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Thermodynamics of Concentrated Electrolyte Solutions

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ABSTRACT

A new equation is derived for the activity coefficient of an electrolyte in a liquid solvent (such as water) as a function of electrolyte concentration. This equation contains contributions from long-range electrostatic forces and from short-range attractive forces; it holds from high dilution to the solubility limit. The new equation is based upon extended Debye-Hückel theory for long-range effects and upon the local-composition concept for short-range effects. For a single-electrolyte solution, the new equation contains only one adjustable energy parameter and three other parameters that are ion-specific, not electrolyte-specific. Therefore, extension to multicomponent electrolyte solutions follows without additional assumptions. Ion-specific parameters are reported for H^+, K^+, Li^+, Br^- and Cl^- ions. Calculated and experimental activity coefficients are in excellent agreement for aqueous solutions of HBr, HCl, KBr, KCl, LiBr and LiCl.

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1. INTRODUCTION

Research leading to an improved absorption heat pump requires a suitable working fluid, which often is a multicomponent, concentrated electrolyte system(1). Recent advances in process-simulation technology can now provide computer-aided heat-pump simulation and optimization. But simulation requires suitable models for representing thermodynamic and transport properties of working fluids. For maximum applicability, these models should

1. predict the properties of mixed-electrolyte systems using only experimental information for single-electrolyte systems.
2. cover the entire concentration range, i.e., infinite dilution to the solubility limits.
3. cover the temperature range 25 ~ 180°C.
4. require only reasonable amounts of computer time.

In the last few decades, much progress has been achieved in representing the thermodynamic properties of electrolyte systems for engineering application. Pitzer(2), Maurer(3) and Renon(4,5) give useful reviews.

There are two fundamentally different methods for calculating vapor-liquid equilibria and related thermodynamic properties(6,7). One is based on activity coefficients for the liquid phase and fugacity coefficients for the vapor phase, and the other is based on fugacity coefficients for both phases obtained from an equation of state. In spite of significant advantages provided by an equation of state, for electrolyte systems, activity-coefficient models have attracted more attention because it is difficult to establish an equation of state for such systems(7).

In developing activity-coefficient models for electrolyte systems, the most popular and successful practice is to combine the electrostatic theory of Debye-Hückel with modifications of well-known methods for non-electrolyte systems(3). We also follow this practice here but with some important modifications beyond those used by others.

In 1973, Pitzer(8,9) proposed a successful model based on combination of an extended Debye-Hückel form (which accounts for long-range forces) with a virial expansion (which accounts for short-range forces). Later, Cruz and Renon(10), Chen et al.(11) and Christensen et al.(12) replaced the virial expansion with various flexible local-composition models.

In the Cruz-and-Renon model, the excess Gibbs energy is assumed to be the sum of a local-composition term(NRTL-equation), a Debye-Hückel term and a Born contribution arising from the composition dependence of dielectric constant of the mixture.

In the Chen model, the excess Gibbs energy is the sum of a NRTL-term and a term of the Debye-Hückel form. In Chen's model, two assumptions are made: "local electroneutrality" and "like-ion repulsion".

Although both the Cruz-Renon model and the Chen model use the NRTL equation to account for short-range forces, there is an important difference between them. Cruz and Renon suggest that ionic species are completely solvated by solvent molecules. Chen et al. note that Cruz and Renon's suggestion becomes unrealistic when applied to high concentrations, since the number of solvent molecules is insufficient to solvate ions completely. In the Chen model, all ions are, effectively, completely surrounded by solvent molecules in the very dilute range but they are only partially surrounded by solvent molecules in the high concentration range. In this work, we adopt the viewpoint of Chen.

Christensen's model is similar to those of Cruz-Renon and Chen. However, Christensen use a UNIQUAC equation instead of a NRTL equation for short-range forces.

Of these models, only that by Chen is claimed to be applicable to the entire concentration range(13). But, when compared with experiment, Chen's model is not successful for a common working fluid, aqueous LiBr, whose activity coefficient rises to 486 at 20 molality. (If converted to a mole fraction basis, the activity coefficient rises to 836).

In this work we develop a new activity-coefficient model similar to that of Chen but based on a more reasonable combination of Debye-Hückel theory and the local-composition concept. Promising applicability of the new model is shown by application to the activity coefficients of some concentrated electrolyte systems. We expect that this model may be useful also for correlating excess enthalpies, heat capacities, solubilities and viscosities of electrolyte systems. All of these properties are important for absorption-heat-pump simulations.

2. INTERMOLECULAR FORCES

Thermodynamic properties of a mixture depend on intermolecular and interionic forces amongst all species of the mixture(6,11). Electrolyte systems contain both uncharged molecular species and charged ionic species; pertinent intermolecular forces are

1. electrostatic forces between ions.
2. electrostatic forces between permanent dipoles, quadrupoles and higher multipoles.
3. induction forces between a permanent dipole (or multipole) and an induced dipole.
4. nonelectrostatic forces of attraction (dispersion forces) and repulsion among molecules and ions.
5. specific (chemical) forces leading to association and complex formation,

i.e., to the formation of "chemical" bonds such as hydrogen bonds.

Electrostatic forces between ions are inversely proportional to the square of the separation distance. All other forces depend on higher powers of the reciprocal distance. Therefore, the forces between ions have a much greater interaction range than all others. The thermodynamic properties of electrolyte systems can be considered as the sum of two parts, one related to long-range forces between ions and the other to short-range forces between all species. It is the long-range nature of the electrostatic forces between ions that has no counterpart in nonelectrolyte systems and that is primarily responsible for the difficulty in constructing a model for concentrated electrolyte systems.

While many authors have considered the thermodynamic properties of electrolyte solutions to be the sum of two contributions, one long-range and the other short-range, most of these authors have considered these contributions independently, ignoring how one contribution affects the other. In this work, we give attention to the effects of short-range forces on the long-range contribution, and vice versa.

3. THERMODYNAMIC BACKGROUND

We seek an expression for the excess Gibbs energy, G. For simplicity, we consider here aqueous single-electrolyte systems. Multi-solvent and multi-electrolyte systems can be handled in the same way.

Throughout this paper, the concentration scale is the true mole fraction defined as

$$x_k = \frac{n_k}{n_T} \tag{3-1}$$

where x_k is the true mole fraction of species k; n_i is the number of moles of species i per unit volume; n_T is the total mole number of all species per unit volume, i.e., the true mole density of the electrolyte solution:

$$n_T=\sum_i n_i.$$

Here $\sum_i$ sums all ionic and molecular species.

Equation (3-1) is based on the assumption that all electrolytes are completely dissociated.

Consider a molecule CA which dissociates into cation C and anion A:

$$CA \rightleftharpoons C^+ + A^-$$

More generally, the molecule has the formula $C_{\omega_c}A_{\omega_a}$ where ω_c and ω_a are stoichiometric coefficients. The dissociation equation now is rewritten

$$C_{\omega_c}A_{\omega_a} \rightleftharpoons \omega_c C^{\nu_c} + \omega_a A^{\nu_a}$$

where ν_c and ν_a are the algebraic valences of cations and anions, respectively.

In this case

$$\nu_c=\omega_a \text{ and } \nu_a=-\omega_c$$

Dissociation is described by the equation of equilibrium

$$\mu_{ca}=\omega_c\mu_c+\omega_a\mu_a \tag{3-2}$$

We relate the chemical potential of an ion to its true mole fraction through activity coefficient γ

$$\mu_c=\mu_c^o+RT\ln\gamma_c x_c \tag{3-3a}$$
$$\mu_a=\mu_a^o+RT\ln\gamma_a x_a \tag{3-3b}$$

where γ_c and γ_a are the individual ionic activity coefficients of cations and anions, respectively; Superscript o denotes the standard state which, for a given system, depends only on temperature;

To obtain an expression for μ_{ca}, we write

$$\mu_{ca}^o=\omega_c\mu_c^o+\omega_a\mu_a^o \tag{3-4}$$

and we define

$$\gamma_{\pm,ca}=\left(\gamma_c^{\omega_c}\gamma_a^{\omega_a}\right)^{\frac{1}{\omega_c+\omega_a}} \tag{3-5}$$

and

$$x_{\pm,ca}=\left(x_c^{\omega_c}x_a^{\omega_a}\right)^{\frac{1}{\omega_c+\omega_a}} \tag{3-6}$$

We then obtain

$$\mu_{ca}=\mu_{ca}^{o}+(\omega_c+\omega_a)RT\ln\gamma_{\pm,ca}x_{\pm,ca} \tag{3-7a}$$

For a real, aqueous, single-electrolyte system, the Gibbs energy, $G_{(real)}$, is given by

$$\begin{aligned}G_{(real)}&=n_w\mu_w+n_c\mu_c+n_a\mu_a\\&=n_w\mu_w+n_{ca}\mu_{ca}\end{aligned} \tag{3-8}$$

where n_{ca} is the number of moles of electrolyte ca in the liquid phase.

The chemical potential of water is related to its true mole fraction through its activity coefficient by

$$\mu_w=\mu_w^{o}+RTln\gamma_w x_w \tag{3-3c}$$

For an ideal, aqueous, single-electrolyte system, the Gibbs energy, $G_{(ideal)}$, is given by

$$\begin{aligned}G_{(ideal)}&=n_w\mu_w^{i}+n_c\mu_c^{i}+n_a\mu_a^{i}\\&=n_w\mu_w^{i}+n_{ca}\mu_{ca}^{i}\end{aligned} \tag{3-9}$$

where

$$\mu_w^{i}=\mu_w^{o}+RTlnx_w \tag{3-10a}$$

$$\mu_c^{i}=\mu_c^{o}+RTlnx_c \tag{3-10b}$$

$$\mu_a^{i}=\mu_a^{o}+RTlnx_a \tag{3-10c}$$

and

$$\mu_{ca}^{i}=\mu_{ca}^{o}+(\omega_c+\omega_a)RTlnx_{\pm,ca} \tag{3-7b}$$

Comparing Equation (3-9) with Equation (3-8), we see that $G_{(ideal)}$ is equivalent to $G_{(real)}$ when all activity coefficients in Equation (3-8) become unity.

For water, we choose the pure liquid as the reference state where $\mu_w=\mu_w^{o}$. It follows from Eq. (3-3c) that

$$\gamma_w\rightarrow 1 \text{ as } x_w\rightarrow 1. \tag{3-11a}$$

However, for the reference state of an electrolyte, the pure solute is not a practical choice since it is frequently a solid or liquid with properties very different from those of aqueous solutions. We here follow common convention(21,6) where the reference state for the cation is a hypothetical ideal dilute solution of unit concentration ($x_c = 1$); we follow a similar convention for the anion. This convention normalizes activity coefficients γ_c, γ_a and $\gamma_{\pm,ca}$ such that they all approach unity as the mole fraction of electrolyte goes to zero:

$$\gamma_c \to 1;\ \gamma_a \to 1 \text{ and } \gamma_{\pm,ca} \to 1 \quad as \quad x_c \to 0;\ x_a \to 0 \text{ and } x_{\pm,ca} \to 0. \tag{3-11b}$$

As shown by Equations (3-11a) and (3-11b), the activity coefficients of water and solute are not normalized in the same way. Equations (3-11a) and (3-11b) give the unsymmetric convention. We here use an asterisk * to denote the normalization given in Equation (3-11b). With this notation, Equation (3-11b) becomes

$$\gamma_c^* \to 1;\ \gamma_a^* \to 1 \text{ and } \gamma_{\pm,ca}^* \to 1 \quad as \quad x_c \to 0;\ x_a \to 0 \text{ and } x_{\pm,ca} \to 0. \tag{3-11c}$$

The unsymmetric excess Gibbs energy, G^{E*}, is defined by

$$\begin{aligned} G^{E*} &= G^*_{(real)} - G^*_{(ideal)} \\ &= n_w RT\ln\gamma_w + n_c RT\ln\gamma_c^* + n_a RT\ln\gamma_a^* \\ &= n_w RT\ln\gamma_w + n_{ca} RT\ln\gamma_{\pm,ca}^* \end{aligned} \tag{3-12}$$

4. NEW MODEL

Many classical models, (e.g. Margules, Van Laar, Redlich-Kister, Scatchard-Hildebrand, Flory-Huggins), have been used for nonelectrolyte systems whose molecules experience only short-range forces. For such systems, better results are often obtained upon using the local-composition concept of Wilson(14) which has led to the development of several flexible local-composition models which are so popular today(15,6). For engineering purposes, such models as Wilson(14), NRTL(16) and UNIQUAC(17) often provide a significant improvement over previous models. But if a local-composition model is used to account for the contribution from long-range electrostatic forces, we expect that the long-range electrostatic forces influence the local composition. In contrast to previous models, our model takes into account the effect of lange-range electrostatic forces on local composition.

Let us arbitrarily choose an ion in the solution which, for simplicity, contains only a single electrolyte. The local composition, in the immediate vicinity of that central ion, is determined by the overall composition of the mixture, by the sizes of the species in the solution and by the energies of interaction between the central ion and all species (ions or uncharged molecules) in the first coordination shell. As shown in Figure 1, at the center, there is a cation C_i, surrounded by near neighbors that form a first coordination shell. The distance between the center of cation C_i and the outer boundary of the first coordination shell is given by r_c^T. The ions, such as C_j and A_j, are located outside the first coordination shell where cation C_i is the center, i.e., their distances from cation C_i are larger than r_c^T. The interaction energy between central cation C_i and anion A_i in the first coordination shell is given by ε_{ca}, which includes contributions from both dispersion and electrostatic forces.

Since ε_{ca} includes an electrostatic contribution, the unsymmetric excess Gibbs energy, $G^{E\circ}$, is given by the sum of two contributions

$$G^{E\circ} = G^{E\circ}_{LR} + G^{E\circ}_{SR} \qquad (4\text{-}1)$$

where $G^{E\circ}_{LR}$ is the contribution from long-range electrostatic interaction forces between each central ion and all ions <u>outside</u> the first coordination shell; $G^{E\circ}_{SR}$ is the contribution from both the short-range interaction forces of all kinds and the long-range electrostatic forces between each central ion and all ions <u>inside</u> the first coordination shell.

For $G^{E\circ}_{LR}$, we use a modified Debye-Hückel expression. For $G^{E\circ}_{SR}$, we use a local-composition expression similar to those proposed by Renon and Prausnitz(19) and Chen(11). Both expressions are based on the assumption of complete dissociation of electrolytes. Through the usual thermodynamic relations, we obtain

$$\ln\gamma^{*}_{\pm,ca}=\ln\gamma^{*}_{ca,LR}+\ln\gamma^{*}_{ca,SR} \tag{4-2}$$

where $\gamma^{*}_{\pm,ca}$ is the unsymmetric mean activity coefficient of the electrolyte, (ca), on a true mole fraction scale.

Subscript (LR) denotes only the contribution from the long-range electrostatic forces which exist between each central ion and all ions <u>outside</u> the first coordination shell. Subscript (SR) denotes the contribution from both the short-range interaction forces of all kinds and the long-range electrostatic forces which exist between each central ion and all ions <u>inside</u> the first coordination shell.

For simplicity, the following expression is developed for a single aqueous electrolyte. The expression can be extended to mixed-electrolyte systems.

5. LONG-RANGE INTERACTION CONTRIBUTION

The long-range interaction contribution is represented by a modified Debye-Hückel expression. The derivation of the modified Debye-Hückel expression is based on the Poisson equation of electrostatic theory, the Boltzmann distribution law and the local-composition concept.

Although the individual ionic activity coefficient cannot be measured separately, if complete dissociation of electrolytes is assumed, it is theoretically preferable to derive first the Debye-Hückel expression for the individual ionic activity coefficient, and then to obtain the mean activity coefficient by Equation (3-5)

We consider first the non-ideal behavior of the cation. We consider two contributions: first, the long-range contribution from electrostatic interaction with ions <u>outside</u> the first coordination shell; second, the contribution from electrostatic interaction with ions <u>inside</u> the first coordination shell plus the contribution from interaction with all species in the first coordination shell due to all kinds of short-range forces. Then we may write the chemical potential of one mole of cations, μ_c, as

$$\mu_c = \mu_c^\circ + RT\ln x_c + RT\ln\gamma^\circ_{c,LR} + RT\ln\gamma^\circ_{c,SR} \tag{5-1}$$

where x_c is the true mole fraction of cations.

From Appendix A, we obtain

$$\ln\gamma^\circ_{c,LR} = \frac{\nu_c e^2}{2Dr_c kT}\left[\left(\nu_c + \frac{\nu_a x_a z_c}{x_a + x_w G_{wc,ac}}\right)\frac{\exp[\kappa(r_c^r - r_c)]}{(1+\kappa r_c^r)} - \nu_c\right] \tag{5-2}$$

where $\gamma^\circ_{c,LR}$ is the individual activity coefficient of the cation arising from the long-range contribution; k is the Boltzmann constant; e is the protonic charge; ν_c and ν_a are the algebraic valences of the cation and the anion, respectively; D is the dielectric constant; κ is defined by (A-10) or (A-16); z_c is the coordination number of the cation; r_c is the radius of the cation; r_c^r is the outer radius of the first coordination shell where the cation is at the center; x_a and x_w are the true mole fractions of anions and water, respectively; $G_{wc,ac}$ is defined by (B-7).

Similarly for anions, we obtain

$$\ln\gamma^\circ_{a,LR} = \frac{\nu_a e^2}{2Dr_a kT}\left[\left(\nu_a + \frac{\nu_c x_c z_a}{x_c + x_w G_{wa,ca}}\right)\frac{\exp[\kappa(r_a^r - r_a)]}{(1+\kappa r_a^r)} - \nu_a\right] \tag{5-3}$$

From (3-5), (5-2) and (5-3), we have

$$\begin{aligned}\ln\gamma^\circ_{ca,LR} = \frac{e^2}{2DkT(\omega_c+\omega_a)}\Bigg\{&\frac{\omega_c\nu_c}{r_c}\left[\left(\nu_c + \frac{\nu_a x_a z_c}{x_a + x_w G_{wc,ac}}\right)\frac{\exp[\kappa(r_c^r - r_c)]}{(1+\kappa r_c^r)} - \nu_c\right]\\ &+ \frac{\omega_a\nu_a}{r_a}\left[\left(\nu_a + \frac{\nu_c x_c z_a}{x_c + x_w G_{wa,ca}}\right)\frac{\exp[\kappa(r_a^r - r_a)]}{(1+\kappa r_a^r)} - \nu_a\right]\Bigg\}\end{aligned} \tag{5-4}$$

Equation (5-4) is a modified Debye-Hückel Equation which differs significantly from the original Debye-Hückel equation. Equation (5-4) gives only the contribution due to electrostatic forces between each central ion and the ions outside its first coordination shell, while the original equation gives the contribution due to electrostatic forces between each central ion and all other ions in the solution.

6. SHORT-RANGE INTERACTION CONTRIBUTION

The local-composition concept is used to account for the contribution due to short-range interaction forces of all kinds, including the electrostatic interaction forces between each central ion and all ions inside the first coordination shell.

Our local-composition expression is superficially similar to that of Chen et al.(11), because it is also based on the NRTL model. But the present work differs from Chen's work in three ways:

First, our local-composition expression is based on a previous derivation of the three-parameter Wilson equation(19). We apply the local-composition concept to excess enthalpy, H^E_{SR}, (instead of excess Gibbs energy, G^E_{SR}); we then integrate the Gibbs-Helmholtz equation

$$\frac{\partial(G^E_{SR}/T)}{\partial(1/T)}=H^E_{SR} \qquad (6\text{-}1)$$

to obtain G^E_{SR}. We use the boundary condition $G^E_{SR}=0$ when $1/T=0$.

Second, we abandon the second assumption of the Chen model wherein the distribution of cations and anions around a central solvent molecule is such that the net local ionic charge is zero. While this assumption may hold for the concentration range near the fused pure electrolyte, we see no reason to assume "local electroneutrality" for the dilute and intermediate concentration range.

Third, as suggested by Guggenheim's quasi-chemical lattice theory, we use a classical definition of the local composition; in our work the definition of the local composition is

$$\frac{x_{ij}}{x_{kj}}=\frac{x_i\exp(-\varepsilon_{ij}/kT)}{x_k\exp(-\varepsilon_{kj}/kT)} \tag{6-2}$$

where x_{ij} is the local mole fraction of i in the first coordination shell surrounding species j; x_i is the true mole fraction of i; ε_{ij} is the characteristic interaction energy between one nearest-neighbor i-j pair[‡].

Equation (6-2) is similar to that used by Chen except that Chen introduces into the argument of the exponential an arbitrary nonrandomness factor.

Both the Debye-Hückel theory and the local-composition concept use the Boltzmann distribution law. Since the Debye-Hückel theory is based on a McMillan-Mayer system while local-composition models are based on a Lewis-Randall system, there is some inconsistency using (4-2) for multicomponent electrolyte systems; fortunately, this inconsistency is usually not significant (22).

From Appendix B, we obtain

$$\ln\gamma^{*}_{c,SR}=-\frac{1}{2}\Bigg[z_w\left[\frac{x_w G_{cw,ww}}{x_w+x_c G_{cw,ww}+x_a G_{aw,ww}}-x_w-G_{cw,ww}+1\right]$$
$$+z_c\ln\frac{(x_a+x_w G_{wc,ac})}{(x_a+x_w)G_{wc,ac}}+\frac{z_a x_a}{x_c+x_w G_{wa,ca}}-\frac{z_a x_a}{x_c+x_w}\Bigg] \tag{6-3}$$

$$\ln\gamma^{*}_{a,SR}=-\frac{1}{2}\Bigg[z_w\left[\frac{x_w G_{aw,ww}}{x_w+x_c G_{cw,ww}+x_a G_{aw,ww}}-x_w-G_{aw,ww}+1\right]$$
$$+\frac{z_c x_c}{x_a+x_w G_{wc,ac}}-\frac{z_c x_c}{x_a+x_w}+z_a\ln\frac{(x_c+x_w G_{wa,ca})}{(x_c+x_w)G_{wa,ca}}\Bigg] \tag{6-4}$$

From (4-1), we obtain

$$\ln\gamma^{*}_{ca,SR}=-\frac{1}{2(\omega_c+\omega_a)}\Bigg\{z_w\left[\frac{x_w(\omega_c G_{cw,ww}+\omega_a G_{aw,ww})}{x_w+x_c G_{cw,ww}+x_a G_{aw,ww}}+(1-x_w)(\omega_c+\omega_a)-\omega_c G_{cw,ww}-\omega_a G_{aw,ww}\right]$$
$$+z_c\left[\omega_c\ln\frac{(x_a+x_w G_{wc,ac})}{(x_a+x_w)G_{wc,ac}}+\frac{\omega_a x_c}{x_a+x_w G_{wc,ac}}-\frac{\omega_a x_c}{x_a+x_w}\right]$$

[‡] Energy parameter g_{ij} is the product of ε_{ij} and Avogadro's number.

$$+ z_a \left[\omega_a \ln \frac{(x_c + x_w G_{wa,ca})}{(x_c + x_w) G_{wa,ca}} + \frac{\omega_c x_a}{x_c + x_w G_{wa,ca}} - \frac{\omega_c x_a}{x_c + x_w} \right] \Bigg\} \tag{6-5}$$

Finally, from (4-2), we have the complete expression for the mean ionic activity coefficient of electrolytes in the single aqueous electrolyte systems. Further, with the Gibbs-Duhem equation, we can obtain the activity coefficient or osmotic coefficient of water in the solution(6).

The sum of Equations (5-4) and (6-5) gives $\ln\gamma^{\circ}_{\pm,ca}$. To use these equations we require the following parameters:

1. radii r_c and r_a for the cation and anion, respectively. Anionic radius r_a comes from crystal data. In this work, we consider only two anions; for Cl^- the radius is 0.181 and for Br^- it is 0.196 nanometers. From fitting of binary data, we obtain five sets of cationic radii, shown in Table 3. Each set corresponds to a series of fixed coordination numbers, as shown in Table 1.
2. energy parameters characterizing the interaction between two species. For example, g_{cw} refers to the interaction between cation (C) and water (W). However, these parameters always appear as differences according to

$$G_{ji,ki} = \exp[-(g_{ji} - g_{ki})/RT]$$

   where subscript (i) denotes the species at the center surrounded by a coordination shell containing species j and/or k (If i stands for water, then species i may also be in the first coordination shell.).
3. the dielectric constant as discussed in Section 7.

To illustrate, consider an aqueous solution of LiCl, we need radii for Li^+ and Cl^-. The dielectric constant is calculated from readily available data as shown in Section 7. Further, we require g_{LiCl}, g_{Liw} and g_{Clw}. The first of these must be obtained from experimental data for LiCl solution but the others could be obtained from experimental data for other salts where lithium is the cation or where chloride is the anion.

7. THE DIELECTRIC CONSTANT

Almost 40 years ago, Hasted et al.(23) observed that for aqueous systems, dielectric constant D is a linear fuction of molarity to 1~2 m, depending on the electrolyte. However, such linearity cannot be used here because we attempt to cover a much large range of concentration.

A highly concentrated aqueous electrolyte may be considered as a molten electrolyte containing a small amount of water. In this condition, the structure of water does not resemble its normal structure; therefore, in a concentrated electrolyte solution, water does not have its usual high dielectric constant but a significantly smaller value, probably not much different from that of the ions(24).

Although there has been extensive experimental study of the concentration-dependence of the dielectric constant of electrolyte solutions, few attempts have been made to take it into account when modeling deviations from ideality for electrolyte solutions. Triolo et al.(25) tried to improve the primitive model within the framework of the Mean Spherical Approximation(MSA), using either a two-parameter, density-dependent dielectric constant or an adjustable (but not density-dependent) dielectric constant up to 2 m. But the calculated values of the dielectric constant are not realistic, since they are greater than that for pure water. In the concentration range to 6 m, an extension of Giese's equation(26) was used by Ball et al.(27) for the MSA model of electrolyte solutions(48). In the Cruz-and-Renon model(10), Cruz and Renon chose Pottel's expression(49) to estimate the variation of the dielectric constant with concentration.

Based on the assumption that ions are dielectric holes, we assume that at high electrolyte concentrations, water becomes steam-like. Therefore, we use here an expression for dielectric constant D based on an equation of Uematsu and Franck(28) that represents the experimental dielectric constant of gaseous and liquid water as a function of temperature and density. In this work, we change density dependence to apparent-mole-fraction dependence. When calculating the apparent mole fraction, an electrolyte is considered as a molecular component; in other words, for calculating the dielectric constant, the electrolyte is considered to be undissociated.

The calculated dielectric constant is a function of temperature and electrolyte concentration but it is the same for all electrolytes

$$\begin{aligned} D = 1 &+ (B_1/T_r)(1-x_{ca}) + (B_2/T_r + B_3 + B_4 T_r)(1-x_{ca})^2 \\ &+ (B_5/T_r + B_6 T_r + B_7 T_r^2)(1-x_{ca})^3 + (B_8/T_r^2 + B_9/T_r + B_{10})(1-x_{ca})^4 \qquad (7\text{-}1) \end{aligned}$$

where x_{ca} is the apparent mole fraction of electrolyte ca; T_r = T / 298.15 with T in Kelvins; Table 6 gives constants B as reported by Uematsu and Franck(28).

Figure 6 shows the dielectric constant as a function of electrolyte concentration at 25 and 50°C.

8. IONIC RADII

In the Debye-Hückel expressions, it is usually assumed that all the ions have the same size. This assumption is reasonable only when electrolyte solutions are dilute, where the distances between ions are so large that the influence of ionic size can be neglected. For moderate and high concentrations, however, the effect of ionic size is significant. There is a large amount of evidence indicating that, for models covering a high concentration range, results are sensitive to the values chosen for ionic radii(35,36).

It has been customary to use crystal ionic radii instead of ionic radii in solution. Several sets of crystal ionic radii are available; the best known and most widely used are those due to Goldschmidt(37), Pauling(38,39), Gourary and Adrian(40) and Waddington(41). In the present model, for anions, we choose Goldschmidt's radii as recommended by the Handbook of Chemistry and

Physics(59th ed.). For cations, we choose radii fit from activity-coefficient data. However, to obtain radii from activity-coefficient data, it is necessary to assign values to the coordination numbers.

Table 3 shows some results of the fit. We can see that, for potassium ion, the values of r_K are not realistic. One reason, we speculate, is that there is some distortion in the simultaneous fit because of the presence of hydrogen ion, a bare proton. Based on complete dissociation, the fit is done as though the hydrogen ion existed by itself as the other cations do. But a bare proton probably does not exist as an entity in aqueous solution. If we fit KBr or KCl separately, we can obtain much more realistic result for r_K.

9. DATA CORRELATION AND DISCUSSION

To obtain binary parameters and cationic radii, we use experimental mean ionic activity coefficient data for six aqueous single-electrolyte systems (HBr, HCl, KBr, KCl, LiBr, LiCl) (42). We use these data to obtain 11 energy parameters and 3 cationic radii; they are obtained by least-square analysis on deviations between calculated and experimental quantities(42):

$$S_\gamma=\sum_i(ln\,\gamma^{\circ,calc}_{\pm,ca,i}-\ln\gamma^{\circ,exp}_{\pm,ca,i})^2 \tag{8-1}$$

The choice of these six aqueous electrolytes follows from several considerations. First, the activity coefficient curves for LiBr and LiCl are different in type from those for KBr and KCl as shown in Figures 4 and 5. Second, there is a large difference in the maximum molalities for these two types of aqueous electrolytes. Therefore, fitting data for these four systems to the present model provides a stringent test. Third, HBr and HCl were chosen to investigate the behavior of H^+ in the present model.

The classical Debye-Hückel expression uses the mass density of water instead of that for the solution. In the high-concentration range, this approximation may cause large deviations. To investigate this effect, we initially chose

Clarke's density model(29) with parameters determined from three sources of experimental density data(30,31,32) to calculate the densities of these six aqueous electrolytes. We found, however, that the true mole density, n_T, does not vary significantly among the six electrolytes or with electrolyte concentrations. If we fix the value of the true mole density as 60 moles per liter, the deviations are within ±5 % for concentration to 20 m. It is therefore not surprising that the fit of activity coefficients using the fixed molar density value is almost as good as that using measured values of the true mole density(see case[5] in Table 1.).

For the system $H_2O-LiBr$ at 25 C, Figure 3 shows the modified Debye-Hückel contribution and the local-composition contribution to the mean ionic activity coefficient. The modified Debye-Hückel contribution is always important, especially at high electrolyte concentrations.

To obtain energy parameters from experimantal activity-coefficient data, it is necessary to specify coordination numbers.

Table 1 gives five sets of coordination numbers for water and the following ions: hydrogen, potassium, lithium, bromide and chloride. The last column in Table 1 gives the standard deviation in fitting experimental activity coefficients $\gamma^*_{\pm,ca}$ to the new equation. For all five sets, the goodness-of-fit is about the same but this conclusion may change when we consider large ions.

The size constant λ is used to determine the radius of the coordination shell shown in Figure 1: $r_c^T = r_c + \lambda r_a$. (Similarly, $r_a^T = r_a + \lambda r_c$.)

Table 2 gives energy parameters g_{ji}/R at 25 C upon setting $g_{ww}=0$.

Table 4 gives a comparison between the present model and that of Chen. Unfortunately, the comparison is not as strict as we might wish because results from the Chen model are obtained from his paper(11), which uses data sources different from ours. Nevertheless, for most systems studied here, the present model gives a much better representation of the experimental data.

9.1. CHARACTERISTICS OF PARAMETERS

Whereas the parameters in the Chen model are salt-specific, those in the present model are ion-specific. There is only one adjustable parameter, g_{ca}, for each electrolyte; other parameters like g_{cw}, g_{aw}, r_c and r_a, are common to all electrolyte systems containing the same cation and/or the same anion (For r_a, we use literature values.).

In the present model, all interaction-energy parameters appear as differences, i.e., $g_{ji}-g_{ki}$, therefore, we can arbitrarily fix one interaction energy parameter; we choose $g_{ww}=0$. All other interaction-energy parameters are relative values.

In view of the semi-empirical nature of our model, we cannot assign definite physical significance to the parameters. We may, however, notice some regularities. The present model suggests that the magnitudes of the attraction energies between various pairs are in the order: $g_{aw}<g_{ca}<g_{cw}$ (Table 2). Also, from Table 2, we see some reasonable attraction-energy sequences: $g_{KBr}<g_{LiBr}$; $g_{KCl}<g_{LiCl}$ and $g_{Kw}<g_{Liw}$.

Table 5 indicates that for accurate results, the interaction energy parameters must be considered to be temperature-dependent if the present model is used over a wide temperature range.

9.2. ION ASSOCIATION

Electrolytes may dissociate partially or completely in solution. With rising temperature, the dielectric constant decreases and association increases. With increasing electrolyte concentration, association rises due to both a mass-action effect and lower dielectric constant.

Molecular-thermodynamic models for electrolyte systems can be divided into two limiting categories: one is based on the assumption of complete dissociation of electrolytes and the other on chemical equilibria to describe the extent of ion association(2). Although the chemical-association models may be regarded as more realistic and flexible(33), they have serious disadvantages(34), especially upon extension to mixed-electrolyte systems.

The complete-ionization assumption has been used consistently in previous work based on the local-composition concept. It has therefore become customary to ascribe inadequacies of local-composition correlations to ion association. However, we believe that the local-composition models can generally represent the contribution due to the short-range forces whether there is some ion association or not.

For nonelectrolyte systems, the UNIFAC model(44), based on the local-composition concept and the group contribution method, often provides a good approximation. If a molecule can be divided into groups, we can similarly divide the ion pair into ionic "groups" and then use the "groups" in our expression representing the contribution from the short-range forces. Therefore, ion association mainly affects the expression representing the contribution from the long-range forces. In the present model, although assuming complete dissociation, the modified Debye-Hückel expression accounts indirectly for ion association, as indicated in Appendix A.

In effect, the present model makes a detour around the problem of ion association. The Cruz-and-Renon model(10) uses a known dissociation constant and six parameters to describe the vapor-liquid equilibrium of HCl-H_2O system at 25 C for acid composition from infinite dilution to 18 m. By contrast, as shown in Figure 2, the present model uses only one specific adjustable parameter in addition to two common parameters and one effective cationic radius to represent the mean ionic activity coefficient of the HCl-H_2O system at 25°C for concentrations from infinite dilution to 16 m. For this system, the specific parameter is g_{HCl} and the two common parameters are g_{Hw} and g_{Clw}.

We cannot claim that the present model has overcome the problem of ion association. But it is probably more flexible than previous strong-electrolyte models for describing electrolyte systems with significant association.

10. CONCLUSION

A new molecular-thermodynamic model has been proposed for aqueous electrolyte solutions. It goes beyond previous models because it is based on a theoretically improved combination of Debye-Hückel theory and the local-composition concept and because it is designed to represent the properties of a wide variety of electrolyte systems over the entire range of electrolyte concentration. As shown here, preliminary application of the new model indicates encouraging results.

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NOTATION

B = constants in Equation (7-1)

D = dielectric constant

G = Gibbs energy

$G_{ji,ki}$ = quantity defined by (B-7)

H = enthalpy

k = Boltzmann constant

N_o = Avogadro's number

R = gas constant

T = temperature(K)

e = protonic charge

g_{ji} = interaction energy parameter of j-i pairs

m = molality

n_i = moles of species i per unit volume (except in Appendix A where n_i denotes the number of species i per unit volume)

r = the distance from the ion which is the origin of the coordinates

$r_c(r_a)$ = radius of cations (or anions) (Å)

r^r = outer radius of the first coordination shell

x_i = true mole fraction of species i based on all species (molecular and ionic)

x_{ji} = local mole fraction of species j where species i is the center

z = coordination number

Greek Letters

γ = activity coefficient on true mole-fraction scale

ε_{ji} = interaction energy for one j-i pair

κ = quantity defined by (A-10)

λ = size constant in (A-4)

μ_k = chemical potential of species k

ν_c, ν_a = algebraic valences of cations and anions respectively

ρ_c = charge density at distance r from the cation which is the origin of the coordinates

σ = standard deviation

ψ = the electric potential

ω_c, ω_a = numbers of cations and anions, respectively, produced by the complete dissociation of one electrolyte molecule

Superscripts

E = excess properties

i = ideal solution

o = standard state

* = unsymmetric convention

∞ = infinite dilution

calc. = calculated value

exp. = experimental value

LR = long-range

SR = short-range

Subscripts

a = anion

c = cation

ca = electrolyte ca

i, j, k = any species (except in Appendix A where j denotes only ionic species)

m = abbreviation for one mole

w = water

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APPENDIX A

Derivation of the Modified Debye-Hückel Expression

Based on the Poisson equation of electrostatic theory, the Boltzmann distribution law and the local-composition concept, the modified Debye-Hückel expression is to account for the long-range electrostatic-interaction contribution to the excess Gibbs energy.

For a charge distribution possessing spherical symmetry about the origin, Poisson's equation has the form

$$\frac{1}{r^2}\frac{d}{dr}\left[r^2\frac{d\psi}{dr}\right]=-\frac{4\pi}{D}\rho \tag{A-1}$$

where ψ is the potential at a point where the charge density is ρ; D is the dielectric constant of the medium in which the charges are immersed; r is the distance from the origin.

If a particular ion is chosen as the origin of coordinates and no external forces act on the ions, the time-average distribution of charges about that ion has spherical symmetry. Equation (A-1) is therefore taken to apply to the time-average values of the potential, ψ, and the charge density, ρ, at distance r from the ion.

Since the electrolyte solution as a whole is electrically neutral, we have

$$\sum_j n_j \nu_j e = 0 \tag{A-2}$$

where n_j denotes the number of ions j per unit volume, (i.e., the bulk concentration); ν_j is the valence of ion j; e is the protonic charge (equal and opposite in sign to that of an electron) and the summation is over all ionic species in the solution.

We select a cation as the center of the coordinates. According to the local composition concept, we consider a cell which consists of the central cation and its first coordination shell. The condition of electrical neutrality tells us that the net charge in the solution outside this central cation cell must be equal but of opposite sign to the net charge inside the cell. Thus (A-2) may be replaced by

$$\int_{r_c^T}^{\infty} 4\pi r^2 \rho_c \, dr + \nu_c e + N_{ac} \nu_a e = 0 \qquad \text{(A-3)}$$

where r_c^T is the outer radius of the central cation cell. This outer radius is given by

$$r_c^T = r_c + \lambda r_a \qquad \text{(A-4a)}$$

where r_c is the radius of the cation; r_a is the radius of the anion; λ is the size constant to account for the effect due to the outside shape of the first coordination shell. This size constant is in the range 1 to 2.

Similarly

$$r_a^T = r_a + \lambda r_c . \qquad \text{(A-4b)}$$

N_{ac} is the time-average number of anions in the first coordination shell of the cell having a cation at the center; it is given by

$$N_{ac} = x_{ac} z_c \qquad \text{(A-5)}$$

where z_c is the coordination number of the cation and x_{ac} is the local mole fraction of anions around the central cation:

$$x_{ac} = \frac{x_a}{x_a + x_w G_{wc,ac}} \qquad \text{(A-6)}$$

Equation (A-6) is discussed further in Appendix B.

Equation (A-3) is related to the 'like-ion repulsion' assumption(11), which states that the local composition of cations around cations is zero, and similarly for anions. This assumption is equivalent to assuming that repulsive forces between ions of like charge are extremely large; equation (A-3) does not include the term $N_{cc} \nu_c e$ because, $x_{cc} = 0$.

According to the Boltzmann distribution law, the average local number of ions j per unit volume, n_j', at distance r, is

$$n_j' = n_j \exp\left[-\frac{\nu_j e \psi_c}{kT}\right] \tag{A-7}$$

where k is Boltzmann constant and T is the absolute temperature.

The product, $\nu_j e \psi_c$, is the electrical potential energy of ion j when the coordinate system is centered on the cation. The product, kT, is its thermal energy.

For the volume element considered, the net-charge density is obtained by summing over all ionic species

$$\rho_c = \sum_j n_j \nu_j e \exp\left[-\frac{\nu_j e \psi_c}{kT}\right] \tag{A-8a}$$

Upon expanding the exponentials in (A-8a), we obtain

$$\rho_c = \sum_j n_j \nu_j e - \sum_j n_j \nu_j e \left[\frac{\nu_j e \psi_c}{kT}\right] + \sum_j \frac{n_j \nu_j e}{2!}\left[\frac{\nu_j e \psi_c}{kT}\right]^2 - \cdots \tag{A-8b}$$

The first term on the right of (A-8b) vanishes by the condition of electrical neutrality (A-2). (For electrolytes with symmetric valence, the third term also vanishes.). If $\nu_j e \psi_c \ll kT$, only the second term (linear in ψ_c) is appreciable, giving the result:

$$\rho_c = -\sum_j \frac{n_j \nu_j^2 e^2 \psi_c}{kT} \tag{A-8c}$$

Since (A-8c) states that ψ_c is directly proportional to ρ_c, this approximate form is consistent with the superposition principle of electrostatics, which says that the potential due to two systems of charges in specified positions is the sum of the potentials due to each system taken separately.

Equation (A-8c) is strictly valid only when the potential energy, $\nu_j e \psi_c$, of the ion j is small compared to its thermal energy, kT. Although this may well be true for the majority of the ions j in the solution, it is questionable for those ions which are close to the central cation. But those ions are not of concern to us because the potential calculated here does not include the ions in the first coordination shell.

Substituting (A-8c) into the Poisson equation (A-1), we have

$$\frac{1}{r^2}\frac{d}{dr}\left\{r^2\frac{d\psi_c}{dr}\right\}=\kappa^2\psi_c \tag{A-9}$$

where κ is defined by

$$\kappa^2=\frac{4\pi e^2\sum_j n_j \nu_j^2}{DkT} \tag{A-10}$$

Equation (A-9) is a linear second-order differential equation relating ψ_c to r. To solve (A-9), we use two physical conditions: first, that the potential must remain finite at large values of r; second, that electroneutrality must hold in the entire solution. We use equation (A-3) for electroneutrality. Finally, we obtain

$$\psi_c=\left\{\nu_c+\frac{\nu_a x_a z_c}{x_a+x_w G_{wc;ac}}\right\}\frac{e}{D}\frac{\exp[\kappa(r_c^T-r)]}{(1+\kappa r_c^T)}\frac{1}{r} \tag{A-11}$$

This fundamental expression is valid only at the region $r \geq r_c^T$. For the case $r=r_c$, we have to add the potentail, $\psi_{c,FCS}$, due to the ions in the first coordination shell.

For an isolated cation in a medium of dielectric constant, D, the potential ψ_c'' at distance r is given by

$$\psi_c''=\frac{\nu_c e}{D\,r} \tag{A-12}$$

By the principle of linear superposition of potential fields, for $r=r_c$, we have

$$\psi_c+\psi_{c,FCS}=\psi_c'+\psi_c''+\psi_{c,FCS} \tag{A-13}$$

where ψ_c' is the potential due to all the ions outside the first coordination shell.

Substituting (A-11) and (A-12) into (A-13), we obtain

$$\psi_c'=\left\{\nu_c+\frac{\nu_a x_a z_c}{x_a+x_w G_{wc,ac}}\right\}\frac{e}{D\,r_c}\frac{\exp[\kappa(r_c^T-r_c)]}{(1+\kappa r_c^T)}-\frac{\nu_c e}{D\,r_c} \tag{A-14}$$

Whithin $r<r_c$, no other ions can penetrate and ψ_c' is therefore constant for all

$r<r_c$ and equal to its value at $r=r_c$. Thus (A-14) accounts for the contribution of all ions outside the first coordination shell on the potential of the central cation.

The change of electrical energy of the central cation, due to interaction with ions outside the first coordination shell, is equal to the product of its charge, $\nu_c e$, and the potential, ψ'_c. However, if we apply the argument to every ion in the solution, we count each ion twice, once as the central ion and once as part of the surrounding ions. Thus the change of the electrical energy for one mole of cations, $\Delta\mu_{c,LR}$, is given by

$$\Delta\mu_{c,LR}=RT\ln\gamma^{*}_{c,LR}=\frac{N_0}{2}\nu_c e\psi'_c \tag{A-15}$$

where N_0 is Avogadro's number.

Substituting (A-14) into (A-15), we obtain (5-2). Similarly, we obtain (5-3).

To maintain concentration scales consistent with the local-composition expression (6-5), we rewrite (A-10) to

$$\kappa^2=\frac{4\pi e^2}{DkT}n_T\sum_j\frac{n_j}{n_T}\nu_j^2=\frac{4\pi e^2}{DkT}n_T\sum_j x_j\nu_j^2 \tag{A-16}$$

where n_T is the total number of all species per unit volume.

$$n_T=\sum_i n_i \tag{A-17}$$

APPENDIX B

Derivation of the Local-Composition Expression

While the derivation that follows may be generalized, the derivation given here is based on a single completely dissociated aqueous electrolyte.

It is assumed that in the solution there are three types of cells as shown in Figure 7. One type consists of a central water molecule with water molecules, w, anions, a, and cations, c, in the first coordination shell. The other two, based on the "like-ion repulsion" assumption, have either an anion or cation at the center and a first coordination shell consisting of water molecules and oppositely-charged ions, but no ions of like charge (i.e., $x_{cc}=x_{aa}=0$). The like-ion repulsion assumption follows from assuming that the attractive interaction energies between ions of like charge are much greater than any other attractive interaction energies.

According to the two-fluid theory(45), we have

$$E_m=N_0(x_w\varepsilon^{(w)}+x_c\varepsilon^{(c)}+x_a\varepsilon^{(a)}) \tag{B-1}$$

where E_m is the interaction energy of one mole of solution; $\varepsilon^{(w)}$ is the interaction energy of one cell where water is the center, with similar definitions for $\varepsilon^{(c)}$ and $\varepsilon^{(a)}$.

The local mole fractions are related to one another by

$$x_{ww}+x_{cw}+x_{aw}=1 \quad (central-water\ cell) \tag{B-2a}$$

$$x_{wc}+x_{ac}=1 \quad (central-cation\ cell) \tag{B-2b}$$

$$x_{wa}+x_{ca}=1 \quad (central-anion\ cell) \tag{B-2c}$$

For each type of cell, we have

$$\varepsilon^{(w)}=\frac{z_w}{2}(x_{ww}\varepsilon_{ww}+x_{cw}\varepsilon_{cw}+x_{aw}\varepsilon_{aw}) \tag{B-3a}$$

$$\varepsilon^{(c)}=\frac{z_c}{2}(x_{wc}\varepsilon_{wc}+x_{ac}\varepsilon_{ac}) \tag{B-3b}$$

$$\varepsilon^{(a)}=\frac{z_a}{2}(x_{wa}\varepsilon_{wa}+x_{ca}\varepsilon_{ca}) \tag{B-3c}$$

where ε_{ji} is the interaction energy of one j-i pair ($\varepsilon_{ji}=\varepsilon_{ij}$).

For one mole of pure water or pure completely dissociated "liquid" electrolyte, we have

$$E_{m,ww}=\frac{z_w}{2}g_{ww} \tag{B-4a}$$

$$E_{m,ac}=\frac{z_c}{2}g_{ac} \tag{B-4b}$$

$$E_{m,ca}=\frac{z_a}{2}g_{ca} \tag{B-4c}$$

where

$$g_{ji}=N_0\,\varepsilon_{ji}$$

The excess interaction energy of one mole of solution, E_m^E, is defined by

$$E_m^E=E_m-x_w E_{ww}-x_c E_{ac}-x_a E_{ca} \tag{B-5}$$

Since we are concerned with low pressures, following Renon and Prausnitz(16), we use the approximation

$$H_m^E=E_m^E \tag{B-6}$$

where H_m^E is the excess enthalpy of one mole solution.

We now define

$$G_{ji,ki}=\exp[-(g_{ji}-g_{ki})/RT] \tag{B-7}$$

where R is the gas constant.

Upon combining (B-2) and (5-2), we have

$$x_{iw}=\frac{x_i\,G_{iw,ww}}{x_w+x_c\,G_{cw,ww}+x_a\,G_{aw,ww}}\quad (i=w,c,a) \tag{B-8a}$$

$$x_{ic}=\frac{x_i\,G_{ic,ac}}{x_a+x_w\,G_{wc,ac}}\quad (i=w,a) \tag{B-8b}$$

$$x_{ia}=\frac{x_i\,G_{ia,ca}}{x_c+x_w\,G_{wa,ca}}\quad (i=w,c) \tag{B-8c}$$

To obtain an expression for the excess mole Gibbs energy, G_m^E, we use the Gibbs-Helmholtz equation

$$\frac{\partial(G_m^E/T)}{\partial(1/T)}=H_m^E \tag{B-9}$$

Assuming g_{ji} independent of temperature, we integrate (B-9), giving

$$\frac{G_m^E}{RT} = -\frac{1}{2}\left[z_w x_w \ln\frac{(x_w + x_c G_{cw,ww} + x_a G_{aw,ww})}{(x_w + x_c + x_a)} + z_c x_c \ln\frac{(x_a + x_w G_{wc,ac})}{(x_a + x_w)} + z_a x_a \ln\frac{(x_c + x_w G_{wa,ca})}{(x_c + x_w)}\right] \tag{B-10}$$

At the low limit of the integration, we use $1/T=0$. Therefore, $G_m^E/T=0$ at this limit.

Through the thermodynamic relations

$$\left(\frac{\partial n_T G_m^E}{\partial n_i}\right)_{T,P,n_{j\neq i}} = RT\ln\gamma_i ,$$

finally, we obtain

$$\ln\gamma_{c,SR} = -\frac{1}{2}\left[z_w\left(\frac{x_w G_{cw,ww}}{x_w + x_c G_{cw,ww} + x_a G_{aw,ww}} - x_w\right) + z_c \ln\frac{(x_a G_{wc,ac})}{(x_a + x_w)} + \frac{z_a x_a}{x_c + x_w G_{wa,ca}} - \frac{z_a x_a}{x_c + x_w}\right] \tag{B-11a}$$

$$\ln\gamma_{a,SR} = -\frac{1}{2}\left[z_w\left(\frac{x_w G_{aw,ww}}{x_w + x_c G_{cw,ww} + x_a G_{aw,ww}} - x_w\right) + \frac{z_c x_c}{x_a + x_w G_{wc,ac}} - \frac{z_c x_c}{x_a + x_w} + z_a \ln\frac{(x_c + x_w G_{wa,ca})}{(x_c + x_w)}\right] \tag{B-11b}$$

Equations (B-11a) and (B-11b) give symmetrically normalized, individual ionic activity coefficients. For consistency with the unsymmetrically normalized modified Debye-Hückel expression, we renormalize the activity coefficients in Equations (B-11a) and (B-11b) using the relations

$$\ln\gamma_{c,SR}^{*} = \ln\gamma_{c,SR} - \ln\gamma_{c,SR}^{\infty} \tag{B-12a}$$

$$\ln\gamma_{a,SR}^{*} = \ln\gamma_{a,SR} - \ln\gamma_{a,SR}^{\infty} \tag{B-12b}$$

where (*) denotes unsymmetric convention and (∞) denotes infinite dilution.

From Equations (B-12a) and (B-12b), we obtain Equations (6-3) and (6-4).

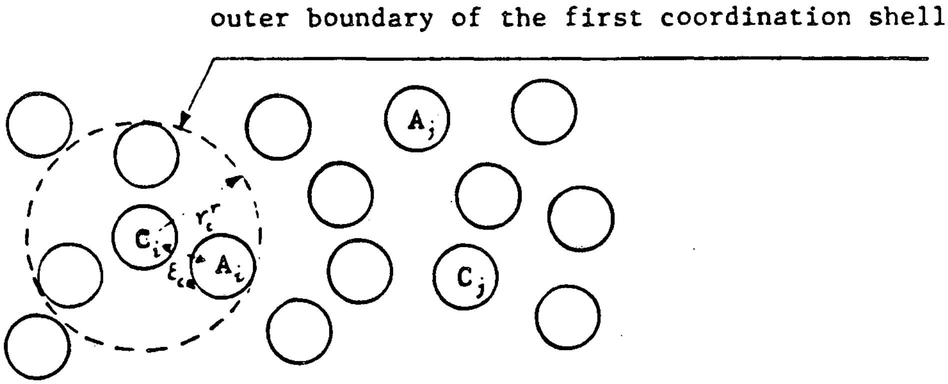


Figure 1. Long-range and Short-range Interaction in a Single-electrolyte System

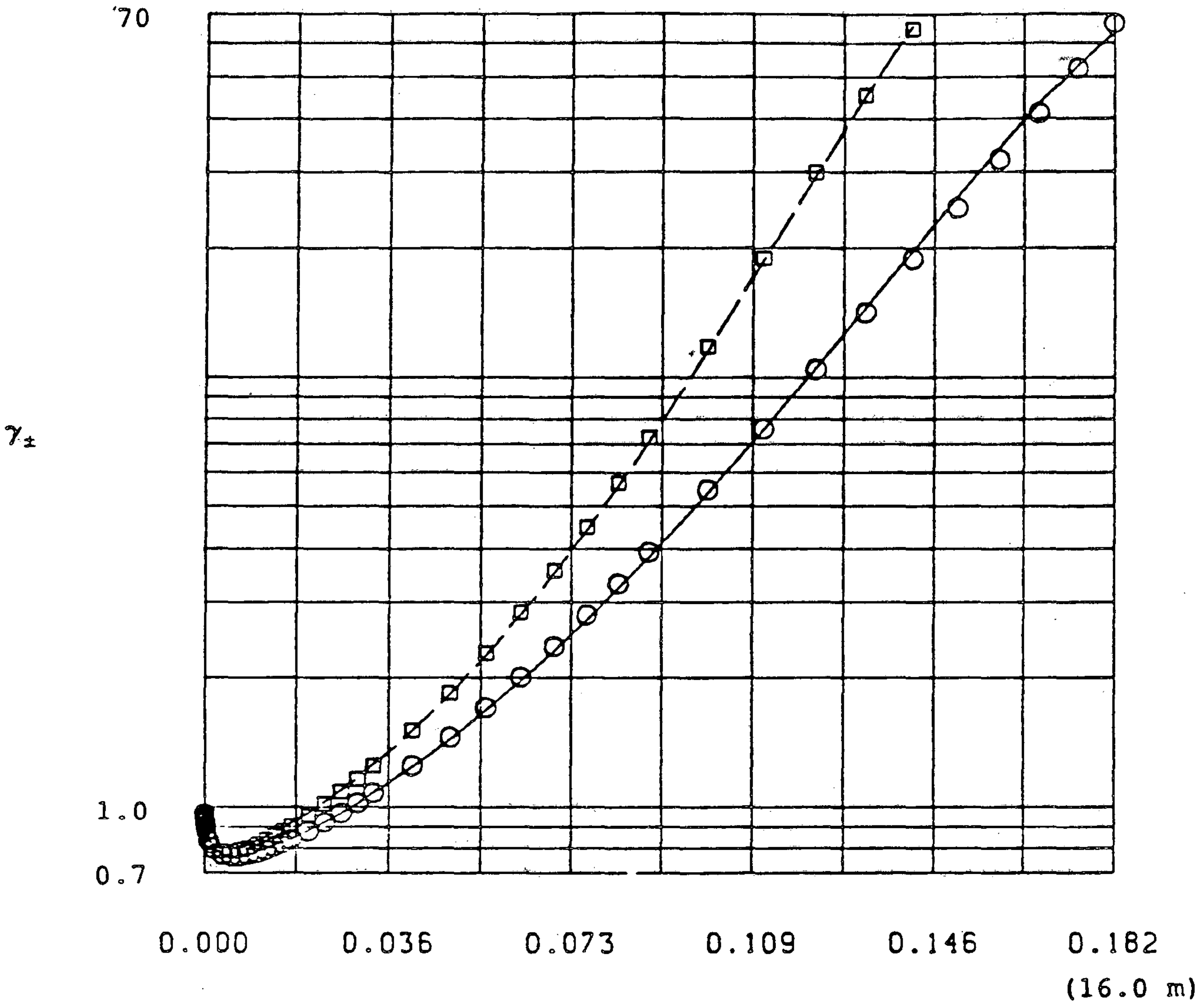


Figure 2. Mean Ionic Activity Coefficient for Hydrochloric Acid and Hydrobromic Acid at 298.15 K

○ Experimental (HCl)

□ Experimental (HBr)

——Calculated (HCl)

-- —Calculated (HBr)

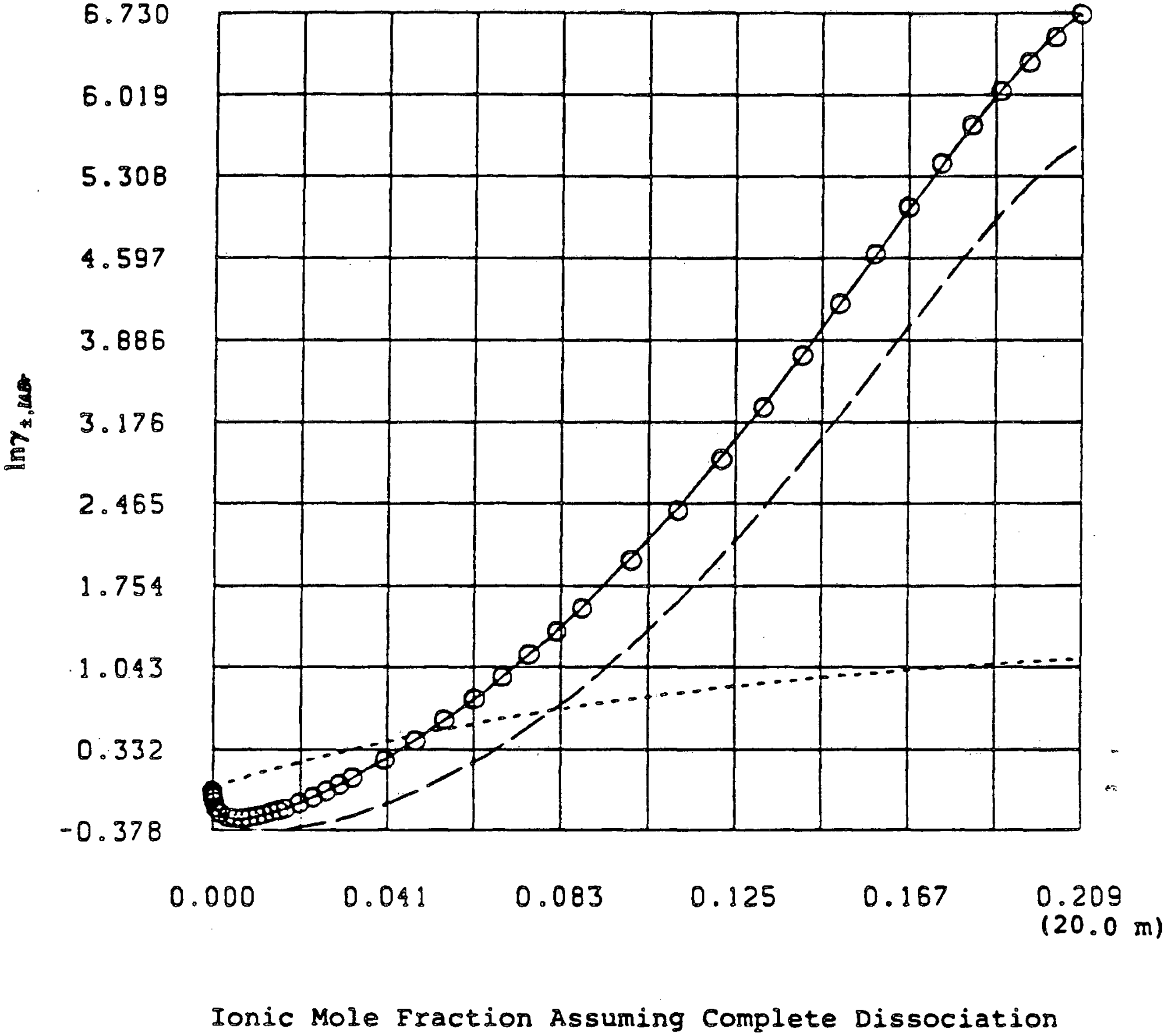


Figure 3. Contributions to Mean Ionic Activity Coefficient for Aqueous Lithium Bromide at 298.15 K

○ Experimental

——Calculated

– – –Modified Debye-Hückel Contribution

-----Local-Composition Contribution

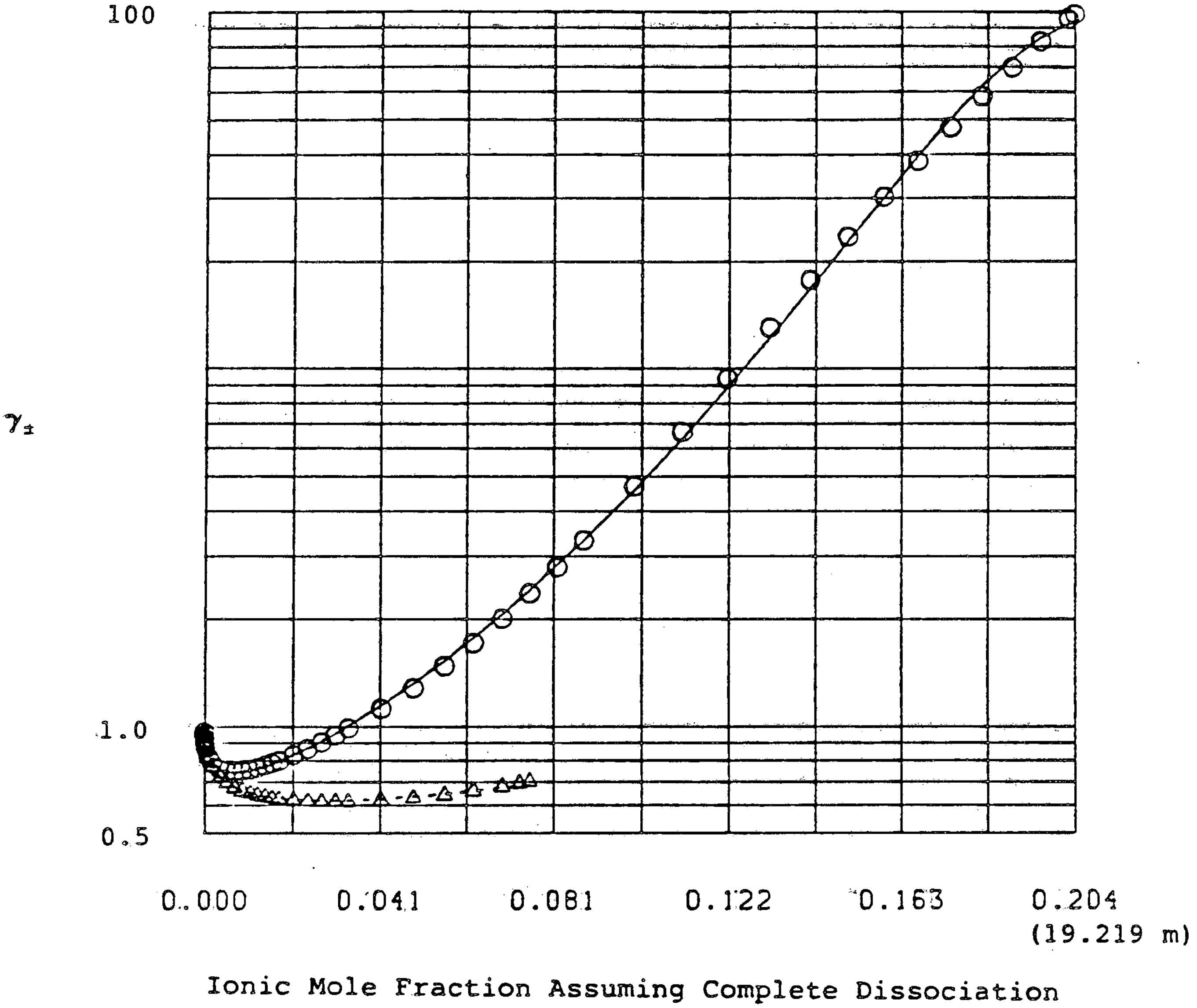


Figure 4. Mean Ionic Activity Coefficient for Aqueous Lithium Chloride and Potassium Chloride at 298.15 K

○ Experimental (LiCl)

△ Experimental (KCl)

—— Calculated (LiCl)

---- Calculated (KCl)

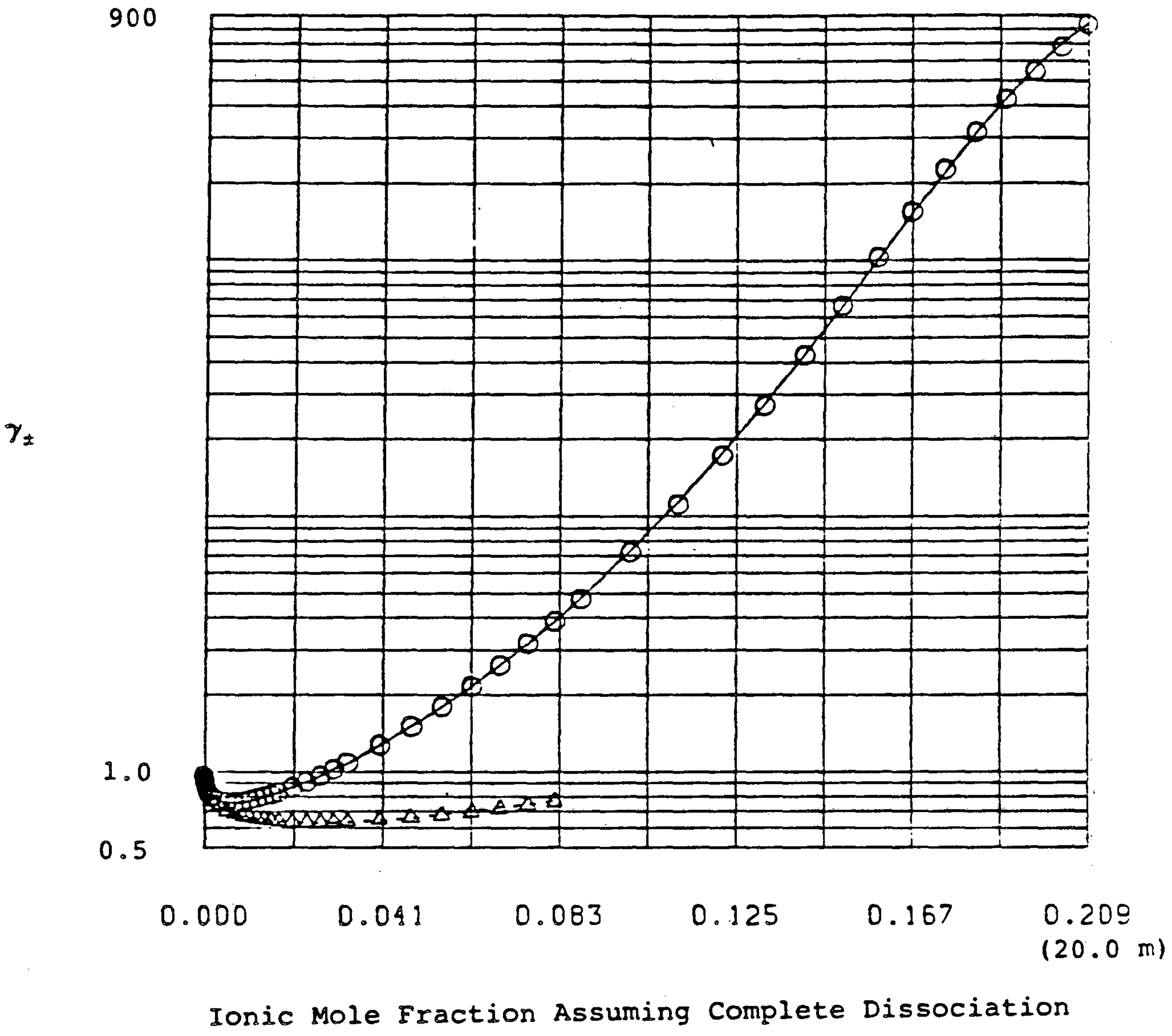


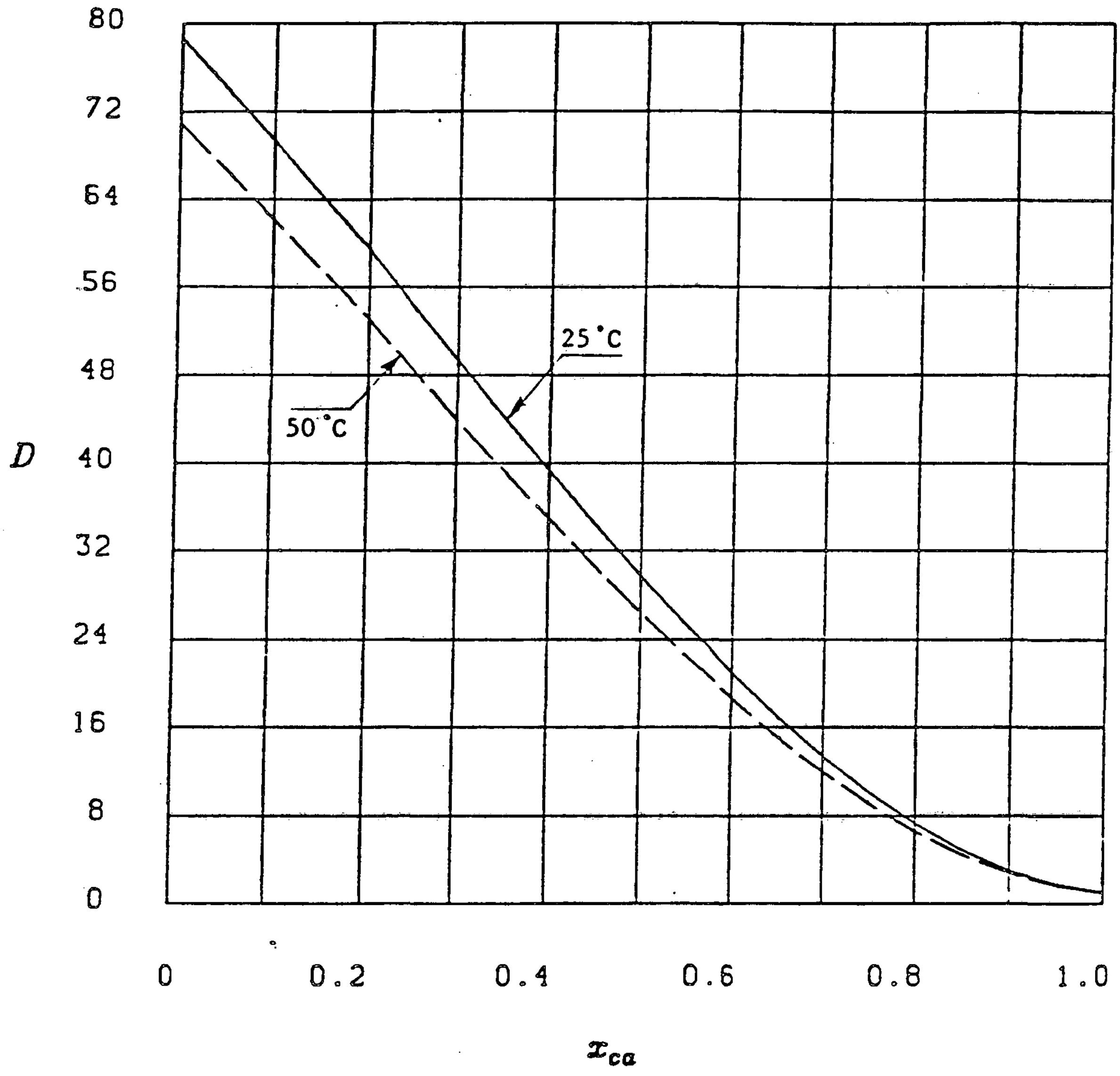
Figure 5. Mean Ionic Activity Coefficient for Aqueous Lithium Bromide and Potassium Bromide at 298.15 K

○ Experimental (LiBr)

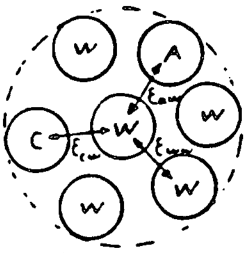
△ Experimental (KBr)

—— Calculated (LiBr)

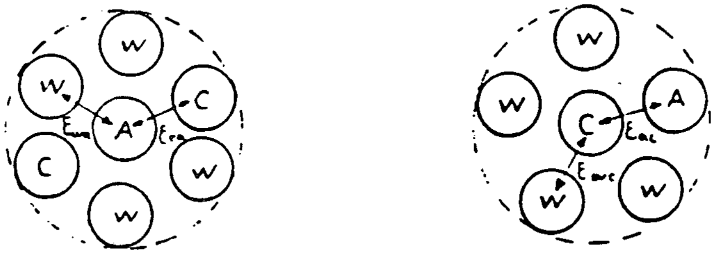
----- Calculated (KBr)



Firure 6. The Dielectric Constant D as a Function of Apparent Electrolyte Mole Fraction at 25 and 50 °C



water at center



anion at center

cation at center

Figure 7. Three Types of Cells.

The lower two cells assume like-ion repulsion.

C=cation, A=anion and W=water.

Table 1. The Influence of Coordination Number on the Simultaneous Fit of Mean-Ionic-Activity-Coefficient Data for Aqueous Electrolytes at 25°C

Set	z_w	z_{H^+}	z_{K^+}	z_{Li^+}	z_{Br^-}	z_{Cl^-}	$\sigma_{\ln\gamma_{\pm,ca}}$
[1]	4.5	4.5	4.5	4.5	4.5	4.5	0.017
[2]	10.0	10.0	10.0	10.0	10.0	10.0	0.018
[3]	4.5	4.0	4.0	5.0	5.0	4.0	0.018
[4]	4.5	4.0	4.0	6.0	7.0	3.0	0.015
[5]	4.5	4.0	4.0	6.0	7.0	3.0	0.016

Date from Hamer et al(42). Maximum molalities are 11.0(HBr), 16.0(HCl), 5.5(KBr), 5.0(KCl), 20.0(LiBr) and 19.2(LiCl).

λ = 1.5 for all electrolytes except HBr where λ = 1.70

In all calculations, the crystal radii of Goldschmidt(37) are used for the radii of anions.

In Set[5], the true density defined by (A-17) is fixed at 60 mol / L.

Table 2. Interaction Energy Parameters, g_{ji}/R (K), from Simultaneous Fit of Mean-Ionic-Activity-Coefficient Data for Aqueous Electrolytes at 25°C, upon Setting g_{ww}=0.

	Br^-		Cl^-		H_2O	
	Set[4]	Set[4]′	Set[4]	Set[4]′	Set[4]	Set[4]′
H^+	-113.86	186.34	14.0	-59.75	-113.33	-137.12
K^+	-203.85	-190.34	-195.82	-175.19	-287.89	-270.69
Li^+	-260.34	-185.66	-274.89	-190.28	-494.51	-443.50
H_2O	315.38	325.13	296.69	316.13	0.00	0.00

Set [4] as in Table 1.

Set [4]′ is the same as *Set* [4] except that maximum molalities are 6.0(HBr), 6.0(HCl), 5.5(KBr), 5.0(KCl), 6.0(LiBr) and 6.0(LiCl).

Table 3. Effective Radii for Cations (Å) from Simultaneous Fit of Mean-Ionic-Activity-Coefficient Data for Aqueous Electrolytes at 25°C

Set	H^+	K^+	Li^+
[1]	0.6991	0.6753	0.7698
[2]	0.6582	0.5542	0.7084
[3]	0.6835	0.6458	0.7447
[4]	0.5924	0.6154	0.6956
[5]	0.5241	1.0301	0.5909

All sets as in Table 1.

Table 4. Comparison Between the Present Model and the Chen Model (Results from Fit of Mean-Ionic-Activity-Coefficient Data of Aqueous Electrolytes at 25°C)

	Set[4]		Set[4]'		Chen Model°	
	$\sigma_{\ln\gamma_{\pm,ca}}$	max.m	$\sigma_{\ln\gamma_{\pm,ca}}$	max.m	$\sigma_{\ln\gamma_{\pm,ca}}$	max.m
HBr	0.013	11.0	0.005	6.0	0.015	3.0
HCl	0.023	16.0	0.003	6.0	0.035	6.0
KBr	0.005	5.5	0.004	5.5	0.004	5.5
KCl	0.007	5.0	0.005	5.0	0.003	4.5
LiBr	0.012	20.0	0.004	6.0	0.050	6.0
LiCl	0.029	19.2	0.004	6.0	0.040	6.0

• From Chen et al.(11)

Set [4] and *Set* [4]' as in Table 1. and 2.

Table 5. Effect of Temperature on Standard Deviation of Mean Ionic Activity Coefficient for Aqueous Potassium Chloride Using Temperature-Independent Parameters Obtained at 25°C

T (°C)	0	18	25	35	50
σ	0.056	0.017	0.005	0.037	0.088

Data from Caramazza(43)

Maximum molality is 4.0 m.

Parameters are those in Set[4] at 298.15 K.

σ denotes the standard deviation of mean ionic activity coefficient for aqueous potassium chloride.

Table 6. Numerical Values of the Constants in Eq. (7-1) for the Dielectric Constant (From Uematsu and Franck(28))

B_1 = 7.62571
B_2 = 244.003
B_3 = -140.569
B_4 = 27.7841
B_5 = -96.2805
B_6 = 41.7909
B_7 = -10.2099
B_8 = -45.2059
B_9 = 84.6395
B_{10} = -35.8644

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