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 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.
Preface

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