A Nonrandom Factor Model for the Excess Gibbs Energy of Electrolyte Solutions

A new approach to represent the deviations from ideality of electrolyte solutions is derived on the basis of the assumptions of specific interactions of Brönsted and of local electroneutrality of Chen. The model consists of two contributions due to long-range forces, represented by the Debye-Hückel theory, and to short-range forces, represented by local compositions through nonrandom factors. With only two adjustable parameters per electrolyte, the model is valid for the whole range of electrolyte concentration, from dilute solution up to saturation. Results are compared with those obtained from two-parameter or one-parameter models of Meissner, Bromley, Pitzer, and Chen et al. The model presented in this work consistently produces better results and reproduces the experimental values from the dilute region up to saturation.

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Introduction

Electrolyte solutions play an important role in the chemical industry and are also relevant in other fields of science and technology. Partitioning processes in biochemical systems; precipitation and crystallization processes in geological systems such as geothermal brines or drilling muds; desalination of water and water pollution control; salting-in and salting-out effects in extraction and distillation, are just a few examples of cases in which the knowledge of the activity of salts or of ionic species are basic for a proper understanding of the phenomena. For some applications, the knowledge of the behavior of dilute solutions is all that is required, while for others the region close to saturation of the solution is important.

Recent models to describe electrolyte solutions are limited in their use to concentrations of the electrolyte below about six molal. At higher molalities, large errors are produced by most models using two parameters for each electrolyte in the solution.

Since the presentation of the Debye-Hückel theory (Debye and Hückel, 1923) for dilute solutions, there have been many attempts to reproduce the behavior of mixtures of higher molalities; Maurer (1983) and Renon (1986) have presented excellent reviews of recent developments. Basically, it is possible to group the models in three categories:

1. Direct extensions of the Debye-Hückel equation
2. Models based on the use of pair correlation functions
3. Models based on the local composition concept

Although certainly arbitrary, this classification helps to follow a systematic pattern in the study of models. However, the possibility that in a near future local compositions may be evaluated from pair correlation functions and used to extend the Debye-Hückel theory, cannot be ignored.

In the first group of models we may include the hydration model of Stokes and Robinson (1948), the graphical correlation of Meissner (Meissner and Kusik, 1972; Meissner, 1980) and the one-parameter model of Bromley (1973).

Within the second group of models, Lebowitz and Percus (1966), based on the earlier theories of Percus and Yevick (1958), proposed the use of the mean spherical approximation (MSA) for potentials of neutral molecules with hard cores. Waisman and Lebowitz (1970, 1972) and Blum (1975) developed the MSA further to account for excluded volume effects. Pitzer (1973, 1980b), in a semiempirical way, proposed to introduce a virial expansion to complement the Debye-Hückel term in the expression of the excess Gibbs energy of electrolyte solutions. Planche and Renon (1981) extended the MSA approach by introducing the consideration of short-range (Dirac) forces.

The third type of models, to which the new model proposed in this work belongs, are models using empirical expressions to express the effect of local composition. As do other models for electrolyte solutions, models of this class recognize the existence of both long-range and short-range forces in electrolyte solutions. The ion-ion interactions are long-range forces that are determinant on the behavior of dilute electrolyte solutions. Short-range forces are mostly due to interactions between the ions and the solvent molecules and, as in systems of nonelectrolytes, may be associated with local composition effects. Cruz and Renon (1978) proposed using the Debye-Hückel and the Debye-McAulary (Harned and Owen, 1958) theories for long-range forces and the NRTL (nonrandom two-liquid) local composition model for short-range forces, which were assumed to cause total hydration of the ionic species. The resulting model had four adjustable parameters and was applicable in all the concentration range for aqueous solutions of a single electrolyte. Chen et al. (1982, 1986) proposed a new local composition model using Pitzer's modification of the Debye-Hückel term for activity coefficients (Pitzer, 1980a) for long-range forces and a modified NRTL for short-range forces. The model of Chen et al. includes two key assumptions. First, it considers that there is no interaction between similar ionic species (like-ion repulsion). This assumption is in agreement with the theory of the specific interactions of Brönsted (1922). Second, it assumes that the distribution of cations and anions around a central solvent molecule is such that the net local ionic charge is zero (local electroneutrality). The resulting model has two adjustable parameters and reproduces well the activity coefficients of single electrolytes in water up to a molality of six. Ball et al. (1985) modified the Cruz-Renon model (Cruz and Renon, 1978) and reduced the adjustable parameters from four to two. The resulting model was used to fit osmotic coefficients of single-electrolyte solutions and compared with other two-parameter models using data up to a molality of six. Other models have extended group methods to electrolytes such as the ASOG version of Kawaguchi et al. (1981, 1984), which assumes total hydration of the ions, or the UNIFAC-type model of Christensen et al. (1983), which uses a Debye-Hückel term for electrostatic interactions and both a Brönsted-Guggenheim term and an UNIQUAC (Abrams and Prausnitz, 1975) term for short-range forces.

A typical limitation of all two-parameter local composition models previously proposed in the literature is the inability to correlate activity coefficients (or osmotic coefficients) beyond a molality of six which, incidentally, is close to the saturation molality of sodium chloride. For many industrial processes, such as crystallization of other salts or work with drilling muds, it is necessary to have models able to represent the thermodynamic behavior at higher molalities. A new formulation meeting this condition is proposed below.

New NRTL-NRF Model

Following the work of Chen et al. (1982, 1986), we assume that the excess Gibbs energy of an aqueous electrolyte solution may be expressed as the sum of a contribution due to long-range coulombic interactions and a contribution due to short-range interactions causing local order. For the long-range interations we use the Debye-Hückel expression and for the short-range interactions we use a new version of the NRTL model of Renon and Prausnitz (1968) in terms of nonrandom factors (NRF) formally similar to those proposed by Panayiotou and Vera (1980), and thus we write,

$$g^{ex} = (g^{ex})_{D-H} + (g^{ex})_{\text{NRTL-NRF}} \tag{1}$$

Although the Debye-Hückel contribution has been discussed in many previous publications, for completeness its main elements are presented in the Appendix.

The short-range effects are originated by molecule-molecule, molecule-ion, and ion-ion interactions at high concentrations. To express these effects, in this work we follow Chen et al. (1982, 1986) and assume the existence of three types of cells, depending on the central species, in the microstructure of an aqueous solution of a single electrolyte. Two types of cells are those with a cation or with an anion as central species. For these cells the like-ion repulsion leads to the assumption that the local mole fraction of cation around cation and of anion around anion is zero. Thus only solvent molecules and counterion species surround a particular ion. The third type of cell has solvent central molecules with anions, cations, and solvent molecules in the surroundings. Thus

$$\left(\frac{g^{ex}}{RT}\right)_{\text{NRTL-NRF}} = x_A \frac{g_A^{ex}}{RT} + x_C \frac{g_C^{ex}}{RT} + x_W \frac{g_W^{ex}}{RT} \tag{2}$$

where g_A^{ex}, g_C^{ex}, and g_W^{ex} represent the contributions of the cells with central anions A, central cations C, and central solvent molecules W to excess Gibbs energy arising from short-range interactions. In a major departure from the NRTL model (Renon and Prausnitz, 1968) and from Chen et al.'s extension (1982, 1986) to electrolytes, we consider here that the excess Gibbs energy contributions of the cells with different central species are expressed with respect to the random case instead of considering them with respect to hypothetical cells of pure central species. Thus

$$g_A^{ex} = g_A - g_A^o \tag{3a}$$

$$g_C^{ex} = g_C - g_C^o \tag{3b}$$

and

$$g_W^{ex} = g_W - g_W^o \tag{3c}$$

Following the approach of Chen et al. (1986), in terms of local mole fractions we may write

$$g_A = X_{WA} g_{WA} + X_{CA} g_{CA} \tag{4a}$$

$$g_C = X_{WC} g_{WC} + X_{AC} g_{AC} \tag{4b}$$

and

$$g_W = X_{WW} g_{WW} + X_{CW} g_{CW} + X_{AW} g_{AW} \tag{4c}$$

for the three types of cells. And, in our case, for the reference cells in the random case

$$g_A^o = X_W g_{WA} + X_C g_{CA} \tag{5a}$$

$$g_C^o = X_W g_{WC} + X_A g_{AC} \tag{5b}$$

and

$$g_W^o = X_W g_{WW} + X_C g_{CW} + X_A g_{AW} \tag{5c}$$

For generality, following Chen et al. (1986), we have used effective mole fractions defined as

$$X_A = Z_A x_A = Z_A Z_C x_s \tag{6a}$$

$$X_C = Z_C x_C = Z_C Z_A x_s \tag{6b}$$

and

$$X_W = x_W \tag{6c}$$

From Eqs. 6a and 6b we observe that $X_A = X_C$, which is the condition of electroneutrality.

In NRTL and related models, a parameter α, closely related to the inverse value of the coordination number Z, is interpreted as a measure of nonrandomness. In this work the nonrandomness of the mixture is represented by means of nonrandom factors (NRF) formally similar to those defined by Panayiotou and Vera (1980). Thus in general, for $i - j$ interactions

$$X_{ij} = X_i \Gamma_{ij} \tag{7a}$$

and similarly

$$X_{\ell j} = X_\ell \Gamma_{\ell j} \tag{7b}$$

From which:

$$\frac{X_{ij}}{X_{\ell j}} = \frac{X_i}{X_\ell} \frac{\Gamma_{ij}}{\Gamma_{\ell j}} \tag{8}$$

However, in this work the NRF are not obtained from the quasichemical theory (Panayiotou and Vera, 1980) but are evaluated using the empirical Wilson (1964) type expressions similar to those used by Renon and Prausnitz (1968) and by Chen et al. (1982). Thus, we write

$$\frac{X_{ij}}{X_{\ell j}} = \frac{X_i}{X_\ell} \beta_{ij,\ell j} \tag{9}$$

with

$$\beta_{ij,\ell j} = \exp\left(-\frac{g_{ij} - g_{\ell j}}{ZRT}\right) \tag{10}$$

Thus, comparing Eqs. 8 and 9

$$\Gamma_{ij} = \Gamma_{\ell j} \beta_{ij,\ell j} \tag{11a}$$

and, in particular, when $\ell = j$,

$$\Gamma_{ij} = \Gamma_{jj} \beta_{ij,jj} \tag{11b}$$

It should be clear that after chosing to use the empirical Wilson-type expressions, Eq. 9, to relate the nonrandom factors, our final model has the same theoretical limitations and practical advantages of all other models based on these expressions (Vera, 1986). Among the practical advantages, it is interesting to observe that the final model has only two adjustable parameters for a system of a single electrolyte dissolved in a single solvent. This can be shown by eliminating variables as follows. For the energy parameters we have the following relations:

$$g_{CA} = g_{AC} \equiv g_E; \quad g_{AW} = g_{WA}; \quad g_{CW} = g_{WC} \tag{12}$$

In addition, assuming local electroneutrality around a central molecule of solvent

$$Z_A x_{AW} = Z_C x_{CW} \tag{13}$$

Combining Eq. 13 with expressions of the form of Eq. 7b, and considering the expression for the overall electroneutrality of the solution ($Z_A x_A = Z_C x_C$), one obtains

$$\Gamma_{AW} = \Gamma_{CW} \tag{14}$$

Equation 14 coupled with expressions of the form of Eq 11b gives

$$g_{AW} = g_{CW} \equiv g_{EW} \tag{15}$$

Thus, relations 12 and 15 reduce to only two independent variables and from Eq. 10 we may write

$$\beta_{CA,WA} = \beta_{AC,WC} \equiv \beta_E \tag{16a}$$

$$\beta_{AW,WW} = \beta_{CW,WW} \equiv \beta_W \tag{16b}$$

To simplify the notation we define the related terms arising from Eq. 10 as

$$\lambda_E \equiv \frac{g_E - g_{EW}}{RT} \tag{17a}$$

and

$$\lambda_W \equiv \frac{g_{EW} - g_{WW}}{RT} \tag{17b}$$

λ_E and λ_W are the only two adjustable parameters for an aqueous solution of a single electrolyte assumed to be completely dissociated. The parameters λ_E and λ_W are designated from here on as the electrolyte and the solvent (water) parameters, respectively.

In order to express the contribution to the excess Gibbs energy due to short-range effects in terms of the above two adjustable parameters, we observe that for the electrolyte the effective (charge) mole fractions of cation and anion are equal due to the condition of overall electroneutrality.

$$X_A = X_C \equiv X_E \tag{18}$$

Thus, either starting with the cation central cells or with the anion central cells we may write a mass balance equation of the form

$$X_E \Gamma_E + X_W \Gamma_W = 1 \tag{19a}$$

where $\Gamma_E \equiv \Gamma_{CA} = \Gamma_{AC}$ and $\Gamma_W \equiv \Gamma_{WW}$. Thus

$$\Gamma_E = \frac{1}{X_E + (X_W \Gamma_W / \Gamma_E)} = \frac{\beta_E}{X_E \beta_E + X_W} \tag{19b}$$

and similarly for the solvent central cells, with $X_E \Gamma_E = X_A \Gamma_{AW} = X_C \Gamma_C$ and $\Gamma_{WW} = \Gamma_W$:

$$2 X_E \Gamma_E + X_W \Gamma_W = 1 \tag{20a}$$

or

$$\Gamma_W = \frac{1}{2(X_E\Gamma_E/\Gamma_W) + X_W} = \frac{1}{2X_E\beta_W + X_W} \qquad (20b)$$

Finally, replacing terms in Eqs. 3 we obtain

$$\frac{g_A^{ex}}{RT} = \frac{g_C^{ex}}{RT} = X_E(\Gamma_E - 1)\lambda_E \qquad (21a)$$

and

$$\frac{g_W^{ex}}{RT} = -X_W(\Gamma_W - 1)\lambda_W \qquad (21b)$$

and Eq. 2 takes the form

$$\left(\frac{g^{ex}}{RT}\right)_{\text{NRTL-NRF}} = (Z_A + Z_C)x_A x_C(\Gamma_E - 1)\lambda_E - x_W^2(\Gamma_W - 1)\lambda_W \qquad (22a)$$

Clearly for the random case, $\Gamma_E = \Gamma_W = 1$, Eq. 22 vanishes in agreement with the local composition concept. However, it must be clearly stated that due to the simplifying assumptions of this phenomenological derivation, mostly the like-ion repulsion assumption and the use of Wilson-type nonrandom factors, the balance equations for each cell do not extend to the overall mixture.

Following Stokes and Robinson (1959), we may express Eq. 21 in terms of a salt mole fraction expressed as

$$x_S = \frac{n_S}{n_W + \upsilon n_S} \qquad (23)$$

from where, the solvent mole fraction is obtained as

$$x_W = 1 - \upsilon x_S \qquad (24)$$

Thus, Eq. 22a takes the form

$$\left(\frac{g^{ex}}{RT}\right)_{\text{NRTL-NRF}} = \upsilon Z_A Z_C x_S^2(\Gamma_E - 1)\lambda_E - x_W^2(\Gamma_W - 1)\lambda_W \qquad (22b)$$

Expressions for the Activity Coefficients

As discussed by Hala et al. (1967) the mean ionic activity coefficient of an electrolyte in an aqueous solution may be obtained from the relation

$$\upsilon \ln \gamma_\pm = \frac{\partial}{\partial n_S}\left(\frac{ng^{ex}}{RT}\right)_{n_W} \qquad (25)$$

Since for the contribution of long-range interactions to the excess Gibbs energy (the Debye-Hückel model) the unsymmetrical normalization is used, it is necessary to normalize the contribution due to short-range interactions on the same basis. Thus we use

$$\left(\frac{g^{ex}}{RT}\right)^*_{\text{NRTL-NRF}} = \left(\frac{g^{ex}}{RT}\right)_{\text{NRTL-NRF}} - \upsilon x_S \ln \gamma_\pm^\infty \qquad (26)$$

From Eqs. 22b and 25 we obtain

$$\ln \gamma_\pm^\infty = \left(\frac{2Z_A Z_C}{\upsilon}\beta_W - 1\right)\lambda_W \qquad (27)$$

and then, from Eqs. 26 and 27

$$\left(\frac{g^{ex}}{RT}\right)^* = \upsilon Z_A Z_C x_S^2(\Gamma_E - 1)\lambda_E - x_W^2(\Gamma_W - 1)\lambda_W + x_S(\upsilon - 2Z_A Z_C\beta_W)\lambda_W \qquad (28)$$

Finally, from Eqs. 25 and 28 the expressions for the activity coefficients in the unsymmetrical convention take the form

$$\begin{aligned}(\ln \gamma_\pm^*)_{\text{NRTL-NRF}} = {} & Z_A Z_C x_S \lambda_E \left[(1 + x_W)(\Gamma_E - 1) + x_S x_W\left(\frac{\upsilon - Z_A Z_C \beta_E}{\beta_E}\right)\Gamma_E^2\right] \\ & + x_W^2\lambda_W(\Gamma_W - 1) \\ & - \lambda_W(x_W^3\Gamma_W^2 - 1)\left(1 - \frac{2Z_A Z_C}{\upsilon}\beta_W\right)\end{aligned} \qquad (29)$$

and

$$\begin{aligned}(\ln \gamma_W^*)_{\text{NRTL-NRF}} = {} & Z_A Z_C \upsilon x_S^2 \lambda_E \cdot \left[1 - \Gamma_E + x_S\left(\frac{Z_A Z_C\beta_E - \upsilon}{\beta_E}\right)\Gamma_E^2\right] \\ & - x_W\lambda_W(2 - x_W)(\Gamma_W - 1) \\ & - x_S x_W^2 \Gamma_W^2 \lambda_W(2\, Z_A Z_C \beta_W - \upsilon)\end{aligned} \qquad (30)$$

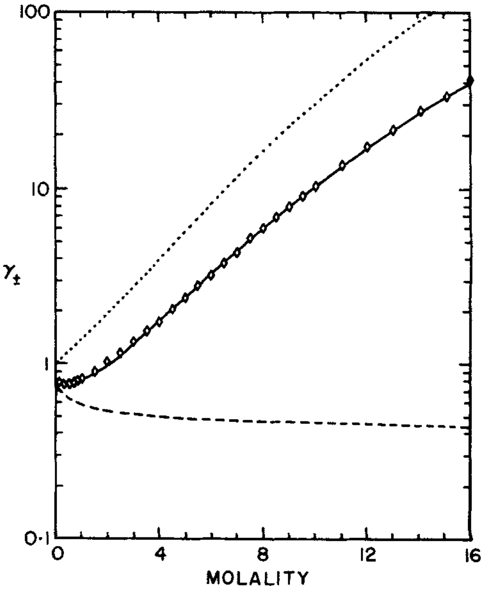

Figure 1. Long-range and short-range contributions to molality mean activity coefficient of aqueous solution of HCl at 298.15 K.

Experimental (Hamer and Wu, 1972); —— calculated
--- Debye-Hückel contribution; .... NRTL-NRF contribution

Although for aqueous solutions of a single electrolyte such as those considered in this work Eqs. 29 and 30 suffice, for the potential extension to multielectrolyte mixtures it would be desirable to have expressions for the individual ionic activity coefficients. These ionic activity coefficients are related to the mean ionic activity coefficient of the electrolyte by the relation:

$$(Z_A + Z_C) \ln \gamma_\pm^* = Z_A \ln \gamma_C^* + Z_C \ln \gamma_A^* \tag{31}$$

As discussed by Prigogine and Defay (1954), the condition of electroneutrality limits the possibility of knowing the values of all partial derivatives of the excess Gibbs energy. In fact it is not possible to change the concentration of cations keeping constant the concentration of anions and simultaneously maintaining the electroneutrality of the mixture. However, if we ignore the condition of electroneutrality and differentiate Eq. 28 with respect to the number of moles of each individual ion we obtain in the unsymmetric convention,

$$\begin{aligned}(\ln \gamma_C^*)_{\text{NRTL-NRF}} = {}& \upsilon x_A (x_A + x_W)(\Gamma_E - 1)\lambda_E \\ & + \upsilon x_A x_C \left(\frac{x_W}{\beta_E} + Z_A x_A\right)\Gamma_E^2 \lambda_E \\ & + x_W^2(\Gamma_W - 1)\lambda_W - (x_W^2 \Gamma_W^2 - 1) \\ & \cdot (1 - Z_C \beta_W)\lambda_W \end{aligned} \tag{32}$$

and

$$\begin{aligned}(\ln \gamma_A^*)_{\text{NRTL-NRF}} = {}& \upsilon x_C (x_C + x_W)(\Gamma_E - 1)\lambda_E \\ & + \upsilon x_A x_C \left[x_W \left(\frac{1 - Z_A \beta_E}{\beta_E}\right) - Z_A x_C\right] \\ & \cdot \Gamma_E^2 \lambda_E + x_W^2 (\Gamma_W - 1)\lambda_W \\ & - (x_W^3 \Gamma_W^2 - 1)(1 - Z_A \beta_W)\lambda_W \end{aligned} \tag{33}$$

Table 1. Fit of the Molality Mean Ionic Activity Coefficient Data of Pure Aqueous Uni-Univalent Electrolytes at $T = 298.15$ K (Hamer and Wu, 1972)

Electrolyte	Max. Molality	λ_E	λ_W	Std. Dev. of ln Values
HCl	16	−9.822	16.151	0.024
HBr	11	−10.722	19.862	0.040
HI	10	−10.433	20.069	0.062
$HClO_4$	16	−11.897	22.251	0.129
$HClO_4$	10	−11.050	20.034	0.060
$HClO_4$	6	−10.154	17.695	0.026
HNO_3	28	−6.971	9.007	0.018
LiCl	20	−10.072	16.262	0.052
LiBr	20	−11.465	20.516	0.095
LiBr	6	−10.651	18.525	0.045
LiI	3	−4.505	9.584	0.020
LiOH	5	−9.898	11.173	0.021
$LiClO_4$	4.5	−7.662	12.996	0.017
$LiNO_3$	20	−7.616	10.450	0.016
NaF	1	−7.382	6.967	0.002
NaCl	6.144	−8.318	10.209	0.011
NaBr	9	−8.357	11.000	0.061
NaI	12	−9.246	13.370	0.028
NaOH	29	−10.217	14.478	0.084
NaOH	20	−10.502	14.952	0.057
$NaClO_3$	3	−3.975	3.390	0.005
$NaClO_4$	6	−7.002	7.461	0.009
$NaBrO_3$	2.617	−7.910	6.778	0.002
$NaNO_3$	10	−9.151	9.169	0.072
NaH_2PO_4	6.5	−9.434	8.458	0.003
NaH_2AsO_4	1.3	−4.477	1.721	0.010
NaCNS	18	−8.046	10.508	0.039
KF	17.5	−9.224	11.750	0.018
KF	6	−8.646	10.705	0.006
KCl	5	−3.806	3.995	0.021
KBr	5.5	−7.329	7.752	0.004
KI	4.5	−.736	3.430	0.005
KOH	20	−10.155	15.710	0.039
$KClO_3$	0.70	−5.558	0.279	0.002
$KBrO_3$	0.4	−6.549	1.894	0.001
KNO_3	3.5	−9.097	6.945	0.004
KH_2PO_4	1.8	−10.794	10.867	0.002
KH_2AsO_4	1.3	−8.723	6.704	0.002
KCNS	5	−6.565	6.252	0.003
KPF_6	0.5	−15.100	30.036	0.000
RbF	3.5	−3.556	5.333	0.009
RbCl	7.8	−7.941	8.144	0.003
RbBr	5	−7.937	7.987	0.001
RbI	5	−8.167	8.342	0.002
$RbNO_3$	4.5	−9.375	7.260	0.007
CsF	3.5	−5.808	7.893	0.007
CsCl	11	−8.430	8.416	0.013
CsBr	5	−8.961	9.225	0.005
CsI	3	−8.874	8.824	0.005
CsOH	1.2	−4.790	7.992	0.012
$CsNO_3$	1.5	−10.894	11.191	0.000
$AgNO_3$	15	−8.527	5.523	0.014
$TlClO_4$	0.5	−11.928	15.157	0.001
$TlNO_3$	0.4	−16.198	40.794	0.002
$TlNO_2$	1.4	−17.167	40.858	0.003
NH_4Cl	7.405	−7.024	7.030	0.002
NH_4ClO_4	2.1	−10.776	12.432	0.007
NH_4NO_3	25	−7.509	5.670	0.010
Li *p*-tol	4.5	−6.231	6.100	0.014
Na *p*-tol	4	−4.276	2.227	0.014
K *p*-tol	3.5	−4.858	0.738	0.020
Na formate	3.5	−3.654	4.755	0.008
Li acetate	4	−6.631	8.202	0.005
Na acetate	3.5	−3.401	6.434	0.009
K acetate	3.5	−3.273	6.844	0.008
Rb acetate	3.5	−2.589	6.708	0.008
Cs acetate	3.5	−3.361	7.165	0.008
Tl acetate	6	−8.357	7.444	0.010
Na propionate	3	−3.340	7.237	0.008
Na butyrate	3.5	−3.300	7.799	0.026
Na valerate	2	−3.321	7.984	0.017
Na caproate	2.3	−3.276	8.156	0.015
Na heptylate	5	−4.643	1.224	0.167
Na heptylate	0.5	−3.170	8.442	0.004
Na caprylate	3	−7.224	0.005	0.149
Na pelargonate	2.5	−14.294	18.325	0.058
Na caprate	1.8	−15.997	24.364	0.020
Na acid maloate	5	−7.461	6.868	0.001
Na acid succinate	5	−8.216	8.495	0.002
Na acid adipate	0.7	−3.755	4.515	0.004
K acid malonate	5	−7.860	6.712	0.004
K acid succinate	4.5	−8.322	8.145	0.003
K acid adipate	1	−3.859	3.798	0.003

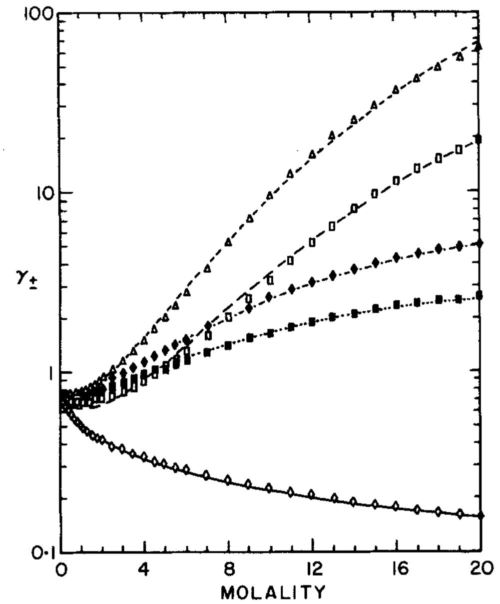

Figure 2. Experimental (Hamer and Wu, 1972) and calculated molality mean activity coefficient of various uni-univalent electrolytes at 298.15 K.

Δ LiCl (exp); --- LiCl (calc)
□ NaOH (exp); --- NaOH (calc)
♦ $LiNO_3$ (exp); - · - $LiNO_3$ (calc)
■ HNO_3 (exp); . . . HNO_3 (calc)
◊ NH_4NO_3 (exp); — NH_4NO_3 (calc)

Notably, Eqs. 32, 33, and Eq. 29 satisfy Eq. 31. Thus, in spite of the mathematical shortcomings, Eqs. 32 and 33 may be used together with the long-range contribution presented in the Appendix to obtain the solvent and the mean ionic activity coefficients as

$$\ln \gamma_i = (\ln \gamma_i)_{D-H} + (\ln \gamma_i^*)_{\text{NRTL-NRF}} \qquad (34)$$

Results and Discussion

The new model developed in this study is based on the Debye-Hückel theory for electrostatic forces (long-range forces) and a new NRTL-NRF model for the effect of local order (short-range forces). The use of the nonrandom factors (NRF) and random liquid as a reference fluid permits the development of a model applicable to the whole range of concentration from the dilute region up to the saturation point of each salt. Figure 1. shows the detail of both contributions, i.e., long- and short-range forces, to the activity coefficients of HCl in an aqueous solution. The model developed in this work has been tested for many salts. Results for the fitting of the mean ionic activity coefficients for uni-univalent electrolytes are shown in Table 1. As can be observed from Table 1, the model is able to predict the mean ionic activity coefficients of salts beyond the traditional molality of six that has been the limit used by most investigators. Some results for uni-univalent electrolytes up to molality 20 are shown in Figure 2. Figures 3 and 4 present a comparison of the results obtained with the most popular models and with new model for HCl and KOH. The two-parameter model of Ball et al. (1985) was not included in the comparisons since its parameters were evaluated using data of osmotic coefficients and a comparison in terms of mean ionic activity coefficient would be unfair. In fact, Ball et al.'s comparison of their model with those of Chen et al. (1982) and Pitzer et al. (1980) was done in terms of osmotic coefficients and used parameters specifically fitted with osmotic coefficient data. The model developed in the present study yields standard deviations of less than 2.5% for HCl and less than 4% for KOH. Table 2 shows the results of the fit for molality mean ionic activity coefficients for nonuni-univalent electrolytes at 298.15 K to maximum molality of six. Figure

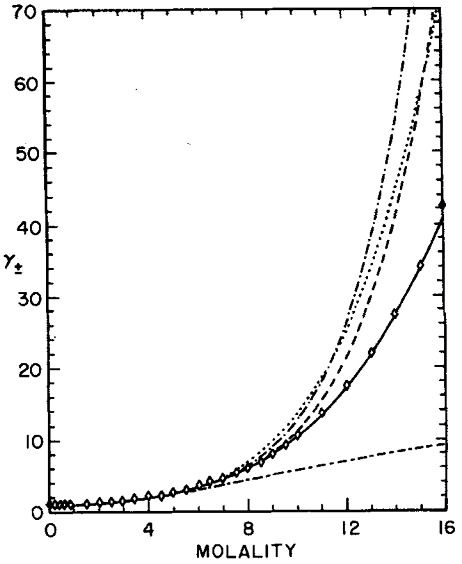

Figure 3. Molality mean activity coefficient of HCl by various models at 298.15 K.

Experimental values and values calculated with models other than the present study are those reported by Zemaites et al. (1986a)
◊ Exp.; —— present study; – · – Pitzer; . . . . Meissner
--- Bromley; —·— Chen

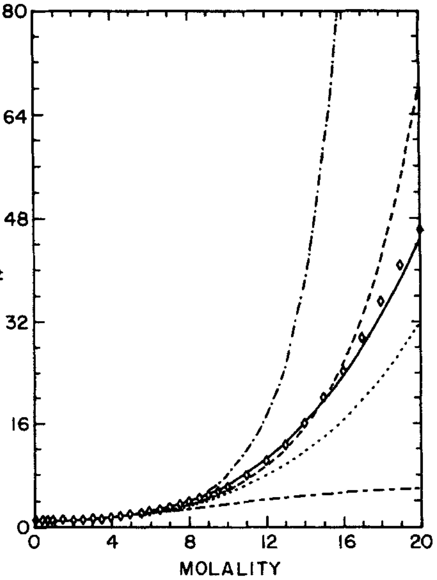

Figure 4. Molality mean activity coefficient of KOH by various models at 298.15 K.

Experimental values and values calculated with models other than the present study are those reported by Zemaites et al. (1986b)
◊ Exp.; —— present study; – · – Pitzer; . . . . Meissner
--- Bromley; —·— Chen

Table 2. Fit of the Molality Mean Ionic Activity Coefficient Data of Pure Aqueous Nonuni-Univalent Electrolytes at $T = 298.15$ K (Robinson and Stokes, 1959)

Bi-Univalent Electrolyte	Max. Molality	λ_E	λ_W	Std. Dev. of ln Values
$BaAc_2$	3.5	−7.896	8.499	0.072
$BaBr_2$	2	−10.165	17.481	0.020
$BaCl_2$	1.8	−10.230	16.172	0.021
$Ba(ClO_4)_2$	4	−8.759	14.128	0.029
BaI_2	2	−10.259	20.725	0.015
$CaBr_2$	6	−11.232	23.444	0.072
$CaCl_2$*	10	−9.571	17.099	0.109
$CaCl_2$*	6	−10.474	19.052	0.021
$Ca(ClO_4)_2$	6	−10.383	22.683	0.005
CaI_2	2	−10.533	23.061	0.007
$Ca(NO_3)_2$	6	−8.728	10.668	0.046
$CdBr_2$	4	−14.308	16.558	0.365
$CdCl_2$	6	−12.640	11.085	0.333
CdI_2	2.5	−17.348	31.222	0.466
$Cd(NO_3)_2$	2.5	−8.970	13.166	0.023
$CoBr_2$	5	−10.021	20.790	0.039
$CoCl_2$	4	−9.451	16.491	0.045
CoI_2	6	−10.190	24.067	0.100
CoI_2	5	−10.686	25.545	0.027
$Co(NO_3)_2$	5	−9.621	16.256	0.026
$CuCl_2$	6	−6.977	8.941	0.048
$Cu(NO_3)_2$	6	−9.252	14.495	0.035
$FeCl_2$	2	−10.565	19.608	0.019
$MgAc_2$	4	−9.840	12.887	0.072
$MgBr_2$	5	−10.967	24.431	0.025
$MgCl_2$	5	−10.851	21.829	0.018
$Mg(ClO_4)_2$	4	−11.071	27.528	0.026
MgI_2	5	−11.353	28.031	0.046
$Mg(NO_3)_2$	5	−9.686	17.143	0.022
$MnCl_2$	6	−7.921	12.044	0.067
$NiCl_2$	5	−9.649	17.326	0.052
$Pb(ClO_4)_2$	6	−9.492	16.470	0.028
$Pb(NO_3)_2$	2	−12.408	15.536	0.064
$SrBr_2$	2	−10.623	20.372	0.013
$SrCl_2$	4	−10.134	17.316	0.020
$Sr(ClO_4)_2$	6	−9.668	18.944	0.042
SrI_2	2	−10.477	22.100	0.006
$Sr(NO_3)_2$	4	−8.977	9.426	0.041
UO_2Cl_2	3	−8.559	15.159	0.024
$UO_2(ClO_4)_2$	5.5	−11.626	33.720	0.029
$UO_2(NO_3)_2$	5.5	−4.451	10.190	0.094
$ZnBr_2$	6	−2.360	5.999	0.058
$ZnCl_2$	6	−8.255	9.249	0.029
ZnI_2	6	−1.888	7.525	0.149
$Zn(ClO_4)_2$	4	−11.372	28.689	0.019
$Zn(NO_3)_2$	6	−9.336	16.105	0.021
Uni-Bivalent Electrolyte				
Cs_2SO_4	1.8	−5.853	5.975	0.011
K_2CrO_4	3.5	−7.033	7.710	0.017
K_2SO_4	0.7	−9.415	11.427	0.004
Li_2SO_4	3	−6.670	8.483	0.019
Na_2CrO_4	4	−7.701	9.464	0.040
Na_2 Fumarate	2	−7.089	10.096	0.004
Na_2 Maleate	3	−8.990	11.278	0.027
Na_2SO_4*	5	−8.191	8.466	0.010
$Na_2S_2O_3$	3.5	−7.597	8.644	0.021
$(NH_4)_2SO_4$	4	−8.378	8.327	0.022
Rb_2SO_4	1.8	−6.419	6.228	0.010
Bi-Bivalent Electrolyte				
$BeSO_4$	4	−5.803	9.781	0.078
$MgSO_4$	3	−4.550	8.075	0.074
$MnSO_4$	4	−5.556	8.542	0.084
$NiSO_4$	2.5	−3.872	6.883	0.072
$CuSO_4$	1.4	−.017	5.332	0.067
$ZnSO_4$	3.5	−5.798	8.826	0.083
$CdSO_4$	3.5	−5.157	7.851	0.073
UO_2SO_4	6	−5.751	8.753	0.054
H_2SO_4**	27.5	−10.032	11.436	0.232
Tri-Univalent Electrolyte				
$AlCl_3$	1.8	−6.825	19.604	0.080
$CeCl_3$	2	−4.237	12.863	0.063
$Co(en)_3Cl_3$	1	−8.371	8.859	0.084
$CrCl_3$	1.2	−1.171	13.339	0.073
$Cr(NO_3)_3$	1.4	−1.181	12.176	0.070
$EuCl_3$	2	−4.383	13.541	0.068
$Ga(ClO_4)_3$	2	−6.863	25.722	0.158
$K_3Fe(CN)_6$	1.4	−1.633	5.288	0.044
$LaCl_3$	2	−4.250	12.874	0.063
$NdCl_3$	2	−4.914	13.572	0.061
$PrCl_3$	2	−4.465	13.002	0.062
$ScCl_3$	1.8	−3.346	13.837	0.059
$SmCl_3$	2	−4.484	13.452	0.064
YCl_3	2	−5.937	15.633	0.064
Tri-Bivalent Electrolyte				
$Al_2(SO_4)_3$	1	−6.369	14.159	0.051
$Cr_2(SO_4)_3$	1.2	0.687	11.116	0.132

*Goldberg (1981)
**Staples (1981)

5 presents results for bi-univalent electrolytes. The model developed in the present study yields standard deviations for $CaBr_2$ and $CaCl_2$ of 7.2 and 2% while Chen's model produces standard deviations of 35.1 and 20.5%, respectively.

For the study of temperature effects, the present model was used without any modification for various electrolytes at different temperatures and model parameters were adjusted at each temperature. Table 3 shows the results of the fit for some salts at temperatures higher than 298.15 K and Figure 6 presents the results for $CaCl_2$ at 474.85 K obtained from the various models. The average standard deviations for the salts shown in Table 4 are within 4.4% for the present study while deviation for Chen's model is 98%. In the Chen et al. model the interaction parameters are those evaluated at 298.15 K and the temperature effect is introduced in parameter A of the Debye-Hückel expression.

The binary parameters presented in Tables 1, 2, and 3 were obtained by minimizing the mean square standard deviation between the calculated and experimental mole fraction mean activity coefficients as,

$$\sigma_\gamma = \left[\frac{\Sigma(\ln \gamma_\pm^{exp} - \ln \gamma_\pm^{calc})^2}{N}\right]^{1/2} \tag{35}$$

Then the results were converted to the molality mean ionic

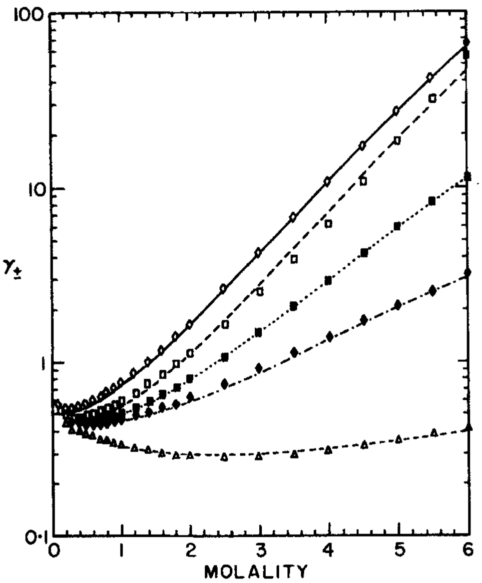

Figure 5. Experimental (Stokes and Robinson, 1948) and calculated molality mean activity coefficient of various bi-univalent electrolytes at 298.15 K.

◊ $Ca(ClO_4)_2$ (exp); — $Ca(ClO_4)_2$ (calc)
□ $CaBr_2$ (exp); --- $CaBr_2$ (calc)
■ $CaCl_2$ (exp); ... $CaCl_2$ (calc)
♦ $Cu(NO_3)_2$ (exp); - · - $Cu(NO_3)_2$ (calc)
△ $ZnCl_2$ (exp); --- $ZnCl_2$ (calc)

activity coefficient as follows:

$$\ln \gamma_{\pm m} = \ln \gamma_\pm - \ln\left(1 + \frac{M_W \nu m}{1{,}000}\right) \tag{36}$$

Attempts were carried out to determine the sensitivity of the results on the value assumed for the closest approach, B, in the Debye-Hückel model and on the coordination number Z in the NRTL-NRF model. A value of 8 for Z and 1.2 for B yield the minimum value of standard deviation for majority of electrolytes. However, with B set to 2 for bi-univalent electrolytes the results improve significantly.

Table 3. Fit of the Molality Mean Ionic Activity Coefficient Data of Pure Aqueous Electrolytes at Various Temperatures

Electrolyte	Max. Molality	Temp. K	λ_E	λ_W	Std. Dev. of ln Values
HCl*	2	323.15	−8.366	12.563	0.002
KCl**	4	353.15	−8.541	9.452	0.008
KOH*	17	353.15	−9.911	14.049	0.072
NaCl†	6	373.15	−8.760	10.599	0.017
NaCl†	6	573.15	−13.412	16.334	0.187
NaOH*	4	308.15	−8.361	10.620	0.011
$MgSO_4$**	2	350.15	−5.957	8.078	0.019
Na_2SO_4**	1.6	350.15	−9.639	11.709	0.021
$CaCl_2$†	3.5	382.00	−8.459	14.260	0.015
$CaCl_2$‡	3.5	475.00	−10.315	14.233	0.092
$MgCl_2$**	2	353.15	−8.513	16.009	0.011

*Harned and Owen (1958)
**Snipes et al. (1975)
†Silvester and Pitzer (1976)
‡Holmes et al. (1978)

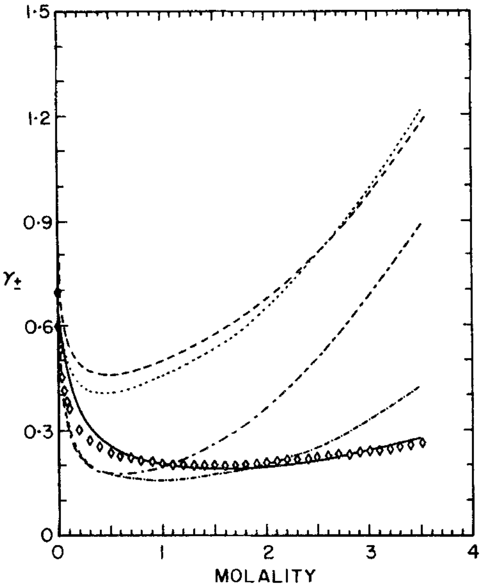

Figure 6. Molality mean activity coefficient of aqueous solution of $CaCl_2$ by various models at 479.85 K.

Experimental values and values calculated with models other than the present study are those reported by Zemaites et al. (1986c)
◊ Exp.; — present study; - · - Pitzer
. . . . Meissner; --- Bromley; —·— Chen

The assumption of a completely dissociated electrolyte may be considered as a limitation for the application of the present model to molecular electrolyte species and to complex ions in solution. However the model was used for electrolytes such as H_2SO_4 and Na heptylate, etc., with good results. The standard deviation for H_2SO_4 for maximum molality 27.5 was 0.232.

The model proposed in this work uses two binary adjustable parameters to fit the mean ionic activity coefficient data. The binary parameter, λ_E, is the difference of the dimensionless interaction energies between cation-anion pair and ion-molecule pair. The solvent parameter, λ_W, is the difference of dimensionless interaction energies between ion-solvent pair and solvent-solvent pair. Adjusting these two parameters presented some difficulties since both parameters are strongly correlated and in some cases the existence of multiple roots was found. As an

Table 4. Comparison of Models for Electrolytes at Various Temperatures (Zemaites et al., 1986)

		Std. Dev. of ln Values of Activity Coeff.				
Electrolyte	Temp. K	Bromley	Meissner	Pitzer	Chen	Present Study
HCl	323.15	0.071	0.032	0.050	0.078	0.002
KCl	353.15	0.179	0.055	0.243	0.182	0.008
KOH	353.15	0.975	0.531	32.440	2.357	0.072
NaCl	373.15	0.266	0.169	0.274	0.154	0.017
NaCl	573.15	4.663	3.202	0.195	0.759	0.187
NaOH	308.15	0.096	0.098	0.038	0.095	0.011
$MgSO_4$	350.15	0.851	0.279	0.038	0.060	0.019
Na_2SO_4	350.15	0.492	0.086	0.223	0.184	0.021
$CaCl_2$	382.00	1.935	2.626	0.629	2.618	0.015
$CaCl_2$	475.00	6.487	6.339	0.823	3.349	0.092
Avg. std. dev.		1.602	1.342	3.495	0.984	0.044

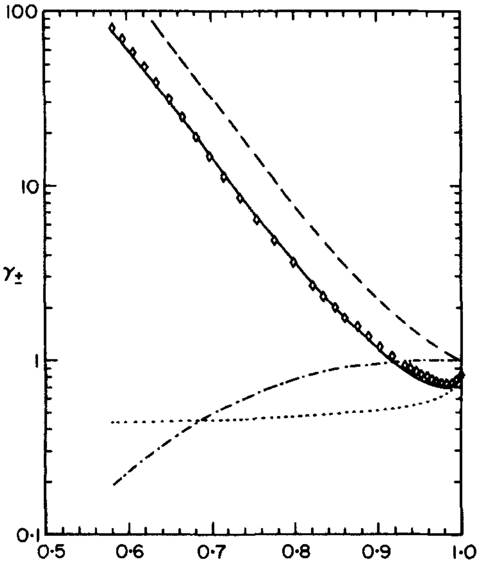

Figure 7. Long-range and short-range contributions on mean activity coefficient of aqueous solution of KOH at 298.15 K.

◇ Exp. (Hamer and Wu 1972); —— calc.;
. . . Debye-Hückel; ---- NRTL-NRF; – · – water

example, two positive values, 12.173 and 11.938, were found for the parameters for $LiClO_4$ with standard deviation of 1.9%, which is close to the value of 1.7% obtained with the parameters reported in Table 1. However for the sake of uniformity it was preferred to report the negative and positive values of the parameters, as shown in Tables 1 and 2. The only rationale for the above choice is that the opposite sign parameters gave the best fit of the data for almost all the systems studied.

Contributions due to long-range forces represented by the Debye-Hückel theory and to short-range forces represented by the NRTL-NRF model to excess Gibbs energy of system seem to be adequate in all the range from dilute solution up to high ionic strengths. Figure 7 shows both contributions to the mole fraction activity coefficient of KOH in an aqueous solution. It is clear that long-range forces dominate at low ionic strength and short-range forces dominate at high concentrations of electrolyte.

In conclusion, the model presented in this work gives a realistic representation of aqueous solutions of a single electrolyte and can be used with confidence up to high ionic strengths.

Conclusions

Recent models for the estimation of the mean ionic activity coefficient of electrolytes in aqueous solutions (Cruz et al., 1978; Chen et al., 1982) have made use of variations of the NRTL model (Renon and Prausnitz, 1968) for the excess Gibbs energy of a liquid mixture. Thus, these models for electrolyte solutions include the basic assumptions of the NRTL expression:

1. Assume the existence of different types of cells depending on the central species considered, and
2. Express the contribution of each cell to the excess Gibbs energy of the mixture by the difference between the Gibbs energy of the cell and that of hypothetical cell of pure central species

With these assumptions, the two-parameter models based on NRTL produce satisfactory results up to six-molal solutions of a single electrolyte and the results rapidly deteriorate for higher molalities.

In this work a new local composition model has been developed. Long-range interactions are accounted for by the Debye-Hückel theory. Local compositions, expressed in terms of nonrandom factors, are used to represent the effect of short-range interactions in aqueous electrolyte solutions. While the assumption of the existence of different types of cells, depending on their central species, has been retained, the contribution to the excess Gibbs energy from each type of cell has been considered differently from the NRTL model. In agreement with the concept of nonrandom factors, the contribution to the excess Gibbs energy by each cell has been expressed by the difference between the Gibbs energy of the cell and that of a cell with the same central particle in a random mixture. The new two-parameter model is able to correlate the mean ionic activity coefficient of electrolytes in aqueous solutions from the dilute region up to saturation. The empirical Wilson-type expressions (Wilson, 1964) used in this work to represent the nonrandom factors have all the theoretical limitations and practical advantages of similar expressions used in the NRTL-type treatments (Vera, 1986). The two-parameter model obtained in this work with the nonrandom factor interpretation of the local composition concept is the best two-parameter model for aqueous solutions of single electrolytes.

Acknowledgment

The authors are grateful to NSERC Canada for financial support.

Notation

a = distance of closest approach, m
A = Debye-Hückel constant
B = distance of closest approach parameter
D = dielectric constant
E = electron charge, 1.6021×10^{-19} C
g_{ij} = interaction energy between two species i and j
g_i^o = reference Gibbs energy of species i
g_i^{ex} = molar excess Gibbs energy of species i
g^{ex} = molar excess Gibbs energy
I = ionic strength
k = Boltzmann constant, 1.38054×10^{-23} J · K
m_i = molality of species i
m = molality of electrolyte
N = number of experimental points
M_W = molecular weight of solvent
n_S = number moles of salt (electrolyte)
N^o = Avogadro's number, 6.02252×10^{23} molecule · mol^{-1}
R = gas constant
T = absolute temperature, K
$\bar{v}_i$ = partial molar volume of species i
x_j = liquid mole fraction of species i
X_i = effective mole fraction of species i
X_{ij} = effective local mole fraction of species i around central species j
Z = coordination number
Z_i = absolute charge number of ionic species i

Greek letters

β_E = electrolyte interaction energy parameter
β_W = solvent interaction energy parameter
γ_i = activity coefficient of species i
$\gamma_\pm$ = mole fraction mean ionic activity coefficient

$\gamma_{\pm m}$ = molality mean ionic activity coefficient
Γ_{ij} = nonrandom factor of species i around j
κ = reciprocal Debye length, m^{-1}
λ = NRTL-NRF parameter
v = stoichometric number of electrolyte, $v = Z_A + Z_C$
ρ_S = density of solution
σ = root mean square deviation of ln values

Superscripts

$*$ = unsymmetrical convention
o = reference state
ex = excess
∞ = infinite dilution

Subscripts

A = anion
E = electrolyte
C = cation
S = salt
W = solvent
i, j, l = any species
$\pm$ = mean ionic, mole fraction basis
$\pm m$ = mean ionic, molality basis

Appendix: Debye-Hückel Model for Long-Range Interactions

Following the charging process approach of Fowler and Guggenheim (1949), Robinson and Stokes (1959) derived the molar excess Gibbs energy of an individual single ion of species j as

$$(g_j^{ex})_{D-H} = -\frac{N^o e^2 Z_i^2}{2D} \frac{\kappa}{1+\kappa a} + \frac{\bar{v}_j k t}{24\pi N^o a^3} (\kappa a)^3 \sigma(\kappa a) \quad \text{(A1)}$$

with

$$\sigma(\kappa a) = \frac{3}{(\kappa a)^3} \left[1 + \kappa a - \frac{1}{1+\kappa a} - 2 \ln (1 + \kappa a)\right] \quad \text{(A2)}$$

$$\kappa = 50.2916 \, X \, 10^8 \frac{\rho_s^{1/2}}{(TD)^{1/2}} I^{1/2} \quad \text{(A3)}$$

and

$$I = \tfrac{1}{2} \sum_i m_i Z_i^2 \quad \text{(A4)}$$

The activity coefficient of ionic species j derived from Eq. A1 has the form

$$(\ln \gamma_j)_{D-H} = -\frac{Z_j^2 e^2}{2 D \kappa T} \frac{\kappa}{(1 + \kappa a)} + \frac{\bar{v}_j}{24\pi N^o a^3} (\kappa a)^3 \sigma(\kappa a) \quad \text{(A5)}$$

As discussed by Robinson and Stokes (1959), the second term of the righthand side is negligible at concentrations of the electrolyte other than the extremely dilute solution and it is conventional to write

$$(\ln \gamma_j)_{D-H} = -\frac{A Z_j^2 I^{1/2}}{1 + B I^{1/2}} \quad \text{(A6)}$$

and thus, the mean ionic activity coefficient of the electrolyte i is written as

$$(\ln \gamma_{i\pm})_{D-H} = \frac{A \, |Z_{Ai} Z_{Ci}| \, I^{1/2}}{1 + B I^{1/2}} \quad \text{(A7)}$$

For the solvent—water in this study—the contribution of the long-range forces to the activity coefficient takes the form

$$(\ln \gamma_W)_{D-H} = \frac{2 A M_W}{B^3} \left[1 + B I^{1/2} - \frac{1}{1 + B I^{1/2}} - 2 \ln (1 + B I^{1/2})\right] \quad \text{(A8)}$$

The parameters A and B are slightly temperature-dependent and their values may be calculated from fundamental data.

Literature Cited

Abrams, D. S., and J. M. Prausnitz, "Statistical Thermodynamics of Liquid Mixtures: A New Expression for the Excess Gibbs Energy of Partly or Completely Miscible Systems," *AIChE J.*, **21,** 116 (1975).

Ball, F. X., W. Fürst, and H. Renon, "An NRTL Model for Representation and Prediction of Deviation from Ideality in Electrolyte Solutions Compared to the Models of Chen (1982) and Pitzer (1973)," *AIChE J.*, **31,** 392 (1985).

Blum, L., "Mean Spherical Model for Asymmetric Electrolytes. I: Method of Solution," *J. Mol. Phys.*, **30,** 1529 (1975).

Bromley, L. A., "Thermodynamic Properties of Strong Electrolytes in Aqueous Solutions," *AIChE J.*, **19,** 313 (1973).

Brönsted, J. N., "Calculation of the Osmotic and Activity Functions in Solutions of Uni-univalent Salts," *J. Am. Chem. Soc.*, **44,** 938 (1922).

Chen, C.-C., H. Britt, J. E. Boston, and L. B. Evans, "Local-Composition Model for Excess Gibbs Energy of Electrolyte Systems," *AIChE J.*, **28,** 588 (1982).

Chen C.-C., and L. B. Evans, "A Local-Composition Model for the Excess Gibbs Energy of Aqueous Electrolyte Systems," *AIChE J.*, **32,** 444 (1986).

Christensen, C., B. Sander, Aa. Fredenslund, and P. Rasmussen, "Toward the Extension of UNIFAC to Mixtures with Electrolytes," *Fluid Ph. Equilib.*, **13,** 297 (1983).

Cruz, J. L., and H. Renon, "A New Thermodynamic Representation of Binary Electrolyte Solutions Nonideality in the Whole Range of Concentrations," *AIChE J.*, **24,** 817 (1978).

Debye, D., and E. Hückel, "Zur Theorie des Elektrolyte," *Phys. Zeitschrift*, **24,** 185 and 305 (1923).

Fowler, R. H., and E. A. Guggenheim, *Statistical Thermodynamics*, Cambridge Univ. Press (1949).

Goldberg, R. N., "Evaluated Activity and Osmotic Coefficients for Aqueous Solutions: Thirty-six Uni-bivalent Electrolytes," *J. Phys. Chem. Ref. Data*, **10**(3), 671 (1981).

Hàla, E., Y. Dick, V. Fried, and O. Vilim, *Vapor-Liquid Equilibiria*, 2nd ed., Pergamon, Oxford (1967).

Hamer, W. J., and Y. C. Wu, "Osmotic Coefficients and Mean Activity Coefficients of Uni-univalent Electrolytes in Water at 25°C," *J. Phys. Chem. Ref. Data*, **1,** 1074 (1972).

Harned, H. S., and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions*, Reinhold, New York (1958).

Holmes, H. F., C. F. Baes, Jr., and R. E. Mesmer, "Isopiestic Studies of Aqueous Solutions at Elevated Temperatures. I: KCl, $CaCl_2$, and $MgCl_2$," *J. Chem. Thermo.*, **10,** 983 (1978).

Kawaguchi, Y., H. Kamar, H. Kasculara, and Y. Arai, "Correlation for Activities of Water in Aqueous Electrolyte Solutions Using ASOG Model," *J. Chem. Eng. Japan*, **14,** 243 (1981).

Kawaguchi, Y., Y. Tashima and Y. Arai, "Supplement to Correlation for Activities of Water in Aqueous Electrolyte Solutions Using ASOG Model," *J. Chem. Eng. Japan*, **15,** 62 (1984).

Lebowitz, J. L., and J. K. Percus, "Mean Spherical Model for Lattice Gases with Extended Hard Cores and Continuum Fluids," *Phys. Rev.*, **144,** 251 (1966).

Maurer, G., "*Electrolyte Solutions,*" *Fluid Ph. Equilib.*, **13**, 269 (1983).

Meissner, H. P., "Prediction of Activity Coefficients of Strong Electrolytes in Aqueous Systems," *Thermodynamics of Aqueous Systems with Industrial Applications*, S. A. Newman, ed., *Am. Chem. Soc. Symp. Ser.*, **133**, Washington, DC, 495 (1980).

Meissner, H. P., and C. L. Kusik, "Activity Coefficients of Strong Electrolytes in Multicomponent Aqueous Solutions," *AIChE J.*, **18**, 294 (1972).

Panayiotou, C., and J. H. Vera, "The Quasichemical Approach for Nonrandomness in Liquid Mixtures. Expression for Local Surfaces and Local Compositions with an Applications to Polymer Solutions," *Fluid Ph. Equilib.*, **5**, 55 (1980).

Percus, J. K., and G. J. Yevick, "Analysis of Classical Mechanics by Means of Collective Coordinates," *Phys. Rev.*, **110**, 1 (1958).

Pitzer, K. S., "Thermodynamics of Electrolytes. I: Theoretical Basis and General Equations," *J. Phys. Chem.*, **77**(2), 268 (1973).

———, "Electrolytes from Dilute Solutions to Fused Salts," *J. Am. Chem. Soc.*, **102**(9), 2902 (1980a).

———, "Thermodynamics of Aqueous Electrolytes at Various Temperatures, Pressures, and Compositions," *Thermodynamics of Aqueous Systems with Industrial Applications*, S. A. Newman, ed., *Am. Chem. Soc. Ser.*, **133**, Washington DC, 495 (1980b).

Planche, H., and H. Renon, "Mean Spherical Approximations Applied to a Simple but Nonprimitive Model of Interactions for Electrolyte Solutions and Polar Substances," *J. Phys. Chem.*, **85**, 3924 (1981).

Prigogine, I., and R. Defay, *Chemical Thermodynamics*, Longmans, Green (1954).

Renon, H., "Electrolyte Solutions," *Fluid Ph. Equili.*, **30**, 181 (1986).

Renon, H., and J. M. Prausnitz, "Local Composition Thermodynamic Excess Functions for Liquid Mixtures," *AICHE J.*, **14**, 135 (1968).

Robinson, R. A., and R. H. Stokes, *Electrolyte Solutions*, 2nd ed., Butterworths, London (1959).

Silvester, L. F., and K. S. Pitzer, "Thermodynamics of Geothermal Brines. I: Thermodynamic Properties of Vapor-Saturated NaCl (aq) Solutions from 0–300°C," Lawrence Berkeley Lab. Rept. LBL-4456 (Jan., 1976).

Snipes, H. P., C. Manly, and D. D. Ensor, "Heats of Dilution of Aqueous Electrolytes: Temperature Dependence," *J. Chem. Eng. Data*, **20**(3), 287 (1975).

Staples, B. R., "Activity and Osmotic Coefficients of Aqueous Sulfuric Acid at 298.15 K," *J. Phys. Chem. Ref. Data*, **10**(3), 779 (1981).

Stokes, R. H., and R. A. Robinson, "Ionic Hydration and Activity in Electrolyte Solution," *J. Am. Chem. Soc.*, **70**, 1870 (1948).

Vera, J. H., "On the Local Composition Concept," *Fluid Ph. Equilib.*, **26**, 313 (1986).

Waisman, E., and J. L. Lebowitz, "Exact Solution of an Integral Equation for the Structure of a Primitive Model of Electrolytes," *J. Chem. Phys.*, **52**, 4307 (1970).

———, "Mean Spherical Model Integral Equation for Charged Hard Spheres. I: Method of Solution," *J. Chem. Phys.*, **56**, 3086 (1972).

Wilson, G. M., "Vapor-Liquid Equilibrium. XI: A New Expression for the Excess Free Energy of Mixing," *J. Am. Chem. Soc.*, **86**, 127 (1964).

Zemaites, J. F. Jr., D. M. Clark, M. Rafal, and N. C. Scrivner, *Handbook of Aqueous Electrolyte Thermodynamics*, DIPPR, AIChE Pub. New York, (a)p. 102, (b)p. 109, (c)p. 158 (1986).

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