

## Thermodynamic behavior of electrolyte solutions

### Part I. Activity coefficients and osmotic coefficients of binary systems

Cheng-Long Lin

*Department of Chemical Engineering, National Taiwan Institute of Technology,  
Taipei 10672 (Taiwan)*

Liang-Sun Lee

*Department of Chemical Engineering, National Central University, Chungli 32054 (Taiwan)*

Hsieng-Cheng Tseng \*

*Department of Chemical Engineering, National Taiwan Institute of Technology,  
Taipei 10672 (Taiwan)*

(Received August 3, 1992; accepted in final form February 15, 1993)

#### ABSTRACT

Lin, C.-L., Lee, L.-S. and Tseng, H.-C., 1993. Thermodynamic behavior of electrolyte solutions. Part I. Activity coefficients and osmotic coefficients of binary systems. *Fluid Phase Equilibria* 90: 57–79.

A predictive model with three parameters for the calculation of activity coefficients and osmotic coefficients of strong electrolytes in binary solutions is developed. In this development, the Poisson–Boltzmann equation was employed to account for the long-range, ion–ion interactions, and the concept of solvation was employed to account for the short-range, ion–molecule interactions.

All three parameters included in the proposed model are expressed clearly with physical explanations. They are (1) the closest distance of approach,  $\tilde{a}$ , (2) the equivalent dielectric constant,  $\tilde{D}_e$ , and (3) the solvation parameter,  $S$ . In the first part of this paper, experimental data obtained from the literature are fitted to the present model. These three parameters are also obtained for 144 aqueous electrolyte solutions and 16 non-aqueous electrolyte solutions. It is found that  $\tilde{a}$  is independent of temperature and solvent, while  $S$  is temperature independent only. It is shown that the proposed model can be applied conveniently to systems other than those at 298.15 K and to non-aqueous electrolyte solutions. In the second part, this model is extended to predict vapor–liquid equilibria of mixed-solvent electrolyte systems.

**Keywords:** theory, application, methods of calculation, activity coefficient, osmotic coefficient, dielectric constant, electrolytes, water.

---

\* Corresponding author.

## INTRODUCTION

To understand the thermodynamic behavior of electrolyte solutions is essential and important to the design and operation of separation processes, such as distillation, extraction, absorption, etc. It is known that the complex behavior of electrolyte solutions is more difficult to describe than that of hydrocarbon mixtures. In an electrolyte solution, the electrolyte will dissociate into cations and anions. Thus there exist complicated interactions between ion and ion, ion and molecule, and molecule and molecule. Since the thermodynamic properties of solutions are strongly dependent upon the particle interactions, it is difficult to predict the thermodynamic properties of electrolyte solutions accurately.

One of the most important thermodynamic properties of an electrolyte solution is the mean activity coefficient of the electrolyte which reflects the non-ideality of the solution. Although mean activity coefficients can be obtained by experiment (Robinson and Stokes, 1959; Hamer and Wu, 1972), the development of theoretical or empirical ways of estimating them is still necessary to supplement the tedious, time-consuming experimental work. Meissner and Tester (1972) have summarized most of the experimental data on electrolyte solutions, and have developed a graphical method to predict activity coefficients of electrolytes. Although the error of this method is approximately 10%, it is still useful when the experimental data are not available. This method was later extended for computer use by Meissner and Kusik (1972, 1973). The earliest theoretical model for estimation is the well-known Debye–Hückel law which takes into account the long-range interactions of ions for activity coefficients of electrolyte solutions. Since this model is suitable only to very dilute solutions, its practical usage is limited. Robinson and Stokes (1959) modified the Debye–Hückel law by introducing the concept of hydration by considering the short-range interaction between ions and water molecules. This model is good for 1–1 and 1–2 type electrolytes with concentrations of up to 4 *m*. Brömley (1973) modified the Debye–Hückel model by adding a parameter to account for particle interactions. This model could predict activity coefficients of 1–1 type electrolyte solutions up to 6 *m*, but is limited to 1 *m* for other types of electrolytes. Pitzer and his coworkers (1973a, 1973b) proposed a model, also based on the Debye–Hückel model, with two additional virial parameters to account for the short-range interactions. This model can be applied to 1–1 and 1–2 types electrolyte solutions satisfactorily up to 6 *m*. Kawaguchi et al. (1981) applied the analytical solutions of groups (ASOG) model and a hydration model to calculate the activity of water in aqueous electrolyte solutions. The mean deviation is within 5% for several systems. Unfortunately, the activity coefficient of the electrolyte was not calculated. Chen and co-workers

(1982, 1986) combined the Pitzer–Debye–Hückel model for the long-range interaction and nonrandom two-liquid (NRTL) model for the short-range interaction. This model can be applied to most of the aqueous electrolyte solutions up to 6 *m*. Recently, Ghosh and Patwardhan (1990) developed a two-parameter model with the concept of solvation and chose LiCl as the reference electrolyte to calculate the activity coefficients of electrolytes in solutions. This model can only be applied to aqueous solutions containing one solute at 298.15 K. Ananth and Ramachandran (1990) extended the self-consistent local composition (SCLC) model (Govindan, 1984) and applied the perturbation theory to calculate those parameters that appeared in their model.

The models of Chen et al. (1982, 1986) and Ananth and Ramachandran (1990) mentioned above are based on the concept of local composition and contain three adjustable interaction parameters for a binary system. These parameters are empirically determined without clear physical explanations. When these models are applied to multicomponent systems, the number of parameters will extensively increase (nine parameters for a ternary system), and become very tedious to estimate.

A drawback of the aforementioned models is that the dielectric constant of the solvent, instead of solution, is used in those models. The composition dependence of the dielectric constant should be taken into account for accurate estimations (Chen and Evans, 1986). For instance, when an electrolyte is added to a solution, the dielectric constant of the solution is decreased and will affect the solution behavior. Only the approach of Cruz and Renon (1978) considered this effect in their model for osmotic coefficient calculations. Their model is able to fit the experimental data of 15 binary systems.

In this study, we propose a model for calculating activity coefficients of electrolytes and osmotic coefficients of solutions, based on the Poisson–Boltzmann equation to account for the long-range, ion–ion interactions, the concept of solvation to account for the short-range, ion–molecule interactions, and the consideration of the effect of dielectric constant. There are three parameters with clear physical meanings involved in the proposed model, and they are applicable to other systems without experimental data, once they are determined.

## POTENTIAL DUE TO ION–ION INTERACTIONS

In the electrolyte solution, the behavior of an ion is affected by its surrounding ions and molecules. The potential energy of an ion can be evaluated by considering the ion–ion interaction contributing to the long-range potential, and the ion–molecule interaction contributing to the short-range potential.

Consider a solution of a strong electrolyte dissociated completely into  $v_+$  cations with electric charge number  $z$ , and  $v_-$  anions with electric charge number  $w$ . The electric potential of a charged cation in an uniform electric field,  $\psi_c$ , can be described by the Poisson–Boltzmann equation (Guggenheim and Stokes, 1969).

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d\psi_c}{dr} \right) = -\frac{Ce}{\epsilon} \{v_+ z \exp(-ze\psi_c/kT) - v_- w \exp(we\psi_c/kT)\} \quad (1)$$

with boundary conditions

$$\text{B.C.1: } r \rightarrow \infty, \quad \psi_c = 0$$

$$\text{B.C.2: } r = \tilde{a}, \quad \frac{d\psi_c}{dr} = -\frac{ze}{4\pi\epsilon r^2}$$

where  $r$  is a radius of a spherical shell in which the ions obey Boltzmann distribution,  $C$  is the number of electrolyte molecules per unit volume of solution and can be approximated by  $C \cong A_v d_s m$  when the concentration of electrolyte solution is not too high, where  $A_v$  is the Avogadro constant,  $d_s$  is the density of the solvent, and  $m$  is the concentration of the solution, expressed in molality. The electrical permittivity  $\epsilon$  can be expressed as  $\epsilon = \epsilon_0 D_e$ , where  $\epsilon_0$  is the electrical permittivity in a vacuum, and  $D_e$  is the dielectric constant of the solution. Parameter  $\tilde{a}$  is the closest distance of approach which means that when  $r$  equals  $\tilde{a}$ , the second boundary condition, the electrical field is entirely due to the central ion, without any contribution from the others. Therefore, the potential energy due to surrounding ions is zero at this hypothetical distance. Equation (1) can be rewritten in a dimensionless form (Guggenheim and Stokes, 1969)

$$\frac{1}{x} \frac{d^2(x\Phi_c)}{dx^2} = \frac{\exp(w\Phi_c) - \exp(-z\Phi_c)}{w + z} \quad (2)$$

$$\text{B.C.1: } x \rightarrow \infty, \quad \Phi_c = 0$$

$$\text{B.C.2: } x = \kappa\tilde{a}, \quad x \frac{d\Phi_c}{dx} = -z\lambda/\tilde{a}$$

where

$$\Phi_c = e\psi_c/kT$$

$$x = \kappa r$$

$$\kappa = \{4\pi(v_+ z^2 + v_- w^2)\lambda C\}^{1/2}$$

$$\lambda = e^2/4\pi\epsilon kT$$

The potential,  $\Phi_c$ , can be considered as the combined contributions of the cation itself,  $\Phi_{ci}$ , and the surrounding ions,  $\Phi_{cr}$ . It can be derived from Coulomb's law that  $\Phi_{ci} = z\lambda/\tilde{a}$ . Therefore  $\Phi_{cr}$  can be expressed as

$$\Phi_{cr} = \Phi_c - z\lambda/\tilde{a} \quad (3)$$

Similarly, the potential considered of an anion can be shown as

$$\Phi_{ar} = \Phi_a - w\lambda/\tilde{a} \quad (4)$$

where  $\Phi_a$  is the dimensionless potential of the anion.  $\Phi_{ar}$  and  $w\lambda/\tilde{a}$  are the potentials contributed by the surrounding ions, and the anion itself respectively (Guggenheim and Stokes, 1969).

#### POTENTIAL DUE TO ION–MOLECULE INTERACTIONS

In an electrolyte solution, the ions may be surrounded by solvent molecules due to the solvent polarity. This specific interaction between ions and molecules is called solvation. By Coulomb's law, the electrical potential between a cation and a solvent molecule can be written as

$$\Gamma_{cs} = h_{cs}ze\mu/s^2 \quad (5)$$

where  $\mu$  is the dipole moment of a solvent,  $s$  is the distance between ion and solvent molecule and  $h_{cs}$  is a proportional parameter. The distance between particles is assumed to be dependent on the concentration of the solution in the following form

$$s = \beta m^{-n} \quad (6)$$

where  $n$  and  $\beta$  are parameters to be determined by experimental data. With substitution of eqn. (6) into eqn. (5), the electrical potential in terms of concentration becomes

$$\Gamma_{cs} = h_{cs}z(e\mu/\beta^2)m^{2n} \quad (7)$$

We define a dimensionless cation potential  $\Phi_{cs} = e\Gamma_{cs}/kT$ , and substitute  $\Gamma_{cs}$  into the numerator, and obtain

$$\Phi_{cs} = h_{cs}z(e^2\mu/\beta^2kT)m^{2n} \quad (8)$$

Similarly, the corresponding formula for the potential of an anion due to solvation is

$$\Phi_{as} = h_{as}w(e^2\mu/\beta^2kT)m^{2n} \quad (9)$$

### MEAN ACTIVITY COEFFICIENT OF ELECTROLYTE

If the theorem of charging process (Guggenheim and Stokes, 1969) is applied, the work needed for increasing the cation charge from 0 to  $ze$  is equal to the electrostatic potential of the surrounding ions,  $kT \ln \gamma_+$ . Therefore, the cation activity coefficient can be expressed as

$$\begin{aligned} \ln \gamma_+ &= \frac{1}{kT} \int_0^z (\psi_{cr} + \Gamma_{cs})e \, dz \\ &= \int_0^z \Phi_{cr} \, dz + h_{cs}(e^2\mu/\beta^2kT)m^{2n}(z^2/2) \end{aligned} \quad (10)$$

Similarly, for the anion activity coefficient

$$\ln \gamma_- = \int_0^w \Phi_{an} \, dw + h_{as}(e^2\mu/\beta^2kT)m^{2n}(w^2/2) \quad (11)$$

According to the definition of the mean activity coefficient of an electrolyte,  $\gamma_{\pm}$ ,

$$(v_+ + v_-) \ln \gamma_{\pm} = v_+ \ln \gamma_+ - v_- \ln \gamma_- \quad (12)$$

the equation to calculate  $\gamma_{\pm}$  can be obtained:

$$(v_+ + v_-) \ln \gamma_{\pm} = v_+ \int_0^z \Phi_{cr} \, dz + v_- \int_0^w \Phi_{ar} \, dw + S \cdot m^{2n} \quad (13)$$

where  $S$  can be considered as a 'solvation parameter', and is defined as

$$S = (e^2\mu/2\beta^2kT)(v_+ h_{cs}z^2 + v_- h_{cs}w^2) \quad (14)$$

The last term in eqn. (13),  $S \cdot m^{2n}$ , represents the short range interaction between the solvent molecule and the electrolyte.  $S$  is characteristic parameter of the electrolyte and the value of  $S$  is a measure of solvation tendency of the electrolyte.

There are four parameters  $n$ ,  $D_e$ ,  $\tilde{a}$ , and  $S$  in eqn. (13). These parameters can be obtained by fitting eqn. (13) to the available experimental data.

### OSMOTIC COEFFICIENT $\phi$ OF THE ELECTROLYTE SOLUTION

Another important thermodynamic property of an electrolyte solution is the osmotic coefficient, which is defined as

$$\phi = \frac{-1000}{vmM_s} \ln(a_s) \quad (15)$$

where  $a_s$  is the activity of the solvent,  $v = v_+ + v_-$ , and  $\phi$  is related to the

mean activity coefficient of the electrolyte by the following equation:

$$\phi = 1 + \frac{1}{m} \int_0^m m \, d \ln \gamma_{\pm} \quad (16)$$

The osmotic coefficient is usually obtained from the experimental value of vapor pressure of an electrolyte solution.

At low pressure, the fugacity coefficient of saturated liquid,  $\phi_s^s$ , and the fugacity coefficient of vapor,  $\phi_s$ , are very close to unity, so the relation of the vapor–liquid equilibrium of a volatile solvent in a binary system can be expressed as

$$a_s P_s^s = P \quad (17)$$

where  $P$  is the vapor pressure of a volatile solvent and  $P_s^s$  is the saturated vapor pressure of pure solvent at temperature  $T$ . Therefore, with known data for  $P_s^s$  and  $P$ , the activity of solvent,  $a_s$ , can be calculated from eqn. (17), and  $\phi$  for the solvent can then be calculated by eqn. (15).

## EVALUATION OF PARAMETERS

The dimensionless Poisson–Boltzmann equation, eqn. (2), is a highly nonlinear differential equation. It can be simplified to eqn. (18) for a very dilute solution

$$\frac{d^2(x\Phi_c)}{dx^2} = x\Phi_c \quad (18)$$

The analytical solution of this equation is the well-known Debye–Hückel law (Guggenheim and Stokes, 1969). However, this model is not of practical use since it is applicable only for concentration of less than 0.01  $m$ . For solutions of high concentration, the original governing equation, eqn. (2), has to be solved. Since the analytical solution is very difficult to obtain, the numerical approach is hence employed. In order to avoid difficulties encountered with the boundary condition of  $x \rightarrow \infty$ , eqn. (2) was transformed into the following form:

$$y^4 \frac{d^2\Phi_c}{dy^2} = \frac{\exp(w\Phi_c) - \exp(-z\Phi_c)}{w + z} \quad (19)$$

$$\text{B.C.1: } y = 0, \quad \Phi_c = 0$$

$$\text{B.C.2: } y = 1/\kappa\tilde{a}, \quad \frac{d\Phi_c}{dy} = z\kappa\lambda$$

where  $y = 1/x$ .

When the values of  $\tilde{a}$ ,  $S$ ,  $\bar{D}_e$  and  $n$  are known (or estimated), the procedures of evaluating the mean activity coefficient of electrolyte,  $\gamma_{\pm}$ , at concentration  $m$  and temperature  $T$  are described as follows:

(1) Equation (19) is solved with the subroutine BVPFD of the IMSL package.

(2)  $\Phi_{cr}$  is calculated by eqn. (3).

(3)  $\Phi_{ar}$  can be calculated by using steps similar to steps (1) and (2).

(4)  $\gamma_{\pm}$  is calculated from eqn. (13).

Figure 1 shows the mean activity coefficients,  $\gamma_{\pm}$ , calculated by the specific parameter set:  $\tilde{a} = 4.0 \text{ \AA}$ ,  $\bar{D}_e = 51.0$ ,  $S = 0.25$  and  $n = 0.645$  for qualitative analysis. Comparisons are made with the results calculated by the Debye–Hückel law, by long-range interactions consideration only, and by short-range interactions consideration only. It can be seen that the contribution of short-range interaction shifts the activity coefficient curve upward. Without the consideration of short-range interactions, such as in curves 1 and 3,  $\gamma_{\pm}$  decreases to a limiting value. This contradicts the experimental findings which show a monotonic increase of  $\gamma_{\pm}$  when  $m$  increases. If both short-range and long-range interactions are considered as shown by curve 4, it can fit experimental data well qualitatively.

In order to quantitatively fit the experimental data, appropriate values of  $\tilde{a}$ ,  $\bar{D}_e$ ,  $S$  and  $n$  should be obtained. This can be done by using the Simplex method of nonlinear programming (Nelder and Mead, 1965). The parameters are viewed as the optimum set of variables to be determined. The

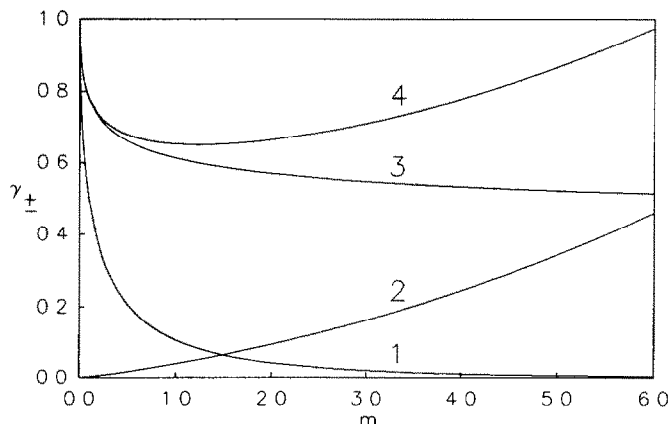


Fig. 1. Calculated mean activity coefficients at 298.15 K using 1. Debye–Hückel law ( $\tilde{a} = 4.0 \text{ \AA}$ ,  $\bar{D}_e = 78.54$ ), 2. short-range contribution ( $S = 0.25$ ,  $n = 0.645$ ), 3. long-range contribution ( $\tilde{a} = 4.0 \text{ \AA}$ ,  $\bar{D}_e = 51.0$ ), 4. the present model ( $\tilde{a} = 4.0 \text{ \AA}$ ,  $\bar{D}_e = 51.0$ ,  $S = 0.25$  and  $n = 0.645$ ).



objective function to be optimized is

$$\text{Min } \sigma \ln \gamma_{\pm} = \left[ \sum_j (\ln \gamma_{\pm_j}^{\text{cal}} - \ln \gamma_{\pm_j}^{\text{exp}})^2 / n_p \right]^{1/2}$$

If the data of osmotic coefficients are used, the objective function becomes

$$\text{Min } \sigma \phi = \left\{ \sum_j [(\phi_j^{\text{cal}} - \phi_j^{\text{exp}}) / \phi_j^{\text{exp}}]^2 / n_p \right\}^{1/2}$$

where  $n_p$  is the number of data points.

During the stage of optimization, it was found that the value of  $n$  did not vary significantly for many aqueous electrolyte systems such as NaCl,  $\text{CaCl}_2$ ,  $\text{Li}_2\text{SO}_4$ ,  $\text{ZnSO}_4$ , etc. Therefore for simplicity, we adopted  $n$  to be a constant value of 0.645 for all the studied systems. Hasted et al. (1948) had measured the dielectric constants of several aqueous electrolyte solutions. Their results show that the dielectric constant is linearly dependent on the concentration of  $m \leq 2$ , and approaches gradually a saturated value (dielectric saturation) at high concentration. Due to insufficient experimental data covering the complete concentration span, it is not possible to establish the functional relation of  $D_e$  and solute concentration. Therefore, the parameter  $D_e$  used in our model is replaced by an equivalent dielectric constant,  $\bar{D}_e$ , over the whole concentration range. After these considerations, only three parameters,  $S$ ,  $\tilde{a}$ , and  $\bar{D}_e$ , are left to be determined.

## RESULTS AND DISCUSSION

The experimental data of activity coefficients and osmotic coefficients of 144 aqueous electrolyte solutions at 298.15 K (Robinson and Stokes, 1959) were used to fit the proposed model. The parameters obtained for each electrolyte by the Simplex method of nonlinear optimization are summarized in Table 1 with corresponding root mean square (RMS) errors. Figures 2 to 5 are the typical results for the 1–1, 1–2, 2–1 and 2–2 types of aqueous solutions of strong electrolytes. It can be seen that the present model fits experimental data fairly well. For very few systems, the RMS errors are relatively large as can be seen in Table 1. This large discrepancy may be attributed to the following factors. 1) For the electrolyte with organic anions, such as sodium caprylate and sodium pelargonate, the size of the anion is much larger than that of the cation, and the shape is so highly nonspherical that the charge density of ions in the solution can no longer be described by the Boltzmann distribution. 2) For some halide electrolytes of transition-metal cations, such as zinc chloride, zinc bromide and cobalt bromide, each electrolyte will form several different complex ions

TABLE 1

Calculated parameters for different aqueous electrolyte solutions at 298.15 K

Electrolyte	$m_{\max}$	$\tilde{a}$ (Å)	$\bar{D}_e$	$S$	$\sigma \ln \gamma_{\pm}$ (%)	$\sigma \phi$ (%)
<i>1-1 electrolytes</i>						
HCl	6.0	4.716	60.348	0.358	3.927	1.940
HBr	3.0	4.000	60.923	0.493	1.415	1.365
HI	3.0	4.065	66.079	0.588	2.568	2.171
HClO <sub>4</sub>	6.0	3.986	57.417	0.434	1.652	1.032
HNO <sub>3</sub>	3.0	4.002	56.107	0.223	0.739	0.665
LiOH	4.0	4.000	42.104	-0.025	2.848	2.443
LiCl	6.0	4.000	58.071	0.320	1.492	1.201
LiBr	6.0	3.988	56.404	0.403	2.175	1.356
LiI	3.0	4.000	67.692	0.479	1.613	1.573
LiClO <sub>4</sub>	4.0	4.000	66.893	0.438	2.510	2.016
LiNO <sub>3</sub>	6.0	4.000	59.825	0.205	3.153	2.524
LiAc	4.0	4.112	48.836	0.177	4.441	1.713
LiTol	4.5	3.786	53.456	0.016	1.796	1.358
NaOH	6.0	3.977	52.280	0.182	1.494	0.888
NaF	1.0	3.997	50.917	-0.187	1.502	1.611
NaCl	6.0	4.056	51.107	0.127	0.546	0.247
NaBr	4.0	4.064	53.345	0.174	0.590	0.498
NaI	3.5	4.031	53.390	0.251	1.078	1.062
NaClO <sub>3</sub>	3.5	3.928	50.490	-0.027	1.100	1.119
NaClO <sub>4</sub>	6.0	3.981	49.773	0.069	1.697	1.325
NaBrO <sub>3</sub>	2.5	4.717	41.521	-0.106	2.185	2.493
NaNO <sub>3</sub>	6.0	3.227	49.369	-0.047	1.856	1.968
Na formate	3.5	4.049	54.396	0.079	1.100	1.056
NaAc	3.5	4.487	57.163	0.237	1.656	1.433
Na propionate	3.0	4.803	57.682	0.309	1.895	1.727
Na butyrate	3.5	6.029	58.846	0.305	4.523	3.691
Na valerate	3.5	3.335	67.225	0.163	8.698	9.359
Na caprylate	4.5	3.991	47.451	-0.607	10.121	4.124
Na pelargonate	2.5	2.986	42.675	-0.683	11.312	8.124
Na caprate	1.8	2.322	34.378	-1.416	7.124	4.332
NaH malonate	5.0	2.677	51.149	0.018	1.768	1.139
NaH succinate	5.0	2.753	51.445	0.058	1.418	0.979
NaH adipate	0.7	3.213	54.086	0.122	0.228	0.407
Na caproate	4.5	9.624	65.293	-0.124	9.017	7.366
NaCNS	4.0	3.927	58.148	0.152	1.451	1.302
NaTol	4.0	4.045	47.267	-0.112	1.481	1.726
NaH <sub>2</sub> PO <sub>4</sub>	6.0	1.712	50.995	-0.047	3.121	4.231
KOH	6.0	3.790	80.826	0.282	2.426	1.613
KF	4.0	1.753	64.232	0.176	2.133	2.032
KCl	4.5	0.043	48.700	0.032	0.855	0.707
KBr	5.5	4.060	49.601	0.070	2.591	2.031
KI	4.5	4.081	51.835	0.074	0.651	0.602

TABLE 1 (continued)

Electrolyte	$m_{\max}$	$\bar{a}$ (Å)	$\bar{D}_e$	$S$	$\sigma \ln \gamma_{\pm}$ (%)	$\sigma\phi$ (%)
KClO <sub>3</sub>	0.7	2.883	59.855	−0.816	3.101	3.418
KBrO <sub>3</sub>	0.5	2.484	57.380	−0.950	2.203	2.855
KNO <sub>3</sub>	3.5	3.176	43.375	−0.224	2.571	3.629
KAc	3.5	4.573	57.775	0.273	1.799	1.613
KH malonate	5.0	2.684	49.496	−0.033	1.838	1.674
KH succinate	4.5	2.783	49.950	0.020	1.407	1.193
KH adipate	1.0	3.413	53.072	0.022	0.339	0.386
KTol	3.5	3.446	51.840	−0.279	4.331	6.074
KCNS	5.0	3.053	59.562	−0.011	3.887	2.873
KH <sub>2</sub> PO <sub>4</sub>	1.8	4.125	39.729	−0.360	2.357	3.191
NH <sub>4</sub> Cl	6.0	4.065	49.296	0.027	0.403	0.468
NH <sub>4</sub> NO <sub>3</sub>	6.0	4.007	40.242	−0.080	2.972	2.940
RbCl	5.0	4.075	46.809	0.029	1.290	1.003
RbBr	5.0	4.000	47.021	0.006	1.142	1.102
RbI	5.0	4.000	46.708	0.007	1.380	1.351
RbNO <sub>3</sub>	4.5	2.252	45.524	−0.182	3.174	4.338
RbAc	3.5	3.998	61.226	0.300	2.005	1.830
CsOH	1.0	4.020	57.555	0.633	0.332	2.423
CsCl	6.0	4.300	41.213	0.007	2.336	2.168
CsBr	5.0	4.000	41.518	0.010	2.528	2.179
CsI	3.0	4.139	42.247	0.002	2.010	1.349
CsNO <sub>3</sub>	1.4	3.987	43.032	−0.242	1.760	2.422
CsAc	3.5	4.013	62.861	0.554	2.157	1.829
TlNO <sub>3</sub>	0.4	3.009	43.840	−1.043	0.774	1.033
TlClO <sub>4</sub>	0.5	5.262	41.937	−0.895	0.640	1.165
TlAc	6.0	2.707	48.177	−0.031	0.933	0.950
AgNO <sub>3</sub>	6.0	3.053	40.457	−0.172	4.954	5.223
<i>2–1 electrolytes</i>						
MgCl <sub>2</sub>	5.0	5.564	75.374	1.465	1.726	0.480
MgBr <sub>2</sub>	5.0	5.846	77.681	1.808	3.328	1.720
MgI <sub>2</sub>	5.0	5.903	78.490	2.246	5.239	1.942
Mg(ClO <sub>4</sub> ) <sub>2</sub>	4.0	5.767	78.306	2.236	6.562	3.669
Mg(NO <sub>3</sub> ) <sub>2</sub>	5.0	5.924	72.526	1.090	4.682	2.458
MgAc <sub>2</sub>	4.0	5.348	64.538	0.352	1.060	1.237
CaCl <sub>2</sub>	6.0	5.657	72.175	1.132	3.747	1.474
CaBr <sub>2</sub>	6.0	5.887	73.343	1.533	3.111	0.964
CaI <sub>2</sub>	2.0	5.822	75.430	1.981	2.287	1.658
Ca(ClO <sub>4</sub> ) <sub>2</sub>	6.0	6.515	77.098	1.662	6.785	3.972
Ca(NO <sub>3</sub> ) <sub>2</sub>	6.0	5.385	68.999	0.276	0.923	0.545
SrCl <sub>2</sub>	4.0	5.500	71.858	1.000	0.563	0.414
SrBr <sub>2</sub>	2.0	5.595	72.886	1.302	0.874	0.602
SrI <sub>2</sub>	2.0	5.885	77.824	1.693	1.254	0.926
Sr(ClO <sub>4</sub> ) <sub>2</sub>	6.0	6.315	76.508	1.279	9.148	5.540

TABLE 1 (continued)

Electrolyte	$m_{\max}$	$\tilde{a}$ (Å)	$\bar{D}_e$	$S$	$\sigma \ln \gamma_{\pm}$ (%)	$\sigma\phi$ (%)
Sr(NO <sub>3</sub> ) <sub>2</sub>	4.0	4.976	67.994	−0.045	2.581	2.957
BaCl <sub>2</sub>	1.8	5.414	74.109	−0.521	2.206	1.075
BaBr <sub>2</sub>	2.0	5.379	75.180	0.917	1.161	1.080
BaI <sub>2</sub>	2.0	5.652	77.766	1.585	1.860	1.678
Ba(ClO <sub>4</sub> ) <sub>3</sub>	5.0	6.255	77.718	7.489	5.861	3.933
Ba(NO <sub>3</sub> ) <sub>2</sub>	0.4	3.820	63.736	0.297	4.776	6.417
BaAc <sub>2</sub>	3.5	5.488	70.508	0.014	4.200	4.456
MnCl <sub>2</sub>	6.0	5.515	73.982	0.674	14.810	8.646
FeCl <sub>2</sub>	2.0	5.575	75.376	1.114	2.477	0.857
CoCl <sub>2</sub>	4.0	7.592	67.175	0.986	4.843	2.779
CoBr <sub>2</sub>	5.0	8.109	68.655	1.466	8.385	3.825
CoI <sub>2</sub>	6.0	6.144	77.929	2.273	9.187	2.830
Co(NO <sub>3</sub> ) <sub>2</sub>	5.0	5.660	75.541	0.931	3.118	1.955
NiCl <sub>2</sub>	5.0	5.600	75.643	1.098	8.901	4.380
CuCl <sub>2</sub>	6.0	5.937	78.100	0.241	6.577	4.931
Cu(NO <sub>3</sub> ) <sub>2</sub>	6.0	5.695	74.800	0.721	4.717	2.761
ZnCl <sub>2</sub>	6.0	5.534	67.003	0.103	9.293	6.778
ZnBr <sub>2</sub>	6.0	5.573	67.265	0.438	25.300	13.483
ZnI <sub>2</sub>	6.0	8.044	72.401	0.331	17.045	11.938
Zn(ClO <sub>4</sub> ) <sub>2</sub>	4.0	5.949	77.409	2.443	4.111	1.584
Zn(NO <sub>3</sub> ) <sub>2</sub>	6.0	5.857	78.146	0.925	6.036	3.460
Cd(NO <sub>3</sub> ) <sub>2</sub>	2.5	5.535	74.265	0.608	1.719	1.589
Pb(ClO <sub>4</sub> ) <sub>2</sub>	6.0	5.990	78.146	0.938	3.171	3.309
Pb(NO <sub>3</sub> ) <sub>2</sub>	2.0	5.308	61.860	−1.467	14.713	10.737
UO <sub>2</sub> Cl <sub>2</sub>	5.5	5.700	77.692	1.248	6.741	4.120
UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	5.5	6.257	78.942	0.860	10.028	8.031
<i>1–2 electrolytes</i>						
Li <sub>2</sub> SO <sub>4</sub>	3.0	3.862	73.967	0.254	1.093	1.080
Na <sub>2</sub> SO <sub>4</sub>	4.0	5.003	58.170	−0.197	4.124	5.192
Na <sub>2</sub> CrO <sub>4</sub>	4.0	3.903	70.224	0.222	5.101	5.390
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	3.5	3.797	70.052	0.093	3.641	4.381
K <sub>2</sub> SO <sub>4</sub>	0.7	3.721	66.622	0.068	3.128	3.674
K <sub>2</sub> CrO <sub>4</sub>	3.5	3.923	70.309	0.023	2.970	3.678
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	4.0	3.281	63.378	−0.050	3.221	4.943
Cs <sub>2</sub> SO <sub>4</sub>	1.8	4.046	70.646	−0.113	1.304	1.613
Rb <sub>2</sub> SO <sub>4</sub>	1.8	3.895	69.208	−0.107	2.537	3.229
Na <sub>2</sub> fumarate	2.0	3.815	74.921	0.533	1.431	1.492
Na <sub>2</sub> maleate	3.0	3.381	70.190	0.205	2.568	1.937
<i>2–2 electrolytes</i>						
BeSO <sub>4</sub>	4.0	4.052	76.738	0.436	2.669	5.026
MgSO <sub>4</sub>	3.0	4.000	76.991	0.306	2.845	6.447
MnSO <sub>4</sub>	4.0	3.946	76.898	0.258	4.449	7.352

TABLE 1 (continued)

Electrolyte	$m_{\max}$	$\bar{a}$ (Å)	$\bar{D}_e$	$S$	$\sigma \ln \gamma_{\pm}$ (%)	$\sigma \phi$ (%)
NiSO <sub>4</sub>	2.5	3.989	75.898	0.152	3.201	5.377
CuSO <sub>4</sub>	1.4	4.066	70.069	0.040	0.980	3.630
ZnSO <sub>4</sub>	3.5	3.920	75.744	0.298	4.872	7.723
CdSO <sub>4</sub>	3.5	4.050	74.860	0.171	3.890	6.349
UO <sub>2</sub> SO <sub>4</sub>	6.0	3.991	75.692	0.249	2.160	1.648
<i>3-1 electrolytes</i>						
AlCl <sub>3</sub>	1.8	9.196	76.315	4.395	4.875	3.984
ScCl <sub>3</sub>	1.8	9.518	76.952	3.335	2.031	2.247
CrCl <sub>3</sub>	1.2	9.464	78.064	3.359	1.582	1.860
YCl <sub>3</sub>	2.0	9.114	75.673	3.079	3.125	2.951
LaCl <sub>3</sub>	2.0	9.197	75.496	2.502	3.056	2.648
CeCl <sub>3</sub>	2.0	9.261	76.288	2.531	2.725	2.742
PrCl <sub>3</sub>	2.0	9.223	75.307	2.516	2.940	3.122
NdCl <sub>3</sub>	2.0	9.012	75.866	2.640	2.828	2.813
SmCl <sub>3</sub>	2.0	9.123	74.734	2.873	3.769	3.407
EuCl <sub>3</sub>	2.0	9.193	75.437	2.825	3.381	2.801
Cr(NO <sub>3</sub> ) <sub>3</sub>	1.4	9.449	77.428	2.692	3.036	1.487
<i>3-2 electrolytes</i>						
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	1.0	7.270	76.773	1.514	8.914	10.295
Cr(SO <sub>4</sub> ) <sub>3</sub>	1.2	8.360	73.209	1.481	11.237	15.994
<i>4-1 electrolytes</i>						
Th(NO <sub>3</sub> ) <sub>4</sub>	5.0	18.589	73.696	1.099	10.011	8.124

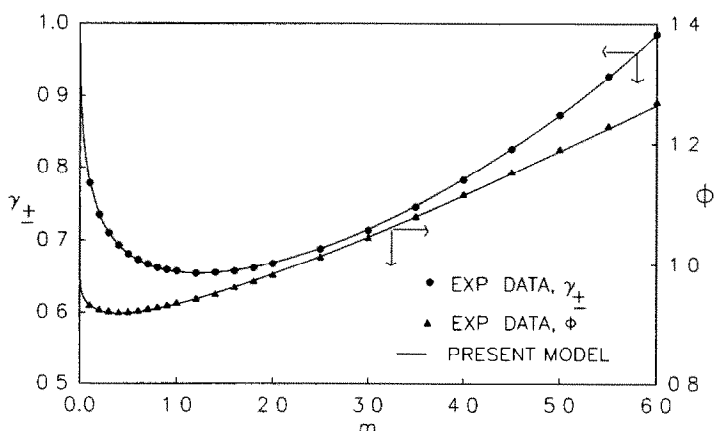


Fig. 2. Comparison of calculated and experimental data (Robinson and Stokes, 1959) of NaCl aqueous solutions at 298.15 K.

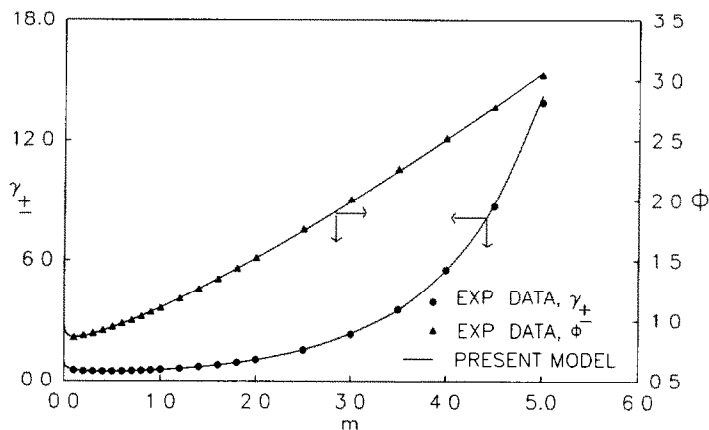


Fig. 3. Comparison of calculated and experimental data (Robinson and Stokes, 1959) of  $\text{MgCl}_2$  aqueous solutions at 298.15 K.

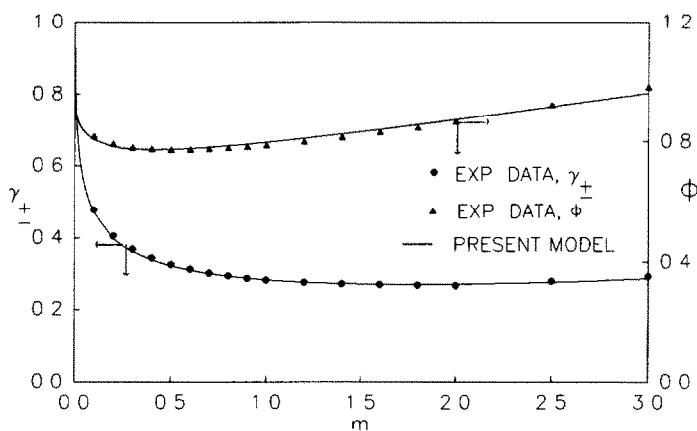


Fig. 4. Comparison of calculated and experimental data (Robinson and Stokes, 1959) of  $\text{Li}_2\text{SO}_4$  aqueous solutions at 298.15 K.

in solution. For example,  $\text{ZnCl}_2$  will form  $\text{Zn}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{ZnCl}^+$ ,  $\text{ZnCl}_2$ ,  $\text{ZnCl}_3^-$  and  $\text{ZnCl}_4^{2-}$  simultaneously in the solution, and the equilibrium concentrations of these species can be calculated from the formation constants (Dean, 1987). The solution behavior of such a system is very complicated, it is not in the scope of our proposed model and appropriate modifications should be developed for such systems.

### *Solvation parameters*

The concept of hydration was introduced by Robinson and Stokes (1959), and the number of hydration ions had been estimated by several re-

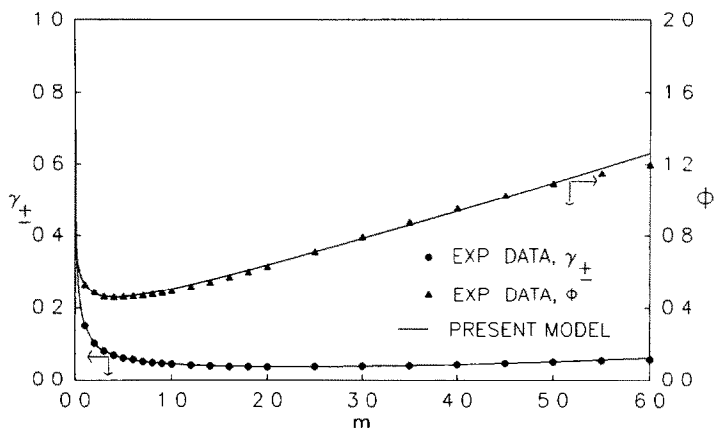


Fig. 5. Comparison of calculated and experimental data (Robinson and Stokes, 1959) of  $\text{UO}_2\text{SO}_4$  aqueous solutions at 298.15 K.

searchers. Unfortunately, the data were not consistent. For example, the hydration number of  $\text{Li}^+$  is 4.6 by Guggenheim and Stokes (1969), but 1.8 by Kawaguchi et al. (1981). This discrepancy is due to the different methods of defining the hydration number, since there is no general method of accounting for the real hydration numbers of each ion in the solution. A more convenient way is probably the adoption of solvation parameter  $S$  to represent the solvation (hydration) tendency. For groups of cations with common anions, the solvation parameters at 298.15 K are listed in Table 2(A). For aqueous electrolyte solutions, the solvation parameter  $S$  is equivalent to the solvation tendency of ions. It can be seen from Table 2 that the order of solvation tendency is  $\text{H}^+ > \text{Li}^+ > \text{Na}^+ > \text{K}^+$ , and for groups of anions with common cations, the order of solvation tendency is  $\text{Cl}^- < \text{Br}^- < \text{I}^-$ , as can be seen in Table 2(B). These orders are consistent with those given by Robinson and Stokes (1959) and Kawaguchi et al. (1981).

#### *The closest distance of approach, $\tilde{a}$*

The closest distance approach,  $\tilde{a}$ , is where the potential energy of an ion due to the surrounding ions is just zero. It has not been possible to measure or estimate this value theoretically so far. In the Debye–Hückel law or its modified models, the value of 4 Å has been well accepted as an estimated value (Bromley, 1973; Pitzer, 1973a; Chen et al. 1982). In the present model, for symmetrical electrolytes such as 1–1 and 2–2 types, the values of  $\tilde{a}$  is approximately 4 Å for over half of the systems, as listed in Table 1. It is known that the size of the anion is much larger than that of the cation.

TABLE 2

Calculated values of  $S$  for electrolytes with common anions or cations at 298.15 K

Electrolyte	$S$	Electrolyte	$S$
(A) <i>Cations with common anions</i>			
HCl	0.358	HI	−0.588
LiCl	0.320	LiI	−0.479
NaCl	0.127	NaI	−0.251
KCl	0.032	KI	−0.074
HBr	0.493	HNO <sub>3</sub>	0.223
LiBr	0.403	LiNO <sub>3</sub>	0.205
NaBr	0.174	NaNO <sub>3</sub>	−0.047
KBr	0.050	KNO <sub>3</sub>	−0.224
(B) <i>Anions with common cations</i>			
HCl	0.358	MgCl <sub>2</sub>	1.465
HBr	0.493	MgBr <sub>2</sub>	1.808
HI	0.588	MgI <sub>2</sub>	2.246
LiCl	0.320	CaCl <sub>2</sub>	1.132
LiBr	0.403	CaBr <sub>2</sub>	1.533
LiI	0.479	CaI <sub>2</sub>	1.981
NaCl	0.127	SrCl <sub>2</sub>	1.000
NaBr	0.174	SrBr <sub>2</sub>	1.302
NaI	0.251	SrI <sub>2</sub>	1.693
KCl	0.032	BaCl <sub>2</sub>	0.521
KBr	0.050	BaBr <sub>2</sub>	0.917
KI	0.074	BaI <sub>2</sub>	1.585

Therefore, if the percentage of anions in the surrounding ions is increased, the value of  $\tilde{a}$  will be large, and vice versa. It is found from Table 1 that most of the  $\tilde{a}$  values are smaller than 4 Å for 1–2 type electrolytes, and are larger than 4 Å for 2–1, 3–1, 3–2 and 4–1 types. As an example, the percentage of Cl<sup>−</sup> in the surrounding ions of Na<sup>+</sup> for NaCl is less than that of Mg<sup>2+</sup> for MgCl<sub>2</sub>; the value of  $\tilde{a}$  for NaCl is therefore smaller than that for MgCl<sub>2</sub>. By the same consideration, the value of  $\tilde{a}$  for AlCl<sub>3</sub> is larger than that for MgCl<sub>2</sub>. Table 3 lists the values of  $\tilde{a}$  for several sets of different electrolytes with the same cations or anions. It is found that, for electrolytes with same cations or anions, the larger the ratio of the number of anions to the number of cations is, the larger the value of  $\tilde{a}$  will be.



TABLE 3

Effect of the anion/cation mole ratio on the closest distance of approach,  $\tilde{a}$ 

Electrolyte	Anion/cation mole ratio	Closest distance of approach, $\tilde{a}$ (Å)
MgBr <sub>2</sub>	2	5.846
MgSO <sub>4</sub>	1	4.000
CrCl <sub>3</sub>	3	9.464
Cr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	1.5	8.360
LiCl	1	4.000
Li <sub>2</sub> SO <sub>4</sub>	0.5	3.862
NaCl	1	4.056
MgCl <sub>2</sub>	2	5.564
AlCl <sub>3</sub>	3	9.196
HNO <sub>3</sub>	1	4.002
Mg(NO <sub>3</sub> ) <sub>2</sub>	2	5.924
Cr(NO <sub>3</sub> ) <sub>3</sub>	3	9.449
Th(NO <sub>3</sub> ) <sub>4</sub>	4	18.589

*Systems at temperatures other than 298.15 K*

In order to explore the temperature effect on these three parameters of the proposed model, the experimental data of KBr, NaCl, LiCl and LiBr at various temperatures (Robinson and Stokes, 1959; Broul et al., 1969; Sada et al., 1975) were fitted to the proposed model. During the optimization process, it was found that the values of  $\tilde{a}$  and  $S$  varied within 0.2% at different temperatures. Therefore, for each electrolyte, the values of  $\tilde{a}$  and  $S$  at different temperatures are adopted to be the values at 298.15 K. The values of parameters and errors in estimated activity coefficients, and osmotic coefficients are listed in Table 4. It can be seen that the average errors for each system at various temperatures are quite small. It shows an important feature that two of the three parameters are temperature independent. It is found that the equivalent dielectric constants,  $\bar{D}_e$ , decrease when the temperature of the system is raised. This trend is consistent with the experimental results of Hasted et al. (1948).

*Comparison with other models*

The concept of local composition in considering short-range interactions between particles in the solution has been adopted by many researchers (Chen et al., 1982; Chen and Evans, 1986; Ananth and Ramachandran,

TABLE 4

Calculated parameters for aqueous electrolyte solutions at various temperatures

Electrolyte	$T$ (K)	$\tilde{a}$ (Å)	$\bar{D}_e$	$S$	$\sigma \ln \gamma_{\pm}$ (%)	$\sigma\phi$ (%)
KBr	298.15	4.060	49.601	0.070	2.591	2.031
	333.15	4.060	44.786	0.070	1.280	0.714
	343.15	4.060	43.096	0.070	1.528	0.924
	353.15	4.060	41.703	0.070	1.711	1.015
	363.15	4.060	40.015	0.070	1.828	1.105
	373.15	4.060	38.441	0.070	1.867	1.162
NaCl	298.15	4.056	51.107	0.127	0.545	0.247
	333.15	4.056	46.445	0.127	1.903	0.883
	343.15	4.056	44.272	0.127	1.705	0.895
	353.15	4.056	41.876	0.127	1.466	0.888
	363.15	4.056	40.015	0.127	1.410	0.766
	373.15	4.056	37.952	0.127	1.320	0.685
LiCl	298.15	4.000	58.071	0.320	1.492	1.201
	333.15	4.000	31.445	0.320		2.130
	348.25	4.000	22.903	0.320		3.442
LiBr	298.15	3.988	56.404	0.403	2.175	1.356
	348.15	3.988	43.827	0.403		3.623

1990). Basically the concept of local composition and the present model are all developed from the Boltzmann distribution. But the proposed method involves a differential equation and three parameters to describe the interactions between particles in a binary system. Table 5 gives a comparison of the calculated results of the present model with those of Chen et al. (1982) and Ananth and Ramachandran (1990). It can be seen that the present model is as good as others. Although three parameters are involved in the present model as with the other models, these three parameters have clear physical meanings and make it possible to predict the vapor–liquid equilibrium of ternary systems (two solvents and one electrolyte) from the known parameters of binary mixtures (solvent and solvent, solvent and electrolyte). This important feature of the present model will be demonstrated in the Part II of this report (Lin et al., 1993).

In this approach, due to the mathematical difficulty, the boundary value ordinary differential equation has to be solved numerically. This seems to be the drawback of the present model. However, it takes only a few seconds to solve this boundary value problem on a PC/486. In lieu of the feasibility for the present model to be extended to ternary systems, it is justified because of the expense of calculation time.

TABLE 5

Comparison of various models for aqueous electrolyte solutions at 298.15 K

Type of electrolyte	No. of systems	$\sigma \ln \gamma_{\pm}$ (%)		
		Chen et al. (1982)	Ananth and Ramachandran (1990)	Present work
1–1	56	1.09	0.86	1.04
2–2	7	3.73	7.35	2.88
1–2	11	1.96	1.64	2.74
2–1	35	12.64	4.79	4.11
3–1	11	8.04	6.57	3.03
3–2	2	12.30	7.12	10.05

*Non-aqueous electrolyte solutions*

For non-aqueous electrolyte solutions, the osmotic coefficients can be calculated from the data of vapor pressures with eqns. (15) and (17). In this research, the experimental osmotic coefficients for 16 non-aqueous systems (Subbotina and Mischchenko, 1969; Sada et al., 1975; Bixon et al., 1979) were used to fit the proposed model. From the physical meaning of

TABLE 6

Calculated parameters for non-aqueous electrolyte solutions

System	Temperature (K)	$m_{\max}$	$\tilde{a}$ (Å)	$\bar{D}_e$	$S$	$\sigma\phi$ (%)	Data source
IPA–LiCl	348.25	2.269	4.000	9.960	1.462	0.792	(1)
IPA–LiBr	348.15	2.936	3.988	8.764	0.922	3.712	(1)
MeOH–LiCl	298.05	5.355	4.000	18.599	0.607	2.868	(2)
MeOH–NaBr	298.05	1.556	4.064	17.442	0.407	0.815	(2)
MeOH–CaCl <sub>2</sub>	298.05	2.635	5.657	29.286	2.090	1.157	(2)
MeOH–NaOH	298.05	5.941	3.977	15.953	0.838	6.442	(2)
MeOH–NaI	298.05	4.520	4.031	20.655	0.666	2.534	(2)
MeOH–KI	298.05	1.122	4.081	18.558	0.051	0.785	(2)
MeOH–CuCl <sub>2</sub>	298.05	3.974	5.937	14.068	0.388	1.310	(2)
EtOH–NaI	278.15	2.842	4.031	49.387	0.656	0.891	(3)
EtOH–NaI	283.15	2.842	4.031	48.510	0.656	0.732	(3)
EtOH–NaI	288.15	2.842	4.031	47.673	0.656	0.934	(3)
EtOH–NaI	293.15	2.842	4.031	28.269	0.656	0.651	(3)
EtOH–NaI	298.15	2.842	4.031	22.214	0.656	0.658	(3)
EtOH–NaI	308.15	2.842	4.031	21.493	0.656	0.587	(3)
EtOH–NaI	318.15	2.842	4.031	14.870	0.656	0.457	(3)

(1) Sada et al. (1975). (2) Bixon et al. (1979). (3) Subbotina and Mischenko (1969).

the closest distance of approach, it is reasonable to assume that  $\tilde{a}$  is mainly dependent on the type of electrolyte, and is nearly independent of the solvent. Therefore, during the optimization process, the value of  $\tilde{a}$  for an electrolyte in alcohols was taken to be the same as that for the same electrolyte in the aqueous solutions. Consequently, only two adjustable parameters remain to be evaluated. The results are summarized in Table 6. The average errors are quite small. This shows that the assumption of  $\tilde{a}$  being independent of solvent type is reasonable, and that the parameter  $\tilde{a}$  evaluated for an electrolyte in aqueous solution can be used for the same electrolyte in alcoholic solutions. Further experimental data are needed to verify this statement when it is applied to other types of solvents.

## CONCLUSION

In the present study, a predictive model was developed to calculate the mean activity coefficients and osmotic coefficients of binary electrolyte solutions. The model has been successfully applied to aqueous and non-aqueous electrolyte solutions over the temperature range 273.15 K to 373.15 K.

In the present model, the long-range and short-range interactions among ions and molecules are accounted for by three parameters; the closest distance of approach,  $\tilde{a}$ , the equivalent dielectric constant,  $\bar{D}_e$ , and the solvation parameter,  $S$ .

The three parameters which are related to the characteristics of an electrolyte in the solution are obtained by fitting the present model to the experimental data from the literature. The values estimated for  $S$  indicate that the solvation tendency for cations and anions follow a trend which is consistent with results reported in the literature. The equivalent dielectric constant is used in the present study instead of the real experimental value as a function of concentration. This simplifies the estimation process and yields satisfactory results. If sufficient experimental data on the dielectric constant are available, it can be adapted easily to the present model. For symmetric electrolytes, the fitted values for the closest distance of approach agree with the widely used value of 4 Å. For other types of electrolytes, it was found that  $\tilde{a}$  depends on the ratio of the number of anions to cations.

The results of the present study show the proposed model is as good as others for aqueous, single electrolyte solutions and is much simpler when applied to systems at temperatures other than 298.15 K and to non-aqueous electrolyte solutions. The extension of the present theory to multisolvent, single electrolyte systems is described in Part II (Lin et al., 1993). It is noted that when the present model is applied to multiple solutes, it must be

modified in order to satisfy the symmetry requirements of the Gibbs–Duhem equation. This is important work to be studied in the future.

#### ACKNOWLEDGMENT

The authors acknowledge with gratitude the National Science Council, Taiwan, for financial support through Grant No. NSC78-0402-E011-07.

#### LIST OF SYMBOLS

$A_v$	Avogadro's constant
$\tilde{a}$	closest distance of approach (Å)
$C$	number of electrolytes per unit volume (particles/m <sup>3</sup> of solution)
$D_e$	dielectric constant
$\bar{D}_e$	equivalent dielectric constant
$d_s$	density of solvent (kg/m <sup>3</sup> )
$e$	electron charge
$h_{cs}$	interaction parameter between cation and solvent molecule
$h_{as}$	interaction parameter between anion and solvent molecule
IPA	iso-propyl alcohol (2-propanol)
$k$	Boltzmann's constant
$M$	molarity (g mol/l of solution)
$m$	molality (g mol/kg of solvent)
$n$	power of $m$ in eqn. (6)
$n_p$	number of data points
$r$	radius of a spherical shell
$S$	solvation parameter
$s$	distance between ion and solvent molecule
$T$	temperature of solution (K)
$w$	absolute value of anionic charge
$x$	$\kappa r$
$y$	$1/x$
$z$	absolute value of cationic charge

#### Greek letters

$\beta$	proportional constant in eqn. (6)
$\Gamma_{cs}$	electrical potential between cation and solvent molecule
$\gamma_+$	activity coefficient of cation
$\gamma_-$	activity coefficient of anion
$\gamma_{\pm}$	mean activity coefficient of electrolyte
$\mu$	dipole moment of solvent

$\nu_+$	stoichiometric number of cations in an electrolyte
$\nu_-$	stoichiometric number of anions in an electrolyte
$\lambda$	$e^2/4\pi\epsilon kT$
$\epsilon$	rationalized electrical permittivity
$\epsilon_0$	electrical permittivity in a vacuum
$\psi$	electrical potential of an ion within an electric field
$\kappa$	$[4\pi(\nu_+ z^2 + \nu_- w^2)\lambda C]^{1/2}$
$\phi$	osmotic coefficient of solution
$\Phi$	dimensionless electrical potential, $=e\psi/kT$
$\sigma$	root mean square error
$\sigma \ln \gamma_{\pm}$	root mean square error of $\ln \gamma_{\pm}$
$\sigma\phi$	root mean square error of $\phi$

### Subscripts

a	anion
c	cation
i	index indicating ion itself
j	index indicating any species
max	maximum value
r	index indicating surrounding ion
s	solvent

### Superscripts

cal	calculated
exp	experimental

### REFERENCES

- Ananth, M.S. and Ramachandran, S., 1990. Self-consistent local composition model of electrolyte solutions. *AIChE J.*, 36: 370–386.
- Bixon, E., Guerry, R. and Tassios, D., 1979. Salt effect on the vapor pressure of pure solvents: methanol with seven salts at 24.9°C. *J. Chem. Eng. Data*, 24: 9–11.
- Bromley, L.A., 1973. Thermodynamic properties of strong electrolytes in aqueous solutions. *AIChE J.*, 19: 313–320.
- Broul, M., Hlavaty, K. and Linek, J., 1969. Liquid–vapour equilibrium in systems of electrolytic components. V. The system  $\text{CH}_3\text{OH}-\text{H}_2\text{O}-\text{LiCl}$  at 60°C. *Collect Czech. Chem. Commun.*, 34: 3428–3435.
- Chen, C.C. and Evans, L.B., 1986. A local composition model for the excess Gibbs energy of aqueous electrolyte systems. *AIChE J.*, 32: 444–454.
- Chen, C.C., Britt, H.I., Boston, J.F. and Evans, L.B., 1982. Local composition model for excess Gibbs energy of electrolytes systems. *AIChE J.*, 28: 588–596.
- Cruz, J.L. and Renon, H., 1978. A new thermodynamic representation of binary electrolyte solutions nonideality in the whole range of concentrations. *AIChE J.*, 24: 817–830.

- Dean, J.A., 1987. *Lange's Handbook of Chemistry*, 13th edn., McGraw-Hill, New York, pp. 5-71–5-76.
- Ghosh, S. and Patwardhan, V.S., 1990. Aqueous solutions of single electrolytes: A correlation based on ionic hydration. *Chem. Eng. Sci.*, 45: 79–87.
- Govindan, A.P., 1984. Study of liquid equilibrium in binary and ternary systems. Ph.D Thesis, Indian Institute of Technology, Madras.
- Guggenheim, E.A. and Stokes, R.H., 1969. *Equilibrium properties of aqueous solutions of single strong electrolytes*, Pergamon Press, Oxford.
- Hamer, W.J. and Wu, Y.C., 1972. Osmotic coefficients and mean activity coefficients of uni-univalent electrolytes in water at 25°C. *J. Phys. Chem. Ref. Data*, 1: 1047–1099.
- Hasted, J.B., Ritson, D.M. and Collie, C.H., 1948. Dielectric properties of aqueous ionic solutions. Parts I and II. *J. Chem. Phys.*, 16: 1–21.
- Kawaguchi, Y., Kanai, H., Kajiwar, H. and Arai, Y., 1981. Correlation for activities of water in aqueous electrolyte solutions using ASOG model. *J. Chem. Eng. Jpn.*, 14: 243–246.
- Lin, C.-L., Lee, L.-S. and Tseng, H.-C., 1993. Thermodynamic behavior of electrolyte solutions. Part II. Prediction of vapor–liquid equilibria for mixed-solvent electrolyte systems. *Fluid Phase Equilibria*, 90: 81–98.
- Meissner, H.P. and Kusik, C.L., 1972. Activity coefficient of strong electrolytes in multicomponent aqueous solutions. *AIChE J.*, 18: 294–298.
- Meissner, H.P. and Kusik, C.L., 1973. Aqueous solutions of two or more strong electrolytes: vapor pressures and solubilities. *Ind. Eng. Chem. Proc., Des. Dev.*, 12: 205–208.
- Meissner, H.P. and Tester, J.W., 1972. Activity coefficients of strong electrolytes in aqueous solutions. *Ind. Eng. Chem. Proc. Des. Dev.*, 11: 128–133.
- Nelder, J.A. and Mead, R., 1965. A simplex method for function minimization. *Comput. J.*, 7: 308–313.
- Pitzer, K.S., 1973a. Thermodynamics of Electrolytes. I. Theoretical basis and general equations. *J. Phys. Chem.*, 77: 268–277.
- Pitzer, K.S. and Mayorga, G., 1973b. Thermodynamics of electrolytes. II. Activity and osmotic coefficients for strong electrolytes with one or both ions univalent. *J. Phys. Chem.*, 77: 2300–2308.
- Robinson, R.A. and Stokes, R.H., 1959. *Electrolyte Solutions*, 2nd edn., Academic Press, New York.
- Sada, E., Morisue, T. and Miyahara, K., 1975. Salt effects of vapor–liquid equilibrium of isopropanol–water system. *J. Chem. Eng. Jpn.*, 8: 196–201.
- Subbotina, V.V. and Mishchenko, K.P., 1969. Activity of solvent in solutions of sodium iodide in ethyl alcohol in the temperature range from 5° to 45°. *Zh. Prikl. Khim.*, 42: 204–206.