

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 Běšter-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 Źarska 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.

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