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Recent Advances in Modeling Thermodynamic Properties of Aqueous Strong Electrolyte Systems

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Theoretical and engineering models for the thermodynamic properties of strong electrolyte solutions have advanced significantly since 1985. This progress is notable in the ability to calculate selected properties of single and mixed strong electrolyte solutions over a wide range of temperatures and compositions, including effects of various nonelectrolytes, solvents and supercritical components. Theoretical studies have begun to consider more realistic fundamental interactions between various components in these systems. There have been several successful conversions of theories based on the mean spherical approximation and perturbation methods into engineering equations, without large numbers of empirical parameters. Other theoretical models seem almost ready for application to real systems. The capability to estimate a wide variety of thermodynamic properties accurately with a consistent set of equations and a small number of adjustable parameters has been achieved by several groups over limited temperature and composition ranges. Much work remains to be done, however, to understand completely the interplay and relative importance of various contributing energy effects.

Introduction

Understanding the thermodynamic properties of aqueous strong electrolyte systems is essential for design and simulation of a wide variety of important chemical processes including wastewater treatment, extractive distillation, solution crystallization, desalination, mineral scale formation in steam systems, and gas scrubbing. Since the 1920s, researchers have sought to model these properties in terms of measurable characteristics of the ions and the solvent molecules. While empirical equations have been constructed that can be used to correlate the thermodynamic properties of aqueous electrolytes over a range of temperatures and compositions, they have done little to improve our theoretical understanding of these systems. Starting with the landmark works of Pitzer (1973) and Helgeson et al. (1981), significant advances have been made in combining theoretical and empirical approaches to these problems. The successes in the past ten years have been particularly noteworthy, as a variety of theoretical techniques have been developed and applied successfully. At least two coherent and theoretically sound approaches have been used to develop equations suitable for engineering applications. In addition, a number of semiempirical equations, which are not as closely grounded in theory, but nonetheless offer improved calculation of various thermodynamic properties, have appeared.

The purpose of this article is to review recent advances in theoretical and empirical approaches for modeling thermodynamic properties of systems containing strong electrolytes. Our intention is to provide a summary of recent developments in both electrolyte theories and engineering equations that will be useful to those who are not specialists in electrolyte thermodynamics but who desire to understand the advances that have been made through recent research in this field. This article is not intended to be an exhaustive survey, but it is a broad sampling of the work in strong electrolyte thermodynamics that has been published in the chemical engineering and chemical physics literature since 1985.

Other Recent Reviews

A number of recent reviews of selected topics in this area should be noted. An introductory review of recent electrolyte

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theories and how they evolved from their predecessors appears in a well-written piece by Mazo and Mou (1991). They discuss the fundamental concepts from statistical mechanics that are the foundation of the most widely used of these theories, show how they are related to thermodynamic properties, and illuminate clearly the problems that the theories have been designed to solve.

Friedman (1981) has written a masterful critical review of advances in theories of electrolyte behavior, which includes suggestions for solving a number of outstanding problems in the area. Here he presents a particularly lucid and very useful discussion of the relationships between the McMillan–Mayer, Born-Oppenheimer, and Schroedinger levels of approximation used to study electrolytes.

The physics and chemistry of ion hydration are thoroughly covered in Conway (1981). This excellent reference work includes interesting discussions of the fundamental physical models that are used to describe ion–solvent and solvent–solvent interactions, as well as the effects of hydration on the thermodynamic properties of electrolyte solutions. Nonaqueous solvation of ions is treated extensively by Marcus (1985). He discusses the solvation of ion pairs, theories that describe selective solvation, and applications of these ideas to real systems.

Empirical and semiempirical equations that can be used to calculate some thermodynamic properties of electrolyte solutions important for industrial applications are reviewed by Renon (1986). An excellent summary of engineering equations that had been formulated prior to 1981 for mean ionic activity coefficients is available in Zemaitis et al. (1986), while the development of theories for activity coefficients of aqueous electrolytes during this period is traced by Conway (1983). Where Zemaitis et al. discuss the origin of the engineering equations and their ability to accurately reproduce experimental data, Conway places special emphasis on modern statistical mechanical treatments.

Rafal et al. (1994) summarize the equations developed by Helgeson and coworkers (Helgeson and Kirkham, 1974a,b, 1976; Halgeson et al., 1981, 1989; Tanger and Helgeson, 1988; Helgeson and Shock, 1988, 1990), and discuss the use of the equations for predicting the standard free energies of electrolytes in calculating solution densities, activity coefficients, and enthalpies and entropies of mixing. This exposition is particularly valuable for chemical engineers, since these equations were originally developed for application to geochemical problems, and were not published in the chemical engineering literature.

Overview of Recent Work

We have chosen to separate recent research in modeling strong electrolyte properties into two broad categories—advances in fundamental theories, and application of theoretical and empirical results to engineering problems. In the first section, we discuss advances in theoretical models for electrolyte solution structural properties along with the semiempirical equations that are derived from them. These are presented under four large headings: Debye–Hückel (Poisson–Boltzmann) methods, perturbation expansions, McMillan–Mayer approaches, and Kirkwood–Buff theories. In the second section, we review progress in semitheoretical and empirical equations that have been developed or extended recently for modeling real electrolyte systems. In this section the works are grouped by the type of systems studied, for example, mixed solvents, mixed electrolytes, systems with supercritical gases. Before discussing the work in each area in detail, it is valuable to note some general trends.

Much of the theoretical work reported since 1985 involves (1) fleshing out and filling in restricted and unrestricted primitive-model formulations of statistical mechanical methods that have been applied successfully to nonelectrolyte systems, and (2) developing nonprimitive formulations of these theories. The restricted primitive model, in which the solvent is regarded as a dielectric continuum and all ions have equal diameters, is the simplest framework for theories derived from statistical mechanical arguments. The goal of such studies often is to develop techniques to solve the difficult mathematical problems caused by the long-range interparticle potential energy in ionic systems, and thereby calculate structural information about the system. This information then is compared with that available from Monte Carlo (MC) and molecular dynamics (MD) computer simulations of the interacting particles, and can be converted into macroscopic thermodynamic properties for comparison with experimental data on real electrolyte systems.

Most of the theoretical work since 1985 that is discussed below has not yielded analytical equations for thermodynamic properties that can be compared with experimental data directly. A notable exception is work reported by Henderson et al. (1985) using perturbation expansion techniques. These results have been used to model aqueous alkali halide activity coefficients by Chan (1991), and form the basis of a successful equation of state for aqueous electrolytes by Jin and Donohue (1989a,b) and Jin (1991). Further development of the RISM (Hirata et al., 1982, 1986; Pettitt and Rossky, 1986) and IPY (Ichiye and Haymet, 1990; Vlachy et al., 1991; Duh and Haymet, 1992) integral-equation techniques so that they can be used in practical applications is an area of research that could be rewarding, given the quality of the structural information available from those methods.

Applications of theories developed before 1985 have continued apace, noteworthy being the continued development of the modified Debye–Hückel theories by Pitzer and coworkers, whose recent work in this area is summarized by Pitzer (1991). This approach has yielded equations for a large number of single and mixed systems, which correlate volumetric properties, enthalpies and entropies of mixing, and osmotic and mean activity coefficients over a wide temperature range, although they require a large number of empirical parameters.

The mean spherical approximation (MSA) integral equation has been extended successfully by Renon and coworkers (Ball et al., 1985; Fuerst and Renon, 1993) to the calculation of osmotic coefficients, and by Copeman and Stein (1986) to activities in liquid–liquid systems containing electrolytes. Hydration models have received new attention recently, with Heyrovska (1989) considering the degree of association and hydration as an alternative to the traditional activity coefficient, Schoenert (1990a,b, 1991a,b, 1993, 1994a,b) developing a set of equations for the excess enthalpy and Gibbs free energy of ion solutions, and Ghosh and Patwardhan (1990) presenting a sort of corresponding states approach for electrolyte solutions based on hydration energies.

One of the most important generalizations reported in this period is that of Patwardhan and Kumar (1986a,b, 1992, 1993) who have shown how to use successful models for single-electrolyte systems to calculate a variety of thermodynamic properties (activity and osmotic coefficients, density, heat capacity, enthalpy of mixing, and compressibility) for solutions of mixed electrolytes.

A number of groups have published theoretically based extensions of nonelectrolyte equations of state or activity coefficient models (Haghtalab and Vera, 1988, 1991; Liu and Gren, 1991; Liu et al., 1989; Harvey and Prausnitz, 1989; Sander et al., 1986; Raatschen et al., 1987). These have been used to calculate activity coefficients of single or mixed electrolytes in aqueous solution or mixed solvents, with or without supercritical gases. In addition, some empirical studies have appeared that focus on very accurate estimation of several thermodynamic properties for one or two selected systems.

Advances in Electrolyte Solution Theory

Research intended to relate properties of electrolytes to the properties of their aqueous solutions has been conducted for more than 70 years. Modern theories can be grouped into four broad categories—those based on the potential energies obtained from solution of various forms of the Poisson–Boltzmann (PB) equation [Debye–Hückel (DH) theories]; those in which the Helmholtz free energy of a system is obtained from a series expansion in inverse temperature about a well-defined reference system (perturbation theories); those that solve the Ornstein–Zernicke equation using relationships between the direct- and pair-correlation function (integral-equation theories); and those that focus on the fluctuations of composition in an open system (Kirkwood–Buff [KB] theories). Because there often is overlap of ideas between the various approaches, this categorization is somewhat artificial. However, it provides a useful framework for classifying the different concepts and approaches that have been used.

From a physical perspective, the theoretical approaches fall into two general categories—continuum-solvent models and discrete-solvent models. Continuum-solvent models view the solvent as a dielectric medium without structure, whereas discrete-solvent models include the presence of solvent molecules explicitly. Continuum-solvent models were the earliest to be developed, due partially to the fact, as Pitzer (1977) points out, that there were no accurate theories that could relate the structure and interparticle interactions in water to its relevant bulk properties. In addition, the long-range effects of the Coulomb interactions between ions posed challenging mathematical problems that had to be solved before these theories could be used to calculate macroscopic thermodynamic properties. These mathematical problems were solved more readily in the continuum-solvent models.

Each of the four theoretical approaches listed earlier has been applied to both continuum and discrete-solvent models. The perturbation and KB techniques are less difficult to apply to the discrete-solvent models than are the DH and integral-theory approaches.

Debye – Hückel theory

In Debye–Hückel theories the ions are assumed to be charged species with a fixed diameter in a continuous dielectric medium. The original Debye–Hückel (DH) formulation assumed the ions were point charges and is valid only for a very limited range of concentrations (< 0.001 m). The extended Debye–Hückel (DHX) theory, which assigns a value to the ion diameter, applies over a somewhat wider range (< 0.1 m), and is considered to be the more useful form of this theory. The interionic potential function used in this approach is divided into two parts: $u_{ij}(r) = u^{SR}$ for $r < a$, and $u_{ij}(r) = z_i z_j e/\epsilon r$ for $r > a$, where r is the distance from a central ion i to another ion j. Here, a is the ion diameter; z_i is the number of charges on ion i including sign; e is the charge of the electron; ϵ is the solvent dielectric constant; and the superscript SR means short range. The Poisson–Boltzmann (PB) equation,

$$\nabla^2 \psi_i(r) = -(4\pi/\epsilon)\Sigma_i \rho_i z_i e \exp[-\beta z_i e \psi_i(r)], \qquad (1)$$

is used to calculate the electrostatic potential energy between the ions. In this equation ∇^2 is the Laplacian operator, $\psi_i(r)$ is the electrostatic potential of the ith ion as a function of the distance from it; ρ_i is the number of ions of type i per unit volume; and $\beta = 1/k_B T$, where k_B is Boltzmann's constant. The free energy of the system is related to the electrostatic potential in these theories by assuming that the electrostatic potential is equal to the potential of mean force (PMF). That is, the electrostatic potential energy of a given ion is the potential energy arising from the *average* force on an ion due to the presence of other ions. Once this connection is made, the radial distribution function, which is proportional to the probability of finding a particle in the spherical shell at distance r from another particle and which can be related to macroscopic thermodynamic properties of the system, becomes

$$g_{ij}(r) = \exp[-\beta z_i e \psi_i(r)]. \qquad (2)$$

Considerable effort has been expended to solve various linearized or otherwise simplified forms of Eq. 1 and to provide a more complete justification for the relationship implied by Eq. 2. Excellent concise discussions of these topics can be found in McQuarrie (1976) and Pitzer (1977, 1991). In addition, the nonlinear form of the equation has been studied in considerable detail (Sharp and Honig, 1990).

In its linearized form, the DH theory is internally consistent for all types of electrolytes, both symmetrically charged (1:1, 2:2, etc.) and unsymmetrically charged (1:2, 2:1, 3:1, 1:3, etc.), but the nonlinear form is not internally consistent for unsymmetrically charged electrolytes (McQuarrie, 1976; Outhwaite, 1987; Outhwaite et al., 1991); or for ions of different sizes. This is due to the assumed equivalence of the potential of mean force and the electrostatic potential energy. The potential of mean force is symmetrical by definition (McQuarrie, 1976), but the series expansion of the exponential in Eq. 1 yields (Martinez et al., 1990)

$$g_{ij}(r) \neq g_{ji}(r) \qquad (3)$$

for unsymmetrically charged electrolytes or electrolytes having different size ions. Outhwaite and coworkers (Outhwaite, 1987; Outhwaite et al., 1991) have derived PB equations that do not suffer from the lack of symmetry in the original theory. These equations can be solved numerically or linearized and then solved analytically and are thermodynamically consistent at low concentrations (< 0.1 M) (Martinez et al., 1990). They also have been used to calculate individual ion activity coefficients, which compare well with values generated by Monte Carlo (MC) simulations at low electrolyte concentrations (Molero et al., 1992). The extension to higher valence and unsymmetrically charged electrolytes does not extend the range of applicability of the DHX theory, but it does remove an inconsistency that had prevented it from being applied properly to these systems (Outhwaite, 1987).

While there is little doubt that Eq. 2 agrees well with MC results for symmetrical electrolytes in the DHX model at moderate molalities (Pitzer, 1977), there has been some uncertainty about the comparison between this model and MC at very low electrolyte concentrations, especially in the region around $r = a$. Sørensen (1990) studied this problem in depth and shows that DHX represents the best MC data for g_{ij} down to very low concentrations.

The PB equation and the DHX theory are the basis of a number of successful semiempirical equations for a variety of thermodynamic properties. The more popular of these are discussed by Zemaitis et al. (1986) and Rafal et al. (1994). Perhaps the most widely applicable of these equations are those developed by Pitzer and coworkers since 1973. Pitzer (1977, 1991) discusses the origin of these equations and their application in some detail. Today, the DH equations provide a limiting law valid at low concentrations and yield first-order structural information about aqueous strong electrolytes. The numerical solutions to the nonlinear form of the PB equation also are used to model ion interactions with large polyelectrolytes in biological systems (Honig and Nicholls, 1995).

Perturbation theories

Perturbation theories use a Taylor series expansion of the Helmholtz free energy in inverse temperature around some known reference state. The major advantage of this approach is that the terms in the series expansion are written as functions of a reference system whose properties are known. Other advantages of this method include its conceptual simplicity and the possibility of associating terms in the expansion with various ion–ion, ion–solvent, and solvent–solvent interactions. In fact, perturbation expansions of the Helmholtz free energy have formed the basis of successful engineering equations for various electrolyte systems, making this technique one of only two non-PB theoretical methods (the other being the MSA integral theory) that have been adapted to the calculation of properties for real systems.

Perturbation theories in which the repulsive part of the intermolecular potential is the reference system were first developed for simple liquids, and two different methods for formulating expansions have been applied successfully within this framework. They differ in the way the pair potential is divided between the repulsive and attractive parts. One, due to Barker–Henderson–Leonard (BHL) (Barker and Henderson, 1967a,b; Leonard et al., 1970), expands the Helmholtz free energy by writing the configuration integral as a double Taylor expansion in two perturbation parameters: a steepness parameter and well-depth parameter. The total potential energy is divided in such a way that the reference system energy is obtained when the two perturbation parameters are zero, while the entire system potential is recovered when they are equal to one.

As applied to model ionic systems, the BHL method results in a series of the form

$$\frac{A - A^o}{Nk_BT} = 2\pi\beta\rho \sum_{ij} x_i x_j \int_\sigma^\infty u_{ij}(r) g_{ij}^o(r) r^2\, dr - \pi\beta\rho \sum_{ij} x_i x_j \int_\sigma^\infty u_{ij}^2(r) g_{ij}^o(r) r^2\, dr + \cdots, \quad (4)$$

in which A^o is the free energy of the reference system; N, the total number of particles in the system; x_i, the mole fraction of i; $u_{ij}(r)$, the pair potential for species i and j; $g_{ij}^0(r)$, the pair radial distribution function for the reference system.

Only the intermolecular pair potential and the radial distribution function of the *reference* system need be known to use this expansion. When the Coulomb potential is substituted for $u_{ij}(r)$, the resulting series becomes a power series in κ, the inverse Debye length:

$$\frac{A - A^o}{Nk_BT} = -\frac{\kappa^3}{12\pi\rho} - \frac{\kappa^4}{16\pi\rho} \int_\sigma^\infty \left[g_{ij}^0(r) - 1 \right] dr + \cdots. \quad (5)$$

where

$$\kappa^2 = 4\pi\beta \Sigma_i x_i z_i^2 e^2\rho/\epsilon. \quad (6)$$

In order to apply the perturbation approach to systems of molecules interacting via coulomb potentials, two major technical problems had to be overcome—the divergence of some configuration integrals appearing in the expansion and the slow convergence of the resulting series. The divergence of the integrals can be eliminated by a resummation technique (Stell and Lebowitz, 1968; Henderson and Blum, 1980). The slow convergence of the series is interpreted as the result of the highly correlated (collective) behavior of large groups of particles that is expected in systems interacting through long-range interactions such as the Coulomb potential. Mazo and Mou (1991) have criticized the perturbation technique for its inherent inability to produce series that converge in a finite number of terms. However, the higher-order terms in the series can be approximated by special polynomials called Padé approximants (Stell and Lebowitz, 1968), yielding useful finite expressions.

Another technique that produces a rapidly converging series is to redistribute the limits of integration of the integrals in Eq. 4, and to write the series expansion in terms of a mathematical transformation of the inverse Debye length κ. This transformed variable called Γ, is related to κ by Eq. 7 (Henderson and Blum, 1980):

$$\kappa = 2\Gamma(1 + \Gamma\sigma), \quad (7)$$

in which σ is the ion diameter. It turns out that Γ is also the characteristic scaling parameter in the mean spherical approximation (MSA) integral-equation theory (see below).

Another approach to solving the convergence problem is to use the short-range terms as the perturbation on a *simplified* model of the long-range interactions. This offers the advantage of rapid convergence of the series, but limits the ion interactions to those in the reference system. Such an approach has been explored by Boyle and McQuarrie (1985), who recast both the BHL (Barker and Henderson, 1967a,b; Leonard et al., 1970) and Weeks-Chandler-Anderson (WCA) (Weeks et al., 1971a,b) perturbation theories for simple fluids in this form by expanding, not about the hard sphere fluid, but rather about the restricted primitive model for electrolytes. In this approach, reference system properties are obtained from a separate theory that had been developed earlier by the same authors. While the results of these studies are not compared to real electrolyte system data, the authors find good representation of osmotic coefficients derived from the hypernetted chain (HNC) integral equation.

This same technique has been used by Wu et al. (1995) to build a perturbation model for the Helmholtz free energy starting with a reference system made from a Mansoori hard-sphere term (Mansoori et al., 1971) and an MSA expression for the ion-ion interactions due to Blum and Høye (1977). The perturbation terms include second- and third-order expressions for the dipole-dipole and charge-dipole interactions, and second-order terms for the quadrupole interactions. Results for the contributions to the internal energy from the several interactions are compared with the MC data of Eggebrecht and Ozler (1990), and are shown to be of about the same order of magnitude as those of Henderson et al. (1985) and Jin and Donohue (1989a,b). The primary advantage of this approach is the use of a convergent charge-charge (MSA) expression.

A study of alternative plausible forms of perturbation expansions in the BHL framework is presented by Henderson et al. (1985). In this work, they model the aqueous electrolyte as a mixture of dipolar hard spheres and ions of equal diameter. The resulting equations are taken to third order and are written in terms of both the inverse Debye length κ and a dimensionless dipole strength y:

$$y = \frac{4\pi\mu^2\rho x_s}{9k_BT}, \tag{8}$$

where x_s denotes the mole fraction of water in the solution. The divergence of several of the integrals in the expansion is eliminated by resummation, and a convergent series is obtained through the use of Padé approximants. Average interparticle potentials required by the second- and third-order mixture terms in the series are given by angle-averaged expressions, and the reference system (hard-sphere) integrals are obtained from the Percus-Yevick (PY) integral theory.

This type of perturbation approach has been revisited in a series of articles by Eggebrecht et al. (Eggebrecht and Ozler, 1993; Eggebrecht and Ozler, 1990; Peters and Eggebrecht, 1993), in which the authors adapt many of the techniques used by Henderson et al. (1985) to obtain a convergent, finite expression for the Helmholtz free energy of aqueous strong electrolytes. They introduce three changes to bring the properties calculated from the series expansion into line with the results of their computer simulations for ion-dipole systems —the Carnahan and Starling (1969) hard-sphere expression replaces the simple hard-sphere result for the repulsive reference system integral, a resummation using an expansion of the solution dielectric constant in terms of the dipole strength y, rather than y itself is used, and the different order effects arising from the resummation are classified in a manner that produces the form of the Padé approximants that best fit the data. The resulting expansion fits their computer simulation calculation results for the free energy of ion-dipole mixtures well, and contains no adjustable parameters.

Some theories derived by perturbation methods have been checked against the thermodynamic properties of real electrolyte solutions after some modification. K. Y. Chan (1990) compared activity coefficients calculated from the Stell and Lebowitz (1968) perturbation expansion of the restricted primitive model with experimental data for several alkali halide solutions. The hard-sphere repulsion term is shown to be the dominant term in the expression for the activity coefficient at moderate ion concentrations, outweighing the ion-ion term. Cation diameters are treated as adjustable parameters in this study, while Pauling crystal diameters are used for the anion sizes. Debye-Hückel limiting behavior is obtained at low concentrations, and experimental data are represented quite well, but the cation diameters are significantly different from the observed crystal diameters.

The same author (Chan, 1991) extended and modified the Henderson et al. (1985) expressions to compare with experimental mean ionic activity coefficient and solution density data for several alkali chlorides. The modifications include an expansion of the solution dielectric constant in terms of the dipole strength, the use of a mixture hard-sphere term derived from the PY integral theory (see below), and the representation of the dipole-dipole, ion-ion, and ion-dipole interactions in the series as individual Padé approximants. Ion sizes are taken as the Pauli crystal diameters and are not adjusted to fit the data. The agreement with experimental data for both the solution density and mean ionic activity coefficient is poor, which is attributed to the inadequate representation of repulsive interactions by the model.

A much more successful extension of Henderson and Blum's (1980) temperature expansion for solutions of primitive electrolytes around a hard-sphere fluid was introduced by Jin and Donohue (1988a,b; Jin, 1991). The perturbation expansion is transformed into an equation of state in the PACT formalism (Vimalchand et al., 1985; Vimalchand, 1986) and contains terms that account for a wide variety of electrostatic interactions between solvent and ions. This model requires one adjustable parameter per ion, and works well in the prediction of mean ionic activity coefficients for solutions of single strong electrolytes, for mixtures of weak electrolytes, including those containing supercritical components, and fairly well for mixtures of strong electrolytes. The adjustable parameter is related to the ion radius and is highly correlated with the Stokes hydrated radii for the same ions. This approach has two main advantages—the potential for extension to mixed solvent systems and higher temperatures through the PACT formalism, and the ready applicability of the equations to mixed electrolyte systems. The agreement between calculated and observed mean ionic activity coefficients is excellent, rivalling Pitzer's equation in accuracy, with significantly fewer adjustable parameters.

Integral equation theories

Integral equation theories, which have been applied in recent years to aqueous electrolyte problems, include those that are derived from the solution of the Ornstein–Zernicke equation (Eq. 9),

$$h_{12} = c_{12} + \rho \int c_{13} h_{13}\, dr_3 \tag{9}$$

in which c_{ij} is called the direct correlation function between particles i and j; $h_{ij} = g_{ij} - 1$; and the integral is over all coordinates of particle 3. This equation relates the direct correlation function to the pair radial-distribution function, and serves as a defining equation for the direct correlation function. This equation can be solved in some cases by providing an additional relationship between g_{ij} and c_{ij} called a *closure*. Three such closures that have been used to derive models for aqueous electrolyte systems are described in this section: Percus–Yevick (PY), hypernetted chain (HNC), and mean spherical approximation (MSA). Of these, only the MSA equations have been applied extensively to real electrolyte systems, although one of the versions of the HNC approach (called RISM) has been used to calculate experimental activity coefficients of alkali halide solutions. Excellent discussions of the origin and early applications of the integral equation approach to aqueous electrolyte systems can be found in McQuarrie (1976) and Mazo and Mou (1991).

Mean Spherical Approximation. MSA is based on this closure of the OZ equation:

$$\begin{aligned} g_{ij} &= 0 & r_{ij} &< a_{ij} \\ c_{ij} &= -\frac{\beta z_i z_j e^2}{\epsilon r_{ij}} & r_{ij} &> a_{ij}, \end{aligned} \tag{10}$$

where a_{ij} is a characteristic hard-sphere diameter for the ions.

An analytic solution for this closure in the restricted primitive model (continuum solvent and equal-size ions) was derived in the early 1970s by Waisman and Lebowitz (1972). It was soon apparent that the equations for the activity coefficients in the dilute solution were closely analogous to those obtained from DHX, but with the inverse Debye length replaced by the MSA parameter Γ (Triolo et al., 1976). Expressions for the pair correlation function, osmotic coefficient, and mean ionic activity coefficients for ions with different sizes in the restricted model were presented by Blum and Høye (1977). Exact and approximate analytical solutions for an arbitrary mixture of ions in a solvent consisting of a hard sphere with a point dipole were obtained by Wei and Blum (1987a,b). Blum et al. (1992) obtained an analytical solution of the MSA for the case of equal-size ions and a different-size solvent. A useful discussion of the MSA theory in relation to the DH and other integral theories and as applied to primitive electrolyte models is given by Blum (1980).

As in the perturbation expansions discussed earlier, expressions for the MSA equations can be written conveniently in terms of scaling parameters whose number is equal to the number of independent interactions in the system. In the MSA solution for an ion–dipole mixture containing ions of equal sizes and hard dipoles of another size, Blum et al. (1992) use two parameters, a polarization parameter that is related to the dielectric constant of the solvent and the MSA screening parameter Γ:

$$\Gamma^2 = \frac{\beta \pi e^2 \rho}{\epsilon} \Sigma_i \frac{x_i z_i^2}{1 + \Gamma \sigma_i}. \tag{11}$$

They derive analytic (but complicated) expressions for the internal energy, Helmholtz free energy, and entropy of this model system in terms of these two parameters.

One of the problems of the MSA approach is the definition of the screening length parameter Γ for mixtures of ions and solvent molecules of unequal sizes (Eq. 11). This equation is itself an approximation, albeit a good one (Corti and Fernandez-Prini, 1986). The complete expression is much more complicated (Triolo et al., 1976). Unlike the expression for Γ used in the restricted primitive model (Eq. 7), Eq. 11 cannot be arranged to produce an explicit relationship between Γ and the particle size and mole fraction. In spite of the rapid convergence of this expression, its implicit nature has been seen as a potential impediment to its widespread use in engineering calculations. Several groups have tried to remedy this situation by proposing approximate explicit relationships between Γ and the Debye screening length κ (Copeman and Stein, 1986; Harvey et al., 1988; Blum, 1988; Sanchez-Castro and Blum, 1989).

Advantages of the MSA approach include the relative simplicity and accuracy of the resulting equations for various thermodynamic properties. This method has been applied successfully to the calculation of osmotic coefficients for 1:1 electrolytes with the help of concentration-dependent hard-sphere diameters (Triolo et al., 1977, 1978), and by adjusting one ion diameter that does not depend on concentration (Triolo et al., 1976). It also has been used successfully to calculate accurate vapor pressures for 26 aqueous alkali and alkaline earth halides out to 3- to 15-m concentration at temperatures in the range 298 K to 343 K with three adjustable parameters per electrolyte (Shiah and Tseng, 1994).

A more empirical but more widely applicable adaptation of the MSA approach has been developed by Planche and Renon (1981) and Ball et al. (1985). They have taken the MSA framework developed by Blum and Høye (1977) and extended it to calculate osmotic coefficients in concentrated (up to 6 molal) solutions of 1:1 and 2:1 electrolytes. The equations used are based on an approximation to the Helmholtz free-energy expression developed by Planche and Renon (1981), which incorporates a simplified, though still implicit equation for the MSA screening parameter. The interaction potential is a combination of long-range Coulomb attractions, short-range contact interactions, and hard-sphere repulsions:

$$\frac{u_{ij}(r)}{k_b T} = \frac{z_i z_j e^2}{4\pi \epsilon_0 \epsilon r k_b T} + \frac{W_{ij}}{2\pi r N_o} - \delta'(r - \sigma_{ij}), \quad \text{for } r = \sigma_{ij} \tag{12a}$$

$$u_{ij}(r) = \infty \quad \text{for } r > \sigma_{ij}, \quad \text{and for } r < \sigma_{ij}. \tag{12b}$$

The parameter δ' is the derivative of the Dirac delta function, and ϵ_0 is the electric permittivity in free space. The size parameter σ_{ij} is given by the arithmetic mean of the two component sizes, each of which is treated as an adjustable parameter. W_{ij} is a parameter that characterizes the contact interactions in the fluid, and is taken to be dependent on temperature in the liquid phase and compressibility in the gas phase, providing two adjustable empirical parameters for the model. The solution dielectric constant varies with concentration, and contains one fitting parameter. Thermodynamic properties are derived from an integration of the internal energy obtained from the energy equation (Eq. 13),

$$\frac{\beta E}{N}=\frac{3}{2}+2\pi\beta\rho\int_0^\infty u_{ij}g_{ij}r_{ij}^2\,dr_{ij}, \tag{13}$$

neglecting terms that are higher than first order in W_{ij}. The resulting equations contain six adjustable parameters. Pure component saturated phase-density data are calculated to within 1% up to reduced temperatures of 0.6, and agreement with experimental osmotic coefficient data for strong electrolytes is very good, 1.4% for 40 sets of 1:1 electrolytes tested, and 2.0% for 28 sets of 2:1 electrolytes.

This approach was extended by Fuerst and Renon (1993) who combined simplified forms of the long-range terms developed by Planche and Ball with a repulsive term and a short-range contribution similar to those in the modified Redlich–Kwong–Soave EOS of Schwartzentruber et al. (1989). They also used a short-range term specific to interactions involving ions, and obtained an expression for the excess Helmholtz free energy of aqueous electrolytes. The equations for the long-range ionic interactions are implicit in the MSA screening-length parameter, and retain the adjustment of the dielectric constant of the solution for composition featured in the earlier development work.

This model has some predictive capability and has been tested against osmotic coefficients for single strong electrolytes and mixed two-electrolyte systems in water. The agreement with the experimental data is very good—mean square deviations in the 2% to 6% range are typical up to 6 molal.

Successful application of an explicit MSA expression in a somewhat different context is given by Copeman and Stein (1987) in an equation of state called the Perturbed Hard-Sphere MSA (PMSA). This equation is intended for use in liquid–liquid systems containing an electrolyte. It is constructed from a two-term expression for the Helmholtz free energy containing the explicit form of the MSA screening parameter and a hard-sphere term derived from the compressibility equation, Eq. 14, with a PY closure (see below).

$$\beta\frac{\partial p}{\partial P}=1+\rho\int_0^\infty (g_{ij}-1)\,dr_{ij}. \tag{14}$$

The equation requires four types of adjustable parameters: one hard-sphere size parameter and three different types of binary-interaction parameters. The sizes for ions are given by the Pauling crystal diameters, while for the solvents, size parameters are empirically determined from vapor pressure and liquid-density data, and are assumed to vary linearly with temperature. All of the binary parameters appear in the attractive term. The authors report good fits (5–15% rms error) for mean ionic-activity coefficients of 13 selected single-salt systems to high molalities (many greater than 12 molal), and are able to calculate values of distribution coefficients for the organic solvent in methanol–water–NaBr, and aniline–water–NH_4Cl systems to within 6% rms error.

Because the equations for thermodynamic properties derived from it are relatively simple, the MSA also has been used to study the effects of ion association on the thermodynamics of electrolyte systems. It is well known that ions can associate and thereby form bonds that exhibit measurable spectroscopic properties, or they can form relatively weakly associated clusters, where the binding energy is on the order of $10k_BT$ or less. The importance of clusters to electrolyte-solution thermodynamics has been recognized for many years (Bjerrum, 1926; Robinson and Stokes, 1965), and results from two effects: the reduction of the effective number of particles in the system, and the nature of the intercluster interaction. Quantitative descriptions of cluster behavior based on statistical mechanics are relatively recent (Friedman and Larsen, 1979; Gillan, 1983; Tani and Henderson, 1983).

Strong electrolytes, especially those containing a multivalent, small-diameter cation, are thought to form weakly associated ion clusters in dilute solution and in the gas phase especially at low reduced temperatures and pressures (Gillan, 1983; Tani and Henderson, 1983). In the liquid phase, these clusters can redissociate at higher concentrations (Laría et al., 1990). Thus, the cluster diameter is not a completely unambiguous concept, and is often made a function of concentration, which has led to substantial discussion in the literature (Corti and Fernández-Prini, 1986; Pitzer and Schreiber, 1987; Laría et al., 1990).

The MSA approach also has been applied to the study of electrolyte-solution behavior near the solution critical point, due to its ability to model solvation effects in a simplified but useful way. Ebeling and Grigo (1980, 1982) combined the mass action law with the Waisman and Lebowitz (1972) MSA description of Coulomb interactions and the hard-sphere expression of Carnahan and Starling (1969) to obtain an equation of state for electrolytes in the restricted primitive model. A liquid-vapor coexistence region is obtained from this equation of state, and the extent of ion pairing is presented as a function of reduced density and temperature for a model 2-2 electrolyte. This approach was improved by Wei and Blum (1995), who discuss explicit solutions to the MSA for a wide range of thermodynamic functions derived from the Helmholtz free energy of solvation. For example, they point out that comparisons with experimental data for solvation Gibbs free energies, enthalpies and entropies for alkali halides in water at 298 K are much better than those obtained with Born equations (Mazo and Mou, 1991), due primarily to the ability to calculate solvent-structure effects. These equations also predict the correct qualitative behavior of the temperature derivative of the apparent molal constant-pressure heat capacity and volume, but predict the solvent critical point poorly. An improved prediction of solvent-critical parameters for both the restricted primitive model and a mixture of ions and hard spheres was obtained by Zhou and Stell (1995a,b) by correcting the MSA for ion association.

Improved Percus–Yevick Theories. The PY closure is given by Eq. 14:

$$c_{ij}=g_{ij}[1-\exp(\beta u_{ij})]. \tag{15}$$

This closure has been used successfully to calculate thermodynamic and structural properties of fluids dominated by short-range interactions; a number of electrolyte models include the hard-sphere fluid results obtained from this closure to account for repulsive interactions. However, until recently this approach has not fared well for ionic systems in comparisons with other methods. For example, it had been used to calculate approximate osmotic coefficients for 1:1 electrolytes in the restricted primitive model (Rasaiah and Friedman, 1968), but was found to be inferior to the hypernetted chain closure (see discussion below) for this purpose.

A new closure similar to the PY closure but intended for ionic liquids called the ionic Percus–Yevick (IPY) closure (Ichiye and Haymet, 1990) has been proposed that remedies this problem. Writing a closure to the OZ equation in its general form:

$$c_{ij} = \exp(-\beta u_{ij} + t_{ij} + B_{ij}) - 1 - t_{ij}, \tag{16}$$

in which $t_{ij} = h_{ij} - c_{ij}$, and B_{ij} is the bridge function (sums of integrals of products of $f_{ij} = \exp(-\beta u_{ij}) - 1$ for selected ij pairs), the PY closure can be regenerated by choosing

$$B_{ij}^{PY} = \ln\left(1 + t_{ij}^{PY}\right) - t_{ij}^{PY}. \tag{17}$$

The IPY closure is given by substituting Eq. 18 into Eq. 16:

$$B_{ij}^{IPY} = \ln(1 + \tau_{ij}) - \tau_{ij} \qquad \tau_{ij} > 0$$

and

$$B_{ij}^{IPY} = \ln[2 - (1 + \tau_{ij})\exp(-\tau_{ij})] \quad \tau_{ij} < 0, \tag{18}$$

in which $\tau_{ij} = t_{ij} - w_{ij} - \phi_{ij}$; w_{ij} is the DH potential of mean force; and ϕ_{ij} is the interionic potential function. This closure includes a soft-sphere repulsive potential and a long-range potential that is the same as that due to the long-range Coulomb force in the MSA direct-correlation function. The pair correlation functions calculated from this closure are closer to those obtained from the MC calculations than are those of HNC for dilute 2:2 electrolytes, due to the capability of IPY to account for ion association in dilute-associating electrolytes. More recent work (Vlachy et al., 1991) demonstrates the poor ability of the HNC closure to provide good approximations to density fluctuations at low ionic concentrations, and shows how to improve these calculations with the IPY closure. The authors disagree with other researchers that the lack of convergence of the HNC equation at low concentrations suggests the existence of a spinodal decomposition of the densities (and the consequent two liquid phases). They point to the IPY's ability to converge in this region as well as the accuracy compared to grand canonical MC results as an indication that the "spinodal decomposition" is an artifact of the approximations used in the HNC. A comparison with excess internal energies and osmotic coefficients generated by MD simulations and those calculated by the HNC and the IPY closure illustrates the usefulness of this approach (Duh and Haymet, 1992) for 2:2 electrolytes.

Advances in Hypernetted Chain Theories. The HNC closure has the form:

$$c_{ij} = g_{ij} - 1 - \ln(g_{ij}) - \beta u_{ij}. \tag{19}$$

Solutions to the OZ equation with this closure provide the most accurate structural information for primitive models of ionic systems when compared with MC results of all the integral theories (Blum, 1980; Friedman, 1981), but the solutions are not analytical, and require special numerical techniques and expertise (Corti et al., 1987). Nevertheless, the thermodynamic and structural properties obtained from other integral equation theories often are compared to those obtained from the HNC approximation. In addition, an analytical approximation to numerical HNC solutions has been suggested and used to calculate thermodynamic and structural properties of 2:2 electrolytes (Corti et al., 1987).

One significant advantage of the HNC approach is its ability to supply accurate structural and thermodynamic properties of primitive electrolytes at low densities and high temperatures, where the simpler MSA theories are not accurate (Blum, 1980; Høye et al., 1994). As a result, the HNC approximation has been used to investigate structural properties in dilute mixed electrolytes (Lim et al., 1986).

A system of equations that is closely analogous to the OZ equation with HNC closure and that has been used to study structural properties of ionic systems at infinite dilution is based on the interaction-site models of Rossky and coworkers (the so-called RISM equations) (Hirata et al., 1982, 1986; Pettitt and Rossky, 1986). The equations make use of atom–atom rather than molecule–molecule interaction potentials, and include the intramolecular as well as intermolecular site-to-site interactions. The equations constitute a set of coupled nonlinear integral equations that can be solved numerically. The RISM approach has been applied successfully to obtain infinite-dilution radial-distribution functions and potentials of mean force (PMF) for the ion–oxygen and ion–hydrogen interactions, and then to derive mean ionic activity and osmotic coefficients and hydration numbers for lithium and sodium chlorides and fluorides in water up to 1 m. The PMF show the effects of polarization saturation of the solvent around the ions and reveal much more structural detail than do primitive model calculations, with peaks in the radial distribution function present at one and two solvent diameters (Pettitt and Rossky, 1986). It would be very interesting to see if these equations could be converted to engineering forms that would exploit the improved structural accuracy to obtain more realistic thermodynamic expressions.

Fluctuation solution theories

Fluctuation solution theories (FST), also known as Kirkwood–Buff theories, relate concentration fluctuations in the statistical mechanical grand canonical ensemble to various observable partial derivatives of thermodynamic functions. These equations are written in terms of the canonical variables T, V^t, and species chemical potentials μ_i, which makes them difficult to apply to mixtures. However, a reformulation of the equations that eliminates this difficulty through the use of the OZ equation and that expresses the partial derivatives of the thermodynamic functions of interest in terms of the more intuitive variables T, V^t, and N^t was proposed by O'Connell (1971). In addition, simultaneous solution of the FST equations and the charge neutrality condition, which is required for electrolytes, produces indeterminate integral equations for the thermodynamic properties. These can be solved, however, through the use of Fourier transforms

(Kusalik and Patey, 1987). These methods have allowed fluctuation theory to be extended successfully to systems containing electrolytes (Perry et al., 1988; Newman, 1989; O'Connell, 1993, 1995).

The major advantage of this approach for electrolyte solutions is the simplicity of the relationships between dimensionless direct-correlation-function integrals (DCFI) and the FST derivatives such as:

$$\rho(\partial \ln \gamma_i/\partial \rho_j)_{T,\rho k \neq i} = 1 - C_{ij}. \tag{20}$$

The DCFI is defined as

$$C_{ij} = \rho \int c_{ij}(\boldsymbol{r}_{12}; T, \rho)\, d\boldsymbol{r}_{12}. \tag{21}$$

A disadvantage to this approach is that the thermodynamic properties that are easily calculated from the equations are not the properties that are useful for engineering applications. Rather, as in Eq. 20, they are products of properties and derivatives of properties. This makes comparisons with experimental data cumbersome, since considerable experimental data for the properties of interest must be available in order to obtain accurate values for the derivatives. However, the FST relations are very powerful correlating tools (if a suitable model for the DCFI is available) when strongly nonideal phase behavior is evident and when density effects are important, such as in highly compressed liquids, near-critical systems, and aqueous electrolytes at high temperatures and pressures (O'Connell, 1995). An excellent and concise discussion of the application of FST to electrolytes has been published by O'Connell (1993).

One model for the DCFI for aqueous NaCl and NaBr solutions due to Perry et al. (1988) produces excellent agreement with experimental data for water and salt activity coefficients and osmotic coefficients at temperatures from 25°C to 85°C, pressures from 1 bar to 1,000 bar, and salt concentrations from 5 wt. % to 25 wt. %. Their approach is to separate the DCFI into several parts: a Carnahan–Starling (1969) repulsive term corrected for the proper infinite-dilution values, and electrostatic terms that force the equations to produce DH limits at low electrolyte concentrations. In these equations both the ion and the water hard-sphere diameters are regarded as temperature-dependent fitting parameters.

Engineering Equations

Our review of recent developments in engineering models for thermodynamic properties of electrolyte solutions is divided into three parts: (1) local composition and hydration models; (2) empirical and semiempirical equations of state for strong electrolytes; and (3) equations for mixed solvents, mixed electrolytes, and mixtures of supercritical gases and electrolytes.

Local composition models

Local-composition concepts for aqueous electrolyte systems were developed first by Chen et al., (1980; Chen and Evans, 1986) and are discussed in detail in Zemaitis (1986). The central idea in this approach is that the interactions between the ions and the solvent can be represented locally and then generalized to the entire solution. While this approach was excellent for reproducing experimental activity coefficients for dilute and moderately concentrated (up to 3 m) solutions of strong electrolytes, it provided relatively poor fits for concentrated single electrolytes and for mixed electrolyte systems. Recent improvements to this approach (Haghtalab and Vera, 1988, 1991; Liu and Gren, 1991) have succeeded in improving the fit to experimental data.

Haghtalab and Vera (1988, 1991) replace Chen's empirical expression for the nonrandom factors with an expression of the Wilson type (Prausnitz et al., 1986). They attribute the effect of the local composition to the difference between the local *average* interaction energy and the bulk (random) average interaction energy. Chen et al. (1980), on the other hand, uses the composition around the individual components as the basis for the local composition energies.

The resulting equations are used to calculate activity coefficients for a large number of 1:1 systems, some out to 15 to 20 molal, and all at 25°C. The fits are quite good with two binary parameters.

Liu et al. (1989) include a modified Debye–Hückel term to account for the effect of long-range electrostatic forces on the local composition, and a short-range term that differs significantly from Chen's short-range term. This expression contains both an adjustable ionic radius and an interaction energy parameter.

The local composition expressions are different from Chen's in three important ways:

1. There is no local electroneutrality condition.
2. The local composition is defined by an expression from quasi-chemical lattice theory, instead of an empirical nonrandomness factor.
3. The local composition is applied to the excess enthalpy, not directly to the Gibbs free energy (GFE). The excess GFE is obtained by integration assuming $G^E = 0$ at $1/T = 0$.

The result is a model that requires five parameters: two ion radii and three interaction parameters. The radii and the ion–water interaction parameters are ion-specific, and do not change from electrolyte to electrolyte. The ion–ion interaction parameter is specific to the electrolyte, however.

Liu and Gren (1991) compare mean ionic-activity coefficients for both the Liu–Harvey–Prausnitz (LHP) model and that of Haghtalab and Vera (1988). They show that the LHP model is significantly better for the 55 systems of 1:1 and 1:2 electrolytes tested.

Hydration models

Hydration models are similar to local composition approaches in that they seek to compensate for the effect of ion–solvent association of the energetics of the whole system. They differ from local composition models in that they often contain specific expressions for the hydration energy and the hydration number (number of solvent molecules associated with the ions). Such models have been available for many years (Robinson and Stokes, 1965). A look at the basic thermodynamics of hydration theory is provided by Wolery and Jackson (1990), and a thorough discussion of hydration effects can be found in Conway (1981) and Marcus (1985).

Recent studies in this area have combined hydration and ion-association concepts (Heyrovska, 1989; Schoenert, 1990a,b; 1991a,b; 1993; 1994a,b) or have sought to improve a simple Pitzer expression by the addition of a hydration energy term (Ghosh and Patwardhan, 1990).

Heyrovska (1989) discusses an alternative view of electrolyte-solution modeling that considers the normal state of the electrolyte in aqueous solution to be hydrated and partially associated. She has derived expressions for the mean ion-activity coefficient, osmotic coefficient, solution density, conductivity, and diffusion coefficient using concepts from early work of Arrhenius and van't Hoff. Heyrovska's approach is to interpret the experimental data directly rather than to try to fit deviations from some ideal limiting behavior. The resulting expressions contain two parameters: the maximum degree of association (α_m) and the hydration number (n_h), both of which are derived from the vapor-pressure lowering by the electrolyte. An intuitively appealing result of this study is the increasing value of the degree of association with higher hydration numbers and higher ionic charge. Ultimately, however, this approach substitutes the search for the temperature and concentration dependence of the activity of the electrolyte with a similar search for the concentration and temperature dependence of the degree of association. Certainly, the implication that hydration and association are responsible for a large proportion of electrolyte behavior is reasonable, and may account for the success of simple extensions of the DH equation over some concentration ranges (Helgeson, 1981; Patwardhan and Kumar, 1986a,b) in representing a variety of thermodynamic properties.

Ghosh and Patwardhan (1990) present a simple equation for the activity and osmotic coefficients of 150 sets of single electrolyte data which takes into account the hydration energy of the individual ions. Their theory develops the excess Gibbs free energy as a combination of a long-range ion–ion term very similar to Pitzer's (1973) and a hydration term consisting of the product of the energy of hydration and a function of the total moles of water involved in ion hydration per kilogram of solution (denoted Q). The hydration contribution is developed in detail for a reference-electrolyte system, in this case LiCl, and then applied to other systems by assuming that Q is the same for all of the systems studied. The resultant scaling requires two parameters, and excellent agreement is obtained with experimental data, some of which extends to very high ionic strengths. The functional form of Q for the reference system is developed from the difference between the experimental data for the reference system and the forms of the long-range interaction appropriate to the experimental data. The mathematical concept of using the difference between a Debye–Hückel long-range term and the experimental data to define a scaling relationship is very similar to that employed by Helgeson (1981).

Schoenert (1990a,b, 1991a,b, 1993, 1994a,b) has developed expressions for the excess Gibbs free energy and excess enthalpy of hydrated and associated ions using a modified version of the hydration model of Robinson and Stokes (1965) along with three major additional assumptions. First, waters of hydration are assumed to be ligands in a stepwise binding process in which the successive binding steps are treated as independent and identical. This assumption results in a simple relationship between the equilibrium constants of successive steps and the equilibrium constant of the first hydration, which itself is related to the difference in Gibbs free energy between the free and bound solvent water molecules. Second, the hydrated ions interact according to the Debye–Hückel potential. Schoenert identifies the average hydration number with the same difference in GFE used to calculate the equilibrium constant for the first binding step. Finally, it is assumed that the hydrated ions and free water form an ideal DH mixture on a mole-fraction basis.

The equations that result contain two fitting parameters—the hydration number at infinite dilution and a binding energy parameter related to the distance of closest approach. Note that estimates of the two fitting parameters for any one set of activity coefficient and osmotic coefficient data are negatively correlated, which implies that higher hydration energies are compensated by smaller contact distances.

The equations can be used to estimate activity and osmotic coefficients for dilute (up to 1 m) single 1:1 electrolytes and mixtures of 1:1 electrolytes with an average error smaller than experimental error. Estimates of the infinite dilution hydration numbers for these electrolytes can be expressed as sums of ion-specific hydration numbers whose values are independent of the electrolyte.

The apparent relative partial molal enthalpy of 1:1 electrolytes also can be estimated quite accurately with this model (to 1 molal), when appropriate expressions for the standard Gibbs free energy and enthalpy are used (Schoenert, 1993a). The model has been modified to permit the calculation of thermodynamic properties over a range of temperatures (Schoenert, 1993b) by assuming a temperature dependence for the binding energy parameter and by assuming that the standard enthapy of hydration of potassium and chloride ions is the same. While activity coefficient data for binary and ternary systems is represented well, ternary enthalpy data are not calculated accurately by this approach.

Aqueous mixed electrolytes

Our discussion of recent progress in representing properties of mixed electrolyte systems is limited to two areas: a generalization of mixing rules based on a reduced activity coefficient, which can be used (in principle) to extend any model for single electrolyte solutions and some work which includes useful discussions of the choice of appropriate standard states for these systems. A brief description of other more empirical recent studies is presented in Table 1.

Extension of models that are appropriate for single electrolyte solutions to multiple salt systems often requires the introduction of extra mixing rules or additional parameters to obtain good fits of the experimental data [see, for example, Zemaitis et al. (1986)]. Patwardhan and Kumar (1986a,b, 1992, 1993) have shown that a new set of mixing rules based on the assumption that single-electrolyte systems of equal ionic strength mix ideally reproduce experimental activity coefficients, vapor pressures, solution densities, heat capacities, enthalpies of mixing, and compressibilities for many two-salt systems exceptionally well using only the property equations for the single electrolytes. The authors have defined a reduced-activity coefficient similar to that used by Meissner and Tester (1972) given by

$$\log \Gamma^* = \log \gamma^* / \Sigma_i x_i^* z_i^2, \qquad (20)$$

Table 1. Recent Empirical and Semiempirical Models for Mixed Electrolytes

Reference	Systems Tested	No. of Parameters	Remarks
Clegg and Pitzer (1990)	Na^+, K^+, NO_3^-, Cl^-, H^+ binaries	4 for single electrolytes, 3 binary, 3 ternary per ion	Good fit for solubilities at 25°C. Complex Margules-like expressions (Prausnitz, 1986). Based on Simonson and Pitzer (1990).
Sako et al. (1987)	Mg^{2+}, Ca^{2+}, Na^+, NO_3^-, OH^-, CO_3^{2-}, Br^-, binaries and ternaries	12 per pair of ions plus 1 ternary	Good fit for VLE data for 20 systems tested up to 160°C and 30 m. Complex Margules-like expressions (Prausnitz, 1986).
Lu and Maurer (1993)	Alkali metal and alkaline earth halides, nitrates, sulfates, hydroxides, singles, binaries, and ternaries	3 per ion, 2 per pair	Excellent fit for mean ionic activity and osmotic coefficients at 25°C and 3 to 26 m. Combines DH and UNIQUAC equations.

in which x_i^* is the water-free mole fraction of the ith electrolyte and γ^* is given by

$$\log \gamma^* = \Sigma_j \nu_j m_j \log \gamma_{\pm,j} / \Sigma_j \nu_j m_j. \tag{21}$$

Plots of Γ^* vs. ionic strength for mixtures lie between the curves for the individual electrolytes in the mixture, permitting the derivation of a mixing rule relating mixture properties to those of the single electrolytes. From such a relationship for the activity coefficient, mixing rules for a number of important thermodynamic properties can be derived. The agreement between values calculated by this method and experimental data for a number of aqueous two-salt systems' activity coefficients, vapor pressure, density, expansibility, and compressibility is very impressive.

Pabalan and Pitzer (1990) present a summary of the use of two different models to represent electrolyte system properties over a very wide range of temperatures and pressures and discuss the appropriate choice of standard states for various types of systems. The authors have found that the use of the dilute solution standard state

$$\ln(\gamma_+^{\nu+} \gamma_-^{\nu-}) \to 0 \quad \text{as} \quad x_{\text{elect}} \to 0 \tag{22}$$

presents difficulties for very concentrated solutions (approaching the fused salts) and high temperatures (more than 300°C). To avoid these problems, they recommend the use of a convention similar to the Lewis–Randall convention for nonelectrolytes in which

$$\ln(\gamma_+^{\nu+} \gamma_-^{\nu-}) \to 0 \quad \text{as} \quad x_{\text{elect}} \to 1. \tag{23}$$

The best results for high temperatures are obtained with the use of this standard state and a Margules-type expansion of the DH model (Simonson and Pitzer, 1986). In this expression, the empirical parameters are treated as temperature and pressure dependent, resulting in complex expressions, but generally very good fits.

Electrolytes in mixed solvents with and without supercritical gases

A number of papers have appeared recently dealing with the thermodynamics of systems containing dissolved supercritical gases and electrolytes both in water and in mixed organic solvent/water systems. With the exception of the studies by Harvey and Prausnitz (1989), and Zerres and Prausnitz (1994), most of this work consists of coupling together empirical modifications of nonelectrolyte equations with electrolyte terms. These are summarized in Table 2. The studies by Prausnitz's group have a more theoretical basis and are discussed separately.

Harvey and Prausnitz (1989) present a theory designed to portray the behavior of aqueous electrolyte systems containing a supercritical component at high temperatures and pressures, using three contributions to the residual Helmholtz free energy: a nonelectrolyte term to account for all interactions except those involving ions, a term that arises from charging the ions, and a charge–charge interaction term.

The intermolecular forces between nonelectrolytes are modeled with a simple Lennard–Jones (LJ) expression using the Barker and Henderson (1967a,b; Henderson and Barker, 1970) form of perturbation theory. The mixing rule for adjusting the attractive energy parameter for the gas–water interaction contains one adjustable parameter that is linear in the reciprocal absolute temperature. The energy, binary interaction, and characteristic size parameters are obtained from binary vapor–liquid equilibrium data.

Charge–charge interactions are given by the explicit MSA expression developed by Harvey et al. (1988) and contain a single effective ion diameter.

The equations require an ion–gas interaction parameter chosen to reproduce the Setchenow constant at room temperature. With this parameter, liquid-phase mole fractions of natural gas in brine can be reproduced to within a few percent. Agreement is not as good, however, for CO_2 in NaCl solutions, probably due, in the authors' opinion, to the manner in which the adjustable parameters have been introduced into the LJ term. The theory is a physical one and does not account explicitly for species formed in equilibria between CO_2 and other components.

An effective model for salt/water/organic solvent systems combined with a thorough examination of the basic thermodynamics and choice of standard states for chemical potentials and activity coefficients in these systems appears in a recent work by Zerres and Prausnitz (1994). Their model divides the excess Gibbs free energy into three contributions—long range, effects, chemical effects, and physical effects. The equations require a minimum of eight parameters per ternary system. The long-range contribution to the excess Gibbs free energy is obtained from a DH expression for the activity coefficient in terms of the osmotic pressure.

Table 2. Recent Empirical and Semiempirical Models for Electrolytes in Mixed Solvents with and without Supercritical Gases

Reference	Systems Tested	No. of Parameters	Remarks
Aasberg-Petersen et al. (1991)	Alkali and alkaline earth halide-CO_2	3 binary per solvent plus 2 binary per electrolyte	Acceptable fits for gas solubilities—generally better than Harvey and Prausnitz (1989). Combines Adachi et al. (1983) EOS with DH.
Simon et al. (1991)	Alkali and alkaline earth halides with NH_3, ethanol, N_2	3 for each nonelectrolyte 1 binary per pair	Good fits for mean ionic activity coefficients. Combines Soave-Redlich-Kwong EOS (Prausnitz et al., 1986) with charging cycle.
Sander et al. (1986)	Alkali and alkaline earth halides with alcohols and water	$(N_{\text{ion}} + N_{\text{solvent}})(N_{\text{ion}} + N_{\text{solvent}} - 1) + N_{\text{salt}} N_{\text{solvent}}$	Good fits for VLE of mixed-solvent systems with salts. Excellent discussion of thermodynamic basis and standard states.
Macedo et al. (1990)	Alkali and alkaline earth halides with alcohols and water	$(N_{\text{ion}} + N_{\text{solvent}})(N_{\text{ion}} + N_{\text{solvent}} - 1) + N_{\text{salt}} N_{\text{solvent}}$	Revision and extension of Sander et al. (1986) using theory from Cardoso and O'Connell (1987).
Raatschen et al. (1987)	LiBr/water/methanol	3 binaries per electrolyte–solvent pair, 5 for each solvent	Good fits for phase compositions of water/methanol binary, osmotic coefficients for LiBr/water, acceptable VLE and ternary compositions.

The chemical contribution (ion–solvent) accounts for hydration equilibria, and an empirical parameter serves the function of an equilibrium constant for the solvation of the ion by the first solvent molecule. In an extension of the statistical arguments proposed by Schoenert (1986), the authors correct for further hydration using the multinomial coefficient, and assume a uniform hydration number of 5 for monovalent cations, 12 for bivalent cations, and 0 for anions.

The physical contribution accounts for water–cosolvent interactions. It is a van-Laar-type expression (Prausnitz et al., 1986), using volume fractions and three parameters for each of the cosolvent–water interactions.

The model works well to predict the vapor pressure and mean ionic-activity coefficients of a number of salt/water/alcohol systems, as well as the concentrations of NaCl in both phases of n-butanol and water. The model is intended for application over a wide range of temperatures, and to very high weight fractions of solids.

While the authors recognize that corrections to these equations are required due to the change in canonical variables from T, V, μ and n (MacMillan–Mayer) to T, P, and n (Lewis–Randall) as suggested by Friedman (1972), Pailthorpe et al. (1984), Cardoso and O'Connell (1987), and Macedo et al. (1990), the need for these corrections is avoided by replacing the partial molar volume of the salt in these equations with the pure-solvent molar volumes.

High temperatures and pressures

In addition to the theoretically based MSA work that has been discussed earlier, the formulation of semiempirical models that can be used to calculate phase behavior of electrolytes and water at high temperatures has been actively pursued since the pioneering studies by Pitzer (1986), and Pitzer and Tanger (1989).

There is not a large amount of experimental data for electrolytes in water at high temperatures. The NaCl–water system has been studied in the most detail, and critically evaluated compilations of phase equilibrium and density data exist for temperatures up to 773 K, while experimental densities and solubilities have been measured at temperatures up to 1173 K (Anderko and Pitzer, 1993a). The KCl–water and KCl–NaCl–water mixtures are much less well defined in this region (Anderko and Pitzer, 1993b), and some vapor pressures and solubilities are available for a number of other salt-water systems (Economou et al., 1995).

Models that are useful at high temperatures include the effects of association of the electrolyte due to the decreasing dielectric constant of water as the temperature increases, and must accommodate the very rapid change in slope of the phase compositions with temperature and pressure as the salt fraction approaches zero (Harvey and Levelt Sengers, 1989). Recent studies employ an equation of state of model this behavior.

The earlier works of Pitzer (1986) and Pitzer and Tanger (1989) used a simple extension of an accurate equation of state for water to obtain the equation of state for the electrolyte water system. Levelt Sengers and Gallagher (1990) applied a modified principle of corresponding states to the prediction of near-critical, critical, and supercritical properties of NaCl–water mixtures. Their approach maps the configurational Helmholtz free energy of the mixture onto that of the reference fluid (water) through the use of shape factors that are functions of the reference-fluid reduced volume and temperature. Using four adjustable parameters, they find reasonably good quantitative agreement properties for dilute NaCl–water in the critical region. This work is completely empirical, with no consideration of the possible mitigating effect of the ion charges on the critical property fluctuations of the mixture.

Equations of state having a somewhat stronger theoretical basis are presented by Anderko and Pitzer (1993a,b) and Economou et al. (1995). Anderko and Pitzer (1993a) assume complete association of the ions into pairs, putting aside the equilibria between clusters of different sizes for the sake of simplicity. They construct an equation for the residual Helmholtz free energy of the system that couples a Mansoori et al. (1971) repulsive term and a modified Wertheim (1971)

MSA dipole–dipole term with a perturbation expression containing a truncated virial expansion. While the experimental dipole moment for water was used in these expressions, all of the remaining parameters are empirical. These expressions are shown to be reasonably accurate for vapor-phase compositions, vapor and liquid densities, compressed liquid volumes, solubilities of NaCl, and apparent molar enthalpies. This approach is extended to KCl-H_2O and the KCl-NaCl-H_2O in a later article (Anderko and Pitzer, 1993b).

The associated-perturbed-anisotropic-chain theory (APACT) (Ikonomou and Donohue, 1986), which takes into account dipole and quadrupole interactions and chemical equilibria, has been used to model aqueous alkali halides at temperatures between 200 and 500°C (Economou et al., 1995). Vapor–liquid and solid–liquid–vapor equilibrium vapor pressures are reproduced to within a few percent for ten different systems with these equations. One advantage of this approach is the use of molecular properties such as the crystal ionic radius, molecular polarizability, and enthalpy and entropy of hydration to derive parameters for the equation. Another arises from the fact that APACT equation of state provides excellent estimates of pure water properties up to the water critical point (374°C) as a limiting case of the electrolyte properties.

Summary

Over the last 10 years there has been substantial progress in modeling strong electrolyte thermodynamics. The breadth of applications that have been tackled is large, and the number and types of systems that can be successfully described by semitheoretical equations has grown dramatically over this period. Substantial advances in several theoretical methods will provide the foundation for future applied work. Some areas that seem fruitful for further investigation are summarized here.

- There is a need for a comparative study of various published equations for properties of engineering interest to give prospective users a means of choosing the best one for a particular application. It would be most helpful if a series of standard applications could be developed for testing these equations over a wide range of temperatures and concentrations. If published reports of new equations claiming wide applicability were to provide the quality of the fits to a set of standard applications, much time and effort would be saved by nonspecialists attempting to use the equations for engineering calculations. We would like to see a cessation of what has become the practice of promoting an equation's strengths without a discussion of its limitations.
- A very important question is the extent to which unifying concepts for mixtures of electrolytes such as those proposed by Patwardhan and Kumar can be applied to a set of such standard applications. If these techniques are widely applicable, then much complexity can be avoided in calculation of mixed-electrolyte properties.
- It would be interesting to know whether the improved solution structural information offered by the IPY and RISM integral-equation theories can be converted to engineering equations that produce better estimates of bulk macroscopic properties than do other approaches.
- With few exceptions, most of the engineering models reviewed here focus on the activity coefficients of the components of systems containing electrolytes, even though a number of authors work with models for the Helmholtz or Gibbs free energies. Scant attention has been given to deriving expressions to accurately represent other properties such as enthalpies, heat capacities, and densities from these models even though these properties are often required for engineering design calculations. Hopefully, some of the theoretical models reviewed here will be extended to permit accurate estimation of these properties with a unified set of equations.

Faced with the large number of studies in the recent literature that claim to have a successful approach to strong electrolyte thermodynamics, it is not easy for the nonspecialist to choose among them for estimating given properties. In addition, the equations often are complex, and using them correctly often requires the expert advice and assistance of their formulators. Thus, there is a need for a critical comparison of the performance of published equations for electrolyte thermodynamic properties with each other and with available experimental data. While there is a large selection of equations for mean ionic-activity coefficients, there are fewer choices for accurate representation of other properties that are important for engineering design. Aside from the extensive empirical and semitheoretical results obtained from the Pitzer equations and the Helgeson formulations, there are as yet no comprehensive theories for the Gibbs or Helmholtz free energies of aqueous strong electrolyte systems that can provide accurate analytical expressions for real electrolyte properties such as density, enthalpies of mixing, and entropies of mixing using the same parameter set over a wide range of compositions and temperatures. This is a difficult but potentially rewarding problem to solve, and one that hopefully will be the focus of research in the coming years.

Notation

d = distance of closest approach
E = total system internal energy
h_{ij} = indirect correlation function
m_i = molality (gmoles/kg solvent) of the ith electrolyte
P = system pressure
t_{ij} = difference between the indirect and direct correlation functions
$\gamma_i, \gamma_{\pm}$ = activity coefficient of the ith component; mean ionic activity coefficient
γ_+, γ_- = activity coefficients for cations and anions
λ = polarization parameter
μ = dipole moment
ν_i = stoichiometric coefficient of the ith ion

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