Local Composition Model for Excess Gibbs Energy of Electrolyte Systems

Part I: Single Solvent, Single Completely Dissociated Electrolyte Systems

An electrolyte local composition model is developed for excess Gibbs energy, which is assumed to be the sum of two contributions, one resulting from long range electrostatic forces between ions and the other from short range forces between all the species. The validity of the model is demonstrated for systems emcompassing the entire range from molecular liquid to fused salt.

CHAU-CHYUN CHEN,
H. I. BRITT,
J. F. BOSTON and
L. B. EVANS

Department of Chemical Engineering and
Energy Laboratory
Massachusetts Institute of Technology
Cambridge, MA 02139

SCOPE

There have been many investigations, both experimental and theoretical, of the thermodynamic properties of aqueous electrolyte systems over the past few decades. Recently, significant developments in the estimation of the molality mean ionic activity coefficients for aqueous electrolyte systems have been made by Meissner (1972), Bromley (1973), Pitzer (1973), and Cruz and Renon (1978). Of these, the Pitzer equation is especially useful. It has been applied successfully to represent data within experimental error from dilute solutions up to an ionic strength of six molal for both aqueous single strong electrolyte systems (Pitzer and Mayorga, 1973) and aqueous mixed strong electrolyte systems (Pitzer and Kim, 1974). Modified forms of the Pitzer equation have been used by Beutier and Renon (1978) and Edwards et al. (1978) as models for the ionic activity coefficients of aqueous weak electrolyte systems. The Pitzer equation was later extended (Chen et al., 1979) in a thermodynamically consistent manner to allow for molecular as well as ionic solutes in the aqueous systems.

Pitzer's excess Gibbs energy equation is a virial expansion equation and is subject to all of the limitations of a virial model. The model parameters are arbitrary, temperature-dependent, and characteristic of the solvent. Binary parameters are empirical functions of ionic strength and ternary parameters are necessary at high ionic strength. The Pitzer equation can not be used for mixed solvent systems because its parameters are unknown functions of solvent composition. Therefore, although the Pitzer equation has been shown to be a convenient and accurate representation of aqueous electrolyte systems, a more versatile model is needed.

In this study a new model is developed that does not have the disadvantages of a virial expression and that is applicable to a wide variety of electrolyte systems over the entire range of electrolyte concentrations and system temperatures. The kinds of systems that have been studied using the new model involve mixed electrolytes, mixed solvents, and partially dissociated electrolytes (Chen, 1980; Chen et al., 1980). It is anticipated that the model is also applicable to systems involving salt precipitation, immiscible liquid phases, and fused salt solutions. However, this paper, part one of a series, is limited to single solvent, single completely dissociated electrolyte systems in order to emphasize the model development, the physical interpretation of the model parameters, and the two critical assumptions on which the model is based. In part two of the series (Chen et al., 1982) the model is extended to multicomponent systems, including partially dissociated electrolytes which involve dissociation equilibria.

CONCLUSIONS AND SIGNIFICANCE

A new model has been developed for the excess Gibbs energy of electrolyte systems. It is based on the local composition concept and is designed to represent the properties of all kinds of electrolyte systems over the entire range of electrolyte concentrations. With only binary parameters, the local composition model may be applied to obtain good data correlation results on many single solvent, single completely dissociated electrolyte systems over wide ranges of concentration and temperature.

Two assumptions about electrolyte systems are critical to the local composition model development. The first is called the like-ion repulsion assumption and states that the local composition of cations (anions) around cations (anions) is zero, which is equivalent to assuming that repulsive forces between like-charged ions are extremely large. The second is called local electroneutrality and states that the distribution of cations and anions around a central solvent molecule is such that the net local ionic charge is zero. It is these realistic assumptions, in conjunction with the local composition concept, that enable the new model to represent all kinds of electrolyte systems.

The proposed excess Gibbs energy expression can represent infinitely dilute electrolyte systems (where it reduces to the Debye-Hückel model), pure molecular systems (where it reduces to the NRTL model), or pure fused salts, and provides a continuous connection between all of these limiting systems.

The authors are presently with Aspen Technology Inc., Cambridge, MA 02139.

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INTRODUCTION

The thermodynamic properties of a mixture depend on the forces that exist between the species of the mixture. Electrolyte systems are characterized by the presence of both molecular species and ionic species, resulting in three different types of interaction: ion-ion, molecule-molecule, and ion-molecule.

Ion-ion interactions are dominated by electrostatic forces between ions. These electrostatic forces are inversely proportional to the square of the separation distance and therefore have a much greater range than other intermolecular forces that depend on higher powers of the reciprocal distance. Except at short range, other forces are relatively insignificant compared to the interionic electrostatic forces.

Many different types of forces arise from molecule-molecule interactions. They may be electrostatic forces between permanent dipoles, induction forces between permanent dipoles and induced dipoles, or dispersion forces between non-polar molecules, etc. (Prausnitz, 1969). All of these forces are known to be short range in nature.

Ion-molecule interaction forces are also short range in nature. The dominant ones are electrostatic forces between ions and permanent dipoles. As suggested by Robinson and Stokes (1970), the short range interaction energies should be large compared with thermal energy (RT).

The excess Gibbs energy of electrolyte systems can be considered as the sum of two terms, one related to long range forces between ions and the other to short range forces between all the species. Long range forces dominate in the region of dilute electrolyte concentration, while short range forces dominate in the region of high electrolyte concentration. It is the long range nature of the electrostatic forces between ions that has no counterpart in nonelectrolyte systems.

SIGNIFICANCE OF CHEMICAL EQUILIBRIUM

Electrolytes may dissociate partially or completely in solution. A mixture of a completely dissociated electrolyte and a solvent consists of cations, anions and solvent molecules. In the case of partial dissociation, however, undissociated electrolyte molecules are also present. In addition to the dissociation chemical equilibrium, in some systems association between cations and anions or between ions and solvent molecules may occur to form ion pairs or complex ions.

Partially dissociating systems and systems in which some form of association occurs are often treated with the assumption of complete dissociation. This may be for simplicity or because there is no information on the dissociation or association equilibrium constants. The assumption of complete dissociation is a great simplification for many electrolyte systems and may result in only very small errors for the quantities of interest such as solvent partial pressure or mean ionic activity coefficient. However, when association among various species are significant, the assumption of complete dissociation can lead to unsatisfactory results.

In this paper only the case of complete dissociation is treated. Systems with partial dissociation or in which association between various species may occur will be treated as multicomponent systems in chemical equilibrium in part two of this series.

NEW MODEL

Nonelectrolyte systems, which are characterized by short range forces between molecules, have frequently been studied using the local composition concept. Models such as Wilson (1964), NRTL (Renon and Prausnitz, 1968), and UNIQUAC (Abrams and Prausnitz, 1975) have resulted. Such models have proven to be a great advancement over older models based on virial type expansions of mole fraction, such as the Margules model. In this study the local composition concept is used to account for the contribution of short range interactions in electrolyte systems with the goal of achieving a similar advancement over the Pitzer equation. In particular, the new model is designed to apply to electrolyte systems over a wide range of electrolyte concentration without the need for ternary or higher order parameters.

The local composition model developed in this study is based on two fundamental assumptions: 1) that the local composition of cations around cations is zero, and similarly for anions, which is equivalent to assuming that repulsive forces between ions of like charge are extremely large, and 2) that the distribution of cations and anions around a central solvent molecule is such that the net local ionic charge is zero. Hereafter, the first assumption is referred to as like-ion repulsion and the second assumption as local electroneutrality. For a pure completely dissociated liquid electrolyte the like-ion repulsion assumption suggests that the local lattice structure around ions in solution is similar to that of a solid salt crystal. When molecules are introduced into the liquid lattice structure, the local electroneutrality assumption suggests that the local lattice structure around molecules is similar to that of interstitial species in a solid salt crystal.

The approach taken in the model development is as follows. The extended Debye-Hückel formula proposed by Pitzer (1980) was used to represent the contribution of long range ion-ion interactions, while the local composition concept is used to represent the contribution of short range interactions of all kinds. The local composition concept and the Debye-Hückel formula are consistent in the sense that they both account for nonrandomness by introducing local compositions through Boltzmann-like factors. The local composition model for the short range interaction contribution is developed as a symmetric model, based on pure solvent and pure completely dissociated liquid electrolyte. The electrolyte reference state may be hypothetical or it may actually exist as a pure fused salt. The model is then normalized by infinite dilution activity coefficients in order to obtain an unsymmetric local composition model. Finally the unsymmetric Pitzer-Debye-Hückel expression and the unsymmetric local composition expression are added to yield the excess Gibbs energy expression proposed in this study:

$$g^{ex*}/RT = g^{ex*,pdh}/RT + g^{ex*,lc}/RT \tag{1a}$$

Similarly,

$$ln\gamma_i = ln\gamma_i^{pdh} + ln\gamma_i^{lc} \tag{1b}$$

LONG RANGE INTERACTION CONTRIBUTION

Many Debye-Hückel type electrostatic excess Gibbs energy expressions have been proposed in the literature to represent the long-range contribution. In this study, the extended form of the Debye-Hückel equation proposed by Pitzer (1973, 1980) was adopted because, like the short range contribution expression, the true mole fraction of all species present, including ions, is used as the measure of composition and also because the equation gives some recognition to the repulsive forces between ions (Pitzer, 1980). The Pitzer-Debye-Hückel formula is normalized to mole fractions of unity for solvent and zero for electrolytes. The expression is

$$g^{ex*,pdh}/RT = -\left(\sum_k x_k\right)(1{,}000/M_s)^{1/2}(4A_\phi I_x/\rho)\,ln(1 + \rho I_x{}^{1/2}) \tag{2}$$

where the sum includes all species, molecular as well as ionic. M_s is the molecular weight of the solvent. A_ϕ is the usual Debye-Hückel parameter:

$$A_\phi = (1/3)(2\pi N_0 d/1{,}000)^{1/2}(e^2/DkT)^{3/2} \tag{3}$$

I_x is the ionic strength on a mole fraction basis:

$$I_x = (1/2)\Sigma Z_i^2 x_i \tag{4}$$

ρ is the "closest approach" parameter. In general, the value of ρ depends on the electrolyte as well as the expression used to represent the short range forces. In order to maintain simplicity in equations for more complex electrolyte systems, it is desirable that

ρ should have the same value for a wide variety of salts.

The expression for the activity coefficient of any species is derived from Eq. 2:

$$ln\gamma_i^{pdh^*} = -(1{,}000/Ms)^{1/2}A_\phi\{(2Z_i^2/\rho)\,ln(1+\rho I_x^{1/2}) + (Z_i^2 I_x^{1/2} - 2I_x^{3/2})/(1+\rho I_x^{1/2})\} \quad (5)$$

SHORT RANGE INTERACTION CONTRIBUTION

The short range interaction contribution is accounted for by using the local composition concept. Among the various approaches used previously to develop local composition models for nonelectrolyte systems, the one used by Renon and Prausnitz (1968) to develop the nonrandom, two-liquid (NRTL) model was adopted for the following reasons. Electrolyte systems are characterized by extraordinarily large heats of mixing. Compared with the heat of mixing the nonideal entropy of mixing is negligible, which is consistent with the basic assumption behind the NRTL approach. In addition, the resulting local composition model is algebraically simple and is applicable to mixtures which exhibit liquid phase splitting. Furthermore, it does not require specific volume or area data, such as that required by the UNIQUAC local composition model (Abrams and Prausnitz, 1975).

In the following development of the new local composition model, the assumptions, terminology, and notation of Renon and Prausnitz are followed as closely as possible. There are small differences in our treatment that arise from the need to consider both cation and anion cells, as well as solvent cells, and more fundamental differences related to the introduction of two principle assumptions about the structure of electrolyte solutions.

The local mole fractions x_{ji} and x_{ii} of species j and i, respectively, in the immediate neighborhood of a central species i are related by

$$x_{ji}/x_{ii} = (x_j/x_i)G_{ji} \quad (6)$$

where

$$G_{ji} = \exp(-\alpha\tau_{ji}) \quad (7)$$

$$\tau_{ji} = (g_{ji} - g_{ii})/RT \quad (8)$$

The quantities g_{ji} and g_{ii} are, respectively, energies of interaction between j-i and i-i pairs of species, and are inherently symmetric ($g_{ji} = g_{ij}$). The nonrandomness factor, α, is fixed at a value of 0.2 in this study.

For convenience in representing other local mole fraction ratios, additional notation is introduced as follows:

$$x_{ji}/x_{ki} = (x_j/x_k)G_{ji,ki} \quad (9)$$

where

$$G_{ji,ki} = \exp(-\alpha\tau_{ji,ki}) \quad (10)$$

$$\tau_{ji,ki} = (g_{ji} - g_{ki})/RT \quad (11)$$

While the derivation that follows may be generalized to handle all types of electrolyte systems, in this paper the derivation will be based on a system of single completely dissociated liquid electrolyte, ca, and single solvent, m. In this type of mixture, it is assumed that there are three types of cells as shown in Figure 1. One type consists of a central solvent molecule with solvent molecules, anions and cations in the immediate neighborhood. The local electroneutrality assumption is applied to cells of this type. The other two are based on the like-ion repulsion assumption and have either an anion or cation as the central species, and an immediate neighborhood consisting of solvent molecules and oppositely-charged ions, but no ions of like charge (i.e., $x_{cc} = x_{aa} = 0$). It should be noted that the like-ion repulsion assumption is equivalent to the assumption that g_{cc} and g_{aa} are much greater than any other interaction energies. The local mole fractions are related by

$$x_{cm} + x_{am} + x_{mm} = 1 \quad \text{(central solvent cells)} \quad (12a)$$

$$x_{mc} + x_{ac} = 1 \quad \text{(central cation cells)} \quad (12b)$$

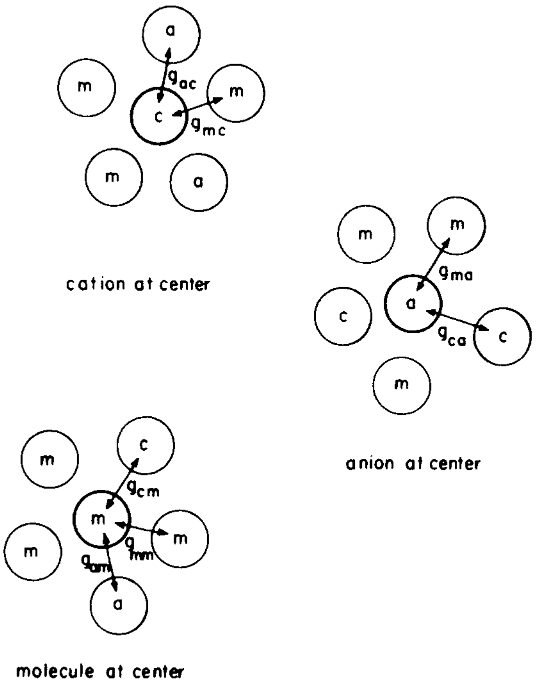

Figure 1. Three types of cells according to like-ion repulsion assumption and local electroneutrality assumption.

$$x_{ma} + x_{ca} = 1 \quad \text{(central anions cells)} \quad (12c)$$

Among the three types of cells there are four distinct local mole fraction ratios: x_{cm}/x_{mm}, x_{am}/x_{mm}, x_{mc}/x_{ac}, and x_{ma}/x_{ca}.

By combining Eqs. 6, 9 and 12, the following expressions for the local mole fractions in terms of overall mole fractions may be derived:

$$x_{im} = x_i G_{im}/(x_a G_{am} + x_c G_{cm} + x_m G_{mm}) \quad (i = c, a, m) \quad (13a)$$

$$x_{ac} = x_a/(x_a + x_m G_{mc,ac}) \quad (13b)$$

$$x_{ca} = x_c/(x_c + x_m G_{ma,ca}) \quad (13c)$$

In order to obtain an expression for the excess Gibbs energy, $g^{(a)}$, $g^{(c)}$, and $g^{(m)}$ are defined as the residual Gibbs energies per mole of cells of central anion, central cation, and central solvent molecule, respectively. These Gibbs energies are related to the local mole fractions as follows:

$$g^{(a)} = Z_a(x_{ma}g_{ma} + x_{ca}g_{ca}) \quad (14a)$$

$$g^{(c)} = Z_c(x_{mc}g_{mc} + x_{ac}g_{ac}) \quad (14b)$$

$$g^{(m)} = x_{am}g_{am} + x_{cm}g_{cm} + x_{mm}g_{mm} \quad (14c)$$

The next step is to determine the reference state Gibbs energies. As discussed previously pure solvent is the reference state for the solvent, and pure completely dissociated liquid electrolyte is the reference state for the electrolyte. The reference Gibbs energies per mole are then

$$g_{ref}^{(c)} = Z_c g_{ac} \quad (15a)$$

$$g_{ref}^{(a)} = Z_a g_{ca} \quad (15b)$$

$$g_{ref}^{(m)} = g_{mm} \quad (15c)$$

In Eqs. 14 and 15 the charge numbers, Z_c and Z_a, are introduced to account for the fact that the ratio of the coordination number of central anion cells to that of central cation cells must be equal to the corresponding ratio of charge numbers. The coordination number of central multivalent ions is that of central univalent ions multiplied by the charge number. In order to account for the difference in the coordination numbers while using the same nonrandomness factor for all ions, the reference Gibbs energy of central multivalent ions is that of central univalent ions multiplied by the charge number.

The molar excess Gibbs energy may now be derived by summing the changes in residual Gibbs energy resulting when x_m moles of solvent are transferred from the solvent reference state to their cells in the mixture, and when x_a moles of anions and x_c moles of cations are transferred from the electrolyte reference state to their respective cells in the mixture. The expression is

$$g^{ex,lc} = x_m(g^{(m)} - g^{(m)}_{ref}) + x_c(g^{(c)} - g^{(c)}_{ref}) + x_a(g^{(a)} - g^{(a)}_{ref}) \quad (16)$$

Substituting Eqs. 14 and 15 into Eq. 16 one obtains

$$g^{ex,lc}/RT = x_m x_{cm} \tau_{cm} + x_m x_{am} \tau_{am} + x_c x_{mc} Z_c \tau_{mc,ac} + x_a x_{ma} Z_a \tau_{ma,ca} \quad (17)$$

The assumption of local electroneutrality applied to the cells of central solvent molecules may be stated as

$$x_{am} Z_a = x_{cm} Z_c \quad (18)$$

Substituting Eq. 6 into this relationship leads to the following equality

$$g_{am} = g_{cm} \quad (19)$$

Since the interaction energies are symmetric, it may be inferred from this result that

$$\tau_{am} = \tau_{cm} = \tau_{ca,m} \quad (20a)$$

$$\tau_{mc,ac} = \tau_{ma,ca} = \tau_{m,ca} \quad (20b)$$

The binary parameters $\tau_{ca,m}$ and $\tau_{m,ca}$ then become the only two adjustable parameters for a binary pair of single completely dissociated electrolyte and single solvent. Hereafter, they will be referred to as the salt-molecule parameter and the molecule-salt parameter, respectively.

In order to combine Eq. 17 with the Pitzer-Debye-Hückel formula, which accounts for the long range contribution, it must be normalized to the infinite dilution reference state for the ions:

$$g^{ex^*,lc}/RT = g^{ex,lc}/RT - x_c \ln\gamma_c^{\infty} - x_a \ln\gamma_a^{\infty} \quad (21)$$

Using Eq. 17 to obtain $\ln\gamma_c^{\infty}$ and $\ln\gamma_a^{\infty}$ and substituting back into Eq. 21 yields the final unsymmetric expression:

$$\begin{aligned} g^{ex^*,lc}/RT = {} & x_m(x_{cm} + x_{am})\tau_{ca,m} \\ & + x_c x_{mc} Z_c \tau_{m,ca} + x_a x_{ma} Z_a \tau_{m,ca} \\ & - x_c(Z_c \tau_{m,ca} + G_{cm}\tau_{ca,m}) \\ & - x_a(Z_a \tau_{m,ca} + G_{am}\tau_{ca,m}) \quad (22) \end{aligned}$$

The corresponding activity coefficient expressions for the three species present are

$$\begin{aligned} \ln\gamma_c^{lc^*} = {} & x_m^2 \tau_{cm} G_{cm}/(x_c G_{cm} + x_a G_{am} + x_m)^2 \\ & - Z_a x_a \tau_{ma} x_m G_{ma}/(x_c + x_m G_{ma})^2 \\ & + Z_c x_m \tau_{mc} G_{mc}/(x_a + x_m G_{mc}) \\ & - Z_c \tau_{mc} - G_{cm}\tau_{cm} \quad (23) \end{aligned}$$

$$\begin{aligned} \ln\gamma_a^{lc^*} = {} & x_m^2 \tau_{am} G_{am}/(x_c G_{cm} + x_a G_{am} + x_m)^2 \\ & - Z_c x_c \tau_{mc} x_m G_{mc}/(x_a + x_m G_{mc})^2 \\ & + Z_a x_m \tau_{ma} G_{ma}/(x_c + x_m G_{ma}) \\ & - Z_a \tau_{ma} - G_{am}\tau_{am} \quad (24) \end{aligned}$$

$$\begin{aligned} \ln\gamma_m^{lc} = {} & x_{cm}\tau_{cm} + x_{am}\tau_{am} \\ & + Z_c x_c G_{mc} \tau_{mc} x_a/(x_a + G_{mc} x_m)^2 \\ & + Z_a x_a G_{ma} \tau_{ma} x_c/(x_c + G_{ma} x_m)^2 \\ & - x_c x_m G_{cm} \tau_{cm}/(x_c G_{cm} + x_a G_{am} + x_m)^2 \\ & - x_a x_m G_{am} \tau_{am}/(x_c G_{cm} + x_a G_{am} + x_m)^2 \quad (25) \end{aligned}$$

Equations 22 and 2 may be combined with Eq. 1a to give the complete local composition model for excess Gibbs energy. Similarly, Eqs. 23 for cation, 24 for anion, or 25 for molecular species and Eq. 5 may be combined with Eq. 1b to give the complete local composition model for activity coefficient.

DISCUSSION OF ASSUMPTIONS

The like-ion repulsion assumption may be justified on the basis that repulsive forces between ions of the same sign are known to be very strong for neighboring species. For example, in the lattice of ionic salt crystals the immediate neighbors of any central ion are always ions of opposite charge. Similarly, the coordination ligands of any central ionic species are either ions of opposite charge or neutral molecules.

For any electrolyte system, the local electroneutrality assumption implies that the net local ionic charge around a central solvent molecule is zero. In other words, the interaction energy between cation and solvent molecule is the same as that between anion and solvent molecule. This is reasonable since the mutual potential energy of a point charge Ze and a dipole of moment μ, is known to be:

$$Ze\,\mu\,\cos\theta/r^2D$$

where θ is the angle between the axis of the dipole and the radius vector passing through the ion (Robinson and Stokes, 1970). In the case of unsymmetric electrolytes, adjustment in the separation distance r or the angle θ can make the interaction energy between cation and solvent molecule equal to that between anion and solvent molecule. Local electroneutrality is also observed for interstitial molecules in ionic salt crystals. An interesting implication of the local electroneutrality assumption, through Eqs. 19 and 20, is that anion-molecule and cation-molecule interaction energies are not independently observable. A further result is that the cation and anion activity coefficients are equal for any single solvent, single symmetric electrolyte system. These observations are consistent with the fact that only mean ionic activity coefficients are observable in this type of system.

DATA CORRELATION USING NEW MODEL

Data of molal mean ionic activity coefficient and vapor pressure depression of various single electrolyte, single solvent systems have been correlated successfully with the assumption that the electrolyte dissociates completely in the solution. Some results are shown in Figure 2 and Tables 1 and 2. The least squares data cor-

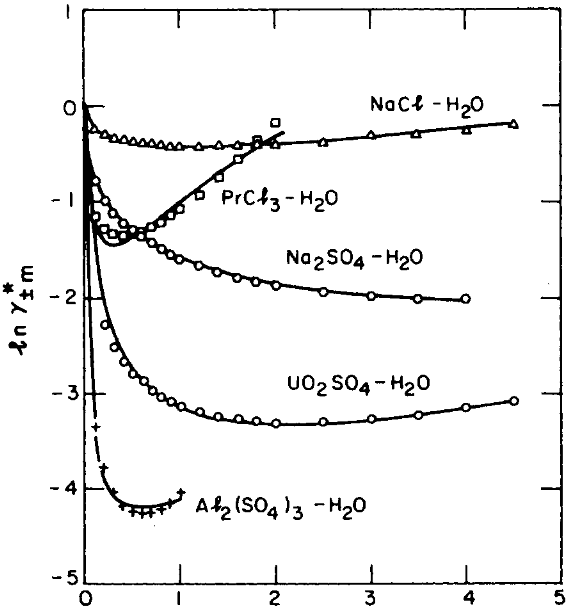

Figure 2. Comparison of experimental and calculated molality mean ionic activity coefficients of various aqueous electrolytes at 298.15 K.

TABLE 1. RESULTS OF FIT FOR MOLALITY MEAN IONIC ACTIVITY COEFFICIENT DATA OF AQUEOUS ELECTROLYTES AT 298.15 K
(DATA FROM ROBINSON AND STOKES, 1970)

1-1 Electrolyte:	$\tau_{m,ca}$	$\tau_{ca,m}$	$\sigma_{ln\gamma}$	max. m
$AgNO_3$	7.420	−3.285	0.010	6.0
CsAc	8.596	−4.626	0.010	3.5
CsBr	8.510	−4.188	0.006	5.0
CsCl	8.530	−4.210	0.006	6.0
CsI	8.337	−4.087	0.007	3.0
$CsNO_3$	8.996	−4.153	0.003	1.4
HBr	9.823	−5.173	0.015	3.0
HCl	10.089	−5.212	0.035	6.0
$HClO_4$	10.601	−5.422	0.063	6.0
HI	9.577	−5.150	0.018	3.0
HNO_3	8.429	−4.463	0.008	3.0
KAc	8.590	−4.602	0.008	3.5
KBr	8.093	−4.143	0.004	5.5
KCl	8.064	−4.107	0.003	4.5
KCNS	7.516	−3.846	0.002	5.0
KF	8.792	−4.500	0.005	4.0
KH Adipate	5.538	−2.986	0.002	1.0
KH Malonate	7.489	−3.661	0.005	5.0
KH Succinate	8.108	−4.022	0.003	4.5
KH_2AsO_4	8.004	−3.735	0.003	1.2
KH_2PO_4	8.932	−4.116	0.004	1.8
KI	7.800	−4.069	0.005	4.5
KNO_3	7.673	−3.479	0.008	3.5
KOH	9.868	−5.059	0.023	6.0
LiAc	8.441	−4.417	0.005	4.0
LiBr	10.449	−5.348	0.050	6.0
LiCl	10.031	−5.154	0.040	6.0
$LiClO_4$	9.579	−5.088	0.023	4.0
LiI	9.257	−4.987	0.024	3.0
$LiNO_3$	8.987	−4.707	0.013	6.0
LiOH	9.008	−4.400	0.026	4.0
LiTol	7.567	−3.895	0.013	4.5
NaAc	8.392	−4.489	0.007	3.5
NaBr	8.793	−4.562	0.009	4.0
$NaBrO_3$	7.593	−3.709	0.002	2.5
Na Butyrate	7.526	−4.300	0.007	3.5
Na Caprate	11.729	−4.836	0.024	1.8
NaCl	8.885	−4.549	0.018	6.0
$NaClO_3$	7.225	−3.692	0.005	3.5
$NaClO_4$	8.021	−4.131	0.010	6.0
NaCNS	7.941	−4.238	0.010	4.0
NaF	7.540	−3.800	0.000	1.0
Na Formate	7.437	−3.942	0.004	3.5
NaH Malonate	7.694	−3.850	0.002	5.0
NaH Succinate	8.226	−4.133	0.002	5.0
NaH_2PO_4	8.277	−3.892	0.003	6.0
NaI	8.862	−4.652	0.010	3.5
$NaNO_3$	7.300	−3.620	0.002	6.0
NaOH	9.372	−4.777	0.029	6.0
Na Pelargonate	10.931	−4.657	0.042	2.5
Na Propionate	8.400	−4.559	0.006	3.0
NH_4Cl	7.842	−4.005	0.001	6.0
NH_4NO_3	7.359	−3.526	0.012	6.0
RbAc	8.728	−4.666	0.009	3.5
RbBr	8.078	−4.063	0.002	5.0
RbCl	8.239	−4.148	0.002	5.0
RbI	8.203	−4.115	0.003	5.0
$RbNO_3$	7.718	−3.464	0.012	4.5
TlAc	7.862	−3.821	0.012	6.0
1-2 Electrolyte:				
Cs_2SO_4	7.254	−4.113	0.009	1.8
K_2CrO_4	8.155	−4.542	0.022	3.5
K_2SO_4	9.247	−4.964	0.008	0.7
Li_2SO_4	8.416	−4.771	0.023	3.0
Na_2CrO_4	8.857	−4.912	0.057	4.0
Na_2 Fumarate	8.834	−5.020	0.003	2.0
Na_2 Maleate	9.375	−5.078	0.020	3.0
Na_2SO_4	8.389	−4.539	0.024	4.0
$Na_2S_2O_3$	8.510	−4.705	0.030	3.5
$(NH_4)_2SO_4$	8.623	−4.602	0.017	4.0
Rb_2SO_4	7.312	−4.086	0.009	1.8

2-1 Electrolyte:	$\tau_{m,ca}$	$\tau_{ca,m}$	$\sigma_{ln\gamma}$	max. m
$BaBr_2$	8.292	−5.022	0.026	2.0
$Ba(ClO_4)_2$	9.709	−5.592	0.072	5.0
BaI_2	9.340	−5.564	0.034	2.0
$CaBr_2$	12.175	−6.553	0.351	6.0
$CaCl_2$	11.396	−6.218	0.205	6.0
$Ca(ClO_4)_2$	12.058	−6.579	0.272	6.0
CaI_2	9.861	−5.809	0.046	2.0
$Ca(NO_3)_2$	8.982	−5.098	0.060	6.0
$CdBr_2$	11.656	−5.498	0.258	4.0
$CdCl_2$	10.621	−5.066	0.214	6.0
CdI_2	13.510	−6.179	0.374	2.5
$CoBr_2$	11.422	−6.339	0.141	5.0
$CoCl_2$	10.111	−5.771	0.055	4.0
CoI_2	12.350	−6.731	0.242	6.0
$Co(NO_3)_2$	10.460	−5.866	0.108	5.0
$CuCl_2$	7.888	−4.771	0.038	6.0
$Cu(NO_3)_2$	10.346	−5.782	0.113	6.0
$FeCl_2$	9.118	−5.377	0.029	2.0
$MgAc_2$	9.148	−5.141	0.013	4.0
$MgBr_2$	11.978	−6.547	0.241	5.0
$MgCl_2$	11.579	−6.338	0.202	5.0
$Mg(ClO_4)_2$	11.948	−6.620	0.208	4.0
MgI_2	12.467	−6.775	0.316	5.0
$Mg(NO_3)_2$	10.655	−5.969	0.125	5.0
$MnCl_2$	9.554	−5.508	0.047	6.0
$NiCl_2$	10.751	−6.013	0.092	5.0
$Pb(ClO_4)_2$	10.853	−6.030	0.147	6.0
$Pb(NO_3)_2$	9.143	−4.695	0.022	2.0
$SrBr_2$	9.305	−5.475	0.036	2.0
$SrCl_2$	10.285	−5.784	0.088	4.0
$Sr(ClO_4)_2$	11.415	−6.305	0.168	6.0
SrI_2	9.655	−5.704	0.046	2.0
$Sr(NO_3)_2$	6.774	−4.000	0.029	4.0
UO_2Cl_2	8.923	−5.386	0.040	3.0
$UO_2(ClO_4)_2$	13.393	−7.184	0.447	5.5
$UO_2(NO_3)_2$	9.216	−5.542	0.041	5.5
$ZnCl_2$	7.997	−4.660	0.119	6.0
$Zn(ClO_4)_2$	12.118	−6.675	0.211	4.0
$Zn(NO_3)_2$	10.750	−5.995	0.148	6.0
2-2 Electrolyte:				
$BeSO_4$	11.556	−6.984	0.039	4.0
$MgSO_4$	11.346	−6.862	0.036	3.5
$MnSO_4$	11.294	−6.805	0.037	4.0
$NiSO_4$	11.378	−6.837	0.031	2.5
$CuSO_4$	11.703	−6.993	0.037	1.4
$ZnSO_4$	11.476	−6.888	0.038	3.5
$CdSO_4$	11.228	−6.755	0.037	3.5
UO_2SO_4	11.201	−6.764	0.050	6.0
3-1 Electrolyte:				
$AlCl_3$	10.399	−6.255	0.115	1.8
$CeCl_3$	9.398	−5.775	0.084	2.0
$Co(en)_3Cl_3$	7.534	−4.278	0.013	1.0
$CrCl_3$	6.567	−4.916	0.069	1.2
$Cr(NO_3)_3$	6.276	−4.777	0.054	1.4
$EuCl_3$	9.555	−5.856	0.091	2.0
$Ga(ClO_4)_3$	11.302	−6.740	0.228	2.0
$K_3Fe(CN)_6$	6.459	−3.806	0.019	1.4
$LaCl_3$	9.290	−5.737	0.082	2.0
$NdCl_3$	9.524	−5.822	0.083	2.0
$PrCl_3$	9.420	−5.779	0.082	2.0
$ScCl_3$	9.664	−5.943	0.078	1.8
$SmCl_3$	9.533	−5.840	0.087	2.0
YCl_3	9.906	−5.991	0.093	2.0
3-2 Electrolyte:				
$Al_2(SO_4)_3$	10.646	−7.116	0.075	1.0
$Cr_2(SO_4)_3$	6.705	−5.568	0.129	1.2

TABLE 2. RESULTS OF FIT FOR VAPOR PRESSURE DEPRESSION DATA OF METHANOL ELECTROLYTE SYSTEMS AT 298.05 K (DATA FROM BIXON ET AL., 1979)

Electrolyte	$\tau_{m,ca}$	$\tau_{ca,m}$	σ_p	max. m
KI	12.221	−5.647	0.003	1.1
LiCl	11.908	−5.616	0.034	5.4
NaBr	11.476	−5.430	0.003	1.6
NaOH	10.534	−5.698	0.017	5.9
NaI	9.958	−5.280	0.010	4.5
$CaCl_2$	10.112	−5.666	0.012	2.6
$CuCl_2$	8.865	−4.897	0.010	4.0

Methanol Dielectric Constant: 32.63
Methanol Density: 786.8 kg/m^3
Methanol Vapor Pressure: 16,732 Pa

relation was carried out on deviations between calculated and experimental quantities:

$$S_\gamma = \sum_i (ln\gamma^{*cal}_{\pm m,i} - ln\gamma^{*exp}_{\pm m,i})^2 \tag{26}$$

$$S_p = \sum_i ((p_i^{cal} - p_i^{exp})/p_i^{exp})^2 \tag{27}$$

The molal mean ionic activity coefficient $\gamma^*_{\pm m}$ is obtained from the mole fraction mean ionic activity coefficient as follows:

$$ln\ \gamma^*_{\pm m} = ln\gamma^*_{\pm} - ln(1 + M_S(\nu_c + \nu_a)m/1{,}000)$$

The Debye-Hückel parameter for aqueous electrolyte systems is calculated by the following expression

$$\begin{aligned} A_\phi = {} & -61.44534\exp((T - 273.15)/273.15) \\ & + 2.864468(\exp((T - 273.15)/273.15))^2 \\ & + 183.5379\ ln(T/273.15) - 0.6820223(T - 273.15) \\ & + 0.0007875695(T^2 - (273.15)^2) + 58.95788(273.15/T) \end{aligned} \tag{29}$$

obtained from data correlation of the Debye-Hückel parameter values reported by Pitzer and Silvester (1976).

As discussed previously, it is desirable that ρ in the Pitzer-Debye-Hückel expression have a fixed value, much as it is desirable for α in the local composition expression to be fixed. A value of 14.9 was used by Pitzer (1980) on his work for the (Ag,Tl)NO_3-H_2O and (Li,K)NO_3-H_2O systems. This value has been found to be quite satisfactory in this study. In an effort to determine the sensitivity of the model to ρ, data correlations were carried out for many electrolyte systems with the two salt-molecule binary parameters and ρ as adjustable parameters. It was found that the results were not enough better to justify ρ as a third adjustable parameter. A different treatment of ρ might be desirable as more experience is gained with the model.

With ρ set to 14.9, data for many binary systems were correlated satisfactorily. For example, with only the two binary salt-molecular parameters as adjustable parameters, the average standard deviation of calculated vs. measured $ln\gamma^*_{\pm m}$ for the 59 uni-univalent aqueous single electrolyte systems listed in Table 1 is 0.01. Although the fit is not as good as that obtained with Pitzer equation, which requires both binary and ternary parameters (Pitzer and Mayorga, 1973) and applies only to aqueous systems, it is quite satisfactory and better than that obtained with Bromley's equation (Bromley, 1973).

It is important to recognize that, while the model may not be dramatically better than others for particular systems, no other model has been designed to be applicable over as wide a range of electrolyte concentrations or to as wide a variety of electrolyte systems. Further, it is emphasized that results shown in Tables 1 and 2 were obtained with the assumption that the binary systems are a mixture of solvent and completely dissociated electrolyte. Neither complex ion formation nor chemical equilibrium between molecular species and ionic species of electrolyte systems are considered. To account for the chemical equilibria rigorously one has to treat these electrolyte systems as multicomponent systems.

BINARY INTERACTION PARAMETERS

In the previous data correlation study, only two binary interaction parameters were adjusted. The salt-molecule parameter, $\tau_{ca,m}$, is the difference of the dimensionless interaction energies between the ion-molecule pair and the molecule-molecule pair. The molecule-salt parameter, $\tau_{m,ca}$, is the difference of the dimensionless interaction energies between the molecule-ion pair and the cation-anion pair.

It is well known that local composition model binary parameters are not well determined for molecular systems, even when the fit is very good. The fitted parameters generally have relatively large standard deviations and are very strongly correlated. In contrast, the binary parameters of this study are very well determined, with parameter standard deivations typically 1% of the parameter value. This result is not surprising since the interaction between the cation and the anion is stronger than the interaction between the solvent molecules and the ionic species which, in turn, is stronger than the interaction between two solvent molecules. Therefore, $\tau_{ca,m}$ should be dominated by g_{cm} (= g_{am}) and $\tau_{m,ca}$ should be dominated by g_{ac}. This is in contrast to molecular systems in which the parameters are always differences between molecule-molecule interactions, presumably of like magnitude. The above discussion is verified by the results of this study which show all $\tau_{ca,m}$'s to be negative and all $\tau_{m,ca}$'s to be positive and to have the expected relative magnitudes.

The relationship between the binary parameters and the interaction energies can also be observed from the significant correlation between values of the binary parameter difference ($\tau_{ca,m} - \tau_{m,ca} = (g_{ac} - g_{mm})/RT$) and the standard deviations of calculated vs. measured data shown in Tables 1 and 2. When absolute values of the binary parameter difference increase, the standard deviations also increase. This is consistent with the proposed physical meaning of the binary parameters. The larger the absolute values of the binary parameter difference, the stronger the interaction between cation and anion, and the greater the tendency for the ions to associate and form complex ions, ion-pairs, or even molecular species. When this association occurs, the assumption of complete dissociation of electrolytes becomes approximate and the local composition model for binary systems is less valid. To be completely rigorous, these electrolyte systems should be considered as multi-

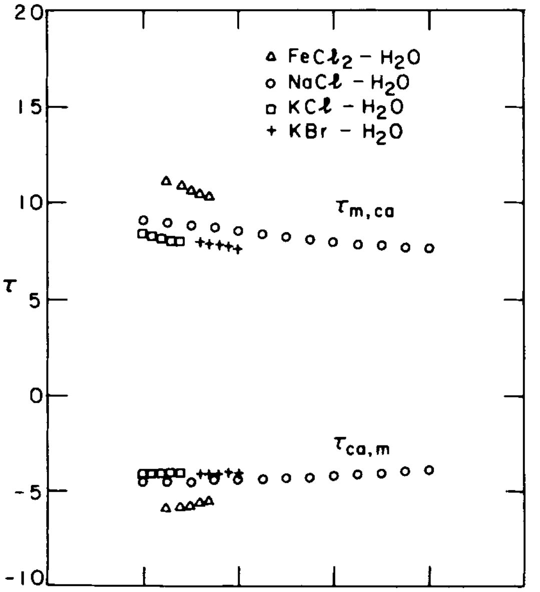

Figure 3. Binary parameters as determined from isothermal fits at various temperatures ($FeCl_2$ data from Susarev et al., 1973; NaCl data from Silvester and Pitzer, 1976; KCl data from Dobos, 1975; KBr data from Robinson and Stokes, 1970).

TABLE 3. COMPARISON OF ACIDIC DISSOCIATION CONSTANTS WITH BINARY PARAMETER DIFERENCE

Acid	$pK_a(= -\log K_a)$*	$\lvert \tau_{m,ca} - \tau_{ca,m} \rvert$
HCl	−6.1	15.301
HBr	−9	14.996
HI	−9.5	14.727

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* (Dean, 1973)

component systems and chemical equilibrium among various species should be taken into account when correlating data.

The relation between the binary parameters and ion association can be further supported by the acidic dissociation constants of three strong acids: HCl, HBr and HI. As shown in Table 3, absolute values of the binary parameter difference increase when ionic association increases and acidic dissociation constants decrease (pK_a increases). The weaker the acid, the less complete the acid dissociation, and the larger the absolute values of the binary parameter difference.

The binary parameters are found to be weak but nonrandom functions of temperature. Figure 3 shows the results of isothermal fits for molality mean ionic activity coefficient data of aqueous KBr, KCl, and NaCl systems along with the results of isothermal fits for water vapor pressure depression of aqueous $FeCl_2$ system at various temperatures. Weak temperature dependence of the binary parameters is observed for all cases, including the aqueous NaCl system data which cover a temperature range from 273 K to 573 K. The weak temperature dependence of the binary parameters is an important and desirable property of the local composition model.

FROM MOLECULAR LIQUID TO FUSED SALT

The local composition model is designed to be applicable to the entire range of electrolyte concentrations. To test the model at high electrolyte concentrations, three electrolyte systems extending in the liquid phase from a dilute solution in water to a pure fused salt were studied. The data are water vapor pressures of the (Ag,Tl)-NO_3-H_2O system (Trudelle et al., 1977), the (Ag,Tl,Na)NO_3-H_2O system (Abraham et al., 1980), and the (Li,K)NO_3-H_2O system (Tripp and Braunstein, 1969; Tripp, 1975). These electrolyte systems are treated as pseudo single electrolyte systems because the cation mixtures have fixed composition and one can assume that the cation mixture behaves like a single cation.

TABLE 4. DATA CORRELATION OF WATER PRESSURE OF (Ag,Tl,Na)-NO_3-H_2O SYSTEM AT 371.65 K (DATA FROM TRUDELLE ET AL., 1977; ABRAHAM ET AL., 1980)

	$\tau_{m,ca}$	$\tau_{ca,m}$	σ_p
Ag/Tl mol ratio = 1.14			
S_0	6.330	−2.753	0.008
Ag/Tl Ratio = 1.06			
$S_{2.5}$	6.431	−2.784	0.005
S_5	6.518	−2.828	0.005
$S_{7.5}$	6.570	−2.871	0.004
$S_{10.1}$	6.595	−2.908	0.003

S_x indicates the mol percentages of $NaNO_3$ in the (Ag,Tl,Na)NO_3 melt.

TABLE 5. DATA CORRELATION OF WATER VAPOR PRESSURE OF (Li,K)NO_3-H_2O SYSTEM (DATA FROM TRIPP, 1975; TRIPP AND BRAUNSTEIN, 1969)

T	$\tau_{m,ca}$	$\tau_{ca,m}$	σ_p
383.15	9.247	−3.979	0.009
392.15	8.807	−4.033	0.006
402.66	8.658	−4.026	0.007
413.15	8.509	−4.037	0.007
423.15	7.988	−4.107	0.019

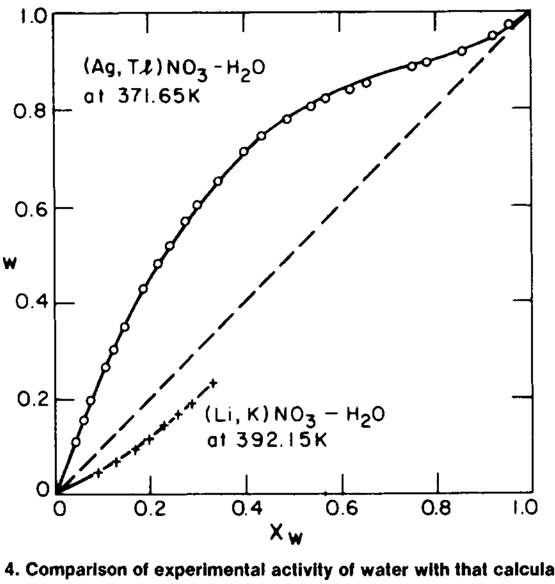

Figure 4. Comparison of experimental activity of water with that calculated from the local composition model.

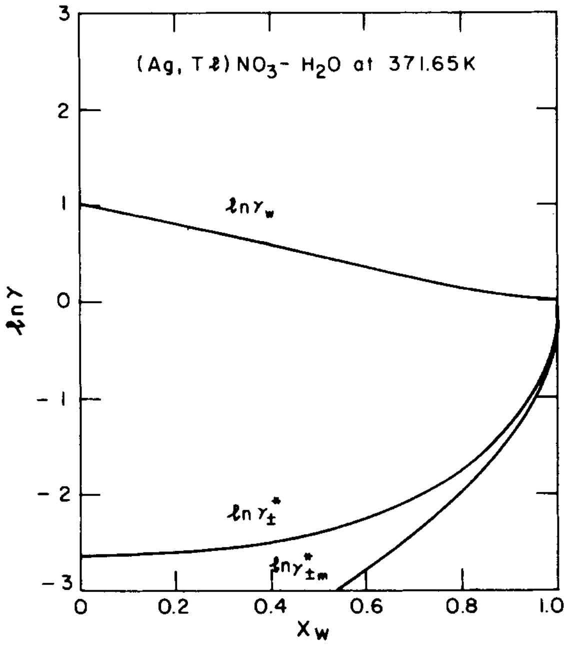

Figure 5. Activity coefficients for both water and salt for system (Ag,Tl)-NO_3-H_2O at 371.65 K.

Tables 4 and 5 show the correlation results. The standard deviations of calculated vs. measured water vapor pressure are less than 0.01, which is within the experimental uncertainty. Table 4 shows the behavior of binary parameters as a function of fused salt composition and Table 5 shows how the binary parameters change as a function of temperature. Figure 4 shows the comparison of the experimental water activity with that calculated from the local composition model. Activity coefficients for both water and fused salt for the (Ag,Tl)NO_3-H_2O system at 371.65 K are shown in Figure 5.

This correlation study of electrolyte systems from dilute solution to fused salt indicates that the local composition model is applicable over the entire range of electrolyte concentrations.

DISCUSSION OF LOCAL COMPOSITION MODEL

The local composition model assumes that the Debye-Hückel formula is adequate to represent the contribution of long range

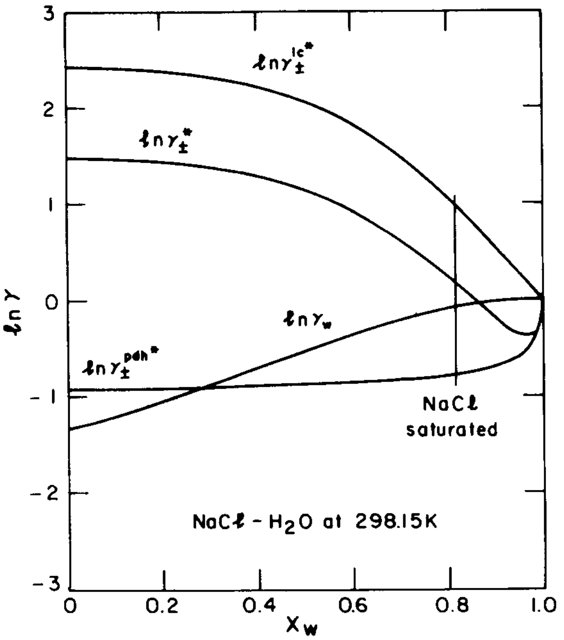

Figure 6. Comparison of short-range contribution and long-range contribution on mean ionic activity coefficients of NaCl-H_2O system at 298.15 K.

ion-ion electrostatic interactions and that the local composition concept can account for the contribution of short range interactions among all species. While both the separation of the long range effect from the short range effect upon excess Gibbs energy and the validity of any specific Debye-Hückel formula at high ionic strength are questionable, it is believed that the short range contribution will dominate at high ionic strength, in which case it is not essential to account for the long range ion-ion electrostatic contribution exactly. A comparison of the short range interaction contribution based on the local composition concept and the long range interaction contribution based on the Pitzer-Debye-Hückel formula is shown in Figure 6 for the mean ionic activity coefficients of the aqueous NaCl system at 298.15 K. The short range interaction contribution increases linearly as ionic strength increases, while the long range interaction contribution increases rapidly in the very dilute region and then levels off at high ionic strength.

It is important to note that both the local composition model and the Debye-Hückel theory adopt the Boltzmann distribution for the local distribution of ions around a central species. Both assume that there are more anions than cations in the immediate neighborhood of a central cation and that there are more cations than anions in the immediate neighborhood of a central anion. In other words, there is a negative ionic atmosphere surrounding a central cation and there is a positive ionic atmosphere surrounding a central anion (Chu, 1967). The fact that the same distribution law was adopted in both the short range and long range interaction models is a significant feature of the approach.

In a recent paper by Cruz and Renon (1978), another local composition model has been presented for electrolyte systems. As in this work, the excess Gibbs energy was decomposed into two contributions: long range interaction contribution and short range interaction contribution. The long range contribution is calculated by a Debye-Hückel expression and a Debye-McAulay term to account for the change of dielectric constant of the solvent due to the presence of ions. The short range contribution is calculated according to the NRTL equation with the solvation theory as the basis for assigning local compositions around ions. The model requires four adjustable parameters to correlate data of isothermal, aqueous single completely dissociated electrolyte systems. Two parameters are involved in the dielectric constant expression of the Debye-McAulay theory and the remaining two are the NRTL parameters related to ion-solvent interaction.

Most importantly, the local composition model presented in this work and the Cruz and Renon model are based on different assumptions about the local lattice structure of electrolyte solutions. Adopting solvation theory, Cruz and Renon suggest that ionic species are completely solvated by solvent molecules for completely dissociated electrolyte binary systems. In other words, the local mole fraction of solvent molecules around a central ion is assumed to be unity. This becomes unrealistic when applied to high concentration electrolyte systems since the number of solvent molecules will be insufficient to completely solvate ions. With the local composition model proposed in this work, all ions are, effectively, completely surrounded by solvent molecules in very dilute electrolyte systems and only partially surrounded by solvent molecules in high concentration electrolyte systems. One consequence is that the Cruz and Renon model, unlike our local composition model, cannot extend all the way to fused salts since their complete solvation assumption becomes meaningless. They were able to obtain good fits at electrolyte concentrations that were relatively high, although far short of the range of the model presented in this paper. This is probably because the adjustable parameters of the Debye-McAulay contribution enabled it to empirically account for short-range effects at high concentration, even though the theory is not intended to apply to short range forces.

In terms of interaction energies, the Cruz and Renon model suggests that the absolute values of the interaction energies between various pairs are in the following order: g_{mc} or $g_{ma} < g_{mm} \ll g_{ca} < g_{cc}$ or g_{aa}, while our local composition model suggests a different order: $g_{mm} \ll g_{mc}$ or $g_{ma} \ll g_{ca}$ or g_{cc} or g_{aa}.

Our local composition model can be readily extended to handle multicomponent electrolyte systems, including both strong electrolytes and weak electrolytes, over the entire range of concentrations. Compared to the model of this paper, the multicomponent model must be able to represent multicomponent behavior with binary parameters determined from subsystem data and must be able to accurately represent individual cation and anion activities and not simply mean ionic activities. The extension of the local composition model to multicomponent systems is the topic of part two of this series.

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NOTATION

A_ϕ = Debye-Hückel constant for the osmotic coefficient
D = dielectric constant
I_x = ionic strength in mole fraction scale
M_s = solvent molecular weight (kg/kg-mol)
N_0 = Avogadro's number
P = pressure (N/m^2)
R = gas constant
T = temperature (K)
Z = absolute value of ionic charge
d = solvent density
e = electron charge
g^{ex} = molar excess Gibbs free energy
k = Boltzmann constant
m = molality (g-mole/kg of solvent)
x = true liquid phase mole fraction based on all species: molecular and ionic

Greek Letters

α = NRTL nonrandomness factor
ϕ = osmotic coefficient
γ = activity coefficient
ν = electrolyte stoichiometric coefficient

ρ = the closest approach parameter of the Pitzer-Debye-Hückel equation
σ = standard deviation
τ = NRTL binary interaction energy parameter

Superscripts

$*$ = unsymmetric convention
∞ = infinite dilution
pdh = long range contribution, represented by the Pitzer-Debye-Hückel equation
lc = short range contribution, represented by the local composition model
cal = calculated value
exp = experimental value

Subscripts

a, a' = anion
c, c' = cation
ca = salt ca
i, j, k = any species
m = any molecular species
ref = reference
$\pm$ = mean ionic, mole fraction scale
$\pm m$ = mean ionic, molality scale

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