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To Ira and Yoram

Preface

Substantial part of my scientific activity was devoted to physicochemical properties of aqueous solutions of citric acid and various inorganic citrates. They included formation of metal-mixed complexes, determinations of solubilities, vapour pressures of water above citric acid and citrates solutions, densities, melting points, sound velocities and electrical conductances. Unquestionably, the industrial and biological importance of citric acid was the main motivation that more than 25 scientific papers I published together with my coworkers on systems with citrate ions. Our results up to 1994, I summarized in the review entitled "Thermodynamic and Transport Properties of Aqueous Solutions of Hydroxycarboxylic Acids." The current book came as a desire to enlarge the information about citric acid properties presented there, to incorporate some subjects which were entirely omitted (chemistry of citric acid and properties of inorganic citrate solutions) and finally to include our and others new relevant results.

My interests in citric acid grew especially after I measured and interpreted electrical conductances of citric acid in aqueous solutions. This actually introduced me for the first time to electrochemistry of unsymmetrical electrolytes, the subject which even today, continue to be an important part of my scientific activity. The idea to write a book about citric acid came also from desire to be involved in something which is applicable oriented. This came from the fact that when I started studying chemical engineering my Father said to me that he expects that I will be successful in "practical chemistry". His intention was clear, that my work will finally lead to a some useful patent. He was satisfied with my career as a chemical engineer, mathematician and physical chemist, but I think in spite that he never said this, he was a little disappointed. In my professional life I meet a number of very interesting and important scientific and engineering problems to solve, but they never resulted in a product finishing on the market. So, writing about citric acid, which evidently is a huge commodity, is in a some way fulfilling his desire that I will be more practical in my work. However, this is once again only partially satisfied, because the present book is mainly devoted to physicochemical properties of solutions and not to engineering and technological aspects of citric acid production or its biological role. These subjects are only marginally treated and the enormous fields of formation of citrate complexes and chemical analysis in systems with citrate ions are also nearly omitted. Nevertheless, I believe that included in this book information, also a very extensive list of references on different aspects dealing with citric acid will be of interest and help not only to people involved with the basic research of systems with citric ions, but also to those who are engaged with its production and use. Thus, there is an intention that this book will serve graduate students and researchers in various domains of chemistry, biotechnology, biochemistry and biology who are studying properties, chemical reactions and applications of hydroxycarboxylic acids, but also engineers who are producing them. Evidently, it is my expectation that that the present book will stimulate further research on chemistry and properties of citric acid and compounds related to it. The book consists of five Chapters, each devoted to different aspects associated with citric acid.

Chapter 1 includes general information about properties, occurrence, importance in living organisms and technological applications of citric acid. It contains also a short history linked with the discovery and development of citric acid production. It lists also most important physicochemical investigations dealing with citric acid solutions.

Chapter 2 is devoted to properties of solid citric acid and aqueous and organic solutions of it. Detailed phase equilibria in the citric acid + water system (melting, freezing, boiling, solubilities and vapour pressures curves) are presented, correlated and thermodynamically analyzed. Dynamic and other physical properties (viscosities, diffusion coefficients, thermal and electrical conductivities, surface tensions and indices of refraction) are examined. Solubilities of citric acid in organic solvents and ternary citric acid + aliphatic alcohol + water and citric acid + tertiary amine + water systems are also discussed.

Chapter 3 is dedicated to comprehensive presentation of mathematical procedures associated with dissociation of citric acid in water and in electrolyte solutions. Available in the literature dissociation constants are tabulated and their accuracy examined. Based on temperature and pressure dependence of dissociation constants, the thermodynamic functions linked with dissociation process are discussed in a detail. It also includes description of many aspects connected with compositions and applications of citrate buffers. Besides, it gives a very extensive number of references related to citric acid complexes.

Chapter 4 offers an extensive description of the citric acid chemistry. It includes presentation of total syntheses of citric acid, preparations of labeled citric acid, typical reactions - neutralization, degradation, oxidation, esterification, formation of anhydrides, amides, citrate-based siderophores and other compounds.

Chapter 5 contains information about applications and physicochemical properties of inorganic citrates. These include solubilities in water, boiling temperatures, freezing points and activity and osmotic coefficients at these temperatures. Presented vapour pressures of water over unsaturated and saturated solutions of alkali metal citrates are thermodynamically analyzed to give activities of components in these systems. From other properties, it also contains sound velocities, densities of binary and ternary solutions and partition data in two-phase ternary systems, namely in the alkali metal citrate + aliphatic alcohol + water and alkali metal citrate + polyethylene glycol (PEG) + water systems. In addition, it includes the literature sources leading to data about crystal structure of many inorganic citrates.

There is a number people who helped me in preparing this book and I am grateful to all of them. First of them is Professor Emanuel Manzurola from Ben-Gurion University of the Negev, Beer Sheva, who during many years participated in our common research on citric acid and various systems with citrate ions. He also helped to prepare chemical formulas of this book An exceptional role played Professor Marija Bĕster-Rogač from Department of Physical Chemistry, Ljubljana University, Slovenia who was able using services of the Ljubljana University libraries, to provide me with a countless number of papers dealing with citric acid or citrates, sometimes from very obscure journals. She also converted graphically presented experimental data from the literature to a digital form. I am deeply indebted to Professor Hirokazu Okamoto from Faculty of Pharmacy, Meijo University, Nagoya, Japan who kindly provided me with his computer program to calculate buffer compositions and corresponding distribution of species in buffer solutions. Dr. Janez Cezar from Department of Physical Chemistry, Ljubljana University, Slovenia slightly modified this program and performed calculations needed to prepare figures representing behaviour of buffers with citrate ions in Chap. 3. I am grateful for this and for his continuous help in understanding the buffer action in general. I am very much obliged to Professor Concetta De Stefano from Department of Inorganic, Analytical and Physical Chemistry, Messina University, Italy who was extremely cooperative in obtaining a large number of papers of Italian scientists which were devoted to the formation of citrate complexes. She also introduced me to the nomenclature applied when stability constants of complexes are reported. I am thankful to Dr. Olga Voskresenskaya, Senior Scientist from Joint Institute for Nuclear Research, Dubno, Russia who helped to obtain a number of not easy available Russian papers. I am very pleased to mention Professor Maria J. Milewska from Department of Organic Chemistry, Technical University of Gdańsk, Poland who was very essential in all aspects related to the synthesis of citric acid and other organic reactions associated with it. I appreciate very much her help with replacing traditional names of organic chemical compounds with those coming from the systematic nomenclature system. I appreciate very much Prof. Gerd Maurer from Department of Mechanical and Process Engineering, University of Kaiserslautern, Kaiserslautern, Germany for helping in clarifications of some points associated with aqueous two-phase systems. I am indebted to Monika Żarska MSc., from Institute of Chemistry, University of Silesia, Katowice, Poland, who on my request, performed measurements of surface tension of aqueous solutions of citric acid in order to include them in this book.

Finally, without continuing help, understanding and support coming from my wife Ira and son Yoram, the appearance of this book would be impossible. I am deeply thankful to them for their love, patience, support and understanding.

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Contents

Chapter 1
Introduction

Among the fruit acids used in beverage, food, pharmaceutical, textile, metal, chemical and other industries, citric acid plays an exceptional role. Worldwide, citric acid is commercially produced in million tones with a steady annual increase in consumption and production. The acid widely occurs in variety of fruits and vegetables, especially in citrus fruits (lemon juice contents 7–9 % of citric acid) and is responsible for their tart taste. From biochemical point of view, citric acid is of tremendous importance considering that in a series of enzymatic reactions (the so-called Krebs cycle or tricarboxylic acid cycle) humans and animals produce citric acid to generate energy through the oxidization of fats, proteins and carbohydrates. Citrate ions can be found in many natural environment situations (plants, roots, leaves) and they have a tendency to be accumulated and present in living organisms, natural waters and various soils [1–9].

The discovery of citric acid is attributed to the eighth century Islamic alchemist Abu Musa Jabir Ibn Hayyan (Geber). Medieval scholars in Europe were aware of the acidic nature of lemon and lime juices already in the thirteenth century. Carl Wilhelm Scheele (1742–1786), the Swedish chemist, was first to isolate and crystallize it from lemon juice in 1784. Famous German chemist Justus Liebig (1803–1873) recognized in 1834 that citric acid is hydroxytricarboxylic acid. British industrial chemist and the author of popular "Chemical Catechism", Samuel Parkes (1761–1825) wrote in 1815 about citric acid "There is a peculiar acid in the juice of lemons, citrons, limes and a variety of other fruits, different in some of its properties from all others, and known to chemist by the name of citric acid. The ancients, it appears, made no use of the juice of these fruits except as an antidote against poison. Formerly, the citric acid was supposed to be identical with the tartaric acid; but the citric acid does not decompose muriate of potash, nor sulphate of lime, like oxalic acid. Georgius in the Stockholm Memoirs proposed the separation of this acid from mucilage of the juice by cold; but the ingenious Scheele was the first who exhibited this acid in a solid form…. Its consists in separating the real acid by means of carbonate of lime and decomposing the citrate of lime by the intermedium of diluted sulphuric acid; a process which has since been followed throughout Europe; for we have no other means of putting this acid into crystalline form" [10].

A. Apelblat, *Citric Acid,* DOI 10.1007/978-3-319-11233-6_1

First chemical synthesis of citric acid was performed by Grimaux and Adam [11] in 1880, in a series of steps starting from hydrochloric acid acting on glycerin to obtain propenyl dichlorohydrin. An alternative synthesis was proposed by Haller and Held [12] in 1890, this time starting with ethyl chloroacetoacetate and potassium cyanide. In 1891 Dunschmann and Pechmann [13] synthesized citric acid from acetonedicarboxylic acid. Lawrence [14] in 1897 used condensation of ethylic oxaloacetate with ethylic bromoacetate in a number of subsequent reactions to obtain ethylic citrate, calcium citrate and finally citric acid, but the yield of this method was very low.

Citric acid production on industrial scale begun in the mid-1800s based on traditional method of preparing citric acid by extraction from the juice of lemons and limes. As mentioned in a number of places in the literature, citric acid was shipped from Sicily and South Italy in the form of calcium citrate to be processed to citric acid at its destinations. Citric acid was recovered from its calcium salt by adding sulfuric acid. The prime destinations from Italy were England, France and United States. However, with regard to England, this is probably not entirely correct because agricultural chemist Robert Warington (1838–1907) (the author of successful book "*Chemistry of the Farm*" and about him later) wrote in 1875 that "…nearly the whole of the citric acid manufactured in this country is made from concentrated lemon-juice" [15]. In 1893, Carl Wehmer [16–20] discovered that citric acid can be produced from sugar by *Penicillium* mold. However, his attempts to produce citric acid industrially in Fabriques Chimiques de Thann et de Mulhouse - Alsace, failed after 2 years, mainly as a result of contamination problems during the fermentation process. First successful fermentation process was achieved only in 1919 by Les Produits Organiques de Tirlemont, Tienen, Belgium. Their strong competition with the Italian lemon-based industry during 10 years finally ended in a joint-venture named Citrique Belge. However, the interruption of citric acid exports from Italian citrus fruit industry during World War I and increasing worldwide demand for it necessitated a new method for producing citric acid in large quantities. This was done in USA by the food chemist James Currie and microbiologist Charles Thom [21, 22]. They found that citric acid can abundantly be produced by certain strains of the filamentous fungus *Aspergillus niger* when grown in acidified solutions containing sucrose and relatively small amounts of inorganic salts. In nature, *Aspergillus niger* is found in soil and liter, in compost and on decaying plant material growing aerobically on organic matter. The Currie-Thom fermentation process was commercialized in 1923 by Pfizer Inc. in Brooklyn, New York and after this the technology was implemented in Europe (England, Belgium, Czechoslovakia, Russia and several other countries) with Italy losing its dominant position in production of citric acid [23–30]. With a largely increasing consumption of citric acid after World War II, to traditionally major producers from Western Europe and North America a new group of manufactures coming from China, India, Indonesia, Japan, Israel, Brazil, Argentina and other countries should be added. The development of citric acid industry was influenced not only by technological aspects but also by economical and legal factors. In each country, its history was marked by takeovers, changing export–import policies, prohibitive tariffs, government subsidies, business cultures, fixing prices procedures, environmental pollution regulations and so on [31].

Most of produced citric acid is used in numerous consumer goods, in food and beverage industries. As an acidulant, it stimulates a natural fruit flavor in soft drinks and syrups and provides the desired degree of tartness. It stabilizes commercially prepared juices, frozen fruits, candies, canned vegetables, fish and meat products. In wines and ciders, citric acid inhibits oxidation, browning and assures their transparency. As an adjusting pH agent, citric acid is constituent of jellies, jams and gelatin desserts. In dairy products, its antioxidant, acidifying and emulsifying properties are used in production of ice creams and cheeses. Being also biodegradable and safe for both industry and consumers, environmentally acceptable, readily metabolized and eliminated from the body, citric acid is ingredient of many pharmaceuticals (e.g. as an anticoagulant is used in transportation and storage of blood plasma), cosmetics and toiletries. Citrate salts of various metals are used to deliver those metals in a biologically available form in many dietary supplements. The widest buffering capacity as compared to other organic acids and the ability of citric acid to form complexes with almost every metal ion are utilized to produce efficient soaps, laundry detergents and household cleaners. Using this property, citric acid is frequently used in analytical chemistry as a buffer masking agent for various metal ions (e.g. an eluting agent in ion-exchange chromatography). In industry, citric acid is used in a broad range of applications, as a cleaner of steam or hot water systems to remove calcium layers, in electroplating, copper plating, metal cleaning, leather tanning, in production of photographic reagents and inks, in construction (additives to cements), in solution of fouling problems, in paper, printing and textile industries. An addition of citric acid or citrates to various aqueous systems produces changes in solubility and dissolution kinetics of sparsely soluble materials, for example such as quartz and gypsum. It influences the crystallization process (crystal morphology and growth), the precipitation (e.g. prevents precipitation of ferric hydroxide and iron sulfide in oilfield treatments) and adsorption of metals on minerals. Citrates frequently serve as precursors for preparation of technologically important ceramic materials. Unique properties of citric are of potential relevance in future applications, in treatment of municipal wastes, in the desulphurization of flue gas and oil recovery, and in treatment of contaminated by heavy metals or radioactive elements soils [32–53].

As raw materials in production of citric acid are utilized inexpensive and readily available carbohydrates. Depending on the country, they included beet and cane molasses, maltose syrups, hydrolyzed starch (corn, wheat, tapioca and potatoes), cellulose hydrolyzates and waste products of the sugar industry. A small amount of citric acid continue to be produced from citrus fruits when they are economically competitive with fermentation processes, for example in Greece, Mexico and South America. Initially, the applied method was the surface fermentation process, but nowadays, starting from 1950s, most of citric acid is coming from the submerged fermentation process. The solid state fermentation method, the Japanese Koji process, is also sometimes used. Batch, fed-batch and continuous modes of production are applied. Usually, from the fermented liquor the mold and other solid impurities are separated by filtration and citric acid is precipitated as calcium citrate by the addition of lime (calcium hydroxide). The precipitate is washed and its aqueous suspension treated with sulfuric acid to regenerate citric acid but also to produce gypsum as an undesired by-product. Recently, to eliminate the formation of gypsum several alternative techniques were studied including solvent extraction, ion-exchange adsorption, membrane filtration, and electrodialysis. Finally, the citric acid solution is concentrated by evaporation and crystallization to give white crystals of citric acid monohydrate [54–87].

In parallel with increasing in citric acid production, an intensive but mainly engineering and technical research was performed to study factors effecting the fermentation process and to improve its efficiency [88–121]. Many parameters were instigated including fermentation mechanism, different types and modifications of strains as applied to different raw materials, fermentation conditions (the oxygen requirement, humidity, salts and trace metal composition, temperature, pH, ionic strength, duration of the process, agitation, heat generation and removal and other factors) and improvements in fermentors and other used equipment. Nowadays, these topics continue to be in an intense study in many places. However, relatively few investigations have dealt with physicochemical properties of citric acid or inorganic citrate solutions. These studies were usually devoted to one or two properties only and they will be discussed and explored in a detail in proper places of this book. There is no doubt, that an extensive and important physicochemical information, which is necessary to produce citric acid, also exists, but unfortunately in the form of unavailable internal reports of citric acid producers.

Five publications are of special interest because of their wide scope of presented material. One has only historical value but other three are of considerable importance. Probably the first information about properties of citric acid and its solutions comes from the above mentioned Robert Warington. He presented to the Chemical Society (London) in 1875 a long paper of 70 pages which was entitled “Note on the Chemistry of Tartaric and Citric Acid” [15]. Evidently, even today, there is an interest to obtain some glance about analytical procedures then used, properties of imported lemon-juice and other solutions (e.g. densities and solubilities), that commercial citric acid was then monohydrate, if prepared from cold water and hemihydrate if crystallized from hot water. Warington also observed that concentrated solutions of citric acid when diluted with water suffer considerable contraction with negligible rise in temperature and that if citric acid is slowly heated to 170 °C, and kept for some time at this temperature, it losses water and aconitic acid is produced.

Modern and comprehensive investigations of physicochemical properties of citric acid solutions actually starts only in 1938 when Marshall published paper entitled “A Phase Study of the System: Citric Acid and Water” [122]. For the first time systematic thermodynamic data were determined in the 10–70 °C temperature range. They included values of enthalpies of hydration and crystallization, determination of the citric acid monohydrate to anhydrous transition point and decomposition pressures of the hydrate. Marshall measured also solubility of citric acid as a function of temperature, densities and vapour pressures of water over saturated solutions. After a long pause, only in 1955, we meet with an extremely important paper of Levien [123] “A Physicochemical Study of Aqueous Citric Acid Solutions.” It contains results of isopiestic measurements (activity and osmotic coefficients), the enthalpy of solution, electrical conductivities, densities, viscosities, partial molar volumes and solubilities. The next step was in 1976, of the Laguerie et al. investigation [124], which includes properties of the citric acid monohydrate + water solutions (solubility, density, viscosity, diffusivity and refractive index). A comprehensive study of thermodynamic properties of the citric acid + water system was performed in 1982 by De Kruif et al. [125]. They reported heat capacities, vapour pressures and solubilities and associated with them the thermodynamic functions for solid citric acid and for aqueous solutions. Contrary to these four papers, the Bates and Pinching study [126] in 1949 is devoted only to determination of dissociation constants of citric acid and associated with them thermodynamic functions in the 0–50 °C temperature range. However, these dissociation constants served in the literature as a basis in practically all calculations when dissociation equilibria in the systems with citric ions are involved.

There is a number of more or less extensive reviews dealing with general properties and production of citric acid [1–6, 56, 86, 99, 119, 127–134], but regrettably two escaped desired attention in the literature, probably, because they appeared in medical journals. First was published in 1949 by Rudy [1] and is entitled “Citric Acid, Occurrence, Preparation Chemistry, Physiology, Pharmacology, Toxicology, Pharmaceutical, and Therapeutic Use”. The second review is from 1953, and it was written by Thunberg [2] “Occurrence and Significance of Citric Acid in the Animal Organism”. In comprehensive review from 1998, the history of citric acid fermentation process and associated with it research was considered by Röhr [133]. Some historical aspects connected with chemistry and development of citric acid production were also discussed by other authors [86, 123, 130]. In 1979 appeared, today practically unavailable, small book having only about 80 pages written by Blair and Zienty [6] “Citric Acid: Properties and Reactions”. The book is an excellent introduction to citric acid subject, especially to the citric acid chemistry. Both authors worked for many years in Citro-tech Division, Miles Laboratories, Inc., Elkhart, Indiana, USA, one of major producers of citric acid. The information contained in this book comes from research performed in Miles Laboratories and from scientific and technical literature available to the authors. A rather small section is only devoted to physical properties of solid citric acid and its aqueous solutions. Most of included material, mainly based on technical and patent literature, deals briefly with the participation of citric acid in many organic reactions.

Physicochemical properties of citric acid solutions and systems with citrate ions which are discussed and analyzed in this book were compiled from variety of sources available in the literature on the subject. Their value, extent, accuracy and reliability is not always even or certain and therefore with only few exceptions when reported data is clearly incorrect, all experimental results of repeated investigations are accessible in tables and figures. This will permit, for a given property, to obtain a some information about scattering of experimental points and the quality of proposed mathematical correlations representing it. As a rule, physical properties are expressed in the SI units, but there are also few exceptions, for example both Kelvin and Celsius degrees are applied when it seems to be more convenient. The same situation exists with chemical names when the IUPAC systematic nomenclature system of organic compounds is not always applied and often traditional names of chemicals are used.

Presented material is not restricted only to liquid phases with citric acid or citrates, but various additional properties associated with solid and gas phases are also taken into account. Besides, but to a limited extent, other related subjects, such as for example the chemical properties of citric acid (its involvement in a variety of chemical reactions), are also considered. A great deal of additional up-to-date information is also available by glancing at titles of numerous investigations cited in references, thus directing readers to the original sources on subjects which are partially or completely omitted in this book. Usually, titles of non-English papers are translated into English, but sometimes they are given in original languages, especially when French investigations are mentioned. From the enormous literature on citric acid and it solutions not all publications were available to the author, especially these in Japanese or Chinese languages. In such way, the authors of omitted and escaped from the author attention investigations have no recognition for their contributions to our knowledge about systems containing citrate ions.

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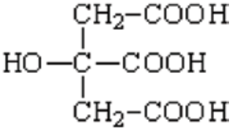
Chapter 2
Properties of Citric Acid and Its Solutions

2.1 Physicochemical Properties of Citric Acid in the Solid State

Citric acid - 2-hydroxy-1,2,3-tricarboxylic acid, $C_6H_8O_7 \equiv H_3Cit$, molar mass 192.12 g mol^{-1}. CAS registry [77-92-9], E 330



$$\begin{array}{c} CH_2-COOH \\ | \\ HO-C-COOH \\ | \\ CH_2-COOH \end{array}$$

Sometimes, also the notation H_4Cit is used for it in the literature, when the hydrogen atom from hydroxyl group is involved in complexation reactions. There are no asymmetric carbon atoms in citric acid or in its anions, i.e. they are optically inactive. However, it is possible to make them asymmetrical by substitution of one of the hydrogen atoms in the methylene groups by another atom or group (the central carbon atom is prochiral).

Citric acid is a natural constituent of many plants, animal tissues and physiological fluids. In trace amounts it appears in a variety of fruits and vegetables, but macroscopic quantities are present in citrus fruits notably lemons and limes. Fruits having above 1 % (on the dry weight basis) are: lemons 4.0–8.0 %, black currents 1.5–3.0 %, grapefruits 1.2–2.1 %, oranges, tangerines, red currents, raspberries and strawberries contain citric acid in the 0.6–1.3 % range. Some typical values for a human body are: blood 10–25 ppm, bones 7500 ppm, semen 2000–4000 ppm, thyroid gland 750–900 ppm, mammary gland 3000 ppm, human milk 500–1250 ppm and urine 100–750 ppm [1].

At first, the crystal structure of anhydrous citric acid was established by Bennett and Yuill [2] in 1935 and later refined by others [3, 4] with an indication of the hydrogen bonding in the crystal. The crystal structure of citric acid monohydrate was reported by Burns and Iball [5] and Roelofsen and Kanters [6]. According to Nordman et al. [3], anhydrous citric acid is monoclinic, crystallizes in the space group $P2_{1/a}$ and citric acid monohydrate is orthorhombic and belongs to the space

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group $P2_12_12_1$, both crystals have four molecules in the unit cell. Bennett and Yuill also found that the transition from citric acid monohydrate to anhydrous citric acid occurs between 36.15 and 36.45 °C with the mean value of 36.3 °C. The Marshall results [7] are slightly higher, from 36.35 to 36.6 °C and he proposed the transition temperature of 36.5 °C when De Kruif et al. [8] gave the value of 36.0 ± 0.5 °C based on the X-ray powder diffraction patterns. Oechler [9] based on solubility and vapour pressure measurements reported the value of 36.7 °C. From solubility determinations Dalman [10] and Slobodin and Novotelnova [11] estimated the transition temperature as 35.8 and 36.6 °C respectively. Using dynamic vapour sorption (DVS) and discontinuous isoperibolic thermal analysis (DITA) techniques Lafontaine et al. [12] gave 37.0 ± 1.0 °C result. Lower values about 34.5 °C, were reported by Nývlt [13] and Helmdach et al. [14] from solubility, ultrasound and turbidity studies.

The used by Bennett and Yuill crystals of anhydrous citric acid had density of $d = 1.665\ \mathrm{g\ cm^{-3}}$ at 18 °C and the melting point was 156–157 °C. The density of citric acid monohydrate as reported by Laguerie et al. [15] was $d = 1.542\ \mathrm{g\ cm^{-3}}$ at 25 °C. Wilhoit and Shiao [16] measured, from 20 to 80 °C, the specific volumes of the solid citric acid by using a glass dilatometer and expressed their results by the following quadratic equation

$$\begin{aligned} &\mathrm{v/cm^3\cdot g^{-1}} = 0.6415 - 4.770\cdot 10^{-5}\,\theta + 2.363\cdot 10^{-6}\,\theta^2 \\ &\theta = (T\,/\,\mathrm{K} - 273.15) \end{aligned} \tag{2.1}$$

The volume expansion and the inner energy coefficients at 25 °C were also determined: $(\partial V/\partial T)_P/\mathrm{cm^3\,g^{-1}\,K^{-1}} = 0.704\cdot 10^{-4}$ and $(\partial U/\partial P)_T/\mathrm{J\cdot g^{-1}\cdot atm^{-1}} = -2.134\cdot 10^{-3}$ with 1 atm = 101.325 kPa. They observed that citric acid decomposes in the 152.9–155 °C temperature region. The elastic and thermoelastic properties of anhydrous and monohydrate citric acid crystals were studied by Khan and Narasimhamurty [17] and Haussuehl and Wang [18].

Citric acid crystallizes from hot aqueous solutions in the anhydrous form as colorless transparent crystals or white crystalline powders. Citric acid monohydrate crystallizes from cold solutions and the crystals lose their hydration water if gently heated at 70–75 °C and melt in the range of 135–152 °C. Fast heating leads to dehydration at about 100 °C, melting at 153 °C and decomposition above 175 °C. Citric acid is deliquescent in wet air. Considering the importance of industrial aspects of crystallization from aqueous solutions, a number of studies of supersaturated or nearly saturated citric acid solutions were performed. It was demonstrated that the structure of these solutions and impurities have a great influence on nucleation kinetics and crystal formation and growth of citric acid crystals [19–32].

Utilization of citric acid in solid dispersions to increase the dissolution and oral absorption of sparingly soluble drugs was first suggested by Chiou and Riegelman [33] in the case of a water-insoluble antifungal antibiotic griseofulvin. A number of other pharmaceutical preparations (e.g. phenobarbital and hexobarbital) in the form of glass dispersions mixtures which include citric acid, were also investigated by various experimental techniques [34–43]. The melted highly viscous citric acid can be drown into threads or sheets and after standing at 37 °C for a few days into a hard, brittle and transparent glass. This glassy state is transformed into a crystalline state after months of standing at room temperature [44]. Thus, a physiologically acceptable and easily soluble carrier and poorly water-soluble drug are melted together and later solidified by cooling to room temperature. The formed glassy solid mixture when exposed to water or gastrointestinal fluids will dissolve rapidly the carrier and disperse drug particles. The competition during a rapid cooling between crystallization and glass formation determines whether a crystal or glass transition occurs. The glass–liquid transition is the reversible transition in amorphous or semicrystalline materials which is accompanied by changes in physical properties (specific heat capacity and viscosity).

The glass transition temperatures T_g and corresponding changes in physical properties were determined for investigated solid mixtures but also for pure citric acid. Simmer and Enever [35] reported $T_g = -23\,°C$ for citric acid monohydrate, but this result was in conflict with the Timko and Lordi [36] findings for anhydrous citric acid. The glass transition for bulk-prepared citric acid glass was $T_g = 13.2\,°C$ and for the *in situ* conditions $T_g = 10.2\,°C$. Repeated determination by Simmer and Enever [37] showed $T_g = 7.0\,°C$ and that water present in citric acid monohydrate strongly reduces the glass temperature. Thermal citric acid studies of Timko and Lordi also indicated that the bulk-prepared melt (an amorphous + crystalline citric acid) exhibits a broad exothermic transition about $-80\,°C$ which is followed by an endothermal effect. On contrary, the *in situ* did not exhibit an exothermic transition. Timko and Lordi [38] also investigated the effect of impurities and thermal history on the value of T_g and found that the lowering of glass transition temperatures is associated with a higher temperature of the melt preparation and with a longer exposure at this temperature. Decrease in T_g is accompanied by a progressive discoloration of the molten citric acid from a clear transparent liquid to a yellowish brown liquid. The effect of impurities was simulated by adding acotinic acid, a dehydration decomposition product of citric acid, which degrades upon melting. With increasing quantities of acotinic acid in the mixture it was observed that the glass transition temperature strongly decreases. A more systematic study of the properties of citric acid at its glass transition in a dry and hydrated states was performed by Lu and Zografi [39]. Their values for anhydrous citric acid are: $T_g = (10.2 \pm 0.2)\,°C$; $\Delta Cp = (0.83 \pm 0.04)\ J\,g^{-1}\,K^{-1}$ and $\Delta H^*_\eta = 733\ kJ\,mol^{-1}$ (the activation energy for viscous flow at T_g) and for citric acid monohydrate are: $T_g = (10.7 \pm 1.0)\,°C$; $\Delta Cp = (0.81 \pm 0.05)\ J\,g^{-1}\,K^{-1}$ and $\Delta H^*_\eta = 410\ kJ\,mol^{-1}$. These values are consistent with the Hoppu et al. [42] results: $T_g = (11.7 \pm 0.9)\,°C$; $\Delta Cp = (0.82 \pm 0.03)\ J\,g^{-1}\,K^{-1}$; $\eta = 2.6 \cdot 10^{10}\ Pa\,s$ and $\Delta E^*_\eta = 156\ kJ\,mol^{-1}$ (flow activation energy at T_g). In the case of amorphous citric acid which contains 8.6 w/w% of residual water (the equimolar composition) the glass transition temperature has the value of $T_g = -25\,°C$ and $\Delta Cp = (0.92 \pm 0.02)\ J\,g^{-1}\,K^{-1}$ which is similar to the Simmer and Enever value [35]. The glass transition of frozen solution of citric acid was estimated to be $T_g = -50\,°C$ [39] which is in an agreement with the Kodoya et al. result $T_g = -55.1\,°C$ as determined in the freeze-drying process study [40]. Lu and Zografi claimed that the relatively low values of T_g are responsible for difficulty to prepare and maintain a large quantity of pure citric acid in the amorphous state without significant crystallization. Evidently, besides drug + citric acid solid dispersions, the values of glass transition temperatures

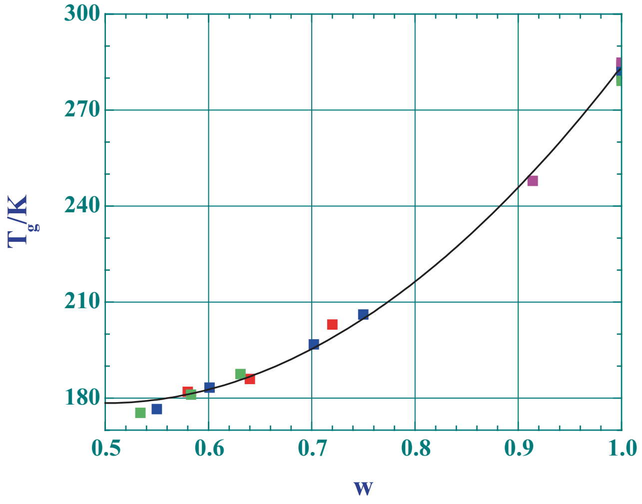

Fig. 2.1 The glass transition temperature T_g as a function of weight fraction of citric acid w in the citric acid + water mixtures. 🟪 - [35–39, 42]; 🟦 - [43]; 🟩 - [45]; 🟥 - [46]; continuous line is calculated using Eq. (2.2)

in the citric acid + water system, are also of great interest in meteorological investigations. Systematic measurements of T_g as a function of added water to citric acid were performed by Lienhard et al. [43], Maltini et al. [45], and Murray [46]. Moreira [47] determined T_g values in the $0.4 < w < 0.8$ concentration range, but unfortunately they are given only in graphical form. All available in the literature T_g values are plotted in Fig. 2.1 and they can be correlated by the following equation

$$T_g/K = 283.15 - 419.36w + 419.89w^2 \tag{2.2}$$

where w is the weight fraction of citric acid in the mixture. This and other fitting equations were evaluated by using an unweighted multivariate least-squares method.

Aerosols in upper troposphere often contain a substantial and variable fraction of organic compounds (ranging from 10 to 70 % of the total dry aerosol mass). They are mixed with inorganic material, usually with ammonium sulfate. Water-soluble organic components of aerosols effect the hygroscopicity, phase transition, light scattering, formation and properties of cloud droplets. Under upper tropospheric conditions, droplets containing dissolved organic substances in aqueous solutions can become glassy. Thus, the impact of organic compounds on the cloud forming and ice cloud nucleation has been widely investigated [46, 48–56]. In this context, citric acid which was identified in aerosol particles, was frequently used as a model substance for atmospheric experiments. Citric acid as well other organic acids received much attention because they are able to absorb water and alter the radiation balance and finally the climate. It is worthwhile also to note that citric acid solutions, as was observed by Corley and Killoy [57], are stable with regards

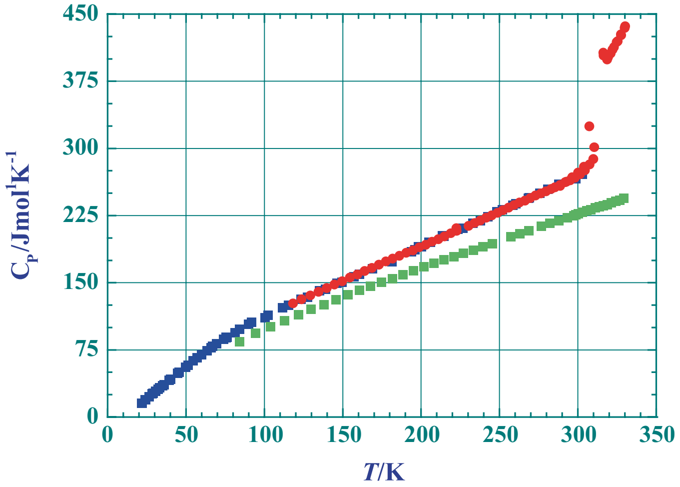

Fig. 2.2 The molar heat capacity of anhydrous and monohydrate citric acid as a function of temperature. Anhydrous citric acid 🟩 - [8]; citric acid monohydrate 🟦 - [58]; 🔴 - [8]

to time, light and air exposure. The studies of the water-citric acid-electrolyte aerosols in atmosphere are also important because they provide significant information about activities, solubilities, surface tension and other properties of aqueous solutions of citric acid [46, 49–51, 53–56].

From thermodynamic properties of solid citric acid monohydrate, the heat capacities, enthalpies and entropies were determined by Evans et al. [58] in the 20–300 K temperature range. De Kruif et al. [8] reported the heat capacities, enthalpies, entropies and the Gibbs free energies from 120 to 300 K for monohydrate, and the corresponding values of the thermodynamic functions from 90 to 330 K for anhydrous citric acid. They observed a slightly superheated large transition at 312.1 K and above this transition, a very large molar heat capacities with a significant temperature dependence (Fig. 2.2). This temperature is higher than that mentioned above from the literature ~309.7 K but probably it indicates that the formation of the monohydrate from the high-temperature solid phase was not complete [8]. As can be seen in Fig. 2.2, both sets of molar heat capacities of citric acid monohydrate agree well and they can be represented by the polynomial expression for 20 K < T < 305 K

$$\begin{aligned} C_P(H_3Cit\cdot H_2O)/\,Jmol^{-1}K^{-1} &= 27.324 + 2.1259(T/K) - 1.0333{\cdot}10^{-2}(T/K)^2 \\ &\quad + 3.3504{\cdot}10^{-5}(T/K)^3 - 3.9008{\cdot}10^{-8}(T/K)^4 \end{aligned} \tag{2.3}$$

For temperatures below 22 K, Evans et al. [58] obtained the molar heat capacities using the Debye function with $T_D = 150$ K. In the case of anhydrous citric acid, in the 84 K < T < 330 K temperature interval, the molar heat capacities can be expressed by

$$\begin{aligned} C_P(H_3Cit)/\,J\cdot mol^{-1}\cdot K^{-1} &= -6.7603 + 1.3632(T/K) - 4.1314{\cdot}10^{-3}(T/K)^2 \\ &\quad + 1.0096{\cdot}10^{-5}(T/K)^3 - 9.4236{\cdot}10^{-9}(T/K)^4 \end{aligned} \tag{2.4}$$

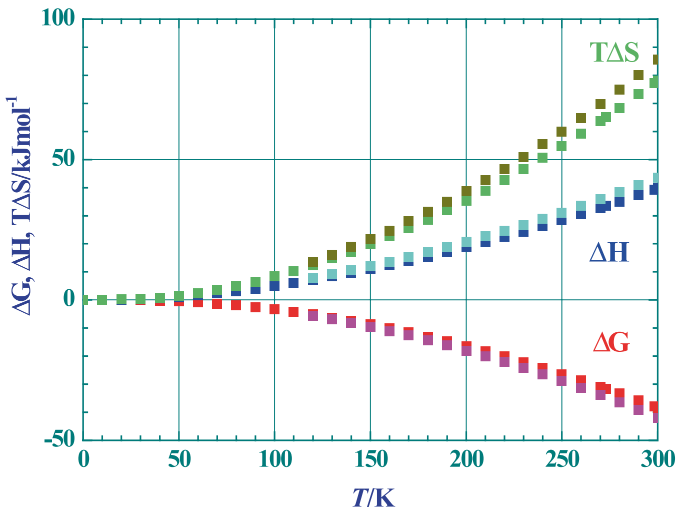

Fig. 2.3 Thermodynamic functions ΔG, ΔH and T·ΔS of citric acid monohydrate as a function of temperature. 🟪, 🟦, 🟩 - [8]; 🟥, 🟦, 🟩 - [58]

Thermodynamic functions ΔG, ΔH and T·ΔS of citric acid monohydrate as a function of temperature were determined by Evans et al. [58] and De Kruif et al. [8] and they are plotted in Fig. 2.3. De Kruif et al. used in calculations of thermodynamic functions the absolute entropy and enthalpy reported by Evans et al. at 120 K. The functions ΔG, ΔH and T·ΔS are consistent in both investigations but there is a noticeable difference between them (Fig. 2.3). As can be observed, the Gibbs free energy is negative $\Delta G<0$ and the enthalpy and entropy are positive and they have similar values with $\Delta H<T\cdot\Delta S$. The absolute values of all thermodynamic functions increase with increasing of temperature *T*. Using the Evans et al. [58] results which cover a more extended temperature range $0<T<300$ K, the thermodynamic functions of citric acid monohydrate are

$$\begin{aligned}\Delta G(\mathrm{H_3Cit\cdot H_2O})/\mathrm{kJmol^{-1}} &= 1.6377\cdot 10^{-2}(T/\mathrm{K}) - 5.1776\cdot 10^{-4}(T/\mathrm{K})^2\\ &\quad +1.2185\cdot 10^{-7}(T/\mathrm{K})^3\\ \Delta H(\mathrm{H_3Cit\cdot H_2O})/\mathrm{kJmol^{-1}} &= -2.7307\cdot 10^{-3}(T/\mathrm{K}) + 5.5329\cdot 10^{-4}(T/\mathrm{K})^2\\ &\quad -3.4548\cdot 10^{-7}(T/\mathrm{K})^3\\ T\Delta S(\mathrm{H_3Cit\cdot H_2O})/\mathrm{kJmol^{-1}} &= -1.9108\cdot 10^{-2}(T/\mathrm{K}) + 1.0710\cdot 10^{-3}(T/\mathrm{K})^2\\ &\quad -4.6733\cdot 10^{-7}(T/\mathrm{K})^3\end{aligned} \tag{2.5}$$

The enthalpy, entropy and the Gibbs free energy of formation of crystalline monohydrate at 298.15 K, as calculated from the values of constituent elements in their standard states are: ΔG_f(s, 298.15 K) = −1472.8 ± 1.3 kJ mol^{-1}, ΔH_f(s, 298.15 K) = −1837.6 ± 0.8 kJ mol^{-1} and ΔS_f(s, 298.15 K) = −1223.8 ± 0.8 J mol^{-1} K^{-1} [58, 59] when Burton

[60] using the enzymatic equilibrium data, gives a slightly higher value for the Gibbs free energy of formation of the crystalline monohydrate ΔG_f(s, 298.15 K) = − 1168.8 ± 6.3 kJ mol^{-1}. The Wilhoit and Shiao value ΔH_f(s, 298.15 K) = − 1543.9 kJ mol^{-1} and the Korchergina et al. [61] value ΔH_f(s, 298.15 K) = − 1551.7 ± 1.3 kJ mol^{-1} for the enthalpy of formation are lower than these given above because they used in calculations the heat of formation of the standard substance for CO_2(gas) and not for C(graphite) as in [58, 59].

Thermodynamic data which exists for anhydrous citric acid is given in the form of relative values. De Kruif et al. [8] reported not absolute values of thermodynamic functions, but changes in the Gibbs free energy, enthalpy and entropy, $\Delta[G(T) - G(90\ K)]$, $\Delta[H(T) - H(90\ K)]$ and $\Delta[S(T) - S(90\ K)]$. They can be represented in the $90\ K < T < 330\ K$ temperature range by the following polynomials

$$\begin{aligned}\Delta[G(T) - G(90\ K)]/kJ\,mol^{-1} &= -8.3675 \cdot 10^{-4}\,\theta - 4.7714 \cdot 10^{-4}\,\theta^2 \\ &\quad + 1.7331 \cdot 10^{-7}\,\theta^3 \\ \Delta[H(T) - H(90\ K)]/kJ\,mol^{-1} &= 9.1225 \cdot 10^{-2}\,\theta + 3.6364 \cdot 10^{-4}\,\theta^2 \\ &\quad - 1.3423 \cdot 10^{-7}\,\theta^3 \\ \Delta[S(T) - S(90\ K)]/J\,mol^{-1}\,K^{-1} &= 9.9208 \cdot 10^{-1}\,\theta - 9.90972 \cdot 10^{-4}\,\theta^2 \\ &\quad + 1.1041 \cdot 10^{-6}\,\theta^3 \\ \theta = T / K - 90 & \end{aligned} \tag{2.6}$$

In order to convert the relative values of entropies of anhydrous citric acid in Eq. (2.6) to absolute values, they must be increased by 75 J mol^{-1} K^{-1}, i.e. S(s, 90 K) = 75 J mol^{-1} K^{-1} and S(s, 298.15 K) = 252.1 J mol^{-1} K^{-1} [8]. Thermal effects associated with the citric acid monohydrate to anhydrous citric acid transition will be discussed later in the context of citric acid dissolution in water.

The Gibbs free energy of formation of citric acid in a saturated solution is given by Evans et al. [58] as ΔG_f(sat. soln, 298.15 K) = − 1235.0 ± 1.3 kJ mol^{-1}. They reported also the corresponding value for the aqueous citrate ion formation in a solution of unit activity, a = 1, as ΔG_f(aq. soln, 3 H^+ + Cit^{3-}, 298.15 K) = − 1161.9 ± 1.4 kJ mol^{-1} (the Burton result is ΔG_f(aq. soln, Cit^{3-}, 298.15 K) = − 1165.5 ± 0.2 kJ mol^{-1} [60]). Kochergina et al. [61] performed a detailed calorimetric study of formation of citrate ions in water and KOH solutions. They presented the following enthalpies of formations ΔH_f(aq. soln, Cit^{3-}, 298.15 K) = − 1534.6 ± 1.6 kJ mol^{-1}; ΔH_f(aq. soln, $HCit^{2-}$, 298.15 K) = − 1526.5 ± 1.6 kJ mol^{-1}; ΔH_f(aq. soln, H_2Cit^-, 298.15 K) = − 1530.0 ± 1.6 kJ mol^{-1} and ΔH_f(aq. soln, undiss. H_3Cit, 298.15 K) = − 1528.5 kJ mol^{-1}.

The equilibrium vapour pressure over crystals of citric acid monohydrate (the decomposition pressure of the hydrate) was determined by Marshall [7] using the dynamic air current method [62, 63]. His results are in a reasonable agreement with those of De Kruif et al. [8]. They used the static method by employing a diaphragm manometer. Oechler [9] applying a direct manometric technique measured vapour pressure of water over solutions saturated with both, the monohydrate and anhydrous citric acid, and obtained practically the same results. These three sets

Table 2.1 Vapour pressures of water over solid citric acid monohydrate

t/°C	*p*/kPa	*t*/°C	*p*/kPa	*t*/°C	*p*/kPa
10.0 [7]	0.669[a]	20.1	1.367	30.1	2.788
13.1	0.809	25.0	1.961	30.2	2.898
13.1	0.895	25.0	1.928	35.0	3.890
13.1	0.852	25.0	1.970	35.0	3.790
13.1	0.852	25.0	1.845	35.0	3.834
15.0	0.964	25.1	1.968	35.0	3.980
20.0	1.377	25.1	1.978	35.0	4.008
20.1	1.384	30.0	2.770	35.05	3.913
20.1	1.367	30.1	2.810	36.50	4.293
4.95 [8]	0.325	24.52	1.748	33.02	3.399
9.73	0.521	25.27	1.760	33.27	3.373
15.96	0.893	28.84	2.332	35.81	3.902
19.97	1.212	30.08	2.582	35.91	3.906
20.60	1.213	33.00	3.240		
26.10 [9]	1.911	33.88	3.546		
31.15	2.836	37.78	4.666		

[a] 1 kPa = 7.5006 mmHg

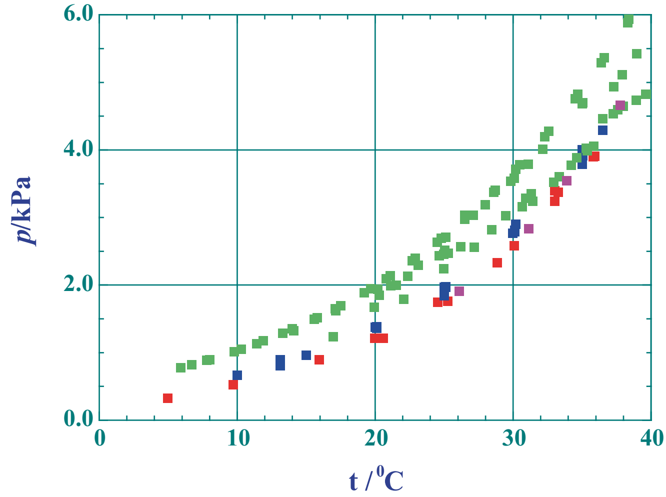

Fig. 2.4 Vapour pressure of water over solid citric acid monohydrate and over aqueous saturated solutions of citric acid as a function of temperature. Vapour–solid equilibrium 🟦 - [7]; 🟥 - [8]; 🟪 - [9, see text] and liquid–solid equilibrium 🟩

of experimental data are presented in Table 2.1 and plotted in Fig. 2.4. They are presented in the temperature range of citric acid monohydrate existence, together with vapour pressures over saturated solutions taken from the literature. As can be observed, especially at higher temperatures with approaching the transition point, the scattering of the experimental points is large and the results are less certain. Melia [64, 65] erroneously claimed that he measured vapour pressures over citric acid monohydrate (above $T > 313$ K) but these vapour pressures are probably over the saturated solutions of citric acid.

The enthalpy change associated with dehydration process is determined from the Clausius–Clapeyron equation

$$\left(\frac{\partial \ln p(T)}{\partial(1/T)}\right)_{s\to g} = -\frac{\Delta H(T)}{R} \tag{2.7}$$

and by assuming that ΔH (T) linearly depends on temperature T, the integral form of Eq. (2.7) gives the temperature dependence of vapour pressures

$$\begin{aligned} \ln[p(T)/\text{kPa}] &= 241.82 - \frac{16262.7}{(T/\text{K})} - 32.757 \ln(T/\text{K}) \\ \Delta H(T)/\text{kJ mol}^{-1} &= 135.22 - 0.2724\,(T/\text{K}) \end{aligned} \tag{2.8}$$

It follows from Eq. (2.8) that ΔH (298.15 K) = 54.0 kJ mol^{-1} when the De Kruif et al. [8] values are ΔH (298.15 K) = 56.8 ± 1.0 kJ mol^{-1} and ΔH (309.5 K) = 55.8 ± 1.0 kJ mol^{-1}. Marshall [7] gives in the 288.15–308.15 K temperature range, the average enthalpy of hydration reaction as ΔH (T) = 51.6 kJ mol^{-1}.

2.2 Melting and Freezing Temperatures of Aqueous Solutions of Citric Acid

The complete phase diagram of the citric acid–water system in the 273–373 K temperature range which includes the liquid and solid phases is plotted in Fig. 2.5. The solid–liquid equilibrium is considered here and the vapour–liquid equilibrium will be discussed later. The temperature–composition curves (in Fig. 2.5, the composition of phases is expressed in the mass fractions of citric acid w) were constructed using experimental data available from the literature. They come from determinations of melting, freezing points, glass transitions and solubilities. The homogenous ice freezing temperatures and the glass transition temperatures were already discussed when other phase relations will be considered in a more detail below. The melting temperatures T_m (Fig. 2.6) and the homogenous ice freezing temperatures T_f are presented in Table 2.2.

Related to determinations of T_m temperatures are cryoscopic measurements where the freezing-point depressions of aqueous solutions of citric acid, $\theta(m) = T_{f.p}(H_2O) - T_{f.p}(m)$, are very accurately measured. This colligative property depends only on the solvent and not on the nature of the solute present in

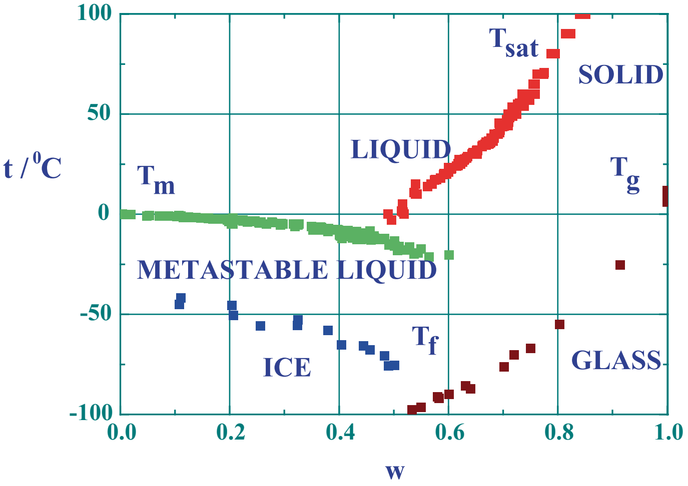

Fig. 2.5 Phase diagram of the citric acid–water system. 🟥 - liquid–solid equilibrium (the solubility curve); 🟩 - equilibrium melting curve; 🟦 - homogenous ice freezing temperature curve; 🟫 - the glass transition curve

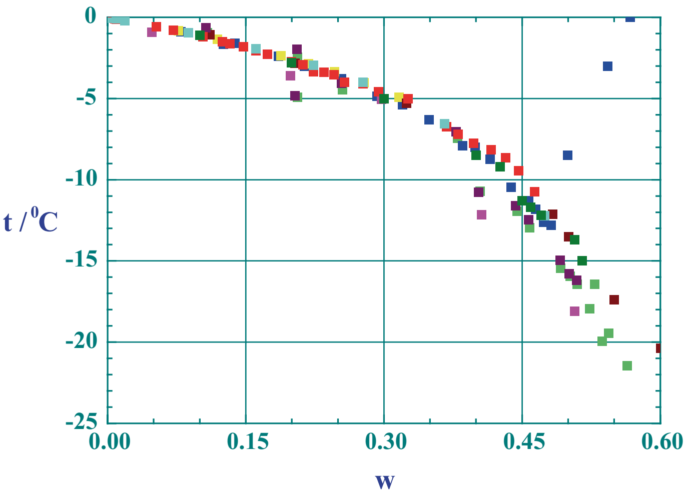

Fig. 2.6 The equilibrium melting-point curve of the citric acid–water system. 🟫 - [43]; 🟪 - [45]; 🟩 - [46]; 🟪 - [53]; 🟨 - [66]; 🟦 - [67]; 🟥 - [68]; 🟦 - [69]; 🟩 - [70]

the solution. Systematic measurements of $\theta(m)$ values for $m < 5.0$ mol kg^{-1} were performed by Apelblat and Manzurola [68], Kendall et al. [66] (in their study, the reported mole fractions are actually molarities of citric acid) and few additional points are given in International Critical Tables [67]. There is a very satisfactory agreement between these sets of data (Table 2.3). In CRC Handbook of Chemistry

Table 2.2 The melting and homogenous ice freezing temperatures in the citric acid–water system

w	T_m/K	w	T_m/K	w	T_f/K
0.1000 [70]	272.05	0.1067 [46, 53]	272.50	0.1080 [46, 53]	228.13
0.2000	270.35	0.2054	271.19	0.2068	222.59
0.3000	268.15	0.2034	268.31	0.2068	222.59
0.4000	264.65	0.2537	269.09	0.2562	217.52
0.4262	263.95	0.3785	266.11	0.3241	217.71
0.4500	261.85	0.4027	262.39	0.3796	215.11
0.4593	261.45	0.4430	261.53	0.4043	207.98
0.4706	260.95	0.4571	260.70	0.4444	207.53
0.5070	259.45	0.4913	258.20	0.4568	205.38
0.5150	258.15	0.5013	257.37	0.4907	197.53
		0.5094	256.95		
0.0727 [69]	272.25			0.1108 [43]	231.34
0.1151	271.48	0.0485 [32]	272.24	0.3250	220.37
0.1263	271.55	0.1983	269.54	0.4833	202.37
0.1694	270.75	0.2976	268.11	0.2037	227.59
0.1954	270.15	0.4058	261.00	0.5008	197.71
0.2322	269.37	0.5068	255.04		
0.2675	268.28				
0.2930	267.75	0.1083 [46, 53]	272.20		
0.3194	266.85	0.2063	268.20		
0.3524	265.24	0.2547	268.70		
0.3647	265.15	0.3803	265.70		
0.3794	264.42	0.4044	262.45		
0.4007	262.70	0.4449	261.20		
0.4179	261.85	0.4583	260.20		
0.4249	261.35	0.4917	257.70		
0.4329	260.52	0.5023	257.20		
0.4401	260.34	0.5100	256.70		
0.4565	264.65	0.5233	255.20		
0.4964	270.15	0.5287	256.70		
		0.5368	253.20		
0.1108 [43]	272.06	0.5439	253.70		
0.3250	267.87	0.5643	251.70		
0.4833	261.03				
0.2037	270.31				
0.5008	259.65				
0.5499	255.75				
0.6009	252.77				

and Physics [71], are presented in the smooth form, the averaged freezing point depressions in the 0–2.2 mol kg^{-1} concentration range.

The experimental freezing-point depressions can be correlated by [68]

$$\begin{aligned}
&\theta(m)/\mathrm{K} = 2.504m^* - 4.224m^{*2}; \quad m^* \le 0.1 \\
&\theta(m)/\mathrm{K} = 0.01827 + 1.88994m^* + 0.09178m^{*2}; \quad 0.1 \le m^* < 5.0 \\
&m^* = m/\mathrm{mol\,kg^{-1}}
\end{aligned} \tag{2.9}$$

Table 2.3 Freezing-point depressions of aqueous citric acid solutions

m/mol kg^{-1}	$\theta(m)$/K	m/mol kg^{-1}	$\theta(m)$/K	m/mol kg^{-1}	$\theta(m)$/K
0.01 [67]	0.0227	0.50	0.967	2.00	3.94
0.02	0.0428	1.00	1.934	3.00	6.53
0.10	0.208	1.50	2.930	4.70	12.24
0.0770 [66]	0.839	0.2179	2.849	0.3165	4.920
0.1193	1.350	0.2462	3.363		
0.1885	2.360	0.2786	4.010		
0.00066 [68]	0.0077	0.5994	1.204	2.000	4.10
0.00256	0.0163	0.7399	1.499	2.170	4.60
0.00356	0.0164	0.7947	1.635	2.519	5.00
0.00514	0.0180	0.9002	1.831	2.520	5.00
0.00522	0.0143	0.9994	1.997	3.03	6.74
0.01057	0.0250	1.0000	2.052	3.20	7.21
0.01998	0.0617	1.0948	2.285	3.43	7.74
0.03033	0.0692	1.3010	2.734	3.71	8.16
0.04050	0.0943	1.4001	2.912	3.96	8.64
0.05000	0.121	1.5006	3.37	4.20	9.44
0.1006	0.216	1.600	3.38	4.50	10.75
0.2920	0.581	1.697	3.54		
0.3996	0.807	1.800	3.99		

It follows that at infinite dilution [72, 73]

$$\lim_{m \to 0} \left(\frac{\theta(m)}{\lambda m} \right) = \nu \tag{2.10}$$

where $\lambda = 1.86$ kg mol^{-1} K is the cryoscopic constant of water and ν is the total number of ions formed from an electrolyte entity. At finite concentrations, values of $\theta(m)/\lambda m$ represent the apparent number of ions and undissociated molecules in the solution. As can be seen in Fig. 2.7, where all available freezing point measurements are plotted, citric acid is dissociated in very dilute solutions. In more concentrated solutions, citric acid behaves as nearly undissociated molecule. Evidently, the observed large scattering of a very sensitive variable $\theta(m)/\lambda m$ results from difficulty to obtain $\theta(m)$ with an adequate precision.

Using thermal properties of pure water it is possible to interrelate $\theta(m)$ values with the water activities a_{w} [72]

$$-\ln a_{\mathrm{w}}(m;T) = 9.687 \cdot 10^{-3}[\theta(m)/\mathrm{K}] + 4.835 \cdot 10^{-6}[\theta(m)/\mathrm{K}]^2 \tag{2.11}$$

The osmotic coefficient of citric acid is directly related to the activity of water

$$\phi(m;T) = -\frac{1000}{\mathrm{M}_{\mathrm{H_2O}}} \cdot \frac{\ln a_{\mathrm{w}}(m)}{\sum_{\mathrm{i}} \nu_{\mathrm{i}} m_{\mathrm{i}}} \tag{2.12}$$

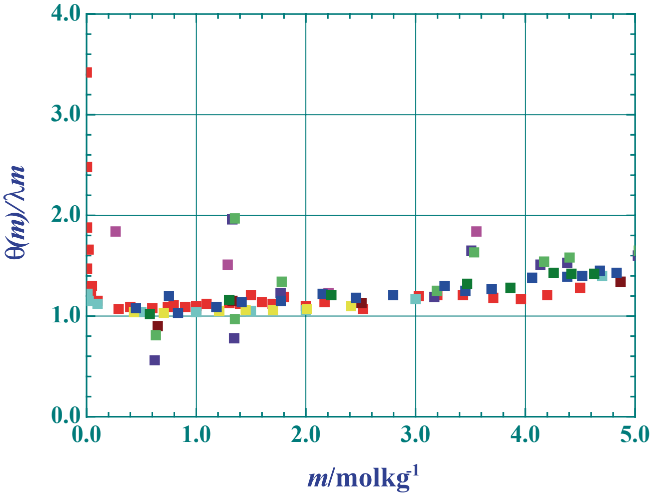

Fig. 2.7 The apparent number of particles in solution as a function of concentration of citric acid. 🟫 - [43]; 🟪 - [45]; 🟩 - [46]; 🟪 - [53]; 🟨 - [66]; 🟦 - [67]; 🟥 - [68]; 🟦 - [69]; 🟩 - [70]

where the sum in Eq. (2.12) expresses the total number of particles in the solution, ν_i are stoichiometric coefficients and m_i are the molalities of corresponding species. In the considered range of concentrations citric acid can essentially be treated as the monobasic weak acid.

This fact can be expressed as

$$\begin{aligned}
&\sum_i \nu_i m_i = \nu_{H^+} m_{H^+} + \nu_{H_2Cit^-} m_{H_2Cit^-} + \nu_{H_3Cit} m_{H_3Cit} \\
&\nu_{H^+} = \nu_{H_2Cit^-} = \nu_{H_3Cit} = 1 \\
&m_{H^+} = m_{H_2Cit^-} = m\,\alpha; \quad m_{H_3Cit} = m(1-\alpha) \\
&\sum_i \nu_i m_i = m(1+\alpha)
\end{aligned} \tag{2.13}$$

and

$$\phi(m;T) = -55.508 \frac{\ln a_w(m;T)}{m(1+\alpha)} \tag{2.14}$$

where α denotes the degree of dissociation of citric acid and $i = 1 + \alpha$ is known as the van't Hoff factor. From the knowledge of the equilibrium constant for the primary step of dissociation $K_1(T)$, it is possible to calculate α values. Using value of $K_1 = 6.0 \cdot 10^{-4}$ mol dm^{-3} at 273.15 K [74], osmotic coefficients at round concentrations were calculated by Apelblat and Manzurola [68] and they are presented in Table 2.4. The functional form of $\phi(m)$ derived from cryoscopic measurements is similar to that determined at higher temperatures by isopiestic and isotenoscopic

Table 2.4 Calculated freezing-point depressions of citric acid solutions, osmotic and activity coefficients of citric acid

m^*	θ^*	ϕ	γ	m^*	θ^*	ϕ	γ
0.01	0.025	1.086	1.037	1.2	2.418	1.059	1.333
0.02	0.048	1.119	1.112	1.4	2.844	1.069	1.360
0.03	0.071	1.126	1.179	1.6	3.28	1.080	1.388
0.04	0.093	1.122	1.218	1.8	3.72	1.090	1.417
0.05	0.115	1.113	1.239	2.0	4.17	1.101	1.446
0.06	0.135	1.102	1.247	2.2	4.63	1.111	1.476
0.07	0.159	1.088	1.248	2.4	5.08	1.121	1.506
0.08	0.173	1.072	1.254	2.6	5.55	1.131	1.537
0.09	0.190	1.056	1.237	2.8	6.03	1.142	1.570
0.10	0.208	1.038	1.219	3.0	6.51	1.153	1.603
0.20	0.400	1.018	1.216	3.2	7.01	1.164	1.637
0.30	0.539	1.016	1.223	3.4	7.51	1.174	1.670
0.40	0.789	1.019	1.232	3.6	8.01	1.184	1.705
0.50	0.986	1.023	1.244	3.8	8.53	1.194	1.740
0.60	1.185	1.028	1.256	4.0	9.05	1.205	1.776
0.70	1.386	1.033	1.268	4.2	9.58	1.215	1.813
0.80	1.589	1.038	1.280	4.4	12.11	1.225	1.851
0.90	1.793	1.043	1.293	4.5	10.38	1.231	1.870
1.00	2.000	1.048	1.306	4.7	10.93	1.241	1.909

$m^* = m/\mathrm{mol\ kg^{-1}}$; $\theta^* = \theta/\mathrm{K}$

methods. Curves are shifted, but unusually, in dilute solutions $\phi(m)$ increases as m decreases when the expected behaviour is $\phi(m) \to 1$ as $m \to 0$. This results from the fact that measurements are performed in not enough dilute solutions. Unfortunately, the applied experimental techniques are unable to reach so diluted solutions where the dissociation of citric acid is a dominant factor.

The activity coefficient of citric acid γ can be evaluated from the Bjerrum form of the Gibbs–Duhem equation [72]

$$\ln \gamma = (\phi - 1) + \int_0^m (\phi - 1)\, d \ln m \tag{2.15}$$

which in terms of $\theta(m)$ values takes the form

$$\begin{aligned} -\ln \gamma &= j + \int_0^m j\, d \ln m - 0.00054\lambda \int_0^\theta (1 - j)\, d\theta \\ j &= 1 - \frac{\theta}{\lambda m (1 + \alpha)} \end{aligned} \tag{2.16}$$

Since at infinite dilution, $m \to 0$, the limiting value of j is uncertain, the numerical integration of Eq. (2.16) was performed by Apelblat and Manzurola [68] from $m = 0.01$ mol kg^{-1} by fixing arbitrarily the value of osmotic coefficient $\phi = 1.086$ (Table 2.4).

Temperature dependence of activity coefficients permits to evaluate the relative partial enthalpies of solution from

$$\overline{\mathrm{L}}_2 = (\overline{\mathrm{H}}_2 - \overline{\mathrm{H}}_2^{\infty}) = -\mathrm{R}T^2\left(\frac{\partial \ln a_2}{\partial T}\right)_{P,m} \tag{2.17}$$

and for citric acid solutions they can be expressed by [68]

$$\begin{aligned}&\overline{\mathrm{L}}_2(m)/\,\mathrm{J\,mol^{-1}} = 4422.8 - 1219.6m^* + 57.157m^{*2} - 57.483m^{*3}\\ &m^* \geq 0.2;\quad m^* = m/\mathrm{mol\,kg^{-1}}\end{aligned} \tag{2.18}$$

The relative partial enthalpies of solution are positive for $m \leq 2.9$ mol kg^{-1}, which means that heat is taken up on mixing of citric acid and water, but for more concentrated solutions $\overline{\mathrm{L}}_2(m)$ is negative and heat is evolved in the mixing process.

2.3 Boiling Points of Aqueous Solutions of Citric Acid

A further colligative property is the elevation of boiling temperatures of aqueous citric acid solutions $\theta(m) = T_{\mathrm{b.p.}}(m) - T_{\mathrm{b.p.}}(\mathrm{H_2O})$. There is a similarity in the analysis of ebullioscopic and cryoscopic measurements, but generally, the boiling-point determinations were less used to obtain thermodynamic quantities. This results from the fact that the ebullioscopic constant of water at its normal boiling point, $\lambda = 0.5128$ kg mol^{-1} K, is about four to five times smaller than the corresponding cryoscopic constant and that the determined boiling point depends strongly on the imposed external pressure p. Complexity of measurements needed to obtain desired precision prevented in many cases evaluations of water activities and osmotic coefficients. Most of investigations were only directed to determination of boiling points and solubilities at high temperatures considering that these quantities are important in chemical engineering practice, especially in the design and control of industrial evaporators.

The activities of water and osmotic coefficients of solute (e.g. undissociated citric acid) are related to the elevation of the boiling point of the solution $\theta(m)$ (determined at $T = T_{\mathrm{b.p.}}(m)$ and under an external pressure p) by [75–77]

$$\begin{aligned}&\ln[a_{\mathrm{w}}(m;T)] = -\frac{\mathrm{M_{H_2O}}}{1000\lambda(T)}\sum_{n=1}^{4} C_n(T)\,\theta(m)^n\\ &\phi(m;T) = -\frac{1000}{\mathrm{M_{H_2O}}m}\ln[a_{\mathrm{w}}(m;T)] = \frac{1}{m\,\lambda(T)}\sum_{n=1}^{4} C_n(T)\,\theta(m)^n\end{aligned} \tag{2.19}$$

where $C_n(T)$ polynomials were evaluated from the temperature dependence of the relative partial molar enthalpies and heat capacities of water in the 333–373 K range. They can be expressed by

$$
\begin{aligned}
&C_1(T) = 1\\
&C_2(T)\cdot 10^3 = -3.1602 + 6.988\cdot 10^{-3}(T/\mathrm{K} - 373.15) - 2.518\cdot 10^{-5}(T/\mathrm{K} - 373.15)^2\\
&C_3(T)\cdot 10^6 = 7.8424 - 5.001\cdot 10^{-2}(T/\mathrm{K} - 373.15) + 5.765\cdot 10^{-4}(T/\mathrm{K} - 373.15)^2\\
&C_4(T)\cdot 10^8 = -1.8440 + 2.047\cdot 10^{-2}(T/\mathrm{K} - 373.15) - 3.850\cdot 10^{-4}(T/\mathrm{K} - 373.15)^2
\end{aligned}
\tag{2.20}
$$

The ebullioscopic constant of water depends on temperature in the following way

$$
\begin{aligned}
\lambda(T)/\mathrm{K}\cdot\mathrm{kg}\cdot\mathrm{mol}^{-1} &= 0.51276 + 3.335\cdot 10^{-3}(T/\mathrm{K} - 373.15)\\
&+ 7.326\cdot 10^{-6}(T/\mathrm{K} - 373.15)^2
\end{aligned}
\tag{2.21}
$$

and the boiling point of water at pressure p is

$$
\begin{aligned}
\mathrm{T}_{\mathrm{b.p.}}(p;\mathrm{H_2O})/\mathrm{K} &= 373.15 + 0.27645(p/\mathrm{kPa} - 101.325)\\
&- 1.13413\cdot 10^{-3}(p/\mathrm{kPa} - 101.325)^2\\
&+ 6.84303\cdot 10^{-3}(p/\mathrm{kPa} - 101.325)^3
\end{aligned}
\tag{2.22}
$$

In the case of aqueous solutions of citric acid, for temperatures above 100 °C, most of reported in the literature boiling points $T_{\mathrm{b.p.}}(m)$ have an accuracy sufficient only for engineering calculations. The Timmermans tabulation [70] includes only two sets of boiling points, but one set is worth to mention. It contains the boiling points determined in 1 K intervals by Gerlach in 1886 and they cover the entire range of solutions, from 0 to 0.914 weight fraction of citric acid (Table 2.5). The second set is that of Baroni from 1932 [70], but this ebullioscopic study is limited only to dilute solutions, $w < 0.14$. As can be observed in Fig. 2.8 all results in the literature are in a reasonable agreement. Only few additional accurate $\theta(m)$ values are tabulated in the International Critical Tables [67] and therefore, there is a very limited ebullioscopic data available for an examination in the citric acid–water system.

Investigating design of industrial evaporators in the case of citric acid, sodium citrate and potassium citrate aqueous solutions, Martinez de la Cuesta et al. [78] reported boiling points by using the Dühring and Othmer plots. These plots give approximately values of boiling points and vapour pressures at $T_{\mathrm{b.p.}}(m)$ using the corresponding values for water in the form

$$
\begin{aligned}
&T_{\mathrm{b.p.}}(m) = \mathrm{a}(m)T_{\mathrm{b.p.}}(\mathrm{H_2O}) + \mathrm{b}(m)\\
&\ln[p(m;T_{\mathrm{b.p.}})] = \mathrm{c}(m)\ln[p(\mathrm{H_2O};T_{\mathrm{b.p.}})] + \mathrm{d}(m)
\end{aligned}
\tag{2.23}
$$

where a, b, c and d constants depend on molality of citric acid m (Table 2.5). The Martinez de la Cuesta et al. [78] study includes boiling points in the 30–120 °C

Table 2.5 Boiling points of citric acid aqueous solutions

w	$T_{b.p.}$/°C	w	$T_{b.p.}$/°C	w	$T_{b.p.}$/°C
0.2063 [70]	101.0	0.8083	118.0	0.0876 [67]	100.285
0.3355	102.0	0.8182	119.0	0.1612	100.585
0.4253	103.0	0.8274	120.0	0.2776	101.210
0.4911	104.0	0.8360	121.0	0.4900	103.512
0.5424	105.0	0.8455	122.0	0.6577	108.41
0.5841	106.0	0.8534	123.0	0.7935	116.72
0.6189	107.0	0.8606	124.0	0.9057	130.77
0.6485	108.0	0.8680	125.0	0.9308	136.25
0.6737	109.0	0.8750	126.0		
0.6957	110.0	0.8813	127.0	0.0216 [70]	100.077
0.7147	111.0	0.8874	128.0	0.0473	100.145
0.7314	112.0	0.8934	129.0	0.0705	100.245
0.7465	113.0	0.8996	130.0	0.1034	100.378
0.7599	114.0	0.9049	131.0	0.1382	100.352
0.7732	115.0	0.9134	132.0		
0.7858	116.0	0.9140	132.5		
0.7977	117.0				
m/mol kg^{-1}	a/°C	b	c	d	t/°C
2.0	1.01362	−0.35374	0.99088	0.02450	30[a]
4.0	1.02637	−0.07796	0.98578	0.00379	35
5.0	1.02441	1.77329	1.00516	−0.15389	35
6.6	1.02441	1.82578	0.99827	−0.14028	50
6.9	1.03117	2.62068	0.99788	−0.17454	50
8.5	1.05185	2.02540	0.98862	−0.19024	50
13.0	1.05963	5.42385	1.00884	−0.45460	70
14.0	1.07646	5.57240	1.00313	−0.47530	70
16.0	1.07663	7.07088	1.01237	−0.59097	70
20.0	1.10043	9.09994	1.01772	−0.77282	80

Table 2.5 (continued)

w	$T_{b.p.}$/°C	w	$T_{b.p.}$/°C	w	$T_{b.p.}$/°C
p/kPa	*20.265*	*40.530*	*60.795*	*81.060*	*101.325*
w			*ΔT*/°C		
0.10 [79, 80]	0.13	0.14	0.15	0.16	0.17
0.20	0.34	0.38	0.40	0.43	0.45
0.30	0.62	0.69	0.74	0.78	0.82
0.40	1.03	1.16	1.22	1.29	1.36
0.50	1.48	1.66	1.75	1.85	1.95
0.60	2.64	2.95	3.12	3.30	3.47
0.70	4.46	5.00	5.28	5.57	5.87
0.80	8.20	9.12	9.68	10.20	10.76
p (kPa)	*121.590*	*141.855*	*151.988*	*162.120*	*202.650*
w			*ΔT* (°C)		
0.10 [79, 80]	0.19	0.20	0.18	0.20	0.20
0.20	0.45	0.47	0.47	0.48	0.49
0.30	0.83	0.84	0.85	0.86	0.89
0.40	1.38	1.41	1.40	1.43	1.65
0.50	2.20	2.26	2.27	2.32	2.40
0.60	3.57	3.63	3.70	3.77	3.93
0.70	6.05	6.22	6.34	6.37	6.69
0.80	10.80	10.90	11.40	11.20	12.00

[a] Constants in Eq. (2.23) to be used for temperatures higher than *t* and up to 120 °C [78]; 1 atm = 101.325 kPa

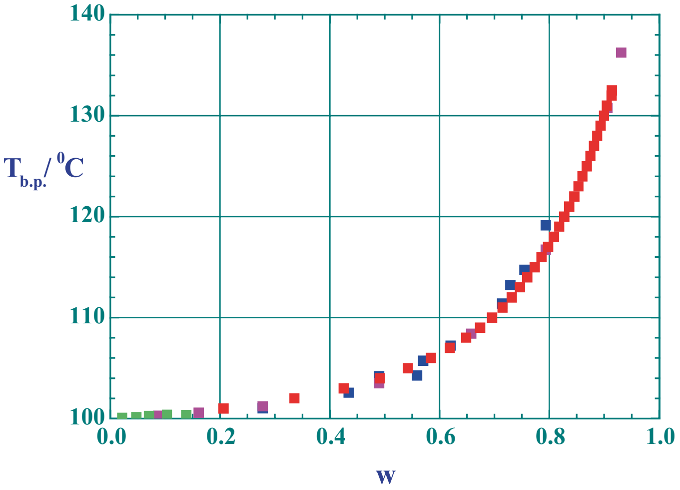

Fig. 2.8 Boiling points of aqueous solutions of citric acid as a function of its weight fraction. 🟪 - [67]; 🟩 - [70]; 🟥 - [70]; 🟦 - [78]

temperature range, for 2.0–20 molal solutions. Bogdanov et al. [79] and Averbukh et al. [80] reported the corresponding thermal depressions ΔT, for the mass fractions of citric acid w from 0.1 to 0.80 and at total pressures in the 20.265–202.650 kPa range (0.2–2.0 atm) (Table 2.5).

Introduction of vapour pressures instead of boiling points leads to an alternative way to describe the colligative properties of solutions. At the boiling point $T_{b.p.}$ (m), the vapour pressure of water above the solution is equal to that of the external pressure p. This pressure is lower than that of pure water at $T = T_{b.p}\cdot(m)$ and the difference in these vapour pressures

$$\Delta P(m) = [p(H_2O;T) - p(m;T)] = [1 - a_w(m;T)]p(H_2O;T) \qquad (2.24)$$

is called the vapour pressure lowering of solution. The values of vapour pressures of water in Eq. (2.25) can be evaluated from a very accurate the Saul and Wagner equation [81]

$$\ln\left(\frac{p(H_2O;T)}{p(H_2O;T_{crit.})}\right) = \frac{\tau}{1-\tau}[-7.85823 + 1.83991\tau^{0.5} - 11.7811\tau^{2} + 22.6705\tau^{2.5} - 15.9393\tau^{3} + 1.77516\tau^{6.5}] \qquad (2.25)$$

$$\tau = \frac{T}{T_{crit.}} \quad ; \quad T_{crit.} = 647.14\mathrm{K} \quad ; \quad p(H_2O;T_{crit.}) = 2.2064 \cdot 10^{4}\,\mathrm{kPa}$$

Using this equation, it is possible to correlate the vapour pressure lowerings $\Delta P(m)$ with the boiling point elevation values $\theta(m)$. Under atmospheric pressure, $p = 101.325$ kPa, the function $\Delta P(m) = f[\theta(m)]$ takes the form

$$\Delta P(m)/\mathrm{kPa} = 3.6298[\theta(m)/\mathrm{K}] + 5.089\cdot 10^{-2}[\theta(m)/\mathrm{K}]^2 \\ +5.209\cdot 10^{-4}[\theta(m)/\mathrm{K}]^3 \tag{2.26}$$

In terms of the vapour pressure lowerings and with assuming that the gaseous phase is ideal, the osmotic coefficients are given using Eq. (2.24) by

$$\phi((m;T) = -\frac{1000}{\mathrm{M}_{\mathrm{H_2O}}m}\ln\left[1-\frac{\Delta P(m;T)}{p(\mathrm{H_2O};T)}\right] \tag{2.27}$$

The boiling points of citric acid solutions (Fig. 2.8) can be correlated with the weight fractions of the acid in the following way

$$\mathrm{T_{b.p.}}/\mathrm{K} = 373.15 - 1.8491\mathrm{w} + 38.774\mathrm{w}^2 - 54.854\mathrm{w}^3 + 67.887\mathrm{w}^4 \tag{2.28}$$

In dilute solutions, the boiling point elevations are

$$\theta(m)/K = 0.7717m^* - 0.5730m^{*2} + 0.4039m^{*3} \\ m^* = m/\mathrm{molkg}^{-1};\quad m^* < 1.5 \tag{2.29}$$

2.4 Solubility of Citric Acid in Water

The knowledge of citric acid solubility in water as a function of temperature is of practical importance and therefore starting from 1923, solubilities of citric acid were repeatedly determined covering the 0–100 °C temperature range or some part of it. A number sets of solubility data are known in the literature (Table 2.6) and as can be observed in Fig. 2.9 there is a reasonably good agreement between them. They include old results of Kremann and Eitel [69], Dalman [10, 82] and Marshall [7], the later measurements of Slobodin and Novotelnova [11], Laguerie et al. [15], DeKruif et al. [8] and Apelblat and Manzurola [83] and recent determinations of Yang and Wang [84], Daneshfar et al. [85], Helmdach et al. [14], Lafontaine et al. [12] (solubilities were determined by the discontinuous isoperibolic thermal analysis (DITA) and the dynamic vapour sorption (DVS) technique), and Oliveira et al. [86]. The Daneshfar et al. [85] solubilities are considerably lower than those of others and they are excluded from Fig. 2.9 because they are clearly incorrect.

The solubility curve has two distinct branches with slightly different slopes (difficult to observe in Fig. 2.9) indicating the solid phase transition from citric acid monohydrate to anhydrous citric acid. The transition temperature as coming from solubility experiments lies between 34.5 and 36.6 °C range [7, 8, 10–12]. There is also a small number of investigations dealing with solubilities of citric acid in pure organic solvents or in mixtures of organics with water [84–87], but they will be treated separately later.

Formally, the solubility curve in the 0–100 °C temperature range can be expressed by

$$\mathrm{w} = 0.4895 + 6.182\cdot 10^{-3}\theta - 3.633\cdot 10^{-5}\theta^2 + 9.899\cdot 10^{-5}\theta^3 \\ \theta = (T/\mathrm{K} - 273.15) \tag{2.30}$$

Table 2.6 Solubilities of citric acid in water as a function of temperature

t/°C	m/mol kg^{-1}	t/°C	m/mol kg^{-1}	t/°C	m/mol kg^{-1}
0.00 [69]	6.835	0.00 [11]	4.989	5.00 [83]	5.546
1.20	6.777	10.00	6.170	10.00	6.151
1.60	6.709	20.00	7.695	15.00	6.861
10.80	7.423	25.00	8.576	20.00	7.534
10.00	7.584	30.00	9.582	25.00	8.449
15.00	7.509	35.80	10.90	30.00	9.765
		38.00	11.23	35.00	10.71
0.00 [10, 82]	4.992	40.00	11.61	40.00	11.26
5.00	5.543	45.00	12.30	45.00	12.38
10.00	6.157	50.00	13.40	50.00	13.05
10.00	6.110	60.00	15.06	55.00	13.80
15.00	6.844	70.00	17.06	60.00	14.78
20.00	7.621	80.00	20.15	65.00	16.01
25.00	8.505	90.00	24.35		
25.00	8.529	100.00	29.66	15.00 [84]	6.896
30.00	9.523			18.00	7.348
35.80	10.90	17.20 [15]	7.133	21.00	7.821
35.80	10.67	17.20	7.079	24.00	8.302
40.00	11.37	19.80	7.528	26.00	8.641
40.00	11.23	20.20	7.546	28.00	8.984
50.00	12.70	22.50	7.951	30.00	9.376
60.00	14.48	22.90	8.003	32.00	9.757
70.00	16.64	25.10	8.401	34.00	10.14
80.00	19.33	25.30	8.418	36.00	10.53
90.00	22.78	27.00	8.808	38.00	10.95
100.00	27.36	27.60	8.842	40.00	11.37
		28.60	9.043	42.00	11.81
10.00 [7]	6.160	30.50	9.472	44.00	12.25
13.80	6.666	30.70	9.456	46.00	12.73
15.00	6.844	31.80	9.717	50.00	13.68

Table 2.6 (continued)

$t/°C$	$m/\text{mol kg}^{-1}$	$t/°C$	$m/\text{mol kg}^{-1}$	$t/°C$	$m/\text{mol kg}^{-1}$
20.00	7.600	33.70	10.15	54.00	14.70
24.30	8.397	34.40	10.48	57.00	15.51
25.00	8.565	35.40	10.84	60.00	16.35
29.95	9.566				
30.00	9.582	16.95 [8]	7.022	23.30 [14]	7.811
35.00	10.71	22.95	7.807	27.40	8.462
35.20	10.79	26.05	8.693	30.20	9.441
36.50	11.11	30.85	9.704	35.00	10.42
40.00	11.56	31.75	9.804	36.50	10.94
40.10	11.61	34.45	10.25	45.50	11.72
43.60	12.06	35.85	10.86	47.20	12.50
45.00	12.29	40.75	11.77	49.70	13.02
48.30	12.82	44.35	12.68	53.50	13.15
50.00	13.09	48.95	13.22	51.50	13.28
55.00	14.04			52.30	13.54
55.30	14.07	20.55 [86]	7.74	54.30	14.06
60.00	15.09	30.15	10.10	56.30	14.58
65.00	16.30	41.25	11.47		
70.00	17.83	49.05	12.72		
70.60	17.94	59.95	14.41		
10.90 [12, DVS]	5.42	4.23 [12, DITA]	5.47	44.41	11.90
20.50	7.26	9.46	6.13	47.18	12.08
20.60	7.28	14.13	6.55	50.04	12.60
25.30	8.07	19.13	7.49	53.30	13.27
30.20	9.20	24.15	8.59	57.02	13.83
32.70	9.53	25.13	8.84		
37.10	10.73	31.12	9.81		
38.00	10.84	35.35	10.84		
39.50	10.97	39.00	11.49		
45.00	11.57	41.49	11.68		
49.00	12.08	44.35	11.00		

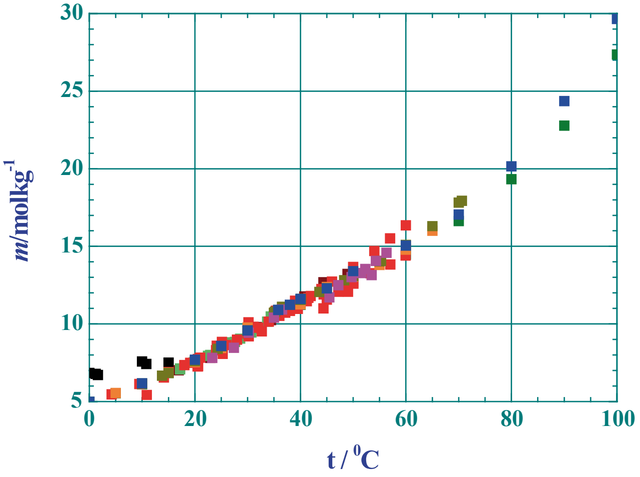

Fig. 2.9 Solubility of citric acid in water as a function of temperature. 🟫 - [7]; 🟩 - [15]; 🟥 - [8]; 🟪 - [14]; ⬛ - [69]; 🟩 - [10, 82]; 🟦 - [11]; 🟧 - [83]; 🟥 - [12, 84, 86]

where w is the weight fraction of citric acid. If the change in solid phase composition is taken into account, then two branches of solubility can be correlated by

$$\begin{aligned}&\ln[m(T)/\mathrm{molkg}^{-1};\mathrm{H_3Cit\cdot H_2O}] = -120.05 + \frac{3785.6}{(T/\mathrm{K})} + 19.217\ln(T/\mathrm{K})\\ &T < 310\mathrm{K}\\ &\ln[m(T)/\mathrm{molkg}^{-1};\mathrm{H_3Cit}] = -100.14 + \frac{3698.7}{(T/\mathrm{K})} + 15.794\ln(T/\mathrm{K})\\ &T > 310\mathrm{K}\end{aligned} \tag{2.31}$$

A rigorous thermodynamic treatment of solubility of anhydrous and hydrated solutes (electrolytes and nonelectrolytes) in water or in other solvent was given in 1944 by Williamson [88]. In a general form, the expression for the molar enthalpy of solution $\Delta\mathrm{H_{sol}}$ of anhydrous or hydrated solute is

$$\begin{aligned}\Delta\mathrm{H_{sol.}} &= -\mathrm{R}T^2\frac{1000}{m\mathrm{M_1}}\left(\frac{\partial m}{\partial T}\right)_{P,\,\mathrm{sat.}}\left(\frac{\partial \ln a_1}{\partial m}\right)_{T,\,\mathrm{sat}}\\ \Delta\mathrm{H_{sol.}} &= \mathrm{R}T^2\left(\mathrm{h}-\frac{1000}{m\mathrm{M_1}}\right)\left(\frac{\partial m}{\partial T}\right)_{P,\mathrm{sat.}}\left(\frac{\partial \ln a_1}{\partial m}\right)_{T,\,\mathrm{sat}}\end{aligned} \tag{2.32}$$

where h is the hydration number and $\mathrm{M_1}$ and a_1 are the molecular mass and activity of solvent. In terms of experimentally available osmotic coefficients ϕ, these equations become

$$\Delta \mathrm{H}_{\mathrm{sol.}} = \nu \mathrm{R} T^2 \left(\frac{\partial m}{\partial T}\right)_{P,\,\mathrm{sat.}} \left[\left(\frac{\phi}{m}\right)_{\mathrm{sat.}} + \left(\frac{\partial \phi}{\partial m}\right)_{T,\,\mathrm{sat}}\right]$$
$$\Delta \mathrm{H}_{\mathrm{sol.}} = \nu \mathrm{R} T^2 \left(1 - \frac{\mathrm{h}\, m \mathrm{M}_1}{1000}\right)\left(\frac{\partial m}{\partial T}\right)_{P,\,\mathrm{sat.}} \left[\left(\frac{\phi}{m}\right)_{\mathrm{sat.}} + \left(\frac{\partial \phi}{\partial m}\right)_{T,\,\mathrm{sat}}\right] \tag{2.33}$$

where v denotes the total number of ions formed by one molecule of solute, and $v = 1$ is introduced for nonelectrolytes. If activity coefficients of electrolyte are considered then

$$\Delta \mathrm{H}_{\mathrm{sol.}} = \nu \mathrm{R} T^2 \left(\frac{\partial m}{\partial T}\right)_{P,\,\mathrm{sat.}} \left[\left(\frac{1}{m}\right)_{\mathrm{sat.}} + \left(\frac{\partial \ln \gamma_\pm}{\partial m}\right)_{T,\,\mathrm{sat}}\right]$$
$$\Delta \mathrm{H}_{\mathrm{sol.}} = \nu \mathrm{R} T^2 \left(1 - \frac{\mathrm{h}\, m \mathrm{M}_1}{1000}\right)\left(\frac{\partial m}{\partial T}\right)_{P,\,\mathrm{sat.}} \left[\left(\frac{1}{m}\right)_{\mathrm{sat.}} + \left(\frac{\partial \ln \gamma_\pm}{\partial m}\right)_{T,\,\mathrm{sat}}\right] \tag{2.34}$$

In the case of nonelectrolytes, the mean activity coefficients are replaced by the activity coefficients of solute *f*. Since in most cases the change of activity of solvent with concentration near the saturation point is unknown, actually are reported only the apparent molar enthalpies of solution ΔH_{sol} from

$$\Delta \mathrm{H}_{\mathrm{sol.}} = \nu \mathrm{R} T^2 \left(\frac{\partial \ln m}{\partial T}\right)_{P,\,\mathrm{sat.}}$$
$$\Delta \mathrm{H}_{\mathrm{sol.}} = \nu \mathrm{R} T^2 \left(1 - \frac{\mathrm{h}\, m \mathrm{M}_1}{1000}\right)\left(\frac{\partial \ln m}{\partial T}\right)_{P,\,\mathrm{sat.}} \tag{2.35}$$

If solubility curves are expressed in the form given by Eq. (2.31)

$$\ln m = \mathrm{A} + \frac{\mathrm{B}}{T} + \mathrm{C} \ln T \tag{2.36}$$

then the apparent molar enthalpy of solution is

$$\Delta \mathrm{H}_{\mathrm{sol.}} = \nu \mathrm{R} \left(1 - \frac{\mathrm{h}\, m \mathrm{M}_1}{1000}\right)(\mathrm{C}T - \mathrm{B}) \tag{2.37}$$

Since in saturated solutions citric acid is practically undissociated, in above equations we have for anhydrous citric acid $v = 1$, $h = 0$ and for citric acid monohydrate $v = 1$, $h = 1$ and $M_1 = M_{H_2O}$ denotes the molar mass of water.

Osmotic coefficients in saturated solutions of citric acid at different temperatures are known from vapour pressure measurements, but not their changes with concentration near the saturation points. At 25 °C, Levien [89] using her ϕ and $\Delta\phi/\Delta m$ values and the Dalman solubilities [10] obtained from Eq. (2.33) the molar enthalpy of solution $\Delta H_{sol} = 29.8\ \mathrm{kJ\,mol^{-1}}$. Similar calculations performed by Apelblat [83] led to lower value $\Delta H_{sol} = 26.0\ \mathrm{kJ\,mol^{-1}}$ and this result is very close to that which was determined from calorimetric measurements, $\Delta H_{sol} = 26.3\ \mathrm{kJ\,mol^{-1}}$, by using the molar enthalpy of solution at infinite dilution of citric acid monohydrate [90] and the molar enthalpy of dilution of citric acid [91]. The apparent molar enthalpies of solution based on Eq. (2.36) are considerably lower than those coming from exact thermodynamic equations. The molar enthalpies of solution in diluted solutions were calorimetrically measured by De Kruif et al. [8] and Apelblat [90] and their results for monohydrate are $\Delta H_{sol} = (29.25 \pm 0.20)\ \mathrm{kJ\,mol^{-1}}$ and $\Delta H_{sol} = (29.06 \pm 0.12)\ \mathrm{kJ\,mol^{-1}}$ respectively. Corresponding values for anhydrous citric acid are $\Delta H_{sol} = (18.47 \pm 0.09)\ \mathrm{kJ\,mol^{-1}}$ and $\Delta H_{sol} = (18.21 \pm 0.07)\ \mathrm{kJ\,mol^{-1}}$. Using these enthalpies, the molar enthalpy of hydration of citric acid is therefore $\Delta H_{hydr.} = -(10.78 \pm 0.29)\ \mathrm{kJ\,mol^{-1}}$ [8] and $\Delta H_{hydr.} = -(10.78 \pm 0.19)\ \mathrm{kJ\,mol^{-1}}$ [90]. Kochergina et al. [61] also calorimetrically measured the molar enthalpies of solution of citric acid in water and KOH dilute solutions. Their values for aqueous solutions in 0.00584–0.0634 $\mathrm{mol\,kg^{-1}}$ concentration range lie between $\Delta H_{sol} = 18.84\ \mathrm{kJ\,mol^{-1}}$ and $\Delta H_{sol} = 17.36\ \mathrm{kJ\,mol^{-1}}$.

2.5 Vapour Pressures of Water Over Saturated Solutions of Citric Acid

Besides solubilities, the knowledge of vapour pressures of water over saturated solutions of citric acid is an essential factor in its production and therefore these vapour pressures were measured a number of times. However, contrary to solubilities, the agreement between Marshall [7], Oechler [9], Williams et al. [92], Melia [64, 65], De Kruif et al. [8], Apelblat et al. [93] and Manzurola and Apelblat [94] sets of data is less satisfactory than can be expected. Determined by the isotenoscopic or hygroscopic techniques, the vapour pressures are presented in two forms, $p = f(t\,°C)$ and $\ln p = f(1/T)$. Differences in absolute values of experimental vapour pressures are clearly evident, especially for temperatures higher than 30 °C (Fig. 2.10), but also the temperature dependence of them is somewhat different (Fig. 2.11). The

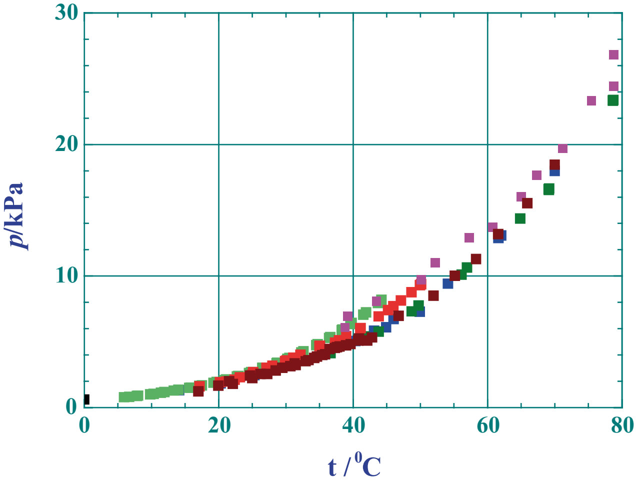

Fig. 2.10 Vapour pressures of water over saturated solutions of citric acid as a function of temperature. 🟦 - [6]; 🟩 - [8]; 🟫 - [53]; 🟪 - [56,57]; 🟥 - [59]; 🟦 - [60]; 🟩 - [61].

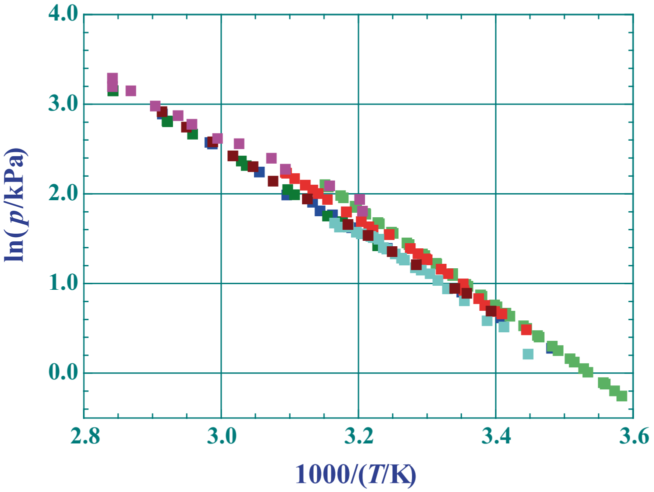

Fig. 2.11 Vapour pressures of water over saturated solutions of citric acid as a function of temperature. ■ - [6]; ■ - [8]; ■ - [53]; ■ - [56,57]; ■ - [59]; ■ - [60]; ■ - [61].

scattering of results is even more pronounced if the water activities or osmotic coefficients are involved.

If all sets of vapour pressures (Table 2.7) are combined, then they formally can be correlated by

$$\ln[p\,/\,\mathrm{kPa}] = -5.8543 + 9.3962\mathrm{w} + 2.4735\mathrm{w}^2 \tag{2.38}$$

or by

$$\ln[p(T)\,/\,\mathrm{kPa}] = 172.21 - \frac{11847}{(T\,/\,\mathrm{K})} - 123.086\ln(T\,/\,\mathrm{K}) \tag{2.39}$$

and then the molar enthalpy of vaporization is

$$\Delta\mathrm{H}_{\mathrm{vap.}}\,/\,\mathrm{kJ\,mol^{-1}} = 98.505 - 0.1919(T\,/\,\mathrm{K}) \tag{2.40}$$

Marshall [7] gives for the molar enthalpy of vaporization $\Delta\mathrm{H}_{\mathrm{vap}} = 39.1\ \mathrm{kJ\,mole^{-1}}$ at 25 °C when the Apelblat et al. [93] value is $\Delta\mathrm{H}_{\mathrm{vap}} = 41.4\ \mathrm{kJ\,mole^{-1}}$.

By assuming that citric acid is undissociated and the gaseous phase is ideal, vapour pressures permit to determine water activities a_{w} and osmotic coefficients ϕ in saturated solutions of citric acid

$$\begin{aligned} a_{\mathrm{w}}(T) &= a_{\mathrm{H_2O}}(T) = \frac{p(T)}{p_{\mathrm{H_2O}}(T)} \\ \phi(T) &= -\frac{1000}{\mathrm{M_{H_2O}}\,m}\ln[a_{\mathrm{H_2O}}(T)] \end{aligned} \tag{2.41}$$

Table 2.7 Vapour pressures of water over saturated solutions of citric acid as a function of temperature

t/°C	*p*/kPa	*t*/°C	*p*/kPa	*t*/°C	*p*/kPa
14.10 [7]	1.321	38.80 [64, 65]	6.098	38.96	5.422
20.30	1.853	39.18	6.942	41.05	6.037
25.30	2.471	43.52	8.073	41.08	6.046
30.90	3.282	50.12	9.731	43.80	6.925
35.30	4.029	52.22	10.998	45.18	7.418
40.30	5.058	57.28	12.928	45.98	7.712
43.10	5.844	60.77	13.692	47.11	8.142
44.90	6.106	64.99	16.039	48.68	8.772
46.00	6.733	67.32	17.674	49.93	9.309
49.90	7.298	71.18	19.686	50.11	9.377
54.10	9.416	75.47	23.312		
61.60	12.887	78.77	24.424	5.90 [94]	0.776
62.00	13.080	78.77	26.819	6.70	0.821
70.00	17.990	84.66	29.658	7.80	0.885
		91.40	35.496	8.00	0.899
21.54 [9]	1.999	94.14	37.326	9.80	1.010
24.65	2.437	98.41	42.024	10.30	1.052
26.22	2.566			11.40	1.131
31.31	3.352	36.62 [8]	4.141	11.90	1.175
34.61	3.881	41.63	5.414	13.30	1.286
37.99	4.651	43.80	5.773	14.00	1.351
40.86	5.248	48.72	7.311	15.60	1.494
46.77	6.974	49.74	7.756	15.80	1.519
51.96	8.502	56.15	10.109	17.10	1.648
55.11	10.015	56.94	10.645	17.50	1.696
58.30	11.299	64.86	14.368	19.20	1.887
61.57	13.195	69.07	16.609	19.70	1.951
65.90	15.542	69.16	16.662	20.80	2.096
70.01	18.466	69.12	16.530	21.10	2.140

Table 2.7 (continued)

t/ °C	*p*/kPa	*t*/ °C	*p*/kPa	*t*/ °C	*p*/kPa
		78.62	23.346	22.70	2.359
16.95 [92]	1.237	78.66	23.333	22.90	2.396
19.94	1.674	78.69	23.386	24.50	2.636
22.07	1.792			24.80	2.690
24.98	2.240	17.15 [93]	1.622	26.50	2.975
27.19	2.560	20.18	1.938	26.50	3.035
28.45	2.816	21.12	1.987	28.60	3.375
29.47	3.029	22.35	2.131	28.70	3.403
30.65	3.157	23.13	2.294	30.20	3.714
31.44	3.242	24.98	2.455	30.50	3.783
32.94	3.520	25.05	2.516	32.30	4.195
33.33	3.605	25.12	2.704	32.60	4.277
34.20	3.776	27.10	3.031	34.50	4.756
35.38	3.989	27.99	3.188	34.70	4.820
35.85	4.053	29.85	3.537	36.40	5.287
36.48	4.458	30.07	3.582	36.60	5.363
37.27	4.533	31.10	3.791	38.30	5.882
37.59	4.597	32.15	4.014	38.40	5.934
38.93	4.736	35.00	4.681	39.60	6.358
39.64	4.821	35.02	4.685	39.80	6.441
40.74	5.098	35.05	4.694	41.50	7.073
42.08	5.098	37.29	4.935	41.90	7.240
42.79	5.333	37.90	5.115	43.70	7.954
				44.20	8.190

Using vapour pressures over saturated solutions from Eq. (2.39) and solubilities of citric acid from Eqs. (2.31), the water activities $a_w(T)$ and osmotic coefficients in two forms $\phi(T)$ and $\phi(m)$, can be represented by

$$\begin{aligned}
&a_w(T) = 0.8382 + 1.013\cdot10^{-3}\theta - 9.805\cdot10^{-5}\theta^2 + 4.637\cdot10^{-7}\theta^3 \\
&\phi(T) = 0.6550 + 1.315\theta^{1/2} - 5.460\cdot10^{-1}\theta + 8.870\cdot10^{-2}\theta^{3/2} - 5.944\cdot10^{-3}\theta^2 \\
&\quad + 1.327\cdot10^{-4}\theta^{5/2} \\
&\phi(m) = -9.5985 + 25.415m^{*1/2} - 18.811m^{*} + 6.187m^{*3/2} - 9.407\cdot10^{-1}m^{*2} \\
&\quad + 5.412\cdot10^{-2}m^{*5/2} \\
&\theta = (T/\mathrm{K} - 273.15); \quad m^{*} = m/\mathrm{mol\cdot kg^{-1}}
\end{aligned} \tag{2.42}$$

2.6 Solubilities of Gases in Aqueous Solutions of Citric Acid

Production of citric acid by the fermentation of carbohydrates with fungus *Aspergillus niger* involves gas–liquid contact operations. In order to establish favorable environment for an effective cell growth and high citric acid yield, it is necessary to control amount of dissolved gases in the liquor. The solubility of gases in liquid foods which is influenced by the presence of citric acid, especially that of oxygen, is also of practical importance [95]. Thus, mostly engineering aspects associated with dissolution of air, oxygen, nitrogen and carbon dioxide and their impact on the microbial production of citric acid were investigated [96–105]. It was observed that with increasing concentration of dissolved oxygen, the amount of formed citric acid also increases when other gases have an opposite effect. However, with an exception of CO_2, the solubility of gases in aqueous solutions of citric acid as a function of concentration, temperature and pressure is unknown. Sada et al. [106] measured solubilities of carbon dioxide at 25 °C and at atmospheric pressure, from 0.19 to 1.35 mol dm^{-3} citric acid solutions and correlated them using the Markham-Kobe equation

$$\begin{aligned}
&\frac{\alpha}{\alpha_{H_2O}} = 0.08789m^{*} + \frac{1}{1 + 0.2251m^{*}} \\
&\alpha_{H_2O} = 0.7597; \quad m^{*} = m/\mathrm{mol\cdot kg^{-1}} < 1.75
\end{aligned} \tag{2.43}$$

Original units in Sada et al. [106] investigation are changed in Eq. (2.43), from molar to molal concentrations and α is the Bunsen absorption (solubility) coefficient defined as the volume of gas, reduced to standard conditions $T = 273.15$ K and $p = 101.325$ kPa, which is absorbed by the unit volume of solvent. Solubilities of gases in pure water, organic solvents and in electrolyte solutions can be obtained from the literature [107–110].

2.7 Volumetric Properties of Aqueous Solutions of Citric Acid

From physicochemical properties of aqueous solutions of citric acid, the volumetric properties based on numerous density determinations are much better documented than other properties. Densities over different concentration and temperature ranges (from 0 to 95 °C and from dilute to nearly saturated solutions) were repeatedly measured and about 850 experimental points (in part of them still unpublished) are analyzed here but probably much more results still exist in the literature. Evidently, most of densities are known in the 15–40 °C temperature range and usually in rather moderately concentrated citric acid solutions $m<1.0$ mol kg^{-1}. The old determinations are tabulated by Timmermans [70] and they include the systematic measurements performed by Gerlach in 1859 and 1898 at 15 °C, Schiff in 1860 at 12 °C, Linebarger in 1898 at 15 °C and Varga in 1912 at 18 °C. These densities are expressed as function of weight per cent of citric acid monohydrate in the solution and they are in an reasonable agreement with those which were reported much later. From modern measurements of density it is worthwhile to mention these performed at 25 °C by Levien [89]; Apelblat and Manzurola [111, 112] and Sijpkes et al. [113]. Densities at 20 °C are tabulated in CRC Handbook of Chemistry and Physics [71]. At more than one temperature, usually in 5 or 10 °C intervals, densities were measured by Patterson and Wooley [114] from 5 to 95 °C; Laguerie et al. [15] at 20 and 25 °C; Palmer et al. [115] and Tadkalkar et al. [116] from 25 to 45 °C; Kharat [117] from 25 to 40 °C; Maffia [118] from 20 to 50 °C and few measurements were performed by Darros-Barbosa et al. [119] from 10 to 60 °C.

At constant temperature T, densities as a function of weight fraction of citric acid w can accurately be represented by

$$\begin{aligned} d(T)/\mathrm{g\cdot cm^{-3}} &= d_w(T) + A(T)w + B(T)w^2 \\ d_w(T) &= d_{H_2O}(T)/\mathrm{g\cdot cm^{-3}} \end{aligned} \tag{2.44}$$

where A and B coefficients are presented in Table 2.8. In this way, the temperature dependence of densities of aqueous solutions of citric acid is expressed by known densities of water. All Eqs. (2.44) from Table 2.8, can be reduced to only one, nearly linear equation

$$\begin{aligned} F(w) &= \left[\frac{1}{d_{H_2O}(T)} - \frac{1}{d(m;T)}\right] \\ F(w)/\mathrm{cm^3\cdot g^{-1}} &= 0.41112w - 0.03700w^2 \end{aligned} \tag{2.45}$$

which is practically independent of temperature. This can be observed in Fig. 2.12 where all experimental densities are included. Thus, from Eq. (2.45) we have directly densities at given temperature T and mass fractions w by using the function F(w) and densities of pure water

Table 2.8 Densities of citric acid aqueous solutions as a function of temperature and concentration. A and B coefficients of Eq. (2.44)

t/°C	d_w	A(*T*)	B(*T*)	w*
0	0.99987	0.3778	0.1943	0.18[a]
5	0.99999	0.4329	0.1328	0.16
10	0.99973	0.4295	0.1142	0.16
12	0.99950	0.4070	0.1831	0.46
15	0.99913	0.4081	0.1636	0.61
18	0.99862	0.3801	0.1270	0.51
20	0.99823	0.4023	0.1590	0.63
25	0.99705	0.4056	0.1554	0.63
30	0.99868	0.4035	0.1526	0.31
35	0.99406	0.3986	0.1580	0.16
40	0.99224	0.3954	0.1603	0.50
45	0.99024	0.3942	0.1272	0.16
50	0.98807	0.3881	0.1604	0.20
55	0.98573	0.3867	0.1349	0.16
60	0.98324	0.3844	0.1292	0.16
65	0.98059	0.3772	0.1550	0.16
75	0.97489	0.3729	0.1550	0.16
85	0.96865	0.3772	0.0734	0.16
95	0.96192	0.3679	0.1420	0.16

[a] Correlated for the 0≤w≤w* mass fraction range

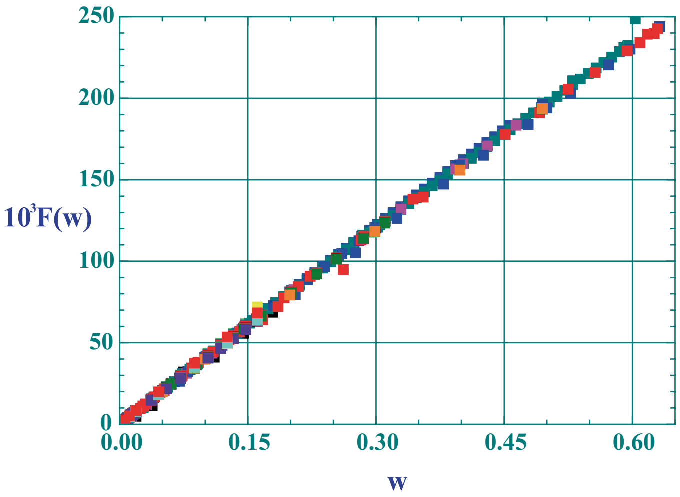

Fig. 2.12 Densities of citric acid aqueous solutions in the 0–95 °C temperature range, as expressed by Eq. (2.45). Each colour represents different temperature

$$\mathrm{d}(m;T) = \frac{\mathrm{d}_{\mathrm{H_2O}}(T)}{1 - \mathrm{d}_{\mathrm{H_2O}}(T)\mathrm{F(w)}}. \tag{2.46}$$

As a consequence, from Eqs. (2.45) and (2.46), it is possible give a good estimation for densities at any temperature and concentration of citric acid. Differentiation of Eq. (2.46) gives an estimation of the cubic expansion coefficient (thermal expansibility) for desired citric acid solutions

$$\begin{aligned} \alpha(m;T) &= -\frac{1}{d(m;T)}\left(\frac{\partial \mathrm{d}(m;T)}{\partial T}\right)_{P,m} \\ \alpha(m;T) &= \frac{\alpha_{\mathrm{H_2O}}(T)}{1 - \mathrm{d}_{\mathrm{H_2O}}(T)\mathrm{F(w)}} \end{aligned} \tag{2.47}$$

where densities and cubic expansion coefficients of pure water can be calculated in the 5–95 °C temperature range from

$$\begin{aligned} \mathrm{d}_{\mathrm{H_2O}}(T)/\mathrm{g{\cdot}cm^3} &= 0.9999727 + 4.035198{\cdot}10^{-5}\,\theta - 7.090436{\cdot}10^{-6}\,\theta^2 \\ &\quad + 3.554779{\cdot}10^{-8}\,\theta^3 - 1.0027098{\cdot}10^{-10}\,\theta^4 \\ \alpha_{\mathrm{H_2O}}(T){\cdot}10^6/\mathrm{K} &= -40.17909 + 14.13821\theta - 0.10439\theta^2 \\ &\quad + 4.26879{\cdot}10^{-4}\,\theta^3 - 3.25786{\cdot}10^{-8}\,\theta^4 \\ \theta &= T/\mathrm{K} - 273.15 \end{aligned} \tag{2.48}$$

These expressions were derived from densities of water given in the Robinson and Stokes book [72].

Since the product $\mathrm{d}_{\mathrm{H_2O}}(T)\mathrm{F(w)} < 1$, it follows from Eq. (2.47) that always for aqueous citric acid solutions we have $\alpha(m;T) > \alpha_{\mathrm{H_2O}}(T)$. Using Eq. (2.47), the cubic expansion coefficients can also be easily calculated by direct differentiation of density polynomials given in Table 2.8.

Aavailable sets of densities are enough accurate for general or engineering purposes, but less satisfactory if the volumetric properties of dilute aqueous solutions of citric acid are considered. The total volume of binary solution V, in terms of the partial volumes of solvent $\overline{V_1}$ and solute $\overline{V_2}$, is given by [120]

$$\begin{aligned} &V = \mathrm{n}_1\overline{V_1} + \mathrm{n}_2\overline{V_2} \\ &\overline{V_1} = \left(\frac{\partial V}{\partial \mathrm{n}_1}\right)_{T,\,P,\,\mathrm{n}_2} \quad ; \quad \overline{V_2} = \left(\frac{\partial V}{\partial \mathrm{n}_2}\right)_{T,\,P,\,\mathrm{n}_1} \end{aligned} \tag{2.49}$$

where n_1 and n_2 are the number of moles of solvent and solute (for concentrations expressed in molal units, numerically n_2 is m moles and n_1 is 55.508 moles).

The partial molar volumes are determined by using the apparent volume defined by

$$V_{2,\phi}(m;T) = \frac{V(m;T) - V_{H_2O}(T)}{m} \tag{2.50}$$

and expressed in terms of densities as

$$V_{2,\phi}(m;T) = \frac{M_2}{d(m;T)} + \frac{1000}{m}\left(\frac{1}{d(m;T)} - \frac{1}{d_{H_2O}(T)}\right) \tag{2.51}$$

At constant *T*, by differentiating Eq. (2.51), the partial volume of solute is

$$\overline{V_2}(m;T) = V_{2,\phi}(m;T) + m\left(\frac{\partial V_{2,\phi}(m;T)}{\partial m}\right)_{T,P} \tag{2.52}$$

and using also Eq. (2.50), the partial molar volume of solvent is

$$\overline{V_1}(m;T) = \overline{V_1}^{\,0}(m \to 0;T) - \frac{m^2}{55.508}\left(\frac{\partial V_{2,\phi}(m;T)}{\partial m}\right)_{T,P} \tag{2.53}$$

where $\overline{V_1}^{\,0}(m \to 0;T)$ is the partial molar volume of water at infinite dilution.

The apparent molar volume is not strongly influenced by errors in determined concentration, but in dilute solutions is very sensitive to experimental uncertainties of measured densities. This is clearly visible in Figs. 2.13 and 2.14 where the

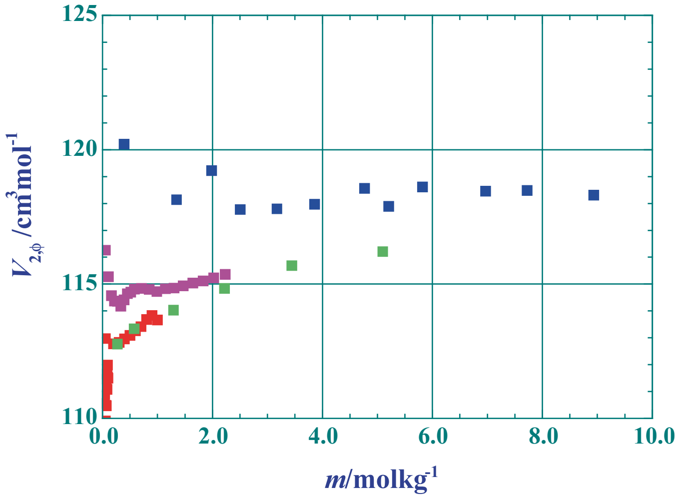

Fig. 2.13 The apparent molar volume of citric acid as a function of concentration at 20 °C. 🟦 - [15]; 🟪 - [71]; 🟩 - [118]; 🟥 - [author's unpublished results].

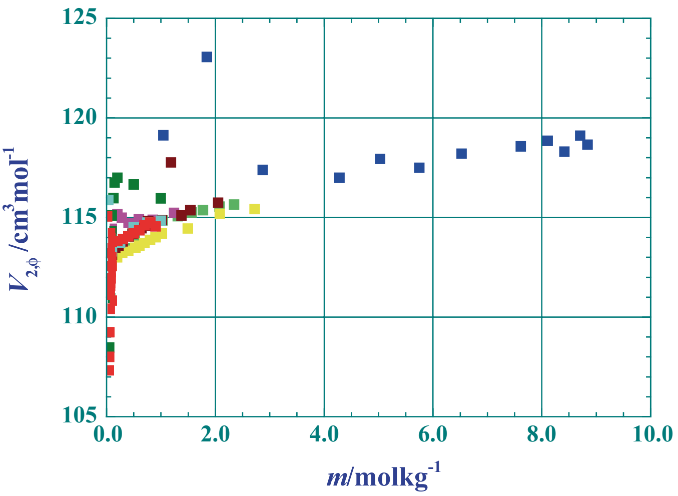

Fig. 2.14 The apparent molar volume of citric acid as a function of concentration at 25 °C. 🟦 - [15]; 🟪 - [89]; 🟩 - [112]; 🟫 - [111]; 🟨 - [113]; 🟦 - [114]; 🟩 - [117].; 🟥 - [author's unpublished results].

apparent molar volumes of citric acid at 20 and 25 °C are plotted as a function of concentration. As can be observed, the molar apparent volumes decrease almost linearly with m in the concentration region where citric acid is undissociated, but $V_{2,\phi}$ decrease much stronger in very dilute solutions due to the dissociation effect. Unfortunately, values of partial molar volumes of citric acid at infinite dilution $\bar{V}_2^{\,0}(m \to 0; T)$, based on the extrapolation of the apparent molar volumes to $m \to 0$ are clearly uncertain. This results from two reasons, the first is an insufficient accuracy of density determinations in dilute solutions of citric acid and the second reason is how the dissociation process is taken into account in the extrapolation of $V_{2,\phi}$ values. With an exception of Sijpkes et al. [113] who treated citric acid solutions as a mixture of molecular and dissociated monobasic acid molecules, all others considered citric acid as a fully dissociated electrolyte (i.e. $V_{2,\phi}$ linearly depends on $\sqrt{m}$). Sijpkes et al. determined the partial molar volume by applying the procedure introduced by King [121] where the experimental $V_{2,\phi}$ values are considered to be sums of two contributions coming from the molecular acid $V_{2,\phi}(H_3Cit)$ and dissociated molecules of citric acid $V_{2,\phi}(H^+ + H_2Cit^-)$

$$V_{2,\phi}(m) = (1-\alpha)V_{2,\phi}(m; H_3Cit) + \alpha V_{2,\phi}(m; H^+ + H_2Cit^-) \tag{2.54}$$

where α is the dissociation degree of the first dissociation step of citric acid. $V_{2,\phi}(H_3Cit)$ is assumed to be linearly proportional to m when $V_{2,\phi}(H^+ + H_2Cit^-)$ is proportional to $\sqrt{m}$ (it is usually assigned that $V^0(H^+) = 0$). Evaluated in such way the partial molar volume of citric acid at infinite dilution at 25 °C was $V^0(H_3Cit) = 113.60 \pm 0.06$ cm^3 mol^{-1}.

Derived differently, as for a fully dissociated electrolyte, Lieven [89] gave 114.7 $cm^3\ mol^{-1}$; Manzurola and Apelblat [111] 112.44 $cm^3\ mol^{-1}$; Apelblat and Manzurola [112] 113.93 $cm^3\ mol^{-1}$; Parmar et al. [115] presented much lower value of 94.76 ± 0.88 $cm^3\ mol^{-1}$ and Kharat [117] 110.32 $cm^3\ mol^{-1}$. Using the conventional basis of partial molar volumes at infinite dilution, Apelblat and Manzurola [112] reported the following values for the citrate ions $V^0(H_2Cit^-) = 98.1 \pm 1.0$ $cm^3\ mol^{-1}$, $V^0(HCit^{2-}) = 88.5 \pm 1.0$ $cm^3\ mol^{-1}$ and $V^0(Cit^{3-}) = 72.0 \pm 1.0$ $cm^3\ mol^{-1}$.

If values of the partial molar volumes at infinite dilution of acidic and neutral citrates are combined with those given here for citric acid, then it is possible to obtain the volume changes occurring in the consecutive steps of dissociation reactions

$$\begin{aligned} \Delta V_1 &= V^0(H_2Cit^-) - V^0(H_3Cit) \\ \Delta V_2 &= V^0(H_1Cit^{2-}) - V^0(H_2Cit^-) \\ \Delta V_3 &= V^0(Cit^{3-}) - V^0(H_1Cit^{2-}) \end{aligned} \tag{2.55}$$

At 25 °C, Apelblat and Manzurola [112] reported $\Delta V_1 = -15.8$ $cm^3\ mol^{-1}$; $\Delta V_2 = -9.6$ $cm^3\ mol^{-1}$ and $\Delta V_3 = -16.5$ $cm^3\ mol^{-1}$ when the Patterson and Woolley [114] values are $\Delta V_1 = -10.5 \pm 1.2$ $cm^3\ mol^{-1}$; $\Delta V_2 = -11.4 \pm 1.3$ $cm^3\ mol^{-1}$ and $\Delta V_3 = -17.0 \pm 1.4$ $cm^3\ mol^{-1}$. Temperature dependence of $\Delta V_i(T)$ is given elsewhere in this book.

As pointed above, Patterson and Woolley [114] performed measurements of density that cover a large temperature range, from 5 to 95 °C. Since they reported the apparent molar volumes at constant molalities, from 0.03 to 1.0 $mol\ kg^{-1}$, it is possible to differentiate their $V_{2,\phi}$ values with regard to temperature in this concentration region. This permits to describe in a more detail the volume-temperature relations in citric acid solutions. Thermal behaviour of these solutions is illustrated by arbitrarily choosing three solutions with the molalities 0.06; 0.5 and 1.0 $mol\ kg^{-1}$. It is observed that at constant m, the apparent molar volumes $V_{2,\phi}(m;T)$ increase with temperature T, $(\partial V_{2,\phi}(m;T)/\partial T)_{P,m} > 0$, but their dependence on m is very weak. Similarly, the cubic expansion coefficients, $\alpha(m;T)$, of aqueous citrate solutions increase with increasing temperature, $\partial \alpha(m;T)/\partial T)_{P,m} > 0$, but they also increase with concentration m and their values markedly differ at lower temperatures, as is illustrated in Fig. 2.15.

If the Maxwell relation is applied to the differential of enthalpy

$$d\,H = C_P dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P \right] dP \tag{2.56}$$

then volumetric and thermal properties of solutions can be interrelated by

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P \tag{2.57}$$

Thus, the second derivatives of volume with respect to temperature are related to changes of isobaric heat capacities with respect to pressure of investigated solutions.

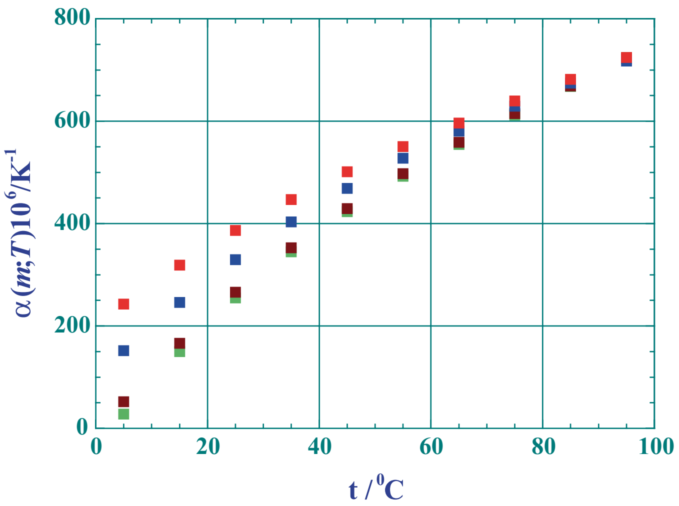

Fig. 2.15 Cubic expansion coefficients of water and citric acid solutions as a function of temperature. 🟩 - water; 🟫 - 0.06 mol kg^{-1}; 🟦 - 0.50 mol kg^{-1}; 114; 🟥 - 1.0 mol kg^{-1}

The product of temperature and the second derivative of the volume V with respect to temperature (denoted as $f(m;T)$ for citric acid solutions and $f(m=0;T)$ for pure water), can be expressed in terms of cubic expansion coefficients [122, 123]

$$\begin{aligned} f(m;T) &= T\left(\frac{\partial^2 V}{\partial T^2}\right)_{P,m} = T\,\mathrm{V}(m;T)\left[\alpha^2(m;T) + \left(\frac{\partial \alpha(m;T)}{\partial T}\right)_{P,m}\right] \\ \mathrm{V}(m;T) &= \frac{1000 + m\mathrm{M}_2}{\mathrm{d}(m;T)} \end{aligned} \tag{2.58}$$

or directly from the derivatives of density

$$\left(\frac{\partial^2 V}{\partial T^2}\right)_{P,\,m} = \frac{(1000 + m\mathrm{M}_2)}{\mathrm{d}^2(m;T)}\left[\frac{2}{\mathrm{d}(m;T)}\left(\frac{\partial \mathrm{d}(m;T)}{\partial T}\right)^2_{P,\,m} - \left(\frac{\partial^2 \mathrm{d}(m;T)}{\partial T^2}\right)\right] \tag{2.59}$$

The function $f(m;T) = -(\partial \mathrm{C}_P/\partial P)_{T,\,m} = T(\partial^2 V/\partial T^2)_{P,\,m}$ as showed by Hepler [124] plays an important role in understanding the effect of dissolved solutes on the structure of water. Similar conclusions were reached by Neal and Goring [125] who used instead of the first and second derivatives of total volume, the derivatives of the apparent specific volume $\phi_2 = V_{2,\phi}/\mathrm{M}_2$.

In a rather simple molecular model, it is assumed that water is a mixture of a structural low density form and an unstructured high density form. Dissolved solutes change the water structure and they are classified as the structure promoters and the structure breakers. The water structure changing is also expected by varying temperature or pressure. The "abnormal" high-heat capacity of water is usually attributed to the fact that water has a highly ordered hydrogen-bonded structure. With increasing pressure, this structure is partially destroyed and therefore it is expected that $(\partial C_P / \partial P)_{T,m}$ will be negative, and the product $f(m;T) = T(\partial^2 V / \partial T^2)_{P,m}$ will be positive. Increase in temperature has a similar effect on the heat capacity of water as pressure, and the product $f(m;T)$ is also positive and decreases with temperature. With an addition of solute, especially at high concentrations, not only solute–water but also solute–solute interactions should be taken into account, and their overall effect on the water structure is rather complex. Therefore, in order to minimize the contribution of the solute-solute interactions, Hepler [124] suggested to replace the second derivatives of the total volume with the second derivatives of the partial molar volume of solute at infinite dilution, $\bar{V}_2^0(T) = \bar{V}_2(m \to 0;T)$. Thus, according to Hepler, since $(\partial \bar{C}_2^0 / \partial P)_T$ is positive, the product $T(\partial^2 \bar{V}_2^0(T) / \partial T^2)_P$ should be negative for the structure-breaking solutes, and the curve is concave downward, $(\partial^2 \bar{V}_2^0(T) / \partial T^2)_P < 0$. For the structure-making solutes, the product should be positive, and the curve is concave upward, $(\partial^2 \bar{V}_2^0(T) / \partial T^2)_P > 0$.

However, these indicative criteria it is difficult to apply directly because the partial molar volumes of solutes at infinite dilution $\bar{V}_2^0(T) = \bar{V}_2(m \to 0;T)$ are usually not specially accurate. They are determined at each temperature T, by an extrapolation of experimental densities in very dilute solutions, $m \to 0$, and evidently their second derivatives with regard to temperature are expected to be even less accurate. In order to overcome this difficulty, it was proposed by the author to change these criteria and apply them for finite, low concentrations of solute in water. It follows from Eq. (2.49) that

$$\left(\frac{\partial^2 V}{\partial T^2}\right)_P = n_1 \left(\frac{\partial^2 \bar{V}_1}{\partial T^2}\right)_P + n_2 \left(\frac{\partial^2 \bar{V}_2}{\partial T^2}\right)_P \tag{2.60}$$

but in dilute solutions of molality m, the number of water moles, $n_1 = 55.508$, is considerably larger than those of solute, $n_1 \gg n_2$. This permits to approximate $n_1 \bar{V}_1$ with the volume of pure water V_1 and Eq. (2.60) becomes

$$\left(\frac{\partial^2 \bar{V}_2}{\partial T^2}\right)_{P,m} \approx \frac{1}{m}\left(\frac{\partial^2 [V - V_1]}{\partial T^2}\right)_{P,} \tag{2.61}$$

Since $[V - V_1]/m$ is the apparent molar volume $V_{2\phi}$, Eq. (2.61) can be written in the form

$$T\left(\frac{\partial^2 [V - V_1]}{\partial T^2}\right)_{P,m} = mT\left(\frac{\partial^2 V_{2,\phi}}{\partial T^2}\right)_{P,m} = -\left(\frac{\partial C_P - C_{P,1}}{\partial P}\right)_{T,m} \tag{2.62}$$

or in the terms of $f(m;T)$ functions as

$$\Delta f(m;T) = f(m;T) - f(m = 0;T) = T\left(\frac{\partial^2 [V - V_1]}{\partial T^2}\right)_{P,m} \tag{2.63}$$

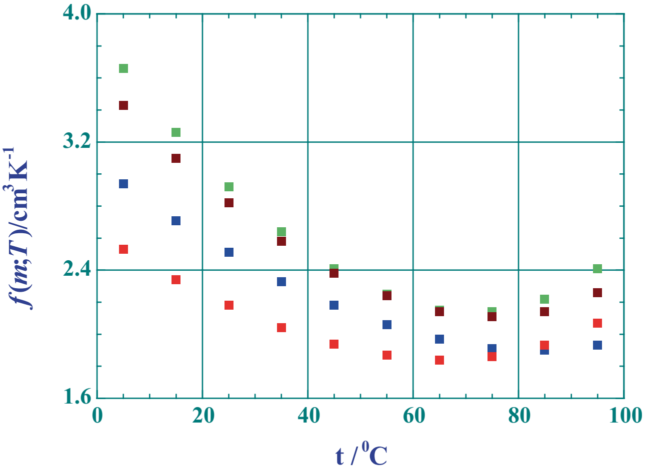

Fig. 2.16 Products of temperature and the second derivative of volume with respect to temperature of water and of citric acid solutions as a function of temperature. 🟩 - water; 🟫 - 0.06 mol kg^{-1}; 🟦 - 0.50 mol kg^{-1}; [114]; 🟥 - 1.0 mol kg^{-1}

where values of $f(m=0;T)$ are given in [122].

Applying Eq. (2.59), the product values, $f(m;T)=T(\partial^2 V/\partial T^2)_{P,m}$ were calculated using the Patterson and Wooley [114] densities in the 5–95 °C temperature range, and they are plotted in Fig. 2.16. As can be observed, all $f(m;T)$ functions behave similarly, they have positive values, decrease with temperature until the minimum value at near 65 °C, and then slightly increase. The curvature of the products $f(m;T)$ is concave upward. Since always $f(m=0;T)>f(m;T)$, the indicative parameter $\Delta f(m;T)$ is always negative and the curvature of curves is concave downward (Fig. 2.17). This clearly indicates the structure-breaking tendency of molecular citric acid in the citric acid–water system, at least in dilute aqueous solutions.

Systematic measurements of densities in ternary systems were performed only by Apelblat and Manzurola [112] who determined at 25 °C the mean apparent molar volumes of citric acid in aqueous solutions with potassium chloride and trisodium citrate.

The mean apparent molar volume is defined by

$$V_{2,3,\phi}(m_2,m_3)=\frac{V(m_2,m_3)-V_{\mathrm{H_2O}}}{m_2+m_3} \tag{2.64}$$

or in terms of densities

$$V_{2,3,\phi}(m_2,m_3)=\frac{m_2\mathrm{M}_2+m_3\mathrm{M}_3}{(m_2+m_3)\mathrm{d}}+\frac{1000}{(m_2+m_3)}\left(\frac{1}{\mathrm{d}}-\frac{1}{\mathrm{d}_{\mathrm{H_2O}}}\right) \tag{2.65}$$

where 2 denotes citric acid and 3 potassium chloride or trisodium citrate.

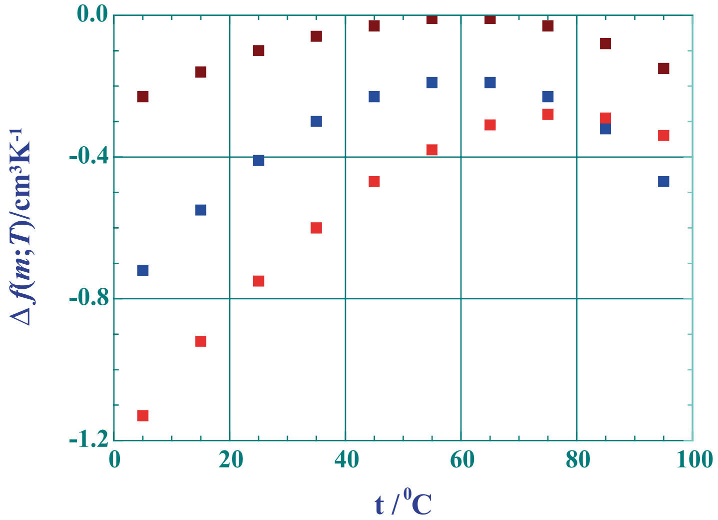

Fig. 2.17 Differences in the products of temperature and the second derivative of volume with respect to temperature of citric acid solutions and of pure water as a function of temperature. 🟫 - 0.06 mol kg^{-1}; 🟦 - 0.50 mol kg^{-1}; [114]; 🟥 - 1.0 mol kg^{-1}

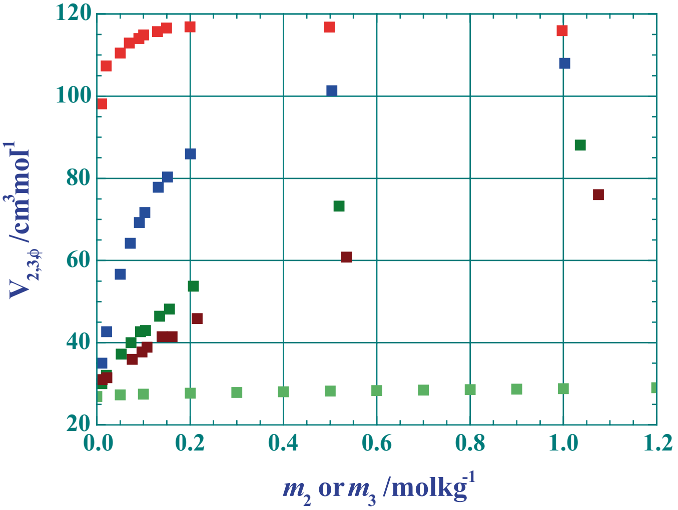

Fig. 2.18 The apparent molar volumes of citric acid and potassium chloride in aqueous solutions and the mean apparent molar volumes in the citric acid–potassium chloride solutions as a function of concentration at 25 °C. 🟥 - citric acid solutions [112]; 🟩 - KCl solutions [126]; citric acid + potassium chloride solutions 🟦 - 0.1012 mol kg^{-1} KCl; 🟩 - 0.5002 mol kg^{-1} KCl; 🟫 - 0.9972 mol kg^{-1} KCl [112].

The influence of different ionic media (KCl and $\mathrm{Na_3Cit}$) on the volumetric properties of citric acid solutions is illustrated in Figs. 2.18 and 2.19. The apparent molar volume of citric acid $V_{2,\phi}(\mathrm{H_3Cit})$ is considerably larger than that of potassium chloride $V_{2,\phi}(\mathrm{KCl})$ and it is always observed that $V_{2,\phi}(\mathrm{KCl}) < V_{2,3,\phi}(m_2,m_3) <$

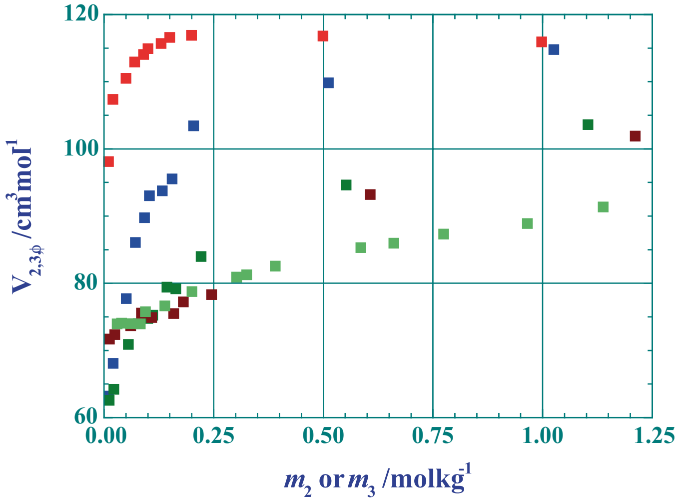

Fig. 2.19 The apparent molar volumes of citric acid and trisodium citrate in aqueous solutions and the mean apparent molar volumes in the citric acid–trisodium citrate solutions as a function of concentration at 25 °C [112]. 🟥 - citric acid solutions; 🟩 - trisodium citrate solutions; citric acid + trisodium citrate solutions 🟦 - 0.08719 mol kg^{-1} Na_3Cit; 🟩 - 0.4243 mol kg^{-1} Na_3Cit; 🟫 - 0.8211 mol kg^{-1} Na_3Cit

$V_{2,\phi}(H_3Cit)$ and the mean apparent volumes increase with citric acid concentration, $\partial V_{2,3,\phi}(m_2,m_3)/\partial m_2 > 0$. At constant m_3, the mean apparent molar volume increases with m_2, and an increase in concentration of KCl causes the difference $V_{2,\phi}(H_3Cit) - V_{2,3,\phi}(m_2,m_3)$ to increase. When potassium chloride is replaced by trisodium citrate, the picture is similar, but the overall effect is much smaller considering that $V_{2,\phi}(KCl) \ll V_{2,\phi}(Na_3Cit)$. At low concentrations of citric acid, $V_{2,\phi}(Na_3Cit) > V_{2,3,\phi}(m_2,m_3)$, and therefore the sign of $\partial V_{2,3,\phi}(m_2,m_3)/\partial m_2$ is expected to be negative and after this to be positive. Only in concentrated solutions of citric acid it is observed that $V_{2,\phi}(Na_3Cit) < V_{2,3,\phi}(m_2,m_3) < V_{2,\phi}(H_3Cit)$.

In three-component solutions, the mean apparent molar volume can be estimated from the Young rule [127]

$$V_{2,3,\phi}(m_2,m_3) = \frac{m_2}{m_2+m_3} V_{2,\phi}(m_2) + \frac{m_3}{m_2+m_3} V_{3,\phi}(m_3) \tag{2.66}$$

where $V_{2,\phi}$ and $V_{3,\phi}$ are the apparent molar volumes of components 2 and 3 in binary solutions of the ionic strength I, of the mixture.

In the case the citric acid–potassium chloride solutions, the formal ionic strength of the mixture is $I = 6m_2 + m_3$, but because citric acid is only partially dissociated, both the acid and KCl should be treated as electrolytes of the type 1:1 and then $I = m_2 + m_3$. Estimated from Eq. (2.66) values of $V_{2,3,\phi}(m_2,m_3)$ are in reasonable agreement with experiment for solutions with KCl and probably this will be also with other strong electrolytes.

However, the Young rule gives incorrect results in the case of trisodium citrate when introduced citrate ions influence dissociation equilibria.

2.8 Compressibility Properties of Aqueous Solutions of Citric Acid

Closely related to volumetric properties are compressibility properties of solutions, and they usually are evaluated from combining sound velocities, densities and heat capacity determinations. Sound velocity measurements in aqueous solutions of citric acid were initiated in 1952 by Miyahara [128] who determined at 20 °C, the isentropic (adiabatic) compressibility coefficients $\kappa_S(T;m)$ and hydration numbers $h(m;T)$ in dilute solutions, $m < 0.25$ mol kg^{-1}. Sound velocities $u(T;m)$ in the same concentration range were measured by Tadkalkar et al. [116] from 30 to 45 °C. In very dilute citric acid solutions $u(T;m)$ and $h(m;T)$ values are reported by Burakowski and Gliński [129, 130]. Parke et al. [131] correlated the taste and properties of solutions, namely the apparent molar compressibilities, hydration numbers, apparent molar volumes and apparent specific volumes of 3 % citric acid solution. In moderately concentrated citric acid solutions, m < 0.5 mol kg^{-1} (in water or in the water + DMSO and water + DMF mixtures), measurements were performed by Bhat et al. [132] at 30 °C. Kharat [117] reported a more complete set of speed velocities, the isentropic (adiabatic) compressibility coefficients and the apparent molar compressibilities $K_{2,\phi}(T;m)$, for $m < 2.35$ mol kg^{-1} citric acid solutions in 25–40 C temperature range. The most systematic investigation of compressibility properties and their thermodynamic analysis ($m < 5.0$ mol kg^{-1} and for 15–50 °C) was performed by Apelblat et al. [133]. The agreement between the reported in the literature sound velocities and derived from them $\kappa_S(T;m)$ values is unsatisfactory. This is easily illustrated when not sound velocities which have a large numerical value, but differences between sound velocities in solutions and in pure water, $\Delta u(T;m) = u(T;m) - u_1(\mathrm{T})$ are compared. This is important because water is usually used as a standard in the calibration of measuring equipment. Over a wide temperature range, based on critical analysis of known in the literature equations, Marczak [134] proposed the following "best" equation for sound velocities of pure water $u_1(T)$

$$\begin{aligned} u_1(T)\,/\,\mathrm{m{\cdot}s^{-1}} &= 1.402385{\cdot}10^{3} + 5.038813{\cdot}10^{0}\,\theta - 5.799136{\cdot}10^{-2}\,\theta^2 \\ &\quad + 3.287156{\cdot}10^{-4}\,\theta^3 - 1.398845{\cdot}10^{-6}\,\theta^4 + 2.78786{\cdot}10^{-9}\,\theta^5 \\ \theta &= T/K - 273.15 \end{aligned} \tag{2.67}$$

As can be seen in Figs. 2.20 and 2.21, it is clear by comparing $\Delta u(T;m)$ values in citric acid solutions, that the Tadkalkar et al. [116] and especially the Bhat et al. [132] sound velocities are considerably less accurate. All available in the literature $u(T;m)$ values are compiled in Table 2.9.

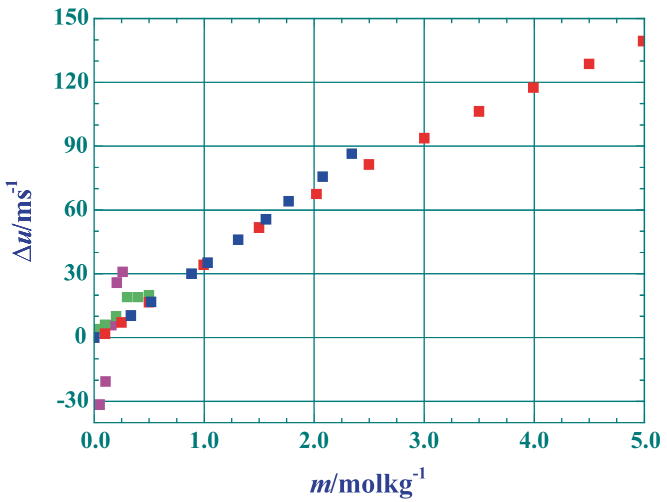

Fig. 2.20 Differences between sound velocities in citric acid solutions and in pure water as a function of concentration, at 30 °C. 🟦 - [117]; 🟪 - [116]; 🟩 - [132] and 🟥 - [133]

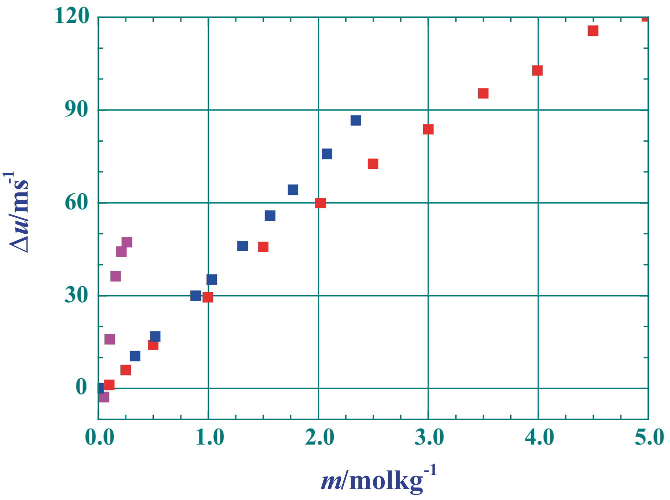

Fig. 2.21 Differences between sound velocities in citric acid solutions and in pure water as a function of concentration, at 35 °C. 🟦 - [117]; 🟩 - [132] and 🟥 - [133]

Sound velocities in citric acid solutions are always higher than those in pure water, i.e. $\Delta u(T;m)=u(T;m)-u_1(\mathrm{T})>0$ (Fig. 2.22), and they monotonically increase with concentration m, but their temperature dependence is more complex. At constant concentration m, up to about 3.0 mol kg^{-1}, they increase with temperature (e.g. if $T_1>T_2$ then $u(T_1;m)>u(T_2;m)$), but in more concentrated

Table 2.9 Sound velocities in water and in citric acid solutions as a function of concentration and temperature

t/°C	*m**	*u**(*T*;*m*)	*m**	*u**(*T*;*m*)	*m**	*u**(*T*;*m*)
15	0.0000 [133]	1465.96	1.5015	1538.01	3.9985	1626.16
	0.1003	1469.94	2.0230	1560.31	4.5063	1640.72
	0.2504	1477.42	2.5023	1578.80	4.9975	1654.69
	0.5006	1490.47	3.0057	1595.36		
	0.9988	1514.98	3.5049	1613.08		
20	0.0000 [133]	1482.38	2.5023	1584.10	0.1746 [128]	1490.24
	0.1003	1485.86	3.0057	1598.92	0.2468	1494.09
	0.2504	1492.46	3.5049	1615.31	0.1601	1489.50
	0.5006	1504.05	3.9985	1628.71	0.1855	1490.83
	0.9988	1526.42	4.5063	1636.65		
	1.5015	1547.09	4.9975	1653.35		
	2.0230	1567.13				
25	0.0000 [130]	1497.00	0.0000 [117]	1496.00	0.0000 [133]	1496.73
	0.0283	1498.30	0.3351	1506.40	0.1003	1499.36
	0.0561	1499.40	0.5175	1512.80	0.2504	1505.51
	0.0828	1500.70	0.8848	1520.80	0.5006	1516.08
	0.1118	1501.90	1.0321	1531.60	0.9988	1535.76
	0.1397	1503.20	1.3109	1542.40	1.5015	1554.41
	0.1653	1504.20	1.5615	1552.00	2.0230	1572.53
	0.1916	1505.50	1.7697	1560.00	2.5023	1587.93
			2.0790	1572.00	3.0057	1602.97
			2.3422	1582.40	3.5049	1616.69
					3.9985	1629.14
					4.5063	1641.01
					4.9975	1651.26
30	0.0000 [116]	1502.28	0.0000 [117]	1509.20	0.0000 [133]	1509.17
	0.0521	1470.77	0.3351	1519.60	0.1003	1510.89
	0.1040	1481.53	0.5175	1526.00	0.2504	1516.22
	0.1580	1508.06	0.8848	1539.20	0.5006	1525.69
	0.2080	1528.10	1.0321	1544.40	0.9988	1543.30
	0.2600	1533.09	1.3109	1555.20	1.5015	1560.82
			1.5615	1564.80	2.0230	1576.67
	0.00 [132, in mol dm^{-3}]	1504.00	1.7697	1573.20	2.5023	1590.50
	0.05	1508.00	2.0790	1584.80	3.0057	1602.98
	0.10	1510.00	2.3422	1595.60	3.5049	1615.58
	0.20	1514.00			3.9985	1626.71
	0.30	1523.00			4.5063	1637.75
	0.40	1523.00			4.9975	1648.59
	0.50	1524.00				

Table 2.9 (continued)

t/°C	m^*	$u^*(T;m)$	m^*	$u^*(T;m)$	m^*	$u^*(T;m)$
35	0.0000 [116]	1511.76	0.0000 [117]	1519.60	0.0000 [133]	1519.85
	0.0521	1509.00	0.3351	1530.00	0.1003	1521.03
	0.1040	1527.62	0.5175	1536.40	0.2504	1525.79
	0.1580	1548.02	0.8848	1549.60	0.5006	1533.91
	0.2080	1556.00	1.0321	1554.80	0.9988	1549.36
	0.2600	1558.96	1.3109	1565.60	1.5015	1565.58
			1.5615	1575.40	2.0230	1579.79
			1.7697	1583.80	2.5023	1592.41
			2.0790	1595.40	3.0057	1603.60
			2.3422	1606.20	3.5049	1615.17
					3.9985	1622.60
					4.5063	1635.46
					4.9975	1640.12
40	0.0000 [116]	1516.72	0.0000	1528.80 [117]	0.0000 [133]	1528.89
	0.0521	1533.28	0.3351	1539.20	0.1003	1529.77
	0.1040	1548.00	0.5175	1545.20	0.2504	1533.86
	0.1580	1552.62	0.8848	1558.40	0.5006	1541.18
	0.2080	1556.35	1.0321	1564.00	0.9988	1554.87
	0.2600	1564.00	1.3109	1574.80	1.5015	1569.46
			1.5615	1584.40	2.0230	1582.25
			1.7697	1592.80	2.5023	1593.65
			2.0790	1604.40	3.0057	1603.77
			2.3422	1615.20	3.5049	1614.16
					3.9985	1621.00
					4.5063	1632.73
					4.9975	1635.65
45	0.0000	1524.05 [116]	0.0000 [133]	1536.43	2.5023	1593.90
	0.0521	1539.92	0.1003	1537.21	3.0057	1599.94
	0.1040	1554.32	0.2504	1540.48	3.5049	1612.59
	0.1580	1563.20	0.5006	1546.14	3.9985	1618.87
	0.2080	1568.29	0.9988	1558.18	4.5063	1629.59
	0.2600	1573.30	1.5015	1571.98	4.9975	1632.06
			2.0230	1583.66		
50	0.0000 [133]	1542.57	1.5015	1573.31	3.9985	1615.37
	0.1003	1542.62	2.0230	1582.59	4.5063	1625.29
	0.2504	1545.93	2.5023	1592.90	4.9975	1626.12
	0.5006	1550.68	3.0057	1598.17		
	0.9988	1561.13	3.5049	1609.72		

$m^* = m/\text{mol kg}^{-1}$; $u^*(T;m) = u(T;m)/\text{m s}^{-1}$

solutions the inversion occurs as can be observed in Fig. 2.22, then for $T_1 > T_2$ we have $u(T_1;m) < u(T_2;m)$.

From the knowledge of sound velocities, $u(T;m)$, densities d(($T;m$), viscosities, η(($T;m$) and specific heats, $c_p(T;m)$, it is possible to evaluate a number of

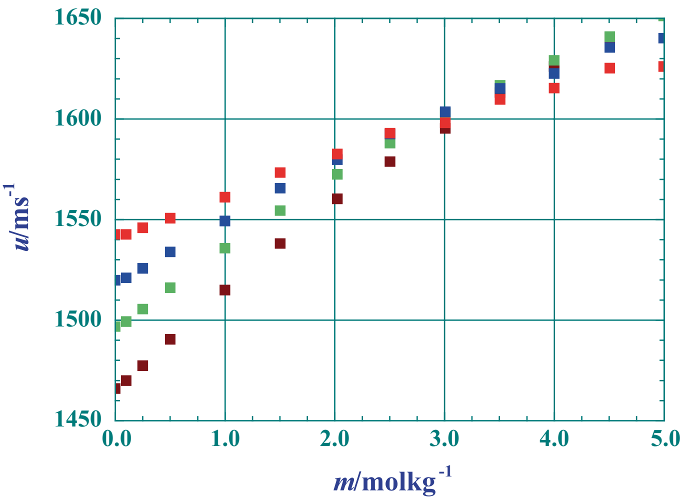

Fig. 2.22 Sound velocities in citric acid solutions as a function of concentration and temperature [133]. 🟫 - 15 °C; 🟩 - 25 °C; 🟦 - 35 °C and 🟥 - 50 °C

thermodynamic quantities which characterize compressibility properties of solutions. Using $u(T;m)$, and d((T;m) values, from the Newton-Laplace equation, the isentropic (adiabatic) compressibility coefficient is determined from

$$\begin{aligned} \kappa_S(T;m) &= -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{S,m} \\ \kappa_S(T;m) &= \frac{1}{u^2(T;m)\,\mathrm{d}(T;m)} \end{aligned} \tag{2.68}$$

The isothermal and isentropic compressibility coefficients are interrelated by

$$\begin{aligned} \kappa_T(T;m) &= -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,m} \\ \kappa_T(T;m) &= \kappa_S(T;m) + \frac{T\alpha^2(T;m)}{C_P(T;m)} \end{aligned} \tag{2.69}$$

where $\alpha(T;m)$ is the cubic expansion coefficient, and $C_p(T;m)$ is the isobaric heat capacity of solution per unit volume given by $C_p(T;m) = \mathrm{d}(T;m)\, c_p(T;m)$. Values of $\kappa_S(T;m)$ and $\kappa_T(T;m)$ based on known speed velocities, densities and heat capacities [79, 80, 135] are presented in Table 2.10. Since the second term in Eq. (2.69) is positive it follows that $\Delta\kappa(T;m) = \kappa_T(T;m) - \kappa_S(T;m) > 0$. The difference in compressibility coefficients $\Delta\kappa(T;m)$ increases with concentration of citric acid and temperature (if $T_1 > T_2$ then $\Delta\kappa(T_1;m) > \Delta\kappa(T_2;m)$), as shown in Fig. 2.23 where are plotted values of $\Delta\kappa(T;m)$ at 35 and 50 °C.

Table 2.10 The isentropic and isothermal compressibility coefficients of water and citric acid solutions as function of concentration and temperature

m^*	$\kappa_S(T;m)\cdot 10^{10}/\text{Pa}^{-1}$							
t/ °C	15	20	25	30	35	40	40	45
0.0000[a]	4.66	4.56	4.48	4.41	4.36	4.31	4.28	4.25
0.1003	4.60	4.50	4.43	4.37	4.32	4.27	4.24	4.22
0.2504	4.50	4.41	4.34	4.29	4.24	4.21	4.18	4.16
0.5006	4.34	4.27	4.21	4.16	4.13	4.10	4.08	4.06
0.9988	4.08	4.02	3.98	3.94	3.92	3.90	3.90	3.89
1.5015	3.85	3.81	3.78	3.75	3.74	3.73	3.73	3.73
2.0230	3.65	3.63	3.60	3.59	3.58	3.58	3.59	3.60
2.5023	3.49	3.48	3.46	3.46	3.46	3.46	3.48	3.49
3.0057	3.36	3.35	3.34	3.34	3.35	3.36	3.39	3.40
3.5049	3.23	3.23	3.23	3.24	3.25	3.26	3.29	3.30
3.9985	3.13	3.13	3.13	3.15	3.17	3.19	3.22	3.23
4.5063	3.04	3.06	3.05	3.07	3.08	3.10	3.14	3.15
4.9975	2.95	2.97	2.97	2.99	3.03	3.05	3.09	3.11
	$\kappa_T(T;m)\cdot 10^{10}/\text{Pa}^{-1}$							
0.0000 [133]	4.67	4.59	4.53	4.48	4.44	4.42	4.42	4.42
0.1003	4.61	4.53	4.48	4.44	4.41	4.39	4.39	4.39
0.2504	4.52	4.45	4.40	4.36	4.34	4.33	4.33	4.34
0.5006	4.36	4.31	4.27	4.25	4.24	4.24	4.25	4.27
0.9988	4.10	4.07	4.05	4.05	4.06	4.08	4.10	4.13
1.5015	3.87	3.86	3.86	3.87	3.90	3.93	3.97	4.01
2.0230	3.68	3.69	3.70	3.73	3.76	3.81	3.87	3.93
2.5023	3.53	3.55	3.57	3.61	3.66	3.72	3.79	3.86
3.0057	3.41	3.43	3.46	3.51	3.57	3.64	3.74	3.83
3.5049	3.29	3.32	3.36	3.42	3.49	3.57	3.67	3.77
3.9985	3.20	3.24	3.28	3.34	3.43	3.52	3.63	3.75
4.5063	3.12	3.17	3.21	3.27	3.35	3.45	3.58	3.71
4.9975	3.04	3.09	3.13	3.21	3.31	3.42	3.57	3.71

$m^* = m/\text{mol kg}^{-1}$

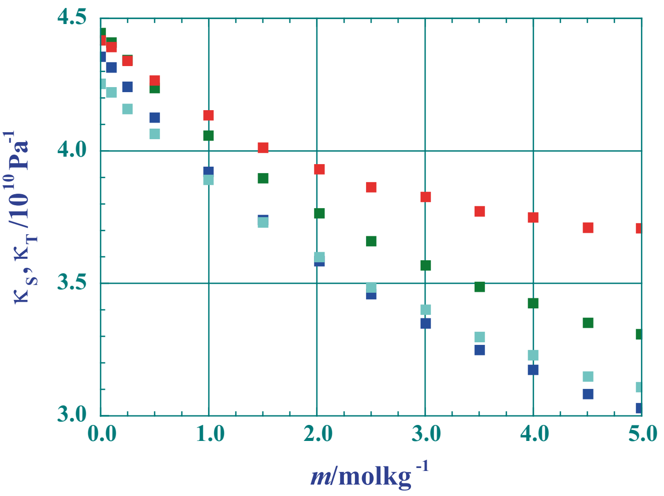

Fig. 2.23 The isothermal compressibility coefficients $\kappa_T(m)$ and the isentropic compressibility coefficients $\kappa_S(m)$ of aqueous solutions of citric acid as a function of concentration at 35 and 50 °C. $\kappa_T(m)$ 🟩 - 35 °C; 🟥 - 50 °C; $\kappa_S(m)$ 🟦 - 35 °C and ▨ - 50 °C

Rao [136, 137] proposed to correlate sound velocities and adiabatic compressibility coefficients of organic liquids or mixtures by the empirical relation

$$R_1(m) = \frac{M_{12} u^{1/3}(T;m)}{d(T;m)} \tag{2.70}$$

or in an alternative form by

$$R_2(m) = \kappa_S^{1/7}(T;m) \cdot d(T;m) \tag{2.71}$$

where $M_{12} = x\ M_1 + (1 - x)\ M_2$ is the average molecular mass. Wada [138] proposed a similar expression

$$R_3(m) = \frac{M_{12}}{\kappa_S^{1/7}(T;m) \cdot d(T;m)} \tag{2.72}$$

$R_1(m)$, $R_2(m)$ and $R_3(m)$ are useful functions because they are weakly dependent on temperature (for theoretical basis of these relations see Mathur et al. [139]). In the case of citric acid solutions, $R_1(m)$ and $R_3(m)$ almost linearly depended on concentration m, $R_1(m) \cdot 10^6/\mathrm{m}^{10/3}\ \mathrm{s}^{-1/3}\ \mathrm{mol}^{-1} = 207.9 + 20.99\ m^*$ and $\sigma[R_1(m) \cdot 10^6/\mathrm{m}^{10/3}\ \mathrm{s}^{-1/3}\ \mathrm{mol}^{-1}] = 1.8$ and $R_3(m) \cdot 10^6/\mathrm{m}^3\ \mathrm{MPa}^{1/7}\ \mathrm{mol}^{-1} = 54.64 + 5.968\ m^*$ and $\sigma[R_3(m) \cdot 10^6/\mathrm{m}^3\ \mathrm{MPa}^{1/7}\ \mathrm{mol}^{-1}] = 0.42$ where $m^* = m/\mathrm{mol\ kg}^{-1}$. $R_2(m)$ function is not given because it has a parabolic form.

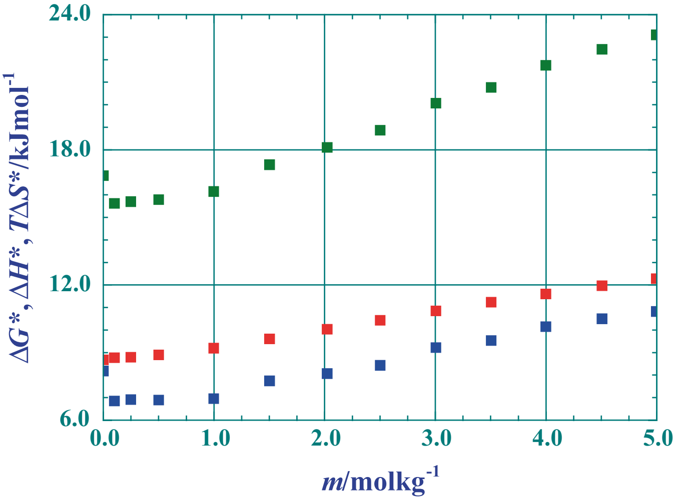

Fig. 2.24 Thermodynamic functions of activation in aqueous solutions of citric acid, at 25 °C [133]. 🟥 - $\Delta G^*(m)$; 🟩 - $\Delta H^*(m)$; 🟦 - $T\Delta S^*(m)$

The ultrasonic (viscous) relaxation times, $\tau(T;m) = (4/3)\kappa_S(T;m)\cdot\eta(T;m)$, can be determined using the isentropic compressibility coefficients and viscosities of solutions. Their values are always larger than those of water, $\tau(T;m) > \tau(T;0)$. At constant m, the ultrasonic relaxation times decrease with increasing T, $(\partial\tau(T;m)/\partial T)_m < 0$ and at constant T, they increase with increasing m, $(\partial\tau(T;m)/\partial m)_T > 0$. In citric acid solutions which are more concentrated that about 1.0 mol kg^{-1}, the ultrasonic relaxation times increase exponentially [133]. According to the Eyring transition state theory, the ultrasonic relaxation times are correlated with the thermodynamic functions of activation of the viscous process in the following way

$$\begin{aligned}
\Delta G^*(T;m) &= -\mathrm{R}T\ln\left[\left(\frac{\mathrm{h}}{\mathrm{k}T}\right)\tau^{-1}(T;m)\right]\\
\Delta S^*(T;m) &= -\left(\frac{\partial\Delta G^*(T;m)}{\partial T}\right)_m\\
\Delta G^*(T;m) &= \Delta H^*(T;m) - T\Delta S^*(T;m)
\end{aligned} \tag{2.73}$$

where h and k denote the Planck and the Boltzmann constants. Over the 0–5.0 mol kg^{-1} range of concentrations and from 15 to 50 °C, the change in $\Delta G^*(T;m)$ is rather small, from 9.0 to11.7 kJ mol^{-1}. All thermodynamic functions increase with increasing m and decrease with increasing T. Since $(\partial\Delta G^*(T;m)/\partial T)_m < 0$ it follows that $T\cdot\Delta S^*(T;m)>0$ and $\Delta H^*(T;m)>\Delta G^*(T;m)>T\cdot\Delta S^*(T;m)>0$. A typical behaviour of the thermodynamic functions of activation in the case of citric acid solutions is shown in Fig. 2.24.

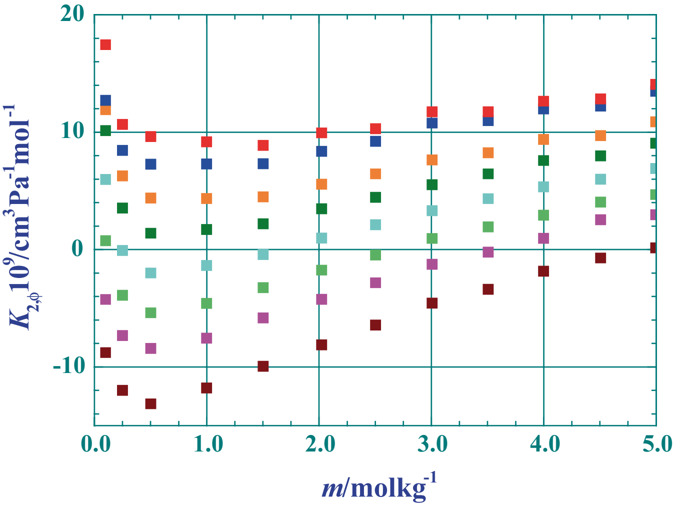

Fig. 2.25 The apparent molar isentropic compressibilities, $K_{2,\phi}$ $(T;m)$ of citric acid solutions as a function of concentration m and temperature T [133]. ■ - 15 °C; ■ - 20 °C; ■ - 25 °C; ■ - 30 °C; ■ - 35 °C; ■ - 40 °C; ■ - 45 °C and ■ - 50 °C

The apparent molar isentropic compressibility is defined similarly as the apparent molar volume

$$K_{2,\phi}(T;m)=\frac{\mathrm{M}_2\kappa_S(T;m)}{\mathrm{d}(T;m)}+\frac{1000}{m}\left(\frac{\kappa_S(T;m)}{\mathrm{d}(T;m)}-\frac{\kappa_{S,1}(T)}{\mathrm{d}_1(T)}\right) \tag{2.74}$$

and it expresses the effect of pressure on the partial volume of solutes. In strong electrolyte solutions $K_{2,\phi}(T;m)$ values are negative, but in aqueous solutions with organic acids, in moderately concentrated solutions when organic acids are undissociated the apparent molar isentropic compressibilities behave differently. As can be observed in Fig. 2.25, initially $K_{2,\phi}(T;m)$ decrease with concentration until the minimal value and after this they increase. The minimum is shifted with increasing temperature to higher concentrations. For $m<2.0$ mol kg^{-1} and temperatures lower than 30 °C the apparent molar isentropic compressibilities have negative values. At higher temperatures and concentrations, $K_{2,\phi}(T;m)$ are positive and increase with m. Similar behaviour was observed in aqueous solutions of other organic acids [140, 141].

Knowing values of the isothermal compressibility coefficients $\kappa_T(T;m)$ and the cubic expansion coefficients $\alpha(T;m)$ it is possible from the thermodynamic relation

$$\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial T}{\partial V}\right)_P\left(\frac{\partial V}{\partial P}\right)_T=-1 \tag{2.75}$$

to evaluate the isochoric thermal pressure coefficient, $\gamma_V(T;m)$ from

$$\gamma_V(T;m) = \left(\frac{\partial P}{\partial T}\right)_{V,\,m} = \frac{\alpha(T;m)}{\kappa_T(T;m)} \tag{2.76}$$

The product of $T \cdot \gamma_V(T;m)$ is very close to the internal pressure of solutions $P_{\text{int}}.(T;m)$ [142]. The isochoric thermal pressure coefficients monotonically increase with m and T, i.e. $\left(\frac{\partial \gamma_V(T;m)}{\partial m}\right)_T > 0$ and $\left(\frac{\partial \gamma_V(T;m)}{\partial T}\right)_m > 0$ and at any given temperature, the isochoric thermal pressure coefficients of pure water is always smaller than those in citric acid solutions, $[\gamma_V(T;m) - \gamma_V(T;0)] > 0$ (Table 2.11, [133]).

By changing the order of differentiation

$$\frac{\partial}{\partial P}\left[\left(\frac{\partial V}{\partial T}\right)_P\right]_T = \frac{\partial}{\partial T}\left[\left(\frac{\partial V}{\partial P}\right)_T\right]_P \tag{2.77}$$

the change of cubic expansion coefficient $\alpha(T;m)$ with pressure is the complement of the change of isothermal compressibility coefficient $\kappa_T(T;m)$ with temperature

$$\left(\frac{\partial \alpha(T;m)}{\partial P}\right)_{T,m} = -\left(\frac{\partial \kappa_T(T;m)}{\partial T}\right)_{P,m} \tag{2.78}$$

In citric acid solutions, the change of expansion coefficients $\alpha(T;m)$ with pressure P decreases with increasing concentration and temperature and they are smaller than those in pure water. Their values are always positive in water, in citric acid solutions they change sign depending on concentration and temperature as can be observed in Table 2.12.

From the differential of internal energy

$$dU = C_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]dV \tag{2.79}$$

by applying the Maxwell relation to it, (similarly as in Eq. (2.56)), it is possible to derive the change of isochoric heat capacity with volume at constant temperature

$$\begin{aligned}\left(\frac{\partial C_V}{\partial V}\right)_{T,m} &= T\left(\frac{\partial^2 P}{\partial T^2}\right)_{V,m} = T\left(\frac{\partial \gamma_V(T;m)}{\partial T}\right)_{V,m} \\ g(T;m) &= T\left(\frac{\partial^2 P}{\partial T^2}\right)_{V,m} = \left(\frac{\partial C_V}{\partial V}\right)_{T,m}\end{aligned} \tag{2.80}$$

Table 2.11 The isochoric thermal pressure coefficients of water and citric acid solutions as a function of concentration and temperature

*m**	$\gamma_V(T;\text{m}) \cdot 10^5/\text{Pa K}^{-1}$							
t/°C	15	20	25	30	35	40	40	45
0.0000 [133]	3.22	4.50	5.69	6.78	7.79	8.71	9.56	10.35
0.1003	3.30	4.61	5.85	7.00	8.05	9.00	9.85	10.58
0.2504	3.42	4.83	6.15	7.36	8.46	9.45	10.31	11.05
0.5006	3.67	5.21	6.65	7.96	9.14	10.17	11.06	11.81
0.9988	4.24	6.01	7.64	9.11	10.41	11.55	12.50	13.31
1.5015	4.94	6.85	8.62	10.21	11.63	12.87	13.92	14.82
2.0230	5.77	7.75	9.59	11.26	12.76	14.09	15.23	16.23
2.5023	6.61	8.58	10.44	12.15	13.71	15.12	16.35	17.49
3.0057	7.52	9.43	11.27	13.00	14.60	16.07	17.34	18.60
3.5049	8.46	10.27	12.07	13.78	15.42	16.98	18.37	19.76
3.9985	9.34	11.06	12.81	14.49	16.12	17.73	19.20	20.69
4.5063	10.21	11.76	13.49	15.20	16.89	18.55	20.08	21.66
4.9975	10.98	12.49	14.16	15.82	17.48	19.15	20.70	22.34

$m^* = m/\text{mol kg}^{-1}$

Table 2.12 The change of the cubic expansion coefficients with pressure in water and citric acid solutions as a function of concentration and temperature

*m**	$(\partial\alpha/\partial P)_{T,m}\cdot10^8/\mathrm{Pa}^{-1}\,\mathrm{K}^{-1}$							
t/°C	15	20	25	30	35	40	40	45
0.0000 [133]	19.1	14.8	11.1	8.0	5.3	2.8	0.7	−1.4
0.1003	18.1	13.5	9.6	6.6	4.3	2.4	0.4	−2.7
0.2504	15.9	12.0	8.3	5.2	2.8	1.0	−0.6	−2.4
0.5006	12.5	9.4	6.1	3.0	0.6	−1.3	−2.6	−3.8
0.9988	8.3	4.9	1.8	−0.9	−3.2	−4.9	−5.9	−6.0
1.5015	3.3	1.4	−0.9	−3.4	−5.8	−7.6	−8.6	−8.1
2.0230	−0.2	−1.7	−3.9	−6.4	−8.7	−10.7	−12.0	−12.6
2.5023	−1.6	−4.1	−6.0	−8.3	−11.0	−13.6	−14.9	−12.7
3.0057	−2.5	−5.8	−7.5	−9.9	−13.7	−17.8	−19.4	−13.9
3.5049	−4.4	−7.5	−9.4	−11.8	−15.2	−18.9	−21.1	−18.4
3.9985	−4.5	−7.6	−10.7	−14.2	−17.9	−21.2	−23.3	−22.6
4.5063	−14.9	−7.8	−8.9	−13.7	−19.2	−23.5	−25.8	−26.7
4.9975	−10.2	−9.2	−12.0	−16.6	−21.8	−26.1	−28.7	−28.8

$m^* = m/\mathrm{mol\,kg^{-1}}$

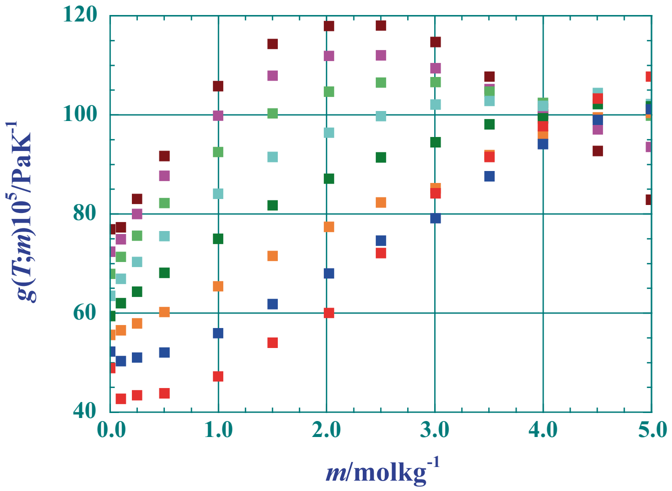

Fig. 2.26 The change of isochoric heat capacity with volume, $g(T = \text{const.}; m)$ of water and citric acid solutions as a function of concentration m and temperature T [133]. 🟥 - 15 °C; 🟪 - 20 °C; 🟩 - 25 °C; 🟦 - 30 °C; 🟩 - 35 °C; 🟧 - 40 °C; 🟦 - 45 °C and 🟥 - 50 °C

Thus, by using thermodynamic relations, in the same way as in the case of volumetric and thermal properties of solutions (see Eq. (2.57)), it is possible to correlate the compressibility and thermal properties. By differentiation of the isochoric thermal pressure coefficient $\gamma_V(T;m)$ with regard to T, the change of isochoric heat capacity with volume at constant temperature can be evaluated. Its value for pure water and citric acid solutions increases with increasing volume because the second derivative of the pressure with respect to temperature is positive, $g(T;m) = T(\partial^2 P / \partial T^2)_{V,m} > 0$.

As can be expected, $g(T;m)$ is rather complex function of both variables, T and m. In Fig. 2.26 are plotted changes of isochoric heat capacity with volume, $g(T = \text{const.}; m.)$ for water and citric acid solutions. As can be observed, for temperatures lower than about 30 °C, $g(T;m)$ curves have curvature concave downward ($g''(T = \text{const}; m) < 0$) with the maximum (at about 2.0 mol kg^{-1} at 15 °C) which is shifted to higher concentrations when temperature increases. After this, the curvature changes gradually to concave upward ($g''(T = \text{const}; m) > 0$). After about 4.0 mol kg^{-1}, the change in temperature has an inverse effect on the isochoric heat capacities of citric acid solutions.

It is interesting also to consider the behaviour of $g(T; m = \text{const.})$ functions because these functions are analogous to those introduced in Eq. (2.58) for the volumetric properties of solutions. Similarly as the function $f(m;T)$, also $g(m;T)$ can give an indication about the structure-breaking or the structure-making character of dissolved solute. As can be observed in Figs. 2.27 and 2.28, the curves $g(T; m = \text{const.})$ behave quite differently for moderately concentrated solutions of citric acid than in more concentrated solutions. If $m < 2.5$ mol kg^{-1}, the change of isochoric heat capacity with volume monotonically decreases with temperature T and increases with concentration m. The curvature of $g(T;m = \text{const.})$ curves is always

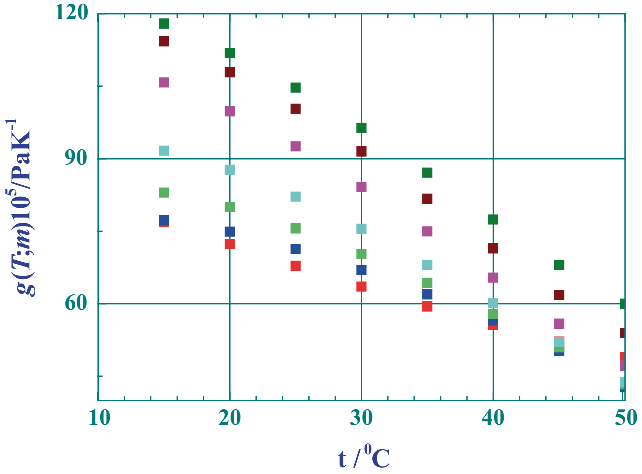

Fig. 2.27 The change of isochoric heat capacity with volume, $g(T;\ m=\text{const})$ of water and citric acid solutions as a function of concentration m and temperature T. 🟥 - pure water; 🟦 - 0.1003 mol kg^{-1}; 🟩 - 0.2504 mol kg^{-1}; 🟦 - 0.5006 mol kg^{-1}; 🟪 - 0.9988 mol kg^{-1}; 🟫 - 1.5015 mol kg^{-1} and 🟩 - 2.0230 mol kg^{-1}

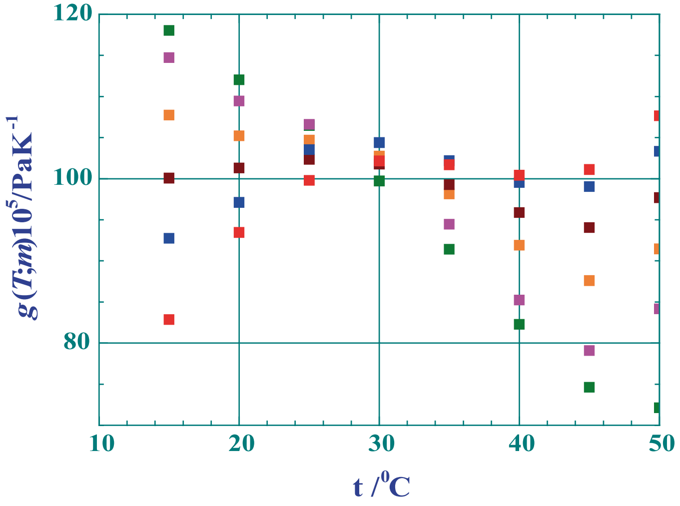

Fig. 2.28 The change of isochoric heat capacity with volume, $g(T;\ m=\text{const})$ of water and citric acid solutions as a function of concentration m and temperature T [133]. 🟩 - 2.5023 mol kg^{-1}; 🟪 - 3.0057 mol kg^{-1}; 🟧 - 3.5049 mol kg^{-1}; 🟫 - 3.99985 mol kg^{-1}; 🟦 - 4.5063 mol kg^{-1} and 🟥 - 4.9975 mol kg^{-1}

concave downward. For more concentrated citric acid solutions, $m > 2.5$ mol kg^{-1}, the curvature gradually changes from concave downward to concave upward with the extremum near 30 °C and dependence on m is rather complex. With an exception of lowest concentrations and highest temperatures, the change of isochoric heat capacity with volume of citric solutions is larger than that of pure water.

Thus, the function $\Delta g(T;m)=[gT;m)-g(T;m=0)]$ is positive and this indicates that molecular citric acid is a structure-making solute. As expected, in dilute solutions, citric acid is a structure-breaking solute due to its partial dissociation when at higher temperatures, the hydrogen-bonded structure of water is gradually destroyed and water starts to behave more and more like a "normal" liquid. The equilibrium between different water species (a structured hydrogen-bonded associated liquid and an "ordinary" liquid) is temperature dependent and the rise in temperature leads to the volume expansion but also to increase in the fraction of unassociated water molecules. As a consequence, the water structure is changed by combined effects of increasing temperature (volume or pressure changes) and of added citric acid.

Frequently, the interpretation of compressibility properties of solutions is expressed not only in terms of the "structure breaking" or the "structure making" solutes but also in terms of the ion hydration numbers. This means to assign to each molecule of solute a finite number of water molecules surrounding it (in primary and secondary hydration shells) and to assume that some properties of the bulk water differ from those of water molecules which are in immediate contact with the molecules of solute. The hydration numbers $h(T;m)$ which are estimated from ultrasonic measurements by different calculation procedures are not always in acceptable agreement. They lie for citric acid in a rather large range from 7.4 to 17.0 [130]. If the Passynski method [143] is chosen, then at given T, in terms of the isentropic compressibility coefficients of pure water and citric acid solutions, the hydration number $h(T;m)$ are given by

$$h(T;m)=\frac{1000}{\mathrm{M}_1 m}\left[1-\frac{\kappa_S(T;m)}{\kappa_{S,1}(T)}\left(\frac{\mathrm{d}_1(T)}{\mathrm{d}(T;m)}\right)\right] \tag{2.81}$$

The hydration numbers of citric acid in aqueous solutions as calculated from Eq. (2.81) decrease with increasing concentration and temperature. Their values vary from 4.0 to 11.5 in the 0–5.0 mol kg^{-1} concentration range and from 15 to 50 °C [133].

2.9 Thermodynamic Properties of Aqueous Solutions of Citric Acid

Thermodynamic functions associated with citric acid solutions are discussed in different contexts in many places of this book. Here, two aspects are considered in a more systematic manner. They will include the water and citric acid activities and the thermal properties of citric acid solutions.

The difference between chemical potential of component j in solution $\mu_j(T, \mathrm{x}_j)$, and its standard chemical potential $\mu_j^0(T)$ is given by a value of measurable quantity, the activity $a_j(T, \mathrm{x}_j)$

$$\Delta\mu_j(T,\mathrm{x}_j)=\mu_j(T,\mathrm{x}_j)-\mu_j^0(T)=\mathrm{R}T\ln a_j(T,\mathrm{x}_j) \tag{2.82}$$

where x_j is the mole fraction of this component.

In the case of binary systems, at constant T, the activities of solvent and solute (components 1 and 2) are determined from integration of the Gibbs–Duhem equation

$$x_1 d \ln a_1 + x_2 d \ln a_2 = 0 \tag{2.83}$$

The integration can be performed if activities of one component as a function of concentration are known. Usually, the activities of solvent (water) $a_1 = a_w$ (or corresponding the relative humidity (RH) $a_w = \mathrm{RH}/100\,\%$) are available from measurements of vapour pressures of water over solutions with known concentrations.

From the equality of chemical potentials of water in liquid and vapour phases and by assuming that the vapour phase behaves ideally, and that the standard chemical potentials in both phases are chosen to be the same, the activity of water is

$$\begin{aligned} a_w(T;x) &= \frac{p(T;x)}{p^0(T)} = \left(1 - \frac{\Delta p(T;x)}{p^0(T)}\right) \\ \Delta p(T;x) &= p^0(T) - p(T;x) \end{aligned} \tag{2.84}$$

where $x = x_2$ and $\Delta p(T;x)$ is the vapour-pressure lowering of citric acid solutions at temperature T and $p^0(T)$ denotes the vapour pressure of pure water.

Water activities of citric solutions were determined by the isopiestic and isotenoscopic methods [89, 93] and recently by applying the electronic hygrometer [144–148], the electrodynamic balance (EDB) [144] and the hygroscopicity tandem differential mobility analyzer (HTDMA) [149]. By using EDB and HTDMA equipment, the hygroscopicity cycles including hydration and dehydration of solid particles can be observed. Such measurements were performed in the context of hygroscopic properties of pharmaceutical solids, atmospheric aerosols and food-related solutions. Vapour pressures of water over citric acid solutions at 25 °C are known for different concentration ranges from investigations of Levien [89], Apelblat et al. [93], Velezmoro and Meirelles [145, 146], Peng et al. [144], Maffia [147, 148] and Zardini et al. [149]. Velezmoro [146] measured water activities at 30 and 35 °C, Apelblat et al. [93] from 30 to 45 °C, and few results exist also at 26.5 °C which were determined by Chirife and Fontan [150]. There are also some vapour pressure measurements performed in ternary aqueous systems with NaCl, $NaNO_3$, Na_2SO_4, and Na_3Cit [151, 152], and with organic acids or sugars [50].

Available from the literature values of relative humidity RH and vapour pressures of water over aqueous citric acid solutions p as a function of mass fraction of citric acid w are presented in Table 2.13. There is a reasonable agreement between reported vapour pressures or water activities coming from different investigations as can be observed in Figs. 2.29 and 2.30 where the vapour-pressure lowerings are plotted as a function of molality or molar fraction of citric acid in aqueous solutions. However, in the case of more sensitive quantity, the apparent osmotic coefficients

Table 2.13 Relative humidity and vapour pressures of water over citric acid solutions as a function of temperature and concentration

t/°C	w	RH%	p/kPa	w	RH%	p/kPa
25	0.0370 [89]	99.61	3.155	0.3656	93.63	2.965
	0.0545	99.43	3.149	0.4021	92.36	2.925
	0.0714	99.25	3.143	0.4345	91.04	2.883
	0.0876	99.05	3.137	0.4637	89.66	2.839
	0.1034	98.86	3.131	0.4900	88.23	2.794
	0.1185	98.67	3.125	0.5138	86.78	2.748
	0.1332	98.48	3.119	0.5355	85.34	2.702
	0.1474	98.29	3.113	0.5553	83.86	2.656
	0.1612	98.09	3.106	0.5735	82.38	2.609
	0.1745	97.89	3.100	0.5903	80.89	2.561
	0.2237	97.06	3.074	0.6058	79.41	2.515
	0.2776	95.99	3.040	0.6199	77.95	2.469
	0.3245	94.84	3.003			
	0.0895 [93]	98.99	3.135	0.4775	89.36	2.830
	0.1445	98.26	3.112	0.5061	87.78	2.780
	0.1869	97.63	3.092	0.5161	87.21	2.762
	0.2194	97.09	3.075	0.5321	86.14	2.728
	0.2623	96.27	3.049	0.5379	85.76	2.716
	0.3131	95.14	3.013	0.5440	85.32	2.702
	0.3673	93.68	2.967	0.5594	84.12	2.664
	0.4067	92.39	2.926	0.5683	83.39	2.641
	0.4406	91.06	2.884	0.5808	82.28	2.606
	0.4514	90.59	2.869	0.5828	82.10	2.600
	0.4738	89.55	2.836	0.5951	80.86	2.561
	0.0224 [146]	99.80	3.160	0.1820	97.50	3.088
	0.0458	99.00	3.135	0.2721	95.90	3.037
	0.0924	98.30	3.113	0.3646	93.60	2.964
	0.1373	98.10	3.107	0.4367	90.80	2.875
	0.1611 [144]	98.10	3.107	0.5037	86.57	2.741
	0.2309	96.80	3.065	0.5225	85.40	2.704
	0.2763	95.70	3.031	0.5445	84.48	2.675
	0.3262	94.30	2.986	0.5480	85.00	2.692
	0.3657	93.10	2.948	0.5923	80.95	2.564
	0.4397	90.20	2.856	0.6023	79.96	2.532
	0.0499 [147]	99.30	3.145	0.2987	95.40	3.021
	0.0995	98.70	3.126	0.3982	92.40	2.926
	0.1990	97.30	3.081	0.4948	87.40	2.768
	0.0370 [149]	99.61	3.155	0.4346	91.02	2.882
	0.0545	99.43	3.149	0.4397	90.20	2.856
	0.0714	99.24	3.143	0.4407	91.07	2.884
	0.0877	99.05	3.137	0.4515	90.60	2.869
	0.0895	98.99	3.135	0.4637	89.64	2.839
	0.1034	98.86	3.131	0.4739	89.56	2.836
	0.1186	98.67	3.125	0.4776	89.37	2.830
	0.1333	98.48	3.119	0.4900	88.21	2.793
	0.1446	98.26	3.112	0.5063	87.79	2.780
	0.1475	98.28	3.112	0.5138	86.76	2.747

Table 2.13 (continued)

t/°C	w	RH%	p/kPa	w	RH%	p/kPa
	0.1611	98.10	3.107	0.5161	87.22	2.762
	0.1612	98.09	3.106	0.5225	85.40	2.704
	0.1745	97.89	3.100	0.5322	86.15	2.728
	0.1869	97.73	3.095	0.5355	85.31	2.702
	0.2195	97.10	3.075	0.5380	85.77	2.716
	0.2238	97.06	3.074	0.5440	85.33	2.702
	0.2309	96.80	3.065	0.5554	83.83	2.655
	0.2624	96.28	3.049	0.5595	84.13	2.664
	0.2763	95.70	3.031	0.5683	83.40	2.641
	0.2776	95.98	3.039	0.5736	82.35	2.608
	0.3131	95.14	3.013	0.5809	82.30	2.606
	0.3245	94.83	3.003	0.5829	82.11	2.600
	0.3262	94.30	2.986	0.5904	80.85	2.560
	0.3657	93.62	2.965	0.5952	80.88	2.561
	0.3657	93.10	2.948	0.6059	79.37	2.514
	0.3674	93.69	2.967	0.6166	78.69	2.492
	0.4021	92.35	2.925	0.6199	77.92	2.467
	0.4067	92.40	2.926			
30	0.0895 [93]	98.92	4.197	0.4775	89.49	3.797
	0.1445	98.33	4.172	0.5061	87.91	3.730
	0.1869	97.78	4.149	0.5161	87.34	3.706
	0.2194	97.29	4.128	0.5321	86.31	3.662
	0.2623	96.51	4.095	0.5379	85.93	3.646
	0.3131	95.43	4.049	0.5440	85.51	3.628
	0.3673	93.92	3.985	0.5594	84.40	3.581
	0.4067	92.60	3.929	0.5683	83.71	3.552
	0.4406	91.23	3.871	0.5808	82.72	3.510
	0.4514	90.76	3.851	0.5828	82.56	3.503
	0.4738	89.68	3.805	0.5951	81.52	3.459
	0.0458 [145]	98.80	4.192	0.2725	95.70	4.060
	0.0924	98.30	4.171	0.3653	93.30	3.959
	0.1822	97.20	4.124	0.4378	90.50	3.840
35	0.0895 [93]	98.88	5.561	0.4775	89.47	5.032
	0.1445	98.33	5.530	0.5061	87.87	4.942
	0.1869	97.79	5.500	0.5161	87.29	4.909
	0.2194	97.31	5.473	0.5321	86.25	4.851
	0.2623	96.55	5.430	0.5379	85.86	4.829
	0.3131	95.45	5.368	0.5440	85.44	4.805
	0.3673	93.95	5.284	0.5594	84.33	4.743
	0.4067	92.62	5.209	0.5683	83.66	4.705
	0.4406	91.23	5.131	0.5808	82.66	4.649
	0.4514	90.75	5.104	0.5828	82.50	4.640
	0.4738	89.67	5.043	0.5951	82.04	4.614
	0.0458 [145]	98.50	5.539	0.2725	95.50	5.370
	0.0924	98.10	5.517	0.3653	93.00	5.230
	0.1822	96.90	5.449	0.4378	90.30	5.078

Table 2.13 (continued)

t/°C	w	RH%	*p*/kPa	w	RH%	*p*/kPa
40	0.0895 [93]	98.86	7.294	0.4775	89.44	6.599
	0.1445	98.31	7.253	0.5061	87.83	6.480
	0.1869	97.78	7.214	0.5161	87.23	6.436
	0.2194	97.29	7.178	0.5321	86.19	6.359
	0.2623	96.54	7.123	0.5379	85.80	6.330
	0.3131	95.43	7.041	0.5440	85.38	6.299
	0.3673	93.94	6.931	0.5594	84.24	6.215
	0.4067	92.60	6.832	0.5683	83.55	6.164
	0.4406	91.22	6.730	0.5808	82.57	6.092
	0.4514	90.73	6.694	0.5828	82.37	6.077
	0.4738	89.63	6.613	0.5951	81.31	5.999
45	0.0895 [93]	98.86	9.477	0.4775	89.51	8.580
	0.1445	98.30	9.423	0.5061	87.90	8.426
	0.1869	97.77	9.372	0.5161	87.29	8.368
	0.2194	97.28	9.325	0.5321	86.25	8.268
	0.2623	96.53	9.253	0.5379	85.85	8.230
	0.3131	95.44	9.149	0.5440	85.43	8.189
	0.3673	93.96	9.007	0.5594	84.28	8.079
	0.4067	92.62	8.879	0.5683	83.58	8.012
	0.4406	91.26	8.748	0.5808	82.55	7.913
	0.4514	90.78	8.702	0.5828	82.37	7.896
	0.4738	89.69	8.598	0.5951	81.30	7.793

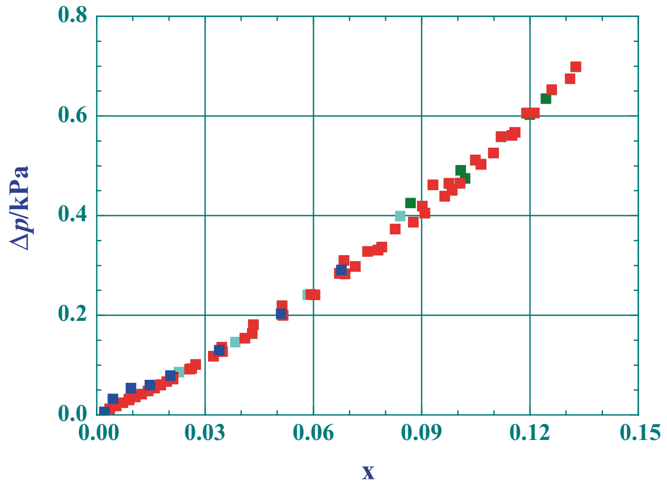

Fig. 2.29 The vapour pressure lowering of citric acid at 25 °C as a function of mole fraction of citric acid in aqueous solutions. 🟩 - [89]; 🟫 - [93]; 🟩 - [144]; 🟦 - [145]; 🟦 - [147] and 🟥 - [149]

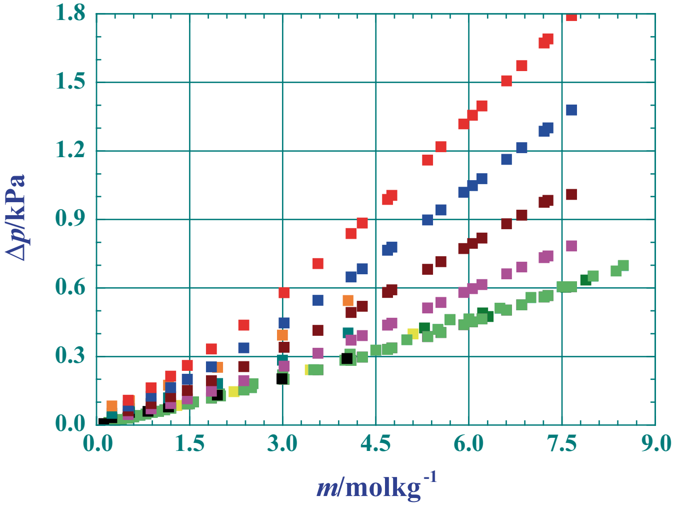

Fig. 2.30 Vapour pressure lowerings in the 25–45 °C temperature range as a function of concentration of citric acid in aqueous solutions. 25 °C 🟦 - [89]; 🟪 - [93]; 🟩 - [144]; ⬛ - [145]; 🟨 - [147]; 🟩 - [149]. 30 °C 🟪 - [93]; 🟩 - [148]; 35 °C 🟫 - [93]; 🟧 - [148]. 40 °C 🟦 - [93]. 45 °C 🟥 - [93]

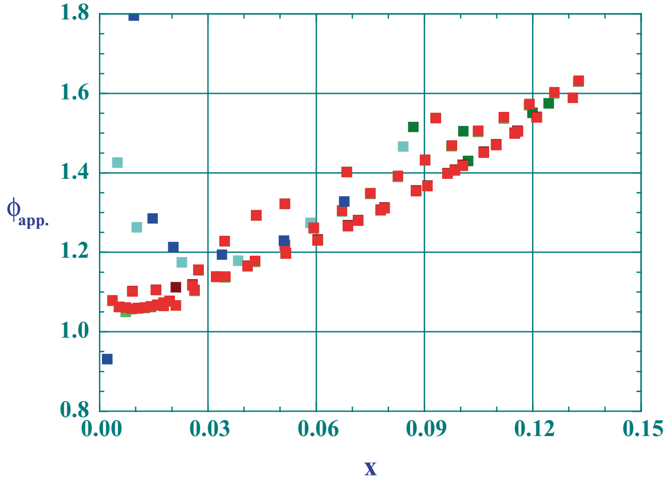

Fig. 2.31 The apparent osmotic coefficients of citric acid at 25 °C as a function of mole fraction of citric acid in aqueous solutions. 🟩 - [89]; 🟫 - [93]; 🟩 - [144]; 🟦 - [145]; 🟦 - [147] and 🟥 - [149]

$$\phi_{\text{app.}}(m;T) = -55.508\,\frac{\ln a_{\text{w}}(m;T)}{m} \tag{2.85}$$

as can be observed in Fig. 2.31, the agreement is less satisfactory [59].

Vapour pressures of water over citric acid solutions, based on measurements from [89, 93, 144, 149] can be represented by the following correlations

$$\begin{aligned}
&p(25^0\,\mathrm{C};m)/\mathrm{kPa} = 3.1668 - 5.9610{\cdot}10^{-2}\,m^* - 2.6473{\cdot}10^{-3}\,m^{*2}\\
&p(30^0\,\mathrm{C};m)/\mathrm{kPa} = 4.2429 - 7.6207{\cdot}10^{-2}\,m^* - 3.5766{\cdot}10^{-3}\,m^{*2}\\
&p(35^0\,\mathrm{C};m)/\mathrm{kPa} = 5.6235. - 9.9298{\cdot}10^{-2}\,m^* - 5.1243{\cdot}10^{-3}\,m^{*2}\\
&p(40^0\,\mathrm{C};m)/\mathrm{kPa} = 7.3778 - 1.3130{\cdot}10^{-1}\,m^* - 6.6817{\cdot}10^{-3}\,m^{*2}\\
&p(45^0\,\mathrm{C};m)/\mathrm{kPa} = 9.5859 - 1.6790{\cdot}10^{-1}\,m^* - 8.8497{\cdot}10^{-3}\,m^{*2}\\
&m^* = m/\mathrm{molkg}^{-1}
\end{aligned} \tag{2.86}$$

The corresponding water activities a_{w} can be calculated using Eqs. (2.84). From these equations it is possible to estimate, at given m, the vapour pressure at other temperatures from a very accurate correlation of the vapour-pressure lowerings which was proposed by the author [153]

$$\begin{aligned}
&\ln(\Delta p/\mathrm{kPa}) = \mathrm{A} + \frac{\mathrm{B}}{(T/\mathrm{K})} + C\left(\ln(T/\mathrm{K}) - \frac{T}{2\mathrm{T_c}}\right)\\
&\mathrm{T_c} = 647.14\mathrm{K}
\end{aligned} \tag{2.87}$$

where A, B and C are adjustable parameters. These coefficients are available from Eq. (2.86) for a chosen number of concentrations m. This permits to obtain vapour pressures of water over citric acid solutions at any temperature.

Vapour pressures of water over citric acid solutions for few more temperatures, others than in Eq. (2.86), are given here

$$\begin{aligned}
&p(10^0\mathrm{C};m)/\mathrm{kPa} = 1.2270 - 2.8366\cdot10^{-2}\,m^* - 7.8552{\cdot}10^{-4}\,m^{*2}\\
&p(20^0\mathrm{C};m)/\mathrm{kPa} = 2.3370 - 4.6168\cdot10^{-2}\,m^* - 1.8323{\cdot}10^{-3}\,m^{*2}\\
&p(50^0\mathrm{C};m)/\mathrm{kPa} = 12.340. - 2.2252\cdot10^{-1}\,m^* - 1.1507{\cdot}10^{-2}\,m^{*2}\\
&p(60^0\mathrm{C};m)/\mathrm{kPa} = 19.927 - 3.8521\cdot10^{-1}\,m^* - 1.18647{\cdot}10^{-2}\,m^{*2}\\
&p(70^0\mathrm{C};m)/\mathrm{kPa} = 31.172 - 6.7080\cdot10^{-1}\,m^* - 2.8500{\cdot}10^{-2}\,m^{*2}\\
&p(80^0\mathrm{C};m)/\mathrm{kPa} = 47.371 - 1.1711m^* - 4.0640{\cdot}10^{-2}\,m^{*2}\\
&p(70^0\mathrm{C};m)/\mathrm{kPa} = 70.117 - 2.0433\,m^* - 5.2607{\cdot}10^{-2}\,m^{*2}\\
&m^* = m/\mathrm{mol{\cdot}kg}^{-1}
\end{aligned} \tag{2.88}$$

The apparent osmotic coefficients ϕ_{app}. (similarly as the apparent molar volumes, Eq. (2.54)) are usually assumed to be the sum of additive contributions coming from the unionized acid molecules H_3Cit and ions $H^+$and H_2Cit^- (high-charged citrate anions are neglected) [89]

$$\phi_{\mathrm{app}}\cdot(m) = \alpha\,\phi_i(\mathrm{H^+} + \mathrm{H_2Cit^-}) + (1-\alpha)\,\phi(m) \tag{2.89}$$

where α is degree of the primary dissociation step of citric acid, $\phi_{\mathrm{i}}(m)$ is the osmotic coefficient of the ions and $\phi(m)$ is the osmotic coefficient of molecular citric acid. Since $\phi_{\mathrm{i}}(m)$ values are unknown, Levien [89] replaced them by the corresponding osmotic coefficients of sodium chloride. The Levien isopiestic measurements were also used by Vaňura and Kuča to calculate the water activities and the activity coefficients of undissociated citric acid in the 0.2–4.2 mol kg^{-1} concentration range [154]. The alternative numerical procedure for dilute citric acid solutions was proposed by Apelblat et al. [93] by using the Debye–Hückel expressions [72] for the osmotic and activity coefficient of citrate ions in dilute solutions

$$\begin{aligned}
&\ln\gamma_{\pm}(T;m) = -\frac{\mathrm{A}(T)\sqrt{m\alpha}}{1+\mathrm{B}(T)a_i\sqrt{m\alpha}}\\
&\phi(T;m) = 1-\frac{\sqrt{m\alpha}}{3}\sigma(\mathrm{B}(T)a_i\sqrt{m\alpha})\\
&\sigma(x) = \frac{3}{x^2}\left[(1+x)-2\ln(1+x)-\frac{1}{1+x}\right]\\
&x = \mathrm{B}(T)a_i\sqrt{m\alpha}
\end{aligned}\tag{2.90}$$

and the Bjerrum equation for the activity coefficients of molecular citric acid $\gamma(m)$.

$$\ln\gamma(T;m) = \phi(T;m)-1+\int_0^m\left(\frac{\phi(T;m)-1}{m}\right)dm. \tag{2.91}$$

Determined in such way, the osmotic and activity coefficients of undissociated citric acid $\phi(m)$ and $\gamma(m)$ are presented in Table 2.14. As can be observed, the influence of temperature is rather small in the 30–45 °C range but it is much stronger at lower temperatures. In moderately concentrated citric acid solutions, values of $\phi(m)$ and $\gamma(m)$ coefficients are nearly unity indicating that deviations from the ideal behaviour are minor. In very dilute solutions when all three steps of dissociation are involved, a quite different theoretical approach should be applied to evaluate osmotic and activity coefficients. Unfortunately, the lack of accurate and reliable experimental results in this concentration range prevents such calculations.

Contrary to other thermochemical properties, the heat capacities of citric acid solutions were determined a number of times. Old values at 18 °C are presented in International Critical Tables [67] for $w<0.52$. At the same temperature few heat capacities were measured by Richards and Mair [155] and their results were thermodynamically analyzed by Rossini [156]. The most detailed values of specific heat capacities C_p (from 20 to 90 °C and for mass fractions in the $0.1<w<0.8$ range) were reported by Bogdanov et al. [79], Averbukh et al. [80] and Gromov [135]. These investigations were associated with engineering aspects of citric acid production. Their specific heat capacities were correlated by the following empirical equation

Table 2.14 Osmotic and activity coefficients of unionized citric acid as a function of temperature and concentration

$t/°C$	25		30		35		40		45	
m^*	ϕ	γ	ϕ	γ	ϕ	γ	ϕ	γ	ϕ	γ
0.2	1.013	1.027	1.002	1.004	1.003	1.005	1.003	1.005	1.003	1.005
0.4	1.027	1.055	1.006	1.010	1.006	1.011	1.007	1.012	1.007	1.013
0.6	1.040	1.083	1.010	1.018	1.011	1.020	1.011	1.021	1.012	1.022
0.8	1.052	1.111	1.016	1.028	1.018	1.031	1.018	1.032	1.018	1.032
1.0	1.065	1.140	1.023	1.039	1.025	1.043	1.025	1.044	1.026	1.045
1.2	1.078	1.170	1.031	1.053	1.033	1.057	1.034	1.059	1.034	1.059
1.4	1.091	1.200	1.040	1.068	1.043	1.074	1.043	1.075	1.043	1.075
1.6	1.103	1.231	1.050	1.085	1.053	1.092	1.054	1.094	1.053	1.093
1.8	1.116	1.263	1.061	1.105	1.064	1.111	1.065	1.114	1.064	1.113
2.0	1.128	1.295	1.073	1.125	1.076	1.133	1.077	1.135	1.076	1.134
2.5	1.159	1.380	1.105	1.185	1.109	1.195	1.110	1.198	1.108	1.196
3.0	1.191	1.469	1.141	1.257	1.145	1.268	1.147	1.272	1.144	1.268
3.5	1.222	1.566	1.180	1.339	1.185	1.353	1.186	1.358	1.183	1.351
4.0	1.255	1.670	1.221	1.432	1.225	1.448	1.228	1.455	1.223	1.446
4.5	1.288	1.782	1.262	1.535	1.267	1.554	1.270	1.563	1.265	1.552
5.0	1.323	1.905	1.303	1.648	1.308	1.670	1.312	1.681	1.307	1.668
5.5	1.359	2.04	1.343	1.769	1.349	1.793	1.353	1.808	1.349	1.764
6.0	1.396	2.19	1.380	1.895	1.386	1.923	1.393	1.942	1.389	1.928
6.5	1.436	2.36	1.415	2.03	1.421	2.06	1.429	2.08	1.427	2.07
7.0	1.478	2.54	1.445	2.16	1.452	2.19	1.461	2.22	1.461	2.21
7.5	1.523	2.75	1.471	2.28	1.477	2.32	1.489	2.36	1.492	2.36
8.0	1.570	2.99	1.490	2.34	1.497	2.44	1.511	2.49	1.518	2.50

$m^* = m/\text{mol kg}^{-1}$

$$C_P(T;w)\,/\,\mathrm{J{\cdot}g^{-1}{\cdot}K^{-1}} = 3.004 - 2.765w + 0.00419(T\,/\,\mathrm{K}) \tag{2.92}$$

Considerably more precise measurements were performed by Patterson and Wooley [114] in a wide temperature range, from 5 to 120 °C, but only for moderately concentrated solutions $m<1.0$ mol kg^{-1}. These and at 25 °C, the heat capacities of Sijpkes et al. [113], and Manzurola [157] (also estimated by Apelblat [90]) are presented in the form of the apparent molar heat capacities

$$C_{P,2,\phi}(T;m) = M_2 C_{P,2}\,(T;m) + \frac{1000}{m}[C_{P,2}(T;m) - C_{P,1}(T;m)] \tag{2.93}$$

where indexes 1 and 2 denote water and citric acid respectively.

If the specific heat capacities citric acid solutions coming from different investigations are compared (available only for $m<2.0$ mol kg^{-1}), the agreement between them is reasonable (Table 2.15 and Fig. 2.32). However, this is not the case of much more sensitive $C_{p,2,\phi}$ quantities. The most accurate sets of $C_{p,2,\phi,}$ the apparent heat capacities of Patterson and Wooley [114] and Sijpkes et al. [113] behave similarly as a function of concentration, but even they are shifted by about 10 J mol^{-1} K^{-1}.

At constant temperature, the specific heat capacities decrease with increasing concentration of citric acid (Fig. 2.32). At constant m, in dilute solutions, similarly as in pure water, the specific heat capacity has the concave upward curvature with the minimum at about 40 °C, but in more concentrated solutions C_p increases nearly linearly with temperature. This is illustrated in Fig. 2.33 where the specific heat capacities which were determined by Patterson and Wooley [114] are plotted.

As comparing with heat capacities, other thermochemical properties of aqueous solutions of citric acid, the enthalpy of solution $\Delta H_{sol\cdot}$, and the enthalpy of dilution $\Delta H_{dil\cdot}$, are less documented in the literature. They were determined in rather difficult calorimetric measurements which are limited to only one temperature, mainly to 25 °C. The enthalpies of dilutions were evaluated by the "short jump" method (adding in the calorimeter a small amount of water to a considerably large quantity of solution to yield a solution that is only slightly more dilute than the original solution) or in the "long jump" method (adding a relatively concentrated solution to a considerably large quantity of water to yield a solution that is considerably more diluted than the original solution) or applying both methods [91]. The enthalpies of dilution are frequently expressed in terms of the relative apparent molar enthalpies (denoted in the literature as ϕ_L, ϕ_H or $L_{2,\phi}$) and they are defined as the negative of the molar enthalpy of dilution from some specific finite composition to a final solution that is infinitely dilute [76]. The positive values of $\Delta H_{dil\cdot}$ indicate that the dilution process is accompanied by the absorption of heat from surroundings.

The enthalpies of solution related to the saturation points (evaluated from solubility measurements) were already discussed, here these determined in dilute solutions will be considered. Pioneering calorimetric measurements with citric acid and alkali citrates were performed by Massol [158] in 1892, but they have only historical value. After prolonged period, in 1929, Richards and Mair [155] performed

Table 2.15 Specific heat capacities of aqueous solutions of citric acid as a function of temperature and concentration

t/°C	w	C_P*	w	C_P*	w	C_P*
5	0.0000 [114]	4.203	0.0114	4.171	0.1259	3.832
	0.0029	4.195	0.0458	4.071	0.1611	3.723
	0.0057	4.187	0.0876	3.949		
10	0.0000 [114]	4.193	0.0114	4.162	0.1259	3.838
	0.0029	4.185	0.0458	4.067	0.1611	3.734
	0.0057	4.178	0.0876	3.949		
15	0.0000 [114]	4.187	0.0114	4.156	0.1259	3.860
	0.0029	4.179	0.0458	4.065	0.1611	3.771
	0.0057	4.171	0.0876	3.958		
18	0.05 [67]	4.03	0.18	3.72	0.42	3.19
	0.10	3.90	0.30	3.45	0.52	2.98
	0.0131 [155]	4.147	0.0503	4.049	0.1747	3.733
	0.0258	4.113	0.0957	3.931		
20	0.0000 [114]	4.182	0.0114	4.153	0.1259	3.864
	0.0029	4.175	0.0458	4.064	0.1611	3.777
	0.0057	4.167	0.0876	3.960		
	0.10 [79, 80]	3.95	0.40	3.13	0.70	2.30
	0.20	3.68	0.50	2.86	0.80	2.01
	0.30	3.40	0.60	2.57		
25	0.0184 [113]	4.132	0.1034	3.922	0.2229	3.630
	0.0366	4.087	0.1181	3.886	0.2858	3.488
	0.0525	4.046	0.1327	3.851	0.3432	3.353
	0.0717	3.999	0.1474	3.814		
	0.0921	3.949	0.1638	3.773		
	0.0191 [157]	4.111	0.1118	3.859	0.2063	3.642
	0.0409	4.058	0.1329	3.788	0.2243	3.611
	0.0641	3.984	0.1630	3.735	0.2474	3.575
	0.0894	3.922	0.1838	3.680	0.2787	3.526

Table 2.15 (continued)

t/°C	w	C_P*	w	C_P*	w	C_P*
	0.0000	4.179	0.0114	4.150	0.1259	3.869
	0.0029	4.172	0.0458	4.064	0.1611	3.783
	0.0057	4.165	0.0876	3.962		
30	0.0000 [114]	4.178	0.0114	4.149	0.1259	3.873
	0.0029	4.170	0.0458	4.065	0.1611	3.789
	0.0057	4.163	0.0876	3.965		
	0.10 [67]	3.99	0.40	3.17	0.70	2.34
	0.20	3.72	0.50	2.89	0.80	2.06
	0.30	3.44	0.60	2.61		
35	0.0000 [114]	4.177	0.0114	4.149	0.1259	3.877
	0.0029	4.170	0.0458	4.066	0.1611	3.794
	0.0057	4.163	0.0876	3.968		
40	0.0000 [114]	4.177	0.0114	4.149	0.1259	3.882
	0.0029	4.170	0.0458	4.068	0.1611	3.800
	0.0057	4.163	0.0876	3.971		
	0.10 [67]	4.03	0.40	3.21	0.70	2.38
	0.20	3.76	0.50	2.93	0.80	2.09
	0.30	3.48	0.60	2.65		
45	0.0000 [114]	4.177	0.0114	4.150	0.1259	3.886
	0.0029	4.170	0.0458	4.070	0.1611	3.805
	0.0057	4.164	0.0876	3.974		
50	0.0000 [114]	4.179	0.0114	4.152	0.1259	3.891
	0.0029	4.172	0.0458	4.073	0.1611	3.811
	0.0057	4.165	0.0876	3.978		
	0.10 [67]	4.07	0.40	3.25	0.70	2.42
	0.20	3.80	0.50	2.97	0.80	2.13
	0.30	3.52	0.60	2.69		

Table 2.15 (continued)

t/°C	w	C_P*	w	C_P*	w	C_P*
55	0.0000 [114]	4.180	0.0114	4.155	0.1259	3.887
	0.0029	4.174	0.0458	4.076	0.1611	3.801
	0.0057	4.167	0.0876	3.978		
60	0.0000 [114]	4.183	0.0114	4.157	0.1259	3.892
	0.0029	4.176	0.0458	4.079	0.1611	3.807
	0.0057	4.170	0.0876	3.982		
	0.10 [67]	4.12	0.40	3.30	0.70	2.47
	0.20	3.85	0.50	3.02	0.80	2.17
	0.30	3.57	0.60	2.74		
65	0.0000 [114]	4.185	0.0114	4.160	0.1259	3.897
	0.0029	4.179	0.0458	4.082	0.1611	3.813
	0.0057	4.173	0.0876	3.986		
70	0.0000 [114]	4.189	0.0114	4.163	0.1259	3.902
	0.0029	4.182	0.0458	4.086	0.1611	3.820
	0.0057	4.176	0.0876	3.991		
	0.10 [67]	4.16	0.40	3.33	0.70	2.51
	0.20	3.89	0.50	3.06	0.80	2.21
	0.30	3.61	0.60	2.78		
75	0.0000 [114]	4.192	0.0114	4.167	0.1259	3.907
	0.0029	4.186	0.0458	4.091	0.1611	3.826
	0.0057	4.180	0.0876	3.996		
80	0.0000 [114]	4.196	0.0114	4.171	0.1259	3.913
	0.0029	4.190	0.0458	4.095	0.1611	3.832
	0.0057	4.184	0.0876	4.001		
	0.10 [67]	4.19	0.40	3.38	0.70	2.55
	0.20	3.93	0.50	3.10	0.80	2.25
	0.30	3.65	0.60	2.82		

Table 2.15 (continued)

t/°C	w	C_P*	w	C_P*	w	C_P*
85	0.0000 [114]	4.201	0.0114	4.176	0.1259	3.919
	0.0029	4.194	0.0458	4.100	0.1611	3.839
	0.0057	4.188	0.0876	4.006		
90	0.0000 [114]	4.205	0.0114	4.181	0.1259	3.925
	0.0029	4.199	0.0458	4.106	0.1611	3.845
	0.0057	4.193	0.0876	4.012		
	0.10 [67]	4.24	0.40	3.48	0.70	2.59
	0.20	3.97	0.50	3.14	0.80	2.29
	0.30	3.69	0.60	2.86		
95	0.0000 [114]	4.211	0.0114	4.186	0.1259	3.931
	0.0029	4.204	0.0458	4.111	0.1611	3.852
	0.0057	4.198	0.0876	4.018		
100	0.0000	4.216	0.0114	4.192	0.1259	3.937
	0.0029	4.210	0.0458	4.117	0.1611	3.858
	0.0057	4.204	0.0876	4.024		
105	0.0000	4.223	0.0114	4.198	0.1259	3.944
	0.0029	4.216	0.0458	4.124	0.1611	3.865
	0.0057	4.210	0.0876	4.031		
110	0.0000	4.229	0.0114	4.205	0.1259	3.951
	0.0029	4.223	0.0458	4.131	0.1611	3.873
	0.0057	4.217	0.0876	4.038		
115	0.0000	4.237	0.0114	4.212	0.1259	3.958
	0.0029	4.230	0.0458	4.138	0.1611	3.881
	0.0057	4.224	0.0876	4.045		
120	0.0000	4.245	0.0114	4.220	0.1259	3.965
	0.0029	4.238	0.0458	4.146	0.1611	3.891
	0.0057	4.232	0.0876	4.053		

$C_P{*} = C_P/\mathrm{J\ g^{-1}\ K^{-1}}$

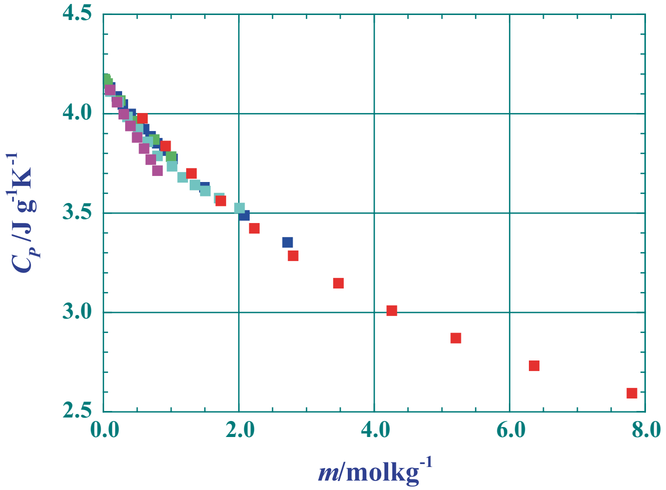

Fig. 2.32 Specific heat capacities of aqueous solutions of citric acid at 25 °C as a function of concentration. 🟥 - [79, 135]; 🟩 - [114]; 🟦 - [113]; 🟫 - [93]; ▨ - [157] and 🟪 - [90]

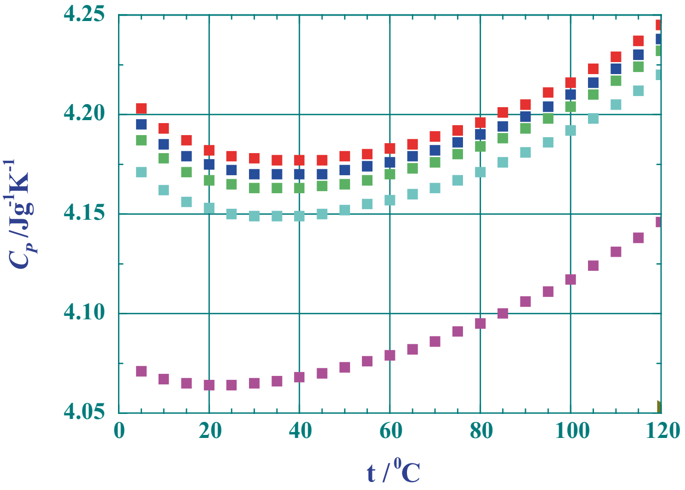

Fig. 2.33 Specific heat capacities of aqueous solutions of citric acid at constant concentrations as a function of temperature [114]. 🟥 - pure water; 🟦 - $m = 0.015$ mol kg^{-1}; 🟩 - $m = 0.03$ mol kg^{-1}; ▨ - $m = 0.06$ mol kg^{-1}; 🟪 - $m = 0.25$ mol kg^{-1}

few calorimetric measurements to evaluate the enthalpy of dilution at 16 and 20 °C. These determinations were critically analyzed by Snethlage [159]. From their results it is evident that ΔH_{dil} strongly depends on temperature.

In the next step in 1986, in rather small concentration regions, from 0.0144 to 0.0254 mol kg^{-1} for anhydrous citric acid and from 0.0151 to 0.0235 mol kg^{-1} for citric acid monohydrate, the molar enthalpies of solution were determined at

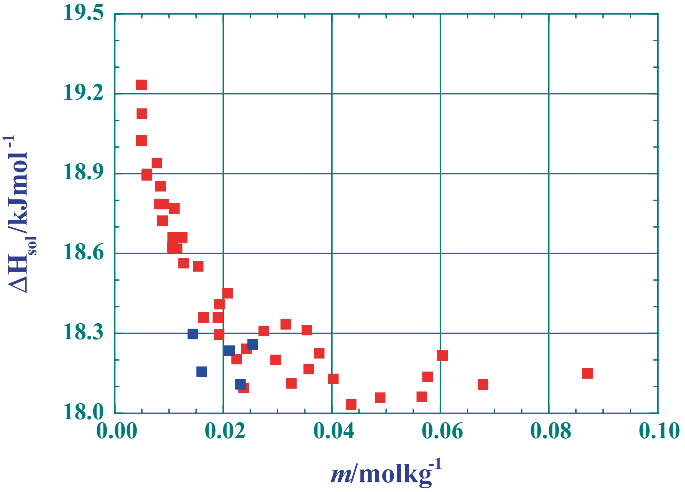

Fig. 2.34 The molar enthalpies of solution of anhydrous citric acid at 25 °C as a function of concentration. 🟦 - [90]; 🟥 - [162]

25 °C by Apelblat [90]. The concentration region was extended in both directions, from 0.0049 to 0.0871 mol kg^{-1} by Bald and Barczyńska [160]. The molar enthalpies of dilution over the nearly entire range of concentrations, from 0.0057 to 7.231 mol kg^{-1}, were measured by Dobrogowska et al. [91]. The only known investigation dealing with heat effects in the ternary systems of citric acid with nitric acid and potassium nitrate is that of Kochergina et al. [161].

Calorimetric measurements performed by Bald and Barczyńska [162] in very dilute solutions showed a steep increase in ΔH_{sol} values for $m \to 0$ (Fig. 2.34). They interpreted such behaviour of the molar enthalpies of solution in terms of contributions coming from the consecutive dissociation steps of citric acid. Over the investigated range of concentrations, Bald and Barczyńska results also permitted to determine the molar enthalpies of dilution. Their values are in an excellent agreement with the ΔH_{dil} values reported by Dobrogowska et al. [91] (Fig. 2.35). The molar enthalpies of dilution change significantly in dilute solutions but in more concentrated solutions their dependence on concentration m is less and less marked with reaching the maximal value at about 5.5 mol kg^{-1} (Fig. 2.36, Table 2.16).

For dilute and concentrated solutions, the molar enthalpies of dilution of citric acid solutions at 25 °C can be represented by the following expressions

$$\begin{aligned}\Delta H_{dil}(m)/\mathrm{Jmol}^{-1} &= 3450.1m^{*1/2} + 42660.8m^{*} - 255670m^{*3/2} \\ &\quad + 399596m^{*2} \quad ; \quad m^{*} < 0.06 \\ \Delta H_{dil}(m)/\mathrm{Jmol}^{-1} &= 1086.0 + 368.16m^{*1/2} + 1115.5m^{*} - 578.4m^{*3/2} \\ &\quad + 76.0m^{*2} \quad ; \quad m^{*} > 0.06 \\ m^{*} &= m/\mathrm{molkg}^{-1}\end{aligned} \tag{2.94}$$

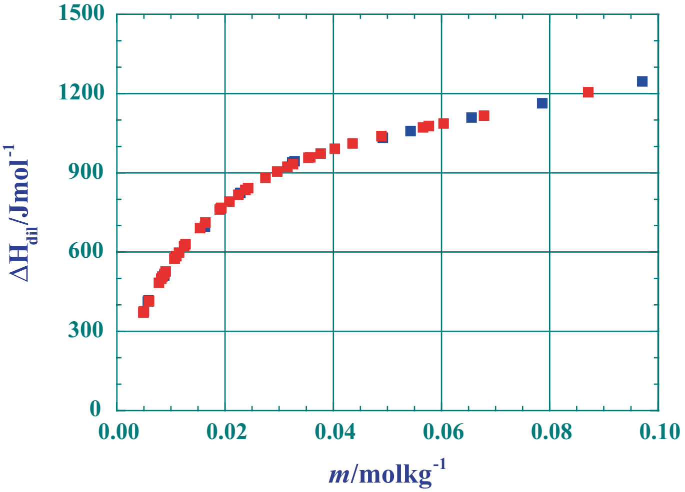

Fig. 2.35 The molar enthalpies of dilution of citric acid solutions at 25 °C as a function of concentration. 🟦 - [91]; 🟥 - [162]

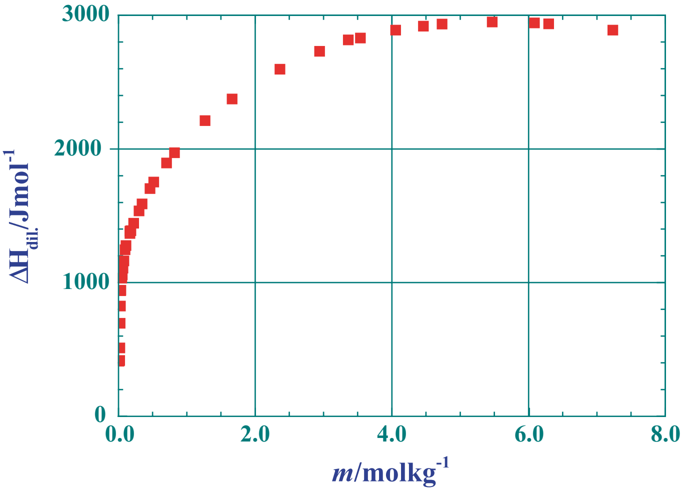

Fig. 2.36 The molar enthalpies of dilution of citric acid solutions at 25 °C as a function of concentration [91]

2.10 Viscosities of Aqueous Solutions of Citric Acid

In the design and operation of fermentation processes to produce citric acid, dynamic properties of its aqueous solutions (viscosities, diffusion coefficients, thermal and electrical conductances) are important parameters and therefore they were repeat-

Table 2.16 The molar enthalpies of solution of anhydrous citric acid, citric acid monohydrate, and the molar enthalpies of dilution of aqueous citric acid solutions at 25 °C

m^*	$\Delta H_{sol}{}^*$	$\Delta H_{dil}{}^*$	m^*	$\Delta H_{sol}{}^*$	$\Delta H_{dil}{}^*$
0.01438 [90]	18.298		0.004897 [162]	19.024	371
0.01602	18.156		0.004903	19.233	372
0.02112	18.235		0.004955	19.024	374
0.02315	18.109		0.004990	19.125	376
0.02541	18.258		0.005887	18.894	413
0.00571 [91]		412	0.005918	18.899	415
0.00583		417	0.007766	18.940	484
0.00875		511	0.008218	18.786	499
0.01627		696	0.008414	18.853	507
0.02280		824	0.008776	18.723	518
0.03240		940	0.009016	18.786	526
0.03283		944	0.01064	18.622	575
0.04915		1033	0.01067	18.660	576
0.05429		1058	0.01099	18.769	585
0.06554		1109	0.01149	18.618	598
0.07862		1163	0.01242	18.660	623
0.09709		1246	0.01270	18.564	630
0.1109		1277	0.01536	18.552	691
0.1656		1367	0.01635	18.359	712
0.1664		1386	0.01899	18.359	761
0.1811		1389	0.01923	18.296	765
0.2222		1444	0.01929	18.410	767
0.3020		1537	0.02079	18.451	791
0.3463		1588	0.02247	18.204	817
0.4614		1703	0.02375	18.095	835
0.5170		1752	0.02427	18.242	842
0.7019		1895	0.02748	18.309	881

Table 2.16 (continued)

m^*	ΔH_{sol}^*	ΔH_{dil}^*	m^*	ΔH_{sol}^*	ΔH_{dil}^*
0.8178		1971	0.02965	18.200	905
1.2656		2211	0.03152	18.334	923
1.6628		2374	0.03255	18.112	933
2.3630		2596	0.03542	18.312	957
2.9433		2730	0.03576	18.166	959
3.3630		2816	0.03765	18.225	973
3.5382		2829	0.04029	18.129	991
4.0562		2888	0.04356	18.033	1011
4.4593		2919	0.04890	18.058	1039
4.7324		2934	0.05657	18.062	1072
5.4676		2950	0.05766	18.137	1077
6.0860		2942	0.06038	18.217	1087
6.2926		2936	0.06784	18.108	1116
7.2307		2889	0.08710	18.150	1205
0.01506 [90—citric acid monohydrate]	29.200		0.02063	28.777	
0.01568	28.847		0.02093	28.824	
0.01899	29.357		0.02151	28.724	
0.01981	29.142		0.02203	29.110	
0.01989	28.841		0.02205	28.871	
0.02027	29.252		0.02336	28.670	
0.02029	28.786		0.02351	28.590	
0.02050	29.188				

$m^* = m/\text{mol kg}^{-1}$; $\Delta H_{sol}^* = \Delta H_{sol}/\text{kJ mol}^{-1}$; $\Delta H_{dil}^* = \Delta H_{dil}/\text{J mol}^{-1}$

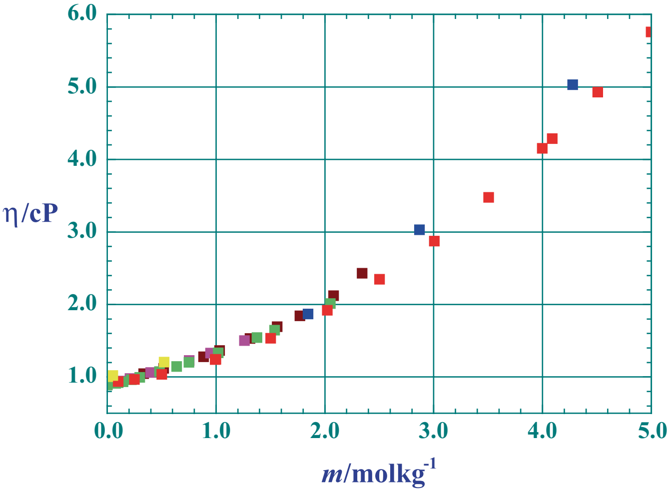

Fig. 2.37 Viscosity of aqueous solutions of citric acid as a function of concentration at temperature 25 °C. 🟦 - [15]; 🟩 - [92]; 🟫 - [117]; 🟪 - [89]; 🟩 - [157]. 🟨 - [163]; 🟥 - [164]

edly measured. However, they were determined with a various accuracy, usually at one temperature, and they cover a limited range of concentrations (Fig. 2.37).

Viscosities of aqueous solutions of citric acid were determined at 25 °C by Levien [89], Laguerie et al. [15] and Manzurola [157], and at 27.5 °C by Kortschak [163]. At 20 °C, they are tabulated in the CRC Handbook of Chemistry and Physics [71] for mass fractions $w \leq 0.30$. Few old measurements of viscosity having only historical value are given for the 20–45 °C temperature range by Taimni [165]. Viscosities in 5° intervals in the 25–40 °C range were determined by Kharat [117]. Similar measurements, from 30–45 °C, were performed by Palmer and Kushwaha [166] but their results are only presented in the form of the Jones–Dole equation coefficients. Viscosities from the above mentioned investigations cover reasonably well dilute and moderately concentrated solutions of citric acid (Fig. 2.38, Table 2.17). Tadkalkar et al. [116] measured viscosities in dilute solutions, but their results are incorrect (viscosities decrease with increasing concentration) and therefore are omitted from Table 2.17.

In more concentrated solutions, the situation is less favorable considering also a small number of experimental determinations (Fig. 2.39). A more detailed engineering study of viscosities in the citric acid-water system was performed by Averbukh et al. [164]. These viscosities were presented graphically, covering highly concentrated solutions, $0.16 \leq w \leq 0.83$ and over a wide temperature range from 20 to 90 °C. Averbukh et al. [164] correlated viscosities by the following empirical expression

$$\eta(w;T)/\mathrm{mPa\cdot s} = 0.0018\exp\left[-3.3\theta + 7.4w^{1.65}(1-\theta)\right]$$
$$\theta = \frac{T/\mathrm{K} - 273.15}{T/\mathrm{K} - 173.15} \tag{2.95}$$

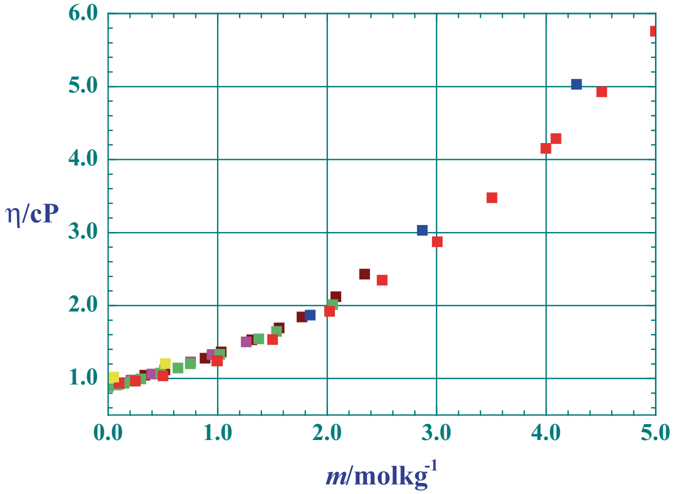

Fig. 2.38 Viscosity of aqueous solutions of citric acid as a function of concentration at temperature 25 °C. 🟦 - [15]; ▨ - [92]; 🟫 - [117]; 🟪 - [89]; 🟩 - [157]. 🟨 - [163]; 🟥 - [164]

Calculated from Eq. (2.95) viscosities are somewhat lower than those given by other authors (Fig. 2.39), but the over-all behaviour of viscosities considering concentration and temperature is satisfactory.

At 25 °C, for moderately concentrated solutions of citric acid, citric acid viscosities can be represented by the Jones-Dole type equation

$$\begin{aligned}&\frac{\eta(m)}{\eta(\mathrm{H_2O})} = 1 - 0.1889\sqrt{m^*} + 0.7228m^*\\&\eta(\mathrm{H_2O})\,/\,\mathrm{mPa{\cdot}s} = 0.8903\\&m^* \le 2.0 \quad ; \quad m^* = m\,/\,\mathrm{mol\cdot kg^{-1}}\end{aligned} \tag{2.96}$$

2.11 Diffusion Coefficients of Citric Acid in Aqueous Solutions

There is only few investigations dealing with diffusion coefficients of citric acid in aqueous solutions. Besides, it is not surprising to observe a large scattering of reported results (Fig. 2.40) considering experimental difficulties to determine them accurately. Measurements in dilute solutions were performed by Muller and Stokes [167] and in a more concentrated solutions by Laguerie et al. [15] and by van Drunen et al. [24].

These diffusion coefficients at 25 °C (Table 2.18), can roughly be approximated by

$$\begin{aligned}&\mathrm{D}\cdot 10^6\,/\,\mathrm{cm^2\cdot s^{-1}} = 6.57 - 0.5901m^* + 0.0183m^{*2}\\&m^* = m\,/\,\mathrm{mol\cdot kg^{-1}}\end{aligned} \tag{2.97}$$

Table 2.17 Viscosities of aqueous solutions of citric acid as a function of concentration and temperature

t/°C	w	η/cP	w	η/cP	w	η/cP
20	0.6169 [165]	24.6	0.040	1.098	0.160	1.525
	0.6403	33.1	0.050	1.125	0.180	1.625
	0.6516	39.9	0.060	1.153	0.200	1.740
	0.6743	56.8	0.070	1.183	0.220	1.872
			0.080	1.214	0.240	2.017
	0.005 [71]	1.013	0.090	1.247	0.260	2.178
	0.010	1.024	0.100	1.283	0.280	2.356
	0.020	1.048	0.120	1.357	0.300	2.549
	0.030	1.073	0.140	1.436		
25	0.6169 [165]	19.4	0.0000 [89]	0.894	0.1880	1.333
	0.6403	20.6	0.0227	0.942	0.2092	1.542
	0.6516	24.0	0.0384	0.978	0.2281	1.647
	0.6743	43.2	0.0545	1.061	0.2826	2.012
			0.1264	1.229		
	0.0000 [15]	0.91	0.1542	1.330	0.0000 [117]	0.894
	0.2617	1.87	0.1949	1.502	0.0605	1.045
	0.3554	3.03			0.0904	1.118
	0.4511	5.03	0.0145 [157]	0.913	0.1453	1.280
	0.4914	7.50	0.0190	0.920	0.1655	1.365
	0.5249	9.45	0.0270	0.934	0.2012	1.532
	0.5564	12.30	0.0408	0.962	0.2308	1.693
	0.5757	14.22	0.0544	0.995	0.2537	1.843
	0.5940	16.87	0.0844	1.073	0.2854	2.122
	0.6090	19.55	0.1092	1.145	0.3103	2.432
	0.6259	23.80	0.1260	1.201		
27.5	0.0010 [117]	1.004				
	0.0100	1.021				
	0.0913	1.205				

Table 2.17 (continued)

t/°C	w	η/cP	w	η/cP	w	η/cP
30	0.6169 [165]	15.8	0.0000 [117]	0.800	0.2012	1.345
	0.6403	20.6	0.0605	0.920	0.2308	1.482
	0.6516	24.0	0.0904	0.985	0.2537	1.631
	0.6743	33.2	0.1453	1.131	0.2854	1.857
			0.1655	1.205	0.3103	2.120
35	0.6169 [165]	12.9	0.0000 [117]	0.722	0.2012	1.193
	0.6403	16.6	0.0605	0.813	0.2308	1.331
	0.6516	19.5	0.0904	0.869	0.2537	1.445
	0.6743	26.0	0.1453	1.002	0.2854	1.632
			0.1655	1.068	0.3103	1.825
40	0.6169	10.8 [165]	0.0000 [117]	0.658	0.2012	1.059
	0.6403	13.6	0.0605	0.725	0.2308	1.179
	0.6516	15.9	0.0904	0.772	0.2537	1.275
	0.6743	16.5	0.1453	0.885	0.2854	1.454
			0.1655	0.943	0.3103	1.613
45	0.6169 [165]	9.1				
	0.6403	11.4				
	0.6743	16.5				

1 cP = 1 mPa · s = 10^{-3} Pa · s

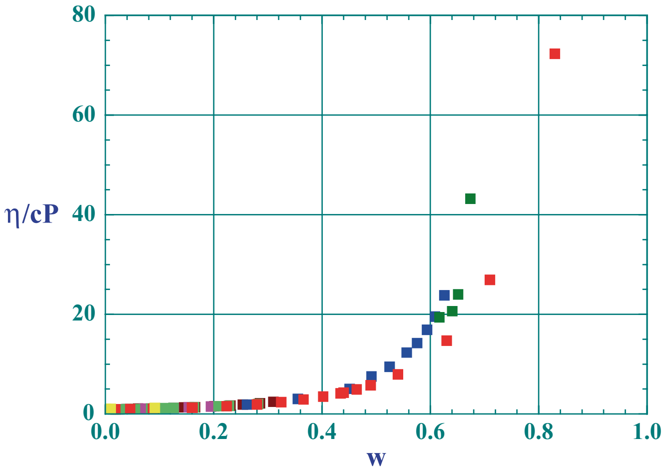

Fig. 2.39 Viscosity of aqueous solutions of citric acid as a function of mass fraction w at temperature 25 °C. 🟦 - [15]; 🟦 - [92]; 🟪 - [89]; 🟫 - [117]; 🟩 - [157]. 🟨 - [163]; 🟩 - [165]; 🟥 - [164]

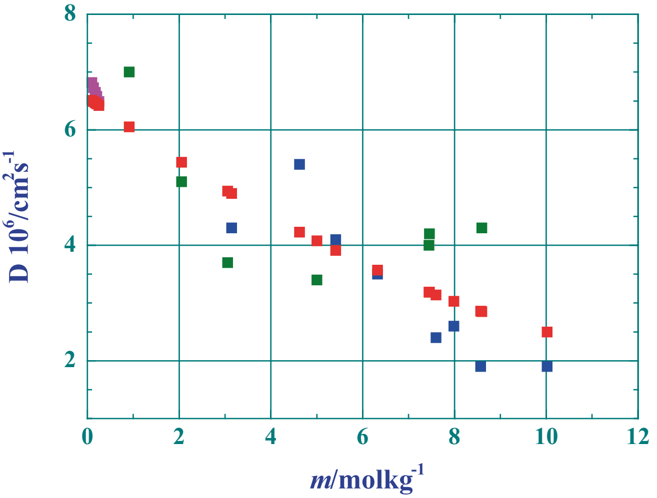

Fig. 2.40 Diffusion coefficients of citric acid in aqueous solutions at 25 °C as a function of concentration. 🟩 - [15]; 🟦 - [24]; 🟪 - [167]; 🟥 - calculated from Eq. (2.97)

From their measurements, Muller and Stokes [167] evaluated the limiting diffusion coefficient for the molecular form of citric acid $D^0(H_3Cit) = 6.57 \cdot 10^{-6}$ cm^2 s^{-1} and for monovalent ion $D^0(H_2Cit^-) = 8.1 \cdot 10^{-6}$ cm^2 s^{-1}. Southard et al. [168] gave $D(H_3Cit) = (7.1 - 8.7).10^{-6}$ cm^2 s^{-1} for the molecular citric acid and for the trivalent ion $D(Cit^{3-}) = (5.9 - 7.6).10^{-6}$ cm^2 s^{-1} values.

Diffusion coefficients were also determined in the mass-transfer investigations, when citric acid reacts with calcite [169], in citric acid solutions saturated with 1-butanol [170] and when citric acid diffuses through polymer membranes [171–173],

Table 2.18 Diffusion coefficients of citric acid in aqueous solutions at 298.15 K as a function of concentration

m/mol kg^{-1}	D · 10^6/cm^2 s^{-1}	*m*/mol kg^{-1}	D · 10^6/cm^2 s^{-1}	*m*/mol kg^{-1}	D · 10^6/cm^2 s^{-1}
0.0989 [167]	6.82	0.913 [15]	7.0	3.14 [24]	4.3
0.1351	6.73	2.053	5.1	4.62	5.4
0.1666	6.65	3.06	3.7	5.41	4.1
0.1759	6.65	5.00	3.4	6.32	3.5
0.2069	6.58	7.45	4.0	7.60	2.4
0.2514	6.49	7.46	4.2	7.99	2.6
		8.59	4.3	8.57	1.9
				10.02	1.9

prepeeled potatoes and heated potato tissues [174, 175]. For engineering purposes, at given T, there is a number of empirical formulas [176–178] and these formulas can be used for reasonable estimation of diffusion coefficients in dilute solutions. For example, using the Wilke and Chang correlation [177] (slightly modified for aqueous solutions by Hayduk and Laudie [178]) for citric acid solutions we have

$$\mathrm{D}(T) = \frac{1.123 \cdot 10^{-7}\sqrt{\mathrm{M}_{\mathrm{H_2O}}}\,T}{\eta(T)V_{\mathrm{H_3Cit}}^{0.6}} \tag{2.98}$$

where V is the molar volume at normal boiling point of solute. Replacing value of V by the molar volume of solid citric acid and considering that the change of specific volume with temperature in rather small (Eq. (2.1)), it is possible to write Eq. (2.98) in the form

$$\mathrm{D}(T)/\mathrm{cm}^2 \cdot \mathrm{s}^{-1} = \frac{4.72 \cdot 10^{-7}\,T/\mathrm{K}}{\eta(T)/\mathrm{cP}} \tag{2.99}$$

For example, for $m = 0.195$ mol kg^{-1} solution, which has viscosity $\eta(298.15\ \mathrm{K}) = 1.502$ cP (Table 2.17) from Eq. (2.99) we have a reasonable value of diffusion coefficient in dilute solutions $\mathrm{D} = 5.2 \cdot 10^{-6}$ cm^2 s^{-1}.

2.12 Thermal Conductivities of Aqueous Solutions of Citric Acid

Thermal conductivities of aqueous solutions of citric acid $\lambda(T;m)$ are only known from the Averbukh et al. [80] investigation, for $0.10 \le \mathrm{w} \le 0.90$, in 10 °C intervals from 20 to 90 °C (Table 2.19). They increase with increasing temperature T and decrease with increasing concentration w. The change in $\lambda(T;m)$ values in dilute solutions is significant considering high values of thermal conductivity of pure water [179]

$$\lambda(T;0)/\mathrm{W \cdot m^{-1} \cdot K^{-1}} = -0.9003 + 8.3869 \cdot 10^{-3}(T/\mathrm{K}) - 1.1180 \cdot 10^{-5}(T/\mathrm{K})^2 \tag{2.100}$$

The thermal conductivities as reported by Averbukh et al. [80] (from Table 2.19) can be expressed by

$$\begin{gathered}\lambda(T;\mathrm{w})/\mathrm{W \cdot m^{-1} \cdot K^{-1}} = 0.4432 + 3.0119 \cdot 10^{-4}(T/\mathrm{K}) \\ -0.8231\mathrm{w} + 0.9084\mathrm{w}^2 - 0.4814\mathrm{w}^3\end{gathered} \tag{2.101}$$

Table 2.19 Thermal conductivity of citric acid aqueous solutions as a function of temperature and concentration

w	$\lambda(T;\mathrm{w})$/W m^{-1} K^{-1}							
t/°C	20	30	40	50	60	70	80	90
0.00 [179]	0.598	0.615	0.630	0.642	0.653	0.661	0.667	0.671
0.10 [80]	0.463	0.466	0.468	0.469	0.471	0.471	0.474	0.475
0.20	0.401	0.403	0.405	0.407	0.409	0.411	0.411	0.413
0.30	0.356	0.358	0.361	0.363	0.365	0.367	0.367	0.370
0.40	0.321	0.325	0.326	0.328	0.332	0.333	0.333	0.336
0.50	0.291	0.293	0.295	0.298	0.300	0.303	0.303	0.308
0.60	0.261	0.264	0.267	0.269	0.272	0.276	0.276	0.278
0.70	0.231	0.237	0.241	0.243	0.247	0.249	0.249	0.255
0.80	0.209	0.212	0.215	0.218	0.222	0.224	0.227	0.230

2.13 Electrical Conductance of Citric Acid in Aqueous Solutions

First determinations of electrical conductivities in dilute aqueous solutions of citric acid were performed in 1892 by Walden [180] and Walker [181]. These measurements were used to estimate the first dissociation constant of citric acid and its limiting molar conductance at 25 °C. In 1912 Jones [182] reported a more comprehensive results (actual measurements were performed by L.D. Smith and E.P. Wightmann) in the 0–65 °C temperature range. Evidently, these conductivities $\Lambda(c)$ have only historical value, but they are comparable with modern determinations (Fig. 2.41) if their values are multiplied by the factor $f = 1.066$ [183, 184]. After a long pause in measurements of $\Lambda(c)$ in dilute aqueous solutions, they were determined by Manzurola [157] at 25, 30 and 35 °C and by Apelblat and Barthel [185] in the 5–35 °C temperature range. They measured also the corresponding conductivities of trilithium citrate, trisodium citrate and tripotassium citrate. If all available sets of conductivity data (Table 2.20) are plotted, they yield a common curve (Fig. 2.41) but differences between different works, especially in very dilute solutions are significant.

Conductivities of moderately concentrated solutions of citric acid were measured only by Levien [89] at 25 °C and by Kharat [117] in the 25–40 °C temperature range, but differences between $\Lambda(c)$ values, as shown in Fig. 2.42, are large. Shamin and Eng [186] reported the limiting molar conductance of the dihydrogen citrate anion $\lambda^0(H_2Cit^-) = 29.2 \pm 0.2$ S cm^2 mol^{-1} and its transference number $t(H_2Cit^-) = 0.074$, which were determined in the 0.011–0.055 mol dm^{-3} concentration

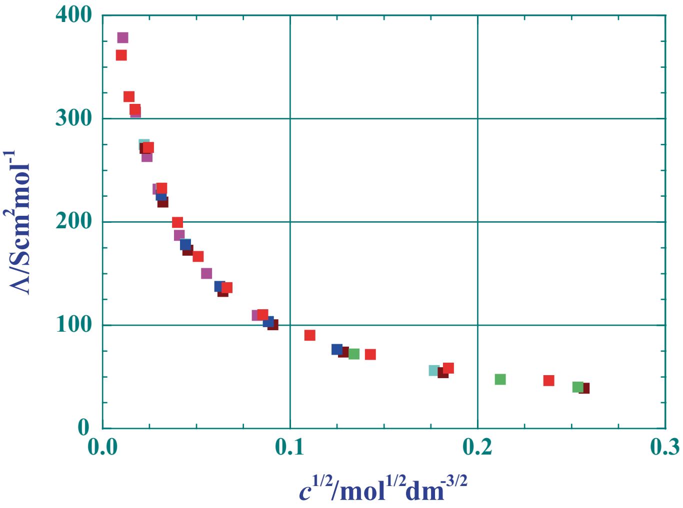

Fig. 2.41 Molar conductivity of citric acid at 25 °C as a function of the square root of concentration. 🟩 - [89]; 🟥 - [157]; 🟦 - [180]; 🟫 - [181]; 🟦 - [182] and 🟪 - [185]

Table 2.20 Molar conductivities of citric acid in dilute aqueous solutions as a function of temperature and concentration

t/°C	(c/mol dm^{-3})^a	Λ/S cm^2 mol^{-1}	*t*/°C	(c/mol dm^{-3})^a	Λ/S cm^2 mol^{-1}
0	0.00049 [182]	169.71	5	0.000116 [185]	259.09
	0.00098	135.70		0.000314	208.09
	0.00195	103.64		0.000563	176.81
	0.00781	59.63		0.000874	155.57
	0.03125	32.27		0.001685	124.57
	0.1250	16.67		0.003075	99.49
				0.006786	72.17
10	0.000116 [185]	289.18	15	0.000116 [185]	320.84
	0.000314	232.80		0.000314	257.56
	0.000563	199.16		0.000563	220.56
	0.000874	174.72		0.000874	193.90
	0.001685	140.20		0.001685	155.91
	0.003075	112.15		0.003075	124.89
	0.006786	81.50		0.006786	90.91
18.1	0.00049 [182]	244.43	20	0.000116 [185]	349.04
	0.00098	206.06		0.000314	282.09
	0.00195	158.09		0.000563	242.13
	0.00781	92.10		0.000874	212.94
	0.03125	49.84		0.001685	171.49
	0.12500	25.96		0.003075	137.55
				0.006786	100.25
25	0.00051 [181]	271.30	25	0.00098 [180]	225.99
	0.00103	219.17		0.00195	178.02
	0.00206	172.69		0.00391	137.51
	0.00412	132.82		0.00781	103.42
	0.00824	100.42		0.01563	76.60
	0.01647	73.98			
	0.03295	54.05			

Table 2.20 (continued)

$t/°C$	$(c/mol\ dm^{-3})^a$	$\Lambda/S\ cm^2\ mol^{-1}$	$t/°C$	$(c/mol\ dm^{-3})^a$	$\Lambda/S\ cm^2\ mol^{-1}$
	0.06592	38.91			
25	0.00049 [182]	274.92	25	0.000116 [185]	378.52
	0.00098	232.49		0.000314	306.36
	0.00195	178.66		0.000563	263.30
	0.00781	103.72		0.000874	231.79
	0.03125	56.24		0.001685	186.94
	0.12500	29.32		0.003075	150.11
				0.006786	109.53
2	0.0001 [157]	361.50	25	0.0180 [89]	72.16
	0.0002	321.30		0.0449	47.57
	0.0003	309.00		0.0642	40.12
	0.0006	272.10		0.1122	30.58
	0.0010	232.80		0.1603	25.46
5	0.0016	199.50		0.2803	18.85
	0.0026	166.50		0.4004	15.26
	0.0044	136.50		0.7000	10.46
	0.0073	110.10		1.0000	7.79
	0.0122	90.30			
	0.0204	71.70	35	0.00049 [182]	317.45
	0.0340	58.50		0.00098	268.53
	0.0566	46.50		0.00195	207.98
	0.0943	33.00		0.00781	120.14
				0.03125	65.47
30	0.000116 [185]	407.15		0.12500	34.17
	0.000314	330.15			
	0.000563	284.05	35	0.000116 [185]	435.88
	0.000874	250.25		0.000314	353.40
	0.001685	202.08		0.000563	304.34

Table 2.20 (continued)

t/°C	(c/mol dm^{-3})^a	Λ/S cm^2 mol^{-1}	*t*/°C	(c/mol dm^{-3})^a	Λ/S cm^2 mol^{-1}
	0.003075	162.40		0.000874	268.32
	0.006786	118.61		0.001685	216.87
				0.003075	174.44
35	0.0004 [157]	243.90		0.006786	127.51
	0.0005	231.30			
	0.0008	212.10	45	0.0003 [157]	308.40
	0.0010	196.50		0.0004	299.70
	0.0016	176.70		0.0006	278.70
	0.0020	162.00		0.0007	268.20
	0.0025	154.80		0.0009	253.50
	0.0031	142.50		0.0011	241.80
	0.0039	132.60		0.0018	215.10
	0.0048	122.40		0.0028	186.30
	0.0060	111.60		0.0035	173.10
	0.0075	102.90		0.0044	160.20
	0.0094	94.50		0.0054	147.90
	0.0147	78.90		0.0068	135.90
	0.0184	72.00		0.0085	125.70
	0.0230	65.70		0.0106	114.60
	0.0288	59.70		0.0166	96.00
	0.0359	54.00		0.0208	87.60
	0.0449	49.20		0.0259	80.70
	0.0562	50.70		0.0324	72.60
	0.0702	46.80		0.0507	60.00
	0.0877	41.40		0.0792	48.60
	0.1097	36.00		0.0990	44.10
50	0.00049 [182]	381.38	65	0.00049 [182]	437.76
	0.00098	325.35		0.00098	361.05

Table 2.20 (continued)

t/ °C	(c/mol dm^{-3})[a]	Λ/S cm^2 mol^{-1}	t/ °C	(c/mol dm^{-3})[a]	Λ/S cm^2 mol^{-1}
	0.00195	249.84		0.00195	284.86
	0.00781	145.45		0.00781	165.88
	0.03125	80.80		0.03125	92.73
	0.1250	40.41		0.1250	46.66

[a] Concentrations at 25 °C, for other temperatures they can be evaluated by using density of pure water

range. Milazzo [187] estimated the limiting conductance of tri-charged citrate anion to be $\lambda^0(1/3\mathrm{Cit}^{3}-) = 71.5$ S cm^2 mol^{-1}.

Without presenting actual conductivities, Bhat and Manjunatha [188, 189] presented only the limiting conductances and the ion association constants of citric acid in water, in water + methanol, water + ethanol, water + acetonitrile and water + dimethylsulphoxide mixtures at 10, 20, 30 and 40 °C. Conductivity measurements of calcium ions in citrate buffers were performed by Davies and Hoyle [190, 191] and Wiley [192]. The citric acid interactions in acetonitrile were studied by Huyskens and Lambeau [193, 194].

With an exception of the Apelblat and Barthel [185] investigation, conductivities of citric acid in water were treated entirely in the framework of a weak, 1:1 type electrolyte models. However, the interpretation of conductivities in aqueous citric acid solutions is supposed to include all three steps of dissociation, by considering the existence of H^+, H_2Cit^-, $HCit^{2-}$ and Cit^{3-} ions and undissociated molecules H_3Cit. As a consequence, at given temperature T, the "correct" representation of molar conductivities $\Lambda(c, T)$ can only be achieved by the solution of a rather complex mathematical problem. Data processing procedure leads to the evaluation of dissociation constants and coefficients of corresponding conductivity equations. This is performed in two steps by simultaneously solving, in an appropriate optimization procedure, the so-called chemical and conductivity problems. In the first step, the concentration fractions of the primary, secondary and tertiary steps of dissociation $\alpha_1 = \alpha(H_2Cit^-)$, $\alpha_2 = \alpha(HCit^{2-})$ and $\alpha_3 = \alpha(Cit^{3-})$ are determined (see Chap. 3). In the second step, these concentration fractions α_j are introduced to the conductivity equations which are suitable to represent a weak, unsymmetrical 1:3 type electrolyte [184, 185, 195].

The electrolyte conductivity $\Lambda(c, T)$ is the sum of the ionic contributions in the solution

$$\Lambda(c,T) = \frac{1000\kappa}{c} = \sum_j \frac{|z_j| c_j \lambda_j(c,T)}{c} \tag{2.102}$$

where κ is the measured specific conductance of solution with a formal analytical concentration c. z_j are the corresponding charges of cations and anions and their molar concentrations are $c_j = \alpha_j c$.

The ionic conductances $\lambda_j(c, T)$ in dilute solutions are represented by

$$\begin{gathered} \lambda_j(c,T) = \lambda_j^0(T) - S_j(T)\sqrt{I} + E_j(T) I \ln I + J_{1j}(T) I - J_{2j}(T) I^{3/2} \\ I = \frac{1}{2}\sum_j z_j^2 c_j \end{gathered} \tag{2.103}$$

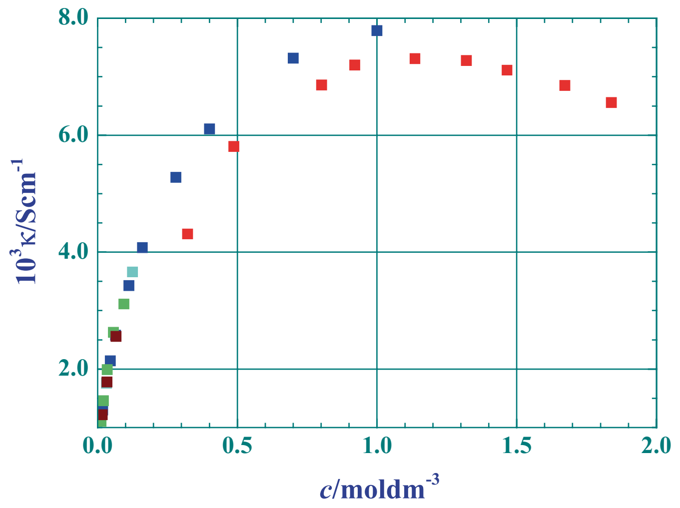

Fig. 2.42 Specific conductivity of citric acid at 25 °C as a function of concentration. 🟦 - [89]; 🟥 - [117]; 🟩 - [157]; 🟫 - [181] and ■ - [182]

where coefficients $S_j(T)$, $E_j(T)$, $J_{1j}(T)$ and $J_{2j}(T)$ are complex functions of the limiting molar ionic conductances $\lambda_j^0(T)$ and distance parameters $a_j(T)$ and physical properties of pure water (dielectric constant $D(T)$ and viscosity $\eta(T)$). The explicit expressions for these coefficients are available from the Quint-Viallard [195] or the Lee-Wheaton [196] theories of unsymmetrical type electrolytes. The single ion conductivities $\lambda_j(c, T)$ are directly proportional to the mobilities of ions, $\lambda_j(c, T) = \mathrm{F} \cdot u_j(c, T)$ where F is the Faraday constant.

In the case of citric acid, the determined molar conductivity $\Lambda(H_3Cit)$ results from pairs of unequally charged ions (cation + anion), namely $H^+ + H_2Cit^-$, $H^+ + HCit^{2-}$ and $H^+ + Cit^{3-}$. These contributions to the molar conductivity of citric acid are

$$\begin{aligned}
\Lambda_1(c) &= [\lambda(\mathrm{H}^+) + \lambda(\mathrm{H_2Cit}^-)] \\
\Lambda_2(c) &= [\lambda(\mathrm{H}^+) + \lambda(1/2\mathrm{HCit}^{2-})] \\
\Lambda_3(c) &= [\lambda(\mathrm{H}^+) + \lambda(1/3\mathrm{Cit}^{3-})] \\
\Lambda(\mathrm{H_3Cit}) &= \alpha_1\Lambda_1(c) + 2\alpha_2\Lambda_2(c) + 3\alpha_3\Lambda_3(c)
\end{aligned} \tag{2.104}$$

where the individual molar conductivities are given in Eq. (2.103) and the ionic strength of solutions is $I = c(\alpha_1 + 3\alpha_2 + 6\alpha_3)$.

Using the Apelblat and Barthel [185] experimental conductivities and by fixing sizes of ions and contact distance parameters as $a(H^+) = 9.0$ Å, $a(H_2Cit^-) = 3.5$ Å, $a(HCit^{2-}) = 4.5$ Å, $a(Cit^{3-}) = 5.0$ Å, $a_1 = 6.25$ Å, $a_2 = 6.75$ Å, $a_3 = 7.0$ Å, in the framework of the Quint-Viallard conductivity equations, from the optimization procedure it is possible to obtain the following dissociation constants at 25 °C,

$K_1 = 6.98 \cdot 10^{-4}$ mol dm^{-3}, $K_2 = 1.40 \cdot 10^{-5}$ mol dm^{-3} and $K_3 = 4.05 \cdot 10^{-7}$ mol dm^{-3} (for other temperatures see [195]). The partial molar conductivities of citric ion pairs (Eq. (2.104)) are

$$\begin{aligned}
\Lambda_1(c) &= 385.72 - 149.24\sqrt{I} + 71.179 I \ln I + 768.72 I - 1646.9 I^{3/2} \\
\Lambda_2(c) &= 400.23 - 230.84\sqrt{I} + 171.28 I \ln I + 1147.7 I - 2367.3 I^{3/2} \\
\Lambda_3(c) &= 421.90 - 304.17\sqrt{I} + 148.74 I \ln I - 952.06 I - 1652.6 I^{3/2} \\
I &= c(\alpha_1 + 3\alpha_2 + 6\alpha_3)
\end{aligned} \tag{2.105}$$

where units of them are S cm^2 mol^{-1} ($1/\Omega = 1$ S). The evaluated limiting conductances at infinite dilution in aqueous solutions of citric acid (Λ^0-values in Eq. (2.105)), are the characteristic parameters of the ionic transport which is undisturbed by interactions between citrate and hydrogen ions.

From the Kohlrausch law of independent migration of ions and considering that the limiting conductance of hydrogen ion in water is known, $\lambda^0(H^+) = 349.85$ S cm^2 mol^{-1}, the limiting conductances of citrate anions at 25 °C are: $\lambda^0(H_2Cit^-) = 35.87$ S cm^2 mol^{-1}, $\lambda^0(1/2HCit^{2-}) = 50.38$ S cm^2 mol^{-1}and $\lambda^0(1/3Cit^{3-}) = 72.05$ S cm^2 mol^{-1}. Due to slightly different optimization procedure, the reported in [184, 185] values of the limiting conductances of citrate anions are somewhat different. Smaller value of $\lambda^0(H_2Cit^-)$ is given by Levien [89] who assumed that the limiting molar conductance of the dihydrogen citrate anion is similar to that of picrate ion 30.39 S cm^2 mol^{-1} and as pointed above, Shamin and Eng [186] reported $\lambda^0(H_2Cit^-) = 29.2$ S cm^2 mol^{-1}. There are no other limiting conductances for di- and tri-charged citrate ions in the literature.

Since in conductivity experiments with citric acid, the contribution coming to determined conductance $\Lambda(H_3Cit)$ from the pair of $H^+ + Cit^{3-}$ ions is small, the limiting molar conductance $\lambda^0(1/3Cit^{3-})$ is derived from measurements with neutral citrates Me_3Cit (Me = Li, Na and K, Table 2.21) by using the Kohlrausch equation

$$\begin{aligned}
\Lambda(c) &= \Lambda^0(\mathrm{Me_3Cit}) - S_{\mathrm{obs.}}\sqrt{I} \\
\Lambda^0_{\mathrm{eq.}} &= \Lambda^0(\mathrm{Me_3Cit})/3 = \lambda^0(\mathrm{Me^+}) + \lambda^0(1/3\mathrm{Cit^{3-}}) \\
I &= 6c
\end{aligned} \tag{2.106}$$

where $S_{\mathrm{obs.}}$ is the slope determined by the least square method at given temperature T. Molar conductivities of alkali metal citrates in dilute aqueous solutions can be represented at 25 °C by [195]

$$\begin{aligned}
\Lambda(c; \mathrm{Li_3Cit}) &= 336.09 - 587.73\sqrt{I} \\
\Lambda(c; \mathrm{Na_3Cit}) &= 368.16 - 554.40\sqrt{I} \\
\Lambda(c; \mathrm{K_3Cit}) &= 732.74 - 524.11\sqrt{I}
\end{aligned} \tag{2.107}$$

Table 2.21 Molar conductivities of alkali metal citrates in dilute aqueous solutions as a function of temperature and concentration [185]

10^4 *m**	Λ/S cm^2 mol^{-1}						
t/°C	5	10	15	20	25	30	35
Li$_3$Cit							
1.1334	189.27	219.87	251.88	285.81	321.18	358.74	397.38
1.2900	187.77	217.92	250.14	283.95	319.26	356.10	394.47
2.8931	183.66	213.09	244.20	277.02	311.52	347.43	384.78
3.7949	181.83	210.99	241.92	274.44	308.52	344.07	380.91
5.2767	178.80	207.36	237.66	269.46	302.91	337.65	373.68
7.1900	175.68	203.70	233.55	264.75	297.48	331.50	366.81
9.5443	172.44	199.92	228.99	259.65	291.69	325.56	359.43
Na$_3$Cit							
0.8857	211.89	245.07	280.29	317.49	356.34	396.75	438.93
2.1369	206.70	239.16	273.27	309.57	347.49	387.09	428.22
5.4841	200.01	231.42	264.45	299.58	336.18	374.25	414.12
9.8680	193.74	224.16	256.05	290.01	325.20	362.04	400.23
16.1087	187.20	216.48	247.32	280.08	314.22	349.56	386.25
K$_3$Cit							
1.9189	254.22	291.81	331.08	372.18	415.08	459.36	505.20
5.4882	247.02	283.44	321.66	361.50	403.08	445.95	490.20
9.8838	240.93	276.21	313.41	352.14	392.43	434.01	476.97
17.0642	233.34	267.60	303.54	340.92	379.77	419.85	461.13

$m^* = m/\text{mol kg}^{-1}$

and the limiting conductances of cations are: $\lambda^0(\mathrm{Li}^+) = 38.64$ S cm^2 mol^{-1}; $\lambda^0(\mathrm{Na}^+) = 50.15$ S cm^2 mol^{-1} and $\lambda^0(\mathrm{K}^+) = 73.50$ S cm^2 mol^{-1} [72, 197] which gives the limiting conductance of tri-charged citrate anion as $\lambda^0(1/3\mathrm{Cit}^{3-}) = 72.24 \pm 1.35$ S cm^2 mol^{-1}.

If the optimization procedure is performed by assuming that alkali metal citrates behave as strong 1:3 type electrolytes (the straight lines of the equivalent conductivities have the Onsager slope [72, 76, 198])

$$\begin{aligned} \Lambda_{\mathrm{eq.}}(c) &= \Lambda^0_{\mathrm{eq.}} - S\sqrt{I} \\ S &= \alpha\Lambda^0_{\mathrm{eq.}} + \beta \end{aligned} \tag{2.108}$$

where

$$\begin{aligned} \alpha &= \frac{4.8047\cdot 10^6}{[D(T)T]^{3/2}} \frac{q}{1+\sqrt{q}} \\ \beta &= \frac{164.954}{\eta(T)\sqrt{D(T)T}} \\ q &= \frac{3[\lambda^0(\mathrm{Me}^+) + \lambda^0(1/3\mathrm{Cit}^{3-})]}{43[\lambda^0(\mathrm{Me}^+) + \lambda^0(1/3\mathrm{Cit}^{3-})]} \end{aligned} \tag{2.109}$$

then the limiting conductance of tri-charged citrate anion is $\lambda^0(1/3\mathrm{Cit}^{3-}) = 72.91 \pm 0.36$ S cm^2 mol^{-1}.

Temperature dependence of limiting conductances of citrate ions in the 0–65 °C range can be accurately evaluated from the Walden products $\eta(T)\cdot\lambda_j^0(T)$ where $\eta(T)$ is viscosity of pure water [197]. These products are practically independent of temperature T: $\eta(T)\cdot\lambda^0(\mathrm{H_2Cit^-}, T) = 0.3189 \pm 0.0023$ S cm^2 mol^{-1} Pa·s; $\eta(T)\,\lambda^0(1/2\mathrm{HCit}^{2-}, T) = 0.4408 \pm 0.0180$ S cm^2 mol^{-1} Pa·s and $\eta(T)\,\lambda^0(1/3\mathrm{Cit}^{3-}, T) = 0.6419 \pm 0.0011$ S cm^2 mol^{-1} Pa s.

Using values of the limiting molar conductances of individual ions $\lambda_j^0(T)$, at temperature T, it is possible to determine mobilities, diffusion coefficients and the Stokes ionic radii. From the Stokes–Einstein laws it follows that [197]

$$\begin{aligned} \mathrm{u_j^0} &= \frac{\mathrm{N_A}\lambda_j^o}{|\mathrm{z_j}|\mathrm{F}^2} \\ \mathrm{D_j^0} &= \frac{\mathrm{RT}\lambda_j^o}{|\mathrm{z_j}|\mathrm{F}^2} \\ \mathrm{r_j} &= \frac{|\mathrm{z_j}|\mathrm{F}^2\mathrm{N_A}\lambda_j^o}{6\pi\mathrm{N_A}\lambda_j^o\eta} \end{aligned} \tag{2.110}$$

where $\mathrm{N_A}$ is the Avogadro number.

From Eq. (2.110), diffusion coefficients of citrate ions are: $D^0(H_2Cit^-)=9.6\cdot10^{-6}$ cm^2 s^{-1}, $D^0(HCit^{2-})=6.7\cdot10^{-6}$ cm^2 s^{-1} and $D(Cit^{3-})=6.4.10^{-6}$ cm^2 s^{-1} and these values are very similar to those mentioned in [167, 168]. The estimated Stokes radii are: $r(H_2Cit^-)=2.6$ Å, $r(HCit^{2-})=3.7$ Å and $r(Cit^{3-})=3.8$ Å.

For the pairs of ions, diffusion coefficients are given by the Nerst–Hartley equation

$$D_{\pm}^{0}=\frac{RT}{F^2}\frac{(|z_+|+|z_-|)\lambda_+^o\lambda_-^o}{|z_+z_-|(\lambda_+^o+\lambda_-^o)} \qquad (2.111)$$

which gives at 25 °C for the hydrogen + citrate ion pairs: $D^0(H^++H_2Cit^-)=1.73\cdot10^{-5}$ cm^2 s^{-1}, $D^0(H^++HCit^{2-})=1.76\cdot10^{-5}$ cm^2 s^{-1} and $D^0(H^++Cit^{3-})=2.12\cdot10^{-5}$ cm^2 s^{-1}. As expected, these values are higher than those for diffusion coefficients of molecular citric acid, $D^0(H_3Cit)=6.57\cdot10^{-6}$ cm^2 s^{-1}, reported by Muller and Stokes [167], At other temperatures, the corresponding diffusion coefficients can be evaluated by combining the Walden products and Eqs. (2.110) and (2.111).

Conductivities of concentrated solutions are usually expressed by empirical equations with parameters having no physical meaning. A widely used the Casteel and Amis equation for specific conductivity curves, $\kappa(c)$ or $\kappa(m)$, have four adjustable parameters a, b, $\kappa_{\max}$ and $c_{\max}$ or $m_{\max}$ ($\kappa_{\max}$ is the maximum of specific conductivity and $m_{\max}$ is the molality at which the maximum is situated) [197]. This equation in the logarithmic form is

$$\ln\left(\frac{\kappa}{\kappa_{\max}}\right)=a\left[\ln\left(\frac{m}{m_{\max}}\right)-\left(\frac{m}{m_{\max}}-1\right)\right]+b(m-m_{\max})^2. \qquad (2.112)$$

An accurate location of the maximum parameters is not easy because usually a broad maximum is observed. Increase in temperature shifts the maximum to higher concentrations as a consequence of decreasing viscosity. The specific conductivities of the 0.4–2.34 mol kg^{-1} citric acid solutions at 25 °C, as measured by Kharat [117], can be represented by Eq. (2.112) using the following parameters: $\kappa_{\max}=0.007289$ S cm^{-1}, $m_{\max}=1.372$ mol kg^{-1}, $a=0.8652$ and $b=0.05464$ mol^{-2} kg^2.

2.14 Index of Refraction of Aqueous Solutions of Citric Acid

Index of refraction $n_D(m;T)$ of aqueous solutions of citric acid as a function of concentration is known in the 20–40 °C temperature range from CRC Handbook of Chemistry and Physics [71] and from investigations of Laguerie et al. [15], Kharat [117] and Lienhard et al. [55] (Table 2.22).

Table 2.22 Refraction index of aqueous solutions of citric acid as a function of concentration and temperature

$t/°C$	$m/\mathrm{mol\ kg^{-1}}$	n_D	$m/\mathrm{mol\ kg^{-1}}$	n_D	$m/\mathrm{mol\ kg^{-1}}$	n_D
20	0.0262 [25 °C, 71]	1.3336	0.3918	1.3420	1.1426	1.3569
	0.0526	1.3343	0.4526	1.3433	1.3012	1.3598
	0.1062	1.3356	0.5148	1.3446	1.4681	1.3626
	0.1610	1.3368	0.5783	1.3459	1.6437	1.3655
	0.2169	1.3381	0.7098	1.3486	1.8288	1.3684
	0.2739	1.3394	0.8473	1.3514	2.0242	1.3714
	0.3322	1.3407	0.9914	1.3541	2.2307	1.3744
25	0.9357 [25 °C, 15]	1.3589	8.159	1.4341	0.3351 [117]	1.3400
	1.9558	1.3764	8.690	1.4375	0.5175	1.3440
	3.0789	1.3908	9.347	1.4402	0.8848	1.3515
	4.017	1.4001			1.0321	1.3542
	4.245	1.4047	0.5453 [55]	1.3346	1.3109	1.3592
	4.784	1.4101	1.3295	1.3597	1.5615	1.3635
	5.353	1.4157	2.1618	1.3729	1.7697	1.3668
	6.250	1.4209	3.5013	1.3899	2.0790	1.3715
	6.743	1.4257	5.1137	1.4311	2.3422	1.3752
	7.187	1.4272	9.0240	1.4530		
	7.317	1.4289	15.3355	1.4056		
	7.492	1.4298				
	0.3351 [30 °C, 117]	1.3395	0.3351[35 °C, 117]	1.3387	0.3351[40 °C, 117]	1.3380
	0.5175	1.3435	0.5175	1.3428	0.5175	1.3420
	0.8848	1.3510	0.8848	1.3502	0.8848	1.3495
	1.0321	1.3537	1.0321	1.3530	1.0321	1.3523
	1.3109	1.3587	1.3109	1.3579	1.3109	1.3572
	1.5615	1.3635	1.5615	1.3622	1.5615	1.3615
	1.7697	1.3663	1.7697	1.3655	1.7697	1.3648
	2.0790	1.3710	2.0790	1.3702	2.0790	1.3695
	2.3422	1.3747	2.3422	1.3740	2.3422	1.3733

Values of $n_D(m;T)$ can be correlated in terms of molar fractions of citric acid in aqueous solution x in the following way

$$\begin{aligned} &n_D(m;T) = n_D(H_2O;T) + 1.2123x - 3.2912x^2 \\ &n_D(H_2O;T) = 0.3346 - 3.2157 \cdot 10^{-5}\theta - 1.4357 \cdot 10^{-6}\theta^2 \\ &\theta = (T/K - 273.15) \end{aligned} \tag{2.113}$$

From the index of refraction it is possible to calculate the molar refractivity [R] using the Lorentz–Lorenz equation

$$\begin{aligned} &[R] = \left(\frac{n_D^2 - 1}{n_D^2 + 2}\right)\frac{\overline{M}}{d} = \frac{4\pi}{3}N_A\alpha \\ &\overline{M} = xM_{H_3Cit} + (1 - x)M_{H_2O} \end{aligned} \tag{2.114}$$

where α is the polarizability and N_A is the Avogadro number. It is interesting to note that for aqueous solutions of citric acid, the molar refractivity is a linear function of mole fraction x and is independent of temperature (Fig. 2.43)

$$[R(x;T)]/\text{cm}^3 \cdot \text{mol}^{-1} = 3.7044 + 33.641x \tag{2.115}$$

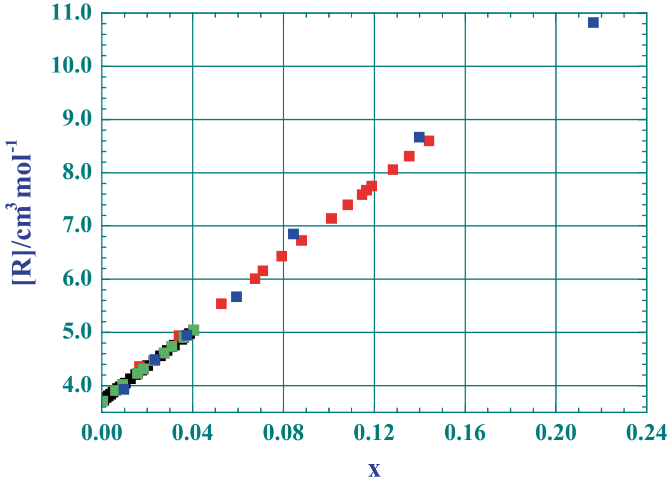

Fig. 2.43 The molar refractivity of aqueous solutions of citric acid as a function of mole fraction in the 20–40 °C temperature range. 20 °C ⬛ - [71]; 25 °C 🟥 - [15]; 25 °C 🟦 - [55]; 🟪 - [117]; 30 °C 🟩 - [117]; 35 °C 🟫 - [117]; 40 °C 🟩 - [117]

2.15 Surface Tension of Aqueous Solutions of Citric Acid

The first measurements of surface tension of citric acid solutions were performed already in 1898 by Traube [199], later by Linebarger [200] in 1898 and by Livingston et al. [201] in 1913. From these investigations, only the Linebarger surface tensions at 15 °C, in the $0.06 < w < 0.65$ mass fraction concentration region, are comparable with modern values. Detailed determinations of surface tension $\sigma(T;w)$, associated with the citric acid production, were performed from 20 to 90 °C and for $0.1 < w < 0.8$ concentration region by the Averbukh group [80, 202] in the 1972–1973 period [80, 202]. Patel et al. [203] reported the parachor values, $P = M\sigma^{1/4}/d$, for a very dilute solutions of citric acid at 30 °C. At boiling temperatures, Sarafraz [204] correlated surface tensions with compositions of citric acid solutions. Since multicomponent aerosol particles in the moist atmosphere (citric acid is one of them) significantly affect the surface tension of cloud droplets, in a number of metrological studies surface tensions of citric acid solutions were also reported [51, 56, 205]. All available surface tensions of citric acid aqueous solutions are presented in Table 2.23.

As can be observed in Fig. 2.44, surface tensions determined in different investigations differ considerably. Recently performed measurements of surface tension in the University of Silesia, from 10 to 50 °C and for $0.1 < w < 0.6$, are consistent with the Averbukh group [80] results, but not with those given by them in other investigation [202]. Thus, determined surface tensions of aqueous solutions of citric acid are uncertain, not sufficiently accurate and therefore more measurements of them are required.

The temperature–concentration dependence of surface tensions $\sigma(T;w)$ was correlated in Averbukh et al. [80] by

$$\sigma(T;\mathrm{w})/\mathrm{mN{\cdot}m^{-1}} = \sigma(T;0)/\mathrm{mN\cdot m^{-1}} - \frac{15\mathrm{w}}{0.5+\mathrm{w}}\left[\frac{T/\mathrm{K}-273.15}{100}\right] \quad (2.116)$$

where the surface tension of water is given by [206]

$$\begin{gathered}\sigma(T;0)/\mathrm{mN\cdot m^{-1}} = 235.8\left(1-\frac{T}{T_c}\right)^{1.256}\left[1-0.625\left(1-\frac{T}{T_c}\right)\right] \\ T_c/K = 647.15.\end{gathered} \quad (2.117)$$

Over wide ranges of temperatures, parachor values for pure substances are nearly constant, but for solutions they depend on concentration of solutes. Using surface tensions and densities from 10 to 50 °C temperature range, which were determined in the Silesian University, the parachor values for aqueous solutions of citric acid can be expressed by

Table 2.23 Surface tension of aqueous solutions of citric acid as a function of concentration and temperature

$\sigma(T;\mathrm{w})$/mN m^{-1}						
t/°C	15		25		25	
w		w		w		
0.0612 [200]	69.35	0.0000 [205]	72.12	0.001 [56]	71.0	
0.0803	68.91	0.0048	71.92	0.005	71.0	
0.1850	66.27	0.0472	70.24	0.01	71.0	
0.2996	65.46	0.0927	69.00	0.05	69.0	
0.3111	65.41	0.1452	67.41	0.10	68.0	
0.4352	65.17	0.1789	66.56	0.30	65.0	
0.5800	65.19	0.2197	66.01	0.40	65.0	
0.6413	65.18	0.2592	65.23			
0.6508	65.19	0.3343	65.22			
		0.4049	64.90			
		0.4714	64.98			
w; t/°C	*10*	*20*	*30*	*40*	*50*	
0.0000[a]	74.08	72.56	70.86	69.21	67.41	
0.0507	71.77	70.33	68.81	67.35	65.94	
0.0988	71.21	70.11	68.89	67.68	66.38	
0.1535	70.54	69.60	68.53	67.33	66.18	
0.2013	69.99	68.92	67.79	66.68	65.42	
0.2499	69.13	67.72	66.27	64.79	63.20	
0.3026	68.72	67.85	66.93	65.88	65.07	
0.3488	68.63	67.39	66.01	64.62	63.36	
0.3990	68.05	66.60	65.60	64.60	63.65	
0.4474	68.22	67.05	65.68	64.26	63.07	
0.5013	67.50	66.57	65.62	64.48	63.39	
0.5513	66.63	65.55	64.50	63.43	62.41	

Table 2.23 (continued)

$\sigma(T;\mathrm{w})/\mathrm{mN\ m^{-1}}$						
t/°C	15		25		25	
w				w		
0.5952	66.29	65.53	64.54	63.66	62.81	
0.6499	0.00	68.06	67.35	66.80	65.98	
0.7032	70.58	69.71	68.84	67.85	67.14	
w; t/°C	*20*	*30*	*40*	*50*	*60*	
0.10 [80]	72.25	70.40	68.85	66.65	64.60	
0.20	71.89	69.86	67.86	65.76	63.50	
0.30	71.63	69.46	67.49	65.10	62.70	
0.40	71.47	69.15	66.90	64.55	62.10	
0.50	71.25	68.90	66.70	64.15	61.60	
0.60	71.12	68.71	66.32	63.81	61.22	
0.70	71.01	68.61	66.05	63.50	60.90	
0.80	70.90	68.39	65.85	63.30	60.61	
	70	*80*	*90*			
0.10	62.66	60.60	58.49			
0.20	61.41	59.20	56.84			
0.30	60.31	58.10	55.54			
0.40	59.71	57.20	54.57			
0.50	59.16	56.60	54.02			
0.60	58.71	56.10	53.44			
0.70	58.31	55.60	52.84			
0.80	58.01	55.20	52.44			
w; t/°C	*20.6*	*30.3*	*38.6*	*43.4*	*48.3*	*54.5*
0.128 [202]	69.77	68.07	67.20	66.62	65.90	65.41
0.200	69.09	67.60	66.73	66.11	65.58	64.72
0.280	69.09	67.60	66.73	66.11	65.58	64.72
0.380	68.13	66.83	66.01	65.43	64.85	64.27

Table 2.23 (continued)

σ(T;w)/mN m^{-1}						
t/°C	15		25		25	
w				w		
0.620	66.75	65.54	65.06	64.34	64.00	63.42
0.800	65.59	64.56	63.78	63.63	62.76	62.80
	64.4	*70.4*	*75.1*	*80.5*	*90.2*	
0.128	63.91	63.19	62.51	61.69	60.48	
0.200	63.52	62.80	62.27		60.30	
0.280	63.51	62.79	62.27		60.30	
0.380	63.12	62.39		61.19	60.08	
0.620	62.31	61.93	61.59	60.63	59.52	
0.800	61.73	60.85	60.36		59.04	

[a] To be published, the University of Silesia

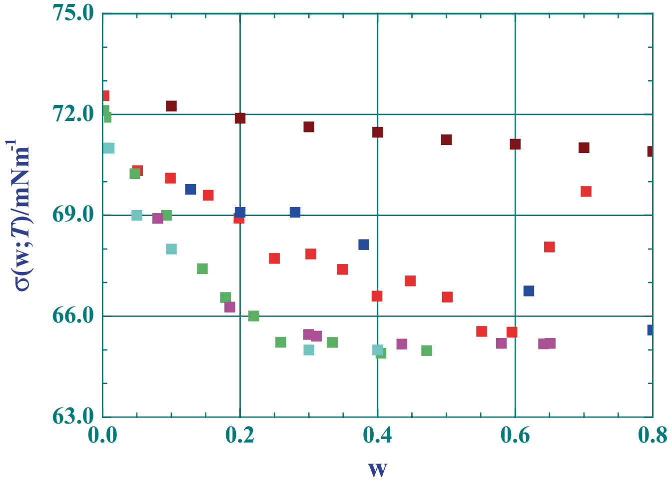

Fig. 2.44 Surface tension of aqueous solutions of citric acid as a function of concentration in the 15–25 °C temperature range. 15 °C ■ - [200]; 20 °C ■ - [80]; 20 °C ■ - [202]; 20 °C ■ - to be published; 25 °C ■ - [56]; 25 °C ■ - [205]

$$P(T;w) = \frac{(x_1M_1 + x_2M_2)\,\sigma(T;w)^{1/4}}{d(T;w)}$$
$$P(T;w)\,/\,g^{1/4}\cdot cm^3\cdot s^{-1/2}\cdot mol^{-1}$$
$$= 52.584 + 1.4289w + 97.470w^2 \qquad (2.118)$$

Thus, from the knowledge of densities as a function of composition at constant temperature (Table 2.7) and parachor values from Eq. (2.118) it is possible to obtain surface tensions for desired temperature and concentration.

2.16 Solubility of Citric Acid in Organic Solvents

Solubilities of citric acid in a number of one-phase liquid systems (in organic solvents or in their mixtures with water) are known in the literature [84–87, 160, 207, 208]. The solubility measurements were performed mainly with aliphatic alcohols but considerably less with other solvents.

Usually, solubilities are known at room temperatures only, but in few cases solubilities of citric acid as a function of temperature is also available (Table 2.24). Nearly all solubility measurements were performed only once and when more results are available, they are in a considerably disagreement. For example, this can be observed in the case of citric acid + ethanol system (Fig. 2.45) where solubilities of Yang and Wang [84], Oliveira [207] and Oliveira et al. [86] are compared with those of Barra et al. [87] and Blair and Zienty [160]. Solubilities of citric acid in

Table 2.24 Solubility of citric acid in organic solvents

Solvent	*t*/°C	x	S	x_{EtOH}	d/g cm^{-3}
Methanol	25	0.1575 [87]			
Ethanol		0.1436			
1-Pentanol		0.0646			
1,2-Propanediol		0.0449			
Ethyl glycole		0.2151			
Propylene glycol		0.0315			
Ethyl acetate		0.0062			
1,4 dioxane		0.1413			
Acetic acid		0.0291			
Formamide		0.1447			
N, N-dimethylformamide		0.1872			
Amyl acetate[a]			5.980 [160]		0.8917
Amyl alcohol[a]			15.430		0.8774
Ethyl acetate[a]			5.276		0.9175
Ether[a]			2.174		0.7228
Chloroform[a]			0.007		1.4850
Amyl acetate			4.220		0.8861
Ether			1.050		0.7160
Ethanol[a]			66.0	0.0891	1.286
			64.3	0.2068	1.258
			62.0	0.3697	1.216
			58.1	0.6100	1.163
			49.8	1.0000	1.068
ethanol			62.3	0.0891	1.297
			59.0	0.2068	1.246
			54.8	0.3697	1.190
			48.5	0.6100	1.120
			38.3	1.0000	1.010

Table 2.24 (continued)

Solvent	*t*/°C	x	S	x_{EtOH}	d/g cm^{-3}
Ethanol	20.6	0.1224 [86]		0.0000	
		0.1721		0.1989	
		0.1876		0.3997	
		0.2482		1.0000	
	30.2	0.1510		0.0000	
		0.1678		0.1997	
		0.1752		0.3997	
		0.1825		0.6005	
		0.2700		1.0000	
	41.3	0.1712		0.0000	
		0.2097		0.1997	
		0.2164		0.3997	
		0.2169		0.6005	
		0.2806		1.0000	
	49.1	0.1864		0.0000	
		0.2395		0.1997	
		0.2661		0.3997	
		0.2919		0.7988	
1-Propanol	20.6	0.2743			
	30.2	0.2794			
	41.3	0.2859			
Ethanol	21.1		57.93 [207]		
	30.8		61.39		
	40.1		61.54		
	49.1		58.73		
	57.6		51.64		
1-Propanol	21.1		55.28		
	30.8		56.15		
	40.1		56.15		

Table 2.24 (continued)

Solvent	*t*/°C	x	S	x_{EtOH}	d/g cm^{-3}
	49.1		40.17		
	57.7		33.74		
x					
		Ethanol	*1-Butanol*	*Acetone*	*Toluene*
	15.0	0.2462 [84]	0.05885	0.05552	0.05670
	18.0	0.2588	0.06626	0.06339	0.06003
	21.0	0.2708	0.07463	0.07726	0.06353
	24.0	0.2826	0.08385	0.08224	0.06720
	26.0	0.2895	0.09057	0.08960	0.06973
	28.0	0.2962	0.09781	0.09755	0.07235
	30.0	0.3027	0.1056	0.1061	0.07505
	32.0	0.3091	0.1139	0.1155	0.07783
	34.0	0.3149	0.1223	0.1254	0.08069
	36.0	0.3201	0.1323	0.1363	0.08363
	38.0	0.3253	0.1414	0.1476	0.08667
	40.0	0.3297	0.1534	0.1605	0.08979
	42.0	0.3341	0.1651	0.1740	0.09031
	44.0	0.3369	0.1773	0.1887	0.09632
	46.0	0.3407	0.1908	0.2044	0.09972
	50.0	0.3458	0.2210	0.2395	0.1068
	54.0	0.3492	0.2538	0.2800	0.1143
	57.0	0.3506	0.2850	0.3145	0.1203
	60.0	0.3509	0.3126	0.3527	0.1265

S grams of citric acid per grams of saturated solution

[a] citric acid monohydrate

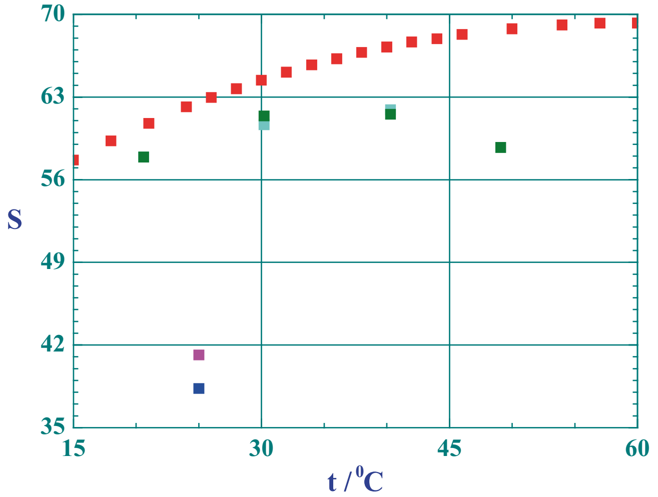

Fig. 2.45 Solubility of citric acid in ethanol, expressed in g/100 g of saturated solution, as a function of temperature. 🟥 - [84]. 🟦 - [86]; 🟪 - [87]; 🟩 - [207]; 🟦 - [160]

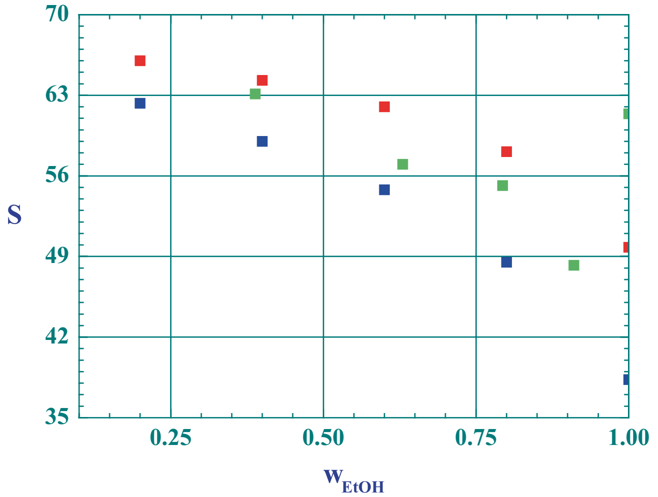

Fig. 2.46 Solubility of citric acid in ethanol + water mixtures, expressed in g/100 g of saturated solution, as a function of temperature. 🟩 - 20.6 °C [207]; 25 °C, 🟥 - citric acid monohydrate; 🟦 - 25 °C anhydrous citric acid [160]

ethanol at 25 °C, from last two investigations, are consistent with the author unpublished determinations. Barra et al. [87] measured solubilities of citric acid in various organic solvents and proposed to estimate their values by applying the Hansen solubility parameters.

It should be taken into account, that known solubilities of citric acid in organic solvents are to a large degree uncertain. This probably results from inadequate analytical procedures which were applied and whether the anhydrous or monohydrate citric acid (one-phase ternary system) were actually dissolved. As can be observed in Fig. 2.46, the hydration water considerably changes solubilities of citric acid in the ethanol + water mixtures. Sometimes, there is not clear whether citric acid solubilities are expressed per mass of solvent or per mass of saturated solution. Therefore, the compiled solubilities of citric acid in organic solvents (Table 2.24) are expressed in original units. Similarly, as with water, the Daneshfar et al. [85] solubilities in other solvents are considered to be incorrect and they are excluded from Table 2.24.

2.17 Two-Phase Citric Acid–Aliphatic Alcohol–Water Systems

Ternary two-phase liquid systems were extensively investigated in the context of recovery of citric acid from fermentation liquors by extraction and back extraction into water at higher temperatures. In this way, extraction is considered as one of alternatives to the classical precipitation technique with the formation of gypsum. From potential extractants mainly two groups of compounds were examined - aliphatic alcohols and long-chain tertiary amines with diluents [154, 208–258], but also few other organic solvents were considered [214, 215]. Extraction of citric acid depends on many parameters (temperature, diluents, addition of strong electrolytes, pH and others) but one aspect is of particular importance, the mutual solubility of components in both phases. For example, in case of lower aliphatic alcohols, a large amount of coextracted water leads to relatively narrow two-phase regions and practically excludes them as possible extractants.

Liquid–liquid equilibrium studies with the citric acid–alcohol–water systems were initiated by Kolossovskii et al. [208, 209] in 1934–1935 and Gordon [210] in 1953. In their investigations, the organic phases at 25 °C included 3-methyl-1-butanol (isoamyl alcohol) and 2-methyl-1-propanol (isobutanol). Systematic distribution studies of citric acid, alcohol and water between aqueous and organic phases were performed by Apelblat and Manzurola [211], in the ternary system with 1-hexanol and 1-octanol, Apelblat et al. [212] with 2-pentanol and Grinberg et al. [213] with 2-butanol. Lintomen et al. [257, 258] determined partition of citric acid and water in systems with 1-butanol and 2-butanol and also extended their measurements by adding the fourth component - sodium chloride or tricaprylin. Kasprzycka-Guttman et al. [214] investigated mutual solubilities in the citric acid-cyclohexanone water system and Tvetkova and Povitskii [215] in the citric acid-water-tributyl phosphate-carbon tetrachloride system. In a number of common solvent-water mixtures, Marvel and Richards [253] studied solubilities of citric acid, but only distribution coefficients were reported. The mentioned here distribution data in ternary systems are presented in (Table 2.25).

Table 2.25 Partition data in the citric acid–water–aliphatic alcohol and citric acid–water ketone systems and solubility of alcohols and ketones in aqueous solutions of citric acid

$m_{aq.}$	$m_{org.}$	$m_{org.}(H_2O)$	$m_{aq.}$	$m_{org.}$	$m_{org.}(H_2O)$	m
1-Butanol						
0.0000 [258]	0.0000	14.04	0.4462	0.1729	15.83	
0.2148	0.0931	15.41	0.6600	0.2932	16.16	
0.3682	0.1550	15.99	1.5906	0.7173	18.72	
2-Butanol						
0.00000 [213]	0.00000	29.1	0.2414	0.2579	39.7	
0.01548	0.01376	29.2	0.2631	0.3107	44.1	
0.01855	0.01564	28.7	0.2774	0.3326	44.6	
0.03148	0.02844	29.6	0.2855	0.3272	46.4	
0.04951	0.04194	30.0	0.2939	0.3560	48.2	
0.05480	0.04799	28.6	0.2987	0.3721	49.7	
0.07422	0.05574	30.5	0.3099	0.3912	52.0	
0.08851	0.07262	31.4	0.3147	0.4038	53.4	
0.08995	0.08283	30.1	0.3274	0.4345	55.7	
0.1086	0.1007	32.4	0.3354	0.4542	57.5	
0.1263	0.1191	31.7	0.3388	0.4636	58.4	
0.1651	0.1615	34.5	0.3410	0.4718	59.0	
0.2018	0.2093	36.9				
0.0000						2.54
0.0454						2.48
0.0500						2.43
0.0716						2.60
0.0914						2.73
0.0955						2.81
0.1037						2.81
0.1260						2.99
0.1567						3.05

Table 2.25 (continued)

$m_{aq.}$	$m_{org.}$	$m_{org.}(H_2O)$	$m_{aq.}$	$m_{org.}$	$m_{org.}(H_2O)$	m
0.1726						0.21
0.1806						3.25
0.2627						3.57
0.2997						3.65
0.3709						4.04
0.3957						4.19
0.4424						4.76
0.0000 [258]	0.0000	31.06	0.1694	0.1506	33.13	
0.0892	0.0795	31.00	0.2870	0.2811	41.08	
2-Pentanol						
0.0000 [212]	0.0000	7.3	2.282	0.6018	9.1	
0.2018	0.0481	7.5	2.584	0.6921	9.9	
0.4017	0.0968	7.6	2.648	0.7162	9.8	
0.5987	0.1433	7.9	2.937	0.8213	10.3	
0.7516	0.1836	7.8	3.327	0.9503	10.7	
0.8194	0.1947	8.2	3.642	1.0736	11.2	
1.0579	0.2500	8.2	4.16	1.2832	11.5	
1.1264	0.2790	8.1	4.61	1.4707	12.3	
1.3048	0.3226	8.7	4.81	1.6204	12.9	
1.4164	0.3472	8.2	5.17	1.7142	12.8	
1.5205	0.3820	8.8	5.63	1.8530	12.8	
1.6875	0.4208	8.6	6.07	2.292	14.5	
1.8215	0.4616	9.2	6.20	2.561	15.1	
1.9544	0.4956	8.5	6.71	2.71	15.4	
2.121	0.5493	9.4	7.65	3.44	17.7	
2.165	0.5669	9.5				
0.0000						0.472
0.0294						0.445

Table 2.25 (continued)

$m_{aq.}$	$m_{org.}$	$m_{org.}(H_2O)$	$m_{aq.}$	$m_{org.}$	$m_{org.}(H_2O)$	m
0.0704						0.444
0.0824						0.456
0.0898						0.448
0.1677						0.453
0.2260						0.437
0.7700						0.502
0.9570						0.583
2.85						0.775
3.78						0.942
4.48						1.088
5.15						1.238
1-Hexanol						
0.0000 [213]	0.00000	4.40	2.608	0.2767	4.85	
0.1943	0.01861	4.45	3.098	0.3285	4.95	
0.5648	0.05324	4.50	3.698	0.4398	5.10	
0.9412	0.09567	4.57	4.30	0.5165	5.24	
1.3368	0.13980	4.64	4.99	0.6498	5.43	
1.7586	0.1908	4.73	5.56	0.8184	5.64	
2.411	0.2484	4.82	6.97	0.9784	5.93	
0.0000						0.051
0.0763						0.053
0.3254						0.058
0.4935						0.072
1.4420						0.073
2.926						0.111
3.59						0.123
4.72						0.154

Table 2.25 (continued)

$m_{aq.}$	$m_{org.}$	$m_{org.}(H_2O)$	$m_{aq.}$	$m_{org.}$	$m_{org.}(H_2O)$	m
1-Octanol						
0.0000 [213]	0.00000	2.91	5.37	0.3720	2.91	
0.1679	0.00707	2.79	6.15	0.4396	2.95	
0.5217	0.02231	2.78	6.63	0.5036	3.00	
0.8729	0.03962	2.77	6.84	0.5360	3.00	
1.2959	0.06104	2.77	7.09	0.5438	3.06	
2.375	0.1188	2.78	7.14	0.5489	3.09	
2.573	0.1335	2.87	7.24	0.5497	3.16	
3.38	0.1877	2.81	7.80	0.5556	3.26	
4.25	0.2643	2.84	8.15	0.5573	3.74	
4.76	0.3120	2.86				
2-Methyl-1-propanol						
0.0371 [210, in mole dm^{-3}]	0.0086		0.725	0.1875		
0.0738	0.0176		1.411	0.3828		
0.1270	0.0308		2.355	0.6600		
0.4350	0.1140					
3-Ethyl-1-butanol						
0.0936 [209, in mole dm^{-3}]	0.0150		3.78	0.8379		
1.4805	0.2797		5.28	1.2033		
1.594	0.3087		7.22	1.922		
2.029	0.4095		8.46	2.847		
2.564	0.5418		10.7	3.68		
3.20	0.7256		11.2	4.89		
Cyclohexanone						
0.0000 [154]	0.0000	3.42	1.1630	0.4543	6.93	
0.1696	0.0619	3.84	1.2303	0.4941	7.31	

Table 2.25 (continued)

$m_{aq.}$	$m_{org.}$	$m_{org.}(H_2O)$	$m_{aq.}$	$m_{org.}$	$m_{org.}(H_2O)$	m
0.3788	0.1321	4.35	1.5236	0.6567	8.64	
0.6612	0.2369	5.12	2.0371	0.8640	10.04	
0.9570	0.3425	6.07	2.1385	0.9592	10.78	
Methyl isobutyl ketone						
0.605 [241]	0.00809	1.16	2.09	0.0313	1.21	
0.606	0.00817	1.14	2.10	0.0318	1.21	
1.22	0.0180	1.06	3.02	0.0506	1.21	
1.29	0.0180	1.18	3.03	0.0500	1.23	
1.29	0.0185	1.19				
0.605						0.21
0.606						0.21
1.29						0.25
1.29						0.25
2.09						0.28
2.10						0.29
3.02						0.34
3.03						0.34

$m_{aq.} = m(H_3Cit)$, moles of citric acid in 1 kg of water; $m_{org.} = m(H_3Cit)$, moles of citric acid in 1 kg of alcohol or ketone; $m_{org.}(H_2O)$, moles of water in 1 kg of alcohol or ketone; m moles of alcohol or ketone in 1 kg of water

A quantitative thermodynamic description of extraction equilibria is complicated, because all components (water - 1, alcohol - 2 and citric acid - 3) are present in aqueous and organic phases and both phases deviate considerably from ideal behaviour.

If component i = 1, 2, 3 is transferred from the aqueous phase to the organic phase, at equilibrium, the chemical potentials of it, are equal

$$\mu_{\mathrm{i\,(aq.)}}[T;\mathrm{x}_{\mathrm{(aq.)}}]=\mu_{\mathrm{i\,(org.)}}[T;\mathrm{x}_{\mathrm{(org.)}}] \tag{2.119}$$

and taking into account that equilibrium states are stable

$$\mu_{\mathrm{i\,(aq.)}}[T;\mathrm{x}_{\mathrm{(aq.)}}]+\mathrm{d}\mu_{\mathrm{i\,(aq.)}}[T;\mathrm{x}_{\mathrm{(aq.)}}]=\mu_{\mathrm{i\,(org.)}}[T;\mathrm{x}_{\mathrm{(org.)}}]+\mathrm{d}\mu_{\mathrm{i\,(org.)}}[T;\mathrm{x}_{\mathrm{(org.)}}] \tag{2.120}$$

it follows from Eqs. (2.119) and (2.120) that

$$\mathrm{d}\mu_{\mathrm{i\,(aq.)}}[T;\mathrm{x}_{\mathrm{(aq.)}}]=\mathrm{d}\mu_{\mathrm{i\,(org.)}}[T;\mathrm{x}_{\mathrm{(org.)}}] \tag{2.121}$$

This equation is an equivalent to the Clausius–Clapeyron equation along the coexistence curve, it correlates the changes of concentration of component i in both phases.

In the chemical modeling approach, the simultaneous extraction of citric acid and water by alcohols is interpreted by the solvation and hydration processes in the alcoholic phase. In a simplest molecular model, it is assumed that only one predominant citric acid complex (solvate) is formed, and the partition process can be treated as the following chemical reaction

$$\mathrm{H_3Cit(aq.)+hH_2O+qROH(org.)}\rightleftharpoons\mathrm{[H_3Cit(H_2O)_h(ROH)_q(org.)]} \tag{2.122}$$

where q and h are the solvation and hydration numbers. Contrary to monobasic carboxylic acids, the dimerization of citric acid in alcoholic phases is very small and can be neglected [211]. In terms of activities, the mass-action law equation for the formation of citric acid complex is given by

$$\mathrm{K}(T)=\frac{a_{\mathrm{H_3Cit\,(H_2O)_h\,(ROH)_q\,(org.)}}}{a_{\mathrm{H_3Cit(aq.)}}\,a^{\mathrm{h}}_{\mathrm{H_2O}}\,a^{\mathrm{q}}_{\mathrm{ROH\,(org.)}}}=\frac{a_{\mathrm{3\,(org.)}}}{a_{\mathrm{3(aq.)}}\,a_1^{\mathrm{h}}\,a^{\mathrm{q}}_{\mathrm{2\,(org.)}}} \tag{2.123}$$

If solubility of alcohol in the aqueous phase is small or its influence neglected (i.e. the aqueous phase is treated as a two component mixture) then the Gibbs–Duhem equations for both liquid phases are

$$\begin{aligned}&\mathrm{x}_{1\mathrm{(aq.)}}\mathrm{d}\mu_{1\mathrm{(aq.)}}+\mathrm{x}_{3\mathrm{(aq.)}}\mathrm{d}\mu_{3\mathrm{(aq.)}}=0\\&\mathrm{x}_{1\mathrm{(org.)}}\mathrm{d}\mu_{1\mathrm{(org.)}}+\mathrm{x}_{2\mathrm{(org.)}}\mathrm{d}\mu_{2\mathrm{(org.)}}+\mathrm{x}_{3\mathrm{(org.)}}\mathrm{d}\mu_{3\mathrm{(org.)}}=0\end{aligned} \tag{2.124}$$

but using Eq. (2.121) we have at constant T

$$
\begin{gathered}
x_{2\,(\text{org.})}\mathrm{d}\mu_{2\,(\text{org.})}+\left[\mathrm{x}_{3\,(\text{org.})}-\frac{x_{1\,(\text{org.})}\mathrm{x}_{3\,(\text{aq.})}}{x_{1\,(\text{aq.})}}\right]\mathrm{d}\mu_{3\,(\text{aq.})}=0\\
\mathrm{d}\mu_{2\,(\text{aq.})}=\mathrm{d}\mu_{2\,(\text{org.})}=\mathrm{d}\mu_{\text{ROH(org.)}}\quad;\quad \mathrm{d}\mu_{3\,(\text{aq.})}=\mathrm{d}\mu_{3\,(\text{org.})}=\mathrm{d}\mu_{\text{H}_3\text{Cit\,(aq.)}}\\
\mathrm{d}\mu_{\text{ROH}}=\mathrm{d}\ln a_{\text{ROH(org.)}}\quad;\quad \mathrm{d}\mu_{\text{H}_3\text{Cit}}=\mathrm{d}\ln a_{\text{H}_3\text{Cit\,(aq.)}}.
\end{gathered}
\tag{2.125}
$$

Finally, changing mole fractions to molalities and performing integration of the Gibbs-Duhem equation in Eq. (2.125), the activity of alcohol in the alcoholic phase can be correlated with the activity of citric acid in aqueous solution

$$
\begin{gathered}
\ln a_{\text{ROH\,(org.)}}(m_{\text{H}_3\text{Cit\,(aq.)}})=\ln a_{\text{ROH(org.)}}(m_{\text{H}_3\text{Cit(aq.)}}\to 0)+\int_{0}^{a_{\text{H}_3\text{Cit(aq.)}}}F\,\mathrm{d}\ln a_{\text{H}_3\text{Cit(aq.)}}\\
F=\frac{\mathrm{M}_{\text{ROH}}}{1000}\left[\frac{m_{\text{H}_2\text{O\,(org.)}}m_{\text{H}_3\text{Cit\,(aq.)}}}{55.508}-m_{\text{H}_3\text{Cit(org.)}}\right].
\end{gathered}
\tag{2.126}
$$

where $a_{\text{ROH(org.)}}(m_{\text{H}_3\text{Cit\,(aq.)}})$ denotes the activity of alcohol saturated by water and their values were determined by Apelblat [217, 218]. The integral in Eq. (2.126) includes only measurable quantities, the composition of both phases and the activities of undissociated citric acid, and therefore can be evaluated numerically.

Examples of $a_{\text{ROH(org.)}}(m_{\text{H}_3\text{Cit\,(aq.)}})$ evaluations for the ternary systems with 2-butanol, 2-pentanol, 1-hexanol and 1-octanol are presented in [211–213]. The solvation number q is determined in dilution experiments (so-called the slope analysis [221]) from $\mathrm{q}=\mathrm{d}\ln m_{\text{H}_3\text{Cit\,(org.)}}/\mathrm{d}\ln m_{\text{ROH(org.)}}$, i.e. by measuring the change in partition of citric acid with the change of concentration of alcohols in organic phase. The concentration of alcohol $m_{\text{ROH(org.)}}$ is changed by additions of a suitable diluent. Determination of hydration numbers h is more complex because the total (analytical) amount of water co-extracted with citric acid is the sum of two different forms of water, namely the "physically" dissolved (free) water and "chemically" bonded, the hydration water. If it is assumed that both processes, the water bonding to the complex and the water dissolved as a result of physical solubility are independent, it is possible to distinguish between them. The physical solubility decreases monotonically with increasing of citric acid concentration in the aqueous phase (correspondingly in the alcoholic phase) because the water activity decreases with increasing of the activity of electrolyte in the aqueous phase. This is a consequence of the equality of water activities in both phases and the Gibbs-Duhem relationship for two component systems in the aqueous phase. The required functional dependence between the water activity and the composition of aqueous phase is known from the binary alcohol-water system investigations [217–220]. The opposite is true for hydrated water which is proportional to the concentration of citric acid in the alcoholic phase. As a result, the amount of bonded to citric acid water always increases when amount of citric acid in the aqueous phase increases. Evidently, this is accompanied by the increase in citric acid concentration in the alcoholic phase. Thus, the difference between determined analytically amount of water in the alcoholic phase and the physically dissolved water gives the amount of water bonded to the citric acid complex and finally the hydration number from

$$h = \lim_{m_{H_3Cit(org.)} \to 0} \left(\frac{[\partial m_{H_2O(org.)} - m_{H_2O(org.,diss.)}]}{\partial m_{H_3Cit(org.)}} \right) \qquad (2.127)$$

Applying described here procedure, it was found that distribution of citric acid between water and alcohols (Table 2.25) is consistent with the formation of the following undissociated citric acid complexes in the alcoholic phase: $H_3Cit(2\text{-}C_4H_9OH)_5$; $H_3Cit(H_2O)_6(2\text{-}C_5H_{11}OH)_5$; $H_3Cit(H_2O)_4(C_6H_{13}OH)_4$ and $H_3Cit(H_2O)_4(C_8H_{17}OH)_4$ [211–213]. An alternative nonstoichiometric hydration model was proposed by Sergievskii and Dzhakupova [154, 216] who proposed a different procedure to represent citric acid partition between water and aliphatic alcohols.

As can be observed in Fig. 2.47, where distribution coefficient of citric acid, $D(H_3Cit) = m_{H_3Cit(org.)} / m_{H_3Cit(aq.)}$, is plotted, the extraction of citric acid by alcohols strongly depends on the length of aliphatic chain. With increasing of aliphatic chain, which is accompanied by a simultaneous decreasing in the water content in the alcoholic phase, the amount of extracted citric acid considerably decreases.

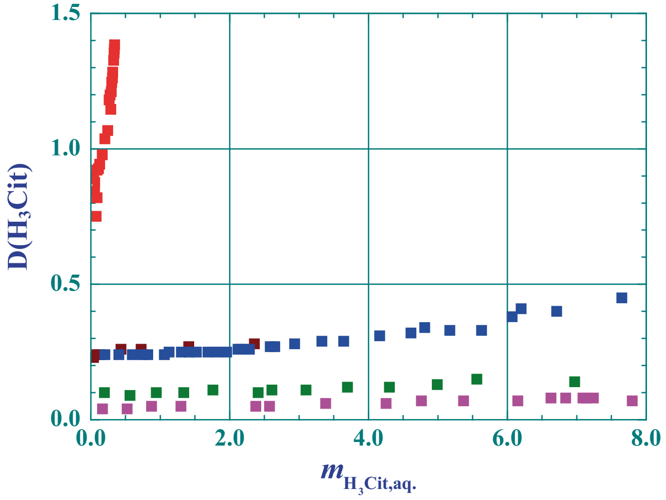

Fig. 2.47 Distribution coefficients of citric acid in aliphatic alcohols at 25 °C as a function of citric acid concentration in the aqueous phase. 🟥 - 2-butanol; 🟦 - 2-pentanol; 🟩 - 1-hexanol; 🟪 - octanol [211–213] and - 2-methyl-1-propanol [210]

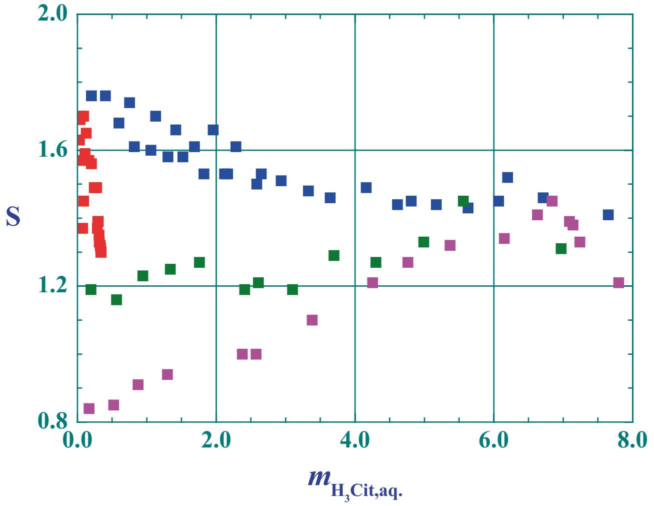

Fig. 2.48 Selectivity coefficients of citric acid in aliphatic alcohols at 25 °C as a function of citric acid concentration in the aqueous phase. 🟥 - 2-butanol; 🟦 - 2-pentanol; 🟩 - 1-hexanol; 🟪 - octanol [211–213]

However, if the selectivity coefficient, $S = D(H_3Cit)/D(H_2O)$, is considered (Fig. 2.48), the citric acid/water behaviour is quite different. For various alcohols, the selectivity coefficient S increases or decreases, but finally tends to the limit value. An exception is 2-butanol, where due to a large mutual solubility of components, the two-phase system disappears and the region of total miscibility is formed. On the other hand, as was shown by Lintomen et al. [257, 258], by adding sodium chloride or tricaprylin, the heterogeneous two-phase region can be considerably enlarged without a significant decrease of extracted amount of citric acid (Fig. 2.49).

The reduction of concentration of citric acid in the organic phase is caused by its competition with sodium chloride which is also extracted by 2-butanol. Simultaneously, with decreasing amount of citric acid in the organic phase, the amount of coextracted water decreases. This results from the fact that the bonded to citric acid water decreases and the physically dissolved water also decreases because the water activity in the aqueous phase decreases (water activities in both phases are equal). Evidently, the decrease in water activities is more significant when sodium chloride, rather than citric acid is dissolved in water. Thus, as a result of added sodium chloride, it is observed the enlargement of the heterogeneous two-phase region and the significant reduction of amount of water which is present in the organic phase (Fig. 2.50).

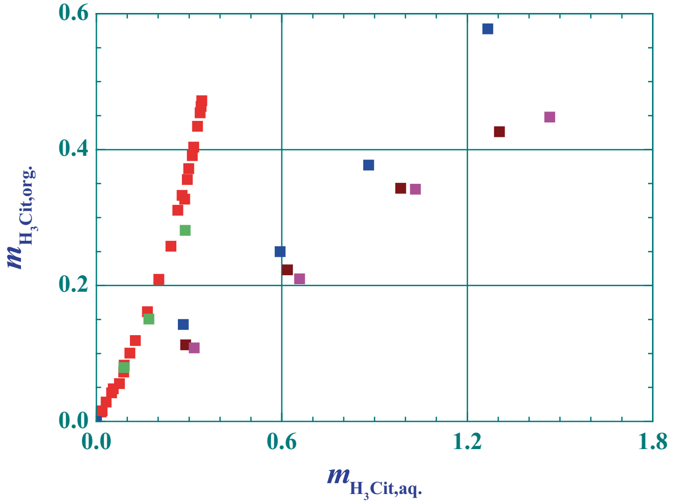

Fig. 2.49 Distribution of citric acid between the organic and aqueous phases in the 2-butanol + sodium chloride + water systems at 25 °C. 🟥 - 2-butanol [213]; 🟩 - 2-butanol [258]; 🟦 - 2-butanol + 5 % NaCl; 🟫 - 2-butanol + 10 % NaCl; 🟪 - 2-butanol + 15 % NaCl [257]

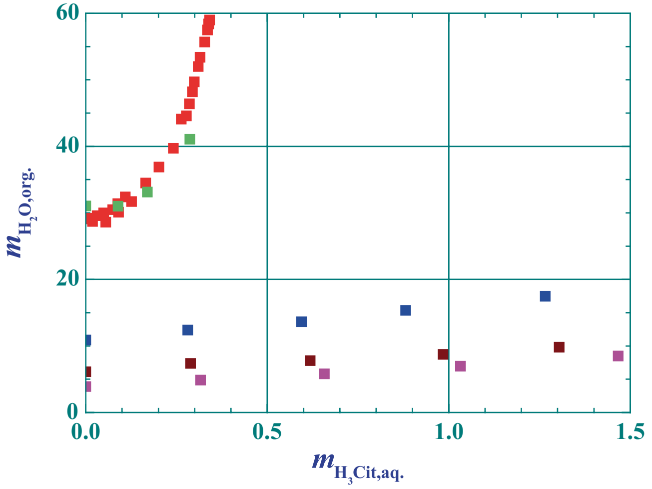

Fig. 2.50 Extracted water in the alcoholic phase in the 2-butanol + sodium chloride + water systems at 25 °C as a function of citric acid concentration in the aqueous phase. 🟥 - 2-butanol [213]; 🟩 - 2-butanol [258]; 🟦 - 2-butanol + 5 % NaCl; 🟫 - 2-butanol + 10 % NaCl; 🟪 - 2-butanol + 15 % NaCl [257]

2.18 Two-Phase Citric Acid–Tertiary Amine–Water Systems

There is a vast literature devoted to extraction of citric acid from aqueous phase by tertiary amines [222–252, 254, 256]. In order to isolate citric acid from fermentation broths only tertiary amines were investigated because primary amines have a high mutual solubility in water, secondary amines form amides at high temperatures when reextraction is performed by distillation and quaternary amines have tendency to produce undesirable and uncontrollable stable emulsions.

With an intention to decrease viscosity and to improve hydrodynamic properties (reduction of emulsion-forming tendency) tertiary amines are mixed with suitable (also to avoid third phase formation) diluent. Tri-n-octalylamine, trilaurylamine, trioctyl methyl ammonium chloride and commercial products such as Alamine 336, Hostarex A 324 and Aliquat 336 (mixture of quaternary amines) received the most attention. From various, with relatively low solubility in water polar and non-polar diluents methyl isobutyl ketone, 1-propanol, 1-octanol, 2-octanol, decanol, isodecanol, hexane, cyclohexane, benzene, toluene, xylenes, chloroform and methylene chloride should be mentioned.

A large number of components in extraction systems and without having direct thermodynamic studies to obtain activities in binary, ternary and quaternary systems, leads only to chemical description of separation processes in terms of the mass-action equations. In many cases, the reported distribution between phases of citric acid, water and other components, is either fragmentary, not specially accurate or presented only in the graphical form. However, there are also few investigations where complete composition of the aqueous and organic phases was reported and these extraction systems were thermodynamically analyzed [241, 247]. Usually, it was assumed that in both phases the extraction mechanism involves only molecular citric acid. The formation of undissociated citric acid-amine complexes is supported by the fact that at low concentrations of citric acid in the aqueous phase, where citrate ions exist, the distribution coefficients of citric acid, D(H_3Cit), are very small. Distribution coefficients increase with increasing concentration of citric acid but later start to decrease with approaching the saturation of the organic phase with citric acid.

A typical case of extraction of citric acid by amines is that when tri-n-octylamine diluted with methyl isobutyl ketone, toluene or chloroform is an extractant. These four component systems were thoroughly investigated theoretically and experimentally by the Maurer group [241–243, 247–249]. Distribution of citric acid between both phases at 25 °C (molalities of tri-n-octylamine in organic phase are nearly equal) is presented in Fig. 2.51. As can be observed, the extraction isotherms for these three diluents are similar and their form resemble those of adsorption isotherms. The maximal loading of organic phase is achieved very quickly and nearly independent of a nature of diluent when its solubility in water is very small (toluene and chloroform). On the contrary, the considerable presence of methyl isobutyl ketone in both phases leads, at the saturation, to significant increase in amounts of citric acid in the organic phase. Correspondingly, the partition of water is similar to that of citric acid (Fig. 2.52), there is less water in the organic phase with toluene or chloroform and much more with methyl isobutyl ketone. As can be seen in Fig. 2.53, amounts of coextracted water and citric acid in the organic phase are proportional.

Difficulties associated with quantitative representation of extraction processes caused that the thermodynamic description (deviations from the ideal behaviour in both phases) was generally replaced by chemical models which include the formation of one or more hydrated or unhydrated complexes in the organic phase. Evidently, the analysis of partition data is not always unique, considering the uncertainty

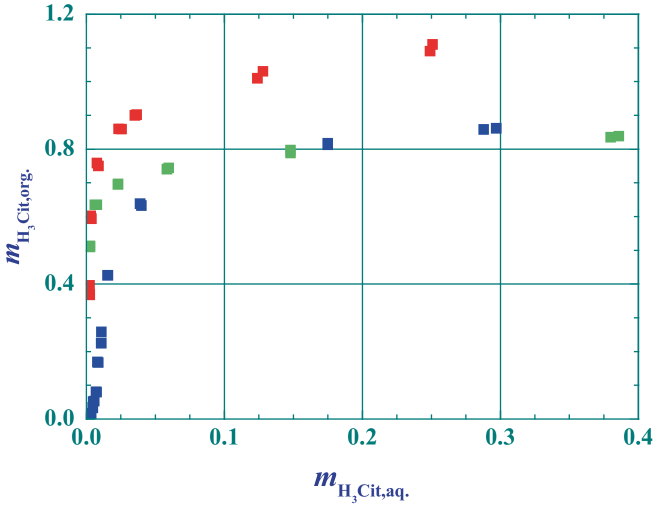

Fig. 2.51 Distribution of citric acid between the aqueous phase and the organic phase (tri-n-octylamine + diluent) at 25 °C [241]. 🟥 - methyl isobutyl ketone, $m_{TOA} = 1.21$ mol kg^{-1}; 🟦 - toluene, $m_{TOA} = 1.13$ mol kg^{-1}; 🟩 - chloroform, $m_{TOA} = 1.23$ mol kg^{-1}

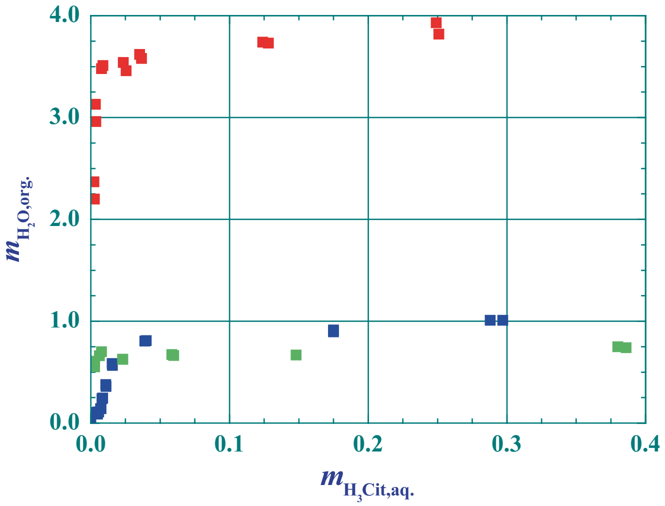

Fig. 2.52 Distribution of water between the aqueous phase and the organic phase (tri-n-octylamine + diluent) at 25 °C as a function of citric acid concentration in the aqueous phase [241]. 🟥 - methyl isobutyl ketone, $m_{TOA} = 1.21$ mol kg^{-1}; 🟦 - toluene, $m_{TOA} = 1.13$ mol kg^{-1}; 🟩 - chloroform, $m_{TOA} = 1.23$ mol kg^{-1}

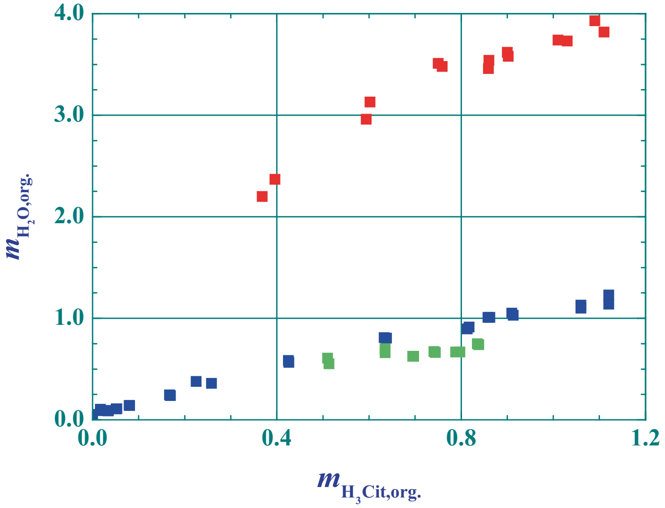

Fig. 2.53 Distribution of water between the aqueous phase and the organic phase (tri-n-octylamine + diluent) at 25 °C as a function of citric acid concentration in the organic phase [241]. 🟥 - methyl isobutyl ketone, $m_{TOA} = 1.21$ mol kg^{-1}; 🟦 - toluene, $m_{TOA} = 1.13$ mol kg^{-1}; 🟩 - chloroform, $m_{TOA} = 1.23$ mol kg^{-1}

coupled with stoichiometry of formed complexes and the differentiation between physically and chemically dissolved water and citric acid in the organic phase. With increasing complexity of chemical models, for correlating experimental data a large number of adjustable parameters is required and they are evaluated by applying appropriate optimization procedures. In chemical models representing reactive extraction, the activities of components are replaced by concentrations in the mass-action equations, and the thermodynamic equilibrium constants K(T) replaced by the apparent equilibrium constants $\beta_{pqh}(T)$. In such description, the quotient of activity coefficients which represents the over-all deviation from non ideal behaviour, is alternatively represented by one or more chemical reactions and incorporated into the equilibrium constant. Thus, in general case of formation of hydrated or unhydrates citric acid–amine complexes, the phase equilibria are expressed by a set of following equations

$$\begin{aligned} & p\left(H_3Cit(aq.)\right) + hH_2O + q\left(R_3N(org.)\right) \rightleftharpoons [\left(H_3Cit\right)_p (H_2O)_h (R_3N)_q (org.)] \\ & p,q = 1,2,3,\ldots \\ & h = 0,1,2,\ldots \end{aligned} \tag{2.128}$$

with

$$\beta_{p,q,h} = \frac{\left[\left(H_3Cit\right)_p (H_2O)_h (R_3N)_q (org.)\right]}{\left[H_3Cit(aq.)\right]^p \left[H_2O\right]^h \left[R_3N(org.)\right]^q}. \tag{2.129}$$

The water concentration term in Eq. (2.129) is usually omitted considering that the change in water activity is small. For extraction systems with the same amine, the reported in the literature stoichiometry and a number of complexes are not always in agreement. This results primarily from an interpretation of similar, but not exactly the same experimental conditions. The factors such as the nature and initial concentration of diluent, pH, temperature, concentration range and coextraction of water change the form of extraction isotherms and such changes are attributed to differences in the stoichiometry of formed complexes. Similar procedures based on the chemical model (formation of complexes and dimers), were also applied to more complicated situations when citric acid is separated from small amounts of carboxylic acids which are always present in fermentation broths [232, 235, 241, 249, 253, 255].

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Chapter 3
Dissociation Equilibria in Solutions with Citrate Ions

3.1 Mathematical Representation of Citric Acid Dissociation

Citric acid as a weak 1:3 type electrolyte dissociates in water in three steps (three ionizable carboxylic groups) when its one hydroxyl is of an importance only in complex formation reactions with various metal ions. The mono-ionizable citrate anions, denoted as H_2Cit^-, may exist in two forms which are in equilibrium. The first form is when hydrogen of terminal carboxylic group (bounded to the methylene group) is ionizated and the second form is when hydrogen is ionizated from the central carboxylic group, bounded to the tertiary carbon atom. Similarly, two forms may exist for di-ionized citrate anion $HCit^{2-}$. The central carboxylic group of citric acid is more acidic than the two terminal carboxylic groups in tri- di- and mono-hydrogen citrate species. The relative concentration of these forms as investigated by NMR, ^{13}C NMR and pH-titration techniques is rather inconclusive. Loewenstein and Roberts [1] postulated that the first and second dissociation steps take place predominantly at the terminal carboxylic groups of citric acid. On contrary, Martin [2] interpreted his results as a predominance of the symmetrical carboxylic groups in the case of mono-ionizable citrate anions and the terminal carboxylic groups in case of di-ionized citrate anions. Pearce and Creamer [3] using the pH-titration method, when titrations were performed with appropriate methyl esters to allow selected ionization or blocking of carboxylic groups, claimed that the mono-ionizable citrate anions are in the symmetrical forms and di-ionized citrate anions are in the asymmetrical forms. Tananaeva et al. [4] concluded that two protons of H_2Cit^- are preferentially localized on two terminal carboxylic groups, when in the case of $HCit^{2-}$, one proton is bound to a greater extent to the central carboxylic group. For both mono- and di-ionized anions the gauche confirmation is postulated. However, in the Cit^{3-} anion, the repulsion of negatively charged carboxylic groups is accompanied by a conformational transition (trans) and the internal hydrogen bonding (ring) does not exist between dissociated carboxylic groups and OH^- groups.

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The successive dissociation of citric acid is schematically represented by

$$\begin{aligned}
&\mathrm{H_3Cit} \rightleftharpoons \mathrm{H^+ + H_2Cit^-} \quad ; \quad \mathrm{K}_1(T)\\
&\mathrm{H_2Cit^-} \rightleftharpoons \mathrm{H^+ + HCit^{2-}} \quad ; \quad \mathrm{K}_2(T)\\
&\mathrm{HCit^{2-}} \rightleftharpoons \mathrm{H^+ + Cit^{3-}} \quad ; \quad \mathrm{K}_3(T)
\end{aligned} \tag{3.1}$$

where the dissociation constants of these reactions from the mass-action law are

$$\begin{aligned}
\mathrm{K}_1(T) &= \frac{a_{\mathrm{H^+}}\, a_{\mathrm{H_2Cit^-}}}{a_{\mathrm{H_3Cit}}} = \frac{[\mathrm{H^+}][\mathrm{H_2Cit^-}]}{[\mathrm{H_3Cit}]} \frac{f_{\mathrm{H^+}}\, f_{\mathrm{H_2Cit^-}}}{f_{\mathrm{H_3Cit}}}\\
\mathrm{K}_2(T) &= \frac{a_{\mathrm{H^+}}\, a_{\mathrm{HCit^{2-}}}}{a_{\mathrm{H_2Cit^0}}} = \frac{[\mathrm{H^+}][\mathrm{HCit^{2-}}]}{[\mathrm{H_2Cit^-}]} \frac{f_{\mathrm{H^+}}\, f_{\mathrm{HCit^{2-}}}}{f_{\mathrm{H_2Cit^-}}}\\
\mathrm{K}_3(T) &= \frac{a_{\mathrm{H^+}}\, a_{\mathrm{Cit^{3-}}}}{a_{\mathrm{HCit^{2-}}}} = \frac{[\mathrm{H^+}][\mathrm{Cit^{3-}}]}{[\mathrm{HCit^{2-}}]} \frac{f_{\mathrm{H^+}}\, f_{\mathrm{Cit^{3-}}}}{f_{\mathrm{HCit^{2-}}}}
\end{aligned} \tag{3.2}$$

and f_{j} are the corresponding activity coefficients of ions and the quotients of them denoted as

$$\begin{aligned}
\mathrm{F}_1(T) &= \frac{f_{\mathrm{H^+}}\, f_{\mathrm{H_2Cit^-}}}{f_{\mathrm{H_3Cit}}}\\
\mathrm{F}_2(T) &= \frac{f_{\mathrm{H^+}}\, f_{\mathrm{HCit^{2-}}}}{f_{\mathrm{H_2Cit^-}}}\\
\mathrm{F}_3(T) &= \frac{f_{\mathrm{H^+}}\, f_{\mathrm{Cit^{3-}}}}{f_{\mathrm{HCit^{2-}}}}
\end{aligned} \tag{3.3}$$

In terms of concentration fractions of the primary, secondary and tertiary steps of dissociation, the concentrations of species present in aqueous solutions of citric acid are

$$\begin{aligned}
&[\mathrm{H_2Cit^-}] = c\alpha_1\\
&[\mathrm{HCit^{2-}}] = c\alpha_2\\
&[\mathrm{Cit^{3-}}] = c\alpha_3\\
&[\mathrm{H_3Cit}] = c(1-\alpha_1-\alpha_2-\alpha_3) = c\alpha_0\\
&[\mathrm{H^+}] = c(\alpha_1+2\alpha_2+3\alpha_3)\\
&\alpha_0+\alpha_1+\alpha_2+\alpha_3 = 1
\end{aligned} \tag{3.4}$$

where c is the total (analytical) concentration of citric acid. Using Eqs. (3.3) and (3.4), the mass-action equations in Eq. (3.2) can be written in the following form

$$
\begin{aligned}
\mathrm{K}_1(T) &= \frac{c(\alpha_1+2\alpha_2+3\alpha_3)\alpha_1}{1-\alpha_1-\alpha_2-\alpha_3}\mathrm{F}_1(T)\\
\mathrm{K}_2(T) &= \frac{c(\alpha_1+2\alpha_2+3\alpha_3)\alpha_2}{\alpha_1}\mathrm{F}_2(T)\\
\mathrm{K}_3(T) &= \frac{c(\alpha_1+2\alpha_2+3\alpha_3)\alpha_3}{\alpha_2}\mathrm{F}_3(T)
\end{aligned}
\tag{3.5}
$$

If the equilibrium constants $\mathrm{K}_i(T)$ and activity coefficients are known, for given values of c, the dissociation fractions can be evaluated by an iterative solution of the following set of quadratic equations

$$
\begin{aligned}
\alpha_1 &= \frac{1}{2}\left[-\left(\frac{\mathrm{K}_1(T)}{c\mathrm{F}_1(T)}+2\alpha_2+3\alpha_3\right)+\sqrt{\left(\frac{\mathrm{K}_1(T)}{c\mathrm{F}_1(T)}+2\alpha_2+3\alpha_3\right)^2+\frac{4\mathrm{K}_1(T)}{c\mathrm{F}_1(T)}(1-\alpha_2-\alpha_3)}\right]\\
\alpha_2 &= \frac{1}{4}\left[-(\alpha_1+3\alpha_3)+\sqrt{(\alpha_1+3\alpha_3)^2+\frac{8\mathrm{K}_2(T)\alpha_1}{c\mathrm{F}_2(T)}}\right]\\
\alpha_3 &= \frac{1}{6}\left[-(\alpha_1+2\alpha_2)+\sqrt{(\alpha_1+2\alpha_2)^2+\frac{12\mathrm{K}_3(T)\alpha_2}{c\mathrm{F}_3(T)}}\right]
\end{aligned}
\tag{3.6}
$$

The activity coefficients of individual ions ($f_{\mathrm{H_3Cit}}$ is assumed to be unity) can be approximated in dilute solutions by the Debye-Hückel expressions

$$
\log_{10}[f_j(c,T)] = -\frac{z_j^2 A(T)\sqrt{I}}{1+a_j B(T)\sqrt{I}}
\tag{3.7}
$$

where z_j and a_j are the charges and ion size parameters and the constants $A(T)$ and $B(T)$ depend on dielectric constant of pure water $D(T)$ in the following way

$$
\begin{aligned}
A(T) &= \frac{1.8246\cdot 10^6}{[D(T)T]^{3/2}}\\
B(T) &= \frac{50.29\cdot 10^8}{[D(T)T]^{1/2}}
\end{aligned}
\tag{3.8}
$$

For more concentrated solutions, the linear term can also be included in Eq. (3.7). The ionic strength I in the case of citric acid solutions is

$$
I = c(\alpha_1+3\alpha_2+6\alpha_3)
\tag{3.9}
$$

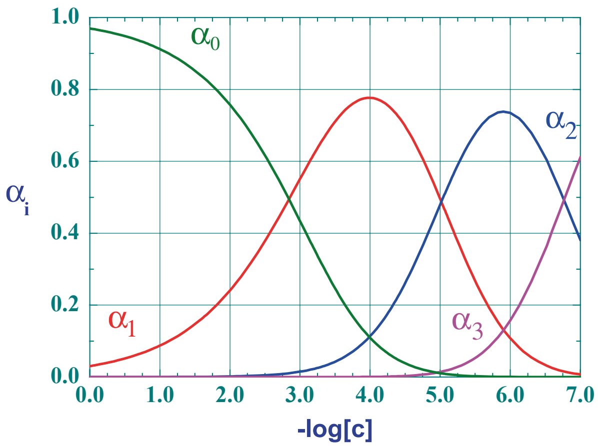


Fig. 3.1 Distribution of H_2Cit^-, $HCit^{2-}$, Cit^{3-} and H_3Cit species as a function of total citric acid concentration in water *c* at 25 °C. The concentration fractions: $\alpha_1 = \alpha(H_2Cit^-)$, $\alpha_2 = \alpha(HCit^{2-})$, $\alpha_3 = \alpha(Cit^{3-})$ and $\alpha_0 = \alpha(H_3Cit) = 1 - \alpha(H_2Cit^-) - \alpha(HCit^{2-}) - \alpha(Cit^{3-})$

Solving the set of equations, Eqs. (3.6)–(3.9), and using $K_1 = 6.98 \times 10^{-4}$ mol dm^{-3}, $K_2 = 1.40 \times 10^{-5}$ mol dm^{-3}, $K_3 = 4.05 \times 10^{-7}$ mol dm^{-3}, $a(H^+) = 9.0$ Å, $a(H_2Cit^-) = 3.5$ Å, $a(HCit^{2-}) = 4.5$ Å and $a(Cit^{3-}) = 5.0$ Å (hereafter units of dissociation constants will be omitted), the evaluated distribution of individual species as a function of total concentration of citric acid at 25 °C is illustrated in Fig. 3.1.

It follows from Fig. 3.1, that for $c > 10^{-3}$ mol dm^{-3}, citric acid behaves actually as the monobasic organic acid. The overlapping between the first and second dissociation steps is extensive (i.e. the equilibrium between H_2Cit and $HCit^{2-}$ anions), it occurs in the $10^{-6} - 10^{-3}$ mol dm^{-3} concentration region and the third step of dissociation is important only in extremely dilute aqueous solutions for $c < 10^{-5}$ mol dm^{-3}.

3.2 Distribution of Citrate Ions in Aqueous Solutions of Acidic and Neutral Citrates

Dissolution of acidic and neutral citrates ($Me_kH_{3-k}Cit$ where Me^+ is alkali metal ion) in water is represented by

$$\begin{aligned} &Me_kH_{3-k}Cit \rightarrow kMe^+ + H_{3\text{-}k}Cit^{-k} \\ &k = 1, 2, 3 \end{aligned} \tag{3.10}$$

In the hydrolysis reactions, considering that citric acid is a weak acid, the formed anions $H_{3-k}Cit^{-k}$ react with water molecules to produce OH^- and citric ions with lower charges up to undissociated citric acid H_3Cit

$$\begin{aligned} H_2Cit^- + H_2O &\rightleftharpoons H_3Cit + OH^- \\ HCit^{2-} + H_2O &\rightleftharpoons H_2Cit^- + OH^- \\ Cit^{3-} + H_2O &\rightleftharpoons HCit^{2-} + OH^- \end{aligned} \tag{3.11}$$

These anions and undissociated citric acid molecules undergo the dissociation process as described in Eq. (3.1), and the hydroxyl ion can be removed from Eq. (3.11) using

$$H^{+} + OH^{-} \rightleftharpoons H_2O; \qquad K_w(T) \tag{3.12}$$

where $K_w(T)$ is the ionization product of water ($K_w = 1.008 \times 10^{-14}$ at 25 °C). This permits to treat equilibrium relations of citric acid and its acidic salts in the same manner as in Eq. (3.2) by taking into account that they depend on the same dissociation constants.

Concentrations of species present in solutions can be expressed in terms of corresponding concentration fractions α_i

$$\begin{aligned}
&[\mathrm{Me}^{+}] = \mathrm{k}c\\
&[\mathrm{H}^{+}] = c\alpha_{\mathrm{H}^{+}}\\
&[\mathrm{OH}^{-}] = c\alpha_{\mathrm{OH}^{-}}\\
&[\mathrm{H_2Cit}^{-}] = c\alpha_1\\
&[\mathrm{HCit}^{2-}] = c\alpha_2\\
&[\mathrm{Cit}^{3-}] = c\alpha_3\\
&[\mathrm{H_3Cit}] = c(1-\alpha_1-\alpha_2-\alpha_3) = c\alpha_0
\end{aligned} \tag{3.13}$$

Using concentration fractions from Eq. (3.13), the dissociation equilibria are represented by

$$\begin{aligned}
&\mathrm{K}_1(T) = \frac{[\mathrm{H}^{+}][\mathrm{H_2Cit}^{-}]}{[\mathrm{H_3Cit}]}\mathrm{F}_1 = \frac{c\alpha_{\mathrm{H}^{+}}\alpha_1}{1-\alpha_1-\alpha_2-\alpha_3)}\mathrm{F}_1\\
&\mathrm{K}_2(T) = \frac{[\mathrm{H}^{+}][\mathrm{HCit}^{2-}]}{[\mathrm{H_2Cit}^{-}]}\mathrm{F}_2 = \frac{c\alpha_{\mathrm{H}^{+}}\alpha_2}{\alpha_1}\mathrm{F}_2\\
&\mathrm{K}_3(T) = \frac{[\mathrm{H}^{+}][\mathrm{Cit}^{3-}]}{[\mathrm{HCit}^{2-}]}\mathrm{F}_3 = \frac{c\alpha_{\mathrm{H}^{+}}\alpha_3}{\alpha_2}\mathrm{F}_3\\
&\mathrm{K_w}(T) = [\mathrm{H}^{+}][\mathrm{OH}^{-}]f_{\mathrm{H}^{+}}f_{\mathrm{OH}^{-}} = c^2\alpha_{\mathrm{H}^{+}}\alpha_{\mathrm{OH}^{-}}f_{\mathrm{H}^{+}}f_{\mathrm{OH}^{-}}
\end{aligned} \tag{3.14}$$

where F_j, j = 1, 2, 3 denote the quotients of the activity coefficients (see Eq. (3.3)) which are calculated by Eq. (3.7) using the ionic strength of solution

$$I = c(\mathrm{k} + \alpha_{\mathrm{H}^{+}} + \alpha_2 + 3\alpha_3) \tag{3.15}$$

The charge balance in terms of the concentration fractions is

$$\mathrm{k} + \alpha_{\mathrm{H}^{+}} = \alpha_{\mathrm{OH}^{-}} + \alpha_1 + 2\alpha_2 + 3\alpha_3 \tag{3.16}$$

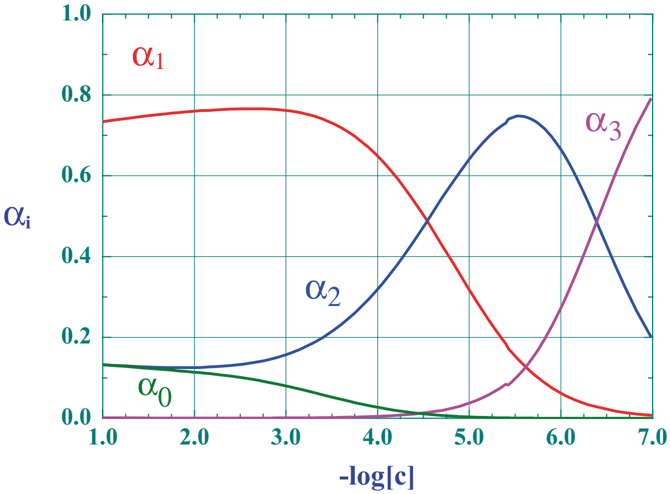


Fig. 3.2 Distribution of H_2Cit^-, $HCit^{2-}$, Cit^{3-} and H_3Cit species as a function of total sodium dihydrogen citrate concentration in water *c* at 25 °C. The concentration fractions: $\alpha_1 = \alpha(H_2Cit^-)$, $\alpha_2 = \alpha(HCit^{2-})$, $\alpha_3 = \alpha(Cit^{3-})$ and $\alpha_0 = \alpha(H_3Cit) = 1 - \alpha(H_2Cit^-) - \alpha(HCit^{2-}) - \alpha(Cit^{3-})$

Thus, the distribution of species in aqueous solutions of acidic and neutral citrates at given temperature *T*, can be determined by the simultaneous solution of the nonlinear set of equations, Eqs. (3.14)–(3.16), and this solution gives the complete set of α_i a function of analytical concentration *c*.

Using values of the ionization product of water K_w, the dissociations constants of citric acid, K_1, K_2 and K_3, the corresponding citrate ions sizes and $a(Na^+) = 5.0$ Å, the distribution of individual species as a function of total concentration of sodium dihydrogen citrate at 25 °C is illustrated in Fig. 3.2. As can be observed, in moderate dilute solutions of sodium dihydrogen citrate, $c > 10^{-3}$ mol dm^{-3}, the monocharged H_2Cit^- is dominant anion, $HCit^{2-}$ is of importance in the 10^{-3} mol dm^{-4}–10^{-6} mol dm^{-3} concentration range and Cit^{3-} only for $c < 10^{-6}$ mol dm^{-3}.

In the case of disodium hydrogen citrate aqueous solutions (Fig. 3.3) for $c > 10^{-6}$ mol dm^{-3}, essentially only $HCit^{2-}$ exists. Three charged anion Cit^{3-} starts to be of importance for $c < 10^{-5}$ mol dm^{-3}. As expected, the neutral salt, trisodium citrate can be considered as a strong electrolyte (see also [5]).

3.3 Dissociation Constants of Citric Acid in Pure Water

Considering importance of solutions with citrate ions, their dissociation constants were determined many times (Tables 3.1, 3.2 and 3.3). However, there is a number of dissociation constants which can be considered as by-products because they are coming indirectly from study of complexation reactions. Dissociation constants of citric acid were mostly evaluated using various variants of potentiometric

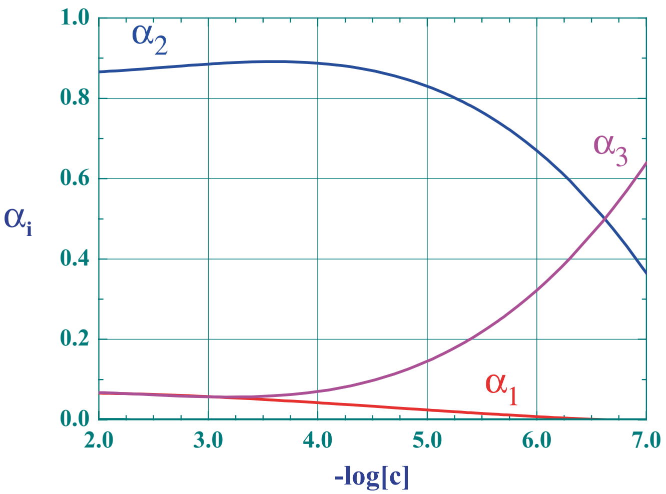


Fig. 3.3 Distribution of H_2Cit^-, $HCit^{2-}$ and Cit^{3-} anions as a function of total disodium hydrogen citrate concentration in water *c* at 25 °C. The concentration fractions: $\alpha_1 = \alpha(H_2Cit^-)$, $\alpha_2 = \alpha(HCit^{2-})$ and $\alpha_3 = \alpha(Cit^{3-})$

Table 3.1 Dissociation constants and thermodynamic functions of the first ionization step of citric acid in water

t °C	pK_1	$K_1 10^4$	ΔG_1	ΔH_1	$T\Delta S_1$	$\Delta C_{P,1}$	References
0	3.229	5.90	16.88				[12]
	3.220	6.03	16.84	7.36	−9.48	−0.12	[6]
	3.232	5.86	16.90	9.10	−7.80	−0.28	[8]
5	3.200	6.31	17.02	6.75	−10.28	−0.12	[6]
	3.131	5.96	17.17	7.39	−9.79		[9]
10	3.176	6.67	17.21	6.12	−11.09	−0.13	[6]
	3.185	6.53	17.22	5.51	−11.71		[10]
	3.191	6.44	17.29				[7]
	3.197	6.27	17.36	6.36	−11.01		[9]
15	3.160	6.92	17.42	5.48	−11.93	−0.13	[6]
	3.157	6.97	17.43	5.08	−12.35		[10]
	3.160	6.92	17.43	5.42	−12.00		[94]
	3.271	6.56	17.56	5.36	−12.19		[9]
18	3.075	8.41	17.14				[86]
	3.087	8.18	17.20				[87]
	3.149	7.10	17.54	5.09	−12.45	−0.13	[6]
	3.146	7.14	17.53	4.06	−13.48	−0.16	[8]
20	3.142	7.21	17.63	4.83	−12.80	−0.13	[6]
	2.960	11.0	16.61				[88]
	3.144	7.18	17.65	4.65	−13.00		[10]

Table 3.1 (continued)

t °C	pK_1	$K_1 10^4$	ΔG_1	ΔH_1	$T\Delta S_1$	$\Delta C_{P,1}$	References
	3.145	7.16	17.65				[7]
	3.357	6.79	17.78	4.40	−13.37		[9]
25	3.080	8.32	17.58				[71]
	3.057	8.77	17.45				[87]
	3.128	7.45	17.85	4.17	−13.68	−0.13	[6]
	3.127	7.47	17.84				[89]
	3.124	7.52	17.83	3.97	−13.85		[90]
	3.124	7.52	17.87	4.20	−13.67		[10]
	3.128	7.45	17.85	5.00	−12.85	−0.18	[7]
	3.060	8.71	17.46				[4]
	3.132	7.38	17.87	5.40	−12.77	−0.14	[16]
	3.460	6.98	18.01	3.47	−14.55		[9]
	2.980	10.5	17.01			1996	[23]
	3.112	7.73	17.76				[11]
	3.130	7.41	17.86				[91]
	3.127	7.46	17.85	4.10	−13.80	−0.16	[8]
	3.130	7.41	17.86				[92]
	3.150	7.08	17.98				[93]
	3.130	7.41	17.86	4.67	−13.18		[94]
30	3.040	9.13	17.64				[95]
	3.116	7.66	18.09	3.50	−14.59	−0.14	[6]
	2.940	11.48	16.78				[96]
	3.117	7.64	18.10	3.75	−14.35		[10]
	3.114	7.69	18.07				[7]
	3.590	7.10	18.27	2.57	−15.70		[9]
35	3.109	7.78	18.33	2.82	−15.52	−0.14	[6]
	3.112	7.73	18.34	3.29	−15.05		[10]
	3.110	7.76	18.34	4.03	−14.31		[94]
	3.770	7.22	18.53	1.70	−16.82		[9]
37	3.042	9.08	18.06				[87]
	3.105	7.85	18.43	2.54	−15.89	−0.14	[6]
	3.098	7.98	17.68				[90]
40	3.099	7.96	18.59	2.12	−16.47	−0.14	[6]
	3.105	7.85	18.59	2.83	−15.76		[10]
	3.094	8.05	18.55				[7]
45	3.097	8.00	18.86	1.42	−17.44	−0.14	[6]
	3.098	7.98	18.85	2.35	−16.49		[10]
50	3.103	7.89	19.19				[12]
	3.095	8.04	19.14	0.70	−18.44	−0.14	[6]
	3.088	8.17	19.11	1.87	−17.24		[10]

Table 3.1 (continued)

t °C	pK_1	$K_1 10^4$	ΔG_1	ΔH_1	$T\Delta S_1$	$\Delta C_{P,1}$	References
	3.084	8.24	19.08				[7]
	3.095	8.04	19.14	0.70	−18.42	−0.12	[8]
65	3.093	8.08	20.02				[12]
75	3.103	7.89	20.68	−2.00	−22.63	−0.10	[8]
100	3.135	7.33	22.39	−4.50	−26.87	−0.11	
125	3.186	6.52	24.28	−7.40	−31.45	−0.13	
150	3.255	5.56	26.36	−11.00	−37.24	−0.16	
200	3.456	3.50	31.30	−21.60	−52.99	−0.27	

Units: K_1 - mol dm^{-3} ; ΔG_1, ΔH_1, $T\Delta S_1$ - kJ mol^{-1} ; $\Delta C_{P,1}$ - kJ mol^{-1} K^{-1}

Table 3.2 Dissociation constants and thermodynamic functions of the second ionization step of citric acid in water

t°C	pK_2	$K_2 10^5$	ΔG_2	ΔH_2	$T\Delta S_2$	$\Delta C_{P,2}$	Ref
0	4.99	1.03	26.07				[12]
	4.837	1.46	25.29	6.92	−18.37	−0.17	[6]
	4.841	1.44	25.31	8.10	−15.02	−0.27	[8]
5	4.813	1.54	25.63	6.06	−19.58	−0.17	[6]
	4.889	1.29	26.03	3.79	−22.25		[9]
10	4.797	1.60	25.99	5.18	−20.82	−0.18	[6]
	4.823	1.50	26.14				[7]
	4.876	1.33	26.43	3.29	−23.13		[9]
15	4.782	1.65	26.37	4.28	−22.09	−0.18	[6]
	4.866	1.36	26.84	2.80	−24.03		[9]
	4.830	1.48	26.64	5.78	−20.93		[94]
18	4.752	1.77	26.48				[86]
	4.769	1.70	26.58				[87]
	4.774	1.68	26.60	3.73	−22.87	−0.18	[6]
	4.772	1.69	26.59	2.19	−24.40	−0.19	[8]
20	4.769	1.70	26.76	3.37	−23.39	−0.18	[6]
	4.380	4.17	24.58				[88]
	4.789	1.63	26.87				[7]
	4.860	1.38	27.27	2.33	−24.95		[9]
25	4.390	4.07	25.05				[71]
	4.759	1.74	27.16				[87]
	4.761	1.73	27.17	2.44	−24.73	−0.19	[6]
	4.780	1.66	27.28				[89]
	4.769	1.70	27.22				[90]
	4.777	1.67	27.26	3.10	−24.16	−0.17	[7]
	3.900	12.6	22.26				[4]
	4.751	1.77	27.11	0.90	−26.21	−0.15	[16]

Table 3.2 (continued)

t°C	pK_2	$K_2 10^5$	ΔG_2	ΔH_2	$T\Delta S_2$	$\Delta C_{P,2}$	Ref
	4.854	1.40	27.70	1.88	−25.82		[9]
	4.320	4.79	24.65				[23]
	4.442	3.61	25.35				[11]
	4.770	1.70	27.22				[91]
	4.759	1.74	27.16	2.20	−24.98	−0.19	[8]
	4.760	1.74	27.16				[92]
	4.790	1.62	27.34				[93]
	4.810	1.55	27.45	3.52	−23.94		[94]
30	4.556	2.78	26.44				[95]
	4.755	1.76	27.59	1.50	−26.09	−0.19	[6]
	4.440	3.63	25.34				[96]
	4.766	1.71	27.65			1990	[7]
	4.848	1.42	28.13	1.44	−26.68		[9]
35	4.751	1.77	28.03	0.54	−27.49	−0.19	[6]
	4.790	1.62	28.25	1.78	−26.47		[94]
	4.845	1.43	28.57	1.02	−27.58		[9]
37	4.747	1.79	28.18				[87]
	4.750	1.78	28.21	0.15	−28.06	−0.19	[6]
	4.758	1.75	27.15				[90]
40	4.750	1.78	28.48	−0.44	−28.92	−0.20	[6]
	4.754	1.76	28.50				[7]
45	4.754	1.76	28.95	−1.43	−30.38	−0.20	[6]
50	4.83	1.48	29.87				[12]
	4.757	1.75	29.43	−2.44	−31.87	−0.20	[6]
	4.749	1.78	29.37				[7]
	4.758	1.75	29.43	−2.00	−31.35	−0.15	[8]
65	4.73	1.87	30.60				[12]
75	4.801	1.58	31.99	−5.40	−37.25	−0.13	[8]
100	4.871	1.35	34.79	−8.70	−43.66	−0.14	
125	4.962	1.09	37.81	−12.30	−50.17	−0.16	
150	5.072	0.85	41.08	−16.70	−57.97	−0.19	
200	5.357	0.44	48.52	−28.90	−77.60	−0.30	

Units: K_2 - mol dm^{-3} ; ΔG_2, ΔH_2, $T\Delta S_2$ - kJ mol^{-1} ; $\Delta C_{P,2}$ - kJ mol^{-1} K^{-1}

techniques, but they also were derived from electrical conductance measurements. Initially, measurements leading to dissociation constants were performed at one or two temperatures only, but there are few sets of them which cover a wide range of temperature. Bates and Pinching [6] reported K_1, K_2 and K_3 values from 0 to 50 °C, De Robertis et al. [7] from 10 to 50 °C, Bénézeth et al. [8] from 0 to 200 °C and Apelblat and Barthel [9], from conductivity measurements, only K_1 and K_2 values,

Table 3.3 Dissociation constants and thermodynamic functions of the third ionization step of citric acid in water

t°C	pK_3	$K_1 10^7$	ΔG_3	ΔH_3	$T\Delta S_3$	$\Delta C_{P,3}$	Ref
0	5.532	29.4	33.69				[12]
	6.393	4.05	33.43	2.76	−30.66	−0.23	[6]
	6.394	4.04	33.43	3.20	−30.32	−0.32	[8]
5	6.386	4.11	34.00	1.58	−32.42	−0.24	[6]
10	6.383	4.14	34.59	0.38	−34.21	−0.24	
	6.411	3.88	34.75				[7]
15	6.384	4.13	35.21	−0.84	−36.05	−0.25	[8]
	6.420	3.80	35.41	−0.35	−35.76		[94]
18	6.407	3.92	35.71				[86]
	6.398	4.00	35.65				[87]
	6.386	4.11	35.59	−1.59	−37.17	−0.25	[8]
	6.385	4.12	35.58	−3.58	−39.16	−0.23	
20	6.388	4.09	35.84	−2.09	−37.93	−0.25	[6]
	5.836	14.6	33.30				[88]
	6.408	3.91	35.96				[7]
25	5.696	20.1	33.05				[71]
	6.400	3.98	36.52				[87]
	6.396	4.02	36.50	−3.36	−39.86	−0.26	[6]
	6.426	3.75	36.67				[89]
	6.419	3.81	36.63				[90]
	6.411	3.88	36.59	−3.00	−39.59	−0.24	[7]
	6.200	6.31	35.38				[4]
	6.418	3.82	36.63	1.60	−35.03	−0.24	[16]
	5.730	18.6	32.70				[23]
	5.637	23.1	33.25				[11]
	5.490	32.4	31.33				[91]
	6.397	4.01	36.51	−3.60	−40.10	−0.23	[8]
	6.400	3.98	36.52				[92]
	6.410	3.89	36.58				[93]
	6.440	3.63	36.75	−2.32	−39.09		[94]
30	5.582	26.2	33.46				[95]
	6.406	3.93	37.18	−4.64	−41.82	−0.26	[6]
	5.820	15.1	33.21				[96]
	6.418	3.82	37.24				[7]
35	6.423	3.78	37.88	−5.95	−43.84	−0.26	[6]
	6.460	3.47	38.10	−4.43	−42.53		[94]
37	6.424	3.77	38.14				[87]
	6.429	3.72	38.17	−6.48	−44.65	−0.27	[6]
	6.445	3.59	36.78				[90]

Table 3.3 (continued)

t°C	pK_3	$K_1 10^7$	ΔG_3	ΔH_3	$T\Delta S_3$	$\Delta C_{P,3}$	Ref
40	6.439	3.64	38.60	−7.29	−45.89	−0.27	[6]
	6.440	3.63	38.60				[7]
45	6.462	3.45	39.35	−8.64	−47.98	−0.27	[6]
50	5.490	32.6	33.94				[12]
	6.484	3.28	40.11	−10.01	−50.12	−0.28	[6]
	6.472	3.37	40.03				[7]
	6.481	3.30	40.09	−8.70	−48.80	−0.19	[8]
65	5.860	13.7	34.02				[12]
75	6.607	2.47	44.03	−13.10	−57.10	−0.17	[8]
100	6.759	1.74	48.28	−17.40	−65.67	−0.17	
125	6.931	1.17	52.82	−22.00	−74.85	−0.20	
150	7.120	0.76	57.67	−27.30	−85.05	−0.23	
200	7.556	0.28	68.43	−41.40	−109.77	−0.34	

Units: K_3 - mol dm^{-3} ; ΔG_3, ΔH_3, $T\Delta S_3$ - kJ mol^{-1} ; $\Delta C_{P,3}$ - kJ mol^{-1} K^{-1}

from 5 to 35 °C. Yadav et al. [10] determined K_1 and K_2 values in the 10–50 °C temperature interval. Saeedudin et al. [11] presented dissociation constants from 25 to 50 °C, but they strongly differ from others and their temperature dependence is incorrect, therefore they are omitted with an exception at 25 °C.

The accuracy of reported dissociation constants of citric acid in water is uneven, and sometimes the observed differences are in one order of magnitude (see for example the scattering of K_i values at 25 °C in Figs. 3.4, 3.5 and 3.6 and Tables 3.1, 3.2 and 3.3). This results from chosen experimental technique, precision of measurements, used mathematical form of activity coefficients and applied numerical procedures in solving of set of algebraic equations. This can be illustrated by presenting the equilibrium constants at 25 °C, the average values coming from the literature are: $K_1 = (7.8 \pm 0.9) \times 10^{-4}$, $K_2 = (2.9 \pm 2.6) \times 10^{-5}$ and $K_3 = (9.7 \pm 9.6) \times 10^{-7}$. Evidently, the scattering of reported results is better demonstrated using K and not $pK = -\log K$ values. In many cases, dissociation constants are actually the apparent dissociation constants which represent only the quotients of concentrations in the mass-action equations.

There is reasonable agreement between results coming from systematic potentiometric determinations performed by Bates and Pinching [6], De Robertis et al. [7], Bénézeth et al. [8] and Yadiv et al. [10]. The reported values from electrical conductivity measurements which were performed by Apelblat and Barthel [9] are similar but systematically lower. However, in the analysis of conductometric measurements, the final results depend not only on chosen molecular model but also on applied conductivity equation. The analysis of old conductivities of citric acid which were determined by Jones [12] was performed by Apelblat et al. [13].

The Bates and Pinching set of K_1, K_2 and K_3 values from 1949 is the most widely used in the literature, and it can be expressed as

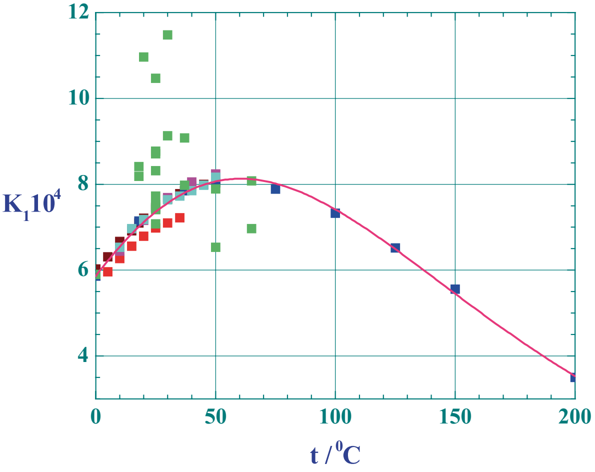


Fig. 3.4 The first dissociation constant of citric acid in pure water as a function of temperature. 🟫 - [6]; 🟪 - [7]; 🟦 - 8]; 🟥 - [9]; 🟦 - [10]; 🟩 - other references from Table 3.1 and the continuous line is calculated using Eq. (3.25)

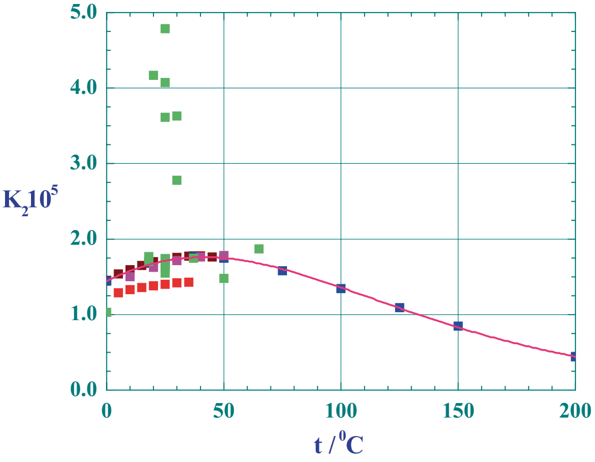


Fig. 3.5 The second dissociation constant of citric acid in pure water as a function of temperature. 🟫 - [6]; 🟪 - [7]; 🟦 - [8]; 🟥 - [9]; 🟦 - [10]; 🟩 - other references from Table 3.2 and the continuous line is calculated using Eq. (3.25)

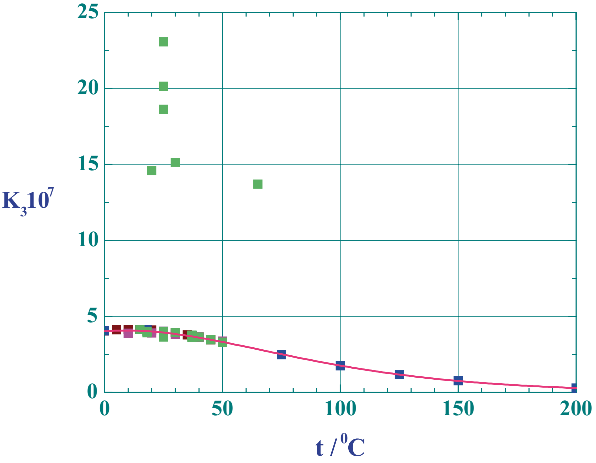


Fig. 3.6 The third dissociation constant of citric acid in pure water as a function of temperature. 🟫 - [6]; 🟪 - [7]; 🟦 - [8]; 🟦 - [10]; 🟩 - other references from Table 3.3 and the continuous line is calculated using Eq. (3.25)

$$\begin{aligned}
\ln[\mathrm{K}_1(T)] &= 10.5078 - \frac{2891.13}{(T/\mathrm{K})} - 0.02688(T/\mathrm{K})\\
\ln[\mathrm{K}_2(T)] &= 12.5399 - \frac{3650.06}{(T/\mathrm{K})} - 0.03776(T/\mathrm{K})\\
\ln[\mathrm{K}_3(T)] &= 14.6592 - \frac{4178.96}{(T/\mathrm{K})} - 0.05155(T/\mathrm{K})
\end{aligned} \tag{3.17}$$

Crea et al. [14] gave an alternative representation of dissociation constants

$$\begin{aligned}
\ln[\mathrm{K}_1(T)] &= -646.52280 + \frac{14264.1855}{(T/\mathrm{K})} + 115.34510\ln(T/\mathrm{K}) - 0.2204(T/\mathrm{K})\\
\ln[\mathrm{K}_2(T)] &= -52.19970 + \frac{1842.97387}{(T/\mathrm{K})} + 11.19421\ln(T/\mathrm{K}) - 0.05487(T/\mathrm{K})\\
\ln[\mathrm{K}_3(T)] &= -129.89305 + \frac{394.04129}{(T/\mathrm{K})} + 25.36088\ln(T/\mathrm{K}) - 0.09394(T/\mathrm{K})
\end{aligned} \tag{3.18}$$

Apelblat and Barthel [9] represented their results as

$$\begin{aligned}
\ln[\mathrm{K}_1(T)] &= -16.862 + \frac{6138.1}{(T/\mathrm{K})} - \frac{9.7725\cdot 10^5}{(T/\mathrm{K})^2}\\
\ln[\mathrm{K}_2(T)] &= -15.722 + \frac{2967.7}{(T/\mathrm{K})} - \frac{4.7613\cdot 10^5}{(T/\mathrm{K})^2}
\end{aligned} \tag{3.19}$$

and Yadav et al. [10] by

$$\ln[\mathrm{K}_1(T)] = 5.2133 - \frac{2106.5}{(T/\mathrm{K})} - 0.01797(T/\mathrm{K}) - 1.9906\cdot 10^5 (T/\mathrm{K})^2 \tag{3.20}$$

If clearly incorrect values of reported in the literature dissociation constants (Figs. 3.4, 3.5 and 3.6) are rejected, it is possible to represent $\mathrm{K}_1(T)$, $\mathrm{K}_2(T)$ and $\mathrm{K}_3(T)$ in terms of thermodynamic functions of dissociation process

$$\begin{aligned}
&\Delta\mathrm{G}(T) = -\mathrm{R}T\ln\mathrm{K}(T)\\
&\Delta\mathrm{G}(T) = \Delta\mathrm{H}(T) - T\Delta\mathrm{S}(T)\\
&\left(\frac{\partial\ln\mathrm{K}(T)}{\partial T}\right)_P = \frac{\Delta\mathrm{H}(T)}{\mathrm{R}T^2}\\
&\left(\frac{\partial\Delta\mathrm{H}(T)}{\partial T}\right)_P = \Delta\mathrm{C}_P(T)\\
&\left(\frac{\partial\ln\mathrm{K}(T)}{\partial P}\right)_T = -\frac{\Delta\mathrm{V}(T)}{\mathrm{R}T}
\end{aligned} \tag{3.21}$$

Using the simplifying assumption that the change in heat capacity in dissociation process is independent of temperature $\Delta C_P(T) = \Delta C_P(T^*) = \text{const}$ (for justification in the case of citric acid solutions see later) we have for the enthalpy and entropy changes

$$\begin{aligned} \Delta H(T) &= \Delta H(T^*) + T\Delta C_P(T^*) \\ \Delta S(T) &= \Delta S(T^*) + \Delta C_P(T^*)\ln T \end{aligned} \tag{3.22}$$

where T^* denotes an arbitrary reference temperature.

From equations Eqs. (3.21) and (3.22), the dissociation constant K(T) can be presented as

$$\ln K(T) = A + B/T + C\ln T \tag{3.23}$$

where three adjustable parameters A, B and C are expressed by

$$\begin{aligned} A &= \frac{\Delta S(T^*) - \Delta C_P(T^*)}{R} \\ B &= -\frac{\Delta H(T^*)}{R} \\ A &= \frac{\Delta C_P(T^*)}{R} \end{aligned} \tag{3.24}$$

Thus, the set of dissociation constants K_1, K_2 and K_3 in the form of Eq. (3.22) is

$$\begin{aligned} \ln[K_1(T)] &= 97.010 - \frac{5100.6}{(T/K)} - 15.290\ln(T/K) \\ \ln[K_2(T)] &= 116.328 - \frac{5931.7}{(T/K)} - 18.852\ln(T/K) \\ \ln[K_3(T)] &= 142.880 - \frac{6701.3}{(T/K)} - 23.721\ln(T/K) \end{aligned} \tag{3.25}$$

The maximal values of dissociation constants can be determined from Eq. (3.22)

$$\begin{aligned} \frac{dK(T)}{dT} &= -\frac{B}{T^2} + \frac{C}{T} = 0 \\ T_{\max} &= \frac{B}{C} \end{aligned} \tag{3.26}$$

Using Eqs. (3.24)–(3.26), the external values of dissociation constants are: $K_{1,\max} = 8.10 \times 10^{-4}$ at 67.65 °C, $K_{2,\max} = 1.76 \times 10^{-5}$ at 41.50 °C and $K_{3,\max} = 4.06 \times 10^{-7}$ at 9.35 °C.

With few exceptions, reported in the literature thermodynamic functions of dissociation, ΔG(T), ΔH(T), TΔS(T) and $\Delta C_P(T)$, result from an appreciate differentiation of K(T) and ΔH(T) fitting correlations. For the three steps of citric acid dissociation, there is a reasonable agreement between changes in the Gibbs free

Fig. 3.7 Changes in the Gibbs free energy, enthalpy and entropy in kJ mol^{-1} as a function of temperature in the first step of dissociation of citric acid (Table 3.1)

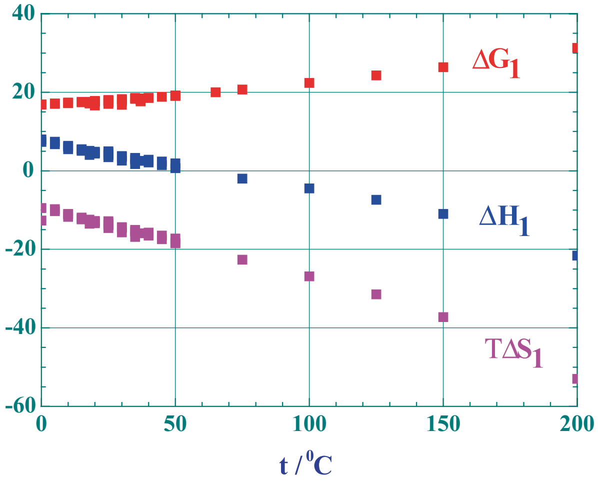
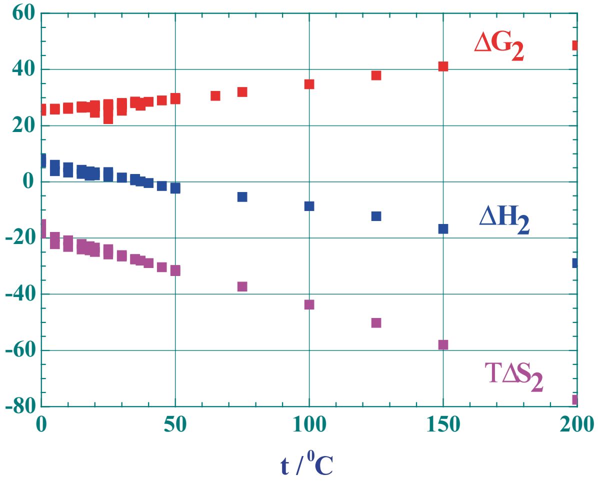
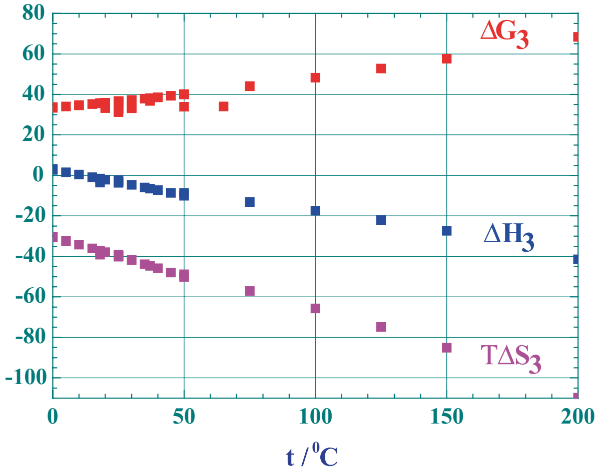


Fig. 3.8 Changes in the Gibbs free energy, enthalpy and entropy in kJ mol^{-1} as a function of temperature in the second step of dissociation of citric acid (Table 3.2)



energies, enthalpies and entropies as reported in various investigations (Figs. 3.7, 3.8 and 3.9). However, since differentiation is always associated with loss of precision, the changes in heat capacities $\Delta C_p(T)$ obtained from the second derivative of K(T) and from calorimetric determinations vary considerably as can be observed in Fig. 3.10. In spite of this, since known $\Delta C_p(T)$ values lie in rather narrow limits, they can be approximated in the 0–200 °C temperature range by the average values: $\Delta C_{P,1} = (-0.133 \pm 0.035)$ kJ mol^{-1} K^{-1}, $\Delta C_{P,2} = (-0.158 \pm 0.072)$ kJ mol^{-1} K^{-1} and $\Delta C_{P,3} = (-0.226 \pm 0.034)$ kJ mol^{-1} K^{-1}. Patterson and Woolley [15] measured densities and heat capacities of citric acid solutions at $p = 0.35$ MPa from 5 °C to 120 °C. Using these data, they reported the "best" values for volume, heat capacity

Fig. 3.9 Changes in the Gibbs free energy, enthalpy and entropy in kJ mol^{-1} as a function of temperature in the third step of dissociation of citric acid (Table 3.3)



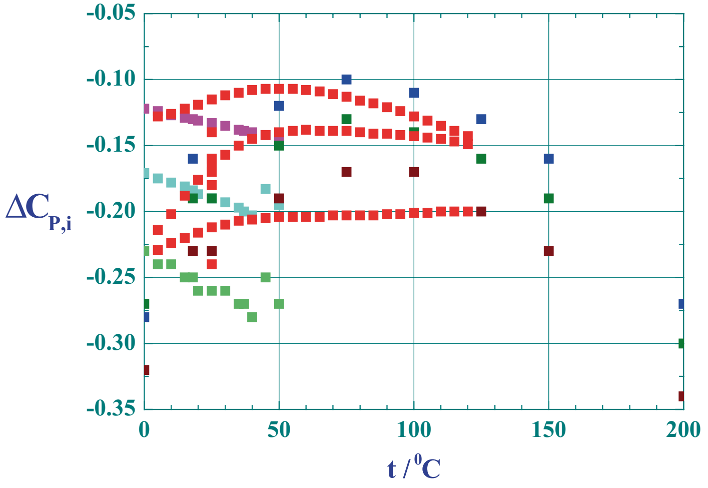


Fig. 3.10 Changes in the heat capacities in kJ mol^{-1} K^{-1} as a function of temperature in three steps of dissociation of citric acid. $\Delta C_{P,1}$ 🟪 - [6]; - 🟦 [8] and 🟥 - [15, 16]; $\Delta C_{P,2}$ 🟦 - [6]; 🟩 - [8] and 🟥 - [15, 16]; $\Delta C_{P,3}$ 🟩 - [6]; 🟫 - [8] and 🟥 - [15, 16]

and enthalpy changes as a function of temperature. The changes in enthalpies were evaluated from integrations of $\Delta C_P(T)$ polynomials

$$\Delta C_P(T) = B + CT + DT^2 + ET^3$$
$$\Delta H(T) = A + BT + \frac{C}{2}T^2 + \frac{D}{3}T^3 + \frac{E}{4}T^4 \tag{3.27}$$

The Patterson and Woolley [15] results for the heat capacity and enthalpy changes in dissociation reactions of citric acid can be correlated by

$$
\begin{aligned}
&\Delta C_{P,1}(T)\,/\,\mathrm{kJ\cdot mol^{-1}\cdot K^{-1}} = -1.0065 + 5.501\cdot 10^{-3}T - 8.421\cdot 10^{-6}T^2 \\
&A_1\,/\,\mathrm{kJ\cdot mol^{-1}} = 134.19 \\
&\Delta C_{P,2}(T)\,/\,\mathrm{kJ\cdot mol^{-1}\cdot K^{-1}} = -7.7865 + 0.06384T - 1.769\cdot 10^{-4}T^2 \\
&\qquad +1.626\cdot 10^{-7}T^3 \\
&A_2\,/\,\mathrm{kJ\cdot mol^{-1}} = 727.86 \\
&\Delta C_{P,3}(T)\,/\,\mathrm{kJ\cdot mol^{-1}\cdot K^{-1}} = -3.0009 + 0.02382T - 6.760\cdot 10^{-5}T^2 \\
&\qquad +6.394\cdot 10^{-8}T^3 \\
&A_3\,/\,\mathrm{kJ\cdot mol^{-1}} = 303.42
\end{aligned}
\tag{3.28}
$$

and for the volume changes as

$$
\begin{aligned}
\Delta V_1(T)\,/\,\mathrm{cm^3{\bullet}mol^{-1}} &= -87.20 + 0.4988T - 8.098{\bullet}10^{-4}T^2 \\
\Delta V_2(T)\,/\,\mathrm{cm^3{\bullet}mol^{-1}} &= -29.64 + 0.1541T - 3.113{\bullet}10^{-4}T^2 \\
\Delta V_3(T)\,/\,\mathrm{cm^3{\bullet}mol^{-1}} &= -84.37 + 0.5648T - 11.347{\bullet}10^{-4}T^2
\end{aligned}
\tag{3.29}
$$

$\Delta G(T)$, $\Delta H(T)$ and $T\Delta S(T)$ as a function of temperature, behave similarly in the three steps of citric acid dissociation process. The change in the Gibbs free energy increases with increasing of temperature, $\partial\Delta G(T)/\partial T>0$ and they are always positive $\Delta G(T)>0$. The enthalpy and entropy changes decrease with increasing of temperature, $\partial\Delta H(T)/\partial T<0$ and $\partial\Delta S(T)/\partial T<0$. The entropies are always negative $\Delta S(T)<0$ but the enthalpies change sign from positive to negative (i.e. dissociation is an exothermic process at high temperatures). The absolute values of thermodynamic changes satisfy $|T\Delta S(T)|>\Delta G(T)>|\Delta H(T)|$. Since $K_1(T)>K_2(T)>K_3(T)$, it follows from Eq. (3.21) that $\Delta G_3(T)>\Delta G_2(T)>\Delta G_1(T)$ and at any temperature, $\Delta H_1(T)>\Delta H_2(T)>\Delta H_3(T)$ and $\Delta S_1(T)>\Delta S_2(T)>\Delta S_3(T)$.

If the enthalpy and entropy changes $\Delta H_i(T)$ and $\Delta S_i(T)$, i = 1, 2, 3 are plotted for three dissociation reactions of citric acid (Fig. 3.11), nearly linear relationships are

$$
\begin{gathered}
\Delta H_i(T) = \alpha_i + \beta_i \Delta S_i(T) \\
i = 1,2,3
\end{gathered}
\tag{3.30}
$$

observed.

The slopes β_i are nearly the same $\beta_i=\beta=(298\pm 1)$ K for $T<323$ K and they are only slightly changed for higher temperatures. Such behaviour is called the enthalpy-entropy effect or enthalpy-entropy compensation. Since β have dimensions of temperature, the constant is often called the isoequilibrium temperature [17].

If ordinary water is replaced by heavy water, there is a change in dissociation constants of citric acid [18, 19]. The deuterium isotope effect, as postulated by Li et al. [18], can be expressed by linear relations

$$
\begin{gathered}
pK_{i,D_2O} = 0.086 + 1.124pK_{i,H_2O} \\
i = 1,2,3
\end{gathered}
\tag{3.31}
$$

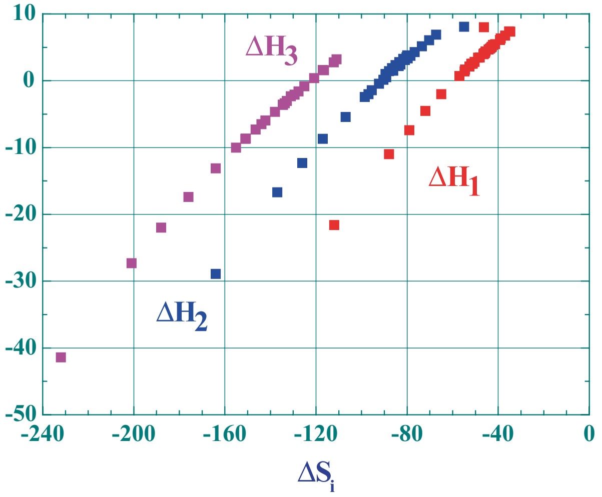


Fig. 3.11 Plots of $\Delta H_i(T)$ in kJ mol^{-1} against $\Delta S_i(T)$ in J mol^{-1} K^{-1}, for the three steps of dissociation of citric acid

3.4 Dissociation Constants of Citric Acid in Electrolyte Solutions

The addition of a neutral salt to solutions of organic acids produces an increase in the extent of ionization and this is expressed by changes in concentration quotients of the corresponding mass-action equations [20]. Thus, the apparent dissociation constants which represent these quotients have very different values according to the background salt (supporting electrolyte) applied in various types of measurements. Since individual activity coefficients of involved ions are usually unknown, the constant-medium method is frequently applied in investigation of complexation, hydrolysis and other similar type reactions. Considering that activity coefficients (in the limiting or extended Debye-Hückel forms) depend on the total ionic strength of solution I, it is assumed that their values are constant when an inert electrolyte (acidic or basic salts would cause large shifts in the dissociation equilibrium of weak acids) is added in sufficiently large and constant amount. In consequence, if during experiments, the concentration of supporting electrolyte considerably exceeds that of reacting species in solutions, the quotients of activity coefficients remain constant and the apparent dissociation constants $K(I \neq 0;T)$ can be determined. Sometimes, using pK values at different I, the thermodynamic constants can be established by the extrapolation to the zero ionic strength, $pK(I=0;T)$.

In case of citric acid, a number of apparent dissociation constants (or equivalent the protonation constants) in different ionic media at different ionic strengths, $K_i(I \neq 0;T)$, considerably exceeds those in pure water. This results from the fact that citrate ions participate in a very large number of complexation reactions and these constants are necessary as a starting point when distribution of species in solution is analyzed. Usually, the apparent dissociation constants of citric acid from the literature, were determined as by-products of various complexation investigations performed at one ionic strength only. However, their dependence on ionic strength and temperature was systematically investigated in few cases: alkali metal chlorides (LiCl, NaCl, KCl, RbCl and CsCl), sodium perchlorate $NaClO_4$, potassium nitrate KNO_3, tetramethylammonium chloride Me_4NCl and tetraethylammonium iodide Et_4NI.

The apparent dissociation constants $K_i(I \neq 0;T)$ which were compiled from the literature are given in Table 3.4 and they are presented together with the corresponding apparent Gibbs free energies $\Delta G_i = -RT \ln[K_i(I \neq 0;T)]$. Similarly as with dissociation constants of citric acid in pure water, differences in reported values of constants can be attributed not only to precision of experiments, but also to differences in applied speciation models, differences in mathematical form of equations used for activity coefficients and the choice of concentration scales (molar or molal). One aspect which was found to be extremely important was that earlier assumption that alkali metal cations do not form complexes with citrate anions is only partially correct. It was established that these cations form weak complexes with citrate anions and sometimes this interfering effect was even taken into account in calculation of $K_i(I \neq 0;T)$ values [16, 21, 22].

Since the apparent dissociation constants are usually reported as $pK_i(I \neq 0;T)$ and not as $K_i(I \neq 0;T)$ values, the scattering of results and differences caused by different ionic media and temperatures are less evident in the literature presentations than they actually are (Figs. 3.12, 3.13, 3.14 and 3.15). Significant differences in the apparent dissociation constants are observed with regard to applied supporting electrolyte, the ionic strength and temperature.

At constant temperature, the apparent dissociation constants as a function of the ionic strength I have a distinct maximum. They have larger values in solutions of alkali metal halides than in solutions of tetraalkylammonium halides. Between different alkali metals, differences in their values are less evident in the first dissociation step of citric acid, but they increase in the second dissociation step and are significant in the third dissociation step. This is clearly illustrated in the case of NaCl and KCl (see Figs. 3.12, 3.13 and 3.14). At constant I, the apparent dissociation constants as a function of temperature have a maximal value, but usually their temperature dependence is rather weak (Fig. 3.15).

Thermodynamic functions associated with dissociation process of citric acid in various ionic media are considerably less known than those in pure water. However, most of them come from direct calorimetric measurements and not from differentiation of $K_i(I \neq 0;T)$ with regard to temperature (see Eq. (3.21)). In Table 3.5 are presented the available ΔH_i and $\Delta C_{P,i}$ values for citric acid solutions with NaCl, $NaClO_4$, KNO_3 and Et_4NI and since the corresponding ΔG_i are given in Table 3.4, the entropic terms, $T\Delta S_i$, is also available.

Table 3.4 Apparent dissociation constants and changes in Gibbs free energies caused by dissociation of citric acid in different ionic media as a function of temperature and ionic strength

t°C	I	$K_1 10^4$	$K_2 10^5$	$K_3 10^6$	ΔG_1	ΔG_2	ΔG_3	Ref
LiCl								
10	0.04	9.44	3.29	1.35	16.39	24.30	31.81	[16]
20		10.3	3.52	1.36	16.77	24.99	32.93	
25		10.6	3.61	1.34	16.97	25.36	33.51	
30		10.9	3.68	1.32	17.19	25.73	34.12	
37		10.5	3.39	1.48	17.69	26.54	34.61	[97]
40		11.4	3.77	1.25	17.64	26.52	35.39	[16]
50		11.7	3.79	1.15	18.13	27.35	36.73	
37	0.09	13.6	4.90	2.40	17.02	25.59	33.36	[97]
10	0.16	11.4	5.08	3.21	15.96	23.27	29.78	[16]
20		12.4	5.50	3.27	16.31	23.90	30.78	
25		12.9	5.66	3.26	16.49	24.24	31.31	
30		13.3	5.81	3.22	16.68	24.58	31.87	
40		14.0	6.03	3.10	17.10	25.29	33.01	
50		14.6	6.14	2.92	17.55	26.05	34.24	
10	0.36	12.4	6.59	5.96	15.75	22.66	28.32	
20		13.7	7.21	6.14	16.07	23.24	29.25	
25		14.3	7.46	6.17	16.24	23.55	29.73	
30		14.8	7.71	6.15	16.42	23.87	30.24	
40		15.7	8.09	6.00	16.81	24.53	31.30	
50		16.4	8.34	5.74	17.23	25.23	32.42	
37	0.49	12.6	7.76	6.17	17.22	24.40	30.93	[97]
10	0.64	12.9	7.80	8.77	15.67	22.26	27.41	[16]
20		14.3	8.61	9.16	15.96	22.81	28.27	
25		15.0	8.97	9.27	16.12	23.10	28.72	
30		15.6	9.31	9.29	16.28	23.39	29.20	
40		16.7	9.89	9.20	16.64	24.01	30.19	
50		17.7	10.3	8.93	17.02	24.65	31.23	
37	0.98	17.0	11.0	11.0	16.44	23.51	29.44	[97]
10	1.00	13.2	8.89	10.1	15.61	21.96	27.08	[16]
20		14.9	9.95	10.7	15.87	22.46	27.89	
25		15.6	10.4	10.9	16.01	22.72	28.32	
30		16.4	10.9	11.0	16.16	22.99	28.77	
40		17.8	11.7	11.1	16.48	23.56	29.71	
50		19.0	12.4	10.9	16.83	24.15	30.69	
NaCl								
10	0.04	9.44	3.21	1.29	16.39	24.35	37.34	[16]
20		10.3	3.47	1.31	16.75	25.03	38.63	
25		10.7	3.56	1.30	16.95	25.38	39.30	
30		11.0	3.65	1.28	17.17	25.75	40.00	

Table 3.4 (continued)

t°C	I	$K_1 10^4$	$K_2 10^5$	$K_3 10^6$	ΔG_1	ΔG_2	ΔG_3	Ref
40		11.5	3.74	1.21	17.63	26.54	41.45	
50		11.7	3.77	1.12	18.14	27.36	42.99	
25	0.075	8.32	1.82	0.55	17.58	27.05	41.43	[98]
0	0.10	9.68	3.71	1.97	15.76	23.17	35.06	[8]
18		12.3	4.34	1.67	16.22	24.31	37.76	[87]
18		11.9	4.30	1.73	16.29	24.34	37.68	[99]
25		12.5	4.60	2.07	16.56	24.75	38.14	[8]
		12.0	4.46	1.69	16.67	24.83	38.65	[100]
		14.0	4.98	2.16	16.28	24.57	32.34	[138]
		12.3	4.75	2.24	16.61	24.67	32.24	[139]
30		9.55	4.90	3.31	17.52	25.01	31.80	[135]
50		13.8	4.82	1.85	17.69	26.70	41.64	[8]
75		14.0	4.62	1.53	19.01	28.89	45.41	
100		13.6	4.23	1.22	20.48	31.24	49.39	
125		12.6	3.74	0.94	22.09	33.74	53.54	
150		11.4	3.21	0.72	23.84	36.40	57.85	
200		8.30	2.17	0.40	27.90	42.24	66.98	
18	0.11	14.6	4.94	2.17	15.81	24.00	37.14	[86]
25		11.2	4.17	1.58	16.84	25.00	33.10	[18]
	0.15	11.5	4.57	2.45	16.78	24.77	37.72	[101]
10	0.16	11.5	4.74	2.77	15.94	23.43	35.54	[16]
20		12.7	5.21	2.84	16.26	24.03	36.73	
25		13.2	5.41	2.85	16.43	24.35	37.35	
		11.5	4.90	2.45	16.78	24.6	32.01	[137]
30		13.7	5.58	2.83	16.62	24.68	37.99	[16]
40		14.4	5.85	2.74	17.03	25.37	39.34	
50		14.9	6.00	2.58	17.49	26.11	40.75	
18	0.20	13.6	5.52	2.90	15.98	23.73	36.43	[99]
	0.26	15.0	6.25	3.31	15.74	23.43	36.11	[86]
10	0.36	12.8	5.93	4.61	15.67	22.91	34.34	[16]
20		14.3	6.59	4.81	15.96	23.46	35.45	
25		15.0	6.89	4.84	16.12	23.75	36.04	
30		15.6	7.16	4.84	16.28	24.05	36.64	
40		16.6	7.60	4.75	16.66	24.69	37.90	
50		17.4	7.93	4.55	17.07	25.37	39.23	
0	0.50	13.1	6.10	5.00	15.07	22.04	32.94	[8]
18		15.7	7.29	5.27	15.63	23.05	34.99	[99]
25		16.9	7.55	5.41	15.82	23.52	35.76	[8]
50		18.7	8.02	5.06	16.87	25.34	38.94	
25		15.2	7.29	3.87	16.08	23.61	36.59	[100]

Table 3.4 (continued)

t°C	I	$K_1 10^4$	$K_2 10^5$	$K_3 10^6$	ΔG_1	ΔG_2	ΔG_3	Ref
75		19.4	7.93	4.47	18.08	27.33	42.32	[8]
100		19.3	7.57	3.86	19.38	29.43	45.80	
125		18.7	7.11	3.34	20.78	31.61	49.35	
150		17.7	6.58	2.90	22.28	33.87	52.95	
200		14.7	5.46	2.25	25.67	38.61	60.20	
18	0.51	16.4	7.98	4.99	15.51	22.84	35.12	[86]
25	0.60	17.0	8.30	6.07	15.80	23.29	35.48	[102]
10	0.64	13.9	6.98	6.38	15.48	22.52	33.57	[16]
20		15.7	7.78	6.70	15.73	23.06	34.64	
25		16.5	8.13	6.78	15.88	23.34	35.21	
30		17.2	8.45	6.81	16.04	23.63	35.78	
40		18.5	9.02	6.73	16.38	24.25	36.99	
50		19.5	9.42	6.50	16.77	24.90	38.27	
15	0.98	15.5	7.94	6.61	15.50	22.61	34.09	[103]
55		20.4	9.77	6.31	16.90	25.19	38.94	
0	1.00	14.9	7.50	6.19	14.78	21.57	32.46	[8]
10		15.4	8.45	7.60	15.24	22.07	33.16	[16]
18		16.7	8.09	7.33	15.48	22.80	34.19	[99]
20		17.3	9.27	7.98	15.49	22.63	34.22	[16]
25		17.0	8.91	7.59	15.81	23.11	34.93	[104]
		18.2	9.62	8.07	15.63	22.92	34.77	[16]
		18.8	9.16	6.65	15.56	23.04	35.25	[8]
30		19.1	9.93	8.11	15.78	23.23	35.34	[2]
40		20.4	10.40	8.02	16.12	23.87	36.54	
50		21.5	10.72	7.76	16.50	24.56	37.79	
50		20.7	9.73	6.28	16.60	24.82	38.36	[8]
75		21.5	9.75	5.68	17.77	26.73	41.62	
100		21.8	9.57	5.11	19.01	28.71	44.94	
125		21.6	9.31	4.65	20.31	30.72	48.26	
150		21.1	9.06	4.30	21.67	32.75	51.57	
200		19.1	8.55	4.00	24.63	36.84	57.94	
25		16.1	8.34	5.31	15.94	23.28	35.81	[100]
	1.23	16.1	8.49	5.77	15.94	23.23	35.60	[14]
15	1.46	15.5	8.13	7.59	15.50	22.56	33.75	[103]
55	1.46	21.9	10.47	7.59	16.71	25.00	38.44	
18	1.50	16.3	8.38	8.28	15.54	22.72	33.89	[99]
15	1.97	14.8	7.76	7.94	15.61	22.67	33.64	[103]
55	1.97	20.4	10.23	8.32	16.90	25.06	38.19	
18	2.00	15.5	8.11	8.38	15.67	22.80	33.87	[99]
25	2.00	15.2	8.07	6.46	16.08	23.36	35.33	[100]

Table 3.4 (continued)

t°C	I	$K_1 10^4$	$K_2 10^5$	$K_3 10^6$	ΔG_1	ΔG_2	ΔG_3	Ref
18	2.50	13.9	7.26	7.93	15.92	23.07	34.00	[99]
15	2.98	12.6	6.31	7.41	15.99	23.16	33.81	[103]
18	3.00	12.3	6.64	7.52	16.22	23.28	34.13	[99]
25	3.00	13.2	6.81	6.47	16.44	23.78	35.32	[100]
55	3.03	18.2	9.12	8.32	17.21	25.38	38.19	[103]
25	3.20	12.6	6.46	6.34	16.54	23.91	35.37	[14]
	4.86	8.91	4.19	5.28	17.41	24.98	35.82	
	5.00	8.61	4.01	5.16	17.49	25.09	35.88	[100]
15	5.06	7.59	3.63	4.37	17.21	24.49	35.08	[103]
55	5.11	12.0	5.89	5.62	18.34	26.57	39.26	
KCl								
10	0.04	9.18	3.10	1.24	16.46	24.43	37.43	[16]
20		10.2	3.42	1.32	16.78	25.06	38.60	
25		10.6	3.52	1.31	16.97	25.42	39.27	
30		10.9	3.56	1.28	17.18	25.82	39.99	
40		11.4	3.53	1.15	17.65	26.68	41.59	
50		11.4	3.36	0.97	18.20	27.67	43.38	
20	0.10	11.0	4.07	2.14	16.61	24.63	37.43	[105]
20		8.32	4.07	3.24	17.28	24.63	36.42	[106]
25		12.8	4.22	2.07	16.50	24.97	38.15	[107]
		12.0	4.43	1.67	16.68	24.85	38.68	[100]
		13.5	4.10	2.26	16.38	25.04	37.93	[108]
		12.0	4.37	2.09	16.66	24.88	38.12	[109]
		11.5	4.87	1.91	16.78	24.94	31.64	[142]
30		11.2	4.17	1.66	17.12	25.42	33.54	[134]
10	0.16	10.7	4.42	2.38	16.10	23.60	35.90	[16]
20		12.1	4.90	2.54	16.38	24.18	37.01	
25		12.6	5.05	2.54	16.55	24.52	37.64	
30		13.1	5.14	2.49	16.73	24.89	38.32	
40		13.7	5.14	2.26	17.16	25.71	39.84	
50		14.0	4.93	1.91	17.65	26.64	41.55	
25	0.20	13.5	5.50	1.02	16.38	24.31	39.89	[110]
	0.50	15.1	7.01	3.64	16.10	23.71	36.75	[100]
10	0.64	13.7	5.75	3.89	15.52	22.98	34.74	[16]
20		15.0	6.53	4.37	15.84	23.48	35.69	
25		15.6	6.81	4.48	16.02	23.78	36.23	
30		15.9	7.01	4.49	16.24	24.10	36.83	
40		16.3	7.19	4.29	16.71	24.83	38.17	
50		16.3	7.08	3.82	17.25	25.67	39.70	
10	1.00	18.3	6.55	3.85	14.83	22.68	34.77	

Table 3.4 (continued)

t°C	I	$K_1 10^4$	$K_2 10^5$	$K_3 10^6$	ΔG_1	ΔG_2	ΔG_3	Ref
20		18.9	7.59	4.61	15.28	23.12	35.55	
25		18.9	8.00	4.89	15.54	23.38	36.02	
30		18.7	8.34	5.08	15.82	23.67	36.52	
40		18.0	8.73	5.18	16.45	24.33	37.68	
50		16.8	8.79	4.94	17.16	25.09	39.00	
25		15.7	7.83	4.71	16.00	23.43	36.11	[100]
	1.25	15.7	7.89	4.99	16.00	23.41	35.96	[14]
	2.00	14.7	7.21	5.15	16.17	23.64	35.88	[100]
	3.00	12.6	5.85	4.74	16.54	24.16	36.09	
	3.31	11.9	5.37	4.52	16.69	24.37	36.21	[14]
	4.50	9.33	3.62	3.70	17.29	25.35	36.71	[100]
	5.12	8.15	3.21	3.30	17.63	25.65	36.99	[14]
RbCl								
37	0.03	10.7	3.47	1.35	17.63	26.48	34.85	[97]
10	0.04	9.62	3.26	1.27	16.35	24.32	31.96	[16]
20		10.4	3.48	1.27	16.73	25.01	33.09	
25		10.8	3.57	1.26	16.93	25.38	33.68	
30		11.1	3.64	1.23	17.15	25.76	34.29	
40		11.5	3.71	1.17	17.63	26.56	35.55	
50		11.6	3.71	1.09	18.15	27.41	36.88	
37	0.10	13.5	4.79	2.04	17.04	25.65	33.78	[97]
10	0.16	12.1	4.90	2.59	15.82	23.36	30.27	[16]
20		13.1	5.27	2.62	16.18	24.00	31.32	
25		13.5	5.41	2.61	16.38	24.35	31.87	
30		13.8	5.53	2.58	16.60	24.70	32.43	
40		14.3	5.68	2.47	17.06	25.45	33.61	
50		14.4	5.71	2.33	17.57	26.24	34.84	
37	0.30	14.5	6.03	3.24	16.86	25.05	32.59	[97]
10	0.36	13.8	6.17	4.01	15.50	22.82	29.25	[16]
20		14.9	6.67	4.06	15.87	23.43	30.25	
25		15.2	6.82	4.06	16.08	23.77	30.77	
30		15.6	6.98	4.02	16.29	24.12	31.31	
40		16.0	7.19	3.89	16.76	24.83	32.43	
50		16.0	7.26	3.69	17.29	25.60	33.60	
10	0.64	15.0	7.10	4.99	15.31	22.49	28.74	
20		15.9	7.64	5.08	15.71	23.10	29.71	
25		16.2	7.85	5.07	15.92	23.43	30.22	
30		16.4	8.22	5.04	16.15	23.70	30.74	
40		16.6	8.26	4.89	16.66	24.47	31.83	

Table 3.4 (continued)

t°C	I	$K_1 10^4$	$K_2 10^5$	$K_3 10^6$	ΔG_1	ΔG_2	ΔG_3	Ref
50		16.5	8.36	4.65	17.21	25.22	32.99	
10	0.90	15.7	8.02	5.22	15.19	22.20	28.63	
20		16.4	8.61	5.31	15.63	22.81	29.60	
25		16.6	8.85	5.31	15.87	23.13	30.10	
30		16.7	9.04	5.26	16.12	23.47	30.63	
40		16.6	9.27	5.12	16.67	24.17	31.71	
50		16.2	9.35	4.88	17.26	24.92	32.86	
CsCl								
37	0.03	11.3	3.52	1.29	17.50	26.44	40.90	[97]
10	0.04	9.55	3.23	1.26	16.37	24.34	37.39	[16]
20		10.4	3.48	1.27	16.73	25.02	38.70	
25		10.8	3.56	1.26	16.93	25.38	39.38	
30		11.1	3.63	1.23	17.15	25.76	40.10	
40		11.5	3.70	1.16	17.62	26.57	41.57	
50		11.6	3.69	1.06	18.15	27.42	43.13	
37	0.10	12.6	4.68	2.00	17.22	25.70	39.77	[97]
10	0.16	11.9	3.70	2.51	15.86	24.02	35.77	[16]
20		12.9	5.15	2.56	16.20	24.06	36.99	
25		13.4	5.30	2.55	16.40	24.40	37.63	
30		13.7	5.42	2.51	16.61	24.75	38.30	
40		14.3	5.57	2.40	17.06	25.50	39.68	
50		14.5	5.61	2.23	17.56	26.29	41.14	
37	0.30	15.8	6.46	3.16	16.62	24.87	38.59	[97]
10	0.36	13.5	5.77	3.73	15.55	22.97	34.84	[16]
20		14.7	6.27	3.83	15.90	23.58	36.01	
25		15.1	6.47	3.83	16.09	23.91	36.62	
30		15.5	6.64	3.79	16.30	24.24	37.26	
40		16.1	6.87	3.66	16.75	24.95	38.58	
50		16.3	6.97	3.44	17.25	25.71	39.98	
10	0.64	14.6	6.30	4.42	15.36	22.77	34.44	
20		15.8	6.87	4.56	15.72	23.36	35.58	
25		16.3	7.11	4.58	15.92	23.67	36.18	
30		16.6	7.31	4.56	16.13	24.00	36.79	
40		17.1	7.59	4.44	16.59	24.69	38.08	
50		17.2	7.62	4.21	17.10	25.47	39.44	
10	0.90	15.6	6.64	4.36	15.21	22.64	34.47	
20		16.7	7.26	4.52	15.58	23.22	35.60	
25		17.1	7.52	4.55	15.79	23.53	36.19	
30		17.4	7.74	4.55	16.01	23.85	36.80	
40		17.7	8.07	4.45	16.49	24.53	38.07	

Table 3.4 (continued)

t°C	I	$K_1 10^4$	$K_2 10^5$	$K_3 10^6$	ΔG_1	ΔG_2	ΔG_3	Ref
50		17.7	8.24	4.26	17.02	25.26	39.41	
$NaClO_4$								
25	0.05	10.7	3.70	1.25	16.96	25.29	33.69	[90]
37		11.4	3.86	1.21	17.47	26.20	35.14	
20	0.10	10.7	4.62	2.19	16.67	24.32	31.76	[133]
25		11.3	4.45	1.69	16.83	24.84	32.93	[90]
		14.1	4.47	1.51	16.26	24.82	38.92	[111]
		13.8	4.17	1.41	16.32	25.00	39.09	
		11.7	4.27	2.29	16.72	24.94	37.89	[112]
15		15.5	7.24	3.02	15.50	22.83	35.96	[113]
20		13.5	4.47	2.09	16.10	24.41	31.87	[117]
25		12.3	5.62	2.24	16.61	24.25	37.95	[113]
35		10.5	4.68	1.82	17.58	25.54	39.75	
37		12.1	4.68	1.64	17.32	25.71	34.35	[90]
25	0.15	11.4	4.91	2.01	16.80	24.59	32.51	
37		12.2	5.18	1.95	17.29	25.44	33.90	
		14.0	6.35	3.41	16.95	24.92	32.46	[140]
25	0.20	11.3	5.19	2.24	16.83	24.45	32.24	[90]
37		12.1	5.48	2.16	17.32	25.30	33.63	
25	0.50	8.55	5.11	2.54	17.42	24.49	31.94	
		24.9	7.13	4.82	14.85	23.67	36.05	[114]
37		9.53	5.41	2.40	17.93	25.33	33.36	[90]
25	1.00	4.80	3.26	1.66	18.94	25.61	32.99	
37		5.15	3.44	1.50	19.52	26.50	34.57	
25	2.00	12.6	6.92	6.61	16.55	23.74	35.27	[115]
		17.8	9.33	9.54	15.69	23.00	28.65	[136]
0	6.60	15.1	7.59	8.32	14.74	21.54	31.79	[116]
25		12.0	5.25	6.17	16.66	24.43	35.44	
45		9.77	4.37	5.25	18.33	26.55	38.24	
60		8.71	3.55	4.47	19.51	28.38	40.49	
KNO_3								
10	0.10	10.5	3.63	1.86	16.15	24.06	36.47	[118]
25		13.5	5.01	2.45	16.38	24.54	37.72	[119]
		16.2	5.01	2.24	15.92	24.54	37.95	[120]
		15.5	4.37	2.00	16.04	24.88	38.24	[121]
		12.0	4.07	1.91	16.66	25.05	38.35	[122]
		12.3	4.37	1.82	16.61	24.88	38.46	[123]
		12.0	4.57	2.04	16.66	24.77	38.18	[118]
35		12.9	4.47	1.86	17.05	25.66	39.69	
45		12.9	3.98	1.48	17.60	26.79	41.59	

Table 3.4 (continued)

t°C	I	$K_1 10^4$	$K_2 10^5$	$K_3 10^6$	ΔG_1	ΔG_2	ΔG_3	Ref
25	0.15	13.5	5.13	2.40	16.38	24.48	37.78	[124]
	0.20	12.0	4.17	2.04	16.66	25.00	32.47	[141]
15	0.50	13.5	5.13	2.40	15.83	23.11	28.57	[94]
25		18.2	8.71	6.76	15.64	23.17	35.21	
35		24.0	11.8	7.08	15.45	23.18	30.38	
15	1.00	12.0	5.13	4.37	16.10	23.66	29.56	
25		16.6	7.08	4.79	15.86	23.68	36.07	[94]
		23.4	7.76	4.57	15.01	23.45	36.18	[120]
31		6.46	7.76	0.65	18.57	23.93	41.86	[125]
35		20.0	10.7	5.89	15.92	23.42	30.85	[94]
15	1.50	8.91	3.98	3.02	16.82	24.27	30.45	
25		12.3	5.62	3.47	16.61	24.25	36.87	
35		15.5	7.94	3.98	16.57	24.18	31.85	
25	2.00	8.32	4.07	3.24	17.58	25.05	37.04	[126]
Me_4NCl								
25	0.10	13.2	4.37	1.45	16.44	24.88	39.03	[127]
		9.12	3.55	1.48	17.35	25.40	33.27	[138]
	0.30	10.4	4.85	1.82	17.03	24.62	38.47	[91]
		12.8	4.88	1.83	16.50	24.61	38.45	
	0.52	13.3	5.43	2.10	16.41	24.34	38.11	
	1.00	12.9	5.64	2.12	16.48	24.25	38.09	
	1.01	13.0	5.61	2.09	16.46	24.26	38.12	
	1.48	11.8	5.57	2.06	16.71	24.28	38.16	
		11.9	5.30	1.92	16.70	24.40	38.33	
	2.14	10.3	5.08	1.86	17.05	24.50	38.41	
		10.2	4.86	1.74	17.07	24.61	38.58	
	2.98	8.53	4.45	1.57	17.51	24.84	38.82	
	2.99	8.28	4.09	1.39	17.59	25.04	39.13	
Et_4NI								
10	0.16	9.51	3.54	1.39	16.38	24.12	37.17	[7]
	0.36	8.95	3.48	1.33	16.52	24.16	37.27	
	0.64	7.73	2.99	1.04	16.87	24.52	37.86	
	1.00	6.34	2.42	0.73	17.33	25.02	38.67	
20	0.04	9.77	3.08	1.02	16.89	25.31	39.23	
	0.16	10.6	3.88	1.42	16.68	24.75	38.42	
	0.36	10.1	3.85	1.38	16.81	24.77	38.50	
	0.64	8.83	3.35	1.09	17.14	25.11	39.08	
	1.00	7.36	2.75	0.78	17.58	25.59	39.89	
25	0.04	10.2	3.18	1.01	17.07	25.67	39.92	
	0.16	11.1	4.02	1.42	16.85	25.09	39.08	

Table 3.4 (continued)

t°C	I	$K_1 10^4$	$K_2 10^5$	$K_3 10^6$	ΔG_1	ΔG_2	ΔG_3	Ref
	0.36	10.6	4.02	1.39	16.97	25.09	39.14	
	0.64	9.35	3.52	1.10	17.29	25.42	39.71	
	1.00	7.83	2.91	0.80	17.73	25.89	40.51	
30	0.04	10.5	3.26	1.00	17.28	26.04	40.62	
	0.16	11.6	4.14	1.41	17.04	25.43	39.75	
	0.36	11.1	4.16	1.39	17.14	25.42	39.79	
	0.64	9.82	3.66	1.11	17.45	25.74	40.36	
	1.00	8.28	3.05	0.81	17.88	26.20	41.16	
37	0.01	10.2	2.70	0.91	17.75	27.12	35.86	[128]
	0.03	10.7	3.16	1.05	17.63	26.71	35.50	
	0.10	12.0	3.98	1.38	17.34	26.12	34.79	
	0.30	12.2	4.27	1.51	17.31	25.94	34.55	
	1.00	8.61	3.13	0.85	18.20	26.74	36.03	
40	0.04	11.0	3.37	0.95	17.72	26.81	42.09	[7]
	0.16	12.2	4.33	1.36	17.45	26.16	41.15	
	0.36	11.9	4.40	1.36	17.54	26.12	41.15	
	0.64	10.6	3.93	1.10	17.83	26.41	41.70	
	1.00	9.10	3.33	0.82	18.23	26.84	42.48	
50	0.04	11.3	3.41	0.89	18.22	27.63	43.62	
	0.16	12.6	4.44	1.29	17.93	26.92	42.61	
	0.36	12.4	4.57	1.31	17.98	26.84	42.58	
	0.64	11.2	4.13	1.08	18.25	27.12	43.10	
	1.00	9.75	3.55	0.81	18.62	27.52	43.87	

Units: K_i and I - mol dm^{-3} ; ΔG_i - kJ mol^{-1}

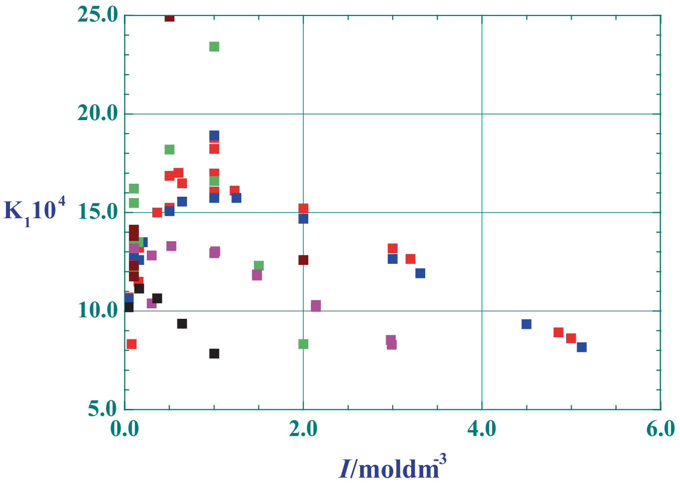


Fig. 3.12 The apparent first dissociation constant of citric acid at 25 °C as a function of ionic strength of electrolyte solution. 🟥 - NaCl; 🟦 - KCl; 🟫 - $NaClO_4$; 🟩 - KNO_3; 🟪 - Me_4NCl and ⬛ - Et_4NI

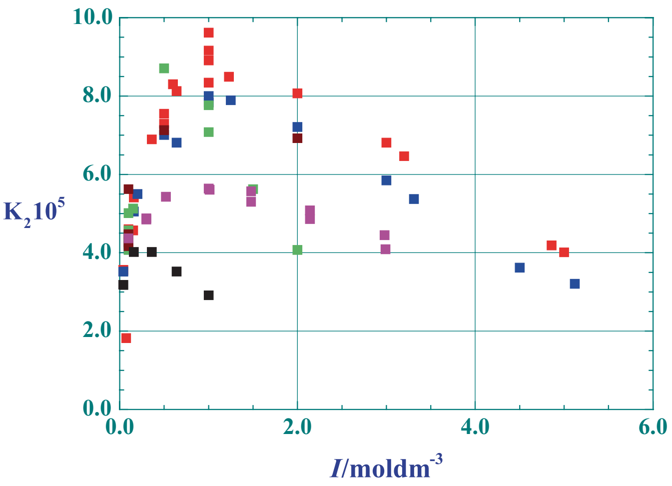


Fig. 3.13 The apparent second dissociation constant of citric acid at 25 °C as a function of ionic strength of electrolyte solution. 🟥 - NaCl; 🟦 - KCl; 🟫 - $NaClO_4$; 🟩 - KNO_3; 🟪 - Me_4NCl and ⬛ - Et_4NI

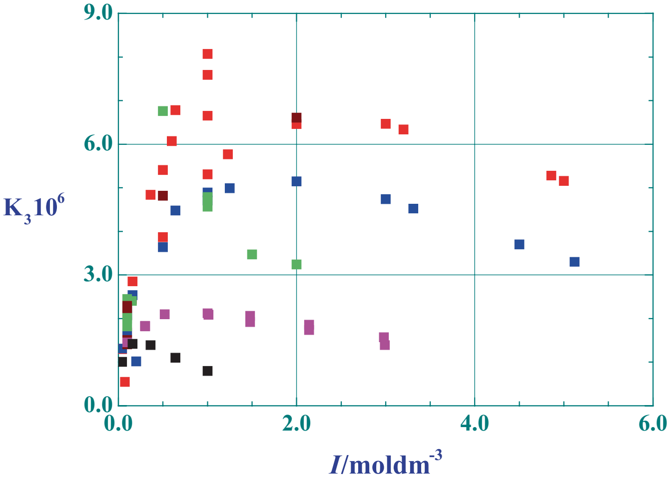


Fig. 3.14 The apparent third dissociation constant of citric acid at 25 °C as a function of ionic strength of electrolyte solution. 🟥 - NaCl; 🟦 - KCl; 🟫 - $NaClO_4$; 🟩 - KNO_3; 🟪 - Me_4NCl and ⬛ - Et_4NI

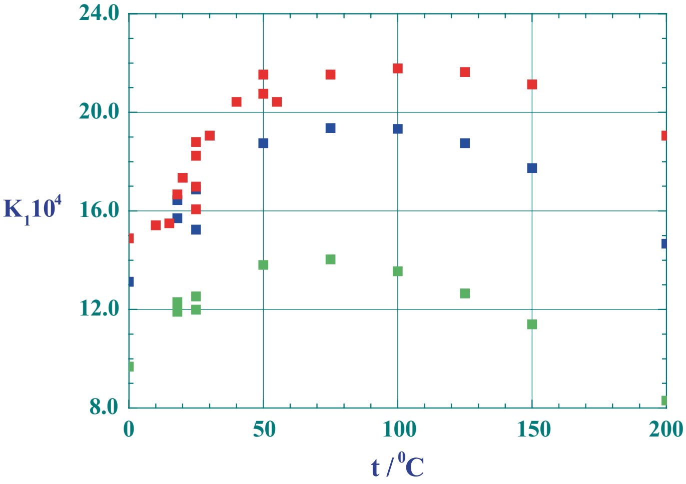


Fig. 3.15 The apparent first dissociation constant of citric acid in sodium chloride solutions as a function temperature. 🟩 - 0.10 mol dm^{-3}; 🟦 - 0.50 mol dm^{-3} and 🟥 - 1.0 mol dm^{-3}

Table 3.5 Changes in enthalpies and heat capacities caused by dissociation of citric acid in different ionic media as a function of temperature and ionic strength

t°C	I	ΔH_1	$\Delta C_{P,1}$	ΔH_2	$\Delta C_{P,2}$	ΔH_3	$\Delta C_{P,3}$	Ref
NaCl								
0	0.10	9.50	−0.24	8.10	−0.27	3.50	−0.31	[8]
10		6.00		4.90		0.40		[103]
25		4.70	−0.15	2.50	−0.18	−3.00	−0.22	
40		2.80		−0.10		−6.30		
50		1.80		−1.70		−8.60		
50		1.60	−0.10	−1.30	−0.13	−7.80	−0.17	[8]
75		−0.50	−0.08	−4.30	−0.11	−11.80	−0.15	
100		−2.40	−0.80	−7.10	−0.11	−15.50	−0.15	
125		−4.60	−0.10	−10.10	−0.13	−19.50	−0.17	
150		−7.40	−0.13	−13.80	−0.16	−24.00	−0.20	
200		−15.40	−0.20	−23.50	−0.23	−35.60	−0.27	
0	0.50	9.20	−0.23	7.50	−0.27	3.20	−0.30	
25		4.70	−0.14	2.10	−0.17	−3.20	−0.21	
50		2.10	−0.08	−1.50	−0.12	−7.70	−0.16	
75		0.50	−0.06	−4.10	−0.10	−11.30	−0.13	
100		−0.80	−0.05	−6.40	−0.09	−14.50	−0.13	
125		−2.30	−0.07	−8.90	−0.11	−17.90	−0.14	
150		−4.20	−0.09	−11.80	−0.13	−21.80	−0.17	
200		−9.70	−0.13	−19.40	−0.17	−31.20	−0.21	
0	1.00	8.60	−0.22	6.80	−0.26	2.40	−0.30	
10		6.80		6.40		2.70		[103]

Table 3.5 (continued)

t°C	I	ΔH_1	$\Delta C_{P,1}$	ΔH_2	$\Delta C_{P,2}$	ΔH_3	$\Delta C_{P,3}$	Ref
25		4.30		4.45		1.32		[104]
25		4.40	−0.12	1.50	−0.17	−3.90	−0.21	[8]
25		5.20		3.90		−0.60		[103]
40		3.50		1.50		−4.00		
50		2.50		−0.20		−6.20		
50		2.10	−0.07	−1.80	−0.11	−8.20	−0.15	[8]
75		0.90	−0.04	−4.10	−0.08	−11.50	−0.12	
100		−0.03	−0.03	−6.00	−0.08	−14.50	−0.12	
125		−0.90	−0.04	−8.00	−0.09	−17.50	−0.13	
150		−2.10	−0.06	−10.40	−0.10	−20.90	−0.15	
200		−5.70	−0.08	−16.30	−0.13	−28.90	−0.17	
10	2.00	7.50		8.00		4.70		[103]
25		5.90		5.50		1.40		
40		4.30		3.00		−2.00		
50		3.30		1.30		−4.20		
10	3.00	8.10		9.40		6.10		
25		6.50		7.00		2.70		
40		4.90		4.50		−0.60		
50		3.80		2.90		−2.90		
10	5.00	8.90		12.10		6.90		
25		7.40		9.60		3.50		
40		5.70		7.10		0.20		
50		4.70		5.40		−2.00		
$NaClO_4$								
25	0.05			3.01		−2.22		[92]
	0.10			3.14		−1.92		
	0.15			3.26		−1.72		
	0.04	5.60	−0.18	4.10	−0.15	−1.50	−0.22	
	0.16	6.10	−0.17	4.90	−0.14	−0.50	−0.21	
	0.36	6.80	−0.16	5.70	−0.13	0.50	−0.20	
	0.64	7.70	−0.16	6.60	−0.12	1.50	−0.18	
	1.00	8.80	−0.15	7.70	−0.11	2.60	−0.17	
KNO_3								
25	0.10	4.00		5.00		−3.00		[118]
15	0.50	6.00		6.65		2.05		[94]
25		5.27		5.06		0.24		
35		4.68		3.60		−1.41		
15	1.00	5.97		6.83		4.30		
25		5.46		5.68		1.43		
35		4.67		4.33		−0.18		

Table 3.5 (continued)

t°C	I	ΔH_1	$\Delta C_{P,1}$	ΔH_2	$\Delta C_{P,2}$	ΔH_3	$\Delta C_{P,3}$	Ref
15	1.50	6.15		6.62		4.20		
25		5.41		5.94		2.80		
35		4.61		4.62		0.63		
Et_4NI								
25	0.04	5.60	−0.18	4.10	−0.15	−1.50	−0.22	[7]
	0.16	6.10	−0.17	4.90	−0.14	−0.50	−0.21	
	0.36	6.80	−0.16	5.70	−0.13	0.50	−0.20	
	0.64	7.70	−0.16	6.60	−0.12	1.50	−0.18	
	1.00	8.80	−0.15	7.70	−0.11	2.60	−0.17	

Units: I - mol dm^{-3} ; ΔH_i - kJ· mol^{-1} and $\Delta C_{P,i}$ - kJ mol^{-1} K^{-1}

3.5 Dissociation Constants of Citric Acid in Pure Organic Solvents and Organic Solvent-Water Mixtures

Considering increasing use of non-aqueous or water-organic solvent media in analytical chemistry (for example in potentiometric titrations and in the high-performance liquid chromatography), dissociation constants of citric acid in few such systems were also determined. Evidently, they are less abundant than those in water. These dissociation constants are actually the concentration quotients, because activity coefficients and activities of water were always ignored.

Dissociation constants of citric acid in pure solvents (methanol (MeOH), ethanol (EtOH), formamide (FA) and dimethylformamide (DMF)) and in aqueous solutions of methanol, 1,4-dioxane (DX), tetrahydrofuran (THF) and acetonitrile (AN) are given in Table 3.6. They are presented together with corresponding ΔG_i values, dielectric constants D and compositions of the mixtures expressed in the molar fraction or weight per cent concentration units.

Values of pK_i in the water–methanol and the water–1,4-dioxane mixtures were determined a number of times [23–27]. However, in mixtures with 1,4-dioxane, the results of Schwarz et al. [23] and Papanastasiou and Ziogas [24] are inconsistent It seems that the Schwarz et al. pK_i values are incorrect. Papanastasiou and Ziogas also determined dissociation constants in the ternary water + methanol + 1,4-dioxane system [28]. pK_i values in the water–methanol mixtures, as obtained by Garrido et al. [27] are slightly shifted with regards to those in other investigations. They also determined dissociation constants of citric acid in the water + methanol + KCl system, but only at one constant ionic strength of $I = 0.15$ M KCl.

In terms of dissociation constants, the change of medium from water to organic solvent or to mixtures, is usually expressed by

$$\Delta pK_i(T) = -\log\left(\frac{K_i(T)}{K_{i,w}(T)}\right) = pK_i(T) - pK_{i,w}(T) \tag{3.32}$$

where $K_{i,w}(T)$ denotes the dissociation constant in pure water.

Table 3.6 Apparent dissociation constants and changes in Gibbs free energies caused by dissociation of citric acid in pure organic solvents and their mixtures with water

x	w/w%	D	pK_1	pK_2	pK_3	ΔG_1	ΔG_2	ΔG_3	Ref
Methanol + Water									
0.0467	8.01	75.08	3.27	4.95	6.59	18.66	28.25	37.61	[24]
0.0983	16.24	71.60	3.41	5.09	6.79	19.46	29.05	38.75	
0.1555	24.67	67.91	3.57	5.26	7.04	20.37	30.02	40.18	
0.2199	33.39	64.00	3.75	5.44	7.30	21.40	31.04	41.66	
0.2936	42.50	59.82	3.94	5.67	7.53	22.48	32.36	42.97	
0.0588	10.00	74.25	3.30	4.96	6.64	18.83	28.31	37.89	[25]
0.1232	20.00	69.97	3.47	5.16	6.90	19.80	29.45	39.38	
0.1942	30.00	65.53	3.66	5.36	7.16	20.89	30.59	40.86	
0.2726	40.00	60.98	3.86	5.57	7.43	22.03	31.79	42.40	
0.3599	50.00	56.34	4.06	5.79	7.70	23.17	33.04	43.94	
0.1000	16.50	71.48	3.41	5.09	6.80	19.46	29.05	38.81	[26]
0.2290	34.57	63.47	3.75	5.44	7.30	21.40	31.04	41.66	
0.3080	44.18	59.05	3.94	5.67	7.53	22.48	32.36	42.97	
0.4000	54.25	54.37	4.12	5.92	7.78	23.51	33.78	44.40	
0.6400	75.97	44.35	4.72	6.59	8.55	26.94	37.61	48.79	
0.0300	5.21	76.24	3.06	4.78	6.46	17.46	27.28	36.87	[27]
0.0629	10.67	73.97	3.19	4.90	6.56	18.20	27.96	37.44	
0.0945	15.66	71.85	3.28	5.00	6.69	18.78	28.53	38.18	
0.1306	21.08	69.49	3.36	4.90	6.83	19.17	27.96	38.98	
0.1633	25.77	67.43	3.49	5.23	6.93	19.92	29.85	39.55	
0.2014	30.96	65.10	3.55	5.29	7.08	20.26	30.19	40.40	
0.2344	35.25	63.15	3.67	5.42	7.15	20.94	30.93	40.80	
0.2741	40.18	60.90	3.75	5.51	7.30	21.40	31.44	41.66	
0.3146	44.95	58.69	3.87	5.61	7.32	22.09	32.02	41.77	
0.3578	49.77	56.45	3.99	5.76	7.48	22.77	32.87	42.69	
0.4091	55.19	53.93	4.12	5.86	7.61	23.51	33.44	43.43	
1,4-Dioxane + Water									
0.0277	12.23	70.25	3.37	5.07	6.70	19.23	28.93	38.24	[24]
0.0493	20.23	61.73	3.63	5.36	7.20	20.72	30.59	41.09	
0.0811	30.15	53.18	3.92	5.72	7.54	22.37	32.64	43.03	
0.1197	39.94	44.71	4.31	6.21	7.92	24.60	35.44	45.20	
0.1680	49.69	36.22	4.82	6.79	8.47	27.51	38.75	48.34	
0.0493	20.23	61.73	3.32	5.03	6.31	18.95	28.71	36.01	[23]
0.1680	49.69	36.22	4.47	5.80	6.81	25.51	33.10	38.86	
0.4575	80.49	11.46	6.72	7.78	8.67	38.35	44.40	49.48	
Tetrahydrofuran + Water									
0.0270	10.00	71.76	3.68	4.98	6.69	21.00	28.42	38.18	[25]
0.0588	20.00	64.60	3.79	5.20	6.83	21.63	29.68	38.98	

Table 3.6 (continued)

x	w/w%	D	pK_1	pK_2	pK_3	ΔG_1	ΔG_2	ΔG_3	Ref
0.0967	30.00	56.59	3.88	5.49	7.29	22.14	31.33	41.60	
0.1428	40.00	48.22	4.06	5.93	7.46	23.17	33.84	42.57	
0.1999	50.00	39.96	4.38	6.06	7.81	25.00	34.58	44.57	
0.2726	60.00	31.97	4.79	6.96	8.37	27.34	39.72	47.77	
0.3683	70.00	24.62	5.61	7.30	8.74	32.02	41.66	49.88	
Acetonitrile + Water									
0.0465	10.00	74.92	3.40	5.01	6.68	19.40	28.59	38.12	[25]
0.1583	30.00	65.57	3.81	5.50	7.29	21.74	31.39	41.60	
0.2264	40.00	60.61	4.06	5.81	7.63	23.17	33.16	43.54	
0.3050	50.00	55.69	4.31	6.08	7.91	24.60	34.70	45.14	
0.5059	70.00	46.83	5.00	7.03	8.86	28.53	40.12	50.56	
MeOH		24.35	6.10	7.42	9.27	34.79	42.36	52.92	[129]
EtOH		32.63	7.58	9.56	11.14	43.26	54.56	63.57	[130]
DMF		36.71	7.17	10.87	12.17	40.89	62.00	69.47	[131]
FA	5/°C	117.19	5.52	7.35	8.35	29.39	39.13	44.46	[132]
	10	115.07	5.50	7.37	8.25	29.81	39.94	44.71	
	15	113.04	5.55	7.34	8.14	30.61	40.48	44.90	
	20	111.00	5.30	7.28	7.99	29.74	40.85	44.83	
	25	109.03	5.27	7.33	8.18	30.07	41.83	46.68	
	30	106.85	5.20	7.17	8.17	30.17	41.60	47.41	
	35	104.89	5.44	6.89	8.02	32.09	40.64	47.30	
	40	102.87	5.47	6.93	8.00	32.79	41.54	47.95	
	45	100.89	5.42	6.87	7.93	33.01	41.84	48.29	

Units: K_i - mol dm^{-3} ; ΔG_i - kJ mol^{-1}

An electrostatic interpretation of the medium effect based on the Born model predicts a linear relation between $\Delta pK_i(T)$ and the reciprocal of the dielectric constant D of organic solvents or water–organic solvent mixtures [20]. Such behaviour is often observed in water-rich mixtures. In the case of citric acid dissociation in water-methanol mixtures, the linear dependence of pK_i on 1/D is illustrated in Fig. 3.16. Besides, for many organic acids, and this is true also for citric acid, it is observed the linear relation between pK and mole fractions of solvent in mixtures (Fig. 3.17). Analyzing pK_i values as a function of dielectric constant D in the mixtures of methanol, 1,4-dioxane, tetrahydrofuran and acetonitrile with water, it is evident that changes in dissociation constants depend only weakly on specific nature of organic solvent (Fig. 3.18). Thus, for mixtures at 25 °C, with less of 50 weight per cent of organic component, it is possible to express the apparent dissociation constants of citric acid, irrespectively of chosen solvent as

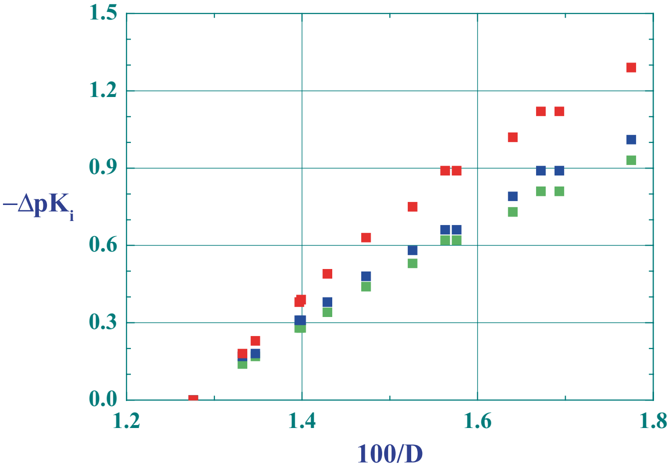


Fig. 3.16 The medium effect in the methanol-water mixtures at 25 °C as a function of reciprocals of dielectric constants D. pK_i values from [24–26]. $-\Delta pK_1$ - 🟩; $-\Delta pK_2$ - 🟦 and $-\Delta pK_3$ - 🟥

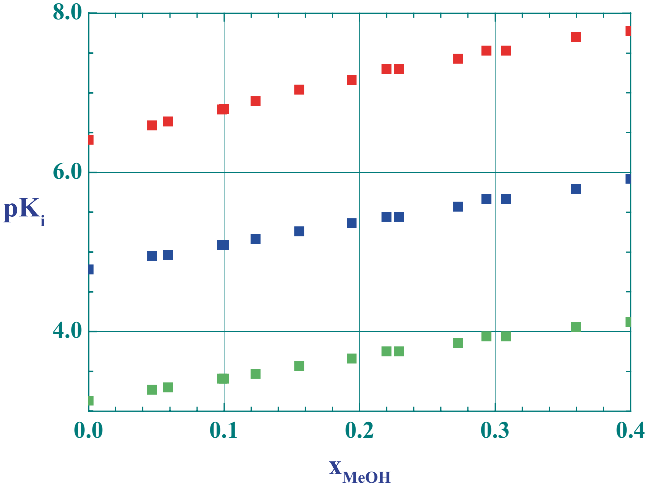


Fig. 3.17 The apparent dissociation constants of citric acid at 25 °C in the methanol-water mixtures as a function of mole fraction of methanol. pK_i values from [24–26]. 🟩 - pK_1; 🟦 - pK_2 and 🟥 - pK_3

$$\begin{aligned} pK_1 &= 3.13 + 0.03895\delta + 1.561 \cdot 10^{-5}\,\delta^2 \\ pK_2 &= 4.78 + 0.04112\delta + 7.988 \cdot 10^{-5}\,\delta^2 \\ pK_3 &= 6.41 + 0.05761\delta - 3.161 \cdot 10^{-4\Delta}\,\delta^2 \\ \delta &= 78.36 - D \end{aligned} \tag{3.33}$$

where D = 78.36 is the dielectric constant of water at 25 °C.

Recently, Kosmulski et al. [29] observed that positively charged particles of metal oxides (alumina, hematite and titania) enhance dissociation of citric acid in 94 w/w% ethanolic solution. This new phenomenon which is manifested by

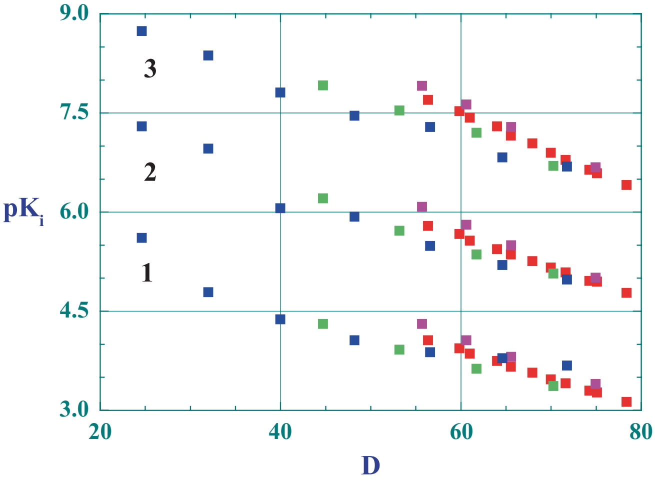


Fig. 3.18 The apparent dissociation constants of citric acid (pK$_1$, pK$_2$ and pK$_3$) at 25 °C in water-organic solvent mixtures as a function of dielectric constant D. pK$_i$ values from Table 3.6. 🟥 - methanol; 🟩 - 1,4-dioxane; 🟦 - tetrahydrofuran and 🟪 - acetonitrile

increasing in electrical conductance of dispersions in solutions they termed as the surface-induced electrolytic dissociation of weak acids.

3.6 Effect of Pressure on Dissociation Constants

Dissociation constants of weak acids increase with increasing applied pressure and the pressure effect for a particular step of dissociation is related by the thermodynamic formula (see Eq. (3.21)) [20, 30]

$$\left(\frac{\partial \ln \mathrm{K}}{\partial P}\right)_T = -\frac{\Delta V(T)}{\mathrm{R}T} \tag{3.34}$$

where $\Delta V(T)$ is the molar volume change accompanying the dissociation reaction. The volume change is itself pressure-dependent and therefore the integral form of Eq. (3.34) from the atmospheric pressure $P^0 = 0.1$ MPa to a higher pressure P is given by [30]

$$\ln\left(\frac{\mathrm{K}_P}{\mathrm{K}_{P^0}}\right)_T = -\frac{\Delta V(T) f(P)}{\mathrm{R}T} \tag{3.35}$$

where different forms of $f(P)$ functions were proposed in the literature [30–35]. Evidently, if $\Delta V(T)$ is independent of pressure then $f(P) = P$.

High pressures are of interest in food industry considering that foods are subjected to high hydrostatic pressures, to inactivate harmful microorganisms, to extend shelf life and freshness of products. Since these products are often buffered and buffer solutions become more acidic with increasing pressure, the pressure-induced changes in pH values were determined by measuring the reaction volumes of buffers or its components. The dissociation volumes at infinite dilution in the 0.1–800 MPa range were determined by Kitamura and Itoh [31]. Their values are: for the first dissociation step of citric acid - 10.4 ± 0.3 $cm^3\ mol^{-1}$; for the second dissociation step - 12.3 ± 0.4 $cm^3\ mol^{-1}$ and for the third dissociation step - 22.3 ± 0.9 $cm^3\ mol^{-1}$. Kauzmann et al. [32, 33] for solutions with $I < 0.1$ mol dm^{-3} obtained −8.7, −12.7 and −18.3 $cm^3\ mol^{-1}$ respectively. Thus, with increasing charge of citrate anion, the change in molar volume increases. Samaranayake and Sastry [34] observed 0.2 pH drop in the 0.09 M citrate buffer in 0.1–785 MPa pressure interval.

3.7 Citrate Buffers

Since the difference between successive pK values of citric acid is less than three units, then at equilibrium, there is an overlap between the pH range of existence of species in solutions (see Fig. 3.1). This overlap is very extensive and buffers having citric acid or citrates as components are suitable to work over a wide range of pH values. The importance of maintaining adequately buffered solutions in analytical chemistry, biochemistry, medicine and technology caused that various citrate buffers are widely used. Due to low undesired reactivity or toxicity, high solubility in aqueous solutions, chemical and thermal stability and easy preparation from inexpensive materials, citric acid and inorganic citrates are common ingredients of pharmaceutical solutions. Buffers are very suitable for biochemical and medical research when buffer solutions are necessary to keep the correct pH values in enzymatic reactions and of body fluids. They are also useful if for certain purposes, it is necessary to maintain the ionic strength of solution relatively constant while varying pH values by varying the composition of buffer system. Buffers serve in chemical analysis, frequently as masking and chelating agents, in pH adjustments in bio-analytical sample preparations [36] and in the calibration of pH meters. In industry, buffer solutions are used in preparation of foods and pharmaceutics, in fermentation processes, in electrolytic deposition of various metals, and in manufacturing textiles by setting correct conditions for applied dyes [37]. Absorption of sulfur dioxide to remove it from industrial waste gases, is performed in citric acid-sodium citrate buffer solutions [38, 39].

From citrate buffers two the most popular are: solutions containing in different proportions 0.1 M citric acid and 0.1 M tri-sodium citrate (pH 3.0–6.2) and the McIlvaine citrate-phosphate buffer [40], having in different proportion 0.1 M citric acid and 0.2 M disodium hydrogen phosphate (pH 2.6–7.6). This buffer is actually a mixture of two buffers, it can be prepared from H_3Cit, H_3PO_4 and NaOH or Na_3Cit and H_3PO_4 or from some other combinations. The citrate-phosphate buffer of constant ionic strength 0.5 and 1.0 M is prepared by adding KCl [41].

Britton and Robinson in 1931–1937 period [42, 43] developed the “universal buffer” covering the pH range from 2.6 to 12. This is a mixture containing four components with multiple pK values: citric acid ($pK_1 = 3.13$, $pK_2 = 4.77$ and $pK_3 = 6.41$), potassium dihydrogen phosphate (H_3PO_4, $pK_1 = 2.148$, $pK_2 = 7.198$

and $pK_3 = 12.375$), boric acid (H_3BO_3, $pK = 9.243$) and 5,5-diethyl barbituric acid ($pK_1 = 7.82$ and $pK_2 = 12.7$), all of them having the same concentration 0.0286 M. The buffer gives an essentially linear pH response to added alkali from pH 2.5 to 9.2 (and for buffers to pH 12). For the Britton-Robinson universal buffer mixture, pH values were reported in the 12.5–91 °C temperature range. They are also given for buffer solutions obtained by the separate neutralization of KH_2PO_4 and constituent acids with 0.2 M NaOH (seven stages of dissociation are successively neutralized with sodium hydroxide) [43].

Potassium dihydrogen citrate 0.05 molal solution ($pH = 3.776$ at 25 °C) is used for calibration purposes because it exhibits better stability than primary pH reference buffer solutions of tartrate or phthalate [44, 45]. The saline sodium citrate buffer (SSC) prepared from tri-sodium citrate and sodium chloride ($pH = 7.0$) is applied in biochemistry. Citric buffers with different H_3Cit:Na_3Cit ratios are clinically effective, for example in reducing gastric acidity [46–48]. Compositions of buffers and corresponding pH values are presented in Table 3.7.

Buffers which include calcium and citrate ions are of special interest in biological systems (for example in the coagulation of blood and in the chemistry of milk) and they received considerable attention in the literature [36, 49–52]. Salt addition to enzymes in buffers is an important subject and in this context Bauduin et al. [53] investigated pH changes in the 0.025 M citrate buffer (0.009 M H_3Cit + 0.016 M Na_3Cit) caused by an addition of different quantities of four sodium salts: NaCl, NaBr, $NaNO_3$ and Na_2SO_4.

Numerous pharmaceuticals are active and stable over a narrow pH and temperature range, either during processing or storage. Buffering of solutions accompanied by cooling to reduce deterioration of drugs and food products is a complex process. Frequently, the freeze-drying method of stabilization (lyophilization) is employed. When solutions containing buffers are frozen, changes in pH and salt composition are observed due a number of simultaneously occurring processes namely formation of ice and its sublimation, selective crystallization (precipitation) of the buffer components, formation of supersaturated solutions and removal of unfrozen water. The final result is observed as a more or less significant shift in pH values. These pH shifts were widely investigated in the context of deterioration during freezing and frozen storage of drugs and foods, by changing cooling conditions and compositions of citrate buffers [54–57].

The use of buffered organic solvent-water mobile phases in high performance liquid chromatography (HPLC) brought out considerable interest in many systems. Measurements of pH in mobile phases, shifts of pH values, changes in buffer compositions and capacities, temperature effects were extensively studied (for details see [25, 26, 58–66]). In the case of citrate buffers (H_3Cit-KH_2Cit, KH_2Cit-KNaHCit, KNaHCit-Na_3Cit), the most attention was paid to the methanol-water [25, 26, 58, 61, 66], acetonitrile-water [25, 59, 63–65] and tetrahydrofuran-water mobile phases [25, 60].

General theory devoted to calculation of pH and distribution of species in particular buffer mixtures can be found in [20, 67–70]. Chemical formulation includes a number of the mass-action equations linked with the mass and charge conservation equations. Limiting or extended forms of the Debye-Hückel expressions for activity

Table 3.7 Composition of buffers

0.050 mol kg^{-1} KH_2Cit[a]

t °C	pH
0	3.863
5	3.840
10	3.820
15	3.802
20	3.788
25	3.776
30	3.766
35	3.759
40	3.760
45	3.740
50	3.749

0.1 M H_3Cit + 0.1 M Na_3Cit

pH	ml H_3Cit	ml Na_3Cit
3.0	82.00	18.00
3.2	77.50	22.50
3.4	73.00	27.00
3.6	68.50	31.50
3.8	63.50	36.50
4.0	59.00	41.00
4.2	54.00	46.00
4.4	49.50	50.00
4.6	44.50	55.50
4.8	40.00	60.00
5.0	35.00	65.00
5.2	30.50	69.50
5.4	25.50	74.50
5.6	21.00	79.00
5.8	16.00	84.00
6.0	11.50	88.50
6.2	8.00	92.00

0.1 M H_3Cit + 0.2 M Na_2HPO_4

pH	ml H_3Cit	ml Na_2HPO_4	*I*/M
2.2	98.00	2.00	0.0108
2.4	93.80	6.20	0.0245
2.6	89.10	10.90	0.0410
2.8	84.15	15.85	0.0592
3.0	79.45	20.55	0.0771
3.2	75.30	24.70	0.0934
3.4	71.50	28.50	0.112
3.6	67.80	32.20	0.128
3.8	64.50	35.50	0.142
4.0	61.45	38.55	0.157
4.2	58.60	41.40	0.173
4.4	55.90	44.10	0.190
4.6	53.25	46.75	0.210
4.8	50.70	49.30	0.232

Table 3.7 (continued)

0.050 mol kg^{-1} KH$_2$Cit[a]

pH	ml H_3Cit	ml Na_2HPO_4	*I/M*
5.0	48.50	51.50	0.256
5.2	46.40	53.60	0.278
5.4	44.25	55.75	0.302
5.6	42.00	58.00	0.321
5.8	39.55	60.45	0.336
6.0	36.85	63.15	0.344
6.2	33.90	66.10	0.358
6.4	30.75	69.25	0.371
6.6	27.25	72.75	0.385
6.8	22.75	77.25	0.392
7.0	17.65	82.35	0.427
7.2	13.05	86.95	0.457
7.4	9.15	90.85	0.488
7.6	6.35	93.65	0.516
7.8	4.25	95.75	0.540
8.0	2.75	97.25	0.559

0.0286 M H$_3$Cit + 0.0286 M KH$_2$P$_4$ + 0.0286 M H$_3$BO$_3$ + 0.0286 M HB[b]

t°C	12.5	18	25	34	53	63	75	91
ml[c]	pH							
0	2.38	2.40	2.42	2.47	2.53	2.55	2.59	2.64
5	2.86	2.88	2.90	2.92	2.94	2.94	2.96	2.96
10	3.36	3.36	3.36	3.36	3.35	3.35	3.35	3.35
15	3.94	3.93	3.92	3.89	3.85	3.84	3.83	3.82
20	4.42	4.41	4.40	4.37	4.35	4.34	4.33	4.33
25	4.83	4.83	4.82	4.80	4.80	4.80	4.80	4.80
30	5.25	5.26	5.27	5.28	5.28	5.30	5.31	5.33
35	5.65	5.67	5.68	5.70	5.73	5.74	5.76	5.75
40	6.10	6.10	6.10	6.10	6.10	6.10	6.10	6.10
45	6.55	6.53	6.51	6.49	6.47	6.46	6.45	6.44
50	6.96	6.93	6.90	6.85	6.80	6.77	6.73	6.72
55	7.38	7.34	7.30	7.24	7.15	7.06	7.02	6.98
60	7.82	7.77	7.71	7.61	7.48	7.42	7.33	7.27
65	8.27	8.21	8.14	8.01	7.87	7.76	7.67	7.59
70	8.77	8.70	8.63	8.48	8.35	8.25	8.16	8.07
75	9.30	9.23	9.15	9.01	8.87	8.77	8.67	8.58
80	9.90	9.81	9.71	9.55	9.40	9.30	9.16	9.06
85	10.90	10.70	10.50	10.27	10.06	9.93	9.77	9.57
90	11.60	11.43	11.25	11.02	10.68	10.48	10.24	9.95
95	11.91	11.75	11.58	11.36	10.98	10.72	10.51	10.17
100	12.10	11.95	11.79	11.56	11.14	10.97	10.69	10.34

[a] 0.04958 M KH$_2$Cit; $\beta = 0.034$ mol OH$^-$ dm^{-3}

[b] HB is 5,5-diethylbarbituric acid

[c] 0.2 M NaOH

coefficients of ions can be used. The corresponding set of non-linear equations is solved numerically by a suitable computer program giving the speciation of buffer solutions (see for example [69]). Essentially, the representation of dissociation equilibria given by Eqs. (3.2) and (3.12) is also valid here.

For buffers of total analytical concentration $c=c_1+c_2$, having as components: citric acid of concentration c_1 and neutral or acidic citrates (NaH_2Cit, Na_2HCit and Na_3Cit or generally $Na_kH_{3-k}Cit$, k = 1, 2, 3) of concentration c_2, the material balance for citrate species is

$$c = c_1 + c_2 = [H_3Cit] + [H_2Cit^-] + [HCit^{2-}] + [Cit^{3-}] \tag{3.36}$$

and charge balance is

$$\begin{aligned} &[Na^+] + [H^+] = [OH^-] + [H_2Cit^-] + 2[HCit^{2-}] + 3[Cit^{3-}] \\ &[Na^+] = kc_2 \quad ; \quad k=1,2,3 \end{aligned} \tag{3.37}$$

The mass-action equations of dissociation reactions are

$$\begin{aligned} K_1 &= \frac{[H^+][H_2Cit^-]}{[H_3Cit]} F_1 \\ K_2 &= \frac{[H^+][HCit^{2-}]}{[H_2Cit^-]} F_2 \\ K_3 &= \frac{[H^+][Cit^{3-}]}{[H_2Cit^{2-}]} F_3 \\ K_w &= [H^+][OH^-] f_{H^+} f_{OH^-} = [H^+][OH^-] F_4 \end{aligned} \tag{3.38}$$

where F_1, F_2, F_3 and F_4 are quotients of corresponding activity coefficients (see Eq. (3.3)).

Thus, for any given c_1 and c_2, the simultaneous solution of equations Eqs. (3.36), (3.37) and (3.38) gives the desired concentrations of all species in the solution and its pH value from

$$pH = -\log\left\{[H^+] f_{H^+}\right\} \tag{3.39}$$

The activity coefficients are calculated from the Debye-Hückel expressions with the total ionic strength

$$I = \frac{1}{2}\left\{[H^+] + [Na^+] + [H_2Cit^-] + 4[HCit^{2-}] + 9[Cit^{3-}] + [OH^-]\right\} \tag{3.40}$$

but using equation Eq. (3.37) we have

$$I = \left\{[H_2Cit^-] + 3[HCit^{2-}] + 6[Cit^{3-}] + [OH^-]\right\} \tag{3.41}$$

which expresses the ionic strength for the mixture of weak 1:1 and 1:3 electrolytes.

Introducing the concentration fractions

$$
\begin{aligned}
&[\mathrm{H_2Cit^-}] = c\alpha\\
&[\mathrm{HCit^{2-}}] = c\beta\\
&[\mathrm{Cit^{3-}}] = c\gamma\\
&[\mathrm{H_3Cit}] = c(1-\alpha-\beta-\gamma)\\
&[\mathrm{H^+}] = c\delta\\
&[\mathrm{OH^-}] = \mathrm{k}c_2 + [\mathrm{H^+}] - [\mathrm{H_2Cit^-}] - 2[\mathrm{HCit^{2-}}] - 3[\mathrm{Cit^{3-}}]\\
&[\mathrm{OH^-}] = \mathrm{k}c_2 + c(\delta-\alpha-2\beta-3\gamma)
\end{aligned}
\tag{3.42}
$$

into Eq. (38) we have

$$
\begin{aligned}
\mathrm{K_1} &= \frac{[\mathrm{H^+}][\mathrm{H_2Cit^-}]}{[\mathrm{H_3Cit}]}\mathrm{F_1} = \frac{c\delta\alpha}{1-\alpha-\beta-\gamma}\mathrm{F_1}\\
\mathrm{K_2} &= \frac{[\mathrm{H^+}][\mathrm{HCit^{2-}}]}{[\mathrm{H_2Cit^-}]}\mathrm{F_2} = \frac{c\delta\beta}{\alpha}\mathrm{F_2}\\
\mathrm{K_3} &= \frac{[\mathrm{H^+}][\mathrm{Cit^{3-}}]}{[\mathrm{H_2Cit^{2-}}]}\mathrm{F_3} = \frac{c\delta\gamma}{\beta}\\
\mathrm{K_w} &= [\mathrm{H^+}][\mathrm{OH^-}]\mathrm{F_4} = c\delta[\mathrm{k}c_2 + c(\delta-\alpha-2\beta-3\gamma)]\mathrm{F_4}\\
I &= \mathrm{k}c_2 + c(\delta+\beta+3\gamma)
\end{aligned}
\tag{3.43}
$$

Denoting

$$
\begin{aligned}
&\mathrm{R} = \frac{\mathrm{k}c_2}{c} \quad ; \quad \mathrm{k} = 1,2,3\\
&\mathrm{S_1} = \frac{\mathrm{K_1}}{\mathrm{F_1}c} \quad ; \quad \mathrm{S_2} = \frac{\mathrm{K_2}}{\mathrm{F_2}c}\\
&\mathrm{S_3} = \frac{\mathrm{K_3}}{\mathrm{F_3}c} \quad ; \quad \mathrm{S_4} = \frac{\mathrm{K_w}}{\mathrm{F_4}c^2}
\end{aligned}
\tag{3.44}
$$

and by applying the successive iteration technique, the concentration fractions of all species in the solution can be evaluated by simultaneous solutions of four algebraic equations

$$
\begin{aligned}
\alpha &= \frac{\mathrm{S_1}(1-\beta-\gamma)}{\delta+\mathrm{S_1}}\\
\beta &= \frac{\mathrm{S_2}\alpha}{\delta}\\
\gamma &= \frac{\mathrm{S_3}\beta}{\delta}\\
\delta &= \frac{\alpha+2\beta+3\gamma-R+\sqrt{(\alpha+2\beta+3\gamma-R)^2+4\mathrm{S_4}}}{2}
\end{aligned}
\tag{3.45}
$$

In an alternative mathematical representation, in terms of $[\mathrm{H}^+]$ only, the concentrations of citrate species are

$$\begin{aligned}
&[\mathrm{H_3Cit}] = c\frac{[\mathrm{H}^+]^3\,\mathrm{F_1F_2F_3}}{\Delta}\\
&[\mathrm{H_2Cit}^-] = c\frac{[\mathrm{H}^+]^2\,\mathrm{K_1F_2F_3}}{\Delta}\\
&[\mathrm{HCit}^{2-}] = c\frac{[\mathrm{H}^+]\mathrm{K_1K_2F_3}}{\Delta}\\
&[\mathrm{Cit}^{3-}] = c\frac{\mathrm{K_1K_2K_3}}{\Delta}\\
&\Delta = [\mathrm{H}^+]^3\,\mathrm{F_1F_2F_3} + [\mathrm{H}^+]^2\,\mathrm{K_1F_2F_3} + [\mathrm{H}^+]\mathrm{K_1K_2F_3} + \mathrm{K_1K_2K_3}
\end{aligned} \tag{3.46}$$

where the electrical neutrality condition is given by

$$\begin{aligned}
&[\mathrm{H}^+] + [\mathrm{Na}^+] = \frac{\mathrm{K_w}}{[\mathrm{H}^+]\mathrm{F_4}} + c\frac{[\mathrm{H}^+]^2\,\mathrm{K_1F_2F_3} + 2[\mathrm{H}^+]\mathrm{K_1K_2F_3} + 3\mathrm{K_1K_2K_3}}{\Delta}\\
&[\mathrm{H}^+] + [\mathrm{Na}^+] = \frac{\mathrm{K_w}}{[\mathrm{H}^+]\mathrm{F_4}} + c\frac{\Lambda}{\Delta}\\
&\Lambda = [\mathrm{H}^+]^2\,\mathrm{K_1F_2F_3} + 2[\mathrm{H}^+]\mathrm{K_1K_2F_3} + 3\mathrm{K_1K_2K_3}
\end{aligned} \tag{3.47}$$

This form of the charge balance equation is appropriate when an expression for the buffer capacity β is needed. The buffer capacity was introduced by Van Slyke [71, 72] in 1922 and it characterizes effectiveness of a buffer (the extent of pH change for small additions of strong base $\mathrm{d}C_\mathrm{b}$ or strong acid $\mathrm{d}C_\mathrm{a}$). A quantitative measure of buffer capacity is given by

$$\beta = \frac{dC_\mathrm{b}}{d\mathrm{pH}} = -\frac{dC_\mathrm{a}}{d\mathrm{pH}} = -\ln(10)[\mathrm{H}^+]\frac{dC_\mathrm{b}}{d[\mathrm{H}^+]} \tag{3.48}$$

Differentiating the charge balance equation (3.47) at constant $\mathrm{K_i}$, T, P and c (in dilute aqueous solutions, changes in the activity coefficient quotients $\mathrm{F_i}$ can be neglected), the buffer capacity is

$$\begin{aligned}
&\beta = \ln(10)\left\{\frac{\mathrm{K_w} + [\mathrm{H}^+]^2\,\mathrm{F_4}}{[\mathrm{H}^+]\mathrm{F_4}} + c[\mathrm{H}^+]\frac{\Lambda\Delta' - \Lambda'\Delta}{\Delta^2}\right\}\\
&\Lambda' = 2[\mathrm{H}^+]\mathrm{K_1F_2F_3} + 2\mathrm{K_1K_2F_3}\\
&\Delta' = 3[\mathrm{H}^+]^2\,\mathrm{F_1F_2F_3} + 2[\mathrm{H}^+]\mathrm{K_1F_2F_3} + \mathrm{K_1K_2F_3}
\end{aligned} \tag{3.49}$$

If an organic solvent is added to an aqueous buffer, its buffer capacity is reduced due to dilution effect (β is proportional to the concentration of the buffer) and the maximal value of β is shifted according to the change in values of dissociation constants.

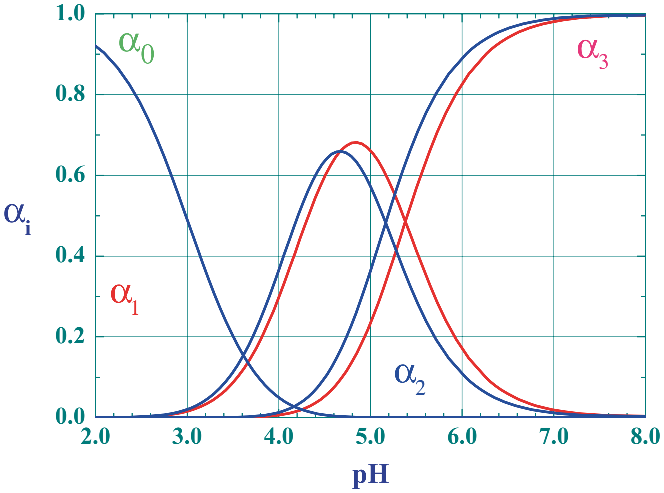


Fig. 3.19 Distribution of H_2Cit^-, $HCit^{2-}$, Cit^{3-} and H_3Cit species as a function of pH. The concentration fractions: $\alpha_1 = \alpha(H_2Cit^-)$, $\alpha_2 = \alpha(HCit^{2-})$, $\alpha_3 = \alpha(Cit^{3-})$ and $\alpha_0 = \alpha(H_3Cit) = 1 - \alpha(H_2Cit^-) - \alpha(HCit^{2-}) - \alpha(Cit^{3-})$. 🟥 0.1 M H_3Cit + 0.1 M Na_3Cit; 🟦 0.2 M H_3Cit + 0.2 M Na_3Cit

In order to illustrate distribution of species in buffers and buffer capacities β, the slightly modified Okamoto et al. [69] computer program was used in the case of two citric acid + tri-sodium citrate buffers with total concentration of $c = 0.1$ M and $c = 0.2$ M. The speciation of both buffers as a function of pH is plotted in Fig. 3.19.

In general, as expected, curves resemble those of citric acid in pure water (Fig. 3.1) and there is only small difference between both buffers. However, if distribution of species is plotted as a function of ionic strength I, then distinction between the buffers is more significant (Fig. 3.20). The same is observed when buffer capacities are expressed as a function of pH or ionic strength I (Figs. 3.21 and 3.22). Since the buffer capacity is proportional to the concentration of the buffering species, therefore β values of $c = 0.2$ M buffer are always higher than those of $c = 0.1$ M buffer.

In the case of McIlvain buffer, the aqueous solution contains citric acid of concentration c_1 and disodium hydrogen phosphate of concentration c_2 and therefore the mass conservation of citrate and phosphate are:

$$\begin{aligned} c_1 &= [H_3Cit] + [H_2Cit^-] + [HCit^{2-}] + [Cit^{3-}] \\ c_2 &= [H_3PO_4] + [H_2PO_4{}^-] + [HPO_4{}^{2-}] + [PO_4{}^{3-}] \end{aligned} \tag{3.50}$$

and the charge balance is given by

$$\begin{aligned} &[H^+] + [Na^+] = [H_2Cit^-] + 2[HCit^{2-}] + 3[Cit^{3-}] + [H_2PO_4{}^-] + \\ &2[HPO_4{}^{2-}] + 3[PO_4{}^{3-}] + [OH^-] \\ &[Na^+] = 2c_2 \end{aligned} \tag{3.51}$$

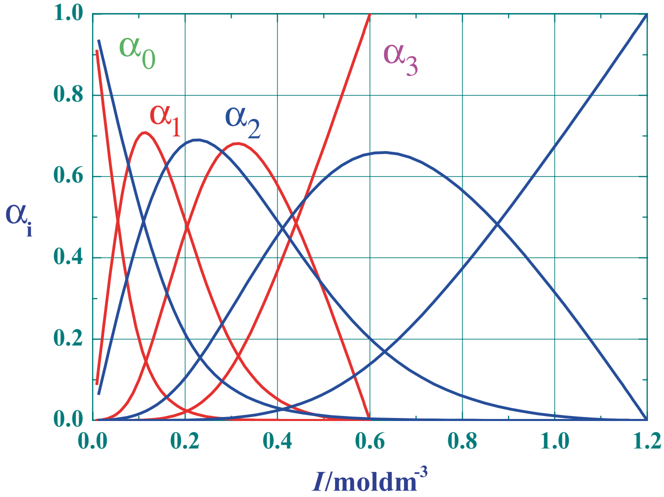


Fig. 3.20 Distribution of H_2Cit^-, $HCit^{2-}$, Cit^{3-} and H_3Cit species as a function of ionic strength *I*. The concentration fractions: $\alpha_1 = \alpha(H_2Cit^-)$, $\alpha_2 = \alpha(HCit^{2-})$, $\alpha_3 = \alpha(Cit^{3-})$ and $\alpha_0 = \alpha(H_3Cit) = 1 - \alpha(H_2Cit^-) - \alpha(HCit^{2-}) - \alpha(Cit^{3-})$. 🟥 0.1 M H_3Cit + 0.1 M Na_3Cit; 🟦 0.2 M H_3Cit + 0.2 M Na_3Cit

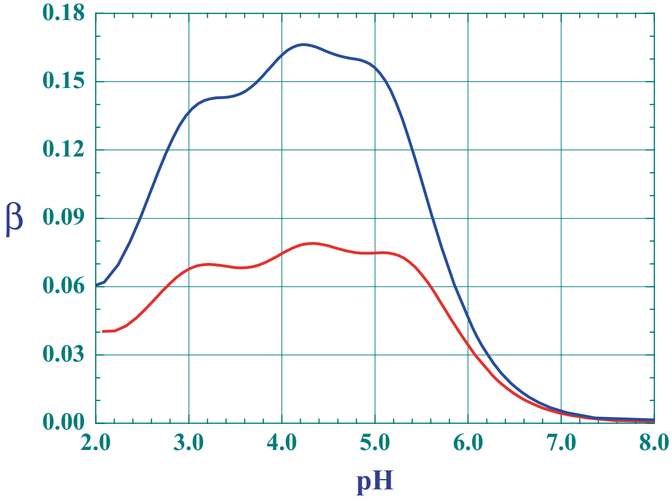


Fig. 3.21 Buffer capacities as a function of pH. 🟥 0.1 M H_3Cit + 0.1 M Na_3Cit; 🟦 0.2 M H_3Cit + 0.2 M Na_3Cit

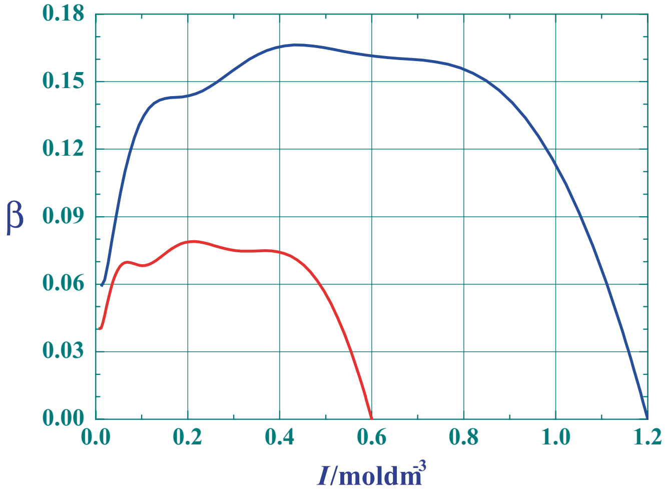


Fig. 3.22 Buffer capacities as a function of ionic strength *I*. 🟥 0.1 M H_3Cit + 0.1 M Na_3Cit; 🟦 0.2 M H_3Cit + 0.2 M Na_3Cit

The ionic strength of the McIlvain buffer is

$$I = \{[H_2Cit^-] + 3[HCit^{2-}] + 6[Cit^{3-}] + [OH^-] + [H_2PO_4^-] + 3[HPO_4^{2-}] + 6[PO_4^{3-}] + [OH^-]\} \tag{3.52}$$

giving an additive contributions of both acids.

If the dissociation constants of citric acid are denoted as K_{iC}, i = 1,2,3 and the quotients of activity coefficients as F_{iC} and the those of phosphoric acid as K_{iP} and F_{iP}, the mass-action equations of dissociation reactions are

$$\begin{aligned}
K_{1C} &= \frac{[H^+][H_2Cit^-]}{[H_3Cit]} F_{1C} \quad ; \quad K_{1P} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} F_{1P} \\
K_{2C} &= \frac{[H^+][HCit^{2-}]}{[H_2Cit^-]} F_{2C} \quad ; \quad K_{2P} = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]} F_{2P} \\
K_{3C} &= \frac{[H^+][Cit^{3-}]}{[H_2Cit^{2-}]} F_{3C} \quad ; \quad K_{3P} = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} F_{3P} \\
K_w &= [H^+][OH^-] f_{H^+} f_{OH^-} = [H^+][OH^-]F_4
\end{aligned} \tag{3.53}$$

Thus, in order to determine concentrations of all species in a given solution, a set of ten algebraic equations in Eqs. (3.50)–(3.53) should be simultaneously solved. Similarly, as in Eq. (3.46), it is possible to write for citrate species

$$\begin{aligned}
&[H_3Cit] = c_1[\frac{H^+]^3 F_{1C}F_{2C}F_{3C}}{\Delta_C}\\
&[H_2Cit^-] = c_1\frac{[H^+]^2 K_{1C}F_{2C}F_{3C}}{\Delta_C}\\
&[HCit^{2-}] = c_1\frac{[H^+]K_{1C}K_{2C}F_{3C}}{\Delta_C}\\
&[Cit^{3-}] = c_1\frac{K_{1C}K_{2C}K_{3C}}{\Delta_C}\\
&\Delta_C = [H^+]^3 F_{1C}F_{2C}F_{3C} + [H^+]^2 K_{1C}F_{2C}F_{3C} + [H^+]K_{1C}K_{2C}F_{3C} + K_{1C}K_{2C}K_{3C}
\end{aligned}\tag{3.54}$$

and analogous expressions for phosphate species are

$$\begin{aligned}
&[H_3PO_4] = c_2\frac{[H^+]^3 F_{1P}F_{2P}F_{3P}}{\Delta_P}\\
&[H_2PO_4^-] = c_2\frac{[H^+]^2 K_{1P}F_{2P}F_{3P}}{\Delta_P}\\
&[HPO_4^{2-}] = c_2\frac{[H^+]K_{1P}K_{2P}F_{3P}}{\Delta_P}\\
&[PO_4^{3-}] = c_2\frac{K_{1P}K_{2P}K_{3P}}{\Delta_P}\\
&\Delta_P = [H^+]^3 F_{1P}F_{2P}F_{3P} + [H^+]^2 K_{1P}F_{2P}F_{3P} + [H^+]K_{1P}K_{2P}F_{3P} + K_{1P}K_{2P}K_{3P}
\end{aligned}\tag{3.55}$$

Introducing Eqs. (3.54) and (3.55) into Eq. (3.51) we have

$$\begin{aligned}
&[H^+] + [Na^+] = \frac{K_w}{[H^+]F_4} + c_1\frac{\Lambda_C}{\Delta_C} + c_1\frac{\Lambda_P}{\Delta_P}\\
&\Lambda_C = [H^+]^2 K_{1C}F_{2C}F_{3C} + 2[H^+]K_{1C}K_{2C}F_{3C} + 3K_{1C}K_{2C}K_{3C}\\
&\Lambda_P = [H^+]^2 K_{1P}F_{2P}F_{3P} + 2[H^+]K_{1P}K_{2P}F_{3P} + 3K_{1P}K_{2P}K_{3P}
\end{aligned}\tag{3.56}$$

and the buffer capacity of the citrate - phosphate buffer, in an analogy with Eq. (3.49), is

$$\begin{aligned}
&\beta = \ln(10)\left\{\frac{K_w + [H^+]^2 F_4}{[H^+]F_4} + c_1[H^+]\frac{\Lambda_C\Delta'_C - \Lambda'_C\Delta_C}{\Delta_C^2} + c_2[H^+]\frac{\Lambda_P\Delta'_P - \Lambda'_P\Delta_P}{\Delta_P^2}\right\}\\
&\Lambda'_C = 2[H^+]K_{1C}F_{2C}F_{3C} + 2K_{1C}K_{2C}F_{3C}\\
&\Delta'_C = 3[H^+]^2 F_{1C}F_{2C}F_{3C} + 2[H^+]K_{1C}F_{2C}F_{3C} + K_{1C}K_{2C}F_{3C}\\
&\Lambda'_P = 2[H^+]K_{1P}F_{2P}F_{3P} + 2K_{1P}K_{2P}F_{3P}\\
&\Delta'_P = 3[H^+]^2 F_{1P}F_{2P}F_{3P} + 2[H^+]K_{1P}F_{2P}F_{3P} + K_{1P}K_{2P}F_{3P}
\end{aligned}\tag{3.57}$$

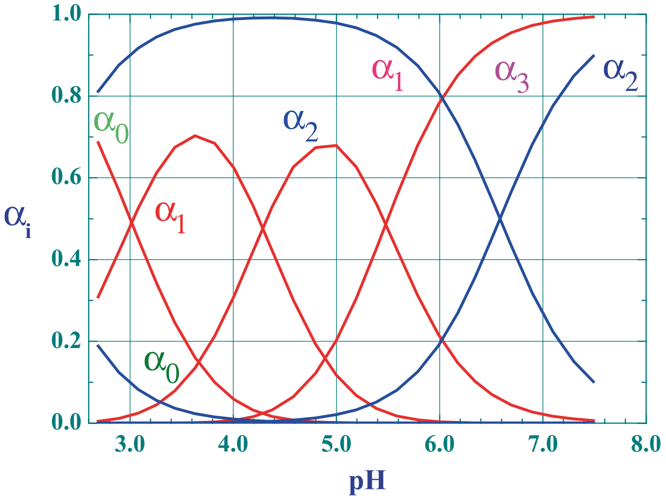
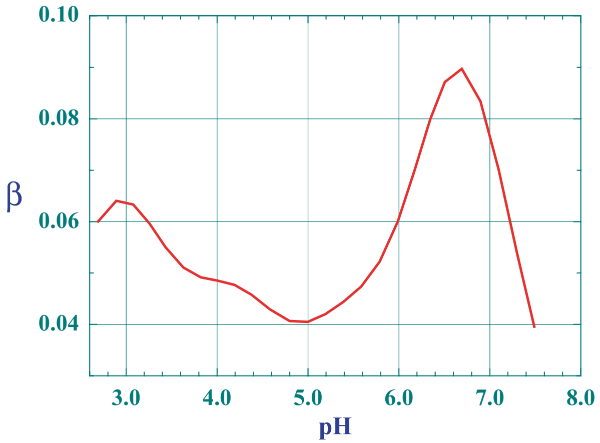


Fig. 3.23 Distribution of H_2Cit^-, $HCit^{2-}$, Cit^{3-}, H_3Cit, $H_2PO_4^-$, HPO_4^{2-}, $PO_4^{3-}$and H_3PO_4 species in the 0.1 M $H_3Cit+0.2$ M Na_2HPO_4 buffer as a function of pH. The concentration fractions: $\alpha_1=\alpha(H_2Cit^-)$, $\alpha_2=\alpha(HCit^{2-})$, $\alpha_3=\alpha(Cit^{3-})$ and $\alpha_0=\alpha(H_3Cit)=1-\alpha(H_2Cit^-)-\alpha(HCit^{2-})-\alpha(Cit^{3-})$ and $\alpha_1=\alpha(H_2PO_4^-)$, $\alpha_2=\alpha(HPO_4^{2-})$, $\alpha_3=\alpha(PO_4^{3-})$ and $\alpha_0=\alpha(H_3PO_4)=1-\alpha(H_2PO_4^-)-\alpha(HPO_4^{2-})-\alpha(PO_4^{3-})$. — citrate species; — phosphate species

Fig. 3.24 Buffer capacities of the McIlvain buffer as a function of pH



Distribution of species in the 0.1 M $H_3Cit+0.2$ M Na_2HPO_4 buffer as a function of pH was evaluated using the Okamoto et al. [69] computer program and is presented in Fig. 3.23. As can be seen, in the pH 2.6–7.6 range where this buffer is applied, one, two and tri-charged citrate anions exist in different proportions, depending on pH values, i.e. all three steps of citric acid dissociation are involved. On the other hand, up to nearly neutral solutions, only $H_2PO_4^-$ is of importance when HPO_4^{2-} starts to be significant only in slightly basic solutions. Buffer capacities of the McIlvain buffer are plotted in Fig. 3.24 and their values are comparable with those observed for the 0.1 M $H_3Cit+0.1$ M Na_3Cit buffer. The maximum buffer capacities, as expected, are located for pH of solutions which are close to pK_i values of citric acid ($pK_1=3.13$, $pK_2=4.77$ and $pK_3=6.41$).

3.8 Citric Acid Complexes

Citrate ions are involved in enormous number of complexation reactions. Devoted to this subject literature is so extensive that cannot be adequately covered in this book considering that citric acid forms complexes with almost all known metal ions. Thus, this topic should be covered by a special and separate treatment. Nevertheless, in spite that citrate complexes are not considered in this book, for convenience of the readers in Table 3.8 are compiled a number of references associated with the formation, stability and structure of citrate complexes in a solid state and in aqueous solutions. These references will be of help when information about particular metal-citrate systems is desired. Besides, they often include summary of previous works on the subject. There is also a number of reviews that are partially dedicated to formation of citrate complexes of different types [21, 73–78] and tabulations of formation constants [79–85].

Citric acid having its hydroxyl group and three carboxylic groups is a multidentate ligand able to form quite stable mononuclear and polynuclear complexes with cations of almost all elements [85]. It forms mixed-metal complexes and also mixed-ligand complexes. In some cases it was possible to isolate complexes in a solid form and their crystal structures were established.

Citric acid complexes are soluble in water, but exist also water-insoluble complexes, their speciation and properties are depending on the oxidation state of metal cation, ionic strength, pH and temperature. Citrate complexes were investigated by a variety of experimental methods but evidently the potentiometric titration technique and spectroscopic methods prevailed. Available in the literature investigations were directed mainly to citrate complexes with alkali metals and alkaline earth metals, Na^+, K^+Ca^{2+} and Mg^{2+}, considering that they are major components of natural waters and biological fluids. Other important group of complexes is these with divalent and trivalent metal cations (Cu^{2+}, Ni^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Al^{3+}, Fe^{3+}, Tl^{3+}). They were studied in the context of chemical processes occurring in soils and aquatic systems, but also considering their importance in other circumstances. Citric acid as a complexing agent is often used in the separation of actinides, lanthanides and other toxic metals from wastes, sediments and contaminated soils. Citric complexes of molybdenum and other metals are components of electrolytic baths used for electrodeposition and cleaning of corrosion resistant alloys.

Specific systems with citrate ions were extensively investigated considering their biological importance. Only few are mentioned here. Ferric-citric systems play a vital role in the iron metabolism of living organisms. Vanadium influences key metabolic processes. Aluminum complexes are suitable for neurobiological applications but also because of their poisoning effects. These effects are also important in the beryllium, cadmium, mercury and lead citrate systems. Magnesium and calcium citrates are involved in the gastrointestinal absorption in humans. Calcium citrate

Table 3.8 Investigations dealing with citric acid complexes of various chemical elements

	References
Li	[16, 97, 175, 364]
Na	[5, 16, 71, 93, [97, 175, 179, 237, 247]
K	[16, 93, 97, 175, 179, 206, 237, 247, 275, 322
Rb	[16, 97, 175]
Cs	[16, 97, 175]
Fr	[97, 206, 210]
NH_4	[97, 206, 210]
Be	[169, 227, 298]
Mg	[111, 114, 117, 127, 138, 152, 162, 171, 179, 184, 185, 190, 192, 196, 197, 233, 235, 237]
Ca	[114, 117, 137, 138, 152, 156, 171, 173, 179, 190, 192, 196, 197, 199, 235, 237, 247, 260, 263, 368, 384, 385]
Sr	[137, 156, 171, 197, 383, 385]
Ba	[117, 137, 157, 163, 197]
Ra	[150, 157]
Sc	[238, 239, 327]
Y	[164, 273, 305, 306, 313, 314, 322, 324, 334, 340, 370, 374]
Ac	[276, 277]
Ti	[211, 307, 309, 320, 321, 360, 370, 386]
Zr	[264, 265, 268, 279, 281, 386]
Hf	[273]
V	[101, 112, 206, 241, 243, 283, 347, 361]
Nb	[310, 311, 312, 328]
Ta	[328]
Cr	[186, 219, 315, 390]
Mo	[104, 204, 209, 236, 242, 350, 351, 367, 386, 389]
W	[209, 230, 362, 386]
Mn	[111, 113, 140, 144, 159, 188, 201, 299, 341, 352, 369]
Tc	[285, 286, 287]
Re	[338]
Fe	[88, 96, 112, 121, 153, 76, 170, 176, 178, 188, 200, 207, 228, 244, 245, 283, 303, 304, 343, 348, 354, 355, 359, 362, 379, 380, 386, 390, 391, 393]
Ru	[266, 302, 386]
Os	[266, 274, 302]
Co	[110, 113, 117, 159, 160, 162, 182, 234, 238, 246, 292, 295, 341, 354, 366, 386]
Rh	[283, 288, 301, 353, 393]
Ir	[386]
Ni	[113, 117, 119, 138, 142, 143, 144, 145, 162, 177, 196, 198, 225, 233, 238, 275, 341, 345, 354, 378, 386, 393]
Pd	[283, 386]
Pt	[386]
Cu	[96, 113, 117, 119, 121, 138, 143, 145, 154, 161, 177, 195, 212, 225, 233, 240, 252, 261, 265, 292, 293, 313, 354, 366, 386]
Ag	[255, 257]
Au	[283]
Zn	[118, 119, 137, 138, 140, 144, 145, 153, 160, 162, 172, 182, 188, 195, 196, 225, 293, 341, 366]
Cd	[117, 118, 136, 144, 145, 153, 162, 166, 293, 366]

Table 3.8 (continued)

	References
Hg	[278, 280, 325]
B	[240, 316, 319]
Al	[102, 149, 75, 180, 202, 204, 220, 227, 254, 392, 308, 342, 344, 349, 372, 386]
Ga	[251, 254, 289, 291, 308, 327, 365, 382]
In	[186, 189, 289, 290, 299, 292, 293, 327]
Tl	[155]
Si	[213]
Ge	[203, 317, 318, 354]
Sn	[147, 148, 176, 266, 302, 346, 363]
Pb	[151, 154, 165, 167, 168, 262, 386, 392]
As	[381]
Sb	[250, 253, 256, 386]
Bi	[181, 218, 265, 283, 386]
Te	[300]
Po	[387, 388]
La	[194, 273, 284, 305, 323, 324, 334, 340, 376]
Ce	[113, 164, 210, 219, 223, 283, 284, 321, 334, 340, 358]
Pr	[164, 259, 276, 284, 323, 339, 376, 78]
Nd	[158, 215, 216, 259, 273, 284, 294, 295, 323, 339, 340, 376]
Pm	[164, 223, 284, 334]
Sm	[258, 259, 273, 284, 322, 340, 371, 374, 376, 377]
Eu	[217, 222, 258, 273, 284, 324, 334, 374, 377]
Gd	[158, 273, 284, 314, 322, 324, 374, 377]
Tb	[164, 217, 223, 273, 284, 314, 322, 324, 334, 373]
Dy	[273, 284, 314, 322, 324, 373, 374]
Ho	[273, 284, 314, 324, 373, 374]
Er	[273, 284, 314, 339, 340, 373]
Tm	[164, 223, 273, 334, 373]
Yb	[273, 276, 322, 374]
Lu	[223, 305]
Th	[267, 269, 272, 326]
U	[120, 146, 159, 162, 174, 182, 183, 189, 200, 208, 229, 231, 232, 244, 248, 249, 270, 271, 283, 292, 293, 303, 304, 330, 356, 357, 375]
Pa	[191, 296]
Np	[221, 329, 330, 331, 375]
Pu	[74, 214, 248, 271, 281, 297, 330, 332, 375]
Am	[187, 193, 205, 217, 222, 226, 332, 333, 334, 335, 336, 375]
Cm	[187, 217, 222, 277, 334]
Bk	[282, 334]
Cf	[187, 217, 334]
Es	[187]
No	[224]
Md	[337]

complexes also were widely studied because they weaken bone structure. Bismuth citrate is used in the treatment of disorders of the alimentary system. Radioisotopes of some elements (for example gallium, ruthenium and others) in the form of citrates are used in medical treatments.

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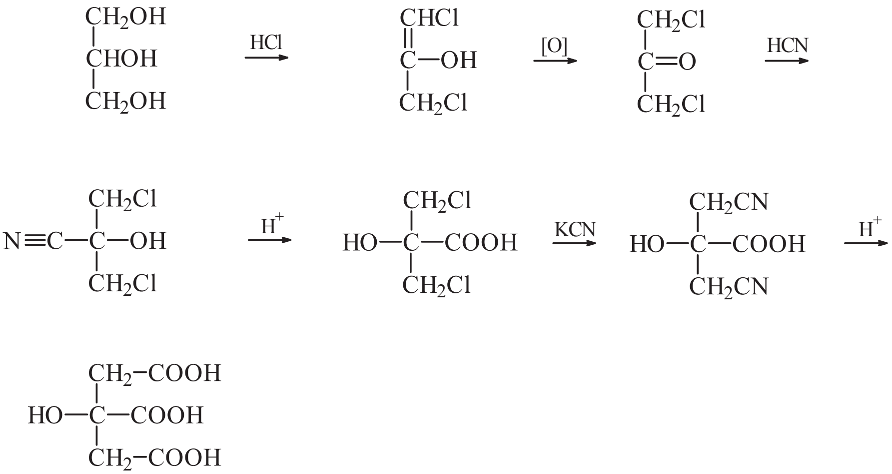
Chapter 4
Citric Acid Chemistry

4.1 Chemical Syntheses of Citric Acid

Citric acid behaves similarly as other hydroxycarboxylic acids in salt formation, esterification, anhydride, amide and other chemical reactions. Its total synthesis was first accomplished by Grimaux and Adam [1] in 1880. They treated glycerol (glycerin) with hydrochloric acid to obtain propenyl dichlorohydrin which is oxidized to 1,3-dichloroacetone. This compound reacts with hydrocyanic acid to form a nitrile which hydrolyses to dichlorohydroxy iso-butyric acid. The acid with potassium cyanide forms corresponding dinitrile which is converted by hydrochloric acid into citric acid. If traditional names of chemical compounds involved in these reactions are expressed by using the systematic nomenclature of organic chemistry then they take the form: 1,2,3-hydroxypropane → 1,3-dichloro-2-propenol → 1,3-dichloro-2-propanone → 1,3-dichloro-2-cyano-2-hydroxypropane → α-chloromethyl-α-hydroxypropionic acid → β-cyano-α-cyanomethyl-α-hydroxypropionic acid → 2-hydroxy-1,2,3-tricarboxylic acid.



$$\begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} \xrightarrow{HCl} \begin{array}{l} CHCl \\ \| \\ C{-}OH \\ | \\ CH_2Cl \end{array} \xrightarrow{[O]} \begin{array}{l} CH_2Cl \\ | \\ C{=}O \\ | \\ CH_2Cl \end{array} \xrightarrow{HCN}$$

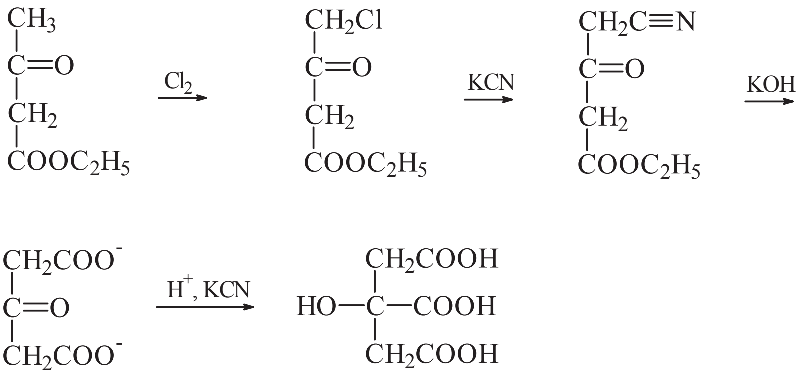
$$N{\equiv}C{-}\begin{array}{l} CH_2Cl \\ | \\ C{-}OH \\ | \\ CH_2Cl \end{array} \xrightarrow{H^+} HO{-}\begin{array}{l} CH_2Cl \\ | \\ C{-}COOH \\ | \\ CH_2Cl \end{array} \xrightarrow{KCN} HO{-}\begin{array}{l} CH_2CN \\ | \\ C{-}COOH \\ | \\ CH_2CN \end{array} \xrightarrow{H^+}$$

$$HO{-}\begin{array}{l} CH_2{-}COOH \\ | \\ C{-}COOH \\ | \\ CH_2{-}COOH \end{array}$$

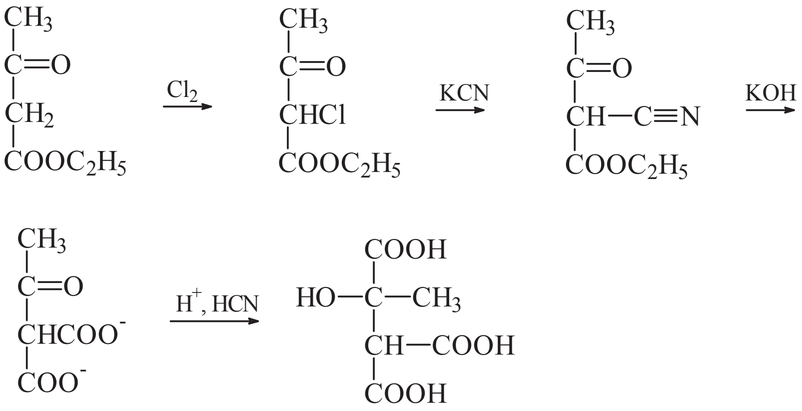
A. Apelblat, *Citric Acid*, DOI 10.1007/978-3-319-11233-6_4

In the same year, the Grimaux and Adam synthesis provoked immediate reactions of Andreoti [2] and Kekulé [3] who in two small notes also dealt with the possibility to prepare citric acid.

The next total synthesis of citric acid was performed 10 years later by Haller and Held [4] in 1890.

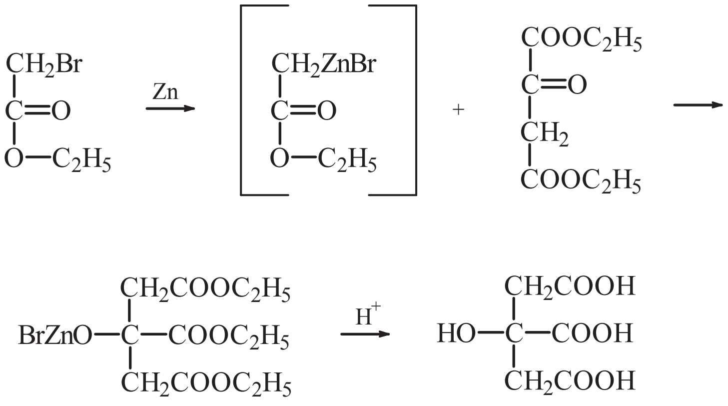


In the series of steps starting with acetoacetic ester reacting with chlorine they obtained ethyl chloroacetoacetate. On heating it with potassium cyanide and saponifying with potassium hydroxide the resulting nitrile was converted to acetone dicarboxylic acid. The acid combined with hydrocyanic acid on hydrolysis gives citric acid (ethyl-β-ketobutyrate → ethyl-γ-chloro-β-ketobutyrate → ethyl γ-cyano-β-ketobutyrate → β-ketoglutaric acid → 2-hydroxy-1,2,3-tricarboxylic acid). However, there is an early warning from 1931, expressed by Favrel and Prevost [5] in 1931, who questioned correctness of an identification of some intermediate products in the Haller and Held synthesis. In the correspondence with the present author, Professor Maria Milewska expressed an opinion that according to the modern views in organic chemistry, the most probably path of these reactions is different and finally leads not to citric acid (2-hydroxy-1,2,3-tricarboxylic acid) but to other isomeric hydroxytricarboxylic acid (3-hydroxy-3-methyl-1,2,4-tricarboxylic acid). And the sequence of reactions will be

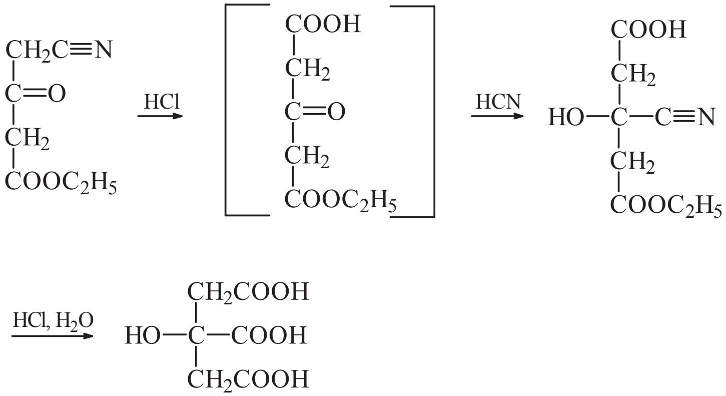


The wrong chemical composition of the final product in the Haller and Held synthesis, comes probably, as pointed out by Professor Maria Milewska, from the fact that in the nineteenth century compounds were identified by an elementary analysis and melting point only. Both hydroxytricarboxylic acids are expected to have these parameters very similar. However their spectra are different and by the modern methods, the difference between them should easily be detected.

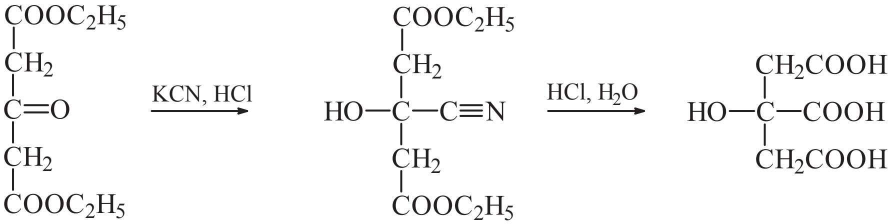
In 1897 Lawrence [6] prepared citric acid differently, by the condensation of ethyl oxalylacetate (diethyl a-ketosuccinate) with ethyl bromoacetate in the presence of zinc. The reaction should be considered at the time of publication to be very advanced because the condensation of ketones or aldehydes with α-halo esters using a metallic zinc to form β-hydroxyesters was introduced only 2 years earlier in 1895 by Reformatsky, and similar reactions are named after him.



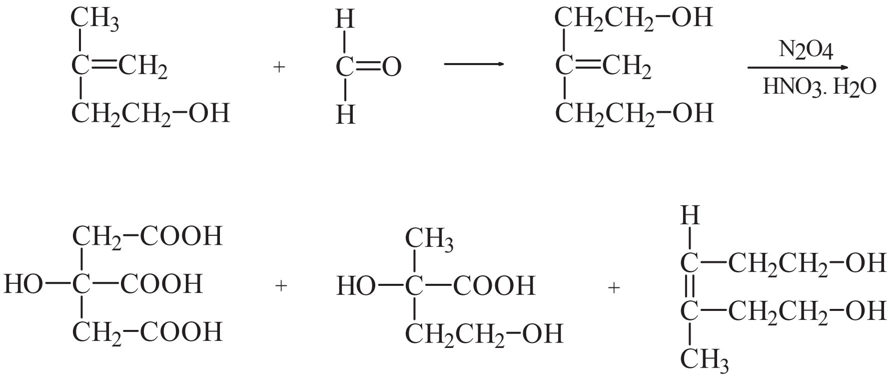
Lawrence regarded that the preparation of citric acid performed by Dunschmann and Pechmann [7] in 1891 can hardly be considered as a synthesis of citric acid. Their series of reactions included an addition of hydrogen cyanide to ethyl acetonedicarboxylate which was following by a hydrolysis of the product. However, they used in experiments ethyl acetonedicarboxylate which was in the first instance prepared from citric acid. These reactions can be presented as (ethyl-γ-chloro-β-ketobutyrate → ethyl β-ketoglutarate → ethyl β-cyano-β-hydroxyglutarate)



and diethyl β-ketoglutarate → diethyl β-cyano-β-hydroxyglutarate.



In 1908 Ferrario [8] in a small note proposed to obtain citric acid by the hydrolysis of triethyl citrate which is prepared by the condensation of ethyl oxalate with ethyl bromoacetate in the presence of magnesium. However, this way of citric acid preparation is rather questionable. It is worth to mention also two more chemical preparations of citric acid, the first was reported by Wiley and Kim [9] in 1973. In this procedure oxaloacetic acid, HOOCCO(COOH)CH(OH)C(COOH)CH$_2$COOH, undergoes a bimolecular decarboxylative self-condensation to give 4-carboxy-4-hydroxy-2-ketohexane-1,6-dioic acid, HOOC(CCH$_2$(OH)C(COOH)CH$_2$COOH, (called by them citroylformic acid). This acid is converted by oxidative decarboxylation to citric acid. In the second method, Wilkes and Wall [10] in 1980 prepared citric acid by reaction of 3-methyl-3-buten-1-ol with formaldehyde to obtain 3-(2-hydroxyethyl)-3-buten-ol which reacts with dinitrogen tetraoxide, N_2O_4, in nitric acid aqueous solution, to give finally citric acid with 64 % yield. 3-methyl-3-buten-1-ol itself, is prepared by reaction of 2-methylpropene (isobutylene) with formaldehyde. However, depending on applied conditions also 2-hydroxy-2-methyl-1,4-butanedioic acid (α-methyl-α-hydroxysuccinic acid) and 3-methyl-3-buten-1,6-diol are formed.



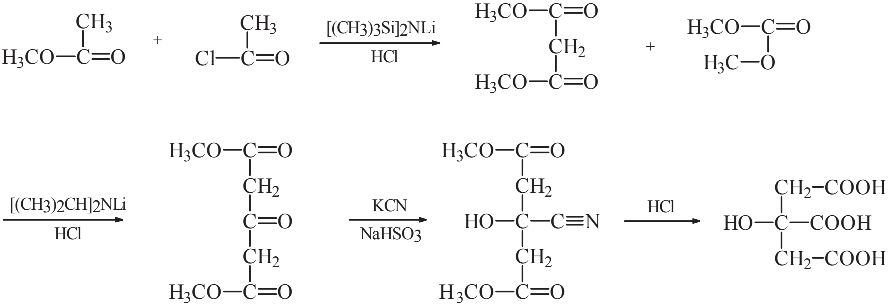
There is a number of similar procedures starting from olefinic diols which by reaction with dinitrogen tetraoxide give citric acid. Sargsyan et al. [11] presented a short account of all known until 1989 synthetic preparations of citric acid. Their paper is based mainly on the patent literature and shows that with an exception of old classical methods, most of other ways to obtain citric acid is characterized by relatively low yield. Evidently, in the context of the Krebs tricarboxylic acid cycle, there is a large number of investigations dealing with enzymatic synthesis of citric acid by condensation of acetate and oxalacetate [12–20].

4.2 Synthesis of Labeled Citric Acid

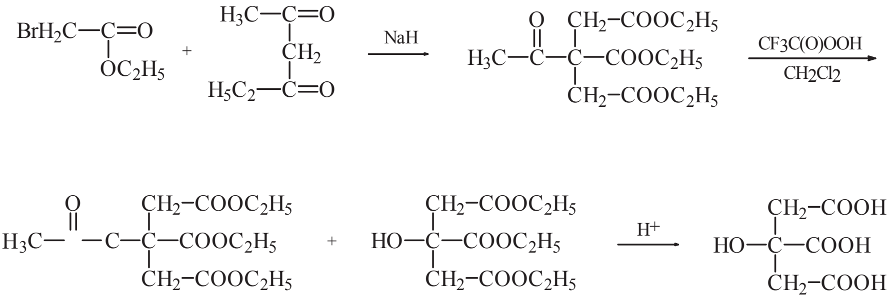
As already mentioned, considering economical aspects, citric acid is actually produced by the fermentation process using *Aspergillus niger* or other funguses and not by using the classical or later modifications of various syntheses (e.g. starting from acetone [21]). However, the knowledge about chemical preparations of citric acid or the chemistry associated with citric acid in general, is important not only for an understanding of different chemical and biological aspects associated with the Krebs cycle or with the citric acid production by microorganisms, but also with tools helping to explore these subjects [22–34]. This is linked with chemical syntheses of

^{13}C and ^{14}C labeled citric acid and citrate compounds or with enzymatic syntheses using the fermentation process with *Aspergillus niger* [35–41]. The labeled citric acid permits to obtain information about carbohydrate metabolism by non-invasive methods using NMR with stable ^{13}C isotope or applying ^{14}C isotope in radioactive investigations. The deuterated or marked with ^{17}O citric acid was also used in various studies using the electron-nuclear double resonance spectroscopy, spin resonance spectroscopy, gas chromatography and other experimental techniques [42–46]. It was observed analyzing citric acid samples different ratios of D/H, $^{13}C/^{12}C$, $^{14}C/^{12}C$ and $^{18}O/^{16}O$ isotopes. These differences in isotope compositions depend on the type of fermentation process, on various additions to commercial citric acid, on common adulteration practices when citric acid is externally added to fruit juices, on climatic changes and geographic locations [47–55].

The chemical operations described in the literature to introduce ^{14}C or ^{13}C into citric acid molecule are based essentially on the Grimaux and Adam synthesis. Labeled citric acid was prepared by Wilcox et al. [35] in the reaction of $Na^{14}CN$ with 3-chloro-2-carboxy-2-hydroxybutyric acid and the formed nitrile was hydrolyzed directly with hydrochloric acid. From this solution, citric acid was isolated in the form of calcium citrate and finally converted to the acid. An alternative procedure was proposed by Rothchild and Fields [36] to obtain trimethyl citrate from labeled sodium cyanide and di-chloromethyl glycolate. A more complex synthesis of ^{13}C labeled citric acid is described by Winkel et al. [39]. They used labeled methyl acetate and acetyl chloride (in the presence of lithium 1,1,1,3,3,3,-hexamethyldisilazide, $[(CH_3)_2Si]_2NLi$ which was dissolved in tetrahydrofuran) to obtain methyl acetoacetate. It reacts in the presence of lithium diisopropylamide, $[(CH_3)_2CH]_2NLi$, also dissolved in tetrahydrofuran, with dimethyl carbonate to give dimethyl 1,3-acetonedicarboxylate. It is dicarboxylated by the action of bisulfite and potassium cyanide is converted to 3-cyano-3-hydroxy-1,5 pentanedioate and finally hydrolyzed by hydrochloric acid to citric acid.



The three step synthesis of ^{13}C labeled citric acid was proposed by Strouse [28]. The sequence of reactions includes the condensation of labeled ethyl bromoacetate with acetoacetate which is followed by conversion of the methyl ketone group to the acetate group by means of the Baeyer-Viliger oxidation reaction. The produced ester is hydrolyzed to citric acid.



4.3 Thermal Decomposition of Citric Acid

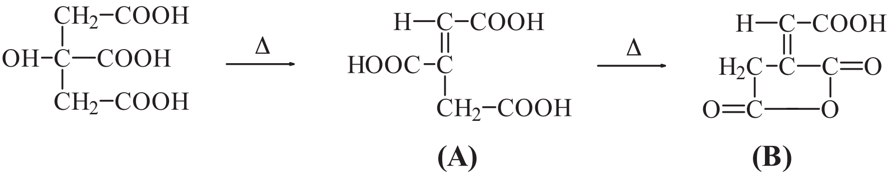
Similarly, as to synthesis of citric acid, a lot of attention was also devoted to decomposition of citric acid. There is a number of reasons to explore this subject in the literature. It includes studies of thermal stability of citric acid and of its organic derivatives including also inorganic citrates (precursors in the high-temperature preparations of ceramic materials and nano-powders doped with rare earths and transition metals). Other related topics are: the mechanism and identification of decomposition products, reactions of citric acid with strong oxidation reagents in analytical procedures, the structural and optical properties of citric acid and its complexes in solid and liquid state, the formation of short-lived radicals of citric acid during photolysis and radiolysis in aqueous solutions, the biodegradation of systems with citrate ions in processes associated with removing various chemical contaminants and treatment of wastewaters from industrial and fermentation plants, the conversion of citric acid to other useful organic compounds, the citric acid degradation reactions under hydrothermal conditions in the reductive citrate cycle (RCC) leading to primordial carbon fixation and many others subjects.

Depending on heating rate, citric acid monohydrate loses hydration water in the 70–100 °C temperature range and melts from 135 to 152 °C. Decomposition of citric acid starts above 175 °C. Early description of the decomposition process is given in 1877 by Fittig and Landolt [56] who during rapid distillation of anhydrous citric acid obtained as main products itaconic, citraconic and mesaconic acids and anhydrides. This observation was supported in 1880 by Anschütz [57] who detected itaconic and citraconic anhydrides. These compounds were formed between 200 and 215 °C and identified after distillation under reduced pressure. Shriner et al. [58] performed syntheses of itaconic anhydride and itaconic acid from citric acid monohydrate. Citric acid monohydrate melts to give itaconic anhydride which can be distilled in the 175–190 °C temperature range and by refluxing it with water is formed itaconic acid. Shriner et al. [58] also observed that superheating tends to increase rearrangement to citraconic anhydride and with adding water, a mixture of itaconic and citraconic acids is formed. These acids and mesaconic acid undergo tautomeric interconversion [59]. Considering to use citric acid monohydrate as reference material in analytical applications, Duval et al. [60] examined its thermal stability by recording infrared absorption spectra. They found that citric acid monohydrate crystals can preserve water up to 56 °C, the hydration water is completely removed at 82 °C, and a negligible loss of weight is observed up to 131 °C. After this, the decomposition of citric acid starts slowly up to 165 °C and is strongly accelerated in the 165–192 °C temperature range.

Because citric acid is considered as relatively cheap and abundant material, it was catalytically dehydrated to aconitic acid in the 120–150 °C temperature range by Umbdenstock and Bruin [61]. Aconitic acid can be readily decarboxylated to a mixture of isomeric itaconic acids (itaconic, citraconic and mesaconic acids). These acids and their esters are used to produce alkyl resins and plasticizers. The mechanism of thermal rearrangement of citraconic acid to itaconic acid in aqueous solution was in a great detail investigated by Sakai [62]. In some cases, the applied catalyst caused excessive pyrolysis of citric acid and in the dehydration and decarboxylation reactions acetone dicarboxylic acid (β-ketoglutaric acid) was initially formed and from it acetone. The catalytic pyrolysis of citric acid monohydrate heated up to 140 °C to obtain itaconic and citraconic acids was reported by Askew and Tawn [63].

At elevated temperatures (from 220 to 400 °C), using near-critical and supercritical water as a reaction medium, Carlsson et al. [64] converted citric acid to itaconic acid and itaconic acid to methacrylic acid. They observed that citric acid slowly reacts below 250 °C in hot compressed liquid water (34.5 MPa) to form itaconic and citraconic acids. In the 230–280 °C temperature region, acetone and acetic acid also appeared. Above 350 °C (the critical temperature of water is 374 °C), the fast decarboxylation of itaconic acid to methacrylic acid is observed, but also with further appearance of degradation products. From itaconic acid were formed acetic acid, pyruvic acid, acetone and acetaldehyde and from methacrylic acid were formed propene and 5-hydroxtisobutyric acid. For the first time, Nakui et al. [65] showed that citric acid can be decomposed at room temperature (20 °C and pH = 3.0) in the presence of coal ash particles to form formic acid, acetic acid and lactic acid. Waddell et al. [66] investigating the chemical evolution of the citric acid cycle, reported that the ultraviolet photolysis of 0.1 M aqueous citric acid solution (the mercury lamp photolysis during 14 h and at about 40 °C) produced 2-methyl-2-hydroxysuccinic acid, 3-hydroxyglutaric acid, tricarballylic acid, malic and succinic acids and volatiles such as acetic acid and carbon dioxide.

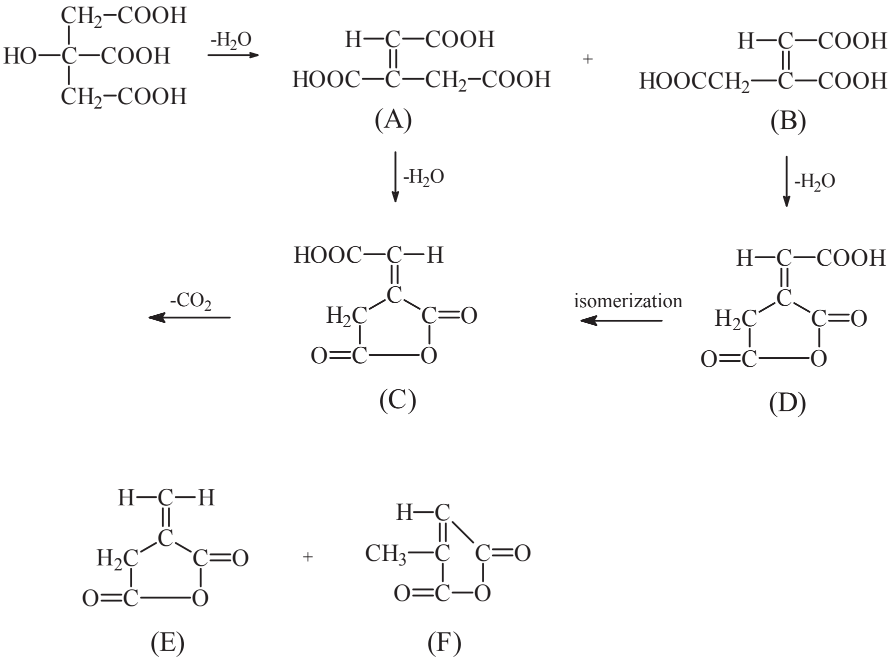
Thermal analysis studies of decomposition process started with the Wendlandt and Hoiberg [67] investigation. Differential thermal analysis (DTA) showed three peaks at 170, 185 and 210 °C, all of them indicating endothermic reactions. First peak was attributed to the fusion of citric acid and other peaks to decomposition products in liquid state. Maslowska [68] performed the derivative thermogravimetric and differential thermal analysis (TG/DTG, DTA) of decomposition reactions of citric acid and found three peaks (endothermic reactions) from 65 to 240 °C and above this temperature the product which is formed in the exothermic reaction. Using the differential scanning calorimetry (DSC) and TG/DGT techniques Barbooti and Al-Sammerrai [69] investigated decomposition of citric acid by considering the formation of (**A**) - aconitic acid by dehydration at 175 °C, and at higher temperatures the formation of (**B**) - 2-methylmaleic anhydride (citraconic anhydride).



They observed that citric acid decomposes slowly above 148 °C and the decomposition rate significantly increases only after the melting point (153 ± 0.1 °C), especially after 165 °C having a maximum at 188 °C, and decreases above 212 °C. Above 480 °C, under oxidizing atmosphere, the decomposition process is exothermic. The thermal pyrolysis of citric acid depends on heating rate and particle size in heated samples. The interpretation of DSC experiments (the rate of weight loss of citric acid samples) is also consistent with competitive reactions when the final product of thermal decomposition is acetone.

Using the thermomicroscopy, Heide et al. [70] demonstrated that the discrepancy between reported in the literature DSC and TD-data can be attributed to superimposing reactions (melting, immiscibility, crystallization and decomposition) which have different reaction rates. The thermolytic decomposition of citric acid in the presence of tin/lead solder was investigated by Fisher et al. [71] using ^{13}C NMR technique. Their results indicate formation of a series of compounds including 3-hydroxyglutaric, citraconic, itaconic and aconitic acids, and anhydrides. The procedure to identify products of citric acid decomposition using the paper chromatography was developed by Popov and Micev [72] and by gas chromatography (GC) by Uno et al. [73].

Combining the thermogravimetric analysis with mass spectrometry TG-MS, the Fourier transform infrared spectroscopy TG-FTIR, and using the differential scanning calorimetry (DSC), Wyrzykowski et al. [62] analyzed thermal properties of citric acid and isomeric aconitic acids. Experiments were performed under a neutral atmosphere of argon and with different heating velocities. They found that decomposition of citric acid is proceeded by melting and its melting point is 160.7 ± 0.2 °C with the enthalpy change of about 40.15 kJ mol^{-1}. This melting point is higher than usually reported in the literature. Wyrzykowski et al. [62] observed that thermal decompositions of involved organic compounds include a complex dehydration and decarboxylation processes, accompanied with the formation of various intermediate products. Thermal stability of citric acid and trans-aconitic acid is larger than that of cis-aconitic acid which undergoes dehydration and finally leads to the formation of cis-aconitic anhydride. The appearance of exothermic peak on the DSC curve was attributed to an existence of isomerisation reaction (cis-aconitic anhydride is transformed into trans-aconitic anhydride). The product of decarboxylation from trans-aconitic anhydride is citraconic anhydride or itaconic anhydride or the mixture of both isomers. Denoting (**A**) - trans-aconitic acid, (**B**) - cis-aconitic acid, (**C**) - trans-aconitic anhydride, (**D**) - cis-aconitic anhydride, (**E**) - itaconic anhydride and (**F**) - citraconic anhydride, the most probable series of chemical reactions, in the thermal decomposition of citric acid and isomeric aconitic acids, according to Wyrzykowski et al. [62] is



Thermoanalytical characteristics of citric acid were also studied by Trask-Morrell and Kottes Andrews [74] in the 60–600 °C temperature range. They found that anhydrous citric acid melted at 152–154 °C and then was decomposed at 228–242 °C. The weight loss of about 96 % of sample size was observed (in an apparent single peak), and at 575 °C, the residue of sample was very small. Thermal analysis of binary systems included in the Krebs tricarboxylic acids cycle was performed by Usol'tseva et al. [75–78]. They investigated systems of fumaric acid, malic acid, succinic acid, cis-aconitic acid and α-ketoglutaric acid with citric acid. They observed three endothermal effects for anhydrous citric acid, the first effect at 35–50 °C (attributed to the citric acid → isocitric acid transformation), the second effect at 150 °C (melting of citric acid) and the third effect in 175–225 °C range (decomposition of citric acid to aconitic acid and finally to anhydrides of itaconic and citraconic acids) [75]. In binary systems, the formation of complexes of citric acid in solid state which have different stoichiometry with malic, succinic and cis-aconitic acids was also detected [76–78].

4.4 Decomposition of Citric Acid by Irradiation

Structure of citric acid in solid and liquid state, in aqueous solutions, its organic derivatives and inorganic complexes, various intermediates in decomposition and enzymatic reactions were intensively investigated by different spectral, computational and electrochemical methods [79–115]. In a part, these structural and kinetic studies were connected with analytical procedures in rather complex biological systems. The radiation damage caused by light exposition, ultraviolet photolysis, gamma and X-ray irradiation, in solid state and in aqueous solutions of citric acid (also with the presence of Fe^{2+}, Fe^{3+}, Ti^{3+}, UO_2^{2+}, $S_2O_8^{2-}$ and other ions [100–109, 116]), and in many biological solutions was widely investigated by applying different experimental techniques. It was observed that in the radiolytic decomposition by gamma rays and accelerated electrons, the degradation of citric acid is weaker when other carboxylic acids or inorganic salts are present. Degradation products during photolysis of citric acid solution (14 h Hg-lamp exposition) include as observed by Waddell et al. [66], 2-methyl-2-hydroxysuccinic acid, 3-hydroxyglutaric acid, tricarballylic acid, malic acid and succinic acid. Radiolysis of citric acid proceeds more efficiently at lower pH, in diluted nitric acid solutions, but bubbling of various gases produces practically no effect [116]. In the connection with chemical origin of life, Negrón-Mendoza and Ramos B [117] investigated radiolytic products of citric acid in aqueous solutions and in solid state. They found that the main irradiation products are tricarballylic, isocitric, carboxysuccinic and succinic acids. In general, citric acid is resistant toward the irradiation and therefore can be accumulated as one of components of primitive hydrosphere.

In an interpretation of the electron spin resonance measurements (ESR) of γ-irradiated trisodium citrate pentahydrate crystals at room temperature, Russell [95] postulated the existence of two long-living radicals, the first arising from hydrogen abstraction from the methylene group $^{-}OOCCH_2(OH)C(COO^{-})C^{\bullet}HCOO^{-}$ (**I**) and second radical coming from the hydroxyl group $^{-}OOCCH_2(O^{\bullet})C(COO^{-})CH_2COO^{-}$ (**II**). No differences were observed between protonated and deuterated citrates except for a difference in the linewidths. Similar measurements with partially deuterated single crystals of citric acid at 4.2 K and at room temperature were performed by Finch et al. [89] using ESR and ENDOR (electron nuclear double resonance) techniques. At low temperature, they proposed the existence of radical which is product of decarboxylation of the central carboxyl group $HOOCCH_2(OH)C^{\bullet}CH_2COOH$

(**III**) or in the form $HOOCCH_2C^{\bullet}(COOH)CH_2COOH$ (**III'**) produced by breaking the C-O bond to the central hydroxyl group. The second radical is the anion radical with unpaired electron on one of the end carboxylic groups $HOOCCH_2(OH)C(COOH)CH_2C^{\bullet}(OH)O^{-}$ (**IV**). At room temperature, the radical (**II**) continue to exist, but in different molecular configuration and the hydrogen abstraction radical (**I**) appears. As showed by Tuner [111], at room temperature, the γ-irradiated polycrystalline powders of anhydrous or monohydrate citric acid have characteristic ESR spectra, when unirradiated samples lack them. In spite that these spectra are different for both solid forms of citric acid, the produced during irradiation radicals have the same structure but different activation energies. Tuner [111] proposed to consider anhydrous citric acid at room temperature as a potential material for the ESR dosimetry. In a similar study performed by Tuner and Korkmaz [110], they found that solid trisodium citrate is less useful as dosimetric material because of a low radical yield and unstable characteristics of produced radicals. The absorption spectra and dissociation constants of formed during irradiation radicals are discussed by Simic et al. [118].

Studying electron paramagnetic resonance (EPR) spectra of radicals present during the photolysis of concentrated aqueous solutions of citric acid and trisodium citrate in the 31–38 °C temperature range, Zeldes and Livingston [88] identified the existence of $HOOCCH_2(OH)C(COOH)C^{\bullet}H_2$ (**V**) and (**III**) radicals. With an addition of radical initiator hydrogen peroxide, it was proposed that from the molecular form of radical (**I**) $HOOCCH_2(OH)C(COOH)C^{\bullet}HCOOH$ (**VI**) is formed. In the case of Na_3Cit solutions, without and with H_2O_2, three different proton coupling of triple ionized derivative of the radical (**VI**) were reported. Analyzing ESR spectra at different pH values, Corvaja et al. [86] observed that in acidic solutions, ($pH=1$, citric acid, hydrogen peroxide and Ti^{3+} ions) the three radicals (**III**), (**V**) and (**VI**) are present. At $pH=6$ (citric acid + H_2O_2 and Fe^{2+} ions) only the radical (**VI**) is identified. They suggested the following mechanism for decarboxylation reactions in the formation of radicals (**III**) and (**V**)

$$\begin{aligned}&HOOCCH_2(OH)C(COOH)CH_2COOH+OH^{\bullet}\rightarrow\\&HOOCCH_2(OH)C(COO^{\bullet})CH_2COOH+HOOCCH_2(OH)C^{\bullet}CH_2COOH+\\&CO_2+H_2O\end{aligned}$$

and

$$\begin{aligned}&HOOCCH_2(OH)C(COOH)CH_2COOH+OH^{\bullet}\rightarrow\\&HOOCCH_2(OH)C(COOH)CH_2COO^{\bullet}+HOOCCH_2(OH)C(COOH)C^{\bullet}H_2+\\&CO_2+H_2O\end{aligned}$$

Irradiation of frozen solutions of citric acid (from 77 to 140 K) in the presence of ferric ions is associated with reduction of iron ions, from Fe(III) → Fe(II), and with formation of radicals (**II**) and (**V**) [106, 107]. It was observed by Glikman et al. [104] that under anaerobic conditions, the radiolysis and ultraviolet photolysis is affected by the presence of ferric complex in citric acid solution. The complex existence is responsible for larger yields of decomposition products (carbon dioxide and probably glycolaldehyde) as compared when citric acid is alone in solutions. The occurrence of iron ions in solutions makes the reduction reaction Fe(III) → Fe(II) suitable to be studied by the Mossbauer spectroscopy, and this was performed by Buchanan [105] who analyzed the spectra of irradiated solid ferric citrate at 77 K.

From practical reasons, aqueous solutions with U(VI) or with both U(VI) and Fe(III) were frequently investigated considering that citric acid is an efficient metal chelator and this property can be used for decontamination of polluted soils, surfaces and iron-containing wastes. Citric acid is also used in cleaning and decontamination mixtures for boilers and cooling circuits of nuclear power plants and removed by the oxidative degradation during various photolytic processes [93, 119]. One of the first such examples is that of Ohyoshi and Ueno [100] who studied the photochemical reduction of uranyl ion from U(VI) → U(IV) and found that final products of photodegradation of citric acid, at acidic pH, are acetone and carbon dioxide. Upon exposure to visible light, the precipitation of uranium trioxide dehydrate $UO_2 \cdot 2H_2O$ was observed by Dodge and Francis [102]. They reported that uranyl ions are reduced to uranous ions and consequently reoxidized to the hexavalent form and precipitated out of solution as uranium trioxide at near-neutral pH. The intermediate and final products of photochemical degradation of uranyl citrate complexes are influenced by the presence of oxygen and by pH values, and they include acetic, acetoacetic, 3-oxoglutatic, malonic acids and acetone. An addition of ferric ion to the system with U(VI), caused precipitation of ferrihydride $Fe(OH)_3$ and during irradiation, when sodium persulfate is added to citric acid solution, citric acid degradation is significantly improved [103, 109].

4.5 Oxidation of Citric Acid

Decomposition process of citric acid is also important in industrial applications because citric acid is one of additives in electroplating baths and takes part in several electrocatalytic reactions. The main focus in electrochemical studies was placed on the electrical oxidation of citric acid on noble metals (Ag and Au) and stainless steel surfaces. Frequently investigated subjects were properties of created electrodeposits, formation of citrate complexes resulting from dissolution of electrode materials, kinetics, temperature, inhibition effects associated with corrosion of aluminum, tin and some other metals (in food industry, their surfaces are in contact with citric acid or with citrate ions) and with evolution of gases during electrochemical processes (hydrogen, oxygen and others) from corroding solutions containing citric acid [96–99, 120–135].

In the context of qualitative and quantitative determination of citric acid in liquid and solid samples, its decomposition by the oxidation with potassium permanganate in sulfuric acid attracted a rather exceptional interest in the literature. The analytical procedure associated with this oxidation reaction is attributed to the prominent and long-living French chemist George Denigès (1859–1951). He worked, in varied areas of analytical, pharmaceutical and biological chemistry and is well-known for the named after him reagent (mercuric oxide, HgO, dissolved in hot and concentrated sulfuric acid). Starting from 1898, Denigès published a number of partially polemical papers [136–142], defending his analytical procedure and rebuffing criticisms of it by others [143–151]. Historically, Denigès is probably not the first person who carried out the oxidation of citric acid by potassium permanganate. The reaction was performed much earlier by the British chemist Thomas L. Phipson [152] who was the recipient of Gold Medal of the Royal Society of Medical and Natural Sciences of Brussels for 1867. In Journal of Chemical Society from 1862, Phipson wrote: "Citric acid oxidized by permanganate of potash at a temperature a little above summer-heat, was found to yield nothing but oxalic acid". Considering that oxidation reactions of citric acid were performed by Phipson and Denigès at different conditions, the identified degradation products are evidently also different. In the Denigès analytical procedure, mainly applied to wines, fruit juices and milk, $KMnO_4$ is acting on citric acid to yield as the intermediate degradation product—acetone dicarboxylic acid (3-oxoglutaric acid) $HOOCCH_2COCH_2COOH$ which is precipitated as an insoluble white mercury compound. In direct titration of citric acid with potassium permanganate in hot sulfuric acid, the formed acetone dicarboxylic acid disintegrates quickly into acetone and carbon dioxide, and acetone to some extent into acetic and formic acids. Various modifications of the Denigès method were introduced, for example, mercuric oxide was replaced by mercuric sulfate, potassium permanganate was substituted by potassium dichromate, instead of mercury salts, the precipitation was performed with lead salts, HCl was added to convert microcrystalline mercury salt into more compact regularly crystallized substance and several others. It was observed that citric acid is detected in the presence of sucrose, glycerin, acetic, aspartic, tartaric, lactic, glycolic, fumaric and succinic acids but aconitic acid, tricarballylic acid and oxalic acid partially react in a similar way as citric acid. In samples with chlorides, bromides and iodides, these acids must be first removed before applying the Denigès method by adding $AgNO_3$ or $MnSO_4$. In the case of chlorides, Kolthoff [153] reported that the oxidation products formed by potassium permanganate treatment are reducing Hg^{2+} to Hg^+ and the later reacts with present chlorides to form insoluble Hg_2Cl_2.

An alternative analytical method, also based on the oxidation with potassium permanganate was introduced in 1895 by Stahr [154] and later developed as quantitative procedure by Kunz [155–157]. In Starh's method, citric acid is oxidized to acetone dicarboxylic acid, which reacts with bromine to give precipitate of pentabromoacetone, $Br_3CCOCHBr_2$.

$$HOOCCH_2COCH_2COOH + 5Br_2 \rightarrow Br_3CCOCHBr_2 + 5HBr + 2CO_2$$

Similarly as with the Denigès method, Stahr was not the first and this reaction was performed many years before by French organic chemist Auguste André Thomas Cahours (1813–1891). In 1847 he published paper entitled "Relatives a l'action du brome sur les citrates et sur les sels alcalins formés par le acides pyrogénés dérivés de l'acide citrique" [158] where described bromination products of several alkali metal citrates and the most important of them can be recognized as pentabromoacetone. In Cahours' words: "…une produit neuter dové d'une odeur aromatique assez semblable a celle du bromoforme. Il est complétement insoluble dans l'eau pure et dans les dissolutions alcalines; l'alcool et l'éther le dissolvent en tout proportions … je propose de la designer sous le nom de *bromoxaforme*". Observing that behaviour of tartaric and malic acid in the bromination reactions is different than that of citric acid, Cahours recommended to use bromine for citric acid analysis "Le brome peut done server à reconnaitre de petites quantités a'acide citrique mélanges a l'acide tartrique". It is also worthwhile to note that Cahours identified oxalic, acetic and oxalacetic acids as decomposition products when citric acid was heated to about 200 °C.

The procedure with pentabromoacetone and many modifications of it, had a huge popularity during a long period as the standard analytical method for detection and quantitative analysis of citric acid in biological and industrial samples [159–196]. The mechanism and kinetics of citric acid oxidation by permanganate was studied mainly to ensure the precision and reliability of the pentabromoacetone method [197–199]. Kuyper [197] observed that oxidation of citric acid by $KMnO_4$ in sulfuric acid is more complete at room temperatures than at high temperatures and the nature of reaction changes above 60 °C. At any temperature in the 20–100 °C temperature range, acetone dicarboxylic acid, carbon dioxide and water are formed according to general scheme

$$\begin{gathered}2HOOCCH_2(OH)C(COOH)CH_2COOH + O_2 \rightarrow \\ 2HOOCCH_2COCH_2COOH + 2CO_2 + 2H_2O\end{gathered}$$

and in this first step, when the oxidation is performed together with potassium bromide, pentabromoacetone is created. In the second step, at low temperatures, the intermediary product acetone dicarboxylic acid, depending on concentration of $KMnO_4$, and the rate of its addition, is oxidized to formaldehyde, formic acid and carbon dioxide according to

$$2HOOCCH_2COCH_2COOH + 5.5O_2 \rightarrow 2HCHO + HCOOH + 7CO_2 + 3H_2O$$

Molecular oxygen takes part in this reaction and no acetone is formed. Acetone appears only above 60 °C

$$2HOOCCH_2COCH_2COOH \rightarrow 2(CH_3)CO + 4CO_2$$

With increasing strength of potassium permanganate solution and temperature, acetone is oxidized to carbon dioxide. Kuyper suggested that the produced carbon dioxide, if determined manometrically, is a measure of citric acid concentration.

In analytical procedures, developed by Berka et al. [200–202] and by others [203–206], potassium permanganate oxidizes citric acid to carbon dioxide and water according to over-all reaction scheme

$$\begin{aligned}&5HOOCCH_2(OH)C(COOH)CH_2COOH + 2MnO_4^- + 6H^+ \rightarrow\\ &30CO_2 + 47H_2O + 18Mn^{2+}\end{aligned}$$

and manganese(III) sulfate to formic acid

$$\begin{aligned}&HOOCCH_2(OH)C(COOH)CH_2COOH + 14Mn^{3+} + 5H_2O \rightarrow\\ &2HCOOH + 4CO_2 + 14Mn^{2+} + 14H^+\end{aligned}$$

where formed Mn^{2+} is titrated potentiometrically or titrated with ferrous sulfate.

If citric acid is oxidized by sulfuric acid alone, then as pointed out by Wiig [207], who investigated this reaction in a detail, citric acid decomposes into carbon monoxide, water and acetonedicarboxylic acid

$$\begin{aligned}&HOOCCH_2(OH)C(COOH)CH_2COOH \rightarrow\\ &HOOCCH_2COCH_2COOH + CO + H_2O\end{aligned}$$

Actually, this reaction is based on the Pechmann findings from 1884 [208]. However, in much earlier investigation from 1839, the French chemist Pierre-Jean Robiquet (1780–1840) observed that on heating sulfuric acid with citric acid, the oxidation is more complete, to give the mixture of carbon monoxide and carbon dioxide. Reaction of citric acid with sulfuric acid is also of interest by considering the combustion of citric acid [209] and the preparation of aconitic acid, by heating both of them at 140–145 °C [210].

There is a number of investigations where potassium permanganate was replaced by other oxidizing agents and few will be mentioned here. Decomposition products of citric acid in the oxidation with cerium(IV) salts [211–217] are according to Ajl et al. [213] acetone and carbon dioxide

$$\begin{aligned}&HOOCCH_2(OH)C(COOH)CH_2COOH + 2Ce^{4+} \rightarrow\\ &(CH_3)_2CO + 3CO_2 + 2Mn^{2+} + 2H^+\end{aligned}$$

but formation of formic acid is more probable [211, 214]

$$\begin{aligned}&HOOCCH_2(OH)C(COOH)CH_2COOH + 14Ce^{4+} + 5H_2O \rightarrow\\ &2HCOOH + 4CO_2 + 14Ce^{3+} + 14H^+\end{aligned}$$

similarly as in the case of manganese sulfate.

Behaviour of cerium and manganese ions in solutions with citrate acid have been thoroughly studied also in the context of oscillation reactions important in biological and chemical systems. The system $Ce_2(SO_4)_3$-$KBrO_3$-H_2SO_4 - malonic acid, $CH_2(COOH)_2$, represents the classical Belousov-Zhabotinskii (B-Z) reaction, the oscillatory oxidation of malonic acid by acidic bromate which is catalyzed by the Ce^{4+}/Ce^{3} redox couple. In many investigations, the substrate malonic acid, is replaced by citric acid or by other carboxylic acids and the cerium Ce^{4+}/Ce^{3+} by manganese Mn^{3+}/Mn^{2+} redox couple [218–231]. The appearance of periodic, aperiodic and chaotic oscillation phenomena leads to considerable difficulty in their interpretation, mathematical representation and mechanism description. Highly complex mechanism of the oxidation reaction is proposed which involves numerous steps, radicals, ions, atomic and molecular species, intermediates and final products. It can be shortly summarized as the Ce(IV) reduction to Ce(III) by a highly reactive organic substrate (carboxylic or hydroxycarboxylic acid) and by the subsequent reverse oxidation from Ce(III) to Ce(IV) by BrO_3^- with production of various bromination and oxidation products [228, 229].

From other oxidation reagents it is possible to mention potassium dichromate in acidic medium or in the presence of Mn^{2+} ions [79, 204, 232–239]. The oxidation process is essentially based on the Cr(VI) to Cr(III) reduction reaction. The reaction mechanism is complicated and intermediates and final products are not well identified but for chromium, the over-all stoichiometry is $Cr_2O_7^{2-} + 14\,H^+ \rightarrow Cr^{3+} + 7\,H_2O$. The presence of Mn^{2+} ions is manifested by the catalytic but also inhibition effects on the chromate oxidation of organic compounds. Other catalytic oxidation agents are vanadium(V) ions which frequently are used in quantitative determinations of small quantities of citric acid but also small quantities vanadium in mineral samples [240–246]. The final products of oxidation are acetone and carbon dioxide and the couple V(V)/V(IV) actually represents the corresponding charged vanadium species in a medium of strong mineral acid. In the aqueous system $VOSO_4 + KBr + H_2SO_4 +$ citric acid, Yatsmirski et al. [244] demonstrated possibility of oscillatory oxidation. Copper-citrate complexes act catalytically to promote oxidation in multistep reactions. The copper(II) catalyzed oxidation of various biological and mineral samples was to a some extent discussed in the literature [247–249].

Diverse nitrates serve as oxidizers, and citric acid or citrates operate as fuels and reducing agents in the nitrate-citrate combustion process to prepare useful ceramic materials (nanostructured powders, spinels, superconductors, alloys and other valuable products). The so-called citrate-nitrate gel combustion process is of an immense practical importance, but only few typical examples it is possible mentioned here [250–264].

Regarding analytical procedures, and the effect of present iodine in aqueous solutions, a special attention was directed to total and partial oxidation of citric acid by periodic acid [265–277]. Huebner et al. [266] and Courtois [267] observed a slow oxidation of citric acid by sodium metaperiodate $NaIO_4$ and by periodic acid HIO_4, with the formation of an intermediate acetone dicarboxylic acid and finally formic acid and carbon dioxide.

$$\mathrm{HOOCCH_2(OH)C(COOH)CH_2COOH + O \xrightarrow{IO_4^-}}$$
$$\mathrm{HOOCCH_2COCH_2COOH + CO_2 + H_2O}$$
$$\mathrm{HOOCCH_2COCH_2COOH{+}6O \rightarrow 2HCOOH + 3CO_2 + H_2O}$$

These oxidation reactions depend on temperature and pH (maximum velocity is in 4–5 pH range). At 100 °C, it was observed that acetone dicarboxylic acid is decarboxylated to acetone [267]

$$\mathrm{HOOCCH_2COCH_2COOH \rightarrow CH_3COCH_3 + 2CO_2}$$

The same products are formed when citric acid is oxidized by acidic solutions containing mixtures of potassium permanganate with KIO_3, KI or I_2, but also yellow solid is precipitated, probably tetraiodoacetone $(CHI_2)_2CO$ [269]. The oxidation reactions of citric acid by periodic acid were also discussed by Melangeau and Rubman [270]. The over-all oxidation process includes an additional product oxalic acid

$$\mathrm{HOOCCH_2(OH)C(COOH)CH_2COOH + O \xrightarrow{IO_4^-}}$$
$$\mathrm{2HCOOH + 4CO_2 + 2H_2O}$$
$$\mathrm{HOOCCH_2(OH)C(COOH)CH_2COOH + O \xrightarrow{IO_4^-}}$$
$$\mathrm{HCOOH + (COOH)_2 + 3CO_2 + 2H_2O}$$

They proposed a number of mechanisms for oxidation of the intermediate product which is acetone dicarboxylic acid. In one route, acetone dicarboxylic acid is oxidized by periodic acid to give 2-hydroxy-3-ketoglutaric acid, HOOCCH(OH) $COCH_2COOH$, which further can be oxidized to glyoxylic acid, HOOCCOH and finally to malonic acid $HOOCCH_2COOH$. In the second path, acetone dicarboxylic acid is oxidized to γ-lactone which in a series of consecutive reactions finally gives carbon dioxide, formic and oxalic acids.

In a series of papers, over the 1904–1923 period, Broeksmit [271–277] proposed a confirmatory test for citric acid in soft drinks, fruits, foods and drugs. Citric acid is oxidized by $KMnO_4$ in acetic acid solution followed by treatment with ammonia in the presence of iodine. As a result, iodoform CHI_3 is precipitated in the case of malic and citric acids but not when other acids or sugars (succinic, lactic, oxalic, tartaric, glucose, lactose and sucrose) are present. Differentiation between malic and citric acids is performed by precipitation of amorphous barium citrate. It was observed by Kalra and Ghosh [230] and Qureshi and Veeraiah [268] that the reaction between citrate and aqueous iodine is accelerated by Cr^{3+}, Mn^{3+} and Mn^{2+} ions. In rather long paper published in 1917, Dhar [278] reported that the oxidation reactions with carboxylic acids including citric acid, take place with $K_2S_2O_8$, MnO_3, KNO_2, and $KMnO_4$. Oxidizing agents such as CrO_2 and HNO_3 act in the presence of Mn^{2+} ions and H_2O_2 and are greatly activated by Fe^{2+} and Fe^{3+} ions. In these reactions $HgCl_2$, $HgBr_2$, $CuCl_2$, $AuCl_3$, $AgNO_3$ and Na_2SeO_3 were reduced to HgCl, HgBr, CuCl, Au, Ag, and Se respectively. These reactions take place at room temperatures, in sunlight, but fail to proceed even at more elevated temperatures in the dark. After optimal concentration of the oxidation agent is reached, further increase is ordinarily accompanied by a decrease in final products which are CO_2 and H_2O.

Degradation, oxidation and complexation reactions with involved citric acid are of considerable interest in the research of origin of life [279–285]. If a chemoautotropic origin of life is accepted, then the central problem within proposed theory is the carbon-fixation pathway. In absence of enzymes, the conversion of carbon dioxide and water to organic compounds is accomplished in a sequence of chemical reactions via the reductive citric acid cycle which is the reverse Krebs tricarboxylic cycle. The required energy source for the reduction of carbon dioxide is, as proposed by Wächtershäuser [279], the oxidative formation of pyrite FeS_2 from pyrrhotite FeS. The Wächtershäuser theory was experimentally tested by Cody et al. [280] with FeS and NiS exposed to hydrothermal conditions. They presented a detailed analysis of kinetically and thermodynamically favorable reactions which are associated with formation and decomposition of citric acid in aqueous solutions at high temperatures and pressures. According to them, citric acid can be synthesized catalytically from a simple molecule like propene. By the aqua-thermolytic degradation, citric acid provides a source for many organic acids (citramalic, itaconic, citraconic, mesaconic, aconitic, methacrylic, oxaloacetic and pyruvic). Thus, the citric acid-water system appears to be well suited as a starting point for primitive metabolism. Thermodynamic and other aspects of the pyrite pulled surface metabolism hypothesis were also discussed by Kalapos [281, 282], Dalla-Betta and Schulte [283] and Marakushev and Belonogova [284].

Cooper et al [285] and Saladino et al. [286] identified pyruvic, oxaloacetic, citric, isocitric and α-ketoglutaric acids (all members of the citric acid cycle) in carbonaceous meteorites and as products of pyruvic acid reactions at low temperatures. Oxaloacetic and pyruvic acids in series of reactions can be converted to citric acid [287, 288]. Considering that meteorites deliver a variety of organic compounds to Earth, most likely, their role in the origin of life and in the evolution of biochemical pathways can not also be excluded.

In many industrialized regions, soils, soil solutions and waters are seriously contaminated with heavy metals which are toxic to humans, animals, plants and microorganisms. In order to remediate and protect these polluted areas, many particular chemical methods and biodegradation procedures are applied. They included conversion of metal complexes from highly to less toxic, ready for microbial decomposition and to organically bounding as micronutrient elements. Vegetation is frequently used by planting appropriate plants which are capable to bioaccumulate, degrade or eliminate heavy metals and toxic materials. Citric acid is one of the most common organic acids in soils, being released from roots of numerous plants, bacteria, fungi and found under plant litter. As a strong chelating agent and participant in various catalyzed degradation, reduction and oxidation reactions, its role is extremely important in the transport, adsorption-desorption, solubility, mobility, precipitation, removal and recovery processes as applied in remediation of polluted soils. Citric acid is non-toxic, easily biodegradable material and usually its concentration in soils is quite large (naturally occurring in soils or intentionally added) as compared to trace concentrations of dispersed metals. This is of great consequence considering citric acid ability to form complexes with practically all elements which are causing serious environmental problems, listing here only Al, Cr, Co, Cu, Mn, Ni, Zn, Th, U, Hg, As and Sb. The bioavailability of metals is affected by pH, mobilities, cation exchange capacities of ions and many other factors in soils. The citric acid presence reduces soil pH values and increases the metal mobility by forming soluble in water complexes, thus influencing transport of metals or their partial or total immobilization when insoluble complexes are formed.

Evidently, two large groups of investigations are devoted to remediation of polluted soils by studing related aspects from the soil chemistry and from the citrate-metabolizing biodegradation. They include a wide spectrum of basic research problems and technological processes in treatment of domestic, industrial (also from citric acid factories) and nuclear wastes. Since some metal-citrates are not readily biodegradable (e.g. Cu, Cd, Pb and U), frequently additional chemical, electrochemical and photodegradation steps are involved, together with bioremediation processes [289–325].

4.6 Qualitative and Quantitative Determination of Citric Acid

As can be expected, many aspects of the citric acid chemistry are linked with chemical analysis of citric acid or citrates in biological materials [169, 172, 179, 326–328], in fermentation media [179, 188, 192, 329–333], in foods [155, 334–340], in fruits [165, 177, 341–347], in tomato-based products [348–350], in musts, wines and beers [155, 174, 351–363], in soft drinks and fruit juices [155, 165, 177, 361, 364–377], in milk and dairy products [155, 170, 173, 176, 378–386], in honey [387, 388], in pharmaceutical formulations [361, 389–391], in medical tests (blood, serum, urine, pancreatic juice and other physiological fluids) [162, 183, 187, 193–195, 392–400], and in mixtures with other carboxylic acids (formic, acetic, tartaric, malic, oxalic, isocitric, succinic, lactic, pyruvic, oxalacetic and others) [160, 184, 211, 265, 401–409].

In the qualitative and quantitative analysis of citric acid [194, 326–346, 348–390, 392–397, 401–474], the neutralization, oxidation, complexation, esterification and other chemical reactions (or combination of them) are applied. However, together with chemical detection and quantification of citric acid in different samples, many biochemical (enzymatic) methods are also employed. Numerous experimental procedures, sampling preparations and detection techniques are used depending on the complexity of analyzed system and concentration levels of citric acid in samples. In research investigations and in various routine separations and determinations, every available analytical technique was and continue to be employed. They include, alone or together, with many modifications, the potentiometric titrations [326, 351, 381, 402, 403, 415–419], ion-exchange separations, electrophoresis [352, 353, 364, 400, 420–423], titrations with selective-electrodes [346, 361, 467–471, 475], polarography [410], mass-spectroscopic [329, 347, 422, 425, 428, 441, 445], gas chromatographic [335, 336, 341, 404, 424–427], thin-layer chromatographic and high-performance liquid chromatographic [332, 333, 337, 338, 342–344, 348, 349, 354–358, 365–375, 382–384, 387, 389, 392, 405–408, 429–445] techniques, many different spectrophotometric procedures [327, 339, 345, 359, 360, 364, 365, 376, 377, 385, 390, 391, 393, 394, 409, 446–463, 466], enzymic methods [194, 195, 328, 340, 350, 362, 363, 386, 388, 395–399, 472–474, 476] and many other analytical techniques.

The enzymatic procedures started in 1929 by Torsten Thunberg (1873–1952) [476] who found that in certain types of seeds (*Cucumis satvus*—cucumber) exists an enzyme which is specific for citric acid. The method was widely applied, especially in determination of citric acid in animal fluids and tissues. Values of citric acid occurrence in biological samples (in a human body and various plants) are mainly coming from the Thunberg method [477]. Practically, in the applied procedure, the concentration of citric acid is related to the rate of decolorization of methylene blue by an enzymatic reaction (isocitrate dehydrogenase). Actually, citric acid first undergoes transformation into isocitric acid, $HOOC(OH)CH(COOH)CH(CH_2COOH)$, by the action of an enzyme that catalyzes the oxidative decarboxylation of isocitric acid to produce α-ketoglutaric acid and carbon dioxide.

Following the literature on relevant analytical procedures, it is observed a continuous improvement in the accuracy, reliability, speed, automation, sampling procedures and widening of concentration levels available for citric acid analysis. However, simultaneously with increased convenience and precision of analytical methods, there is an increasing investment cost, sophistication and complexity of applied equipment. Considering its practical importance, a number of investigations dealing with chemical analysis of citric acid, as reported for various routine determinations or for many specific situations, is enormous. Evidently, from a huge amount of published analytical investigations, it was possible to mention only a very small part, only some representative examples.

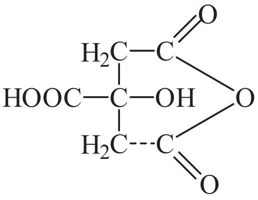
From many topics connected with citric acid analysis, there is one which is not so frequently associated with other chemical compounds. Its importance started to be immediately evident from a very early analytical studies on the subject. Citric acid was initially determined in wines and later in milk, beverages, fruit juices and other natural products, and in part, these determinations were linked with the regulatory and adulteration problems in food industry. Common practices of adulteration include an addition of water, colorants, sugar, citric acid (sometimes added to prevent iron salt precipitation) and other chemicals, mixing of natural wines and pure juices with cheaper products and other undeclared additives. Thus, ensuring authenticity of wines and detecting adulteration is of considerable interest to producers, consumers and regulatory officials. For example, this raised necessity to establish authenticity of wines and fruit juices and the assessment of performed fraud. As mentioned above, adulteration practices can be detected by isotopic techniques, but besides them, conventional methods of analysis are also suitable for such purposes [136, 144, 413, 423, 463].

Evidently, an adulteration is only a secondary concern in citric acid analysis, the main bulk of determinations is associated with citric acid production, during and after fermentation process, analysis of drinks and foods and routine control of citrate levels in urine and blood. From other examples, it is worthwhile to mention citric acid concentration in honey, which is needed for differentiation between two main types of honey (floral and honeydew honeys). There are numerous methods devoted to citric acid analysis in dairy products, in view of its intentional additions or as a result of normal bovine biochemical metabolism. Considering that citric acid is used in many detergent additives and able to form toxic complexes with heavy metals, its monitoring in tap water and sewage effluents is also necessary.

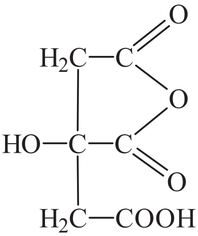
4.7 Formation of Citric Acid Anhydrides

As mentioned above, behaviour of citric acid in chemical reactions is similar to that expected from other hydroxycarboxylic acids. However, the tertiary sterically hindered hydroxyl group does not undergo all the common reactions being mainly important only in complex formation reactions. The natural and synthetic derivatives of citric acid and different reactivities of the carboxylic groups were reviewed by Milewska [478] (see also [479]) and therefore only the most important chemical reactions involving citric acid are shortly discussed here.

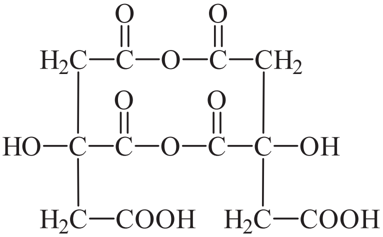
Dehydration of organic acids leads to corresponding anhydrides, but as stated by Repta and Higuchi [480, 481], the mentioned in the literature dehydrated citric acid is actually anhydrous crystalline form of citric acid or aconitic acid, but not a true anhydride of citric acid. They were able to synthesize and isolate the monomolecular unsymmetrical anhydride of citric acid. The conversion of citric acid to its anhydride is performed by interacting of the solid acid with an excess of acetic anhydride in glacial acetic acid at 36–38 °C. The melting point of prepared white crystalline solid anhydride is at 121–123 °C. The identification of thise compound was performed by elementary analysis, potentiometric titration, cryoscopic and NMR measurements. From three possible anhydride structures (**A**) - symmetrical anhydride, (**B**) - unsymmetrical anhydride and (**C**) - intermolecular anhydride.



(A)



(B)



(C)

Repta and Higuchi postulated that the unsymmetrical anhydride (**B**) is predominantly formed. This is based on the fact that anhydride of citric acid reacted readily with aniline to yield expected monoanilides and hydrolyzed in water to give back ionized citric acid [481]. They also observed that anhydride of citric acid is more soluble in water, alcohols, diethyl ether, tetrafuran, dioxane and acetone than in chloroform, benzene, carbon tetrachloride and petroleum ether. If the reaction mixture is heated for several hours at about 120 °C, largely acetylcitric anhydride is formed. Auterhoff and Swingel [482] demonstrated that citric acid gives with acetic anhydride and pyridine a red color solid. A different way to produce citric acid anhydride was proposed by Schroeter [483], by using $CH_3OOCCH_2(OH)C(COOH)CH_2COOCH_3$, the symmetrical dimethyl ester which reacts with acetic acid anhydride in the presence of sulfuric acid serving as a catalyst. The alcoholysis of citric acid anhydrides leads to the formation of unsymmetrical monoesters. Formaldehyde or acetyl chloride reacts with citric acid to give methylene-citric acid, this acid and its anhydride are involved in the formation of aniline and other derivatives of citric acid. This was illustrated by Dulin and Martin [484] in the case of aromatic methylene citrates (monobenzyl-, monophenylethyl- and monoallyl methylene citrate). Acetylcitric anhydride was also prepared by heating powdered citric acid with acetic chloride by Klingemann [485]. Aldehydes or ketones, normally, form with citric acid 1,3-dioxolan-4-ones which are acetals and lactones at the same time and therefore they also can serve in preparation of corresponding amides [478, 484, 486, 487].

Actually, an interest in the anhydride of citric acid synthesis started when Repta et al. [488] and Robinson et al. [489] analyzed behaviour of acetic anhydride and gluraric anhydride in citrate buffers. It was suggested by Repta and Higuchi [480], that the anhydride can be used as a latentiated acidifier in spontaneous carbonation of aqueous systems, as a desiccant in food and drug products and finally as a reagent in synthesis of various citric acid derivatives.

4.8 Esterification and Neutralization Reactions Associated with Citric Acid

From all types of chemical reactions involving citric acid, the esterification reactions are most discussed in the literature. Various esters or polyesters of citric acid are of large practical importance because organic citrates having numerous applications are usually non-toxic, environment friendly materials [490–494]. Citric acid esters are used as plasticizers in preparation of plastic tubes employed in medical practice, as crosslinkers for starch, cellulose, cotton fabrics and as biodegradable materials used for packing of foods. They are also used as food additives, as ingredients in drugs, as cosmetic sprays, deodorants, skin conditioning agents, fragrance ingredients, in lipstick formulations, in ink printing compositions and as lubrication and antifreeze liquids [495–517]. The direct food additives (called as citroglycerides) are obtained by esterification of glycerol with citric acid and edible fatty acids. The formation of volatile esters is essential when samples containing citric acid are analyzed by the gas chromatographic technique [518].

In esterification reactions there are produced neutral tri-esters of citric acid $ROOCCH_2(OH)C(COOR)CH_2COOR$, with the same or different organic groups ($R=R_1,R_2$ and R_3 or $R=R_1=R_2$ and R_3) and the acidic mono- or di-esters where R denotes identical or dissimilar groups. Depending on esterificated carboxylic group position in the citric acid molecule, the mono- and di-esters are symmetrical or unsymmetrical. The synthezed alkyl citrates (with short alkyl groups) are oily liquids, but with increasing the chain, they are oily to waxy and powdery solids with varying solubility in water and organic solvents.

Similarly as with esters, in neutralization reactions, citric acid reacts with many inorganic ions forming mono-, di- and tribasic salts: MeH_2Cit, Me_2HCit and Me_3Cit. Usually, these inorganic citrates are prepared by partial or complete neutralization of aqueous citric acid solutions with the appropriate base or amine, but special preparation procedures are also known (double decomposition, mixed salt formation and other procedures) [494, 519–524]. From a large number of known and offered commercially citrates (ammonium citrate, lithium citrate, potassium citrate, calcium citrate, magnesium citrate, copper citrate, ferric citrate, ferric ammonium citrate, manganese citrate, cobalt citrate, nickel citrate, zinc citrate, lead citrate, tin citrate, bismuth citrate) trisodium citrate hydrates ($Na_3Cit\ 2H_2O$ and $Na_3Cit\ 5.5H_2O$) are more widely prepared and used than other salts of citric acid.

The esterification of citric acid started with simple aliphatic alcohols and was followed with more complex alcohols and finally expended to a wide diversity of polyester resins with various applications [506–516, 525–534]. Initial work with simple esters was performed in the 1902–1905 period by Schroeter and Schmitz [483, 535] who prepared dimethyl hydrogen ester of citric acid by heating citric acid with methanol in sulfuric acid solution. They called it "citrodimethyl ester acid" to emphasize that this ester still continue to be acid. Schroeter with coworkers obtained calcium, silver and copper salts of dimethyl ester, and a number of organic derivatives (acetyl dimethyl esters and amides) and measured their solubilities in water and some organic solvents. Wolfrum and Pinnow [536] by boiling anhydrous citric acid with absolute ethanol prepared citrate esters, mainly diethyl hydrogen citrate. The esters were identified by precipitation of silver, copper and zinc salts. Industrial continuous esterification process to yield tributyl and trihexyl esters of citric acid was described by Canapary and Bruing [537]. The kinetics and mechanism of the catalytic esterification of citric acid with ethanol is discussed by Kolah et al. [538]. Melting D-glucose with citric acid, Maier and and Ochs [539] prepared mono-glucose citrates. The preparation methods of these and many other esters is reviewed by Milewska [478]. Sometimes, desired symmetrical or unsymmetrical mono- and di-esters are also obtained by partial hydrolysis of various tri-esters of citric acid. Evidently, in such procedures a mixture of esters is produced and different separation methods are involved. The identification of acyl groups in esters as N-benzylamides was described by Dermer and King [540]. The hydrolysis processes of few simple tri-esters was investigated by Pinnow [541], Pearce and Creamer [542] and Hirata et al. [543]. A knowledge about physical properties of citric acid esters is very limited, usually only experimental or predicted boiling points at reduced pressure, sometimes melting points, densities and refraction indices were also reported [493, 544]. Citric polyesters are prepared by reactions with 1,2-epoxides (ethylene oxide, propylene oxide, styrene oxide and others), which are catalyzed by small amounts of BF_3, $SnCl_2$ or NaOH [494].

4.9 Formation of Amides Citrate-Based Siderophores and Other Compounds

If one or more hydroxyl groups -OH in citric acid or in its esters are replaced by the nitrogen group $-NH_2$, amides of citric acid are formed. They are synthesized by heating citric acid, citric acid anhydride and various esters with concentrated aqueous ammonia and amine solutions. From other groups of citric acid derivatives, the synthesis of amides by different paths is reasonably well established in the literature [478, 487]. Amides and polyamides, as other compounds associated with citric acid, have a wide spectrum of applications. They serve as components in stable, enzyme-compatible detergents, soaps, shampoos, disinfectants, cosmetic antiperspirant gels, oil well drilling fluids, defoamers in papermaking, anticorrosion agents, in making leather impermeable to water and in many other applications.

First works related to the citric acid amides started already in 1852 by Pebal [545] who synthesized citranilic cid (N-phenylcitric acid imide). Further investigations, in the 1872–1905 period, with various amides and rather sporadic, are these of

Sarandinaki [546], Kaemmerer [547], Behrmann and Hofmann [548], Ruhemann [549], Conen [550], Klingemann [485] and Bertram [551]. A more systematic investigation of the mechanism and kinetics of citric acid amide synthesis was performed Higuchi and coworkers [552–554]. They found that interactions of carboxylic groups of citric acid and aromatic amines in aqueous solutions at 95 °C are relatively fast and depend on pH (exhibits a strong maximum). The equilibria and reactions involved appear to be rather complex, but over-all scheme in the case of warm aqueous solutions of aniline and citric acid can be represented by a series of following reversible reactions: citric acid (or dihydrogen citrate anion) $\rightleftharpoons$ cyclic citric anhydride (**B**) $\rightleftharpoons$ citric acid monoanilide ($HOOCCH_2(OH)C(CONHC_6H_5)CH_2COOH$) $\rightleftharpoons$ citranilic acid (oxygen atom of cyclic ring in (**B**) is replaced by $N\text{-}C_6H_5$ group). Citric acid monoanilide in the presence of aniline can be involved in next series of reactions: citric acid monoanilide $\rightleftharpoons$ citric acid dianilide ($C_6H_5NHCOCH_2(OH)C(CONHC_6H_5)CH_2COOH$) $\rightleftharpoons$ citranilic acid anilide (carboxylic group of citrinalic acid is now $CO\text{-}NHC_6H_5$ group). The possible mixed anilide-imide and dianilide are formed in relatively small quantities.

If citric acid is heated in an autoclave with aqueous NH_3 in the 140–160 °C temperature range, initially ammonium citrate is formed, and when dehydrated, the amide is produced. Further elimination of ammonia leads to preparation of citrazinic acid (2,6-dihydroxyisonicotinic acid) [494]. Dissolving methylene citric acid or its ahydride in the desired amine, Dulin and Martin [484] prepared a number of monoamides (N-monomethylenecitryl anthranilic acid, N-monomethylenecitryl p-aminobenzoic acid and allyl methylene citramide). Distillation of diethyl citric amide under reduced pressure and hydrolysis with alkali leads to imide of citric acid (citrimic acid-3-hydroxy-2,5-diketo-pyrolidyl-3-acetic acid) [494]. Methods of preparation of mono-, di- and triamides and some aspects associated with their physiological role were described by Cier and Drevon [555, 556].

Syntheses of many symmetrical and unsymmetrical diamides of amino acids were reported by Milewska and Chimiak [32]. They used in reactions 2-tert-butyl-1,3-di(N-hydroxysuccinimidyl) citrate and 1-tert-butyl-2,3-di(N-hydroxysuccinimidyl) citrate. In few steps, from mixed triesters of citric acid, $R_1OOCCH_2(OH)(COOR_2)CH_2COOR_3$, acting with amino acid esters, the respective symmetrical and unsymmetrical diamides of citric and amino acids were prepared, and they have the following molecular formulas $R_1OOCCH_2(OH)C(CONHCHR_5COOR_4)CH_2CONHCHR_5COOR_4$ or $R_4OOCCHR_5CO\ NHCH_2(OH)C(COOR_2)CH_2CONHCHR_5COOR_4$ where R_1, R_2, R_3, R_4 and R_5 denote various group including H, Me, Et, t-Bu and others. For isolated and identified diamides of citric and amino acids, melting points, solubilities in organic solvents and specific rotations α_D^{20} were determined.

These and similar syntheses made possible preparation, isolation, identification and characterization of various citrate-based siderophores [478, 557–589, and many references therein]. However, this group of compounds is only to a certain extent linked with the ordinary citric acid chemistry. Siderophores are more connected with biochemical aspects of the iron-transport in living organisms. Considering their biological importance, clinical applications and potential use in agriculture, a huge literature is devoted to various siderophores, but here, it is possible to present only a brief description of citrate-based siderophores [560, 567, 569, 576, 582, 584–588].

Iron in biologically relevant ferrous form (soluble, bioavailable and non-toxic) is an essential micronutrient for growth and metabolism of virtually all organisms. To fulfill this nutritional requirement in iron-deficient conditions, bacteria, fungi, algae and grasses release a low molecular weight, high-affinity ferric iron chelating compounds named siderophores. The iron uptake from an extracellular environment includes three main steps, the release of siderophores from the cell, a membrane receptor that is able to transport ferric chelate across the membrane and an enzymatic system which is capable to free iron from the chelate and disperse it within the cell. Most siderophores are either hydroxamates, catechols, α-hydroxycarboxylates or with mixed functional groups. In the case of hydroxamates and catechols, the -CONHOH groups or derivatives of isomers of dihydroxybenzene $C_6H_4(OH)_2$ are inserted in the matching carboxylic acid. There is an evidence, that citric acid behaves as a siderophore [231]. Although siderophores differ to a large extent in the structure, all of their formed ferric chelates are characterized by the exceptional thermodynamic stability.

There is a large number of naturally produced terrestrial and marine siderophores but only a small group of them are derivatives of citric acid. The marine siderophores containing "citrate skeleton", when coordinated with the Fe(III) chelate are photoreactive in natural sunlight conditions of seawater [582, 586–588, 590]. The photolysis of ferric chelate generates an oxidized ligand and an acceptable by cells iron in the ferrous Fe(II) form. Most of citrate-based siderophores are coming from biosynthetic procedures, but few of them were chemically synthesized and isolated in pure state [475, 564, 565, 567, 568, 573, 574, 579, 580, 591–594].

The structure of siderophores of citric acid can be presented formally as the following configuration: **CBABC** where **A** denotes the citrate diamide backbone $-HNCOCH_2(OH)C(COOH)COCH_2CONH-$ and **B** and **C** represent: **B**= $-CHR(CH_2)_n-$ and **C** is N-hydroxyamide group $-N(OH)COCH_3$. For example, a siderophore named schizokinen has $R=H$, and $n=2$ [558, 559, 561, 564, 566, 568, 572, 574, 577, 579, 580, 595, 596]; awaitin B has $n=3$, and anthrobactin has $n=4$ [564, 596]. If R is carboxylic group COOH, then awaitin A has $n=3$ and aerobactin is with $n=4$ [557, 565, 574, 579, 580, 596].

There are also unsymmetrical situations, when two different groups, $R=R_1$ and $R=R_2$ exist in **B** segments and similarly in **C** segments of siderophores. If one of the N(OH) groups of schizokinen is replaced by NH- group then deoxyschizokinen is formed [568]. Carboxylate type siderophore (two citrate skeleton groups) named rhizoferrin posseses the structure **ABA** which includes two symmetrical amides **A**$=HOOCCH_2(OH)C(COOH)CH2CONHCH_2$ which are separated by four methylene groups, **B**$=(CH_2)_4$ [578, 581, 592, 596–600].

From a large list of more complex siderophores which are related to citric acid skeleton it is worthwhile to note staphyloferrin A which consists of two citric residues linked by two amide bonds [570]. Aerobactin and nannochelins have $\mathbf{B_1AB_2}$ structure where **A**$=HNCOCH_2(OH)C(COOH)CH_2CONH$, $\mathbf{B_1}$ and $\mathbf{B_2}$ denote different ester groups $\mathbf{B_1}=R_1OCO(CH_2)_4NOHCOR$ and $\mathbf{B_2}=R_2OCO(CH_2)_4NOHCOR$

[573, 589, 591, 593, 596]. They are named aerobactin if $R_1 = R_2 = R = H$; nannochelin C if $R = \text{-CHCHC}_6H_5$, $R_1 = R_2 = H$; nannochelin A if $R_1 = R_2 = CH_3$ and nannochelin B if $R_1 = H$, $R_2 = CH_3$. Similar structure have various petrabactins, but with a longer chain including more amino groups and different final complex R segments, in the form of differently substituted 2,3-dihydroxybenzenes [579, 583, 589, 594, 596, 601]. There is also a number of amino analogs of citric acid siderophores [572].

There is no doubt that increased interest in citrate-based siderophores, with many possibilities to synthesize them with different combinations of organic groups, will have a stimulating effect on the ordinary chemistry of citric acid and its derivatives. Certainly, various modern experimental techniques which were applied for identification and characterization of siderophores, will also be used in the case of other organic and inorganic citrate-based compounds.

In addition to more or less systematic investigations dealing with anhydrides, esters, amides and siderophores, it should be to mention few and rather sporadic, but important studies which are also associated with citric acid. Citrazinic acid amide was prepared by De Malde and Alneri [602] by treating citric acid with urea, under pressure at 130–150 °C or with a large excess of ammonia in the 165–200 °C temperature range. In this case, considering that citrazinic acid (dihydroxypyridine-4-carboxylic acid) is heterocyclic compound, the dihydropyridine ring was established. Similarly, heating urea and citric acid in the presence of sulfuric acid uracil-acetic acid is formed [494]. The citric acid—urea system was also investigated by Paleckiene et al. [603], but in the context of liquid fertilizers containing urea and the influence of citric acid on corresponding phase equilibria. It was observed by Brettle [604] that citric acid reacts with chloral Cl_3CCHO, to give citric acid chloralide (actually, from condensation of citric acid with chloral hydrate in concentrated sulfuric acid). Two compounds were formed: 1,3-dioxalan-4-on ring with CCl_3 and two CH_2COOH groups and 1,3-dioxan-4-one ring with CCl_3, two CH_2COOH groups and H. The structure and some properties of the first compound, (5,5-bis(methylcarboxy)-2-trichlormethyl-1,3-dioxalan-4-one) were studied by Koh et al. [605].

To preparation of dialkyl-, trialkyl-, benzyl substituted citric acids was devoted investigation of Habicht and Schneeberger [606]. Brändange et al. [607] studied the absolute configuration of fluorocitric acids. By condensation of aldehydes with citric acid under influence of P_2O_5 Pette [608] prepared benzal-, 3-nitrobenzal and 4-nitrobenzalcitric acids. Katritzky et al. [609] synthesized monosubstituted L, L-aspartame citric amide. Fisher and Dangschat [610] showed that quinic acid by a number of chemical reactions can be degraded to citric acid.

Treatment of citric acid with phosphorous pentachloride PCl_5 leads to cyclic intermediate dioxachlorophosphorane which is transformed into mono-3-cytril chloride-3-dichlorophosphate ($HOOCH_2(COCl)C(OPOCl_2)CH_2COOH$. The last compound when heated gives $ClCOHC{=}C(OPOCl_2)COCl$ maleychloride-2-dichlorophosphate [494]. If citric acid is dissolved in hot melamine (2,4,6-triamino-1,3,5-triazine) then after cooling and evaporating, crystals of melaminium citrate are formed [611]. The structure of melaminium citrate was investigated by Marchewka and Pietraszko [611] and Atalay and Avci [612]. Melamine itself has a wide application in polymer industry as constituent of automobile paints.

Starting with the isolation of citric acid by Scheele in 1784 to modern times, chemical reactions involving citric acid were similar to those performed with other carboxylic or α-hydroxycarboxylic acids. Initially, they included neutralization reactions with formation of various inorganic citrates. Later on, a great deal of energy was devoted to preparation of esters and amides, but contrary to other carboxylic acids, significantly less attention was dedicated to chemical synthesis of citric acid. This can be justified by the fact that actually citric acid was and is produced in the fermentation process with *Aspergillus niger*. There is no doubt, that citric acid chemistry also was driven strongly forward considering that citric acid is an important participant of the Krebs cycle. However, with passing time, a number of investigations associated with formation of citrates, esters, amides and other compounds rapidly declined. However, this is not the case when degradation processes and analytical methods are considered. Chemical analysis of industrial and biological samples containing citric acid were and continue to be a very active field, similarly as thermal degradation of various citrates which are serving as precursors in preparations of important ceramic materials. Studies dealing with complexation reactions of various metals with citric acid were always very popular in the literature. However, the discovery of siderophores put them on a quite different level, not only in the case of iron-citrate complexes, and beyond doubt, citrate-based siderophores are responsible for revitalization of entire citric acid chemistry.

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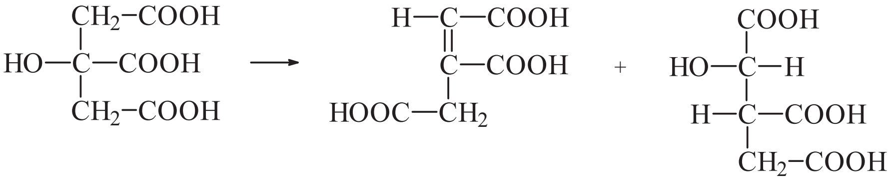
Chapter 5
Physicochemical Properties of Inorganic Citrates

5.1 Application of Inorganic Citrates and Their Crystal Structures

Physicochemical properties of solid inorganic salts of citric acid (neutral and acidic citrates) is less documented in the literature than those of citric acid, but citrates of alkali, alkaline earths and some transitional and other metals were intensively investigated considering their biological, pharmaceutical, chemical, industrial, and environmental importance. Specifically, citrates similarly as citric acid are used in production of soft drinks and in food industry as nutrients and food additives, as acidity regulators, antioxidants, buffering, firming, preservative and stabilizing agents. Many of them serve as dietary or nutritional supplements against iron, copper, zinc and other trace mineral deficiencies. They are also used in producing of cosmetics, medicaments, plastics, photographic and other materials. Inorganic citrates are produced by direct neutralizations of aqueous solutions of citric acid by the corresponding bases or by titrations of soluble in water salts with solutions containing citrate ions.

There is a large group of X-ray studies leading to the crystal structures of simple solid citrates and various rather complex citrates (Table 5.1). These investigations include also preparation and isolation procedures for considered crystals and sometimes also their magnetic or other properties. Initially, most of investigations were motivated by biological interest associated with the aconitase, the enzyme that catalyses stereo-specific isomerization of citrate to isocitrate and establishes equilibrium between ions of citric acid (**A**), cis-aconitic acid (**B**) and d-isocitric acid (**C**) in the Krebs tricarboxylic acid cycle. This is essential step in the cycle which is mainly responsible for the conversion of the combustion energy of carbohydrates, proteins and fats into the form which is suitable for living organisms.



$$\begin{array}{l} \mathrm{CH_2{-}COOH} \\ \mathrm{HO{-}C{-}COOH} \\ \mathrm{CH_2{-}COOH} \end{array} \longrightarrow \begin{array}{r} \mathrm{H{-}C{-}COOH} \\ \mathrm{C{-}COOH} \\ \mathrm{HOOC{-}CH_2} \end{array} + \begin{array}{r} \mathrm{COOH} \\ \mathrm{HO{-}C{-}H} \\ \mathrm{H{-}C{-}COOH} \\ \mathrm{CH_2{-}COOH} \end{array}$$

A **B** **C**

A. Apelblat, *Citric Acid,* DOI 10.1007/978-3-319-11233-6_5

Table 5.1 References to the crystal structures of inorganic citrates

Citrate	Ref.
$Li_3Cit\cdot 2H_2O$	[1]
$Li_3Cit\cdot 5H_2O$	[2]
LiH_2Cit	[1, 3]
$LiH_2Cit\cdot H_2O$	[1, 4]
$Li(NH_4)HCit\cdot H_2O$	[1, 5]
$LiRbHCit\cdot H_2O$	[1]
$(NH_4)_3Cit$	[6]
$(NH_4)H_2Cit$	[1]
$(NH_4)_2HCit$	[1]
$LiKHCit\cdot KH_2Cit\cdot H_2O$	[7]
$Na_3Cit\cdot 2H_2O$	[8, 1, 9]
$Na_3Cit\cdot 5H_2O$	[8, 1]
$Na_3Cit\cdot 5.5H_2O$	[10, 11]
NaH_2Cit	[1, 12]
$Na_2HCit\cdot H_2O$	[1]
$K_3Cit\cdot H_2O$	[8, 1]
K2HCit	[13]
KH_2Cit	[1]
$Rb_3Cit\cdot H_2O$	[1]
RbH_2Cit	[14, 15]
$Mg_3(Cit)_2\cdot 10H_2O$	[16]
$Ca_3(Cit)_2\cdot 4H_2O$	[17, 18]
$CaHCit\cdot 3H_2O$	[19]
$Ca[B(HCit)_2]\cdot 4H_2O\cdot HCl$	[20]
$Sr_3(Cit)_2\cdot 5H_2O$	[21]
$LaCit\cdot 3H_2O$	[22]
$K[B(HCit)_2]\cdot 2H_2O$	[23]
$Sr[BHCit\cdot Cit]\cdot 7H_2O$	[24]
$Cu[B(HCit)_2]\cdot 10H_2O$	[25]
$NdCit\cdot 3H_2O$	[26]
$(NH_4)_4[Ti_2O_4(Cit*)_2]\cdot 2H_2O$	[27]
$(NH_4)_8[Ti_4O_8(Cit*)_4]\cdot 8H_2O$	[28]
$Na_3[Ti(HCit)_2\cdot Cit]\cdot 9H_2O$	[29]
$Na_7[TiH(Cit*)_3]\cdot 18H_2O$	[30]
$Na_8[Ti(Cit*)_3]\cdot 17H_2O$	[31]
$K_4[TiHCit(Cit)_2]\cdot 4H_2O$	[32]
$K_5[Ti\ (Cit)_3]\cdot 4H_2O$	[33]
$K_7[Ti_2(Cit\cdot HCit)_3]\cdot 10H_2O$	[34]
$Ba_2[TiHCit(Cit)_2]\cdot 8H_2O$	[35]
$(NH_4)_7Ba_3[Ti_{2(}Cit\cdot Cit*)_3]\cdot 15H_2O$	[36]

Table 5.1 (continued)

Citrate	Ref.
$(NH_4)_2Mn[Ti_2(HCit)_6] \cdot 12H_2O$	[30]
$(NH_4)_2Fe[Ti_2(HCit)_6] \cdot 12H_2O$	[30]
$(NH_4)_5Fe[Ti_2(HCit \cdot Cit)_3] \cdot 9H_2O$	[32]
$(NH_4)_2Co[Ti_2(HCit)_6] \cdot 12H_2O$	[30]
$(NH_4)_2Ni[Ti_2(HCit)_6] \cdot 12H_2O$	[30]
$(NH_4)_2Cu[Ti_2(HCit)_6] \cdot 12H_2O$	[30]
$(NH_4)_2Zn[Ti_2(HCit)_6] \cdot 12H_2O$	[30]
$(NH_4)_4[V_2O_4(Cit^*)_2] \cdot 2H_2O$	[33]
$(NH_4)_4[V_2O_4(Cit)_2] \cdot 4H_2O$	[34]
$(NH_4)_6[V_2O_4(Cit)_2] \cdot 6H_2O$	[34]
$(NH_4)_2[V_2O_4(HCit)_2] \cdot 2H_2O$	[35]
$(NH_4)_4K_2[V_2O_4(Cit^*)_2] \cdot 6H_2O$	[36]
$Na_4[V_2O_2(Cit^*)_2] \cdot 6H_2O$	[38]
$Na_4\ [V_2O_4(Cit^*)_2] \cdot 12H_2O$	[33]
$Na_2K_2[V_2O_4(HCit)_2] \cdot 9H_2O$	[37]
$K_2[V_2O_4(HCit)_2] \cdot 4H_2O$	[38]
$Na_{10}[NaPd_3(Cit)_3]_2 \cdot 31H_2O$	[39]
$[Co(NH_3)_6]_2K[Nd_3(Cit)_4].21H_2O$	[40]
$(NH_4)_6[Be_2Al_2(Cit)_4]$	[41]
$K_3[V_2O_2Cit.Cit^*] \cdot 7H_2O$	[33]
$K_4[V_2O_4(Cit)_2] \cdot 5.6H_2O$	[42]
$K_2[V_2O_6(HCit)_2] \cdot 4H_2O$	[35]
$K_2[V_2O_6(HCit)_2] \cdot 2H_2O$	[43]
$(NH_4)_4[CrCit \cdot Cit^*] \cdot 3H_2O$	[44, 45]
$Na_3[Cr(Cit)_2] \cdot 8.5H_2O$	[44, 45]
$K_4[MoO_3Cit^*] \cdot 2H_2O$	[46]
$K_4[Mo_2O_5(Cit)_2Cit^*] \cdot 4H_2O$	[46]
$K_2Na_4[Mo_2O_5(Cit)_2] \cdot 5H_2O$	[47]
$Na_6[W_2O_5(Cit^*)_2] \cdot 10H_2O$	[48, 49]
$K_4[WO_3Cit^*] \cdot 2H_2O$	[50]
$NaK_3[W_2O_5(Cit)_2] \cdot H_2O$	[50]
$(NH_4)_4[WO_3Cit^*] \cdot 2H_2O$	[51]
$(NH_4)_3[LiWO_3 \cdot Cit^*] \cdot 3H_2O$	[52]
$Mn_3(Cit)_2 \cdot 10H_2O$	[53, 54]
$(NH_4)_4[Mn(II)(Cit)_2]$	[55]
$(NH_4)_5[Mn(III)(Cit^*)_2]$	[55]
$Fe_3(Cit)_2 \cdot 10H_2O$	[56]
$(NH_4)_5[Fe(III)(Cit^*)_2] \cdot 2H_2O$	[57]
$Na_2[Co_2(Cit)_2] \cdot 10H_2O$	[58]
$(NH_4)_2[Ni_2(Cit)_2] \cdot 6H_2O$	[59]

Table 5.1 (continued)

Citrate	Ref.
$(NH_4)_4[Ni\ (Cit)_2] \cdot 2H_2O$	[59]
$[Co(NH_3)_6][Sb(Cit)_2] \cdot 5H_2O$	[60]
$K_2[Co_2(Cit)_2] \cdot 10H_2O$	[58]
$K_2[Ni_2(Cit)_2] \cdot 8H_2O$	[61]
$Cu_2Cit*2H_2O$	[62]
$(NH_4)_4[Cu(Cit)_2]$	[63]
$[CuSbH_2Cit \cdot Cit] \cdot 4.5H_2O$	[64]
$(NH_4)_4[Zn(Cit)_2]$	[65]
$Na_4[Zn(Cit)_2] \cdot 5.5H_2O$	[11]
$K_4[Zn(Cit)_2]$.	[11]
$[Cd_3(Cit)_2] \cdot 6H_2O$	[66]
$NH_4[CdCit] \cdot 2H_2O$	[66]
$(NH_4)_5[Al(Cit*)_2] \cdot 2H_2O$	[67, 68]
$(NH_4)_4[AlCit \cdot Cit*] \cdot 3H_2O$	[68]
$K_4[Al \cdot Cit \cdot Cit*] \cdot 4H_2O$	[68]
$(NH_4)_3[Ga\ (Cit)_2] \cdot 4H_2O$	[69, 70]
$(NH_4)_5[Ga\ (Cit*)_2] \cdot 2H_2O$	[68]
$(NH_4)_4[Ga \cdot Cit \cdot Cit*] \cdot 3H_2O$	[68]
$K_4[Ga \cdot Cit \cdot Cit*] \cdot 4H_2O$	[68]
$Fe[Ge(HCit)_2] \cdot 10H_2O$	[71]
$[Sn_2Cit*]$	[72]
$(NH_4)_2[SnCit*]$	[72]
$Na_2[SnCit*]$	[72]
$K_2[SnCit*]$	[72]
$[ZnSnCit*]$	[72]
$Na[Pb_5(HCit.Cit)_3] \cdot 15.5H_2O$	[73]
$Li[Sb(Cit)_2] \cdot 3H_2O$	[74]
$K_2[Sb_4(Cit)_8] \cdot 2H_2O$	[74]
$Na[Sb\ (HCit)_2] \cdot 3H_2O$	[75]
$Ag_2[Sb_2(HCit)_4]$	[75]
$K[BiCit*] \cdot 3.5H_2O$	[76]
$K(NH_4)[BiCit*]_2 \cdot 4H_2O$	[77]
$K(NH_4)[BiCit*]_2 \cdot 6H_2O$	[77]
$(NH_4)_{12}[Bi_{12}O_8\ (Cit*)_8] \cdot 10H_2O$	[78]
$Sr[B(Cit)_2] \cdot 7H_2O$	[79]
$[(UO_2)_3(HCit)_2] \cdot 5H2O$	[80]
$[Co(NH_3)_6]_6K[Am_3(Cit)_4].21H_2O$	[40]
$(NH_4)_{18}[Be_6Al_6(Cit*)_6(PO_4)_8]$	[41]

$Cit = C_6H_5O_{7,}$ $Cit* = C_6H_4O_7$

These early X-ray crystal structure studies were summarized and reviewed by Glusker [81]. In later investigations, the reason to perform structural analysis of particular citrate is explained by its applicability, physiological functions and bioactivity, taking into account that many citrates play an important role in the metabolism of metals in living organisms (V, Cr, Mo, Fe, Co, Zn and others). Sodium, potassium, magnesium, calcium, iron, copper and zinc citrates are used as food additives and dietary supplements. Calcium citrate serves also as a water softener. Sodium citrate is used as an anticoagulant for collection and preservation of blood, as buffer in diverse applications and in photography as a supplement in galvanic solutions. Disodium hydrogen citrate can be applied in the stabilization of penicillin-salt solutions [82]. Potassium citrate is primarily used as a buffering agent in soft drinks, but it reduces a highly acidic urine and therefore is useful in the treatment of mild urinary tract infections. Lithium citrate is a mood stabilizer in psychiatric treatment of manic states and bipolar disorder. A number applications in medicine are associated with magnesium citrate. This citrate is a powerful laxative and for this reason is used to empty the bowel prior a major surgery or colonoscopy. Magnesium citrate aids also in fighting depression and in relaxing of muscles. Ammonium ferric citrate as a source of iron is used in cell culture procedures.

In connection with the bio-toxicity of aluminum, copper, chromium, nickel, cadmium and lead elements, their citrates are intensively studied. Zinc citrate is linked to the genetic disorder to zinc metabolism (acrodennatitis enteropathica). Zinc citrate due to its antimicrobial and anti-inflammatory behaviour is also used in dental care products such as toothpastes and chewing gums. Bismuth citrates are used in a variety of gastrointestinal disorders (e.g. for treatment of peptic ulcers). Gallium and technetium citrate complexes are important in nuclear medicine because ^{67}Ga accumulates in soft tumor tissues and Tc^{99m} in bones and therefore they can be used in radiodiagnostic procedures. Titanium(IV) citrates serve as soluble precursors in the preparation of titanium oxide materials (e.g. $MeTiO_3$, Me = Mg, Ca, Sr, Ba, Pb; $La_2Ti_2O_7$ and $Y_2Ti_2O_7$) but on the other side, titanium damages and raptures red blood cells [83]. Similarly, rare-earth citrates (e.g. $LaCr(Cit)_2 \cdot 2H_2O$) are used as precursors in a low-temperature preparation of useful perovskite oxides. Citrates are precursors in the colloid synthesis of gold and silver nanoparticles by using citrate ions in reduction reactions [84, 85–92]. Vanadium and molybdenum systems with citrate ions are important because these metals are involved in the nitrogen fixation (nitrogenase).

Thermal decomposition of simple citrates or mixed-metal citrates is in many cases associated with preparation of technologically useful ceramic and other materials. A very large number of studies is devoted to applications of citrates as precursors, only few additional examples, to already mentioned above are given here. Nickel iron hexahydrate $Ni_3Fe_6O_4(Cit)_8 \cdot 6H_2O$ is precursor in the synthesis of ultrafine $NiFe_2O_4$ ferrites [93]. Barium titanium citrates $BaTi(HCit)_3 \cdot 6H_2O$ and $Ba_2Ti(HCit \cdot Cit) \cdot 7H_2O$ were transformed at high temperature into barium titanate $BaTiO_3$ [94, 95]. Ultrafine rare-earth iron garnets $RE_3Fe_5O_{12}$, RE = Sm, Tb, Dy, Ho, Er and Yb, were synthesized from citrate $Fe_3Fe_5(Cit)_{25} \cdot (36+n) \cdot H_2O$ gels [96–99]. Bismuth citrate $BiCit \cdot 2H_2O$ served to produce bismuth sulfide Bi_2S_3 nanorods [98].

Spinel ferrites $MeFe_2O_4$, Me = Mn, Co, Ni Cu were prepared by thermal decomposition of $Me_3[Fe(Cit)_2]_2 \cdot xH_2O$ citrates [99, 100] and there are many other similar investigations [101].

In addition to a vital information required to produce solid materials of desired properties, the first and foremost reason to perform thermal analysis is linked with the knowledge about the change in stoichiometry, dehydration, properties and stability of citrates. These studies help to understand the mechanism of decomposition process, its intermediate and final products. Maslowska et al. [102] reported about thermal decomposition of hydrates of alkaline-earth and transition metal citrates, $Mg_3(Cit)_2 \cdot 4H_2O$, $Ca_3(Cit)_2 \cdot 4H_2O$, $Mn_3(Cit)_2 \cdot 9H_2O$, $Co_3(Cit)_2 \cdot 8H_2O$, $Ni_3(Cit)_2 \cdot 10H_2O$, $Cu_3(Cit)_2 \cdot 5H_2O$, $Zn_3(Cit)_2 \cdot H_2O$, $FeCit \cdot 3H_2O$, $CrCit \cdot 6H_2O$ and $AlCit \cdot 4H_2O$. Calcium, barium, zinc, iron and bismuth citrates $Ca_3(Cit)_2 \cdot 4H_2O$, $Ba_3(Cit)_2 \cdot 2H_2O$, $Zn_3(Cit)_2$, $FeCit \cdot 2H_2O$ and $Bi_3(Cit)_2 \cdot H_2O$ were investigated by Strivastava et al. [103–105]. Mansour [106–108] studied magnesium, and calcium citrates $Mg_3(Cit)_2 \cdot 14H_2O$, $Ca_3(Cit)_2 \cdot 4H_2O$ and anhydrous bismuth citrate BiCit. Thermal decomposition of citrates used in medicine, $Li_3Cit \cdot 5H_2O$, $K_3Cit \cdot H_2O$, $Mg_3(Cit)_2$ and $BiCit \cdot 2H_2O$, were examined by Tabón-Zapata et al. [109], Duval [110], Szynkaruk et al. [111] and Radecki and Wesolowski [112]. Thermal pyrolysis of lead citrates, $Pb_3(Cit)_2 \cdot 2H_2O$ and $Pb_3(Cit)_2 \cdot 4H_2O$ to obtain the pyrophosporic lead as the final product, is described by Charles et al. [113] and Brown [114]. Thermal decomposition of iron citrate pentahydrate using the Mössbauer technique was performed by Bassi et al. [115]. Devi and Rao [116] investigated degradation of $LaCit \cdot 4H_2O$ and $CrCit \cdot 5H_2O$ at higher temperatures, up to 600 °C. Thermoanalytical properties of triammonium citrate were established by Erdey et al. [117]. Thermal studies of citrates of rare-earth elements of the type $RECit \cdot xH_2O$ and $RE_2(HCit)_3 \cdot 2H_2O$ (RE = La, Ce, Pr, Nd, Sm and Eu) were also studied [118–120, 121].

5.2 Solubilities of Inorganic Citrates in Water

As mentioned above, physical properties of aqueous solutions of inorganic citrates were systematically investigated only in few cases. These are aqueous solutions of neutral and acidic sodium and potassium citrates and diammonium hydrogen citrate. Mostly, the volumetric and compressibility properties are reported, and they are based on measured densities and speed velocities. In dealing with a particular physical property, all available citrates are considered together.

Solubilities of inorganic citrates in water or in aqueous electrolyte solutions as a function of temperature are known for a small number of citrates. They include very soluble in water trisodium citrate hydrates, tripotassium citrate and potassium dihydrogen citrate dihydrate and sparingly soluble trimagnesium dicitrate hydrates, tricalcium dicitrate tetrahydrate and iron(III) citrate monohydrate [85, 122–133]. Besides solubilities, Gao et al. [131] also reported that the transition temperature from the $Na_3Cit \cdot 5.5H_2O$ to $Na_3Cit \cdot 2H_2O$ hydrate appears at 42.2 °C (Table 5.2).

Considering importance of calcium citrates ($Ca_3(Cit)_2 \cdot 4H_2O$ and $Ca_3(Cit)_2 \cdot 6H_2O$) in citric acid production, milk products and in medical procedures [134], its

Table 5.2 Solubility of inorganic citrates in water as a function of temperature

t/°C	*m*/mol kg^{-1}	t/°C	*m*/mol kg^{-1}	*t*/°C	*m*/mol kg^{-1}
$Mg_3(Cit)_2 \cdot 14H_2O$ [129]		$Ca_3(Cit)_2 \cdot 4H_2O$ [129]		$FeCit \cdot H_2O$ [129]	
13.20	0.0295	10.24	0.0017	11.74	0.0073
15.90	0.0314	10.89	0.0021	13.39	0.0090
20.61	0.0393	13.58	0.0018	14.93	0.0100
22.08	0.0416	16.56	0.0019	18.79	0.0099
25.11	0.0446	16.66	0.0019	19.45	0.0147
29.77	0.0514	22.80	0.0018	28.07	0.0260
38.19	0.0642	28.64	0.0017	36.11	0.0365
41.01	0.0777	36.32	0.0017	39.86	0.0435
43.08	0.0836	41.55	0.0016	43.59	0.0515
47.19	0.1016	50.18	0.0015	49.39	0.0590
49.23	0.1028	58.62	0.0014	52.18	0.0680
53.14	0.1077	18.00	0.0018 [123]		
58.35	0.1414	25.00	0.0020		
$Mg_3(Cit)_2 \cdot 9H_2O$ [129]		18.00	0.0020 [126]	K_3Cit [133]	
13.04	0.0467	25.00	0.0023	15.0	4.582
24.93	0.0482	25.00	0.0015 [123]	20.0	4.840
37.76	0.0546			25.0	5.095
44.22	0.0563			30.0	5.398
52.74	0.0643				
57.85	0.0705				
$Na_3Cit \cdot 5.5H_2O$ [131]		$Na_3Cit \cdot 2H_2O$ [131]		$KH_2Cit \cdot 2H_2O$ [132]	
10.0	1.2323	35.0	1.5609	15.0	0.6638
15.0	1.2692	40.0	1.5735	25.0	1.0552
20.0	1.3112	45.0	1.5878	35.0	2.0208
25.0	1.3567	50.0	1.6048	35.0	1.7927
30.0	1.4099	55.0	1.6251	45.0	3.4322
35.0	1.4760	60.0	1.6478	55.0	6.3891
40.0	1.5472	65.0	1.6738	55.0	6.3634
45.0	1.6210	70.0	1.7014		

solubility and dissociation equilibria were discussed by Chatterjee and Dhar [122], Shear and Kramer [123, 134], Hastings et al. [124], Joseph [125], Boulet and Marier [126], Meyer [127], Singh et al. [128], Wiley [135], Muus and Lebel [136] and Al-Khaldi et al. [137]. Chatterjee and Dhar [122] observed that solubility of $Ca_3(Cit)_2 \cdot 6H_2O$ increases with temperature and $Ca_3(Cit)_2 \cdot 4H_2O$ decreases, which was also observed by others. Their only measured values of solubility at 30 and 93 °C are incorrect, and should be lower at least by factor two. Boulet and Marier [126] measured solubilities in aqueous solutions of variable ionic strength at 21 and 93 °C and found that the solubility products are unaffected by pH and temperature, and can be expressed by the following expression $pK_{sp} = 17.63 - 10.84\sqrt{I}$. Ciavatta et al. [130] determined solubilities of $Ca_3(Cit)_2 \cdot 4H_2O$ in the 0–3.5 molal solutions of $NaClO_4$ at 25 °C, and reported the value of $pK_{sp} = 17.81$ for pure water. Their solubilities can correlated by

$$
\begin{aligned}
&m[\mathrm{Ca_3(Cit_2)}, 298.15\mathrm{K}] / \mathrm{mol \cdot kg^{-1}} = 1.530 \cdot 10^{-3}\sqrt{m^*} - 3.759 \cdot 10^{-4} m^* \\
&m^* = m(\mathrm{NaClO_4}) / \mathrm{mol \cdot kg^{-1}}
\end{aligned}
\qquad (5.1)
$$

Difficulty to measure very low solubilities is clearly illustrated in the case of dissolution of calcium citrate at 25 °C in pure water (Fig. 5.1). The scattering of experimental solubilities for more soluble magnesium and iron citrates is less pronounced (Fig. 5.2). From similar investigations, it is worthwhile to mention also the Bolton [138] detailed solubility study in systems included trisodium citrate, acetylsalicylic acid (aspirin) and benzoic acid.

Solubility products K_{sp} of Mg, Ca, Zn, Cd, Hg and Th citrates and those of the rare earth element citrates (La, Ce, Pr, Nd, Eu, Gd, Tb, Dy, Ho, Er and Y) in 0.1 M (H, Na) ClO_4 solutions were reported at 25 °C by the Skornik group [139–146] (Table 5.3). They also determined solubilities of some rare earth citrates in HCl and KOH solutions and found that these solubilities are larger than those in pure water and increase with

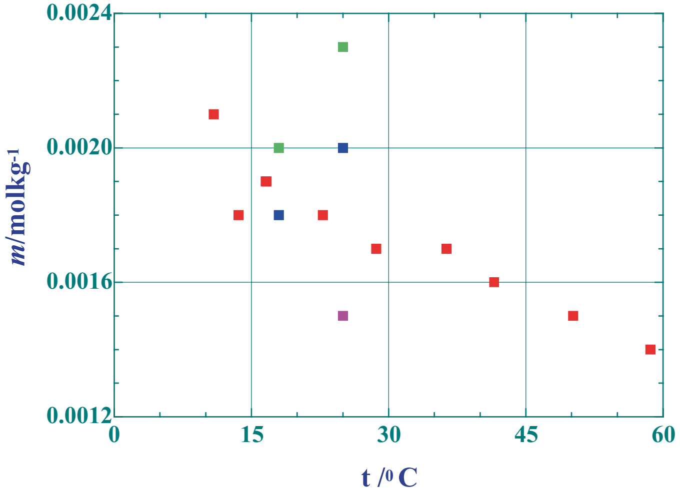


Fig. 5.1 Solubility of calcium citrate tetrahydrate in water as a function of temperature. 🟦 - [123], 🟩 - [126], 🟥 - [129], 🟪 - [130]

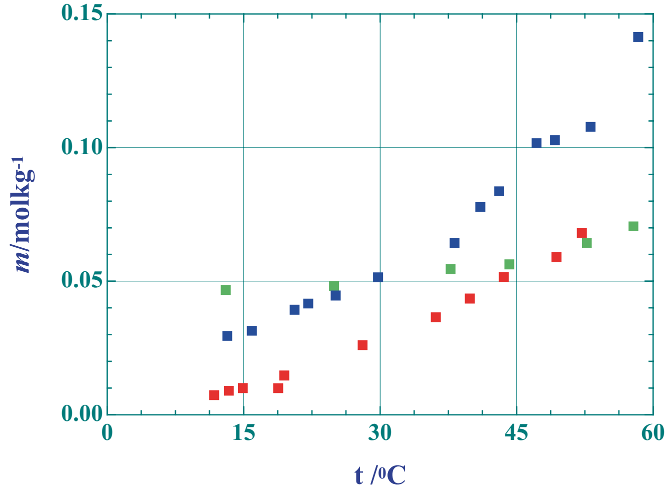


Fig. 5.2 Solubility of magnesium and iron citrates in water as a function of temperature. 🟩 - magnesium citrate nonahydrate, 🟦 - magnesium citrate tetradecanehydrate and 🟥 - iron(III) citrate monohydrate [129]

the added electrolyte. Furthermore, the common-ion effect and the influence of pH on the solubility was investigated (Table 5.4) by measuring solubilities in solutions of Li, Na, K, Cs, Mg, Ca, Ba, Zn, Cd and Hg citrates. At constant ionic strength, a distinct minimum in the solubility was observed in the $pH_{sat.}$ 5.0–6.5 region (Fig. 5.3).

In most reported solubility determinations, the solid phase compositions in equilibrium with saturated solutions were not established. And therefore, they are uncertain with regard to transition temperatures of different hydrates. Thus, in the investigated temperature range, solubilities presented in Tables 5.2 and 5.3 describe not only thermodynamically stable but probably also metastable states.

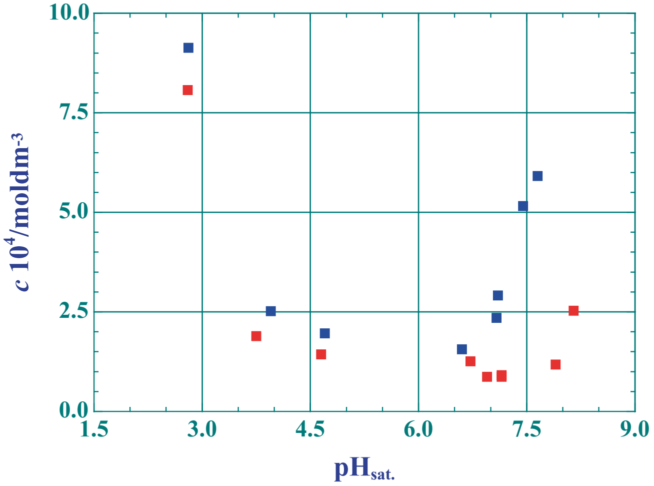


Fig. 5.3 Solubility of lanthanum and neodymium citrates in sodium perchlorate solutions of total ionic strength I = 0.1 M, as a function of pH of saturated solutions [141]. 🟥 - $LaCit \cdot 3H_2O$, 🟦 - $NdCit \cdot 3H_2O$

Table 5.3 Solubility products of inorganic citrates in 0.1 M (H, Na)ClO_4 solutions at 25 °C

Citrate	K_{sp}	Reference
$Mg_3(Cit)_2 \cdot 15H_2O$	$(7.94 \pm 0.72) \cdot 10^{-12}$	[146]
$Ca_3(Cit)_2 \cdot 4H_2O$	$(2.18 \pm 0.57) \cdot 10^{-15}$	
$Zn_3(Cit)_2 \cdot 2H_2O$	$(3.01 \pm 1.33) \cdot 10^{-20}$	
$Cd_3(Cit)_2 \cdot 2H_2O$	$(7.55 \pm 1.88) \cdot 10^{-19}$	
$(Hg_2)_3(Cit)_2 \cdot 4H_2O$	$(8.92 \pm 3.03) \cdot 10^{-28}$	
$Hg_3(Cit)_2 \cdot 3.5H_2O$	$1.6 \cdot 10^{-33}$	
$Th_3(Cit)_4 \cdot 7.5H_2O$	$(7.08 \pm 2.85) \cdot 10^{-56}$	[144]
$LaCit \cdot 3H_2O$	$(1.96 \pm 0.08) \cdot 10^{-11}$	[142]
$LaCit \cdot 3H_2O^a$	$8.6 \cdot 10^{-13}$	
$CeCit \cdot 3.5H_2O$	$(1.56 \pm 0.05) \cdot 10^{-11}$	[143]
$PrCit \cdot 3.5H_2O$	$(1.06 \pm 0.12) \cdot 10^{-11}$	
$PrCit \cdot 3.5H_2O^a$	$4.6 \cdot 10^{-13}$	[142]
$NdCit \cdot 3.5H_2O$	$(1.30 \pm 0.07) \cdot 10^{-11}$	[143]
$NdCit \cdot 3.5H_2O^a$	$5.7 \cdot 10^{-13}$	[142]
$EuCit \cdot 4H_2O$	$(0.97 \pm 0.60) \cdot 10^{-12}$	
$GdCit \cdot 4H_2O$	$(1.32 \pm 0.04) \cdot 10^{-12}$	
$TbCit \cdot 5H_2O$	$(1.51 \pm 0.12) \cdot 10^{-12}$	
$DyCit \cdot 4H_2O$	$(3.20 \pm 0.04) \cdot 10^{-12}$	
$HoCit \cdot 4H_2O$	$(2.99 \pm 0.21) \cdot 10^{-12}$	
$YCit \cdot 5H_2O$	$(0.94 \pm 0.04) \cdot 10^{-11}$	[16]

[a] Extrapolated to $I = 0$

Since activity coefficients of citrates in saturated solutions are usually unknown, the apparent molar enthalpy of solution ΔH_{sol} is only available from the temperature dependence of solubility [147]

$$\Delta H_{sol.} = \nu R T^2 \left(1 - \frac{h\, m\, M_1}{1000}\right) \left(\frac{\partial \ln m}{\partial T}\right)_{P,\, sat.} \tag{5.2}$$

where h denotes the hydration number and ν is the total number of ions formed by one molecule of citrate.

If solubilities are expressed by

$$\ln m = A + \frac{B}{T} + C \ln T \tag{5.3}$$

then from Eqs. (5.2) to (5.3), it follows that

$$\Delta H_{sol.} = \nu R \left(1 - \frac{h\, m\, M_1}{1000}\right)(CT - B) \tag{5.4}$$

Table 5.4 Solubilities of rare-earth element citrates at 25 °C as a function of pH in aqueous solutions of electrolytes

Citrate	$pH_{initial}$	$pH_{sat. solution}$	$c.10^4$/mol dm^{-3}	
$LaCit \cdot 3H_2O$		6.70	1.8	H_2O, [145]
	2.0	2.4	27	HCl^a, [139]
	3.2	3.7	1.94	
	3.5	4.0	1.22	
	4.1	7.2	1.23	
		8.20	13.5	KOH^b, [145]
		8.62	26.5	
		8.38	37.6	
		6.84	3.06	0.000246 M Na_3Cit^c
		6.89	8.75	0.00123 M Na_3Cit^c
		6.73	8.70	0.00123 M Na_3Cit^c
		7.18	8.14	0.00123 M Na_3Cit^c
		6.68	26.5	0.00492 M Na_3Cit^c
		7.14	62.2	0.0123 M Na_3Cit^c
		8.70	44.8	Na_3Cit^d, [145]
		8.64	32.9	
		8.40	17.5	
		8.68	75.0	
	8.0	6.5	41.0	1.0 M Li_3Cit, [140]
	5.9	5.5	12.0	0.25 M Na_3Cit
	6.0	5.6	19.0	0.50 M Na_3Cit
	6.2	5.6	31.0	0.75 M Na_3Cit
	8.0	6.5	47.0	1.0 M Na_3Cit
	7.8	6.5	61.0	1.0 M K_3Cit
	6.4	5.5	65.0	1.0 M $Cs_3(Cit)_2$
	5.6	6.8	1.7	$Zn_3(Cit)_2{}^e$, [140]
	6.2	6.8	1.8	$Cd_3(Cit)_2{}^e$
	5.7	6.8	1.9	$Hg_3(Cit)_2{}^e$
	2.3	2.80	8.07	$NaClO_4{}^f$, [141]
	3.15	3.75	1.89	
	4.10	4.65	1.43	
	6.15	6.95	0.87	
	7.15	6.72	1.26	
	7.65	7.15	0.87	
	9.2	7.15	0.91	
	9.67	7.90	1.18	
	10.6	8.15	2.53	
$CeCit \cdot 3.5H_2O$		2.32	19.2	0.1 M (H, Na)ClO_4,
		2.39	4.51	[143]
		2.62	3.40	
		2.73	2.06	
		2.88	3.01	
		3.24	2.08	
		6.00	2.16	
		6.20	2.81	
$PrCit \cdot 3.5H_2O$	2.0	2.4	6.02	HCl^a, [139]

Table 5.4 (continued)

Citrate	$pH_{initial}$	$pH_{sat.\ solution}$	$c.10^4$/mol dm^{-3}	
	3.0	3.0	5.27	
	2.9	3.7	6.03	
	3.5	5.8	3.26	
	4.1	5.4	2.48	
	3.8	6.0	3.12	
	2.30	2.80	9.07	$NaClO_4$[f], [141]
	3.15	3.58	2.32	
	4.10	4.50	1.50	
	5.20	6.60	1.33	
	6.15	7.05	1.33	
	7.15	6.85	1.23	
	7.65	7.40	1.68	
	9.20	7.40	1.85	
	9.65	7.15	3.45	
	10.6	7.60	4.52	
		7.40	5.5	0.000123 M Na_3Cit[c]
		7.45	6.3	0.00250 M Na_3Cit[c]
		6.82	4.92	0.00066 M Na_3Cit[c]
		7.43	4.9	0.00072 M Na_3Cit[c]
		7.25	23.0	0.00246 M Na_3Cit[c]
		7.35	35.5	0.00355 M Na_3Cit[c]
$NdCit \cdot 3.5H_2O$	2.0	2.5	41.0	HCl[a], [139]
	2.9	3.3	6.78	
	3.6	6.8	6.16	
	3.8	5.0	3.67	
	4.3	7.0	3.53	
	2.30	2.81	9.13	$NaClO_4$[f], [141]
	3.15	3.95	2.52	
	4.10	4.70	1.96	
	5.20	6.60	1.56	
	7.17	7.10	2.91	
	9.20	7.08	2.35	
	9.65	7.65	5.91	
	10.6	7.45	5.16	
		6.3	5.07	0.000332 M Na_3Cit[c]
		6.3	6.03	0.000415 M Na_3Cit[c]
		6.3	8.85	0.00083 M Na_3Cit[c]
		6.3	16.9	0.00166 M Na_3Cit[c]
		6.3	67.0	0.0083 M Na_3Cit[c]
$SmCit \cdot 3.5H_2O$	1.6	2.3	28.5	HCl[a], [139]
	1.6	2.0	28.3	
	2.0	2.5	27.9	
	3.0	4.2	6.18	
	4.4	6.6	3.72	
$SmCit \cdot 4H_2O$		2.13	38.5	0.1 M (H, Na)ClO_4,
		2.20	28.1	[143]
		2.33	20.3	
		2.44	15.1	
		3.10	4.0	

Table 5.4 (continued)

Citrate	$pH_{initial}$	$pH_{sat. solution}$	$c.10^4$/mol dm^{-3}	
		4.18	3.4	
		6.46	1.7	
$GdCit \cdot 4H_2O$	2.0	2.5	27.3	HCl[a], [139]
	3.0	6.2	5.8	
	4.0	6.3	5.6	
		6.4	8.2	$Zn_3(Cit)_2$[e], [140]
		6.8	8.6	$Cd_3(Cit)_2$[e]
		6.5	7.5	$Hg_3(Cit)_2$[e]
	8.0	6.3	61.0	1.0 M Li_3Cit, [140]
	8.0	6.6	79.0	1.0 M Na_3Cit
	7.8	6.8	92.0	1.0 M K_3Cit
		1.89	93.5	0.1 M (H, Na)ClO_4,
		2.20	37.0	[143]
		2.33	26.3	
		2.44	21.0	
		2.46	18.7	
		2.47	15.3	
		2.69	7.6	
		2.89	4.3	
		6.62	3.7	
		6.63	3.6	
		6.76	3.5	
	2.3	3.25	6.75	$NaClO_4$[f], [141]
	5.2	6.77	3.03	
	7.15	6.5	2.70	
	9.2	7.25	2.92	
	10.6	7.0	8.93	
$TbCit \cdot 5H_2O$		2.03	3.99	0.1 M (H, Na)ClO_4,
		2.30	23.0	[143]
		2.35	23.3	
		2.36	21.5	
		2.48	18.0	
		3.14	4.5	
		6.5	1.5	
$DyCit \cdot 4H_2O$		2.16	59.0	0.1 M (H, Na)ClO_4,
		2.39	27.6	[143]
		2.51	18.4	
		3.18	3.4	
		4.28	1.5	
		4.43	1.8	
		5.94	1.4	
		6.29	1.6	
		6.34	1.5	
$HoCit \cdot 4H_2O$		1.99	100.5	0.1 M (H, Na)ClO_4
		2.07	69.7	[143]
		2.30	37.4	
		2.36	31.6	
		2.63	14.8	
		2.63	14.7	
		3.19	6.0	
		6.03	2.2	

Table 5.4 (continued)

Citrate	$pH_{initial}$	$pH_{sat. solution}$	$c.10^4$/mol dm^{-3}	
$ErCit \cdot 4H_2O$	2.1	3.3	9.14	$NaClO_4$[f], [141]
	3.15	5.20	2.84	
	7.15	6.05	2.94	
	7.65	6.20	3.25	
	9.2	6.35	4.87	
$YbCit \cdot 4H_2O$	1.9	4.1	157.0	HCl[a], [139]
	3.0	5.3	35.2	
	4.0	5.6	24.2	
$YCit \cdot 5H_2O$	1.9	2.8	5.62	HCl[a], [139]
	3.0	5.5	3.82	
	1.5	6.1	2.02	
	7.5	5.7	70.2	$Mg_3(Cit)_2$[e], [140]
	6.7	5.7	71.3	$Ca_3(Cit)_2$[e]
	6.7	5.7	71.8	$Ba_3(Cit)_2$[e]
	5.6	5.6	29.5	$Zn_3(Cit)_2$[e]
	6.3	5.6	28.3	$Cd_3(Cit)_2$[e]
	5.7	5.6	97.1	$Hg_3(Cit)_2$[e]
	8.0	5.7	56.0	1.0 M Li_3Cit, [140]
	8.0	5.5	72.0	1.0 M Na_3Cit
	7.8	5.7	84.0	1.0 M K_3Cit
		1.99	179.0	0.1 M (H, Na)ClO_4,
		2.09	129.0	[143]
		2.39	49.6	
		2.44	48.6	
		2.49	41.4	
		2.54	37.8	
		2.55	36.3	
		2.61	32.2	
		2.83	16.2	
		2.88	14.7	
		5.73	2.5	
		6.29	3.8	
	3.15	3.80	6.90	$NaClO_4$[f], [141]
	4.15	4.58	1.04	
	5.20	6.30	0.92	
	7.15	6.65	1.84	
	7.65	6.72	1.78	
	9.2	6.80	3.99	
	9.75	6.75	3.99	
	10.6	6.87	4.91	

[a] Various concentrations of HCl, pH 2–4.4

[b] Various concentrations of KOH, total ionic strength of aqueous solutions $I = 0.1$ M

[c] Various concentrations of Na_3Cit, total ionic strength $I = (0.1 - 0.12)$ M [16]

[d] Various concentrations of Na_3Cit, total ionic strength $I = 0.1$ M

[e] Concentrations of Me^{2+} $(2.60 - 2.75) \cdot 10^{-3}$ equiv. dm^{-3} ; [f] Various concentrations of $NaClO_4$, total ionic strength $I = 0.1$ M

Using such representations, solubilities of highly soluble in water citrates can be correlated by

$$\ln[m(T)/\text{mol}\cdot\text{kg}^{-1};\text{Na}_3\text{Cit}\cdot 5.5\text{H}_2\text{O}] = -113.82 + \frac{4506.4}{(T/\text{K})} + 17.377\ln(T/\text{K}) \quad T < 315.4\ \text{K} \tag{5.5}$$

$$\ln[m(T)/\text{mol}\cdot\text{kg}^{-1};\text{Na}_3\text{Cit}\cdot 2\text{H}_2\text{O}] = -53.075 + \frac{2344.3}{(T/\text{K})} + 8.012\ln(T/\text{K}) \quad T > 315.4\ \text{K} \tag{5.6}$$

$$\ln[m(T)/\text{mol}\cdot\text{kg}^{-1};\text{K}_3\text{Cit}\cdot 2\text{H}_2\text{O}] = -72.493 + \frac{2465.8}{(T/\text{K})} + 11.558\ln(T/\text{K}) \quad T > 285.15\ \text{K} \tag{5.7}$$

$$\ln[m(T)/\text{mol}\cdot\text{kg}^{-1};\text{KH}_2\text{Cit}\cdot 2\text{H}_2\text{O}] = -483.03 + \frac{17507}{(T/\text{K})} + 74.867\ln(T/\text{K}) \tag{5.8}$$

and for citrates with a very low solubility in water, similar expressions are

$$\ln[m(T)/\text{mol}\cdot\text{kg}^{-1};\text{Mg}_3\text{Cit}_2\cdot 9\text{H}_2\text{O}] = -267.86 + \frac{11381}{(T/\text{K})} + 39.782\ln(T/\text{K}) \tag{5.9}$$

$$\ln[m(T)/\text{mol}\cdot\text{kg}^{-1};\text{Mg}_3\text{Cit}_2\cdot 14\text{H}_2\text{O}] = -129.97 + \frac{3056.5}{(T/\text{K})} + 20.466\ln(T/\text{K}) \tag{5.10}$$

$$\ln[m(T)/\text{mol}\cdot\text{kg}^{-1};\text{Ca}_3\text{Cit}_2\cdot 4\text{H}_2\text{O}] = 110.29 - \frac{4815.7}{(T/\text{K})} - 173.633\ln(T/\text{K}) \tag{5.11}$$

$$\ln[m(T)/\text{mol}\cdot\text{kg}^{-1};\text{FeCit}\cdot 2\text{H}_2\text{O}] = 691.56 - \frac{35793}{(T/\text{K})} - 100.99\ln(T/\text{K}) \tag{5.12}$$

For each citrate the composition of solid phase is indicated and m denotes molality of anhydrous citrate. Equation (5.7) for tripotassium citrate, is based on only five measured solubilities in the 15–30 °C temperature region and they were taken from the Linke tabulation of solubilities [133].

Derived from solubility determinations, performed by Apelblat [129], the molar enthalpies of solution at 298.15 K are: $\Delta H_{\text{sol.}}(m = 0.0483\ \text{mol kg}^{-1}) = 4.0\ \text{kJ mol}^{-1}$ for trimagnesium dicitrate nonahydrate; $\Delta H_{\text{sol.}}(m = 0.0443\ \text{mol kg}^{-1}) = 25.1\ \text{kJ mol}^{-1}$ for trimagnesium dicitrate tetradecanehydrate; $\Delta H_{\text{sol.}}(m = 0.0018\ \text{mol kg}^{-1}) = -6.2\ \text{kJ mol}^{-1}$ for tricalcium dicitrate tetrahydrate and $\Delta H_{\text{sol.}}(m = 0.0198\ \text{mol kg}^{-1}) = 47.3\ \text{kJ mol}^{-1}$ for iron(III) citrate monohydrate. Apelblat [148] also obtained the molar enthalpies of solution from calorimetric measurements: $\Delta H_{sol.}(T=298.22\ \mathrm{K},\ m=0.01491\ \mathrm{mol\ kg^{-1}})=-51.42\pm1.34\ \mathrm{kJ\ mol^{-1}}$ for trilithium citrate tetrahydrate; $\Delta H_{sol.}(T=298.14\ \mathrm{K},\ m=0.02817\ \mathrm{mol\ kg^{-1}})=23.28\pm0.63\ \mathrm{kJ\ mol^{-1}}$ for trisodium citrate dihydrate; $\Delta H_{sol.}(T=298.41\ \mathrm{K},\ m=0.01759\ \mathrm{mol\ kg^{-1}})=-51.42\pm1.34\ \mathrm{k\ J\ mol^{-1}}$ for disodium hydrogen citrate; $\Delta H_{sol.}(T=298.37\ \mathrm{K},\ m=0.01175\ \mathrm{mol\ kg^{-1}})=27.79\pm0.23\ \mathrm{kJ\ mol^{-1}}$ for sodium dihydrogen citrate; $\Delta H_{sol.}(T=298.19\ \mathrm{K},\ m=0.01272\ \mathrm{mol\ kg^{-1}})=7.09\pm0.20\ \mathrm{kJ\ mol^{-1}}$ for tripotassium citrate monohydrate and $\Delta H_{sol.}(T=298.08\ \mathrm{K},\ m=0.01795\ \mathrm{mol\ kg^{-1}})=35.43\pm0.52\ \mathrm{kJ\ mol^{-1}}$ for potassium dihydrogen citrate.

Considering the precipitation equilibrium of sparingly soluble inorganic citrates

$$\mathrm{Me_kCit_n} \rightleftharpoons \mathrm{kMe^{n+}} + \mathrm{nCit^{k-}} \tag{5.13}$$

and expressing [Me] = kc and [Cit] = nc where c is the molar concentration of a given citrate, the solubility product is expressed by

$$\mathrm{K_{sp}}=[\mathrm{Me}]^{\mathrm{k}}[\mathrm{Cit}]^{\mathrm{n}} = \mathrm{k^k n^n} c^{\mathrm{k+n}} \tag{5.14}$$

and

$$c=\left(\frac{\mathrm{K_{sp}}}{\mathrm{k^k n^n}}\right)^{1/(k+n)} \tag{5.15}$$

These expressions can be expressed in terms of molality m by using the density of pure water because in very dilute solutions $c \approx m\mathrm{d}_{H_2O}(T)$.

The common-ion effect is observed if citrate $\mathrm{Me_kCit_n}$ is dissolved in solutions already containing $\mathrm{Me^{n+}}$ or $\mathrm{Cit^{k-}}$ ions (from other salts or citrates), then the metal and citrate concentrations in [Me] and [Cit] should be correspondingly changed in Eq. (5.13). If $\mathrm{Me_kCit_n}$ is dissolved in solutions of electrolytes having no common ions, then their effect on the solubility can be quantitatively taken into account only if the solubility product is expressed in Eq. (5.14) by activities and not by concentrations. Frequently, in such cases, the solubility product $\mathrm{K_{sp}}$ is expressed as a function of total ionic strength of solution I. Solubility of citrates depends also on pH of solutions because with changing the hydrogen ion concentration, various citrate complexes with different stability and stoichiometry are formed and an examination of such cases is rather complex (see for example [126, 128, 130]).

5.3 Activities of Alkali Metal Citrates at Freezing Point Temperatures

Systematic determination of freezing points is known only in case of aqueous solutions of alkali metal acidic and neutral citrates. Apelblat and Manzurola [149] measured freezing-point depressions $\theta(m)=T_{\mathrm{f.p.}}(\mathrm{H_2O})-T_{\mathrm{f.p.}}(m)$ for sodium dihydrogen citrate, disodium hydrogen citrate, trisodium citrate, potassium dihydrogen citrate and tripotassium citrate and their values are presented in Table 5.5. These experimental freezing-point depressions can be correlated by

Table 5.5 Freezing temperatures in the alkali metal citrate - water systems [149]

w	T_m/K	w	T_m/K	w	T_f/K
NaH_2Cit		*Na_2HCit*		*Na_3Cit*	
0.0012	273.13	0.0012	273.11	0.0012	273.11
0.0024	273.10	0.0024	273.08	0.0024	273.06
0.0095	272.96	0.0048	273.01	0.0048	272.99
0.0189	272.78	0.0095	272.89	0.0095	272.79
0.0370	272.44	0.0187	272.67	0.0189	272.60
0.0545	272.14	0.0368	272.24	0.0368	272.06
0.0714	271.84	0.0540	271.88	0.0539	271.62
0.0876	271.62	0.0866	271.12	0.0704	271.25
0.1032	271.36	0.1012	270.78	0.0853	270.68
0.1187	271.08	0.1165	270.42	0.1014	270.24
0.1331	270.85			0.1159	269.70
0.1472	270.56			0.1298	269.38
0.1611	270.24			0.1433	268.71
				0.1559	268.21
KH_2Cit		*K_3Cit*		0.1686	267.81
0.0012	273.12	0.0012	273.10	0.1796	267.10
0.0024	273.08	0.0024	273.07	0.1926	266.39
0.0048	273.01	0.0048	272.98	0.2036	266.06
0.0095	272.89	0.0095	272.85	0.2147	265.01
0.0187	272.67	0.0189	272.56	0.2352	264.01
0.0368	272.24	0.0370	272.01	0.2638	263.56
0.0540	271.88	0.0545	271.50	0.3058	263.35
0.0866	271.12	0.0714	270.93		
0.1012	270.78	0.0876	270.26		
0.1165	270.42	0.1033	269.71		
		0.1185	269.26		
		0.1332	268.73		
		0.1473	267.88		
		0.01830 [150]	272.62		
		0.05191	271.68		
		0.07729	270.93		
		0.11389	269.68		
		0.14937	268.20		
		0.15858	267.79		
		0.19539	265.89		

$$
\begin{aligned}
&\theta(m,\mathrm{NaH_2Cit})/\mathrm{K} = 4.086m^* - 2.6896m^{*2};\;\; m^* \le 0.1\\
&\theta(m,\mathrm{NaH_2Cit})/\mathrm{K} = 3.3886m^* - 0.5479m^{*2};\;\; 0.1 \le m^* < 1.0\\
&\theta(m,\mathrm{Na_2HCit})/\mathrm{K} = 5.825m^* - 10.436m^{*2};\;\; m^* \le 0.1\\
&\theta(m,\mathrm{Na_2HCit})/\mathrm{K} = 4.6626m^* - 1.0373m^{*2};\;\; 0.1 \le m^* < 0.7\\
&\theta(m,\mathrm{Na_3Cit})/\mathrm{K} = 7.9165m^* - 23.582m^{*2};\;\; m^* \le 0.1\\
&\theta(m,\mathrm{Na_3Cit})/\mathrm{K} = 3.3029m^* + 3.3066m^{*2} - 1.2468m^{*3};\;\; 0.1 \le m^* < 2.3\\
&m^* = m/\mathrm{mol\cdot kg^{-1}}
\end{aligned}
\tag{5.16}
$$

and

$$
\begin{aligned}
&\theta(m,\mathrm{KH_2Cit})/\mathrm{K} = 5.8122m^* - 10.296m^{*2};\ m^* \le 0.1\\
&\theta(m,\mathrm{KH_2Cit})/\mathrm{K} = 4.6624m^* - 1.037m^{*2};\ 0.1 \le m^* < 0.7\\
&\theta(m,\mathrm{K_3Cit})/\mathrm{K} = 6.407m^* - 4.9711m^{*2};\ m^* \le 0.1\\
&\theta(m,\mathrm{K_3Cit})/\mathrm{K} = 6.0475m^* - 1.6634m^{*2} + 1.5151m^{*3};\ 0.1 \le m^* < 0.9\\
&m^* = m/\mathrm{mol\cdot kg^{-1}}
\end{aligned}
\tag{5.17}
$$

Few freezing-point depressions of tripotassium citrate were also reported by Fricke and Schützdeller [150] in 1924 (Table 5.5). These values are consistent with those of Apelblat and Manzurola [149], but they are systematically lower by about 0.1 K.

Using the cryoscopic constant of water $\lambda = 1.86$ kg mol^{-1} K, the values of $\theta(m)/\lambda m$ represent the apparent number of ions and undissociated molecules in the solution. If it is assumed that acidic and neutral citrates are fully dissociated, then at infinite dilution, it is expected that the total number of ions will be $\nu = 4$. At low concentrations, this happens only for $\mathrm{Na_3Cit}$ and $\mathrm{K_3Cit}$ ($\mathrm{Me^+}$ and $\mathrm{Cit^{3-}}$), but in more concentrate solutions ν is nearly 3, and therefore mainly $\mathrm{Me^+}$, $\mathrm{H_2Cit^-}$ and $\mathrm{HCit_2^{2-}}$ ions exist in solutions (Fig. 5.4). Disodium hydrogen citrate and potassium dihydrogen citrate behave similarly at low concentrations with $\nu \sim 3$, but sodium dihydrogen citrate is dissociated only to $\mathrm{Na^+}$and $\mathrm{H_2Cit^-}$ having $\nu \le 2$ (Fig. 5.5). In all cases, sodium salts have lower value of ν than corresponding potassium salts.

From the knowledge of $\theta(m)$ values, by using thermal properties of pure water, it is possible to determine the water activities a_w of inorganic citrates from [151]

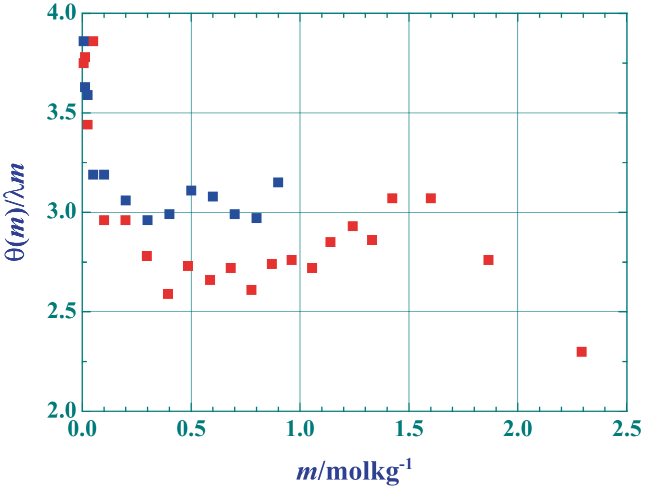


Fig. 5.4 The apparent number of particles in solution as a function of concentration of neutral alkali metal citrates. 🟥 - trisodium citrate, 🟦 - tripotassium citrate

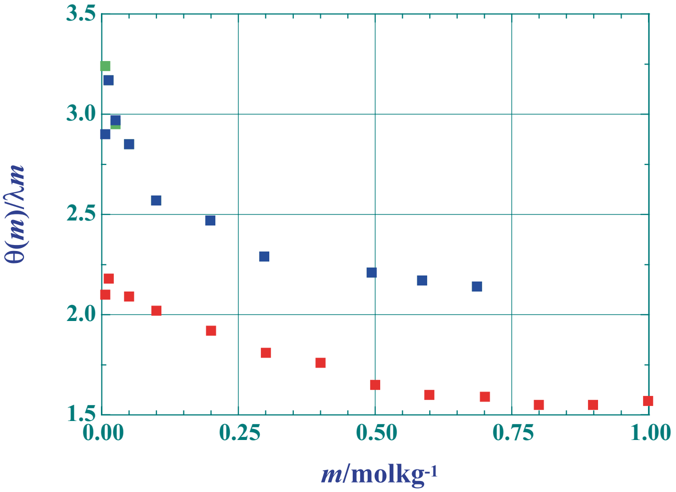


Fig. 5.5 The apparent number of particles in solution as a function of concentration of acidic alkali metal citrates. 🟥 - sodium dihydrogen citrate, 🟦 - potassium dihydrogen citrate and 🟩 - disodium hydrogen citrate

$$-\ln a_w(m;T) = 9.687\cdot 10^{-3}\left[\theta(m)/\mathrm{K}\right] + 4.835\cdot 10^{-6}\left[\theta(m)/\mathrm{K}\right]^2 \tag{5.18}$$

and the water activity is related to osmotic coefficients

$$\phi(m;T) = -\frac{1000}{\mathrm{M}_{\mathrm{H_2O}}}\cdot\frac{\ln a_w(m)}{\sum\limits_{\mathrm{i}} \nu_{\mathrm{i}} m_{\mathrm{i}}} \tag{5.19}$$

where the sum in Eq. (5.18) expresses the total number of particles in the solution, ν_i are stoichiometric coefficients and m_i are the molalities of corresponding species.

However, in calculations, Apelblat and Manzurola [149] assumed that all alkali metal citrates can be treated as strong electrolytes, but of different types, NaH_2Cit and KH_2Cit are 1:1 electrolytes, Na_2HCit is 1:2 electrolyte and Na_3Cit and K_3Cit are 1:3 electrolytes. In this case, the osmotic coefficients can be written in the usual form

$$\phi(m) = -55.508\left[\frac{\ln a_w(m)}{m\,\nu}\right] \tag{5.20}$$

and ν has values for fully dissociated electrolyte. Using a similar numerical procedure as for citric acid, the activity coefficients of alkali metal citrates $\gamma_\pm(m)$ were determined by solution of the corresponding Gibbs-Duhem equations. Since at infinite dilution, $m \to 0$, the limiting values of $\theta(m)/\lambda m$ are uncertain, the numerical integration of the Gibbs-Duhem equations was performed by fixing arbitrarily values of osmotic coefficients at $m = 0.01$ mol kg^{-1}.

Table 5.6 Osmotic coefficients of alkali metal citrates at freezing temperatures

m*	$\phi(m)$				
	NaH_2Cit	Na_2HCit	Na_3Cit	KH_2Cit	K_3Cit
0.01	1.081	0.904	0.904	0.908	0.810
0.02	1.074	0.899	0.893	0.907	0.808
0.03	1.067	0.894	0.882	0.905	0.806
0.04	1.06	0.888	0.872	0.904	0.804
0.05	1.053	0.883	0.861	0.903	0.802
0.06	1.047	0.878	0.852	0.901	0.800
0.07	1.040	0.873	0.842	0.899	0.798
0.08	1.033	0.868	0.833	0.898	0.796
0.09	1.027	0.864	0.824	0.896	0.794
0.10	1.021	0.859	0.815	0.895	0.792
0.15	0.990	0.836	0.776	0.886	0.784
0.20	0.962	0.816	0.743	0.877	0.776
0.25	0.935	0.797	0.715	0.867	0.770
0.30	0.911	0.780	0.693	0.857	0.764
0.35	0.888	0.766	0.676	0.846	0.760
0.40	0.868	0.753	0.663	0.834	0.756
0.45	0.851	0.743	0.655	0.823	0.754
0.50	0.833	0.733	0.648	0.809	0.753
0.60	0.807	0.721	0.645	0.781	0.753
0.70	0.788	0.717	0.651	0.750	0.766
0.80	0.778		0.664	0.717	0.779
0.90	0.776		0.680		
1.00	0.783		0.698		
1.10			0.715		
1.20			0.731		
1.30			0.742		
1.40			0.750		
1.50			0.751		
1.60			0.747		
1.70			0.737		
1.80			0.721		
1.90			0.699		
2.00			0.673		
2.10			0.642		
2.20			0.609		
2.30			0.574		

m^* m/mol kg^{-1}

Results of such calculations are presented in Tables 5.6 and 5.7 where values of osmotic and activity coefficients are given at round concentrations. As can be observed, the osmotic coefficients of sodium dihydrogen citrate behave differently than those expected for strong electrolyte and probably a better molecular model needs to take in account the partial dissociation of sodium dihydrogen citrate in dilute solutions.

Table 5.7 Activity coefficients of alkali metal citrates at freezing temperatures

m^*	$\gamma_{\pm}(m)$				
	NaH_2Cit	Na_2HCit	Na_3Cit	KH_2Cit	K_3Cit
0.01	0.906	0.731	0.542	0.906	0.542
0.02	0.954	0.676	0.497	0.844	0.469
0.03	0.976	0.644	0.469	0.811	0.432
0.04	0.987	0.621	0.448	0.787	0.407
0.05	0.993	0.602	0.431	0.769	0.388
0.06	0.996	0.586	0.415	0.754	0.374
0.07	0.966	0.572	0.402	0.741	0.362
0.08	0.994	0.559	0.390	0.730	0.351
0.09	0.991	0.548	0.378	0.720	0.354
0.10	0.987	0.537	0.368	0.711	0.334
0.15	0.961	0.495	0.325	0.674	0.303
0.20	0.928	0.460	0.294	0.645	0.282
0.25	0.893	0.432	0.269	0.621	0.267
0.30	0.860	0.409	0.249	0.599	0.254
0.35	0.828	0.389	0.233	0.579	0.244
0.40	0.798	0.372	0.220	0.560	0.235
0.45	0.772	0.358	0.211	0.546	0.222
0.50	0.746	0.344	0.201	0.525	0.212
0.60	0.703	0.323	0.188	0.492	0.205
0.70	0.669	0.308	0.179	0.460	0.200
0.80	0.643		0.173	0.430	0.198
0.90	0.625		0.169		
1.00	0.615		0.167		
1.10			0.165		
1.20			0.163		
1.30			0.162		
1.40			0.160		
1.50			0.158		
1.60			0.154		
1.70			0.150		
1.80			0.146		
1.90			0.140		
2.00			0.135		
2.10			0.128		
2.20			0.122		
2.30			0.118		

m^* m/mol kg^{-1}

5.4 Vapour Pressures of Water Over Saturated Solutions of Alkali Metal Citrates

Vapour pressures of water over saturated solutions of trisodium citrate, tripotassium citrate and disodium hydrogen citrate were determined in 5–45 °C temperature range by Manzurola and Apelblat [152] (Table 5.8).

Table 5.8 Vapour pressures of water over saturated solutions of trisodium citrate, tripotassium citrate and disodium hydrogen citrate as a function of temperature

t/°C	p/kPa	t/°C	p/kPa	t/°C	p/kPa
Na_3Cit		Na_2HCit		K_3Cit	
5.80	0.772	5.80	0.806	6.50	0.608
6.20	0.795	6.00	0.811	6.50	0.603
7.60	0.875	7.70	0.924	8.40	0.692
7.70	0.889	7.80	0.918	8.60	0.699
9.50	0.996	9.70	1.066	10.30	0.791
9.90	1.042	9.80	1.058	10.50	0.801
11.40	1.131	11.30	1.194	12.10	0.901
11.60	1.166	11.50	1.187	12.30	0.907
13.20	1.273	13.00	1.343	14.00	1.029
13.30	1.304	13.40	1.351	14.20	1.035
15.30	1.474	15.00	1.536	15.90	1.169
15.40	1.496	15.30	1.532	17.80	1.325
17.10	1.665	16.90	1.741	18.00	1.342
17.20	1.680	17.10	1.726	19.70	1.497
19.00	1.883	19.20	1.983	19.90	1.504
19.50	1.947	20.70	2.212	21.60	1.685
20.90	2.131	20.90	2.208	21.80	1.693
22.10	2.292	22.50	2.475	23.60	1.903
22.70	2.387	22.80	2.485	23.80	1.914
22.80	2.404	24.60	2.812	25.50	2.132
24.60	2.686	24.90	2.825	25.70	2.147
24.70	2.705	26.50	3.152	27.40	2.384
26.50	3.013	26.60	3.142	27.80	2.433
26.70	3.052	28.50	3.506	29.10	2.592
28.40	3.371	28.50	3.523	29.30	2.663
28.70	3.438	30.30	3.939	30.90	2.878
30.50	3.814	30.50	3.958	31.20	2.969
30.70	3.875	32.10	4.368	32.80	3.210
32.20	4.220	32.40	4.414	33.10	3.305
32.40	4.292	34.20	4.919	34.70	3.575
34.00	4.689	34.30	4.930	34.90	3.676
34.20	4.763	36.10	5.464	36.40	3.932
35.70	5.164	36.30	5.494	36.80	4.081
35.90	5.238	38.00	6.066	38.50	4.413
37.80	5.804	38.30	6.158	38.60	4.499
37.90	5.875	39.50	6.576	40.40	4.886
39.90	6.505	40.00	6.754	40.50	4.980
40.20	6.654	41.80	7.437	42.20	5.390
41.60	7.159	41.90	7.493	42.40	5.514
41.90	7.281	43.80	8.274	44.20	5.991
43.50	7.925	44.00	8.361	44.30	6.086
43.80	8.084				

For sodium citrates it is possible to express the vapour pressures from Table 5.8 by the following correlations

$$\begin{aligned}&\ln[p(T)/\mathrm{kPa}, \mathrm{Na_3Cit}] = 48.826 - \frac{6768.9}{(T/\mathrm{K})} - 4.408\ln(T/\mathrm{K})\\&\Delta\mathrm{H_{vap.}}/\mathrm{kJ\cdot mol^{-1}} = 56.280 - 0.0366\,(T/\mathrm{K})\end{aligned} \tag{5.21}$$

$$\begin{aligned}&\mathrm{n}[p(T)/\mathrm{kPa}, \mathrm{Na_2HCit}] = 80.283 - \frac{8131.7}{(T/\mathrm{K})} - 9.119\ln(T/\mathrm{K})\\&\Delta\mathrm{H_{vap.}}/\mathrm{kJ\cdot mol^{-1}} = 67.611 - 0.0758\,(T/\mathrm{K})\end{aligned} \tag{5.22}$$

and for tripotassium citrate

$$\begin{aligned}&\ln[p(T)/\mathrm{kPa}, \mathrm{K_3Cit}] = 111.193 - \frac{9498.3}{(T/\mathrm{K})} - 13.797\ln(T/\mathrm{K})\\&\Delta\mathrm{H_{vap.}}/\mathrm{kJ\cdot mol^{-1}} = 78.973 - 0.1147\,(T/\mathrm{K})\end{aligned} \tag{5.23}$$

Using these equations and vapour pressures of pure water from [153], the water activities $a_\mathrm{w}(T)$ of sodium and potassium citrates are

$$\begin{aligned}&a_w(T, \mathrm{Na_3Cit}) = 0.8262 + 1.4138\cdot 10^{-3}\,\theta^{1/2} + 1.3735\cdot 10^{-3}\,\theta\\&a_w(T, \mathrm{Na_2HCit}) = 0.8289 + 1.8993\cdot 10^{-2}\,\theta^{1/2} - 8.379\cdot 10^{-4}\,\theta\\&a_w(T, \mathrm{K_3Cit}) = 0.6181 - 7.2901\cdot 10^{-3}\,\theta^{1/2} + 5.5479\cdot 10^{-3}\,\theta - 5.5887\cdot 10^{-4}\,\theta^{3/2}\\&\theta = (T/\mathrm{K} - 273.15)\end{aligned} \tag{5.24}$$

Since solubilities of trisodium citrate and tripotassium citrate are given in Eqs. (5.5) and (5.7), the corresponding osmotic coefficients $\phi(T)$ are

$$\begin{aligned}&\phi(T, \mathrm{Na_3Cit}) = 2.358 - 0.07752\,\theta^{1/2} - 0.02043\,\theta\\&\phi(T, \mathrm{K_3Cit}) = 1.979 - 0.1735\,\theta^{1/2} + 0.002379\,\theta\\&\theta = (T/\mathrm{K} - 273.15)\end{aligned} \tag{5.25}$$

5.5 Boiling Points, Activities and Vapour Pressure Lowerings in Aqueous Solutions of Alkali Metal Citrates

Similarly as for citric acid, Martinez de la Cuesta et al. [154] reported boiling points for $\mathrm{Na_3Cit}$ and $\mathrm{K_3Cit}$ by using the Dühring and Othmer plots. These plots give approximately values of boiling points and vapour pressures at $\mathrm{T_{b.p.}}(m)$ using the corresponding values for water in the form

Table 5.9 Coefficients of Eq. (5.26) for trisodium citrate and tripotassium citrate solutions at boiling temperatures

m/mol kg^{-1}	a /°C	b	c	d	t/°C
Trisodium citrate					
1.6 [154]	1.01367	0.56526	0.99691	−0.04821	50[a]
2.3	1.02808	1.82684	0.99888	−0.15570	60
2.7	1.01665	3.96298	1.01779	−0.31887	70
3.5	1.02035	4.20815	1.01860	−0.34563	80
3.9	1.02128	4.91606	1.02239	−0.39970	80
Tripotassium citrate					
2.4 [154]	1.03197	1.99628	0.99600	−0.15685	50
3.1	1.04635	2.87773	0.99424	−0.24641	70
3.7	1.05261	4.09473	0.99853	−0.31695	80
4.0	1.06594	4.08687	0.99076	−0.30879	80
4.4	1.06813	5.08488	0.99711	−0.39264	80
4.7	1.06178	6.65042	1.01098	−0.52139	80
5.2	1.07812	6.78302	1.00336	−0.52602	80
6.4	1.08201	9.82278	1.02621	−0.79897	80

[a] Constants in Eqs. (5.26) to be used for temperatures higher than t and up to 120 °C 1 atm = 101.325 kPa

$$\begin{aligned} &\mathrm{T_{b.p.}}(m) = \mathrm{a}(m)\mathrm{T_{b.p.}}(\mathrm{H_2O}) + \mathrm{b}(m) \\ &\ln[p(m\,;\mathrm{T_{b.p.}})] = \mathrm{c}(m)\ln[p(\mathrm{H_2O}\,;\mathrm{T_{b.p.}})] + \mathrm{d}(m) \end{aligned} \tag{5.26}$$

where a, b, c and d constants depend on molality of citrates (Table 5.9). These boiling points lie in the 50–120 °C temperature range for 1.6–3.9 molal solutions of trisodium citrate and for 2.4–6.4 molal solutions of tripotassium citrate.

At constant temperatures T, vapour pressures of water over unsaturated solutions $p(T;m)$ are known only for sodium and potassium citrates and for diammonium hydrogen citrate. Gustav Tammann (1861–1938) determined at 100 °C, vapour pressures for trisodium citrate and tripotassium citrate. These vapour pressures were measured in 1885, and they are presented in the Timmermans tabulation [155] (Tables 5.10 and 5.11). As can be observed in Fig. 5.6, there is no significant difference in the vapour-pressure lowering $\Delta p(T;m)=p^0(T)-p(T;m)$ for both citrates. In the 25–45 °C temperature range, the vapour pressures of sodium and potassium acidic and neutral citrate solutions are coming from the Sadeghi group [156–162]. They also determined the water activities for aqueous solutions of diammonium hydrogen citrate at 25 °C [162]. Some ternary systems, when the third component is polymer or ionic liquid, were studied and a number of solutions having the same water activity were also reported. Schunk and Maurer [163] measured at 25 °C the water activities for trisodium citrate solutions and also for the ternary $Na_3Cit + H_3Cit + H_2O$ system. At the same temperature, Salabat et al. [164] determined vapour pressures for trisodium citrate solutions, but these values are incorrect as can be observed in Fig. 5.7. They differ considerably from those given by Schunk and Maurer [164], Sadeghi et al. [157, 160] and Kazemi et al. [165], even if concentrations are recalculated assuming that trisodium citrate dihydrate was used in experiments.

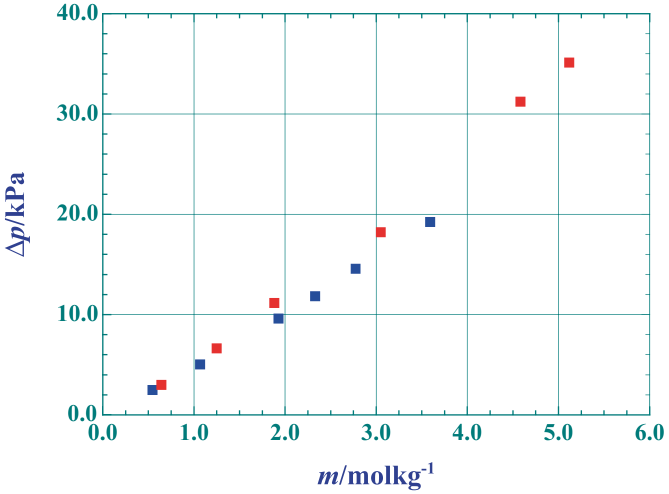


Fig. 5.6 The vapour pressure lowerings of metal alkali citrates at 100 °C as a function of their molality in aqueous solutions [155]. 🟦 - trisodium citrate and 🟥 - tripotassium citrate

Vapour pressure determinations in ternary systems with poly (vinylpyrrolidine) [157], 1-alkyl (butyl-, heptyl- and octyl-)-3-3methylidazolium bromide [161] and poly (ethylene glycol) PEG - 6000 [165] are reasonably consistent with those of the binary $Na_3Cit + H_2O$ systems when the vapour-pressure lowerings $\Delta p(T;m)$ are considered (Fig. 5.7). However, the agreement when expressed in terms of osmotic coefficients $\phi(T;m)$, as will discussed later, is less satisfactory. Actually, all reported

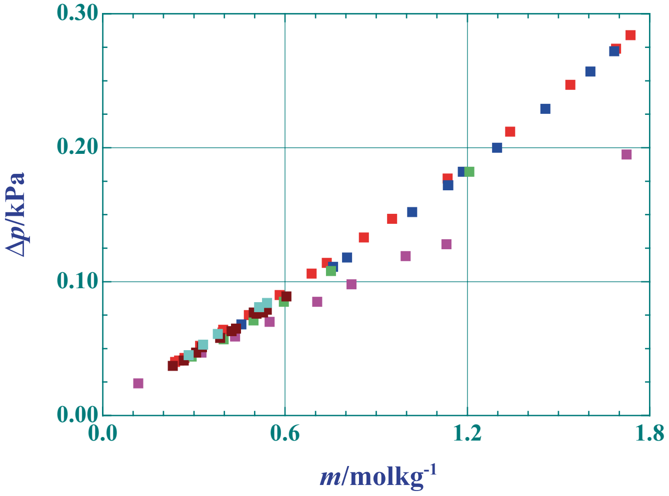


Fig. 5.7 The vapour pressure lowerings of trisodium citrate at 25 °C as a function of its molality in aqueous solutions. 🟦 - [163], 🟪 - [164], 🟥 - [157], 🟦 - [157*], 🟩 - [161*] and 🟫 - [165*]. * - from isopiestic experiments in ternary systems

Table 5.10 Relative humidities and vapour pressures of water over sodium citrates solutions as a function of temperature and concentration

t/°C	w	RH%	p/kPa	w	RH%	p/kPa
Trisodium citrate						
25	0.1053 [163]	97.85	3.099	0.1173	97.40	3.086
	0.1636	96.48	3.055	0.1224	97.29	3.083
	0.1718	96.27	3.049			
	0.2080	95.20	3.015	0.0293 [164]	99.23	3.142
	0.2267	94.57	2.995	0.0773	98.51	3.120
	0.2269	94.56	2.995	0.1009	98.15	3.108
	0.2342	94.25	2.985	0.1242	97.78	3.097
	0.2509	93.70	2.967	0.1541	97.31	3.082
	0.2733	92.77	2.938	0.1744	96.91	3.069
	0.2929	91.90	2.910	0.2046	96.24	3.048
	0.3028	91.42	2.895	0.2260	95.96	3.039
				0.3079	93.85	2.972
	0.0578 [157]	98.70	3.127			
	0.0609	98.65	3.126	0.0610 [161][a]	98.81	3.131
	0.0648	98.59	3.124	0.0703	98.56	3.123
	0.0764	98.32	3.115	0.0931	98.19	3.110
	0.0922	97.99	3.105	0.1135	97.71	3.096
	0.0928	97.94	3.103	0.1333	97.26	3.082
	0.1104	97.58	3.092	0.1624	96.54	3.059
	0.1306	97.10	3.077			
	0.1506	96.60	3.061	0.0562 [165][a]	98.83	3.130
	0.1599	96.35	3.053	0.0644	98.71	3.126
	0.1815	95.75	3.034	0.0734	98.53	3.120
	0.1973	95.33	3.020	0.0777	98.40	3.116
	0.2265	94.38	2.990	0.0906	98.18	3.109
	0.2571	93.27	2.955	0.0986	98.00	3.103
	0.2843	92.16	2.920	0.1017	97.96	3.102
	0.3036	91.30	2.893	0.1136	97.56	3.090
	0.3095	91.01	2.883	0.1155	97.59	3.090
	0.3305	89.90	2.848	0.1198	97.58	3.090
				0.1222	97.52	3.088
	0.0680 [157][a]	98.52	3.122	0.1349	97.19	3.078
	0.0786	98.28	3.114			
	0.0890	98.04	3.106			
	0.3262	94.30	2.986	0.5480	85.00	2.692
	0.3657	93.10	2.948	0.5923	80.95	2.564
	0.4397	90.20	2.856	0.6023	79.96	2.532
35	0.0622 [157]	98.61	5.548	0.1622	96.40	5.423
	0.0802	98.25	5.528	0.1690	96.39	5.423
	0.0975	97.90	5.508	0.2234	94.86	5.336
	0.1217	97.41	5.480			
	0.1274	97.23	5.470	0.0062 [161][a]	99.85	5.618
	0.1459	96.80	5.446	0.0089	99.81	5.616
	0.1515	96.63	5.436	0.0268	99.44	5.595
	0.1636	96.36	5.421	0.0437	99.14	5.578
	0.2119	94.92	5.340	0.0616	98.78	5.558

Table 5.10 (continued)

t/°C	w	RH%	*p*/kPa	w	RH%	*p*/kPa
	0.2554	93.33	5.250	0.0718	98.59	5.547
	0.2934	91.82	5.165	0.0730	98.57	5.546
	0.3332	89.84	5.054	0.0796	98.41	5.537
	0.3625	88.10	4.955	0.0802	98.43	5.538
				0.0828	98.36	5.534
	0.0661 [161][a]	98.59	5.547	0.0855	98.32	5.532
	0.0706	98.38	5.535	0.0964	98.04	5.516
	0.0763	98.36	5.534	0.1133	97.67	5.495
	0.0855	98.32	5.531	0.1150	97.63	5.493
	0.0877	98.07	5.517	0.1176	97.63	5.493
	0.1086	97.63	5.493	0.1503	96.82	5.447
	0.1088	97.76	5.500	0.1628	96.46	5.428
	0.1133	97.67	5.495	0.1690	96.39	5.423
	0.1180	97.63	5.493	0.1696	96.31	5.418
	0.1343	97.07	5.461	0.2234	94.86	5.337
	0.1510	96.49	5.428			
45	0.0612 [157]	98.66	9.461	0.3153	90.75	8.700
	0.0985	97.95	9.392	0.3292	90.06	8.634
	0.1053	97.81	9.379	0.3380	89.61	8.590
	0.1136	97.69	9.367	0.3584	88.46	8.480
	0.1193	97.54	9.353	0.3773	87.24	8.363
	0.1243	97.47	9.346	0.3833	86.79	8.319
	0.1593	96.57	9.260			
	0.1607	96.45	9.248	0.0618 [157][a]	98.63	9.458
	0.1685	96.30	9.234	0.0799	98.23	9.419
	0.2117	94.99	9.108	0.1048	97.85	9.383
	0.2501	93.66	8.980	0.1219	97.47	9.346
	0.2625	93.24	8.939	0.1311	97.21	9.321
	0.2956	91.78	8.799	0.1514	96.54	9.257
100	0.1236 [155]	97.54	98.832	0.3754	88.32	89.486
	0.2160	95.03	96.285	0.4172	85.63	86.766
	0.3322	90.53	91.726	0.4811	81.03	82.100
Disodium hydrogen citrate						
25	0.0642 [161][a]	98.82	3.131	0.1509	97.15	3.078
	0.0647	98.81	3.131	0.1740	96.72	3.065
	0.0745	98.56	3.123	0.1794	96.54	3.059
	0.0745	98.65	3.126	0.2103	95.83	3.036
	0.1000	98.19	3.111	0.2112	95.41	3.023
	0.1043	98.08	3.108	0.2590	94.64	2.999
	0.1077	98.02	3.106	0.2705	94.22	2.985
	0.1193	97.81	3.099	0.2988	93.37	2.958
	0.1228	97.71	3.096	0.3354	92.20	2.921
	0.1424	97.34	3.084	0.3492	91.56	2.901
	0.1451	97.26	3.082			
35	0.0089 [161]	99.83	5.617	0.1841	96.38	5.422
	0.0090	99.83	5.617	0.1864	96.39	5.423
	0.0269	99.53	5.600	0.1866	96.31	5.418
	0.0359	99.36	5.590	0.2207	95.53	5.374

Table 5.10 (continued)

t/°C	w	RH%	p/kPa	w	RH%	p/kPa
	0.0449	99.20	5.581	0.2519	94.86	5.337
	0.0583	98.95	5.567	0.3334	92.52	5.205
	0.0808	98.52	5.543			
	0.0892	98.35	5.533	0.0893 [161][a]	98.32	5.531
	0.0893	98.32	5.532	0.0897	98.36	5.534
	0.0897	98.36	5.534	0.1011	98.12	5.521
	0.0990	98.18	5.524	0.1077	97.97	5.531
	0.1011	98.12	5.520	0.1267	97.63	5.493
	0.1077	97.97	5.512	0.1284	97.67	5.495
	0.1163	97.83	5.504	0.1423	97.35	5.477
	0.1267	97.63	5.493	0.1790	96.49	5.428
	0.1284	97.67	5.495	0.1820	96.48	5.428
	0.1347	97.46	5.483	0.1841	96.38	5.422
	0.1423	97.35	5.477	0.1864	96.39	5.423
	0.1650	96.82	5.447	0.2207	95.53	5.374
	0.1790	96.49	5.428	0.2519	94.86	5.336
	0.1820	96.48	5.428	0.3334	92.52	5.205
Sodium dihydrogen citrate						
25	0.0675 [161][a]	98.71	3.128			
	0.0773	98.52	3.122			
	0.0978	98.19	3.111			
	0.1329	97.95	3.104			
	0.1876	97.04	3.075			
	0.1901	96.84	3.068			
35	0.0200 [161]	99.67	5.608	0.1334	97.91	5.508
	0.0299	99.52	5.599	0.1371	97.90	5.508
	0.0401	99.36	5.590	0.1394	97.85	5.505
	0.0501	99.22	5.582	0.1449	97.70	5.497
	0.0600	99.07	5.574	0.1501	97.63	5.493
	0.0806	98.78	5.558	0.1713	97.14	5.465
	0.0900	98.63	5.549	0.0936	98.57	5.546
	0.0902	98.63	5.549	0.1371	97.70	5.496
	0.0936	98.57	5.546	0.0900	98.53	5.543
	0.1002	98.46	5.539	0.1371	97.90	5.508
	0.1224	98.07	5.517	0.1742	97.14	5.465
	0.1255	98.00	5.514	0.1831	96.86	5.449
	0.1299	97.97	5.512			

[a] From isopiestic experiments in ternary systems

in these investigations $p(T;m)$ values were calculated using the water activities $a_w(T;m)$ which were determined in isopiestic experiments and known pressures $p^0(T)$ of pure water. In isopiestic determinations, sodium chloride solutions always served as reference solutions [166, 167].

As can be expected, at constant temperature, citric acid has the lowest vapour pressure lowering and $\Delta p(T;m)$ increase with increasing the sodium content in citrate salts: $\Delta p(T;m;\ \mathrm{Na_3Cit}) > \Delta p(T;m;\ \mathrm{Na_2HCit}) > \Delta p(T;m;\ \mathrm{NaH_2Cit}) > \Delta p(T;m;$

Table 5.11 Relative humidities and vapour pressures of water over potassium citrates solutions as a function of temperature and concentration

t/°C	w	RH%	*p*/kPa	w	RH%	*p*/kPa
Tripotassium citrate						
20	0.0471 [156]	99.21	2.320	0.0761	98.66	2.307
	0.0547	99.08	2.317	0.0770	98.62	2.306
	0.0678	98.89	2.313	0.0829	98.46	2.302
	0.0974	98.33	2.299	0.0886	98.45	2.302
	0.0986	98.26	2.298	0.0980	97.99	2.291
	0.1156	97.90	2.289	0.0986	98.22	2.297
	0.1187	97.85	2.288	0.1080	98.02	2.292
	0.1143	97.80	2.287	0.1087	98.02	2.292
	0.1370	97.43	2.278	0.1096	97.85	2.288
	0.1591	96.85	2.265	0.1111	97.91	2.290
	0.2061	95.54	2.234	0.1126	97.92	3.103
	0.2671	93.40	2.184	0.1163	97.83	2.288
	0.2854	92.48	2.162	0.1327	97.46	2.279
	0.3806	87.18	2.038	0.1339	97.46	3.088
	0.3986	85.42	1.997	0.1364	97.40	3.086
	0.5116	70.31	1.644	0.1379	97.21	2.273
				0.1423	96.92	2.266
	0.0477 [156, 158][a]	99.17	2.319	0.1469	97.16	3.079
	0.0711	98.72	2.309	0.1537	96.99	2.268
	0.0758	98.66	2.307	0.1701	96.48	2.256
25	0.0418 [156]	99.18	3.143	0.0598	98.92	3.134
	0.0531	99.04	3.138	0.0605	98.80	3.131
	0.0650	98.88	3.133	0.0695	98.73	3.128
	0.0773	98.63	3.125	0.0682	98.68	3.127
	0.0775	98.62	3.125	0.0751	98.55	3.123
	0.1030	98.19	3.111	0.0788	98.57	3.123
	0.1154	97.90	3.102	0.0808	98.45	3.119
	0.1475	97.12	3.077	0.0859	98.38	3.117
	0.1577	96.75	3.066	0.0870	98.32	3.115
	0.2162	95.31	3.020	0.0963	98.25	3.113
	0.2843	92.89	2.943	0.1126	97.92	3.103
	0.3207	90.89	2.880	0.1144	97.87	3.101
	0.3779	87.44	2.770	0.1180	97.94	3.103
	0.4334	83.33	2.640	0.1202	97.75	3.097
	0.4850	79.01	2.503	0.1339	97.46	3.088
	0.5069	75.31	2.385	0.1364	97.40	3.086
	0.5110	75.16	2.381	0.1391	97.34	3.084
				0.1469	97.16	3.079
	0.0441 [156, 158][a]	99.21	3.144	0.1505	96.99	3.073
	0.0491	99.03	3.138	0.1529	96.91	3.071
	0.0556	99.02	3.138			
30	0.0523 [156]	99.09	4.206	0.0475 [156, 158, 159][a]	99.03	4.204
	0.0598	98.84	4.196	0.0495	99.01	4.203
	0.0635	98.81	4.194	0.0531	98.98	4.202
	0.0700	98.78	4.193	0.0587	98.94	4.200
	0.0804	98.55	4.183	0.0635	98.81	4.194
	0.0917	98.34	4.175	0.0652	98.82	4.195

Table 5.11 (continued)

t/°C	w	RH%	*p*/kPa	w	RH%	*p*/kPa
	0.0963	98.25	4.171	0.0708	98.66	4.188
	0.1164	97.85	4.154	0.0738	98.64	4.187
	0.1215	97.73	4.149	0.0754	98.45	4.179
	0.1262	97.54	4.140	0.0762	98.65	4.188
	0.1429	97.23	4.127	0.0857	98.33	4.174
	0.1691	96.67	4.103	0.0918	98.36	4.175
	0.1875	96.31	4.088	0.0997	98.18	4.168
	0.2213	95.12	4.038	0.1035	98.10	4.164
	0.2246	95.11	4.037	0.1105	97.96	4.158
	0.2647	93.46	3.967	0.1138	97.89	4.156
	0.3616	89.05	3.779	0.1213	97.76	4.150
	0.3806	87.46	3.712	0.1215	97.73	4.149
	0.3943	86.61	3.676	0.1288	97.42	4.135
	0.4103	84.71	3.595	0.1366	97.40	4.135
	0.4524	81.13	3.443	0.1383	97.24	4.128
	0.4836	78.16	3.317			
35	0.0528 [156]	99.08	5.574	0.4687	79.48	4.420
	0.0682	98.73	5.555			
	0.0857	98.45	5.539	0.0462 [156, 158, 159][a]	99.09	5.575
	0.1030	97.98	5.512	0.0472	99.12	5.567
	0.1037	98.07	5.517	0.0499	99.06	5.573
	0.1587	96.87	5.450	0.0536	98.98	5.569
	0.1601	96.85	5.449	0.0559	98.85	5.562
	0.1706	96.44	5.426	0.0578	98.95	5.567
	0.1766	96.45	5.426	0.0645	98.81	5.559
	0.2075	95.50	5.373	0.0627	98.81	5.560
	0.2099	95.15	5.353	0.0762	98.63	5.549
	0.2362	94.24	5.302	0.0767	98.61	5.548
	0.2605	93.54	5.262	0.0791	98.49	5.541
	0.2781	92.89	5.225	0.0804	98.53	5.543
	0.2856	92.59	5.209	0.0877	98.39	5.536
	0.3088	91.15	5.127	0.0914	98.36	5.534
	0.3183	90.59	5.096	0.0917	98.29	5.530
	0.3585	88.44	4.975	0.1012	98.18	5.524
	0.3872	86.19	4.848	0.1034	98.11	5.520
	0.3909	86.63	4.873	0.1044	97.94	5.510
	0.4015	85.62	4.816	0.1213	97.76	5.500
	0.4217	84.33	4.743	0.1242	97.65	5.494
40	0.0397 [156]	99.27	7.327	0.4649	80.14	5.912
	0.0427	99.20	7.320	0.4969	76.99	5.679
	0.0588	98.93	7.302	0.5144	75.07	5.537
	0.0625	98.87	7.297			
	0.0676	98.78	7.291	0.0473 [156, 158, 159][a]	99.00	7.307
	0.0690	98.72	7.286	0.0473	99.16	7.319
	0.0699	98.76	7.289	0.0488	99.08	7.313
	0.0906	98.33	7.258	0.0601	98.91	7.300

Table 5.11 (continued)

t/°C	w	RH%	p/kPa	w	RH%	p/kPa
	0.0997	98.13	7.243	0.0605	98.84	7.295
	0.1091	98.01	7.234	0.0620	98.86	7.297
	0.1713	96.44	7.118	0.0701	98.67	7.283
	0.2266	94.61	7.004	0.0756	98.65	7.281
	0.2375	94.45	6.970	0.0777	98.62	7.279
	0.2670	93.73	6.917	0.0814	98.47	7.268
	0.2863	92.60	6.834	0.0912	98.35	7.259
	0.3180	90.95	6.711	0.0922	98.36	7.260
	0.3788	87.04	6.422	0.1027	98.13	7.243
	0.3808	86.96	6.416	0.1112	97.97	7.231
	0.4081	84.65	6.245	0.1264	97.61	7.204
	0.4530	81.44	6.008			
100	0.1646 [155]	97.04	98.325	0.4833	82.03	83.113
	0.2770	93.46	94.699	0.5841	69.18	70.101
	0.3657	88.99	90.166	0.6106	65.32	66.181
Potassium dihydrogen citrate						
20	0.0413 [158]	99.36	4.218	0.2058	97.72	4.127
	0.0463	99.29	4.215			
	0.0563	99.16	4.209	0.0628 [158][a]	99.11	4.207
	0.0575	99.16	4.209	0.0658	98.98	4.202
	0.0583	99.16	4.209	0.0866	98.84	4.196
	0.0698	98.96	4.201	0.0879	98.73	4.193
	0.0931	98.68	4.189	0.0942	98.72	4.191
	0.1006	98.56	4.184	0.0946	98.70	4.190
	0.1200	98.34	4.175	0.1002	98.65	4.188
	0.1261	98.21	4.169	0.1208	98.37	4.176
	0.1471	97.97	4.159	0.1326	98.22	4.169
	0.1633	97.72	4.148	0.1348	98.21	4.169
	0.1938	97.38	4.134	0.1574	97.75	4.150
25	0.0475 [158]	99.29	3.146	0.0755	98.95	3.135
	0.0607	99.07	3.139	0.0836	98.73	3.128
	0.0925	98.73	3.128	0.0837	98.81	3.131
	0.1123	98.52	3.122	0.0998	98.54	3.122
	0.1370	98.19	3.111	0.1054	98.57	3.123
	0.1478	98.06	3.107	0.1156	98.43	3.119
	0.1547	97.97	3.104	0.1367	98.14	3.110
				0.1541	97.62	3.105
	0.0649 [158][a]	99.08	3.139	0.1556	97.94	3.103
	0.0707	99.02	3.138	0.1832	97.62	3.093
30	0.0413 [158]	99.36	4.218	0.2058	97.72	4.127
	0.0463	99.29	4.215			
	0.0563	99.16	4.209	0.0628 [158][a]	99.11	4.207
	0.0575	99.16	4.209	0.0658	98.98	4.202
	0.0583	99.16	4.209	0.0866	98.84	4.196
	0.0698	98.96	4.201	0.0879	98.73	4.193
	0.0931	98.68	4.189	0.0942	98.72	4.191
	0.1006	98.56	4.184	0.0946	98.70	4.190
	0.1200	98.34	4.175	0.1002	98.65	4.188

Table 5.11 (continued)

t/°C	w	RH%	*p*/kPa	w	RH%	*p*/kPa
	0.1261	98.21	4.169	0.1208	98.37	4.176
	0.1471	97.97	4.159	0.1326	98.22	4.169
	0.1633	97.72	4.148	0.1348	98.21	4.169
	0.1938	97.38	4.134	0.1574	97.75	4.150
35	0.0485 [158]	99.27	5.585	0.0514 [158][a]	99.27	5.585
	0.0540	99.23	5.583	0.0698	99.04	5.572
	0.0553	99.21	5.582	0.0717	98.85	5.620
	0.0596	99.16	5.579	0.0772	98.82	5.560
	0.0683	99.03	5.572	0.0797	98.81	5.560
	0.0833	98.85	5.562	0.0950	98.67	5.551
	0.0964	98.67	5.551	0.0996	98.61	5.548
	0.1137	98.43	5.538	0.1071	98.55	5.545
	0.1195	98.35	5.533	0.1179	98.35	5.533
	0.1357	98.11	5.520	0.1242	98.32	5.532
	0.1606	97.79	5.502	0.1321	98.16	5.523
	0.1703	97.69	5.496	0.1614	97.82	5.504
	0.1824	97.52	5.487	0.1869	97.51	5.486
40	0.0451 [158]	99.24	7.325	0.1287	98.24	7.251
	0.0492	99.21	7.323	0.1523	97.90	7.226
	0.0508	99.17	7.320			
	0.0533	99.16	7.319	0.0589 [158][a]	99.08	7.313
	0.0588	99.12	7.316	0.0702	98.97	7.305
	0.0643	99.06	7.312	0.0754	98.86	7.297
	0.0730	98.94	7.303	0.0756	98.95	7.304
	0.0838	98.78	7.291	0.0804	98.78	7.291
	0.0886	98.75	7.289	0.0916	98.70	7.285
	0.0893	98.73	7.287	0.0990	98.62	7.279
	0.0928	98.68	7.284	0.1110	98.48	7.269
	0.1081	98.50	7.270	0.1264	98.21	7.249
	0.1139	98.44	7.266	0.1540	97.85	7.220
	0.1157	98.42	7.264	0.1561	97.85	7.220
	0.1244	98.29	7.255	0.1801	97.52	7.198

[a] From isopiestic experiments in ternary systems

H_3Cit). This is illustrated in Fig. 5.8, where the vapour pressure lowerings at 35 °C of citric acid and sodium citrates are plotted together. Changes in the water activity of trisodium citrate solutions $a_w(T;m)$ with temperature, in the 25–100 °C range, are very small. As a consequence, the reduced pressure lowering $\Delta p(T;m;\,\mathrm{Na_3Cit})/p^0(T)$ is only function of concentration. This means that at given concentration, its value is the same for any temperature (Figs. 5.9 and 5.10).

Vapour pressures of water over trisodium citrate solutions, based on data from Table 5.10, (the Salabat et al. [164] results are excluded in calculations) can be represented by the following correlations

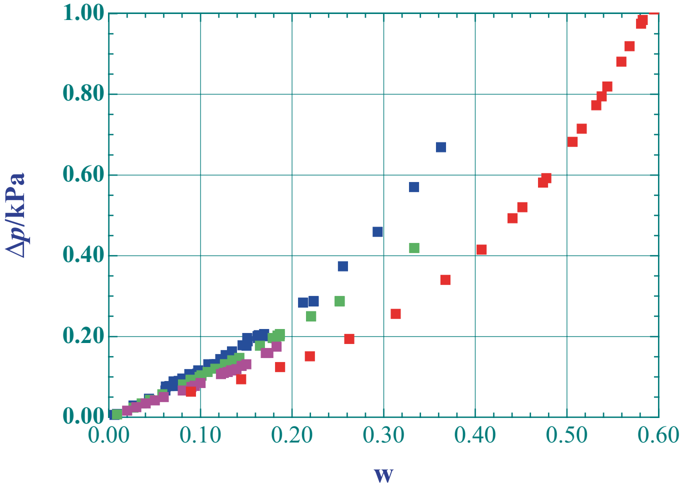


Fig. 5.8 The vapour pressure lowerings of citric acid and sodium citrates at 35 °C as a function of their weight fractions in aqueous solutions. 🟦 - trisodium citrate, 🟩 - disodium hydrogen citrate, 🟪 - sodium dihydrogen citrate and 🟥 - citric acid

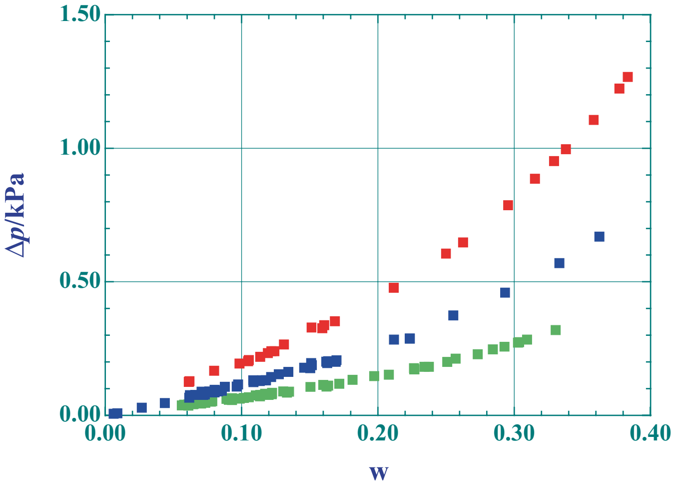


Fig. 5.9 The vapour pressure lowerings of trisodium citrate as a function of temperature and its weight fraction in aqueous solutions. 🟩 - 25 °C, 🟦 - 35 °C and 🟥 - 45 °C

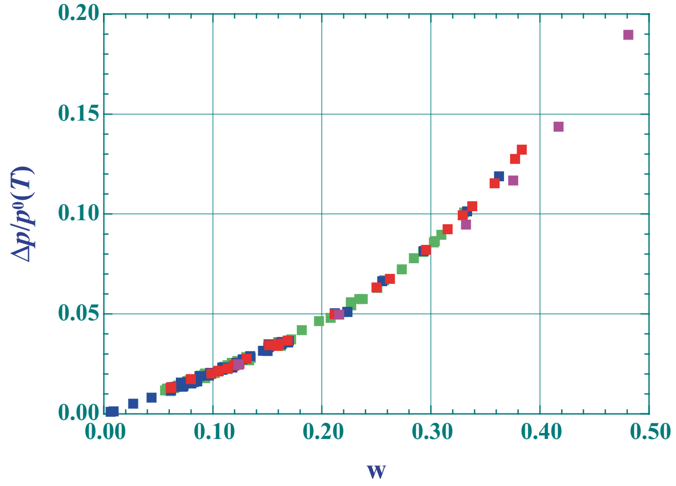


Fig. 5.10 The reduced vapour pressure lowerings of trisodium citrate as a function of temperature and its weight fraction in aqueous solutions. 🟩 - 25 °C, 🟦 - 35 °C, 🟥 - 45 °C and 🟪 - 100 °C

$$
\begin{aligned}
&p(25°\mathrm{C};\mathrm{w})/\mathrm{kPa} = 3.1668 - 0.6713\mathrm{w} + 0.6182\mathrm{w}^2 - 4.5424\mathrm{w}^3 \\
&\mathrm{w} < 0.34 \\
&p(35°\mathrm{C};\mathrm{w})/\mathrm{kPa} = 5.6236 - 1.1556\mathrm{w} + 0.9107\mathrm{w}^2 - 7.7483\mathrm{w}^3 \\
&\mathrm{w} < 0.37 \\
&p(45°\mathrm{C};\mathrm{w})/\mathrm{kPa} = 9.5859 - 2.0014\mathrm{w} + 1.5685\mathrm{w}^2 - 12.9158\mathrm{w}^3 \\
&\mathrm{w} < 0.40 \\
&p(100°\mathrm{C};\mathrm{w})/\mathrm{kPa} = 101.325 - 19.1054\mathrm{w} + 1.3637\mathrm{w}^2 - 93.062\mathrm{w}^3 \\
&\mathrm{w} < 0.48
\end{aligned}
\tag{5.27}
$$

Similar polynomial expressions for vapour pressures over disodium hydrogen citrate solutions are

$$
\begin{aligned}
&p(25°\mathrm{C};\mathrm{w})/\mathrm{kPa} = 3.1668 - 0.4734\mathrm{w} - 0.7759\mathrm{w}^2 \\
&p(35°\mathrm{C};\mathrm{w})/\mathrm{kPa} = 5.6236 - 0.8929\mathrm{w} - 1.0612\mathrm{w}^2 \\
&\mathrm{w} < 0.35
\end{aligned}
\tag{5.28}
$$

and for sodium dihydrogen solutions they are

$$
\begin{aligned}
&p(25°\mathrm{C};\mathrm{w})/\mathrm{kPa} = 3.1668 - 0.6316\mathrm{w} - 0.6688\mathrm{w}^2 \\
&p(35°\mathrm{C};\mathrm{w})/\mathrm{kPa} = 5.6236 - 0.7268\mathrm{w} - 1.0709\mathrm{w}^2 \\
&\mathrm{w} < 0.20
\end{aligned}
\tag{5.29}
$$

The reduced pressure lowering of trisodium citrate, $\Delta p(T;m;\ \mathrm{Na_3Cit})/p^0(T)$, if concentrations are expressed in the weight fractions w takes the following form

$$\begin{aligned}
&\frac{\Delta p(T;\mathrm{w})}{p^0(T)} = 1 - a_w(T;\mathrm{w}) = F(\mathrm{w})\\
&F(\mathrm{w}) = 0.1791\mathrm{w} + 0.1543\mathrm{w}^2 + 0.6247\mathrm{w}^3\\
&p(T;w) = p^0(T)\left[1 - F(\mathrm{w})\right]
\end{aligned} \tag{5.30}$$

Probably, similar expressions can also be evaluated for other sodium citrates, but the available data is known only for narrow temperature range to verify this assumption.

Vapour pressure depressions of potassium citrates were measured in the 20–40 °C temperature range by Sadeghi and Ziamajidi [156] and Sadeghi and Goodarzi [158, 159] and they are presented in Table 5.11. Their values were determined in isopiestic experiments in the binary $\mathrm{K_3Cit + H_2O}$ and $\mathrm{KH_2Cit + H_2O}$ systems, but also in the ternary systems with alanine and polypropylene oxide 400.

Vapour pressures of water over tripotassium citrate solutions as a function of temperature and weight fraction of the salt in water can be correlated by

$$\begin{aligned}
&p(20°\mathrm{C};\mathrm{w})/\mathrm{kPa} = 2.3370 - 0.5010\mathrm{w} + 1.3028\mathrm{w}^2 - 45.7635\mathrm{w}^3\\
&p(25°\mathrm{C};\mathrm{w})/\mathrm{kPa} = 3.1668 - 0.5958\mathrm{w} + 0.6923\mathrm{w}^2 - 4.9286\mathrm{w}^3\\
&p(30°\mathrm{C};\mathrm{w})/\mathrm{kPa} = 4.2429 - 0.8244\mathrm{w} + 1.2366\mathrm{w}^2 - 7.2580\mathrm{w}^3\\
&p(35°\mathrm{C};\mathrm{w})/\mathrm{kPa} = 5.6236 - 0.9550\mathrm{w} - 0.02361\mathrm{w}^2 - 6.5070\mathrm{w}^3\\
&p(40°\mathrm{C};\mathrm{w})/\mathrm{kPa} = 7.3778 - 1.2587\mathrm{w} + 0.3213\mathrm{w}^2 - 9.4342\mathrm{w}^3\\
&p(100°\mathrm{C};\mathrm{w})/\mathrm{kPa} = 101.325 - 26.4861\mathrm{w} + 62.9516\mathrm{w}^2 - 185.9632\mathrm{w}^3\\
&\mathrm{w} < 0.48
\end{aligned} \tag{5.31}$$

Similar equations for potassium dihydrogen citrate are

$$\begin{aligned}
&p(20°\mathrm{C};\mathrm{w})/\mathrm{kPa} = 2.3370 - 0.3201\mathrm{w} + 0.1365\mathrm{w}^2 + 0.3228\mathrm{w}^3\\
&\mathrm{w} < 0.15\\
&p(25°\mathrm{C};\mathrm{w})/\mathrm{kPa} = 3.1668 - 0.5655\mathrm{w} + 0.5590\mathrm{w}^2 - 4.7839\mathrm{w}^3\\
&\mathrm{w} < 0.19\\
&p(30°\mathrm{C};\mathrm{w})/\mathrm{kPa} = 4.2429 - 0.5909\mathrm{w} + 0.2714\mathrm{w}^2 - 0.7522\mathrm{w}^3\\
&\mathrm{w} < 0.21\\
&p(35°\mathrm{C};\mathrm{w})/\mathrm{kPa} = 5.6234 - 0.7536\mathrm{w} - 0.1570\mathrm{w}^2 + 1.1592\mathrm{w}^3\\
&\mathrm{w} < 0.19\\
&p(40°\mathrm{C};\mathrm{w})/\mathrm{kPa} = 7.3778 - 1.2454\mathrm{w} + 3.7608\mathrm{w}^2 - 13.8687\mathrm{w}^3\\
&\mathrm{w} < 0.18
\end{aligned} \tag{5.32}$$

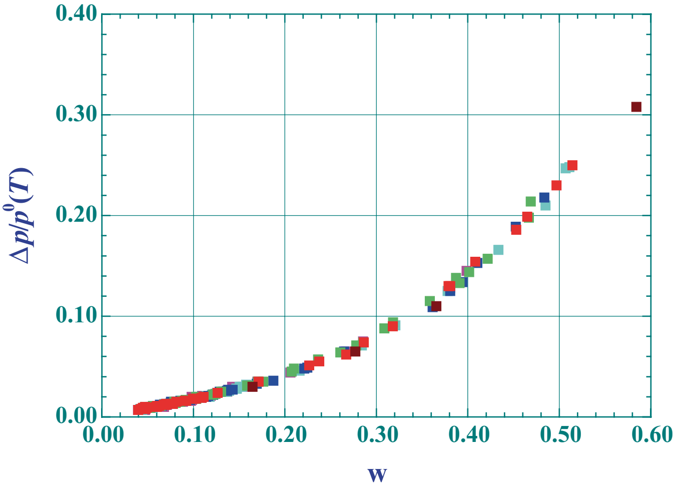


Fig. 5.11 The reduced vapour pressure lowerings of tripotassium citrate as a function of temperature and its weight fraction in aqueous solutions. 🟪 - 20 °C, 🟦 - 25 °C, 🟦 - 30 °C, 🟩 - 35 °C, 🟥 - 40 °C and 🟫 - 100 °C

Also in the case of tripotassium citrate, the change of water activity with temperature is weak and therefore it is possible to present its reduced pressure lowering $\Delta p(T;m;K_3Cit)/p^0(T)$ as an unique function F(w). This function is nearly independent of temperature (Fig. 5.11)

$$\begin{aligned} \frac{\Delta p(T;\mathrm{w})}{p^0(T)} &= 1 - a_w(T;\mathrm{w}) = F(\mathrm{w}) \\ F(\mathrm{w}) &= 0.1514\mathrm{w} + 0.1394\mathrm{w}^2 + 0.9380\mathrm{w}^3 \\ p(T;w) &= p^0(T)\left[1 - F(\mathrm{w})\right] \end{aligned} \tag{5.33}$$

In the case of potassium dihydrogen citrate, the reduced pressure lowering depends somewhat on temperature but still it can give a reasonable well approximation for desired vapour pressure using known $\Delta p(T;w;KH_2Cit)$ values.

At constant temperature, the vapour pressure lowering of potassium citrates is similar to that observed for sodium citrates $\Delta p(T;m;\ K_3Cit) > \Delta p(T;m;\ KH_2Cit) > \Delta p(T;m;\ H_3Cit)$. As a rule, in moderately concentrated solutions, there are no significant differences between sodium and potassium salts, but in the case of neutral citrates, these differences are more pronounced with increased concentration of salts ($\Delta p(T;m;\ K_3Cit) > \Delta p(T;m;\ Na_3Cit)$). This is shown in Fig. 5.12 where the vapour pressures of K_3Cit, KH_2Cit, Na_3Cit, NaH_2Cit, $(NH_4)_2HCit$ and H_3Cit, at 25 °C are plotted.

From ammonium citrates, the vapour pressure lowerings are known only for diammonium hydrogen citrate in water and in ternary solutions with glycine, L-alanine

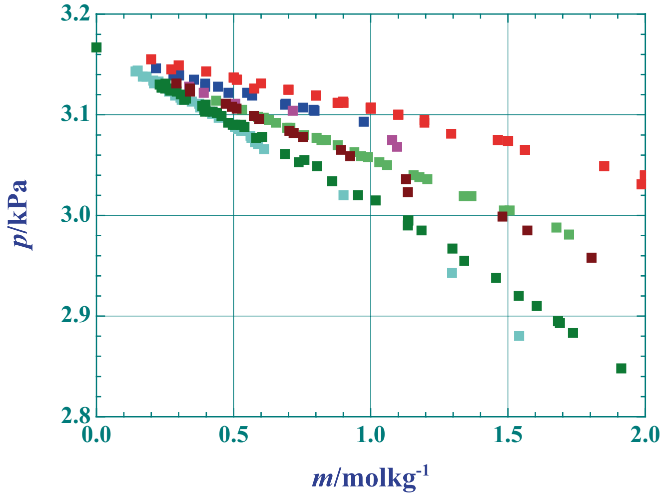


Fig. 5.12 Vapour pressures of ammonium citrate, sodium, potassium citrates and citric acid at 25 °C. 🟥 - citric acid, 🟦 - potassium dihydrogen citrate, 🟪 - sodium dihydrogen citrate, 🟩 - diammonium hydrogen citrate, 🟫 - disodium hydrogen citrate, 🟩 - trisodium citrate and 🟩 - tripotassium citrate

and L-serine. These $\Delta p(T;m)$ values are based on isopiestic determinations performed at 25 °C by Sadeghi and Gholamireza [162] (Table 5.12). The vapour pressure lowerings of disodium hydrogen citrate are slightly larger than those of diammonium hydrogen citrate and the same is probably true in the case of dipotassium hydrogen citrate (Fig. 5.12).

Table 5.12 Relative humidities and vapour pressures of water over diammonium hydrogen citrate solutions as a function of temperature and concentration. ([162] - From isopiestic experiments in binary and ternary systems)

t/°C	w	RH %	*p*/kPa	w	RH %	*p*/kPa
25	0.0898	98.28	3.114	0.1828	96.51	3.058
	0.1073	98.00	3.105	0.1891	96.35	3.053
	0.1174	97.76	3.098	0.1933	96.25	3.050
	0.1212	97.74	3.097	0.2072	95.96	3.040
	0.1245	97.68	3.095	0.2103	95.88	3.038
	0.1288	97.59	3.092	0.2144	95.81	3.036
	0.1360	97.44	3.087	0.2324	95.28	3.019
	0.1378	97.43	3.087	0.2361	95.27	3.019
	0.1462	97.21	3.080	0.2515	94.84	3.005
	0.1536	97.10	3.077	0.2541	94.83	3.005
	0.1565	97.05	3.075	0.2750	94.30	2.988
	0.1594	97.04	3.075	0.2804	94.08	2.981
	0.1659	96.88	3.070	0.3583	91.66	2.904
	0.1755	96.67	3.063	0.3723	91.18	2.889
	0.1791	96.54	3.059	0.4218	89.20	2.826

The vapour pressure of water over diammonium hydrogen citrate solutions at 25 °C can be correlated by

$$p(25°\text{C}; \text{w}) / \text{kPa} = 3.1668 - 0.5777\text{w} + 0.2133\text{w}^2 - 1.7999\text{w}^3 \qquad (5.34)$$
$$\text{w} < 0.18$$

As mentioned above, the accuracy of measured values $\Delta p(T;m)$ when expressed in terms of more sensitive osmotic coefficients is not sufficiently accurate for the extrapolation of $\phi(T;m \rightarrow 0)$ from the low concentration region. This is clearly evident when the experimental values of water activities are used to calculate osmotic coefficients of citrates. Formally, the osmotic coefficients are evaluated from Eq. (5.20)

$$\phi(m) = -55.508\left[\frac{\ln a_\text{w}(m)}{m\nu}\right] \qquad (5.35)$$

by treating acidic citrates as 1:1 and 1:2 and neutral citrates as 1:3 type strong electrolytes with $\nu = 1$ for MeH_2Cit, $\nu = 2$ for Me_2HCit and $\nu = 3$ for Me_3Cit salts.

In Figs. 5.13 and 5.14 are plotted osmotic coefficients of several citrates at 25 °C (at other temperatures osmotic coefficients of citrates behave in similar way) which were calculated directly from Eq. (5.35) without taking into account the incomplete dissociation of acidic citrates. As can be observed, the scattering of $\phi(m)$ values is large and they always lie far from the concentration region which permits a certain extrapolation $\phi(m \rightarrow 0)$. The necessity of accurate $\phi(m)$ values in the low concentration region is associated with the integration of the Gibbs-Duhem equation which allows to evaluate thermodynamically consistent activity coefficients.

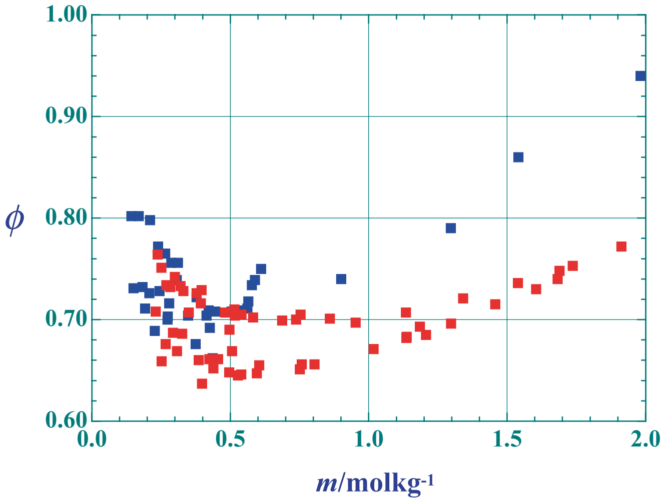


Fig. 5.13 Osmotic coefficients calculated from experimental water activities at 25 °C. 🟥 - trisodium citrate and 🟦 - tripotassium citrate

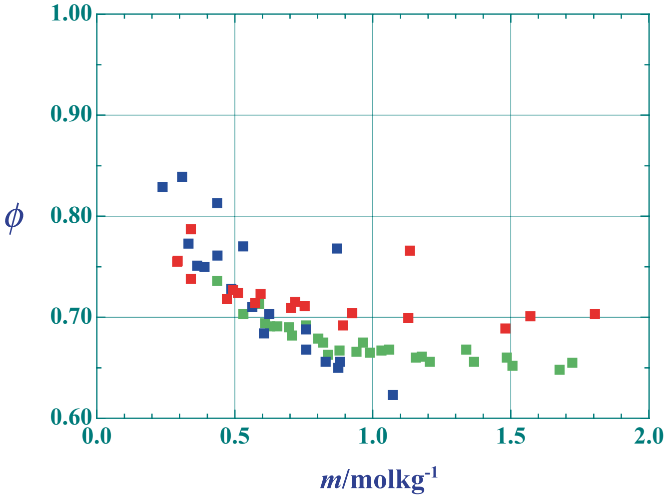


Fig. 5.14 Osmotic coefficients calculated from experimental water activities at 25 °C. 🟥 - disodium hydrogen citrate, 🟦 - potassium dihydrogen citrate and 🟩 - diammonium hydrogen citrate

If determination of osmotic and activity coefficients is limited only to Na_3Cit and K_3Cit salts then the Pitzer formalism [167] can be applied. In this procedure trisodium citrate and tripotassium citrate are treated as fully dissociated electrolytes and the water activities $a_w(T;m)=p(T;m)/p^0(T)$, at constant temperature are calculated using Eqs. (5.27) and (5.31). These equations represent the best fit of vapour pressures as a functions of concentration.

For a strong 1:3 type electrolyte, the Pitzer equations for osmotic coefficients are

$$\phi(T;m) = 1 - \frac{3A_\phi(T)\sqrt{I}}{1+b\sqrt{I}} + \frac{3}{2}\left[\beta^{(0)}(T) + \beta^{(1)}(T)e^{-\alpha\sqrt{I}}\right]m + \frac{3^{3/2}}{2}C^{\phi}(T)m^2 \tag{5.36}$$

$$I = 6\,m; \quad \alpha = 2.0\ \mathrm{kg}^{1/2}\mathrm{mol}^{-1/2}; \quad b = 1.2\ \mathrm{kg}^{1/2}\mathrm{mol}^{-1/2}$$

and for activity coefficients are

$$\ln\gamma_\pm(T;m) = -3A_\phi(T)\left[\frac{\sqrt{I}}{1+b\sqrt{I}} + \frac{2}{b}\ln(1+b\sqrt{I})\right] + 3\left\{\beta^{(0)}(T) + \frac{\beta^{(1)}(T)}{\alpha^2 I}\left[1 - \left(1+\alpha\sqrt{I} - \frac{\alpha^2 I}{2}\right)e^{-\alpha\sqrt{I}}\right]\right\}m + \frac{3^{5/2}}{4}C^{\phi}(T)m^2 \tag{5.37}$$

Table 5.13 Pitzer parameters for alkali metal citrates[a]

t/°C-	$A_\phi(T)$	$\beta^{(0)}(T)$	$\beta^{(1)}(T)$	$C^\phi(T)$
Trisodium citrate				
25	0.3913	0.2856	5.5950	−0.03111
35	0.3981	0.3018	5.0889	−0.03336
45	0.4058	0.2878	6.3473	−0.02761
Tripotassium citrate				
20	0.3878	0.2577	6.7580	−0.00262
25	0.3913	0.3026	5.8856	−0.01920
30	0.3944	0.2955	6.3015	−0.01707
35	0.3981	0.3660	5.0199	−0.03266
40	0.4017	0.3465	5.0510	−0.02637

[a] Units: $A_\phi(T)$ $\text{kg}^{1/2}\ \text{mol}^{-1/2}$, $\beta(^0)\ (T)$, $\beta(^0)\ (T)$ kg mol^{-1} and $C^\phi\ (T)$ $\text{kg}^2\ \text{mol}^{-2}$

where $A_\phi(T)$ is constant which depends on physical properties of water (the Debye-Hückel parameter for the osmotic coefficient) and $\beta^{(0)}(T)$, $\beta^{(0)}(T)$ and $C^\phi(T)$ are three adjustable parameters at given temperature T. Values of these parameters are presented in Table 5.13.

Typical behaviour of osmotic and activity coefficients as calculated using Eqs. (5.36) and (5.37), is illustrated for trisodium citrate and tripotassium citrate in Fig. 5.15. It can be observed, that values of the $\phi(m)$ and $\gamma_\pm(m)$ coefficients after a strong fall in very dilute solutions depend rather weakly on the citrate concentration. Since $a_w(T;m)$ values are nearly temperature independent, the same is observed in the case osmotic and activity coefficients. It is worthwhile to mention that the Pitzer model was also used by Schunk and Maurer [163] when they determined water activities at 25 °C in ternary systems (citric acid + inorganic salt). The interactions parameters between ions, which were applied to represent activities in ternary systems, were calculated by taking into account the dissociation steps of citric acid and the formation of bisulfate ions for solutions with sodium sulfate.

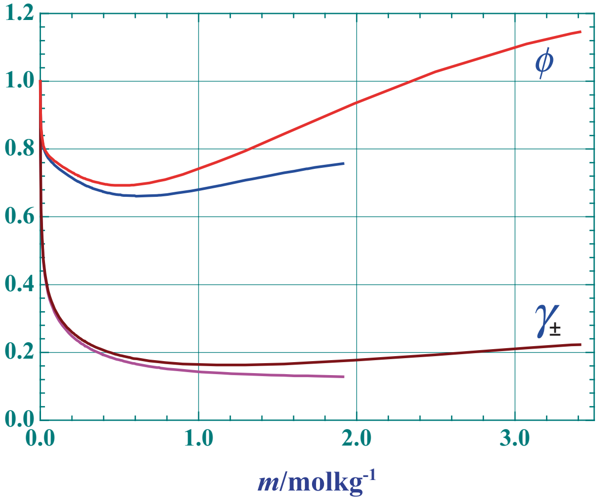


Fig. 5.15 Osmotic and activity coefficients of trisodium citrate and tripotassium citrate at 25 °C, calculated using Eqs. (5.36) and (5.37). — K_3Cit, — Na_3Cit, — K_3Cit and — Na_3Cit

5.6 Volumetric Properties of Aqueous Solutions of Alkali Metal Citrates

Volumetric and compressibility studies in aqueous solutions of alkali metal citrates and ammonium citrates are relatively well documented in the literature [160, 162, 164, 168–187]. Usually, they were performed in the context of separation and purification of biomaterials in various two-phase aqueous systems with different polyethylene glycols, polypropylene glycols, polyvinylpyrrolidone, room temperature ionic liquids and amino acids.

Densities and calculated from them the apparent molar volumes of trisodium citrate and disodium hydrogen citrate at 25 °C and in the 0.03–1.68 mol kg^{-1} and 0.03–1.67 mol kg^{-1} concentration ranges were reported in 1990 by Apelblat and Manzurola [170]. In dilute and moderately dilute solutions, and over a large range of temperatures, from 5 to 95 °C, Patterson and Wooley [184] presented in 2001 a detailed thermodynamic analysis of volumetric properties of the trisodium citrate + water, disodium hydrogen citrate + water and sodium dihydrogen citrate + water systems. Their determinations included the following concentration ranges from 0.006 to 0.43 mol kg^{-1} for Na_3Cit, from 0.0015 to 0.64 mol kg^{-1} for Na_2HCit and from 0.03 to 0.98 mol kg^{-1} for NaH_2Cit. Densities and sound velocities in trisodium citrate solutions, in the 10–35 °C temperature range and from 0.025 to 1.32 mol kg^{-1} were measured by Sadeghi and Ziamajidi [171, 185] They also considered the effect of small additions of polyvinylpyrrolidone on densities of Na_3Cit solutions. Aqueous solutions of acidic sodium citrates were considered by Sadeghi et al. [160] who measured densities and sound velocities in the 15–35 °C temperature range, from 0.0095 to 0.34 mol kg^{-1} for disodium hydrogen citrate and from 0.0093 to 0.39 mol kg^{-1} for sodium dihydrogen citrate. Kumar et al. [182] determined densities and sound velocities of trisodium citrate solutions, and also with additions of N-acetyl glycine, in the 10–30 °C temperature range, from 0.0025 to 0.87 mol kg^{-1}. Their molal concentrations and calculated the apparent molar volumes are based on the $Na_3Cit \cdot 2H_2O$ and $K_3Cit \cdot H_2O$ hydrates and not on anhydrous salts. Determinations of densities, viscosities and refraction indices of Na_3Cit solutions were also performed by Salabat et al. [164] (at 25 °C, from 0.0025 to 1.92 mol kg^{-1}) but their results differ considerably from all others (Fig. 5.16).

In the case of tripotassium citrate aqueous solutions, the first measurements of density and viscosity at 25 °C and in the 0.3–3.3 mol kg^{-1} concentration range were reported in 1924 by Fricke and Schützdeller [150]. Sister Halasey [168] in 1941 determined densities of a number of potassium salts by the dilatometric method, in the context of the Hofmeister series. She obtained that in the 5–30 °C temperature range, the molar volume of K_3Cit at infinite dilution is about 112.3 dm^3 mol^{-1}. The apparent molar volumes tripotassium citrate at 25 °C and in the 0.03–1.73 mol kg^{-1} concentration range were reported by Apelblat and Manzurola [170]. Most of recent investigations which are dealing with densities, sound velocities and viscosities is associated with the Sadeghi group [172, 173–175, 178, 179]. Sadeghi and Ziamajidi [172] measured densities and sound velocities of aqueous solutions of tripotassium citrate in the 15–40 °C range, from 0.0185 to 0.75 mol kg^{-1} and together with polypropylene oxide 400. Sadeghi and Goodarzi [173–175] also studied the influence of KH_2Cit and K_3Cit on the volumetric and compressibility properties of L-alanine solutions.

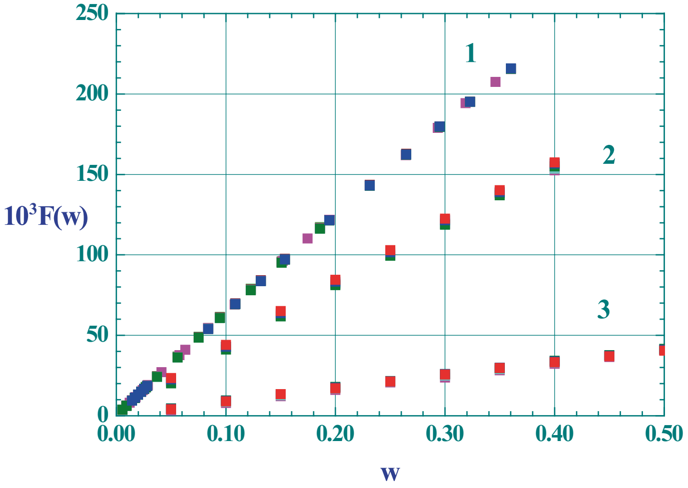


Fig. 5.16 Densities of aqueous solutions of citrates in the 0–50 °C temperature range, as expressed by Eqs. (5.40). 1-tripotassium citrate, 2-diammonium hydrogen citrate and 3-triammonium citrate. 🟩 - 15 °C, 🟥 - 20 °C, 🟪 - 25 °C, 🟩 - 30 °C, 🟩 - 35 °C, 🟦 - 40 °C, 🟥 - 45 °C, ⬛ - 50 °C

The effect of KCl, KBr and KNO_3 on densities, sound velocities and viscosities of tripotassium citrate solutions, in the 20–40 °C range, from 0.047 to 0.1.84 mol kg^{-1}. was investigated by Zafarami-Moattar and Izadi [178, 179]. Few values of densities, viscosities and surface tensions in the 20–50 °C range are reported by Lu et al. [180]. Similarly as for trisodium citrate, Kumar et al. [182] studied the volumetric and acoustic properties of tripotassium citrate solutions and in the presence of N-acetyl glycine, in the 10–30 °C temperature range and from 0.036 to 0.87 mol kg^{-1}. Sound velocities in trilithium, trisodium and tripotassium solutions were measured by Dhake and Padmini [169] but their ultrasonic parameters are mainly given in graphical form. They recommended, basing on adiabatic compressibilities, the following hydration numbers of ions in aqueous solutions $h(Cit^{3-}) = 9.54$; $h(Li^+) = 4$ and $h(Na^+) = h(K^+) = 5$. From other alkali metal citrates, the author unpublished densities of trilithium citrate aqueous solutions, in the 5–70 °C temperature range, and from 0.013 to 1.74 mol kg^{-1} are also considered here.

Volumetric properties of triammonium citrate solutions were considered by Govindarajan et al. [183] in the 25–45 °C temperature range, and from 0.21 to 4.1 mol kg^{-1}. However, the accuracy of their densities which were determined by the pycnometric method is not enough to calculate the apparent molar volumes. In case of diammonium hydrogen citrate, Sadeghi and Gholamireza [163] determined densities in dilute solutions from 0.0059 to 0.09 mol kg^{-1} and over the 10–35 °C temperature range, but the concentration dependence of their $V_{2,\phi}(m)$ values has an usual form (some densities are lower than those of pure water) and therefore their results were excluded from the data analysis. Kalaivani et al. [182] measured densities and viscosities od diammonium hydrogen citrate solutions in the 25–45 °C temperature range, and from 0.036 to 0.87 mol kg^{-1}. There are also densities of ammonium citrates in ternary systems with polyethylene glycols 400, 2000 and 6000 [176, 181, 183] and with glycine, L-alanine and L-serine [162, 188].

Densities of aqueous solutions of citrates, taken from above mentioned investigations, can be at constant temperature *T*, to correlated as a function of weight fractions of citrates w in the following way

$$\begin{aligned} &\mathrm{d}(T)/\mathrm{g}\cdot\mathrm{cm}^{-3} = \mathrm{d}_\mathrm{w}(T) + \mathrm{A}\mathrm{w} + \mathrm{B}\mathrm{w}^2 \\ &\mathrm{d}_\mathrm{w}(T) = \mathrm{d}_{\mathrm{H_2O}}(T)/\mathrm{g}\cdot\mathrm{cm}^{-3} \end{aligned} \tag{5.38}$$

where A and B coefficients are presented in Table 5.14.

Similarly as for citric acid, temperature dependence of densities can be reduced to the known temperature dependence of pure water densities

$$\begin{aligned} &\mathrm{d}(m;T) = \frac{\mathrm{d}_{\mathrm{H_2O}}(T)}{1-\mathrm{d}_{\mathrm{H_2O}}(T)\mathrm{F}(\mathrm{w})} \\ &\mathrm{F}(\mathrm{w})/\mathrm{cm}^3\cdot\mathrm{g}^{-1} = \left[\frac{1}{\mathrm{d}_{\mathrm{H_2O}}(T)} - \frac{1}{\mathrm{d}(m;T)}\right] = \mathrm{a}\,\mathrm{w} + \mathrm{b}\mathrm{w}^2 \end{aligned} \tag{5.39}$$

where a and b are constants given in Eqs. (5.40)

$$\begin{aligned} &\mathrm{F}(\mathrm{Li_3Cit;w})/\mathrm{cm}^3\cdot\mathrm{g}^{-1} = 0.64366\mathrm{w} - 0.23620\mathrm{w}^2\ ;\ \mathrm{w} < 0.27 \\ &\mathrm{F}(\mathrm{NaH_2Cit;w})/\mathrm{cm}^3\cdot\mathrm{g}^{-1} = 0.47570\mathrm{w} + 0.18151\mathrm{w}^2\ ;\ \mathrm{w} < 0.17 \\ &\mathrm{F}(\mathrm{Na_2HCit;w})/\mathrm{cm}^3\cdot\mathrm{g}^{-1} = 0.61252\mathrm{w} - 0.15341\mathrm{w}^2\ ;\ \mathrm{w} < 0.29 \\ &\mathrm{F}(\mathrm{Na_3Cit;w})/\mathrm{cm}^3\cdot\mathrm{g}^{-1} = 0.71050\mathrm{w} - 0.26731\mathrm{w}^2\ ;\ \mathrm{w} < 0.26 \\ &\mathrm{F}(\mathrm{KH_2Cit;w})/\mathrm{cm}^3\cdot\mathrm{g}^{-1} = 0.51588\mathrm{w} - 0.10256\mathrm{w}^2\ ;\ \mathrm{w} < 0.15 \\ &\mathrm{F}(\mathrm{K_3Cit;w})/\mathrm{cm}^3\cdot\mathrm{g}^{-1} = 0.65936\mathrm{w} - 0.16956\mathrm{w}^2\ ;\ \mathrm{w} < 0.36 \\ &\mathrm{F}((\mathrm{NH_4})_2\,\mathrm{HCit;w})/\mathrm{cm}^3\cdot\mathrm{g}^{-1} = 0.43878\mathrm{w} - 0.12638\mathrm{w}^2\ ;\ \mathrm{w} < 0.40 \\ &\mathrm{F}((\mathrm{NH_4})_3\,\mathrm{Cit;w})/\mathrm{cm}^3\cdot\mathrm{g}^{-1} = 0.08843\mathrm{w} - 0.01291\mathrm{w}^2\ ;\ \mathrm{w} < 0.51 \end{aligned} \tag{5.40}$$

The accuracy of densities, as calculated from Eqs. (5.39) to (5.40), depends evidently on the accuracy of experimental densities coming from various investigations. How good is the estimation of densities at different temperatures *T* and weight fractions w is illustrated in Figs. 5.16 and 5.17. As can be observed, Eqs. (5.39) and (5.40) give for densities at any temperature and concentration, reasonable good predictions for all citrates, with an exception of sodium dihydrogen citrate in the 0.10<w<0.17 concentration range. For this citrate densities will probably be less accurate (Fig. 5.17).

Determined densities of aqueous solutions of citrates are usually expressed in terms of the apparent molar volumes

Table 5.14 Densities of aqueous solutions of lithium, sodium, potassium and ammonium citrates as a function of temperature and concentration. A and B coefficients of Eq. (5.38)

t/°C	d_w	A	B	w*
Trilithium citrate				
5	0.99999	0.66170	0.11236	0.27
10	0.99973	0.65297	0.12484	
15	0.99913	0.64651	0.13386	
20	0.99823	0.64193	0.13917	
25	0.99705	0.63792	0.14379	
30	0.99568	0.63437	0.14938	
35	0.99406	0.63181	0.15254	
40	0.99224	0.62961	0.15584	
45	0.99024	0.62798	0.15811	
50	0.98807	0.62704	0.15947	
55	0.98573	0.62639	0.16066	
60	0.98324	0.62623	0.16126	
65	0.98059	0.62686	0.16009	
70	0.97781	0.62751	0.16075	
Sodium dihydrogen citrate				
5	0.99999	0.55505	0.13430	0.17
15	0.99913	0.47127	0.55252	
20	0.99823	0.47713	0.18337	0.09
25	0.99705	0.45926	0.55194	0.17
30	0.99568	0.46513	0.19883	0.09
35	0.99406	0.44853	0.55797	0.17
45	0.99024	0.50047	0.19204	
55	0.98573	0.49351	0.19421	
65	0.98059	0.48777	0.19513	
75	0.97489	0.48327	0.19493	
85	0.96895	0.47975	0.19368	
95	0.96192	0.47720	0.18992	
Disodium hydrogen citrate				
5	0.99999	0.64880	0.05050	0.13
15	0.99913	0.64155	−0.00424	
20	0.99823	0.62901	0.12807	0.08
25	0.99705	0.61068	0.23268	0.29
30	0.99568	0.61498	0.15675	0.08
35	0.99406	0.61530	0.23490	0.13
45	0.99024	0.58854	0.16208	
55	0.98573	0.57939	0.18783	
65	0.98059	0.57621	0.17880	
75	0.97489	0.57322	0.17494	
85	0.96895	0.57024	0.18021	
95	0.96192	0.56899	0.18040	
Trisodium citrate				
5	0.99999	0.74030	0.00878	0.10
10	0.99973	0.72870	0.19331	0.26
15	0.99913	0.71696	0.21659	
20	0.99823	0.71257	0.21190	
25	0.99705	0.70509	0.22265	0.31
30	0.99568	0.70068	0.22440	0.26
35	0.99406	0.69609	0.22873	
45	0.99024	0.68690	0.08978	0.10

Table 5.14 (continued)

t/°C	d_w	A	B	w*
55	0.98573	0.68149	0.09798	
65	0.98059	0.67921	0.09053	
75	0.97489	0.67737	0.09220	
85	0.96895	0.66403	0.19542	
95	0.96192	0.67982	0.06869	
Potassium dihydrogen citrate				
10	0.99973	0.52852	0.15294	0.15
15	0.99913	0.52106	0.16202	
20	0.99823	0.51466	0.16811	
25	0.99705	0.50971	0.16888	
30	0.99568	0.50364	0.17910	
35	0.99406	0.49921	0.18174	
Tripotassium citrate				
15	0.99913	0.66861	0.23874	0.19
20	0.99823	0.65745	0.28355	0.36
25	0.99705	0.65309	0.28883	
30	0.99568	0.64812	0.29560	
35	0.99406	0.64482	0.29754	
40	0.99224	0.64174	0.30104	
Diammonium hydrogen citrate				
25	0.99705	0.43941	0.02835	0.40
30	0.99568	0.43845	0.03336	
35	0.99406	0.43245	0.06261	
40	0.99224	0.43717	0.04874	
45	0.99024	0.44942	0.01882	
Triammonium citrate				
25	0.99705	0.07935	0.00794	0.51
30	0.99568	0.08536	−0.00083	
35	0.99406	0.09215	−0.01323	
40	0.99224	0.09089	−0.01308	
45	0.99024	0.08973	−0.01336	

[a] Correlated for the $0 \le w \le w^*$ mass fraction range

$$
\begin{aligned}
V_{2,\phi}(m;T) &= \frac{V(m;T) - V_{\mathrm{H_2O}}(T)}{m} \\
V_{2,\phi}(m;T) &= \frac{\mathrm{M}_2}{\mathrm{d}(m;T)} + \frac{1000}{m}\left(\frac{1}{\mathrm{d}(m;T)} - \frac{1}{\mathrm{d}_{\mathrm{H_2O}}(T)}\right)
\end{aligned}
\tag{5.41}
$$

and they are used to determinate the partial volumes of water $\overline{V_1}$ and dissolved salt $\overline{V_2}$.

$$
\begin{aligned}
\overline{V_1}(m;T) &= \overline{V_1}^0(m \to 0;T) - \frac{m^2}{55.508}\left(\frac{\partial V_{2,\phi}(m;T)}{\partial m}\right)_{T,P} \\
\overline{V_2}(m;T) &= V_{2,\phi}(m;T) + m\left(\frac{\partial V_{2,\phi}(m;T)}{\partial m}\right)_{T,P}
\end{aligned}
\tag{5.42}
$$

where $\overline{V_1}^0(m \to 0;T)$ is the partial molar volume of water at infinite dilution.

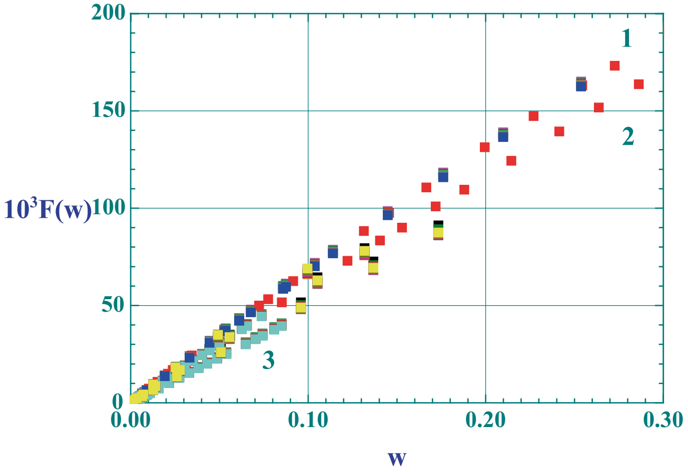


Fig. 5.17 Densities of aqueous solutions of sodium citrates in the 0–95 °C temperature range, as expressed by Eqs. (5.40). 1-trisodium citrate, 2-disodium hydrogen citrate and 3-sodium dihydrogen citrate. ⬛ - 5 °C, 🟪 - 10 °C, 🟩 - 15 °C, 🟩 - 20 °C, 🟥 - 25 °C, 🟫 - 30 °C, 🟦 - 35 °C, 🟦 - 45 °C, 🟧 - 55 °C, 🟩 - 65 °C, 🟪 - 75 °C, ⬛ - 85 °C, 🟨 - 95 °C

The apparent molar volumes strongly depend on the accuracy of measured densities. As can be observed in Fig. 5.18, where are plotted $V_{2,\phi}$ values of trisodium citrate at 25 °C, the discrepancies between different investigations are evident and as mentioned above, the Salabat et al. [164] results are shifted with regard to all others and they clearly incorrect. The best agreement exists between $V_{2,\phi}$ values of trisodium citrate coming from the Apelblat and Manzurola [170] and Sadeghi and Ziamajidi [171] densities. In the case of tripotassium citrate, disodium hydrogen citrate and sodium dihydrogen citrate [160, 170, 172, 178, 184], the evaluated apparent

Fig. 5.18 The apparent molar volume of trisodium citrate as a function of concentration at 25 °C. 🟩 - [164], 🟪 - [170], 🟥 - [71], 🟫 - [182], 🟩 - [184], —— fully dissociated 1:3 type electrolyte with the Debye-Hückel slope

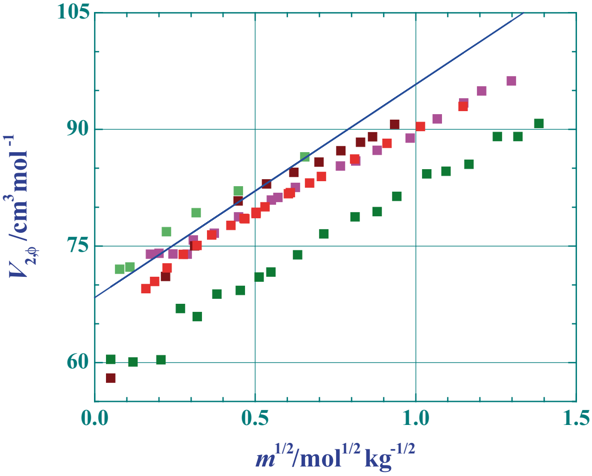


Fig. 5.19 The apparent molar volume of tripotassium citrate (1) and trilithium citrate (2) as a function of concentration at 25 °C. 🟥 - [170], 🟫 - [172], 🟪 - [178], 🟩 - [author's unpublished results], —— fully dissociated 1:3 type electrolyte with the Debye-Hückel slope

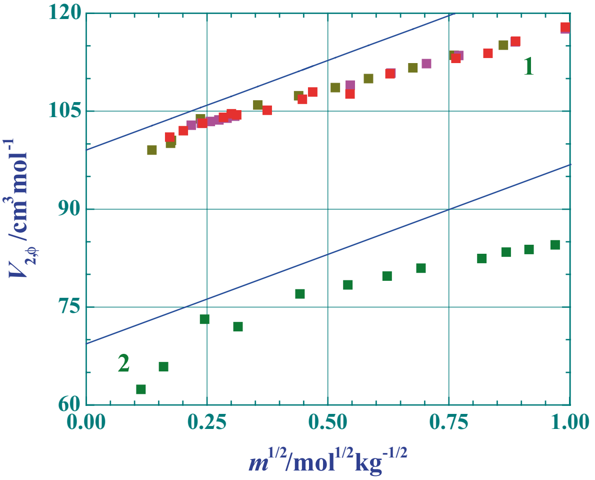
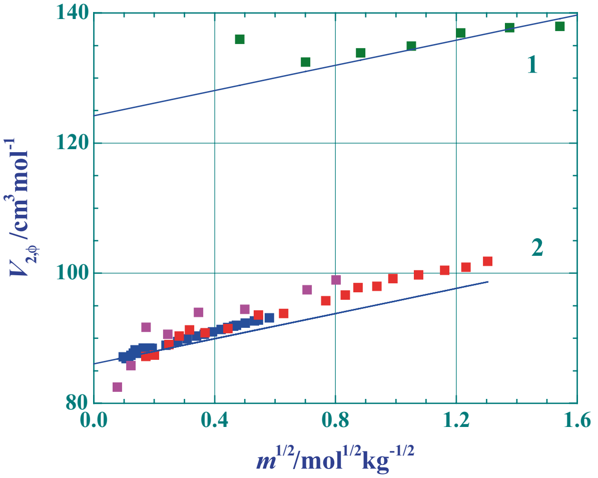


Fig. 5.20 The apparent molar volume of diammonium hydrogen citrate (1) and disodium hydrogen citrate (2) as a function of concentration at 25 °C. 🟩 - [181], 🟦 - [160], 🟥 - [170], 🟪 - [184], —— fully dissociated 1:2 type electrolyte with the Debye-Hückel slope



molar volumes are in a reasonably good agreement (Figs. 5.19, 5.20, and 5.21). Unfortunately, it is impossible to compare $V_{2,\phi}$ values for other citrates, because their densities were reported only once (trilitium citrate, triammonium citrate, diammonium hydrogen citrate and potassium dihydrogen citrate).

It is expected from the Debye-Hückel theory, that in dilute solutions of fully dissociated electrolyte, the apparent molar volumes depend on concentration in the following form [189]

$$\begin{aligned} V_{2,\phi}(m;T) &= V^0(T) + A_V(T)\sqrt{m} \\ A_V(T) &= S_V(T)\mathrm{d}_{\mathrm{H_2O}}^{1/2}(T) \end{aligned} \tag{5.43}$$

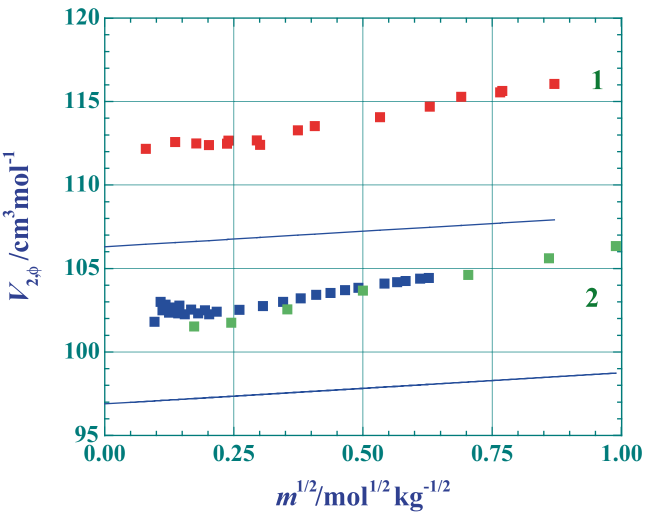


Fig. 5.21 The apparent molar volume of potassium dihydrogen citrate (1) and sodium dihydrogen citrate (2) as a function of concentration at 25 °C. 🟥 - [174], 🟦 - [160], 🟩 - [184], —— fully dissociated 1:1 type electrolyte with the Debye-Hückel slope

where $S_V(T)$ are the limiting Debye-Hückel slopes and $V^0(T)$ are the partial molar volumes of electrolytes at infinite dilution. At 25 °C, values of the Debye-Hückel slopes are 1.868 cm^3 mol$^{-1/2}$ kg$^{1/2}$ for 1:1 type electrolytes, 9.706 cm^3 mol$^{-1/2}$ kg$^{1/2}$ for 1:2 type electrolytes and 27.454 cm^3 mol$^{-1/2}$ kg$^{1/2}$ for 1:3 type electrolytes.

Using the conventional basis of partial molar volumes at infinite dilution, $V^0(\mathrm{H}^+)=0$ cm^3 mol^{-1}, the corresponding values for cations are: $V^0(\mathrm{Li}^+)=-0.88$ cm^3 mol^{-1}; $V^0(\mathrm{Na}^+)=-1.21$ cm^3 mol^{-1}; $V^0(\mathrm{K}^+)=9.02$ cm^3 mol^{-1} and $V^0(\mathrm{NH_4}^+)=17.86$ cm^3 mol^{-1} [189]. Since the partial molar volumes at infinite dilution of citrate ions at 25 °C are known, $V^0(\mathrm{H_2Cit}^-)=98.1\pm1.0$ cm^3 mol^{-1}, V^0 $(\mathrm{HCit}^{2-})=88.5\pm1.0$ cm^3 mol^{-1} and $V^0(\mathrm{Cit}^{3-})=72.0\pm1.0$ cm^3 mol^{-1}, then due to the additivity principle we have

$$\begin{aligned} V^0(\mathrm{Me_3Cit}) &= 3V^0(\mathrm{Me}^+)+V^0(\mathrm{Cit}^{3-}) \\ V^0(\mathrm{Me_2HCit}) &= 2V^0(\mathrm{Me}^+)+V^0(\mathrm{HCit}^{2-}) \\ V^0(\mathrm{MeH_2Cit}) &= V^0(\mathrm{Me}^+)+V^0(\mathrm{H_2Cit}^-) \end{aligned} \tag{5.44}$$

Thus, considering that the partial molar volumes of electrolytes are equal to the sum of its ionic components, it follows for the neutral citrates from Eqs. (5.44) that

$$\begin{aligned} V^0(\mathrm{Li_3Cit}) &= 69.4\ \mathrm{cm^3{\cdot}mol^{-1}} \\ V^0(\mathrm{Na_3Cit}) &= 68.4\ \mathrm{cm^3{\cdot}mol^{-1}} \\ V^0(\mathrm{K_3Cit}) &= 99.1\ \mathrm{cm^3{\cdot}mol^{-1}} \\ V^0((\mathrm{NH_4})_3\mathrm{Cit}) &= 125.6\ \mathrm{cm^3{\cdot}mol^{-1}} \end{aligned} \tag{5.45}$$

and for the acidic citrates

$$\begin{aligned} V^0(\mathrm{Na_2HCit}) &= 86.1\,\mathrm{cm^3 \cdot mol^{-1}} \\ V^0(\mathrm{K_2HCit}) &= 106.5\,\mathrm{cm^3 \cdot mol^{-1}} \\ V^0(\mathrm{(NH_4)_2HCit}) &= 122.2\,\mathrm{cm^3 \cdot mol^{-1}} \end{aligned} \tag{5.46}$$

and

$$\begin{aligned} V^0(\mathrm{NaH_2Cit}) &= 96.9\,\mathrm{cm^3 \cdot mol^{-1}} \\ V^0(\mathrm{KH_2Cit}) &= 107.1\,\mathrm{cm^3 \cdot mol^{-1}} \\ V^0(\mathrm{NH_4H_2Cit}) &= 116.0\,\mathrm{cm^3 \cdot mol^{-1}} \end{aligned} \tag{5.47}$$

The partial molar volumes at infinite dilution of citrates can be arranged in the following order $V^0(\mathrm{MeH_2Cit}) > V^0(\mathrm{Me_2HCit}) > V^0(\mathrm{Me_3Cit})$ and with regard to cations $\mathrm{NH_4^+} > \mathrm{K^+} > \mathrm{Na^+} \geq \mathrm{Li^+}$.

The apparent molar volumes of the 1:3, 1:2 and 1:1 citrates at 25 °C, as evaluated from Eq. (5.43), by using the partial molar volumes of citrates at infinite dilution and the corresponding the Debye-Hückel slopes are plotted in Figs. 5.18, 5.19, 5.20, and 5.21. They are compared with $V_{2,\phi}(m)$ values based on experimental densities. As can be seen, the partial molar volumes of $V^0(\mathrm{Me_3Cit})$ and $V^0(\mathrm{Me_2HCit})$ citrates have acceptable values but not those of $V^0(\mathrm{MeH_2Cit})$ (Fig. 5.21). This can be expected taking into account that measurements are performed in not enough dilute solutions and the complicity of dissociation processes observed for mono-charged citrates in this concentration region.

The observed slopes differ somewhat from the Debye-Hückel slopes which is a typical situation for many electrolyte solutions. However, it should be taken into account that the apparent molar volume are very sensitive to experimental uncertainties of measured densities in dilute solutions and practically all determinations were performed outside the concentration range where the Debye-Hückel slopes are expected. A reasonably good agreement between the Debye-Hückel slopes, as observed in the case two-charged citrates (Fig. 5.20) is probably accidental. The apparent molar volumes of potassium dihydrogen citrate are determined only in concentrated solutions and those of disodium hydrogen citrate show a large scattering of $V_{2,\phi}(m)$ values in dilute solutions. The same is observed in the case of trisodium citrate (Fig. 5.18).

In spite of the fact that densities of aqueous solutions of citrates as a function of temperature were determined in the literature many times and over various ranges of temperature in 5 or 10 °C intervals, no special attention was directed to examine more closely their temperature dependence. The only exceptions are Sadeghi. and Gholamireza [162] for diammonium hydrogen citrate and Kumar et al. [182] for trisodium citrate and tripotassium citrate. However, they only postulated that the apparent molar expansibilities at infinite dilutions are positive $V_{2,E} = \left(\partial V_{2,\phi}(m;T)/\partial T\right)_{P,m\to 0} > 0$ and the second derivatives of the partial molar volume of solute at infinite dilution,

$\bar{V}_2^0(T) = \bar{V}_2(m \to 0; T)$, are negative $\left(\partial^2 \bar{V}_2^0(T) / \partial T^2\right)_P < 0$. This indicates according to Hepler [190], that these citrates are the structure-breaking solutes.

Considering that Patterson and Woolley [184] performed measurements of density that cover a large temperature range, from 5 to 95 °C for sodium citrates and others for smaller temperature ranges: Sadeghi. and Ziamajidi [173] for tripotassium citrate from 15 to 35 °C, Sadeghi and Goodarzi [175] for potassium dihydrogen citrate from 10 to 40 °C and.the author densities for trilithium citrate from 5 to 70 °C, it is possible to perform a more detailed analysis of the volume-temperature relations.

Some general, a rather qualitative description of such relations, for all citrates treated together, is presented here. The volume-temperature relations are based on numerical differentiation of experimental densities, and evidently accuracies of the first and second derivatives of densities with regard to temperature strongly depend on the accuracy of d(*m*;*T*) values coming from different investigations. The first derivative of densities leads to the cubic expansion coefficients (thermal expansibilities) of aqueous solutions of citrates

$$\alpha(m;T) = -\frac{1}{d(m;T)}\left(\frac{\partial \mathrm{d}(m;T)}{\partial T}\right)_{P,m}$$
$$\alpha_{\mathrm{H_2O}}(T) = \frac{1}{\mathrm{d}_{\mathrm{H_2O}}(T)}\left(\frac{\partial \mathrm{d}_{\mathrm{H_2O}}(T))}{\partial T}\right)_{P,m} \tag{5.48}$$

Calculated values of cubic expansion coefficients at 25 °C are plotted in Fig. 5.22 and as can be observed they increase with increasing concentration and they are larger than the cubic expansion coefficient of pure water. In general, at constant

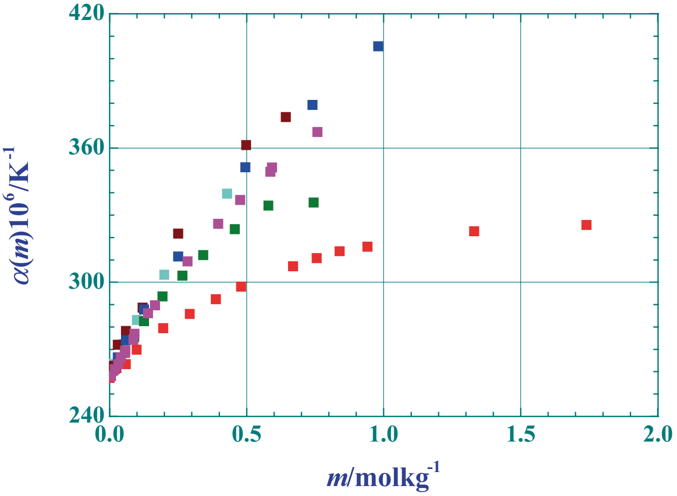


Fig. 5.22 Cubic expansion coefficients of aqueous solutions of citrates as a function of concentration at 25 °C. 🟥 - trilithium citrate, 🟩 - tripotassium citrate, 🟪 - potassium dihydrogen citrate, 🟦 - trisodium citrate, 🟦 - sodium dihydrogen citrate and 🟫 - disodium hydrogen citrate

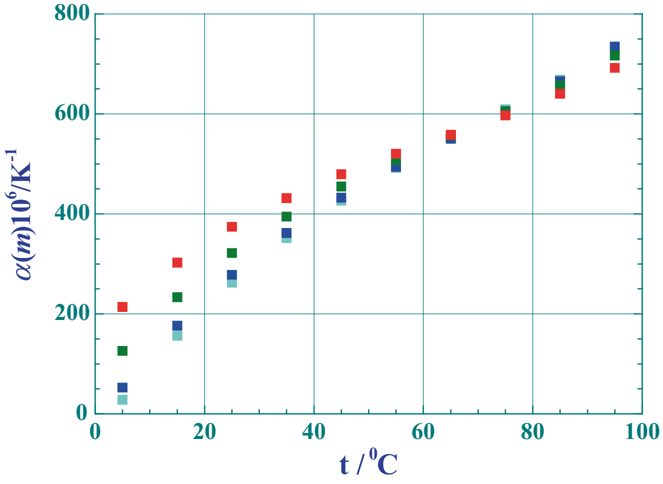


Fig. 5.23 Cubic expansion coefficients of aqueous solutions of disodium hydrogen citrate as a function of temperature. 🟩 - $m = 0.3000$ mol kg^{-1}, 🟦 - $m = 0.1201$ mol kg^{-1}; 0.2499 mol kg^{-1} and 🟧 - $m = 0.6427$ mol kg^{-1}

temperature, cubic expansion coefficients increase with m, but they are approaching some limiting value. Thermal expansibilities of sodium citrates are larger than those of other citrates $\alpha(Na_2HCit) > \alpha(NaH_2Cit) > \alpha(Na_3Cit) > \alpha(KH_2Cit) >> \alpha(K_3Cit) > \alpha(Li_3Cit)$. Cubic expansion coefficients of acidic citrates are larger than those of neutral citrates with the following order of cations $Na^+ > K^+ > Li^+$.

At constant concentration, when the temperature dependence is examined, usually $\alpha(m_2;T) > \alpha(m_1;T)$ if $T_2 > T_1$, but the difference between them decreases rapidly with increasing T and sometimes the inverse behaviour is observed at high temperatures, as for example in the case of disodium hydrogen citrate (Fig. 5.23). Differences in cubic expansion coefficients, $\Delta\,\alpha(m;T) = \alpha(m;T) - \alpha_{H_2O}(T)$, have positive values, but they strongly decrease with T. Above temperature of about 60 °C, $\Delta\alpha(m;T)$ values can be negative or positive, but if positive they are nearly constant (Fig. 5.24). The apparent molar volumes $V_{2,\phi}(m;T)$ having the concave downward curvature (i.e. $\left(\partial^2 V_{2,\phi}(m;T)/\partial T^2\right)_{P,m} < 0$) initially increase with temperature, $\left(\partial V_{2,\phi}(m;T)/\partial T\right)_{P,m} > 0$, but for $T > 60$ °C, they have constant values or even slightly decrease with T.

According to Hepler [190], in order to obtain a qualitative characterization of the citrate—water interactions, the second derivatives of the volume with respect to temperature are needed

$$f(m;T) = T\left(\frac{\partial^2 V}{\partial T^2}\right)_{P,m} = -\left(\frac{\partial C_P}{\partial P}\right)_{T,m} \tag{5.49}$$

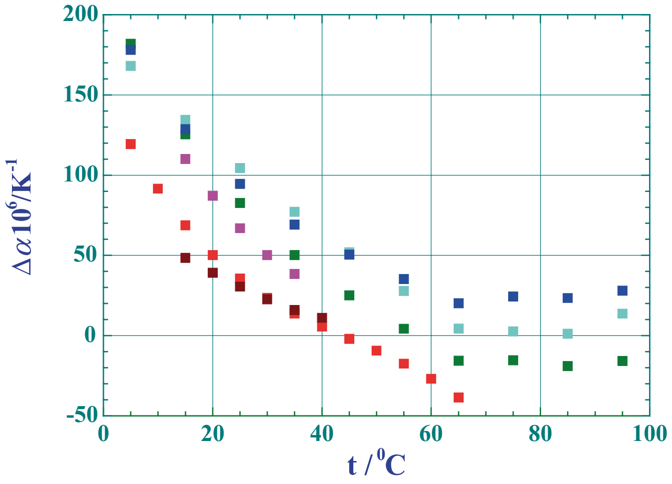


Fig. 5.24 Differences in cubic expansion coefficients of $m = 0.5$ mol kg^{-1} solutions of citrates and pure water as a function of temperature. 🟧 - trilithium citrate, 🟩 - tripotassium citrate, 🟪 - potassium dihydrogen citrate, 🟩 - trisodium citrate, 🟦 - sodium dihydrogen citrate and 🟥 - disodium hydrogen citrate

These second derivatives are related to changes of isobaric heat capacities with respect to pressure. Since densities of sodium citrates and trilithium citrate are known over a large temperature range, the products $f(m;T) = T\left(\partial^2 V/\partial T^2\right)_{P,m}$ and that of pure water $f(0;T)$ [191] can be evaluated. In Fig. 5.25 are plotted these products for 0.1 mol kg^{-1} solutions and as can be observed for all citrates, that $f(0;T) > f(m;T)$.

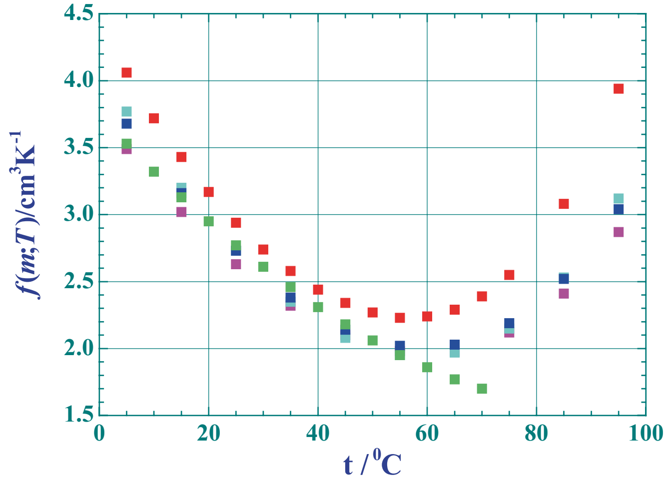


Fig. 5.25 Products of temperature and the second derivatives of volume with respect to temperature of water and of $m = 0.1$ mol kg^{-1} citrate solutions as a function of temperature. 🟥 - water, 🟩 - trilithium citrate, 🟪 - trisodium citrate, 🟩 - disodium hydrogen citrate and 🟦 - sodium dihydrogen citrate

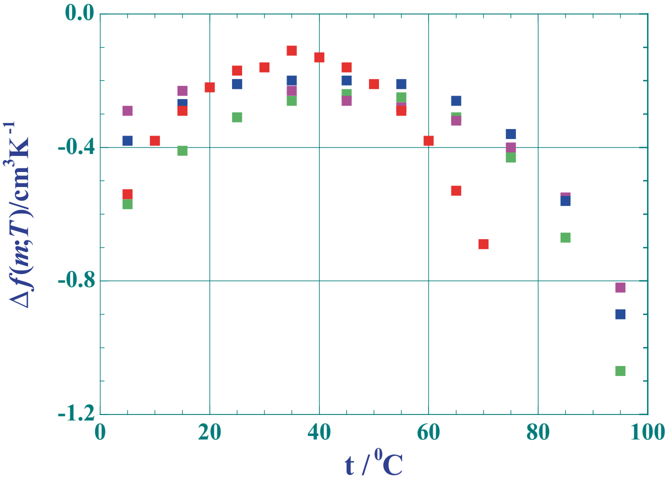


Fig. 5.26 Differences in the products of temperature and the second derivative of volume with respect to temperature of $m = 0.1$ mol kg^{-1} citrate solutions and of water as a function of temperature. 🟥 - trilithium citrate, 🟩 - trisodium citrate, 🟪 - disodium hydrogen citrate and 🟦 - sodium dihydrogen citrate

All $f(m;T)$ functions behave similarly, they have positive values irrespectively of concentration of citrate and what citrate is considered. Initially, they decrease with temperature until the minimum value at near 60 °C, and then increase. The curvature of the products $f(m;T)$ is concave upward ($f'(m;T) > 0$). The indicative parameter $\Delta f(m;T) = f(m;T) - f(0;T)$. is always negative and the curvature of curves is concave downward ($f'(m;T) < 0$), the extremal values of it are shifted to lower temperature, about 40 °C (Fig. 5.26). Considering that in dilute solutions the indicative parameter $\Delta f(m;T)$ is nearly equal to $\left(\partial^2 \overline{V}_2^0(T) / \partial T^2\right)_P$, then according to the Hepler criteria, it is possible to postulate that neutral and acidic lithium, sodium, potassium and ammonium citrates, when dissolved in water, are the structure-breaking solutes.

5.7 Volumetric Properties of Ternary Aqueous Solutions with Alkali Metal Citrates

Measured densities of aqueous solutions in ternary systems with alkali metal citrates [171–174, 176, 178, 179, 181–183, 186, 188] can be divided into three main groups when one component (denoted as - components 3) is a strong electrolyte (KCl, KBr and KNO_3), or amino acid - alanine, glycine, serine and valine (in zwitterion forms), or a dissoluble in water polymer. They can also be classified by considering effects of these components on the volumetric properties of citrates or effects of citrates on the volumetric properties of other components in aqueous solutions. Actually, only the changes in the apparent molar volumes with an addition of different amounts of citrate or other components were discussed in the literature. The influence of temperature was not considered, in spite of the fact that density determinations were performed at different temperatures.

Actually, in the listed above investigations, three component systems were treated as the pseudo-binary systems by regarding solutions of water (1) + citrate (2) or water (1) + component (3) as solvents. Thus, in determinations of $V_{2,\phi}$ or $V_{3,\phi}$ values, the density of pure water was replaced by the corresponding densities of (1 + 2) or (1 + 3) solutions and the apparent molar volumes are defined as for binary solutions

$$V_{j,\phi}(m_j;T) = \frac{V(m_2,m_3) - V(\text{solvent})}{m_j} \quad ; \quad j = 2,3 \tag{5.50}$$

However, this is unsatisfactorily description of volumetric properties of citrate solutions considering that both components which are dissolved in water are in comparable and macroscopic quantities. In such cases, the over-all change in the volume of solutions is better represented by using the mean apparent molar volume, $V_{2,3,\phi}$, where water continue to be solvent and then [189]

$$\begin{gathered} V_{2,3,\phi}(m_2,m_3;T) = \frac{V(m_2,m_3;T) - V_{\mathrm{H_2O}}(T)}{m_\mathrm{T}} \quad ; \quad m_\mathrm{T} = m_2 + m_3 \\ V_{2,3,\phi}(m_2,m_3;T) = \frac{m_2\mathrm{M}_2 + m_3\mathrm{M}_3}{m_\mathrm{T}\mathrm{d}(m_2,m_3;T)} + \frac{1000}{m_\mathrm{T}}\left(\frac{1}{\mathrm{d}(m_2,m_3;T)} - \frac{1}{\mathrm{d}_{\mathrm{H_2O}}(T)}\right) \end{gathered} \tag{5.51}$$

where M_2 is the molar mass of citrate and M_3 is the molar mass of component (3). M_3 in the case of polymers denotes the molar masses of monomers.

From a relatively large number of ternary systems where densities were measured, only some representative examples at 25 °C are presented here. The first three cases, tripotassium citrate is dissolved in an ionic medium of strong electrolytes KCl, KBr and KNO_3. Densities in these ternary systems were measured by Zafarami-Moatter and Izadi [178, 179]. In Figs. 5.27, 5.28, and 5.29 are plotted the mean apparent molar volumes of the $K_3Cit + KCl + H_2O$, $K_3Cit + KBr + H_2O$ and $K_3Cit + KNO_3 + H_2O$ systems as a function of total molal concentration of solutions, $m_T = m_2 + m_3$.

Since behaviour of the $V_{2,3,\phi} = f(m_T)$ and $V_{2,3,\phi} = g(I)$ functions is similar, it is possible to replace m_T by the ionic strength of solution, $I = 6m_2 + m_3$. However, the use of m_T is preferable, considering that for citrates usually we have $I >> m_T$, which leads to reduction of concentration scales in figures. As can be observed, in all cases of strong electrolytes, with increasing m_T, the expected order of the mean apparent molar volumes $V_{3,\phi}(m_3) < V_{2,3,\phi}(m_2,m_3) < V_{2,\phi}(m_2)$ is achieved only for dilute solutions. In concentrated solutions, $V_{2,3,\phi}(m_2, m_3)$ values are even larger than $V_{2,\phi}(m_2)$ values. The effect is more significant for smaller concentrations of added electrolyte, with reaching rapidly the $V_{3,\phi}(m_3) < V_{2,\phi}(m_2) < V_{2,3,\phi}(m_2,m_3)$ order. This means that even small quantities of strong electrolytes have a large influence on the volumetric properties of aqueous solutions of neutral citrates. The mean apparent volumes always increase with increasing tripotassium citrate concentration,

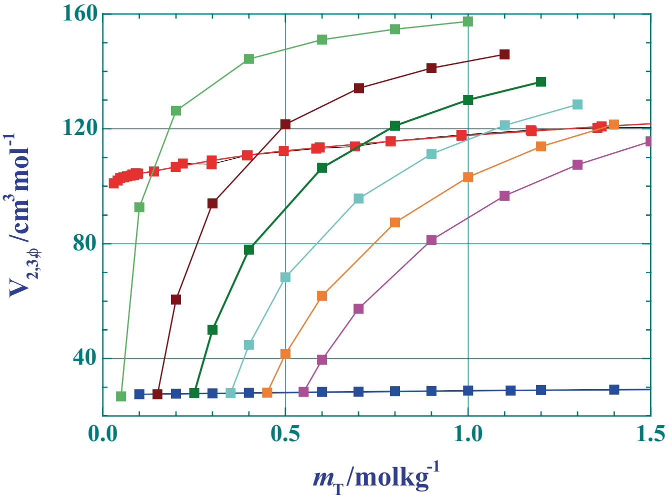


Fig. 5.27 The mean apparent molar volumes in the tripotassium citrate + potassium chloride + water systems at 25 °C as a function of the total molal concentration in solutions. 🟥 - K_3Cit, 🟦 - KCl, 🟩 - K_3Cit + 0.05 mol kg^{-1} KCl, 🟫 - K_3Cit + 0.15 mol kg^{-1} KCl, 🟩 - K_3Cit + 0.25 mol kg^{-1} KCl, 🟩 - K_3Cit + 0.35 mol kg^{-1} KCl, 🟧 - K_3Cit + 0.35 mol kg^{-1} KCl, 🟪 - K_3Cit + 0.55 mol kg^{-1} KCl

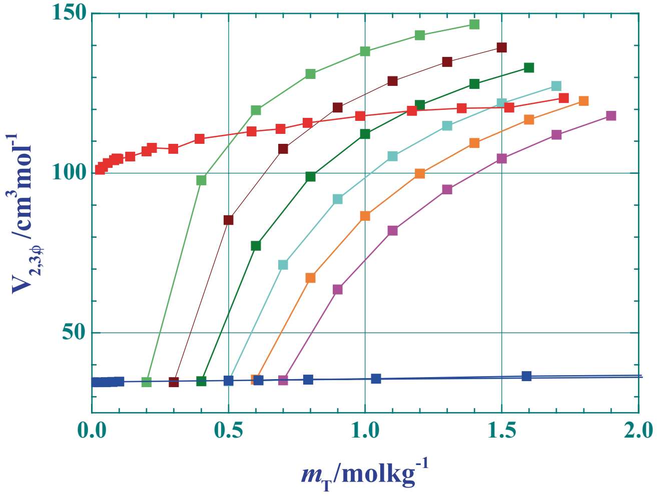


Fig. 5.28 The mean apparent molar volumes in the tripotassium citrate + potassium bromide + water systems at 25 °C as a function of the total molal concentration in solutions. 🟥 - K_3Cit, 🟦 - KBr, 🟩 - K_3Cit + 0.20 mol kg^{-1} KBr, 🟫 - K_3Cit + 0.30 mol kg^{-1} KBr, 🟩 - K_3Cit + 0.40 mol kg^{-1} KBr, 🟩 - K_3Cit + 0.50 mol kg^{-1} KBr, 🟧 - K_3Cit + 0.60 mol kg^{-1} KBr, 🟪 - K_3Cit + 0.70 mol kg^{-1} KBr

$\partial V_{2,3,\phi}(m_2,m_3)/\partial m_2 > 0$, but at constant m_3, the difference $V_{2,\phi}(K_3Cit) - V_{2,3,\phi}(m_2,m_3)$ is only positive for concentrated solutions and rapidly becomes negative for dilute citrate solutions.

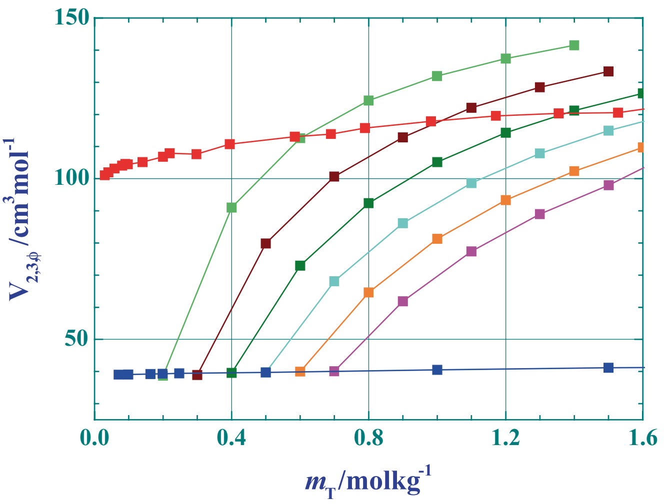


Fig. 5.29 The mean apparent molar volumes in the tripotassium citrate + potassium nitrate + water systems at 25 °C as a function of the total molal concentration in solutions. 🟥 - K_3Cit, 🟦 - KNO_3, 🟩 - K_3Cit + 0.20 mol kg^{-1} KNO_3, 🟫 - K_3Cit + 0.30 mol kg^{-1} KNO_3🟩 - K_3Cit + 0.40 mol kg^{-1} KNO_3, 🟩 - K_3Cit + 0.50 mol kg^{-1} KNO_3, 🟧 - K_3Cit + 0.60 mol kg^{-1} KNO_3, 🟪 - K_3Cit + 0.70 mol kg^{-1} KNO_3

The behaviour of ternary systems with citrates and amino acids is illustrated in Figs. 5.30, 5.31, and 5.32. An addition of L-alanine to tripotassium citrate or to potassium dihydrogen citrate solutions (always $V_{2,\phi}(m_T) > V_{3,\phi}(m_T)$) produces the expected order of the mean apparent molar volumes $V_{3,\phi}(m_3) < V_{2,3,\phi}(m_2,m_3) < V_{2,\phi}(m_2)$ and the concave downward curvature of the $V_{2,3,\phi}$ functions. However, the effect of added citrates to amino acid solutions is very strong and increases with amounts of citrate in solutions. The mean apparent volumes in L-alanine solutions have unusual concave upward curvature and the difference $V_{2,\phi}(m_T) - V_{2,3,\phi}(m_2,m_3)$ becomes rapidly negative, i.e. $V_{2,3,\phi}(m_2,m_3) > V_{2,\phi}(m_T) > V_{3,\phi}(m_T)$ (Figs. 5.30 and 5.31).

There is a large diversity in the form of $V_{2,3,\phi}(m_2,m_3)$ functions in the amino acid + citrate systems. They depend on the nature of added citrate or amino acid and evidently on temperature and concentration.

One additional example illustrates changes in behaviour of the mean apparent molar volumes produced by replacement of potassium citrates by trisodium citrate. In Fig. 5.32 are plotted $V_{2,3,\phi}(m_2,m_3)$ functions of glycine and L-analine solutions which contain 0.2 mol kg^{-1} and 0.8 mol kg^{-1} of trisodium citrate. For both amino acids, the difference $V_{2,\phi}(m_T) - V_{2,3,\phi}(m_2,m_3)$ is always positive when with added tripotassium citrate they are also negative. There is also observed for glycine and L-alinine, a significantly larger concentration dependence of $V_{2,3,\phi}(m_2,m_3)$ functions. The apparent molar volume of trisodium citrate significantly exceeds those of amino acids $V_{2,\phi}(Na_3Cit) > V_{3,\phi}$(L-Ala) $> V_{3,\phi}$(Glu) producing not only $V_{2,3,\phi}$(L-Ala) $> V_{2,3,\phi}$(Glu) but also large changes in the apparent molar volumes $V_{2,\phi}(Na_3Cit) > V_{2,3,\phi}$(L-Ala, Na_3Cit) $>> V_{3,\phi}$(L-Ala) and similarly $V_{2,\phi}(Na_3Cit) > V_{2,3,\phi}$(Glu, Na_3Cit) $>> V_{3,\phi}$(Glu) (Fig. 5.32).

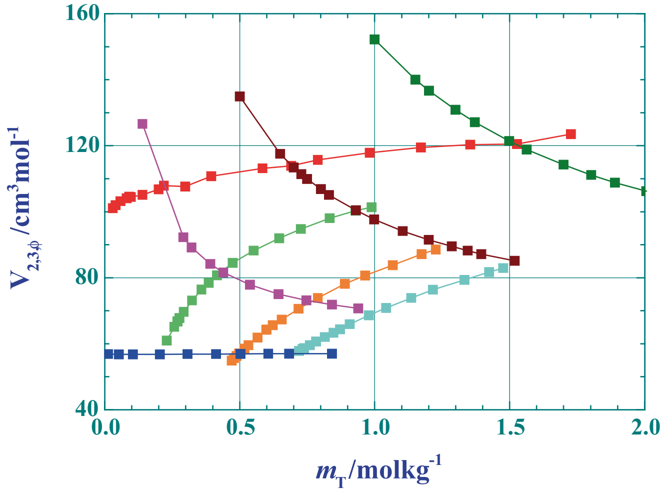


Fig. 5.30 The mean apparent molar volumes in the tripotassium citrate + L-alanine + water systems at 25 °C as a function of the total molal concentration in solutions. 🟥 - K_3Cit, 🟦 - L-alanine, 🟩 - K_3Cit + 0.23 mol kg^{-1} L-alanine, 🟧 - K_3Cit + 0.47 mol kg^{-1} L-alanine, 🟩 - K_3Cit + 0.72 mol kg^{-1} L-alanine, 🟪 - L-alanine + 0.14 mol kg^{-1} K_3Cit, 🟫 - L-alanine + 0.5 mol kg^{-1} K_3Cit, 🟩 - L-alamine + 1.0 mol kg^{-1} K_3Cit

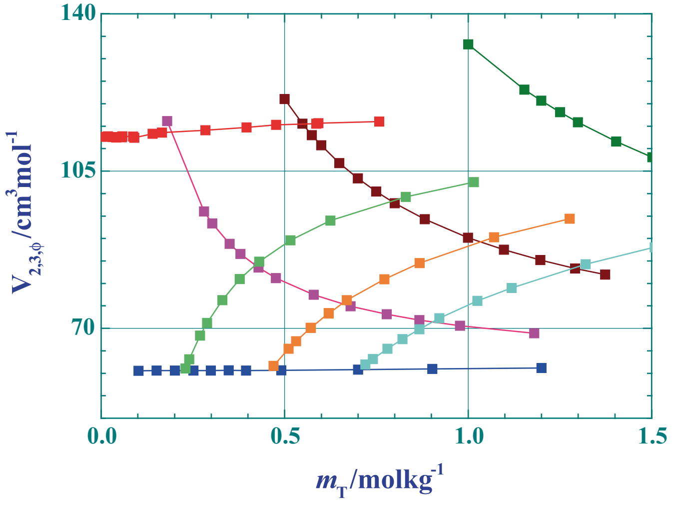


Fig. 5.31 The mean apparent molar volumes in the potassium dihydrogen citrate + L-alanine + water systems at 25 °C as a function of the total molal concentration in solutions. 🟥 - KH_2Cit, 🟦 - L-alanine, 🟩 - KH_2Cit + 0.23 mol kg^{-1} L-alanine, 🟧 - KH_2Cit + 0.47 mol kg^{-1} L-alanine, 🟩 - KH_2Cit + 0.72 mol kg^{-1} L-alanine, 🟪 - L-alanine + 0.18 mol kg^{-1} KH_2Cit, 🟫 - L-alanine + 0.5 mol kg^{-1} KH_2Cit, 🟩 - L-alamine + 1.0 mol kg^{-1} KH_2Cit

In the case of ternary systems with polymers, Sadeghi and Ziamajidi [171, 172] measured densities in the trisodium citrate + polyvinylpyrrodone + water and tripotassium citrate + polypropylene oxide 400 + water systems. Small amounts of

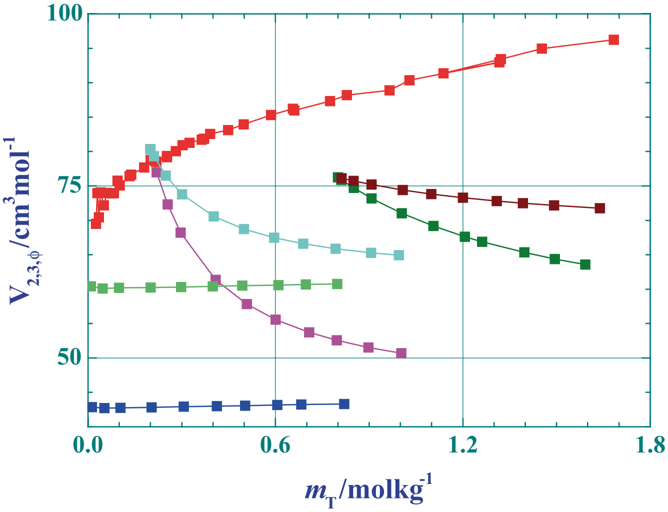


Fig. 5.32 The mean apparent molar volumes in the trisodium citrate + L-alanine + water and trisodium citrate + glycine + water systems at 25 °C as a function of the total molal concentration in solutions. 🟥 - Na_3Cit, 🟦 - glycine, 🟩 - L-alanine, 🟪 - glycine + 0.2 mol kg^{-1} Na_3Cit, 🟩 - glycine + 0.8 mol kg^{-1} Na_3Cit, 🟩 - L-alanine + 0.2 mol kg^{-1} Na_3Cit, 🟫 - L-alanine + 0.8 mol kg^{-1} Na_3Cit

polymeric substances are more important in dilute solutions of citrates. With increasing concentration of citrates, $V_{2,3,\phi}(m_2,m_3)$ values are slowly approaching the limit values of $V_{2,\phi}(Na_3Cit)$ and $V_{2,\phi}(K_3Cit)$ (Fig. 5.33).

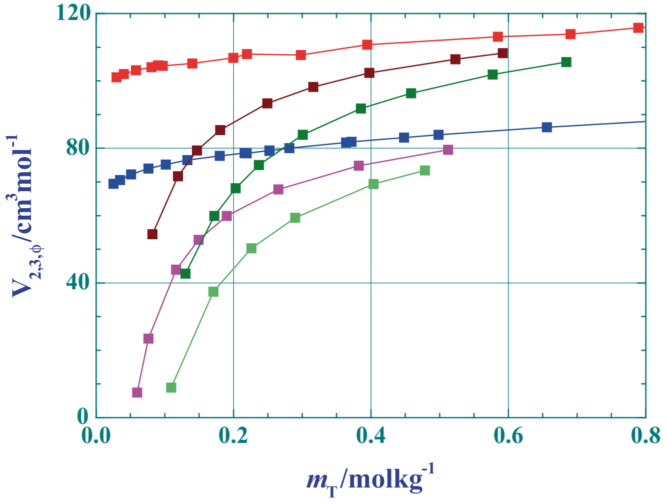


Fig. 5.33 The mean apparent molar volumes in the trisodium citrate + polyvinylpyrrolidone (PVP) + water and tripotassium citrate + polypropylene oxide (PPO) 400 + water systems at 25 °C as a function of the total molal concentration in solutions. 🟦 - Na_3Cit, 🟥 - K_3Cit, 🟪 - Na_3Cit + 0.002 mol kg^{-1} PVP, 🟩 - Na_3Cit + 0.004 mol kg^{-1} PVP, 🟫 - K_3Cit + 0.051 mol kg^{-1} PPO 400, 🟩 - K_3Cit + 0.104 mol kg^{-1} PPO 400

5.8 Compressibility Properties of Aqueous Solutions of Alkali Metal Citrates

Ultrasonic characterization of aqueous solutions of citrates was carried out by performing measurements of sound velocities $u(T;m)$ together with densities $d(T;m)$ [160, 171, 172, 174, 178, 181]. In these investigations are presented in 5 °C intervals $u(T;m)$ and $d(T;m)$ values and they permit to determine the isentropic compressibility coefficients $\kappa_S(T;m)$ and the apparent molar compressibilities $K_{2,\phi}(T;m)$ from

$$\begin{aligned} \kappa_S(T;m) &= \frac{1}{u(T;m)^2 \, \mathrm{d}(T;m)} \\ K_{2,\phi}(T;m) &= \frac{\mathrm{M}_2 \kappa_S(T;m)}{\mathrm{d}(T;m)} + \frac{1000}{m}\left(\frac{\kappa_S(T;m)}{\mathrm{d}(T;m)} - \frac{\kappa_{S,\mathrm{H_2O}}(T)}{\mathrm{d}_{\mathrm{H_2O}}(T)}\right) \end{aligned} \tag{5.52}$$

Other compressibility parameters, like the isothermal compressibility coefficients, are not available because the specific heats of solutions are unknown.

Measurements of sound velocities in trisodium citrate solutions were performed by Sadeghi and Ziamajidi [171] and Kumar et al. [182]. Tripotassium citrate solutions were investigated by Sadeghi and Ziamajidi [172], Zafarami-Moattar and Izadi [178] and Kumar et al. [182]. Sadeghi et al. [160] measured sound velocities in disodium hydrogen citrate and sodium dihydrogen solutions and Sadeghi and Goodarzi [174] in potassium dihydrogen solutions. Sound velocities in dilute solutions of diammonium hydrogen citrate were reported by Sadeghi and Gholamireza [162]. There are also determinations of $u(T;m)$ and $d(T;m)$ values in ternary systems with amino acids and polymers [162, 171, 173, 174, 179, 182, 188]. Only in the case of Na_3Cit or K_3Cit solutions, measurements were performed more than once, and a good agreement between different investigations is observed.

In spite of a large amount of experimental data, unfortunately due to absence of heat capacities and sometimes viscosities, only restricted compressibility properties can be determined and they are also limited to one temperature. In Table 5.15 are presented values of $d(m)$ and $u(m)$ at 25 °C (for other temperatures they are available in the original papers) and they permit to evaluate the isentropic compressibility coefficients $\kappa_S(T;m)$ and the apparent molar compressibilities $K_{2,\phi}(T;m)$ using Eqs. (5.52).

Sound velocities in solutions of neutral citrates are larger than those in acidic citrates or citric acid solutions. They increase with temperature and concentration. The sound velocities in aqueous solutions can be arranged in the following order $u(\mathrm{Na_3Cit}) \approx u(\mathrm{K_3Cit}) > u(\mathrm{Na_2HCit}) > u((\mathrm{NH_4})_2\mathrm{HCit}) > u(\mathrm{NaH_2Cit}) > u(\mathrm{KH_2Cit}) > u(\mathrm{H_3Cit}) > u(\mathrm{H_2O})$.

Determined sound velocities and densities can be correlated by the Rao empirical relations [192, 193]

$$\begin{aligned} \mathrm{R}_1(m) &= \frac{\mathrm{M}_{12} u^{1/3}(T;m)}{\mathrm{d}(T;m)} \\ \mathrm{M}_{12} &= x\mathrm{M}_1 + (1-x)\mathrm{M}_2 \end{aligned} \tag{5.53}$$

Table 5.15 Sound velocities in aqueous citrate solutions at 25 °C as a function of concentration

m/mol kg^{-1}	d/g cm^3	u/m s^{-1}	*m*/mol kg^{-1}	d/g cm^3	*u*/m s^{-1}
Sodium dihydrogen citrate					
0.0093 [160]	0.99809	1497.87	0.0470	1.00227	1501.51
0.0117	0.99834	1498.11	0.0681	1.00459	1503.50
0.0125	0.99844	1498.15	0.0937	1.00738	1505.92
0.0138	0.99858	1498.33	0.1194	1.01015	1508.31
0.0155	0.99877	1498.48	0.1440	1.01277	1510.55
0.0163	0.99886	1498.55	0.1678	1.01530	1512.73
0.0187	0.99913	1498.80	0.1911	1.01776	1514.86
0.0202	0.99930	1498.91	0.2165	1.02042	1517.01
0.0209	0.99936	1499.01	0.2412	1.02298	1519.27
0.0240	0.99972	1499.31	0.2934	1.02836	1523.96
0.0279	1.00015	1499.70	0.3205	1.03113	1526.34
0.0327	1.00069	1500.09	0.3395	1.03306	1528.00
0.0376	1.00122	1500.61	0.3728	1.03641	1530.90
0.0409	1.00160	1500.93	0.3936	1.03850	1532.68
Disodium hydrogen citrate					
0.0095	0.99846	1498.47	0.0771	1.00825	1508.80
0.0114	0.99874	1498.78	0.0953	1.01084	1511.45
0.0133	0.99902	1499.12	0.1157	1.01371	1514.42
0.0150	0.99927	1499.34	0.1332	1.01617	1516.89
0.0172	0.99959	1499.72	0.1542	1.01909	1519.76
0.0187	0.99980	1499.94	0.1773	1.02227	1523.04
0.0210	1.00015	1500.33	0.1964	1.02488	1525.70
0.0229	1.00042	1500.59	0.2144	1.02733	1528.22
0.0267	1.00097	1501.14	0.2229	1.02848	1529.41
0.0307	1.00156	1501.79	0.2509	1.03226	1533.24
0.0344	1.00210	1502.35	0.2830	1.03655	1537.59
0.0374	1.00254	1502.86	0.2965	1.03834	1539.39
0.0570	1.00538	1505.81	0.3375	1.04377	1544.92
Trisodium citrate					
0.0253 [171]	1.00180	1502.50	0.656	1.10361	1617.35
0.0347	1.00353	1504.50	0.8285	1.12803	1646.89
0.0507	1.00642	1507.75	1.0294	1.15480	1680.28
0.0760	1.01094	1512.79	1.3173	1.19060	1726.67
0.1014	1.01543	1517.78			
0.1327	1.02087	1523.83	0.0025 [182]	0.99754	1497.16
0.1799	1.02900	1532.70	0.0487	1.00609	1507.19
0.2160	1.03511	1539.43	0.0974	1.01465	1516.78
0.2191	1.03566	1540.01	0.201	1.03180	1536.66
0.2524	1.04120	1546.11	0.2898	1.04601	1552.43
0.2523	1.04123	1546.15	0.3899	1.06160	1570.23
0.2812	1.04593	1551.33	0.4966	1.07760	1587.10
0.3639	1.05927	1566.28	0.6007	1.09245	1603.49
0.3716	1.06049	1567.60	0.7036	1.10671	1617.63
0.4483	1.07255	1581.25	0.7698	1.11558	1628.07
0.4985	1.08024	1590.06	0.9013	1.13231	1646.03

Table 5.15 (continued)

m/mol kg^{-1}	d/g cm^3	u/m s^{-1}	m/mol kg^{-1}	d/g cm^3	u/m s^{-1}
Potassium dihydrogen citrate					
0.0063 [174]	0.99779	1497.32	0.1399	1.01315	1508.83
0.0186	0.99923	1498.46	0.1655	1.01600	1510.90
0.0314	1.00073	1499.59	0.2840	1.02900	1520.45
0.0407	1.00182	1500.36	0.3960	1.04081	1529.04
0.0561	1.00361	1501.76	0.4766	1.04898	1534.98
0.0574	1.00375	1501.86	0.5861	1.06000	1543.01
0.0868	1.00715	1504.37	0.5922	1.06056	1543.47
0.0905	1.00760	1504.69	0.7578	1.07659	1555.24
Tripotassium citrate					
0.0472 [178]	1.00659	1506.63	0.0899	1.01502	1514.73
0.0566	1.00846	1508.48	0.1258	1.02190	1522.43
0.066	1.01033	1510.27	0.1931	1.03465	1534.27
0.0754	1.01219	1512.04	0.2653	1.04799	1546.75
0.0849	1.01406	1513.87	0.3412	1.06156	1560.22
0.0943	1.01590	1515.67	0.4565	1.08154	1581.18
0.2984	1.05402	1552.82	0.5796	1.10181	1601.35
0.3971	1.07135	1570.1	0.7446	1.12811	1629.25
0.4955	1.08807	1587.04			
0.5936	1.10421	1603.76	0.0036 [182]	0.99784	1497.31
0.7877	1.13465	1636.17	0.0543	1.00798	1507.64
0.9823	1.16314	1667.51	0.0968	1.01612	1515.82
1.1745	1.18977	1697.47	0.2001	1.03559	1534.61
1.3656	1.21446	1725.72	0.2914	1.05192	1550.64
1.5551	1.23769	1752.64	0.3859	1.06902	1567.66
1.8373	1.26996	1790.26	0.4948	1.08646	1584.79
			0.5799	1.10020	1598.79
0.0185 [172]	1.00087	1500.77	0.6983	1.11845	1618.29
0.0304	1.00329	1503.17	0.7576	1.12736	1627.73
0.0310	1.00340	1503.32	0.8939	1.14696	1649.37
0.0558	1.00827	1508.14			
Diammonium hydrogen citrate					
0.0059 [182]	0.99763	1497.72	0.0423	1.00123	1502.40
0.0071	0.99775	1497.92	0.0446	1.00146	1502.71
0.0087	0.99791	1498.14	0.0468	1.00167	1502.95
0.0129	0.99833	1498.70	0.0492	1.00192	1503.26
0.0177	0.99880	1499.28	0.0562	1.00256	1504.11
0.0222	0.99926	1499.86	0.0645	1.00338	1505.16
0.0266	0.99968	1500.31	0.0748	1.00434	1506.36
0.0311	1.00013	1500.96	0.0797	1.00483	1506.96
0.0354	1.00055	1501.49	0.0900	1.00581	1508.22

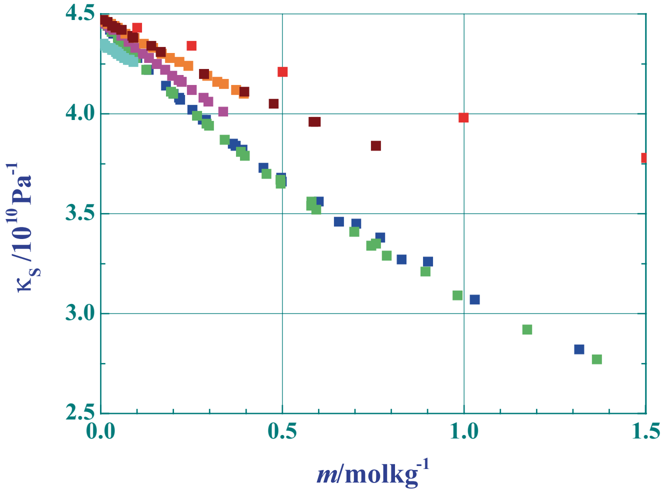


Fig. 5.34 The isentropic compressibility coefficients of citric acid and of aqueous inorganic citrate solutions at 25 °C as a function of concentration. 🟥 - citric acid, 🟦 - trisodium citrate, 🟩 - tripotassium citrate, 🟪 - disodium hydrogen citrate, 🟩 - diammonium hydrogen citrate, 🟧 - sodium dihydrogen citrate, 🟫 - potassium dihydrogen citrate

They vary linearly with concentration and are nearly independent of temperature.

$$
\begin{aligned}
&\mathrm{R_1\,(NaH_2Cit};m)\cdot 10^6\,/\,\mathrm{m^{10/3}s^{-1/3}\,mol^{-1}} = 206.6 + 26.34m^*\\
&\mathrm{R_1\,(Na_2HCit};m)\cdot 10^6\,/\,\mathrm{m^{10/3}s^{-1/3}\,mol^{-1}} = 207.1 + 21.98m^*\\
&\mathrm{R_1\,(Na_3Cit};m)\cdot 10^6\,/\,\mathrm{m^{10/3}s^{-1/3}\,mol^{-1}} = 205.9 + 23.43m^*\\
&\mathrm{R_1\,(KH_2Cit};m)\cdot 10^6\,/\,\mathrm{m^{10/3}s^{-1/3}\,mol^{-1}} = 206.2 + 24.81m^*\\
&\mathrm{R_1\,(K_3Cit};m)\cdot 10^6\,/\,\mathrm{m^{10/3}s^{-1/3}\,mol^{-1}} = 206.7 + 29.14m^*\\
&\mathrm{R_1\,((NH_4)_2HCit};m)\cdot 10^6\,/\,\mathrm{m^{10/3}s^{-1/3}\,mol^{-1}} = 206.9 + 30.56m^*\\
&m^* = m\,/\,\mathrm{mol\cdot kg^{-1}}
\end{aligned}
\tag{5.54}
$$

The isentropic compressibility coefficients of citric acid and citrates, as can be observed in Fig. 5.34, strongly decrease with increasing concentration $\left[\partial\kappa_S(T;m)/\partial m\right]_T < 0$, and they can be arranged similarly as velocities, but in the inverse order. They are lower than those of pure water $\kappa_S(T;m) < \kappa_S(T;0)$ and decrease with increase of temperature, $\left[\partial\kappa_S(T;m)/\partial T\right]_m < 0$.

The apparent molar isentropic compressibilities of citrates in aqueous solutions are always negative, $K_{2,\phi}(T;m) < 0$, (Fig. 5.35). This behaviour is opposite to that which is mostly observed in citric acid solutions. The positive values of $K_{2,\phi}(T;m)$ are attributed to the presence of undissociated molecules of citric acid. The apparent molar isentropic compressibilities of citrates in aqueous solutions decrease with increase of temperature and concentration. It is observed that strong electrolytes

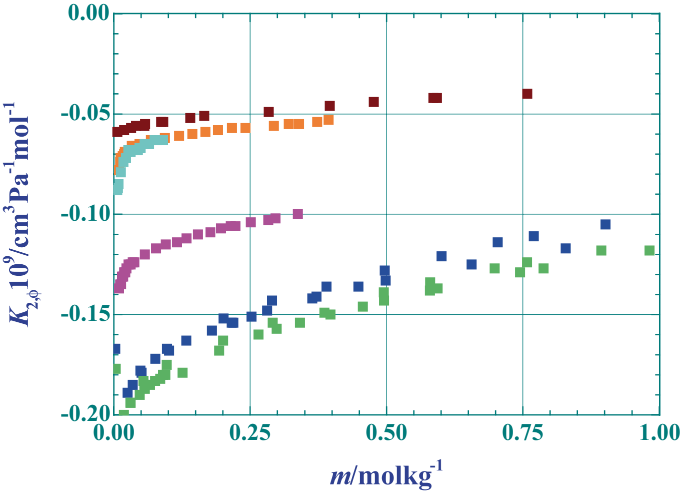


Fig. 5.35 The apparent molar isentropic compressibilities of aqueous inorganic citrate solutions at 25 °C as a function of concentration. 🟦 - trisodium citrate, 🟩 - tripotassium citrate, 🟪 - disodium hydrogen citrate, 🟩 - diammonium hydrogen citrate, 🟧 - sodium dihydrogen citrate, 🟥 - potassium dihydrogen citrate

(usually the "structure breaking" solutes) have larger negative values of the apparent molar isentropic compressibilities than weak electrolytes. This is confirmed also in the case of citrates. If solutions of acidic citrates and neutral citrates are compared (Fig. 5.35) then it is possible to arrange the apparent molar isentropic compressibilities in the following order $K_{2,\phi}(\mathrm{KH_2Cit}) > K_{2,\phi}(\mathrm{NaH_2Cit}) > K_{2,\phi}((\mathrm{NH_4})_2)$ HCit) $> K_{2,\phi}(\mathrm{Na_2HCit}) > K_{2,\phi}(\mathrm{Na_3Cit}) > K_{2,\phi}(\mathrm{K_3Cit})$. Thus, the incomplete dissociation of acidic citrates in water leads to less destruction of water structure and this is expressed by less negative values of $K_{2,\phi}(T;m)$.

From the knowledge of densities and the isentropic compressibility coefficients it is possible to estimate from ultrasonic measurements the hydration numbers of citrates in water by using the Passynski method [194]

$$h(T;m) = \frac{1000}{\mathrm{M}_{\mathrm{H_2O}}m}\left[1 - \frac{\kappa_S(T;m)}{\kappa_{S,\mathrm{H_2O}}(T)}\left(\frac{\mathrm{d}_{\mathrm{H_2O}}(T)}{\mathrm{d}(T;m)}\right)\right] \tag{5.55}$$

Hydration numbers of citrates have large values, they are considerably greater than those of citric acid (Fig. 5.36). As expected, the hydration numbers decrease with increase of temperature and concentration, but contrary to the apparent molar isentropic compressibilities, the hydration numbers of neutral citrates are greater than those of acidic citrates. Determined by Dhake and Padmini [169], also from acoustic measurements, hydration numbers in one molal solutions: $h(\mathrm{Li_3Cit}) = 20.87$, $h(\mathrm{Na_3Cit}) = 24.49$ and $h(\mathrm{K_3Cit}) = 25.36$, are consistent with those plotted in Fig. 5.36.

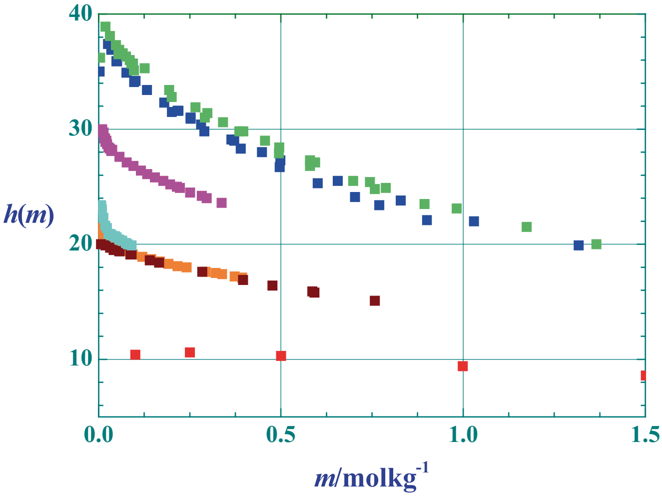


Fig. 5.36 Hydration numbers of citric acid and inorganic citrates at 25 °C as a function of concentration. 🟥 - citric acid, 🟦 - trisodium citrate, 🟩 - tripotassium citrate, 🟪 - disodium hydrogen citrate, 🟩 - diammonium hydrogen citrate, 🟧 - sodium dihydrogen citrate

5.9 Viscosities of Aqueous Solutions of Alkali Metal Citrates

Available in the literature transport properties of citrates in aqueous solutions such as viscosity or diffusion are very limited and unreliable, especially in concentrated solutions where considerable differences are observed (Figs. 5.37 and 5.38). The first measurements of viscosity (tripotassium citrate solutions at 25 °C) were performed in 1924 by Fricke and Schützdeller [150]. These were followed only in 1973 by Barradas et al. [195] who determined viscosities of trilithium citrate, trisodium citrate and tripotassium citrate in the 0.005 to 1.5 mol dm^{-3} concentration range. Viscosities of trisodium citrate solutions at 25 °C are known only from the Salabat et al. [164] investigation. All results reported in this work are questionable, but in dilute solutions, their viscosities are consistent with those determined by Barradas et al. [195]. In the case of aqueous solutions of tripotassium citrate, viscosities were measured few times [150, 175, 178, 180, 195, 196], but discrepancies between various investigations are very large. Viscosities of other citrates (potassium dihydrogen citrate, diammonium hydrogen citrate and triammonium citrate) were measured only once [175, 176, 181]. All known viscosities, measured over different temperature and concentration ranges, are collected in Table 5.16. Viscosity determinations are frequently reported using molarities c and not molalities m, but concentrations of citrates can be converted to a desired concentration scale by using densities from Table 5.14. At the same temperature and in dilute solutions, determined viscosities can be arranged in the following series $\eta(\mathrm{Na_3Cit}) > \eta(\mathrm{Na_3Cit}) > \eta((\mathrm{NH_4})_2\mathrm{HCit}) > \eta(\mathrm{KH_2Cit}) > \eta((\mathrm{NH_4})_3\mathrm{Cit})$.

Measured viscosities are frequently represented by the Jones-Dole equations which are valid for dilute solutions, usually for $c < 0.5$ mol dm^{-3} [151].

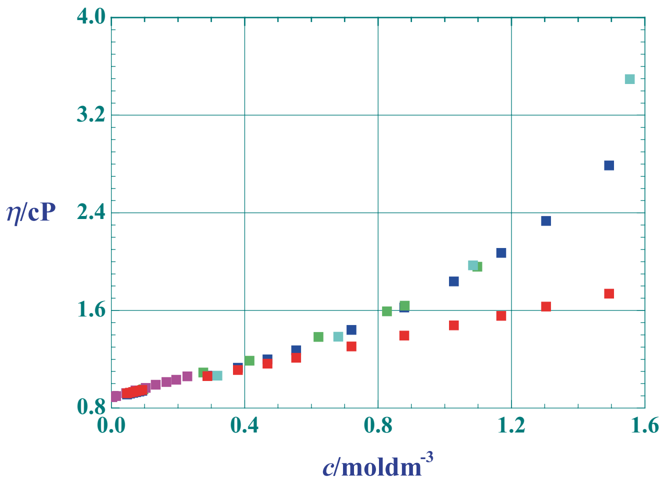


Fig. 5.37 Viscosity of aqueous solutions of tripotassium citrate as a function of concentration in molarity units at 25 °C. 🟩 - [150], 🟪 - [175], 🟦 - [178], 🟧 - [195], 🟩 - [196]

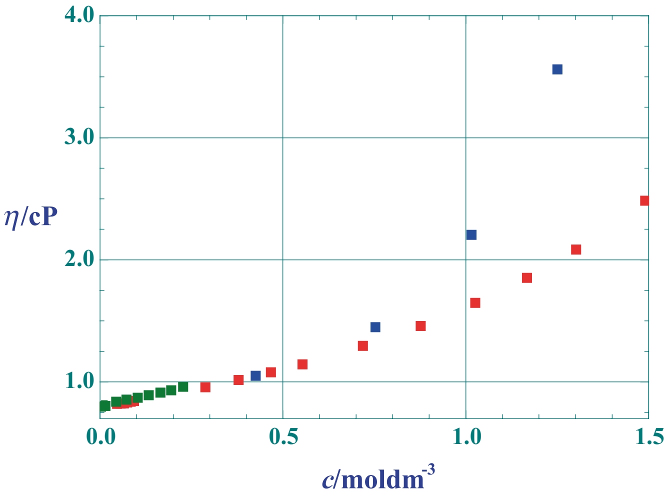


Fig. 5.38 Viscosity of aqueous solutions of tripotassium citrate as a function of concentration in molarity units at temperature 30 °C. 🟩 - [175], 🟥 - [178], 🟦 - [180]

$$\eta_{\rm rel}(T;c) = 1 + \mathrm{A}(T)\sqrt{c} + \mathrm{B}(T)c$$
$$\eta_{\rm rel}(T;c) = \frac{\eta(T;c)}{\eta_{\rm H_2O}(T)} \tag{5.56}$$

The viscosity A-coefficient depends on solvent properties, ionic charges (an indication about long-range electrostatic interactions and an ability to promote ion-pairing in solution) and temperature when the viscosity B-coefficient is highly

Table 5.16 Viscosities of aqueous solutions of citrates as a function of concentration and temperature [176]

Trisodium citrate							
25 °C							
m	*η*	*m*	*η*	*m*	*η*	*m*	*η*
0.0025 [164]	0.891	0.1447	1.052	0.5090	1.236	1.1976	2.563
0.0142	0.946	0.2058	1.082	0.6573	1.515	1.3583	3.410
0.0427	0.964	0.2625	1.102	0.7737	1.617	1.5724	4.315
0.0714	1.044	0.3011	1.134	0.8857	1.888	1.7373	5.848
0.1018	1.020	0.3991	1.174	1.0695	2.218	1.9146	6.963
Potassium dihydrogen citrate							
20 °C		*25 °C*		*30 °C*		*35 °C*	
c	*η*	*c*	*η*	*c*	*η*	*c*	*η*
0.0000 [175]	1.002	0.0000	0.890	0.0000	0.797	0.0000	0.719
0.0215	1.013	0.0215	0.897	0.0214	0.806	0.0214	0.727
0.0659	1.040	0.0658	0.923	0.0657	0.831	0.0656	0.751
0.1082	1.064	0.1080	0.942	0.1079	0.851	0.1077	0.763
0.1540	1.087	0.1538	0.963	0.1535	0.869	0.1533	0.778
0.1998	1.113	0.1996	0.986	0.1992	0.886	0.1989	0.795
0.2460	1.142	0.2457	1.014	0.2453	0.907	0.2448	0.815
0.2872	1.169	0.2868	1.040	0.2863	0.928	0.2858	0.831
0.3390	1.201	0.3385	1.067	0.3379	0.957	0.3373	0.854
Tripotassium citrate							
25 °C							
c	*η*	*c*	*η*	*c*	*η*	*c*	*η*
0.0960 [150]	0.955	0.4143	1.188	0.8270	1.593	1.0980	1.958
0.2760	1.091	0.6215	1.383	0.8800	1.639		
0.3178 [196]	1.065	0.6803	1.385	1.0850	1.970	1.5551	3.496
2.0652	5.350						
20 °C		*25 °C*		*30 °C*		*35 °C*	
0.0000 [175]	1.002	0.0000	0.890	0.0000	0.797	0.0000	0.719
0.0073	1.015	0.0072	0.900	0.0072	0.809	0.0072	0.729
0.0145	1.014	0.0145	0.899	0.0145	0.804	0.0144	0.728
0.0441	1.043	0.0441	0.922	0.0440	0.838	0.0439	0.752
0.0726	1.064	0.0725	0.945	0.0724	0.855	0.0723	0.767
0.1035	1.084	0.1034	0.966	0.1032	0.871	0.1031	0.784
0.1335	1.106	0.1333	0.991	0.1331	0.891	0.1329	0.800
0.1655	1.133	0.1653	1.013	0.1650	0.912	0.1647	0.817
0.1949	1.158	0.1947	1.032	0.1944	0.932	0.1940	0.831
0.2281	1.192	0.2278	1.060	0.2274	0.959	0.2270	0.850
m	*20 °C*	*25 °C*	*30 °C*	*35 °C*	*40 °C*	*50 °C*	
0.0472 [178]	1.027	0.911	0.821	0.739	0.665		
0.0566	1.027	0.918	0.822	0.741	0.668		
0.0660	1.029	0.924	0.825	0.744	0.672		
0.0754	1.033	0.930	0.832	0.749	0.675		
0.0849	1.037	0.935	0.837	0.754	0.680		
0.0943	1.041	0.942	0.843	0.760	0.684		
0.2984	1.132	1.065	0.956	0.861	0.783		
0.3971	1.183	1.130	1.016	0.916	0.832		
0.4955	1.238	1.200	1.080	0.975	0.887		

Table 5.16 (continued)

m	*20 °C*	*25 °C*	*30 °C*	*35 °C*	*40 °C*	*50 °C*	
0.5936	1.295	1.274	1.145	1.036	0.940		
0.7877	1.423	1.441	1.295	1.168	1.063		
0.9823	1.575	1.624	1.458	1.316	1.196		
1.1745	1.733	1.837	1.647	1.486	1.351		
1.3656	1.920	2.072	1.853	1.671	1.516		
1.5551	2.121	2.334	2.085	1.875	1.697		
1.8373	2.476	2.788	2.484	2.231	2.013		
0.45 [180]	1.342		1.050		0.845	0.695	
0.83	1.891		1.448		1.127	0.925	
1.16	2.933		2.205		1.644	1.291	
1.48	4.989		3.560		2.597	1.986	
Diammonium hydrogen citrate							
m	*25 °C*	*30 °C*	*35 °C*	*40 °C*	*45 °C*		
0.0000 [181]	0.890	0.801	0.723	0.656	0.599		
0.2327	1.026	0.926	0.835	0.784	0.715		
0.4913	1.146	1.025	0.934	0.862	0.781		
0.7802	1.303	1.155	1.057	0.955	0.836		
1.1053	1.536	1.353	1.225	1.085	0.927		
1.4738	1.907	1.611	1.492	1.294	1.091		
1.8948	2.448	2.105	1.879	1.641	1.383		
2.3807	3.215	2.737	2.430	2.128	1.788		
Triammonium citrate							
m	*25 °C*	*30 °C*	*35 °C*	*40 °C*	*45 °C*		
0.0000 [176]	0.894	0.801	0.723	0.656	0.599		
0.0839	0.924	0.827	0.748	0.690	0.631		
0.1713	0.931	0.837	0.764	0.695	0.645		
0.2624	0.949	0.875	0.795	0.737	0.671		
0.3575	0.964	0.950	0.889	0.831	0.770		
0.4568	1.010	1.161	1.102	1.038	0.975		

Units: m mol kg$^{-1,}$ c mol dm^{-3} , η cP, 1 mPa s = 1cP

specific for the present electrolyte and temperature and it has additive properties with regard to the constituent ions. Barradas et al. [195] reported the following coefficients: A(Li_3Cit) = 0.042 mol$^{-1/2}$ dm$^{3/2}$ and B(Li_3Cit) = 1.057 mol dm^{-3}; A(Na_3Cit) = 0.036 mol$^{-1/2}$ dm$^{3/2}$ and B(Na_3Cit) = 0.873 mol dm^{-3} and A(K_3Cit) = 0.027 mol$^{-1/2}$ dm$^{3/2}$ and B(K_3Cit) = 0.615 mol dm^{-3}. From B(Me_3Cit) = 3B(Me^+) + B(Cit^{3-}) and using B(Li^+) = 0.146 mol dm^{-3}, B(Na^+) = 0.085 mol dm^{-3} and B(K^+) = −0.009 mol dm^{-3} at 25 °C [197], the value of B(Cit^{3-}) is about 0.62 mol dm^{-3}. This result differs considerably from that given by Sadeghi et al. [175], B(Cit^{3-}) = 0.846 mol dm^{-3}. Basing on large positive values of A and B coefficients, Barradas et al. [195] interpreted their results by an existence of ion-association, and that water is highly structured in alkali metal citrate solutions.

5.10 Diffusion Coefficients and Indices of Refraction of Alkali metal Citrates in Aqueous Solutions

Diffusion coefficients are only known in the case of aqueous solutions of tripotassium citrate. They were determined at 25 °C by McDonald and Hsu [196] and for $c < 2.0$ mol dm^{-3}, and these diffusion coefficients can be correlated by

$$\begin{aligned} &\mathrm{D}\cdot 10^{6} / \mathrm{cm}^{2}\cdot\mathrm{s}^{-1} = 2.305 + 3.685c^{*} - 3.358c^{*2} + 1.000c^{*3} \\ &c^{*} = c / \mathrm{mol}\cdot\mathrm{dm}^{-3} \end{aligned} \tag{5.57}$$

For other temperatures, it was suggested by McDonald and Hsu to use $\mathrm{D}(c;T)\eta(c;T)/T = \text{constant}$, equation.

From other properties of citrate solutions it should be mentioned the index of refraction which frequently served for analytical purposes. In the Timmermans tabulation [155] are given old measurements of n_D in tripotassium citrate solutions at 16.5, 18 and 25 °C and in triammonium citrate solutions at 17.5 °C [198]. Recent determinations of n_D values come from investigations dealing with ternary systems. Trisodium citrate aqueous solutions were considered by Salabat et al. [164] at 25 °C and Sadeghi et al. [199] at 35 °C. Kalaivani et al. [181] measured index of refraction of diammonium hydrogen citrate in the 25–45 °C temperature range. The difference in refractive indices of solution and water $\Delta n_D(T;m) = n_D(\mathrm{T};m) - n_D(T;0)$ very weakly depends on temperature and therefore can be used to estimate n_D values at other temperatures. Differences $\Delta n_D(T;m)$ for mentioned here citrates and refraction indices of water can be correlated by the following expressions

$$\begin{aligned} &\Delta n_D(\mathrm{Na_3Cit};T;m) = 0.04531m^{*} - 0.006231m^{*2} \\ &\Delta n_D(\mathrm{K_3Cit};T;m) = 0.04514c^{*} - 0.003683c^{*2} \\ &\Delta n_D((\mathrm{NH_4})_3\mathrm{Cit};T;m) = 0.04685c^{*} - 0.003182c^{*2} \\ &\Delta n_D((\mathrm{NH_4})_2\mathrm{HCit};T;m) = 0.03826m^{*} - 0.003898m^{*2} \\ &n_D(\mathrm{H_2O};T) = 1.33432 - 1.3798\cdot 10^{-5}\theta - 1.7644\cdot 10^{-6}\theta^{2} \\ &m^{*} = m / \mathrm{mol}\cdot\mathrm{kg}^{-1} \quad ; \quad c^{*} = c / \mathrm{mol}\cdot\mathrm{dm}^{-3} \\ &\theta = T/\mathrm{K} - 273.15 \end{aligned} \tag{5.58}$$

Among different citrates, differences in indices of refraction are very small in dilute solutions, for $m < 0.5$ mol kg^{-1}, but they are clearly evident with increasing concentration.

Other physical properties of citrate solutions are only sporadically reported in the literature. Usually, they are by-products of investigations, rarely dealing with the concentration or temperature dependence. It is possible to mention here only measurements of surface tension of tripotassium citrate performed by Livingston et al. [200] and Lu et al. [180] and the Bhat and Manjunatha [201].determinations of electrical conductivities of citrates in the water + dimethyl formamide mixtures (Table 5.17).

Table 5.17 Refraction index of aqueous solutions of citrates as a function of concentration and temperature

Trisodium citrate						
t/°C	*m*/mol kg^{-1}	n_D	*m*/mol kg^{-1}	n_D	*m*/mol kg^{-1}	n_D
25	0.00250 [164]	1.33338	0.26250	1.34441	1.06950	1.37377
	0.01420	1.33336	0.30110	1.34624	1.19760	1.37805
	0.04270	1.33474	0.39910	1.35023	1.35830	1.38287
	0.07140	1.33597	0.50900	1.35428	1.57240	1.38797
	0.10180	1.33734	0.65730	1.35976	1.73730	1.39308
	0.14470	1.33935	0.77370	1.36395	1.91460	1.39721
	0.20580	1.34205	0.88570	1.36792		
35	0.0000 [199]	1.3311	0.1424	1.3379	0.2847	1.3438
	0.0340	1.3328	0.1771	1.3393	0.3319	1.3456
	0.0682	1.3345	0.2157	1.3410	0.3674	1.3469
	0.1015	1.3361	0.2524	1.3425		
Diammonium hydrogen citrate						
25	0.00000 [181]	1.3435	0.72556	1.3695	1.76207	1.3975
	0.21639	1.3515	1.02788	1.3790	2.21389	1.4090
	0.45683	1.3610	1.37050	1.3870		
30	0.00000	1.3430	0.72556	1.3685	1.76207	1.3970
	0.21639	1.3500	1.02788	1.3780	2.21389	1.4085
	0.45683	1.3605	1.37050	1.3865		
35	0.00000	1.3415	0.72556	1.3675	1.76207	1.3965
	0.21639	1.3495	1.02788	1.3775	2.21389	1.4080
	0.45683	1.3595	1.37050	1.3860		
40	0.00000	1.3410	0.72556	1.3670	1.76207	1.3960
	0.21639	1.3485	1.02788	1.3770	2.21389	1.4075
	0.45683	1.3590	1.37050	1.3855		
45	0.00000	1.3400	0.72556	1.3665	1.76207	1.3955
	0.21639	1.3480	1.02788	1.3765	2.21389	1.4068
	0.45683	1.3585	1.37050	1.3850		
Tripotassium citrate						
t/°C	*c/mol dm*$^{-3}$	n_D	*c/mol dm*$^{-3}$	n_D	*c/mol dm*$^{-3}$	n_D
16.5	0.0200 [155]	1.3340	0.1667	1.3410	1.33333	1.38670
	0.0400	1.3350	0.3333	1.3478		
	0.0833	1.3370	0.6667	1.3618		
18	0.0000	1.33348	0.4871	1.35492	1.0404	1.37663
	0.1491	1.34040	0.6868	1.36303	1.3554	1.38810
	0.3466	1.34908	0.8202	1.36820	1.4457	1.39135
20	0.31663	1.34622	1.09497	1.37770	2.13113	1.41272
	0.68479	1.36315	1.56643	1.39536		
	0.31663 [195]	1.34622	1.09497	1.37770	2.13113	1.41272
	0.68479	1.36315	1.56643	1.39536		
25	0.0000 [155]	1.33291	0.48610	1.35935	1.03790	1.38151
	0.14880	1.34463	0.68530	1.36765	1.35220	1.39312
	0.34590	1.35348	0.81830	1.37291	1.44230	1.39638
Triammonium citrate						
17.5	0.02067 [198]	1.33440	0.16667	1.34110	1.33333	1.39030
	0.04167	1.33520	0.33333	1.34870		
	0.08333	1.33720	0.66667	1.36360		

5.11 Two-Phase Alkali Metal Citrate - Aliphatic Alcohol - Water Systems

For many years, the two-phase liquid systems which are mostly composed of water are extensively used in biotechnological applications (separation, purification, concentration and recovery of biomaterials), as a reaction media, in separation of metal ions, in environmental remediation procedures and in various other separation practices. Such biphasic aqueous systems contain one or two polymeric substances (usually, polyethylene glycols (PEG) of various degree of polymerization) and inorganic salts. A number of factors such as temperature, type of polymer and its polymerization extent were extensively studied to find their influence on the separation characteristics of aqueous two-phase systems. From technological point of view, the most important are the existence of a rather wide regions of mutual immiscibility, high distribution coefficients and appropriate hydrodynamic properties of both liquid phases (interfacial tension, viscosity and emulsion formation).

In determination of phase diagrams, the binodal curves, which permit to establish concentration range of phase separation, are considerably better documented than the equilibrium curves (tie-line compositions). This results from the fact that analytical procedures to obtain binodal points are less complicated than those used to determine the equilibrium compositions. Binodal curves and tie-line compositions were represented with various different correlations having two or three adjustable parameters [202–209].

Expressed in weight fractions, the compositions of alcohol-rich phases (top phases) and salt-rich phases (bottom phases) at equilibrium are presented in Table 5.18. There is a reasonable good agreement between different investigations, especially in the ethanol + tripotassium citrate + water system [203, 204, 206] (Fig. 5.41), but reported by Nemati-Kande and Shekaari [207] and by Zafarami-Moattar and Jafari [209] tie-lines for the systems with disodium hydrogen citrate differ considerably (Figs. 5.41 and 5.43). Only a short and qualitative description of aliphatic alcohol—citrate—water two-phase ternary systems is given below.

Partition of citrates and water between both phases is very similar for neutral and acidic citrates. With increasing concentration of citrate in the salt-rich phase its concentration in the alcohol-rich phase and that of water strongly decreases (Figs. 5.39, 5.40, and 5.41). The available for separation mutual immiscibility regions depend on used alcohol and the extent of the two-phase area decreases in the following order ethanol > 2-propanol > 1-propanol > 2-methyl-2-propanol > 2-butanol. If solubilities of citrates in the salt-rich phases with 2-propanol are compared, then acidic citrates are more soluble than neutral citrates and they can arranged in the following order $(NH_4)_2HCit > Na_2HCit > (NH_4)_3Cit > Na_3Cit > K_3Cit$ (Figs. 5.42 and 5.43).

Table 5.18 Equilibrium compositions in the alcohol (1) + citrate (2) + water (3) systems at 25 °C

$w_{1,salt}$	$w_{2,salt}$	$w_{1,ROH}$	$w_{2,ROH}$	$w_{1,salt}$	$w_{2,salt}$	$w_{1,ROH}$	$w_{2,ROH}$
Ethanol + trisodium citrate + water							
0.0856 [206]	0.3193	0.4289	0.0449	0.0707	0.3420	0.4833	0.0270
0.0815	0.3253	0.4427	0.0399	0.0683	0.3460	0.4970	0.0245
Ethanol + tripotassium citrate + water							
0.1410 [206]	0.2915	0.4208	0.0741	0.0503	0.4310	0.6262	0.0116
0.1046	0.3366	0.4858	0.0455	0.0420	0.4518	0.6511	0.0085
0.0638	0.4024	0.5819	0.0189				
0.0215 [204]	0.5612	0.7998	0.0010	0.0593	0.4193	0.6147	0.0142
0.0224	0.5389	0.7792	0.0009	0.0622	0.4130	0.6049	0.0147
0.0267	0.5246	0.7641	0.0019	0.0759	0.3855	0.5602	0.0237
0.0301	0.5118	0.7514	0.0026	0.1003	0.3464	0.5015	0.0444
0.0347	0.4884	0.7211	0.0042	0.1238	0.3071	0.4370	0.0632
0.0445	0.4488	0.6768	0.0074	0.1465	0.2772	0.3914	0.0917
0.0540	0.4326	0.6454	0.0092				
0.0536 [203]	0.4405	0.6467	0.0104	0.0948	0.3444	0.4842	0.0439
0.0749	0.3801	0.5548	0.0268	0.1249	0.3088	0.4454	0.0589
Ethanol + triammonium citrate + water							
0.1268 [205]	0.3724	0.5630	0.0454	0.11880	0.3830	0.5786	0.0401
0.1000	0.4102	0.6129	0.0300	0.15340	0.3397	0.5137	0.0653
1-propanol + trisodium citrate + water							
0.0655 [203]	0.1642	0.5943	0.0066	0.0931	0.1337	0.5393	0.0107
0.0798	0.1478	0.5674	0.0092	0.1331	0.1196	0.4742	0.0196
1-propanol + disodium hydrogen citrate + water							
0.1519 [203]	0.1332	0.5284	0.0197	0.0865	0.2136	0.6267	0.0096
0.1201	0.1648	0.5844	0.0134	0.0803	0.2397	0.6603	0.0073
0.13207 [207]	0.1529	0.4237	0.03651	0.07739	0.2062	0.5082	0.02020
0.14440	0.1721	0.4656	0.02828	0.06890	0.2361	0.5466	0.02046
1-propanol + tripotassium citrate + water							
0.0927 [209]	0.1448	0.5950	0.00085	0.1537	0.1008	0.5363	0.0157
0.1215	0.1288	0.5842	0.01240	0.2142	0.0782	0.4479	0.0277
1-propanol + diammonium hydrogen citrate + water							
0.09500 [203]	0.2118	0.5898	0.02510	0.0657	0.3012	0.7005	0.0144
0.07750	0.2375	0.6320	0.02130	0.0620	0.3367	0.7198	0.0137
0.06800	0.2716	0.6676	0.01720	0.0579	0.3507	0.7391	0.0115
2-propanol + trisodium citrate + water							
0.0329 [208]	0.2688	0.5294	0.0122	0.1265	0.1654	0.3475	0.0509
0.0411	0.2536	0.4866	0.0173	0.1508	0.1486	0.3009	0.0650
0.0613	0.2220	0.4366	0.0287				
2-propanol + disodium hydrogen citrate + water							
0.11130 [203]	0.2393	0.4603	0.0371	0.07680	0.3011	0.5596	0.0178
0.08990	0.2749	0.5255	0.0227	0.06860	0.3421	0.6135	0.0113
0.08749 [207]	0.2713	0.4574	0.03971	0.07336	0.3254	0.5105	0.01829
0.07636	0.2932	0.4849	0.02845	0.06806	0.3703	0.5425	0.01362
2-propanol + tripotassium citrate + water							
0.0939 [207]	0.1994	0.6585	0.0087	0.1285	0.1568	0.5506	0.0222
0.1012	0.1871	0.6269	0.0120	0.2400	0.1031	0.4616	0.0362

Table 5.18 (continued)

$w_{1,salt}$	$w_{2,salt}$	$w_{1,ROH}$	$w_{2,ROH}$	$w_{1,salt}$	$w_{2,salt}$	$w_{1,ROH}$	$w_{2,ROH}$
0.1113	0.1736	0.6007	0.0143				
0.1363 [203]	0.1922	0.4543	0.0332	0.0731	0.2630	0.5827	0.00096
0.0990	0.2298	0.5272	0.0177	0.0846	0.2472	0.5590	0.01270
2-propanol + triammonium citrate + water							
0.1268 [205]	0.2370	0.5404	0.0280	0.0558	0.3474	0.7014	0.0048
0.0443	0.3764	0.7228	0.0032	0.1674	0.1968	0.4653	0.0464
2-propanol + diammonium hydrogen citrate + water							
0.1770 [205]	0.2395	0.4749	0.0643	0.1272	0.2975	0.5507	0.0406
0.1570	0.2613	0.5048	0.0547	0.1187	0.3123	0.5742	0.0373
0.1383	0.2790	0.5298	0.0478	0.0962	0.3393	0.5932	0.0336
1-butanol + disodium hydrogen citrate + water							
0.0520 [208]	0.0795	0.6982	0.00279	0.0456	0.1457	0.7442	0.00051
0.0482	0.1067	0.7188	0.00155	0.0524	0.1635	0.7486	0.00020
0.0496	0.1275	0.7328	0.00122				
2-butanol + trisodium citrate + water							
0.1058 [203]	0.0161	0.7415	0.00005	0.1287	0.0336	0.6908	0.0003
0.1190	0.0228	0.7367	0.00004	0.1388	0.0439	0.6851	0.0003
0.1204	0.0293	0.6954	0.00030				
2-butanol + disodium hydrogen citrate + water							
0.0486 [209]	0.1513	0.6777	0.00145	0.0438	0.2314	0.7385	0.00083
0.0450	0.1790	0.7032	0.00122	0.0429	0.2551	0.7446	0.00058
0.0446	0.2100	0.7280	0.00095				
2-butanol + tripotassium citrate + water							
0.1163 [203]	0.0406	0.4939	0.0004	0.1472	0.0158	0.4819	0.0002
0.1278	0.0306	0.4913	0.0003	0.1579	0.0076	0.4736	0.0002
0.1269	0.0265	0.4864	0.0003				
2-butanol + diammonium hydrogen citrate + water							
0.1048 [208]	0.0664	0.7313	0.0111	0.0690	0.1541	0.7972	0.0055
0.0925	0.0938	0.7491	0.0095	0.0553	0.1925	0.8106	0.0043
0.0860	0.1155	0.7702	0.0079				
2-methyl-2-propanol + trisodium citrate + water							
0.1947 [123]	0.0690	0.4750	0.0153	0.1073	0.1135	0.5808	0.0062
0.1271	0.1080	0.5566	0.0067	0.0737	0.1351	0.6055	0.0052
2-methyl-2-propanol + disodium hydrogen citrate + water							
0.1877 [207]	0.0931	0.5160	0.0153	0.0981	0.1508	0.6239	0.0074
0.1303	0.1226	0.5727	0.0101	0.0589	0.1920	0.6648	0.0052
0.14284 [209]	0.1128	0.4567	0.02100	0.06151	0.2118	0.5792	0.01184
0.10557	0.1474	0.5118	0.01611	0.04929	0.2434	0.6110	0.01088
0.07696	0.1774	0.5454	0.01412				
2-methyl-2-propanol + tripotassium citrate + water							
0.0976 [203]	0.1417	0.6290	0.0032	0.1527	0.0943	0.5488	0.0094
0.1273	0.1121	0.5768	0.0062	0.1996	0.0754	0.5075	0.0134
2-methyl-2-propanol + diammonium hydrogen citrate + water							
0.1806	0.1189	0.5414	0.0238	0.1360	0.1662	0.6189	0.0163
0.1630	0.1343	0.5749	0.0187	0.1186	0.1856	0.6380	0.0140
0.1411	0.1517	0.5989	0.0171	0.1103	0.2041	0.6601	0.0133

w_i, i=1, 2, 3 weight fractions in the salt-rich and alcohol-rich phases. $w_1+w_2+w_3=1$

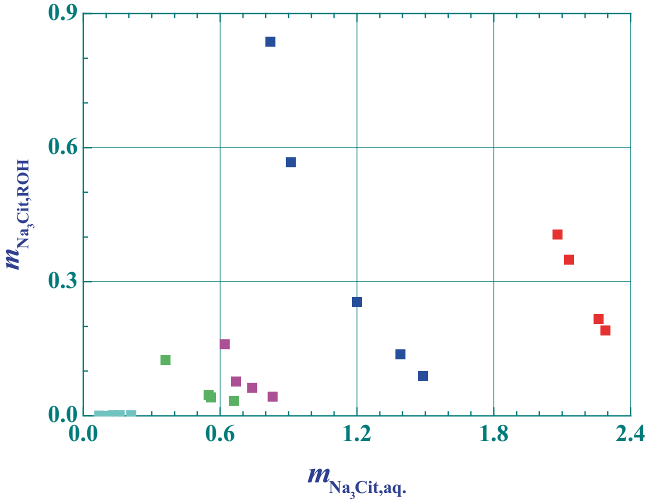


Fig. 5.39 Partition of trisodium citrate in aqueous two-phase systems with different alcohols at 25 °C. Equilibrium compositions are expressed in moles of Na_3Cit in the alcohol-rich phase per kg of alcohol and in the salt-rich phase per kg of water. 🟥 - ethanol [206], 🟪 - 1-propanol, 🟦 - 2-propanol, 🟩 - 2-butanol, 🟩 - 2-methyl-2-propanol [203]

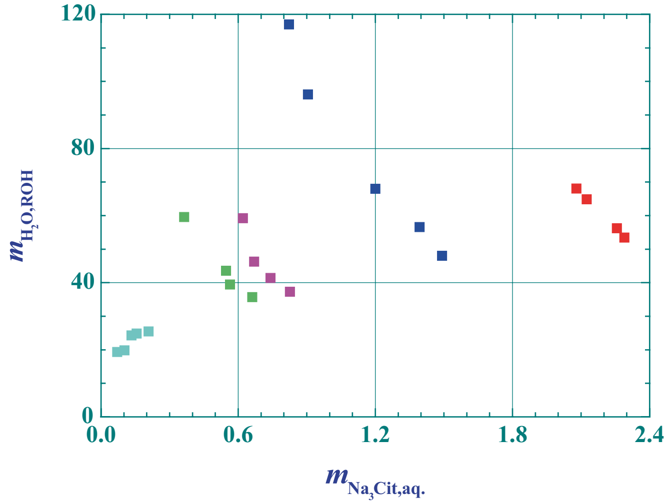


Fig. 5.40 Water dissolved in the alcohol-rich phases as a function of trisodium citrate concentration in the salt-rich phases at 25 °C. Equilibrium compositions are expressed in moles of water in the alcohol-rich phase per kg of alcohol and moles of Na_3Cit in the salt-rich phase per kg of water. 🟥 - ethanol [206], 🟪 - 1-propanol, 🟦 - 2-propanol, 🟩 - 2-butanol, 🟩 - 2-methyl-2-propanol [203]

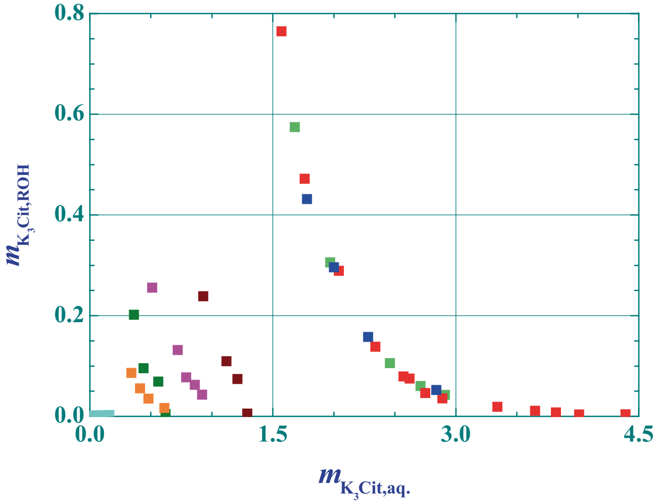


Fig. 5.41 Partition of tripotassium citrate in aqueous two-phase systems with different alcohols at 25 °C. Equilibrium compositions are expressed in moles of K_3Cit in the alcohol-rich phase per kg of alcohol and in the salt-rich phase per kg of water. 🟥 - ethanol [205], 🟩 - ethanol [207], 🟦 - ethanol [204], 🟩 - 1-propanol, 🟪 - 2-propanol, 🟩 - 2-butanol, 🟧 - 2-methyl-2-propanol [204], 🟫 - 2-propanol [206]

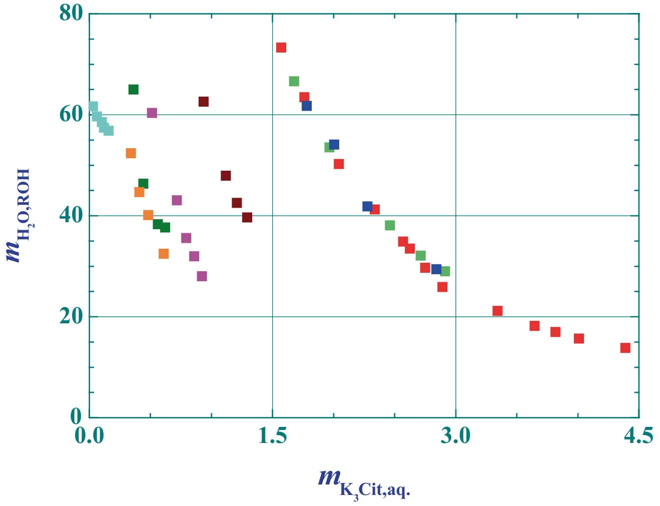


Fig. 5.42 Water dissolved in the alcohol-rich phases as a function of tripotassium citrate concentration in the salt-rich phases at 25 °C. Equilibrium compositions are expressed in moles of water in the alcohol-rich phase per kg of alcohol and moles of K_3Cit in the salt-rich phase per kg^1 of water. 🟥 - ethanol [204], 🟩 - ethanol [206], 🟦 - ethanol [203], 🟩 - 1-propanol, 🟪 - 2-propanol, 🟩 - 2-butanol, 🟧 - 2-methyl-2-propanol [203], 🟫 - 2-propanol [205]

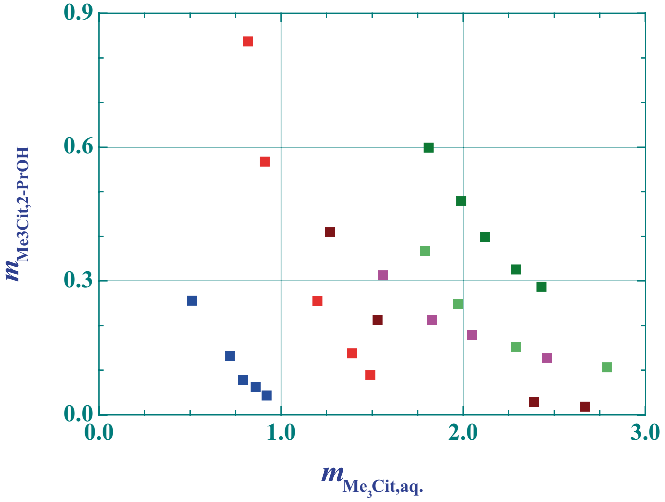


Fig. 5.43 Partition of citrates in aqueous two-phase systems with 2-propanol at 25 °C. Equilibrium compositions are expressed in moles of citrate in the alcohol-rich phase per kg of alcohol and in the salt-rich phase per kg of water. 🟥 - trisodium citrate [203], 🟦 - tripotassium citrate [203], 🟫 - triammonium citrate [205], 🟩 - diammonium hydrogen citrate [208], 🟪 - disodium hydrogen citrate [207], 🟩 - disodium hydrogen citrate [207]

5.12 Two-Phase Alkali Metal Citrate - Polyethylene Glycol (PEG) - Water Systems

To aqueous two-phase systems with various polyethylene glycols (PEG) it was devoted more attention than to the corresponding systems with alcohols [210–229]. Recently, an additional group of two-phase systems, which include different ionic liquids and inorganic citrates, is extensively investigated [230–233]. Only a general behaviour of aqueous two-phase systems with PEG is illustrated and discussed below. At present, the aqueous polymer - salt systems, with ammonium, potassium or sodium salts, are more preferred in separation of biomaterials than previously applied the two-phase aqueous polymer - polymer systems. Comparing with frequently used polymer + dextran + sodium phosphate or ammonium sulfate systems, they offer lower viscosity and interfacial tension, relatively low material cost and better separation rates. The reason to replace phosphates, sulfates or carbonates by citrates is that they are biodegradable, nontoxic, and the effluent streams containing ammonium, potassium or sodium citrates are environmentally safe.

Similarly, as with alcohols, the binodal curves are much better documented than data about equilibrium compositions. It should be taken into account that, in systems with polyethylene glycols, in an addition to not always adequate analytical procedures, the applied PEG or other polymer is not sufficiently characterized. Polymers with the same average mass have a certain distribution of molecular masses which evidently varies depending on theirs producers. The effect is expected to be more pronounced with increasing the molecular mass of polymer. The final result of different polydisperse samples is that if two or more investigations are compared, considerable differences in reported distributions of components between phases are observed. Unfortunately, even such comparisons of data can be performed only in few cases, because most of studies are devoted to different polymers only once. In view of a large but not always certain and comparable experimental data, only a general behaviour of the PEG - citrate - water systems is presented. The binodal curves and tie-lines are not tabulated here and should be taken from original publications [138, 210–229, 230–233, 234–238].

Investigated aqueous two-phase systems include trisodium citrate with different molecular mass polyethylene glycols ranging from PEG 400 to PEG 8000 and in the 5–50 °C temperature range. Zafarani-Moattar et al. [211] studied and correlated systems with PEG 6000 at 25, 35 and 45 °C and Murugesan and Perumalsamy [212] with PEG 2000 at 25, 30, 35, 40 and 45 °C. The same authors reported partition data and some physicochemical properties in the systems with PEG 2000 at 25, 35 and 45 °C [214, 221, 228]. Liquid-liquid equilibria containing polyethylene glycols of different molecular mass (PEG 600, 1000, 1450, 3350 and 8000) at 22, 37 and 50 °C were investigated by Tubio et al. [213]. Partition data for systems with PEG 6000 at 20, 30 and 40 °C were given by Perumalsamy et al. [215]. Compositions of coexisting phases in systems with PEG 1500 and PEG 4000 at temperatures from 5 to 45 °C were determined by Oliveira et al. [218]. Experimental results and modeling of systems with PEG 600, PEG 1500 and PEG 3000 at 25 °C were reported by Alves et al. [219]. At 25, 35 and 45 °C, Souza et al. [224] measured the liquid-liquid equilibrium in systems with PEG 400. Duraiayya et al. [223] compared partition of components in the aqueous two-phase systems containing PEG 4000 and trisodium, tripotassium and triammonium citrates at 25 °C. Polyethylene glycols with much more higher molecular masses, PEG 20000 and PEG 30000, were investigated as potential systems for partitioning of penicillin G acylase [229]. Porto et al. [234] demonstrated possibility to remove toxin-activating proteases from *Clostridium perfringens* fermented broths by using polyethylene glycols having molecular masses ranging from 400 to 8000. The kinetics of phase demixing and the influence of physical properties (densities, viscosities and interfacial tensions) were studied by Nagaraja and Iyyaswami [226]. Phase diagrams at 25, 35 and 45 °C, in the systems with disodium hydrogen citrate and PEG 600, PEG 2000 and PEG 4000 were determined and correlated by Zafarani-Moattar and Jafari [227].

There is much less investigations devoted to the two-phase tripotassium citrate + polymer + water systems than to those with trisodium citrate or triammonium citrate. Jayapal et al. [216] considered the liquid-liquid equilibrium in systems with PEG 2000 at 25, 35 and 45 °C and Zafarami-Moattar and Hamidi [210] with PEG 6000 at 25, 30 and 35 °C. The effect of temperature on the phase equilibrium of the aqueous two-phase poly (polythene glycol) + tripotassium citrate system was studied by Zafarami-Moattar et al. [217]. The phase compositions and densities in the PEG 4000 + triammonium citrate + water systems in the 25–45 °C temperature range were determined by Govindarajan et al. [183]. Similar measurements, but with PEG 6000 were performed by Regupathi et al. [220]. Phase compositions, some physicochemical properties and temperature effects in the triammonium citrate + PEG 2000+ water systems at 25, 35 and 45 °C were reported by Perumalsamy and Murugesan [221, 225]. Comparable investigation, but with diammonium hydrogen citrate was performed by Regupathi et al. [222].

Apart from polyethylene glycols, Sadeghi et al. [185, 235, 236] used polyvinyl pyrrolidone (PVP) with trisodium and tripotassium citrates in establishing the aqueous two-phase systems. The binodal curves and tie-lines in these systems were determined in the 25–55 °C temperature range. Polyethylene oxide (PEO) and polypropylene oxide (PPO) were also utilized to form the aqueous two-phase systems with trisodium citrate. For example, da Rocha Patricio et al. [237] investigated PEO 1500 systems at 10, 25 and 40 °C. Two-phase systems consisting water, triblock copolymers formed from ethylene oxide and propylene oxide units and trisodium citrate were studied at 15, 35 and 45 °C by Virtuoso et al. [238].

Essentially, the behaviour of aqueous two-phase systems with polymers is very similar to that with alcohols. The increase in concentration of citrate in the salt-rich phase is accompanied with a strong decrease in the citrate concentration in the PEG-rich phase (Figs. 5.44 and 5.46). The water behavior is similar, the amount of water in the PEG-rich phase strongly decreases when the citrate concentration in the salt-rich phase increases (Figs. 5.45 and 5.47). As is illustrated in these figures, polymer components with lower molecular mass have a more wide regions

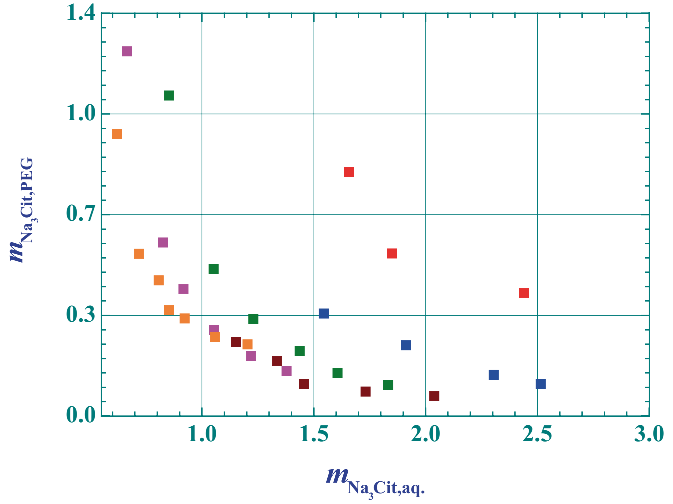


Fig. 5.44 Partition of trisodium citrate in the $Na_3Cit+PEG+H_2O$ systems at 25 °C. Equilibrium compositions are expressed in moles of Na_3Cit in the PEG-rich phase per kg of PEG and in the salt-rich phase per kg of water. 🟥 - PEG 400 [224], 🟦 - PEG 600 [219], 🟩 - PEG 1500 [219], 🟪 - PEG 3000 [219], 🟫 - PEG 4000 [218], 🟧 - PEG 6000 [219]

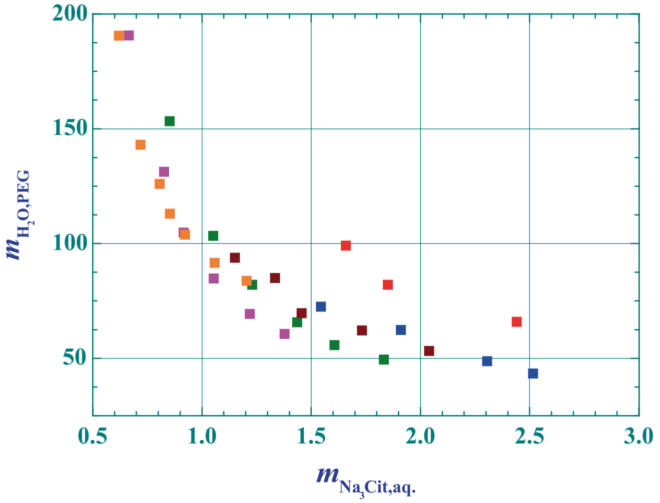


Fig. 5.45 Water dissolved in the PEG-rich phases as a function of trisodium citrate concentration in the salt-rich phases at 25 °C. Equilibrium compositions are expressed in moles of water in the PEG-rich phase per kg of PEG and moles of Na_3Cit in the salt-rich phase per kg of water. 🟥 - PEG 400 [224], 🟦 - PEG 600 [219], 🟩 - PEG 1500 [219], 🟪 - PEG 3000 [219], 🟫 - PEG 4000 [218], 🟧 - PEG 6000 [219]

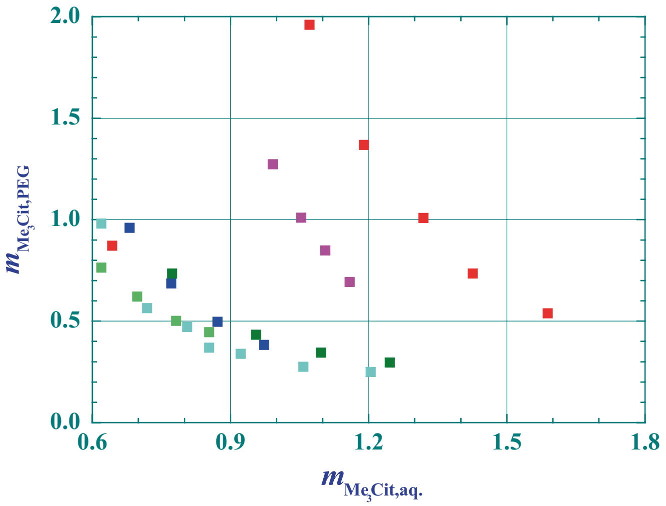


Fig. 5.46 Partition of citrates in the $Na_3Cit+PEG+H_2O$, $K_3Cit+PEG+H_2O$ and $(NH_4)_3Cit+PEG+H_2O$ systems at 25 and 30 °C. Equilibrium compositions are expressed in moles of citrates in the PEG-rich phase per kg of PEG and in the salt-rich phase per kg of water. 30 °C, PEG 4000, 🟦 - Na_3Cit [223], 🟩 - K_3Cit [223], 🟪 - $(NH_4)_3Cit$ [223]. 25 °C, PEG 6000, 🟩 - Na_3Cit [211], 🟩 - K_3Cit [210], 🟥 - $(NH_4)_3Cit$ [220]

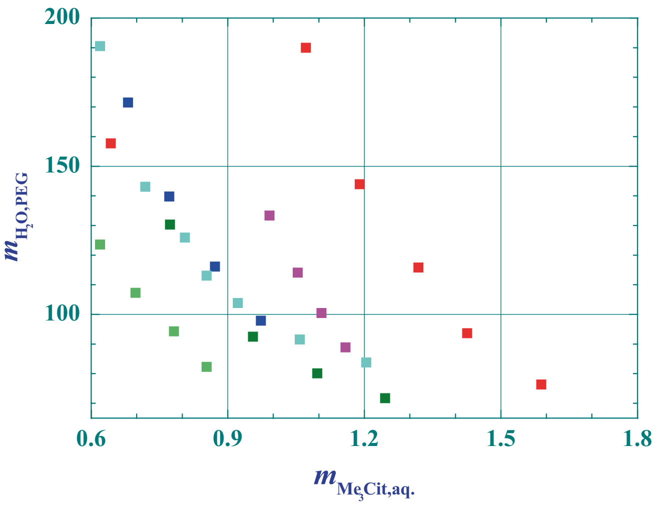


Fig. 5.47 Water dissolved in the PEG-rich phases as a function of citrate concentration in the salt-rich phases at 25 and 30 °C. Equilibrium compositions are expressed in moles of water in the PEG-rich phase per kg of PEG and moles of citrates in the salt-rich phase per kg of water. 30 °C, PEG 4000, 🟦 - Na_3Cit [223], 🟩 - K_3Cit [223], 🟪 - $(NH_4)_3Cit$ [223]. 25 °C, PEG 6000, 🟩 - Na_3Cit [211], 🟩 - K_3Cit [210], 🟧 - $(NH_4)_3Cit$ [220]

of mutual immiscibility than those with large molecular masses. However, then the citrate partition is less and less influenced by the molecular mass of polymer. With increasing of molecular masses of polymer components, the lowest (minimal) compositions of citrates in the salt-rich phases tend to a mutual limit (Figs. 5.44 and 5.46). With regard to extent of mutual immiscibility regions, citrates can be arranged in the following order $(NH_4)_3Cit > K_3Cit > Na_3Cit$ (Fig. 5.46). The expansion of two-phase regions, can be achieved not only by reduction of molecular mass of polymeric components but also by increasing temperature in the citrate - polymer - water systems.

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