

Preface

Electrolytes and salt solutions are ubiquitous in chemical industry, biology, and nature. However, their thermodynamic properties and applications have not been adequately covered in the undergraduate curricula. Possibly, it was due to the theoretical level and difficulty in treating long-range Coulomb interactions; and partly it was due to the historical emphasis on hydrocarbon processing for oil-and-gas industry. Into the 21st century, the chemical industry becomes highly specialized and much diversified. Many new processes and products are developed that require the application of the electrolyte solutions and knowledge of their properties.

This book is written for the purposes of a learning primer on electrolyte solutions, connection to the modern molecular approaches in the field, and giving examples of some important industrial applications. There is in actuality a dearth of introductory textbooks on electrolyte solutions. The earlier books* by Harned and Owen and by Robinson and Stokes, valuable as they are, were written in the 1950s and 60s. They do not contain many of the modern materials. Other recent books are at an advanced level and restricted to specialized topics. There is indeed a need for a general introductory book to serve as the first course on electrolyte thermodynamics as well as a beginner's guide to it.

How do we harmonize the diametrically opposed demands of, on the one hand, an introduction and on the other, advanced molecular theories? We divide the book into three parts. The first five chapters are introductory, thus suitable for undergraduate education. They also provide practicing engineers who did not have training in this subject with a quick self study to “catch up”. It can supplement an undergraduate thermodynamics course. Chapters 6 to 10 pave the way to molecular theories. We are heavy on applied statistical mechanics and light on

*H. S. Harned, B. B. Owen, “*The physical chemistry of electrolyte solutions*” (Reinhold Publishing, New York, 1950). R. A. Robinson, R. H. Stokes, “*Electrolyte solutions*” (Butterworths, London, 1959).

advancing theories. Chapters 12 and 13 are industrial applications: absorption refrigeration and natural gas processing; both utilizing electrolyte solutions. We give more description below.

We introduce the classical Debye-Hückel theory, not due to its accuracy, but for historical reasons. The contribution of Debye and Hückel is remarkable in their ability to explain the $(-\sqrt{I})$ behavior of the activity coefficients (I being the ionic strength). This behavior arises due to the long-range Coulomb interaction and cannot be accounted for by classical thermodynamic theories. It is now recognized as the *Debye-Hückel limiting law*. For higher concentrations, we choose the formulation due to Pitzer. Pitzer has correlated salt solution data for many common salts with a virial type equation. The equation is relative simple and can be programmed on a hand-held calculator (e.g. a TI-89). For simple systems, the results are quite accurate. It is hoped that after the five chapters, the reader will acquire adequate working skills with salt solutions and be able to apply equations to calculate accurately electrolyte solution properties with confidence.

To understand modern electrolyte theory, we must learn the molecular aspects of ionic solutions. The next five chapters (6 to 10) form an advanced part of the book and are more suitable for a graduate level course. It introduces the statistical mechanics of electrolyte solutions. Some elementary knowledge of physical chemistry, such as probability distribution, partition function, and statistical ensembles, is needed as prerequisites. Here we go beyond the Debye-Hückel theory and discuss the integral equation approaches that give more accurate activity coefficients for concentrated electrolyte solutions (greater than 0.001 molal). We also try to keep the mathematics on a moderate level, by using the mean spherical approach (MSA) as the staple method where analytical formulas are available for numerical calculations. Chapter 10 gives a general description of the Ornstein-Zernike integral equation for the molecular distributions. We describe the hypernetted-chain closure (HNC), the numerical solution techniques, and the origin and treatment of the bridge function that is essential in any closure equation. Once the integral equations are solved, the correlation functions can be used to obtain the thermodynamic properties of the electrolyte solution: such as the electrostatic internal energy, the osmotic coefficient, and the activity coefficient. Since the activity coefficients play a central role, just as in the conventional solution thermodynamics, we can decipher the behavior of electrolyte solutions from these properties. The reader should be able

to connect comfortably with other modern treatments with a molecular bend after studying these chapters.

Many industrial processes employ mixed solvents: water, methanol, amines, ethylene glycol, ammonia, etc. in the presence of salt species, such as in inhibition of gas hydrates, dehydration, gas sweetening, azeotrope distillation, and refrigeration. Chapters 8 and 9 deal with the “salting-out” behavior for these solvents and the necessary conversion of thermodynamic scales: from the McMillan-Mayer scale to the Lewis-Randall scale. Our approach automatically satisfies the Gibbs-Duhem relation and thermodynamic consistency. We examine the Setchenov and Furter coefficients, which are rederived, improved, and put on a firm theoretical basis.

Chapter 11 is an introduction to the electric double layers that are at the basis of cellular interactions, biochemistry, and electrochemistry on electrodes. We start with the Poisson-Boltzmann equation and go into some details on the derivations to achieve a sound understanding. We then discuss the ζ -potential and the DLVO (Derjaguin-Landau-Verwey-Overbeek) theory that are much used in colloid and biochemistry. Finally we cite some recent developments in protein chemistry on using the Yukawa potentials to model the colloidal interactions. The molecular approach introduced in Chapter 10 finds its application here.

A unique feature of this text book is the inclusion of two chapters (12 and 13) on industrial applications: (i) the absorption refrigeration using electrolytes as working fluids, and (ii) the removal, from raw natural gas streams, of the acid gases (hydrogen sulfide and carbon dioxide) by aqueous amine solutions. There is urgent need in the HVAC (heating, ventilation, & air conditioning) industry in finding alternative working fluids other than the CFC's (chlorofluorocarbons) and HCFC's (hydrochlorofluorocarbons) that are ozone depleting and are subject to banning by 2030 according to an international accord. Ionic solutions, such as water-lithium bromide solutions, can be use in the absorption refrigeration cycle to achieve cooling. In natural gas processing, the acid gases must be neutralized and removed before being used as fuel. Aqueous amines, which contain ionic species, are used to “wash” and “sweeten” the raw gas, to remove the CO_2 and H_2S . This process also has implications in environmental engineering. We have included some software in the CD accompanying this book for calculations of the loading of amines and acid gas vapor pressures. It can

be put on a laptop computer by an engineer and carried around in the field for fast answers. The programs also provide detailed outputs (such as speciation and activity coefficient information).

This text book is introductory. However it connects to modern approaches. It lays out the basic theories, but also gives industrial applications. It provides ready-to-use software* and computer programs that give immediate applications and alleviate the complicated programming. We hope that it will enhance the thermodynamics education and put the tools of accurate electrolyte modeling into the hands of practicing engineers.

The field of electrolyte solutions is vast and spanned many centuries. It is impossible to cite, let alone study, all the extant literature. Due to the introductory nature of this book, we mentioned only a bare minimum of previous works in the bibliography. The sin of omission is not to be interpreted as a lack of respect for all the brilliant and indispensable contributions to this field. I sincerely thank the careful review by Dr. Frank T.H. Chung who showed keen interest in its success, and many typing and editing help by my dear wife, Chi-Ming. Some of the programming has been carried out by my former colleagues, Kevin Gering, D. J. Ghonasgi, Lester Landis, Bill Li-Jun Lee, Frank Chung, and Rong-Song Wu. Many of them have pioneered in the developments of this branch of electrolyte solution studies. I am grateful for their contributions.

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*A Windows-interactive (GUI) software for acid gas treating with amine solutions is available for distribution at cost. Contact profllee@yahoo.com for ordering.