Handbook of

AQUEOUS ELECTROLYTE SOLUTIONS

Physical Properties, Estimation and Correlation Methods

A. L. HORVATH, B.Sc., M.Sc.

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Preface

The purpose of this book is to bring together the advances that have been made in estimating and correlating the physical properties of aqueous electrolyte solutions during the last century. The various methods presented are integrated and arranged to provide the coherence essential for current progress in a field as dynamic and important as electrochemistry.

Until now there has been no journal, serial, or other publication reserved exclusively for the diversified literature on estimation and correlation methods for the properties of electrolyte solutions. As a consequence of the increasingly large number of publications in this field, there has grown up an inescapable need for a comprehensive treatise in which one could expect to find the latest important world literature compiled and the methods for estimations and correlations evaluated.

The time is not available to most researchers to scan the large number of technical publications that might contain articles important to a current problem. Therefore, the objective of this monograph is to survey the entire field from a single viewpoint and to present current information in a consistent format. The author's aim is to promote a basic understanding of the properties and behavior of aqueous electrolyte solutions which underlie the selection of the estimation and correlation methods. The various trends and regularities existing among physical, thermodynamic, and transport properties are emphasized and mathematical equations are used for expressing the relevant relationships developed throughout the century.

The goal of this book is to present a systematic and comprehensive collection of the more important methods reported in the published literature and to make a selection of them with recommendations.

To produce a book of manageable proportions it was necessary to limit it in scope. Some thermodynamic properties, e.g. enthalpy, heat of formation, free energy of formation, heat of solution, heat of fusion, etc., have been excluded. These thermodynamic properties of aqueous electrolyte solutions deserve a separate volume.

The book is directed toward graduate students in science and engineering and toward workers engaged in the chemical industries and related disciplines. Although this book will be of greatest use to electrochemists and process engineers, it is hoped that environmental chemists, geochemists, biochemists, and other scientists and technologists will also find the information gathered to be of interest. This treatise will also serve as a reference source for many scientists in various disciplines, as well as for students, who will find it helpful in gaining a better knowledge of the aqueous electrolyte solutions and in understanding the interrelationships among the various physical, thermodynamic, and transport properties.

I am indebted to several authors and the following publishers for their consent to the publishing of figures and tables: the American Chemical Society, Academic Press, the American Institute of Chemical Engineers, Springer-Verlag, the National Research Council of Canada, the Canadian Society for Chemical Engineering, and Pergamon Press.

I wish to acknowledge the support provided by Imperial Chemical Industries PLC and constructive discussions with a number of scientists and engineers in the company, especially Drs P.O. Kane, P. Rathbone, and G.E. Edward. I am very grateful to my wife Joan for her patience, constant support, and help during the past years.

January, 1985 Ari L. Horvath

Introduction

NEED FOR PHYSICAL DATA

The inorganic salts (e.g. NaCl, $CaCl_2$, Na_2CO_3) when dissolved in water form aqueous electrolyte solutions. They play a significant role not only in chemical laboratories and industries, but also in Nature, as geothermal systems and in the biological processes of all living organisms. Consequently, these solutions are of particular interest to geologists, electrochemists, and chemical engineers. If water is present in a system, then it is most likely that it contains ions, at least in minute quantities as impurities. The oceans are the largest reservoir of aqueous electrolyte solutions.

Very few people realize the enormous cost which mankind has to pay for not having sufficient information on the behavior and properties of aqueous electrolyte solutions. The lack of data on the physical, thermodynamic, and transport properties of these solutions – and the consequence in monetary terms (annually the cost would amount to many millions of pounds) in the electrical industries alone – were recently reported by Turner (1980). There is no doubt that this field of science and technology requires further investigation in order that we may widen our knowledge and consequently save on unnecessary expenses (Cobble, 1966; Hill, 1979; Touloukian, 1979; Horvath, 1973).

In this book references are given in most chapters where experimental or evaluated data have been reported. In some cases, e.g. thermal conductivity, the list of references has been updated with new material. For surface tension a comprehensive bibliography has been compiled, because there is considerable difficulty in finding experimental data in the literature.

Despite the large number of reported experimental data, there is still a great demand for methods which will enable scientists and engineers to extrapolate or interpolate the available data to other conditions, or to estimate the missing properties of the aqueous electrolyte solutions at the desired conditions (Newman, 1980).

For the estimation of the properties of aqueous electrolyte solutions, in most cases the properties of pure water are required. Therefore they are tabulated in Appendix 6 for easy access.

To illustrate the difficulties, it is worthwhile to compare the conditions required for pure substances and aqueous electrolyte solutions. The physical properties of a pure compound are defined by two variables: temperature and pressure. This can be expressed by the equation

$$F(\text{property, temperature, pressure}) = 0.$$

In the case of an aqueous electrolyte solution (binary system) the expression becomes

$$F(\text{property, temperature, pressure, concentration}) = 0.$$

That is, while for pure substances two variables determine the condition, for binary aqueous electrolytes an additional parameter, the concentration, will be needed to describe the properties. Therefore, it is not surprising that it is difficult to find thermodynamically sound relationships and more and more empirical equations are used for the representation of the various properties of aqueous solutions.

The mixing rules proved to be very useful for dealing with binary and multicomponent systems. However, the mixing rules can not be used if one of the components is solid and the other is liquid in the pure state, as in the case of aqueous salt solutions. It will be shown later in the book that most of the more reliable and practical correlations or representations of physical properties of aqueous electrolyte solutions are based more upon mathematical than upon physicochemical principles. In particular, the double polynomial has proved very successful for the representation of the transport properties of aqueous salt solutions. However, the effect of pressure has not been included in the formula.

The best sources of reliable physical properties can be traced among experimental determinations. In general, it is not difficult to measure the most common properties of aqueous salt solutions (density, viscosity, surface tension, etc.) at room temperature. However, difficulty arises when the measurements are carried out at higher temperatures and pressures. The purity of the material is usually no problem (contrary to the case in making measurements with organic compounds). Despite the easy availability of the aqueous solutions, even in large quantities, there are many properties of numerous solutions which have never been determined experimentally. For example, aqueous Li, Na, and Ca hypochlorite solutions are important bleaching agents used widely in industry and households. There is little reported on their various physical properties in the published literature. Their annual production is well over thousands of tons and they are frequently transported in bulk quantity in roadtankers, by rail, and by sea. Due to the lack of experimental data, all the necessary design and safety calculations needed have been based upon estimated physical, thermodynamic, and transport property values. Similarly, very limited experimental data are available on aqueous solutions of $AgNO_3$, LiCl, KBr, KNO_3, NaBr, NaCN, Na_2S and $ZnSO_4$.

It is most unlikely that an extensive experimental program will start in the near future; therefore the designers and scientists who require the information discussed above have to rely on the available estimation techniques. Unfortunately, until now no compilation or book had been published on estimation methods for the physical, thermodynamic, and transport properties of aqueous electrolyte solutions. However, estimation methods were and are published in journals (see Appendix 5); many of these methods have been well studied and evaluated. The main purpose of this book is to provide the readers with a review on the available estimation and correlation methods and give recommendations as to the calculations which could provide the best answers for the required physical properties.

SOURCES OF DATA

While there are several compilations on the physical properties of aqueous electrolyte solutions, there is no one book devoted to the estimation, prediction and correlation methods. The bibliographies most often cited on the literature sources of physical, thermodynamic, and transport properties of aqueous electrolyte solutions are listed in Appendix 1, which includes the multivolume handbooks on the data. However, these compilations also contain chemical and physical information in general; that is, they are not special books on aqueous electrolyte solutions.

The tabulation and presentation of the physical, thermodynamic, and transport properties of aqueous solutions of electrolytes are not easy tasks. Therefore, it is not surprising that there is a lack of compilations for easy use by scientists and engineers. The data collected and evaluated in preparing the *International Critical Tables* (Washburn, 1926–33) have not been updated. The existing seven volumes consist of about 500 pages each. According to a recent estimate by the National Bureau of Standards, Washington, a comparable compilation today would consist of 200 volumes (Abelson, 1981).

To find the data needed in the open literature requires access to a technical library. Most of the multivolume handbooks – Gmelin (1926–), Mellor (1922–), Pascal (1956–), Landolt-Börnstein (1950–), and Washburn (1926–33) – contain properties of electrolyte solutions. However, the reader will find, in most cases, that the required data are not available in these handbooks, or that the concentration and temperature ranges are not covered by the experimental results. In these cases, the reader has to interpolate, extrapolate, or estimate the property needed.

In addition to the multivolume handbooks, there are several special books on the physical, thermodynamic, and transport properties of aqueous electrolyte solutions. These are listed in Appendix 2.

Furthermore, in association with the available multivolume handbooks, bibliographies, and specific compilations, the sources of published articles in the literature can be retrieved through searching the various abstract journals:

Chemical Abstracts
Physical Abstracts
Pollution Abstracts
Water Quality Abstracts
Chemisches Zentralblatt
Referativnyi Zhurnal
Dissertation Abstracts
Theoretical Chemical Engineering Abstracts
Nuclear Science Abstracts
Analytical Abstracts
Citation Index.

The list of relevant sources on the properties of aqueous electrolyte solutions would not be complete without reference to the numerous industrial and trade brochures, phamphlets, and booklets. Most of the larger industrial manufactures of aqueous solutions of inorganic compounds issue promotion leaflets of some type on their products, e.g. aqueous solutions of sulfuric acid, sodium hydroxide, ammonia, hydrochloric acid, sodium hypochlorite, etc. In general these information leaflets are normally available only to the purchasers and potential purchasers of the products. However, some of these brouchures contain valuable unpublished (albeit unsubstantiated) experimental data, which have not been reported in the open literature. It is worthwhile to mention a few of those firms which produce such brochures:

Allied Chemical Corporation, USA
Dow Chemical Company, USA
Imperial Chemical Industries PLC, UK
Farbwerke Hoechst, Germany
Hooker Chemical Company, USA
Lurgi Chemie und Huttentechnik GmbH, Germany
Mathieson Chemical Corporation, USA
Minnesota Mining and Manufacturing Company, USA
Montecatini, Italy
Pennsalt Chemical Corporation, USA
du Pont de Nemours and Company, USA
Solvay et Cie, France
Union Carbide Corporation, USA.

PRODUCTION OF CHEMICALS

The importance of the inorganic compounds and their aqueous solutions is well illustrated in the annual list of the top 50 chemical products, prepared for the journal *Chemical and Engineering News* (Webber, 1983). These compounds, their ranks, and their production in billions of pounds during 1982 are given below. The last column gives the production data quoted by Hyman (1973), for comparison.

Compound	Rank	1982	1973
Sulfuric acid	1	64.74	60.09
Ammonia	3	30.99	—
Sodium hydroxide	7	18.45	20.53
Phosphoric acid	9	17.10	12.53
Sodium carbonate	10	15.79	14.92
Nitric acid	12	15.24	14.04
Ammonium nitrate	13	14.67	13.74
Hydrochloric acid	25	4.97	4.40
Ammonium sulfate	29	3.57	—

SPECIFIC PROBLEMS

In the following subsections a short account is given to outline through some typical examples the application of and need for physical, thermodynamic, and transport properties of aqueous electrolyte solutions.

Geology

To obtain useful results related to hydrothermal activity, hot springs, and ore deposits, geologists have to know the physical properties of aqueous solutions. The interpretation of hydrothermal processes, the origin of ore deposits, the synthesis and decomposition of particular minerals, etc., are difficult without reliable thermodynamic property data on the solutions and systems in question. For the evaluation of various geothermal systems in order to use them for the production of energy, various properties of the systems are needed. Information is also required for the study of aqueous salt solutions as a result of nuclear explosions in underground salt beds (Benedict, 1939; Keevil, 1942; Zen, 1957; Criss & Cobble, 1964a, b; Zarembo & Fedorov, 1976; Ozbek *et al.*, 1977; Kestin *et al.*, 1977, 1978; Ozbek & Phillips, 1979, 1980; Potter & Haas, 1978; Grimes *et al.*, 1979; Jenne, 1979; Gokcen *et al.*, 1981; Tödheide, 1982; Phillips *et al.*, 1982).

Desalination

The physical, thermodynamic, and transport properties of saline water are necessary for the design of desalination plants. The economy and efficiency of operation, and the capacity of the equipment, will depend upon the maximum temperature of the operation. The higher temperature region is advantageous because of low viscosities, higher diffusion rates, shifts in chemical equilibria, and some other properties depending upon the temperature. However, the higher temperature will cause scale formation, which is a deterrent. It is relevant to know more about the scale-forming ingredients in solutions at various concentrations and temperatures (Anonymous, 1965; Fabuss & Körösi, 1967; Körösi & Fabuss, 1968; Lindsay & Liu, 1968; Fabuss *et al.*, 1969; Latysheva, 1973).

Humidity

For the measurement and control of humidity of gases, it is necessary to know the vapor pressures of the solutions of inorganic salts. Furthermore, vapor pressure data are also required for the calibration of infrared hygrometers. Binary saturated aqueous solutions (primarily of single salts) are often used for humidity control in a working space. These binary solutions provide a relatively inexpensive and simple method for humidity control, through control of the temperature and concentration of a saturated solution (Leopold & Johnston, 1927; Linge, 1929; Acheson, 1965a, b; Wexler, 1965; Boryta *et al.*, 1975; Greenspan, 1977; Yusufova *et al.*, 1978).

Drying

The properties of aqueous salt solutions (e.g. aqueous LiCl, LiBr, and $CaCl_2$ solutions) are needed for the study of gas drying (Bogatyk *et al.*, 1966) and spray drying (Schlünder, 1965).

Crystallization

The various physical properties of crystallizing aqueous systems are used for the design of continuous crystallizers (Phillips, 1972; Basargin *et al.*, 1976; Ishii & Fujita, 1978).

Fuel Cells

A fuel cell is an electrochemical device in which electric power is produced from some suitable fuel, which can be a gas, a solid, or a liquid electrolyte. Physicochemical properties of aqueous electrolytes are also needed in the calculation of process characteristics in fuel cell operation (Kirkpatrick *et al.*, 1933; Kelly *et al.*, 1965; Vogel *et al.*, 1967; MacMullin, 1969).

Concentrators

The design of the Dowtherm-heated caustic high concentrator requires a knowledge of the properties of caustic soda solutions for all concentrations and temperatures up to the molten anhydrous state (Standiford & Badger, 1954). During the evaporation of aqueous electrolytes in commercial practise, it is important to know the vapor pressure–temperature–concentration relationship, particularly in the range of very low water concentration (Badger & Baker, 1920; Pershke & Kalinin, 1932; Rothbaum, 1958; Hoyt, 1967; Chou & Rowe, 1969).

Refrigeration

The thermodynamic properties of ammonia–water mixtures in the form of the saturated liquid and vapor are of considerable technical importance, because of the use of these mixtures in refrigeration (Scatchard *et al.*, 1947). Other aqueous solutions, e.g. those of lithium bromide and lithium iodide, also have very low vapor pressures (high hydroscopicity) and, therefore, they are used in air-conditioning units of the absorbing - cooling type in order to create the pressure drop between the evaporator and absorber necessary to move the refrigerant vapor. Consequently, the physical and thermodynamic properties, e.g. vapor pressure, latent heat of vaporization, enthalpy, solubility, etc., are necessary for the design of the air-conditioning units (Rau, 1948; Riedel, 1950a, b, c; Bach & Boardman, 1967; Latysheva, 1973).

Equilibrium

Knowledge of the changes in thermodynamic functions accompanying a chemical reaction is required in order to investigate the equilibrium conditions of that reaction. Inorganic solids are often deposited in pipelines during the transport of gases and solutions. For example, in the manufacture of chlorine gas, information is needed with regard to the solid - gas equilibrium between $NaHSO_4$ and H_2O, since this affects transport processes (Hejtmankova & Cerny, 1974). The molal activity coefficients and the vapor pressure depression in electrolytic solutions are often needed in phase and/or chemical reaction equilibrium calculations and in ion–solvent and ion–ion interactions (Kaminsky, 1957a, b, c; Mandal *et al.*, 1977; Lo Surdo & Wirth, 1979; Rastogi & Tassios, 1980). Recently, a new catalytic route has been reported for the epoxidation of simple olefins with diluted solutions of NaOCl as an easy-to-handle oxygen source (Meunier *et al.*, 1984).

Structures of Solutions

There is a steadily growing interest in understanding the structures of solutions, the structures of surface layers, and the surface characterization of solutions. In order to carry out the requisite investigations, model building processes, simulations, etc., knowledge of the properties of the relevant solution is necessary. Probably the largest number of investigations in the field of aqueous electrolyte solutions are related to this subject (Harkins &

McLaoghlin, 1925; Harkins & Gilbert, 1926; Jones & Dole, 1929; Onsager & Fuoss, 1932; Oka, 1932a, b; Ariyama, 1937a, b; Dole, 1938; Vand, 1948; Pozinov & Tumarkina, 1954; Schäfer *et al.*, 1955; Rusanov & Faktor, 1965; Ostroff *et al.*, 1969; Clementi & Popkie, 1972; Faktor & Rusanov, 1973a, b, c; Kistenmacher *et al.*, 1973a, b, c, 1974a, b, c; Popkie *et al.*, 1973; Molyneux, 1973; Pugachevich & Tsurkin, 1973; Ralston & Healy, 1973; Robertson, 1973; Fortier *et al.*, 1974; Berecz, 1975; Williams, 1975; Aveyard & Saleem, 1976; Broers *et al.*, 1976; Celeda & Zilkova, 1977; Goldsack & Franchetto, 1977a, b, 1978; James & Frost, 1978; Liphard *et al.*, 1977; Singh *et al.*, 1977; Aleshko-Ozhevskii, 1979; Lee *et al.*, 1979; Marcus, 1979; Lyashchenko *et al.*, 1981; Szasz *et al.*, 1981; Ciccariello *et al.*, 1982; Leyendekkers, 1982b, 1983a, b; Watanasiri *et al.*, 1982).

Sizing Equipment

The basic properties of aqueous solutions most frequently required are solubility, density, surface tension, vapor pressure, specific heat, latent heat of vaporization, viscosity, thermal conductivity, and the molecular diffusion coefficient. These properties are required for calculating flow, heat transfer, and mass transfer rates in various pieces of equipment (Unterberg, 1964, 1966). Accuracy in the design or performance of industrial equipment for handling operations or processes involving aqueous salt solutions requires accurate physical data on the solutions involved. For engineering utility, reliable methods for estimation of the important thermodynamic properties of solutions over wide ranges of concentrations and temperatures would be extremely valuable (Johnson & Molstad, 1951; Bump & Sibbitt, 1955; Kirschbaum, 1955; Othmer & Naphtali, 1956; Vargaftik & Os'minin, 1956; Vieweg, 1960, 1963a, b; Gel'perin *et al.*, 1969, 1972; Fedotov & Maksimova, 1971; Chernen'kaya & Vernigora, 1973a, b; Castelli *et al.*, 1974; Jamieson *et al.*, 1975; Krönert & Schuberthy, 1977; Venart & Prasad, 1980; Newman, 1980, 1983; Chen, 1980).

Turbine Design

Thermophysical data are also required for the minimization of scaling and corrosion in the design of turbines and in establishing the best available operating temperatures, pressures, and flow rates of the aqueous solutions (Potter & Haas, 1978; Turner, 1980).

Separation

For the removal and separation of gaseous products of a chemical reaction, the wet method is often used, i.e. scrubbing the gases out with water or aqueous solutions. To determine the separation potential of the mixture, it is important