Activity Coefficient Model of Concentrated Electrolyte Solutions

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Since Debye and Huckel proposed their simple limiting law predicting the activity coefficients of dilute electrolyte solutions, there have been many attempts to extend their theory to solutions of high concentration. Little success had been achieved until the last two decades during which a number of models utilizing methods of statistical mechanics were developed. The most successful of these are the virial model of Pitzer (1973), the NRTL (Nonrandom two-liquid) model of Cruz and Renon (1978), the NRTL model of Chen et al. (1982), and the UNIQUAC model of Sander (1986).

Generally speaking, the development of these models is based on the summation of the excess Gibbs free energy of the electrolyte solution coming from the following contributions:

- Long-range interactions or electrostatic interactions
- Short-range interactions (Virial, NRTL, or UNIQUAC model)
- Concentration dependence of dielectric constants.

In all of the four above-mentioned models, the long-range and short-range interactions are taken as independent: i.e., they assume that long-range interactions have little effect on short-range interactions and short-range interactions have little effect on long-range interactions.

Liu et al. (1989a) proposed a different approach. Their model was based on the assumption that long-range and short-range interactions would interact. The local composition, NRTL model was used to accommodate these effects. The NRTL model they used abandoned the "local electroneutrality" assumption which was made by Chen and coworkers. In addition all the model parameters used were ion-specific.

The main limitation of the Liu et al.'s model is lack of extensive model parameter database. Using the "ion-specific" parameters has the advantage that no additional parameter is needed to extend the activity coefficient model for multicomponent prediction. But from a practical point of view, the disadvantage of ion-specific parameters is that they are difficult to correlate from experimental data since the ion-solvent energy parameters would tend to have different values when correlated with different salts with common ions. Even if it was possible to correlate the experimental activity coefficient data from a large number of salts with the same ion at the same temperature so that universal ion-solvent interaction parameters could be obtained, it would not be practical at temperatures other than 25°C due to lack of extensive experimental data. From a theoretical point of view, the same ion-solvent interaction might have different values in different environments since all ions are not acting independently.

A new method of correlating data using the Liu et al.'s (1989) NRTL model was used in this analysis. The parameters of this analysis are electrolyte-specific, rather than ion-specific, making the model more practical to use. The relationship between the proposed electrolyte-specific parameters and the ion-specific parameters is given. The salt-salt interaction parameters in the multicomponent prediction can be obtained from the corresponding binary parameters.

Modified Liu et al.'s NRTL Model

The modification of the Liu et al.'s NRTL model is in the formulation of the energy parameter in the original model. The structure of the Liu et al.'s NRTL model is left unchanged. Four new parameters, $\tau_{w,ca}$, $\tau_{ca,w}$, $\tau'_{w,ca}$, and $\tau'_{ca,w}$, are defined, which are electrolyte-specific, instead of ion-specific. The new parameters and the equations for calculating activity coefficients are defined as follows.

Long-range interaction contribution

The long-range interaction contribution is obtained by modifying the original Debye-Huckel model. It is the combination of classical Poisson-Boltzmann theory and the local-composition concept.

The activity coefficients of cation c_i and anion a_i due to long-range interaction are given as (Liu et al., 1989b)

$$\ln \gamma_{c_i,LR} = \frac{e^2}{2DkT} \cdot \left(\frac{z_{c_i}}{r_{c_i}} \left[(z_{c_i} + C_{c_i} \sum_{a_j} x_{a_j c_i} z_{a_j}) \frac{\exp[\kappa(r^r_{c_i} - r_{c_i})]}{(1 + \kappa r^r_{c_i})} - z_{c_i} \right] \right) \quad (1)$$

$$\ln \gamma_{a_i,LR} = \frac{e^2}{2DkT} \cdot \left(\frac{z_{a_i}}{r_{a_i}} \left[(z_{a_i} + C_{a_i} \sum_{c_j} x_{c_j a_i} z_{c_j}) \frac{\exp[\kappa(r^r_{a_i} - r_{a_i})]}{(1 + \kappa r^r_{a_i})} - z_{a_i} \right] \right) \quad (2)$$

where

$$x_{a_j c_i} = \frac{x_{a_j}}{x_w G_{wc_i,a_j c_i} + x_{a_k} G_{a_k c_i,a_j c_i}}$$

$$x_{c_j a_i} = \frac{x_{c_j}}{x_w G_{wa_i,c_j a_i} + x_{c_k} G_{c_k a_i,c_j a_i}}$$

$$r^r_{a_i} = r_{a_i} + \frac{\Sigma_{c_j} \lambda_{c_j} r_{c_j} x_{c_j}}{\Sigma_{c_j} x_{c_j}}$$

$$r^r_{c_i} = r_{c_i} + \frac{\Sigma_{a_j} \lambda_{a_j} r_{a_j} x_{a_j}}{\Sigma_{a_j} x_{a_j}}$$

$$\kappa^2 = \frac{4\pi e^2}{DkT} n_T \left(\sum_{c_j} x_{c_j} z^2_{c_j} + \sum_{a_j} x_{a_j} z^2_{a_j} \right)$$

Short-range interaction contribution

The short-range interaction contribution is based on the local-composition concept. It is similar to the Chen's NRTL model except that "local electroneutrality" is not assumed.

The activity coefficients of cation c_i and anion a_i due to short-range interaction are given as (Liu et al., 1989b)

$$\ln \gamma_{c_i,SR} = -\frac{C_w}{2} \left(\frac{x_w G_{c_i w,ww}}{x_w + \Sigma_{c_j} x_{c_j} G_{c_j w,ww} + x_{a_j} G_{a_j w,ww}} - x_w - G_{c_i w,ww} + 1 \right) - \frac{C_{c_i}}{2 \Sigma_{a_j} x_{a_j}} \sum_{a_k} x_{a_k} \ln \frac{x_w G_{wc_i,a_k c_i} + x_{a_j} x_{a_j} G_{a_j c_i,a_k c_i}}{(1 - \Sigma_{c_j} x_{c_j}) G_{wc_i,a_k c_i}} + \frac{1}{2(\Sigma_{c_j} x_{c_j})^2} \sum_{a_k} C_{a_k} x_{a_k} \cdot \left[\sum_{c_k} x_{c_k} \ln \frac{x_w G_{wa_k,c_k a_k} + \Sigma_{c_j} x_{c_j} G_{c_j a_k,c_k a_k}}{(1 - \Sigma_{a_j} x_{a_j}) G_{wa_k,c_i a_k}} \right] - \frac{1}{2\Sigma_{c_j} x_{c_j}} \sum_{a_k} C_{a_k} x_{a_k} \left[\ln \frac{x_w G_{wa_k,c_i a_k} + \Sigma_{c_j} x_{c_j} G_{c_j a_k,c_i a_k}}{(1 - \Sigma_{a_j} x_{a_j}) G_{wa_k,c_i a_k}} + \sum_{c_k} x_{c_k} \left(\frac{G_{c_i a_k,c_k a_k}}{x_w G_{wa_k,c_k a_k} + \Sigma_{c_j} x_{c_j} G_{c_j a_k,c_k a_k}} - \frac{1}{1 - \Sigma_{a_j} x_{a_j}} \right) \right] \quad (3)$$

$$\ln \gamma_{a_i,SR} = -\frac{C_w}{2} \left(\frac{x_w G_{a_i w,ww}}{x_w + \Sigma_{c_j} x_{c_j} G_{c_j w,ww} + \Sigma_{a_j} x_{a_j} G_{a_j w,ww}} - x_w - G_{a_i w,ww} + 1 \right) - \frac{C_{a_i}}{2 \Sigma_{c_j} x_{c_j}} \sum_{c_k} x_{c_k} \ln \frac{x_w G_{wa_i,c_k a_i} + \Sigma_{c_j} x_{c_j} G_{c_j a_i,c_k a_i}}{(1 - \Sigma_{a_j} x_{aj}) G_{wa_i,c_k a_i}} + \frac{1}{2(\Sigma_{a_j} x_{a_j})^2} \sum_{c_k} C_{c_k} x_{c_k} \cdot \left[\Sigma_{a_k} x_{a_k} \ln \frac{x_w G_{wc_k,a_k c_k} + \Sigma_{a_j} x_{a_j} G_{a_j c_k,a_k c_k}}{(1 - \Sigma_{c_j} x_{c_j}) G_{wc_k,a_k c_k}} \right] - \frac{1}{2\Sigma_{a_j} x_{a_j}} \sum_{c_k} C_{c_k} x_{c_k} \left[\ln \frac{x_w G_{wc_k,a_i c_k} + \Sigma_{a_j} x_{a_j} G_{a_j c_k,a_i c_k}}{(1 - \Sigma_{c_j} x_{c_j}) G_{wc_k,a_i c_k}} + \sum_{a_k} x_{a_k} \left(\frac{G_{a_i c_k,a_k c_k}}{x_w G_{wc_k,a_k c_k} + \Sigma_{a_j} x_{a_j} G_{a_j c_k,a_k c_k}} - \frac{1}{1 - \Sigma_{c_j} x_{c_j}} \right) \right] \quad (4)$$

Then the activity coefficient for salt $c_i a_i$ is obtained as

$$\ln \gamma_{c_i a_i} = \frac{1}{(\nu_{c_i} + \nu_{a_i})} [\nu_{c_i} (\ln \gamma_{c_i,LR} + \ln \gamma_{c_i,SR}) + \nu_{a_i} (\ln \gamma_{a_i,SR} + \ln \gamma_{a_i,SR})]$$

The model parameter $G_{ji,ki}$ is defined as

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

where the energy parameter g_{ji} accounts for the interaction between two species i and j.

Here we define the following relations,

$$(g_{wc} - g_{ac})/RT = \tau_{w,ca} \quad (5)$$

$$(g_{wa} - g_{ca})/RT = \tau'_{w,ca} \quad (6)$$

$$(g_{cw} - g_{ww})/RT = \tau_{ca,w} \quad (7)$$

$$(g_{aw} - g_{ww})/RT = \tau'_{ca,w} \quad (8)$$

where τ and τ' are the new parameters, which are electrolyte-specific. And the following relation holds:

$$\tau'_{w,ca} - \tau_{w,ca} = \tau'_{ca,w} - \tau_{ca,w} \quad (9)$$

Those relations differ from the Chen's NRTL model in the sense that the following relations do not necessarily hold:

$$g_{wc} = g_{wa} = g_{ca}$$

and

$$g_{cw} = g_{aw} = g_{ww}$$

which are the results of the local electroneutrality assumption. This is reflected by the fact that τ does not have the same values as τ'.

Table 1. Parameters for 1-1 Type Electrolyte at 25°C*

Salt	$\tau_{w,ca}$	$\tau_{ca,w}$	$\tau'_{w,ca}$	$\tau'_{ca,w}$	Max m	$\sigma_{\ln\gamma}$
HBr	−1.7797	−1.0630	0.2715	0.9881	3.0	0.010
HCl	−0.7649	−1.4127	1.6674	1.0196	6.0	0.002
HI	−0.9262	−1.0722	0.5215	0.3755	3.0	0.011
HNO_3	−0.8164	−0.7205	0.6033	0.6992	3.0	0.007
KBr	−1.0952	−1.1504	1.5313	1.4761	5.5	0.011
KCl	−1.2436	−1.5801	1.9821	1.6457	6.0	0.000
KI	−1.5565	−1.3583	1.6087	1.8060	4.5	0.002
KNO_3	−0.0840	−1.7639	2.5079	0.8280	3.5	0.010
LiBr	−2.1481	−0.8308	0.2660	1.5833	6.0	0.009
LiCl	−0.8052	−0.9061	1.1960	1.0951	6.0	0.002
$LiNO_3$	−0.8982	−0.7323	0.5998	0.7657	6.0	0.008
NaBr	−0.8455	−1.4758	1.9201	1.2899	4.0	0.000
NaCl	−1.0511	−1.4521	1.8366	1.4356	6.0	0.002
NaI	−2.7038	−1.0488	1.1556	2.8107	3.5	0.006
$NaNO_3$	−0.9565	−1.4924	2.0043	1.4684	6.0	0.005
NH_4Cl	−3.8275	−0.8782	1.1434	4.0927	6.0	0.023
NH_4NO_3	−12.0185	−1.8198	2.4882	12.6869	6.0	0.007

*Experimental Data from Robinson and Stokes (1970)

If we assume $g_{ww} = 0$, we have the following equations:

$$g_{cw}/RT = \tau_{ca,w} \tag{10}$$

$$g_{aw}/RT = \tau'_{ca,w} \tag{11}$$

$$g_{ac}/RT = \tau_{ca,w} - \tau_{w,ca} \tag{12}$$

which relate the proposed electrolyte-specific parameters to the ion-specific parameters.

Binary Solutions

The parameters of the modified Liu et al.'s NRTL model, $\tau_{w,ca}$, $\tau_{ca,w}$, $\tau'_{w,ca}$, and $\tau'_{ca,w}$, are obtained by least-square analysis on deviations between calculated and experimental values:

$$S_r = \sum_i (\ln \gamma^{\text{cal}}_{\pm,ca} - \ln \gamma^{\text{exptl}}_{\pm,ca})^2$$

where the experimental activity coefficient data are taken from Robinson and Stokes (1970).

Table 2. Parameters for High Valence Electrolyte at 25°C*

Salt	$\tau_{w,ca}$	$\tau_{ca,w}$	$\tau'_{w,ca}$	$\tau'_{ca,w}$	Max m	$\sigma_{\ln\gamma}$
$MgBr_2$	−0.1564	−1.0089	1.6597	0.8072	5.0	0.019
$MgCl_2$	0.3886	−1.5094	2.6870	0.7891	5.0	0.183
MgI_2	0.1246	−0.4527	2.0752	1.4979	5.0	0.036
$Mg(NO_3)_2$	0.1361	−1.7172	2.3617	0.5084	5.0	0.070
$CaBr_2$	−0.8806	−0.7248	1.2933	1.4492	6.0	0.040
$CaCl_2$	0.0066	−1.9034	2.4935	0.5767	6.0	0.026
CaI_2	−0.4501	−0.1280	1.6972	2.0193	2.0	0.009
$Ca(NO_3)_2$	−0.3779	−0.7421	1.9126	1.5484	6.0	0.020
K_2SO_4	−0.9120	−1.1784	2.5549	2.2885	0.7	0.008
Li_2SO_4	−0.2089	−0.6220	2.4055	1.9922	3.0	0.063
Na_2SO_4	−0.4884	−0.5596	2.4056	2.3315	4.0	0.047
$MgSO_4$	0.7006	−0.9831	3.6784	1.9948	3.0	0.317

*Experimental data from Robinson and Stokes (1970)

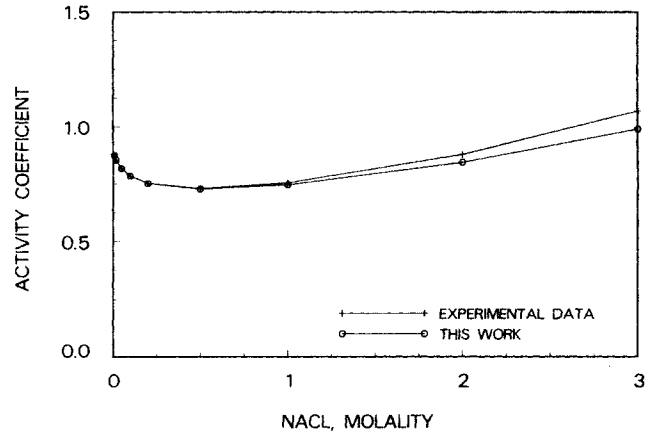

Figure 1. Activity coefficients of HCl in NaCl at 298.15 K (HCl = 0.01 m).

The conversion of the values of the activity coefficients between true-mole-fraction scale, which is the scale of the current model, and the molality scale, which is the scale of the experimental data, is given as follows:

$$\ln \gamma_{\pm,m} = \ln \gamma_{\pm,x} - \ln (1 + M_w(\nu_c + \nu_a)m/1{,}000)$$

where M_w is the molecular weight of water.

The concentration dependence of the dielectric constant is

$$D = 31.65 + 46.65 x_w$$

following the suggestion by Liu et al. (1989b).

The densities of the electrolyte solutions used in this analysis were the density of pure water, instead of the real densities of the solutions that are usually not available. The density of pure water at 25°C is 0.9970449 g/cm^3 (Kell, 1975).

It has been customary to use crystal ionic radii as the actual ionic radii in the solution since the latter are not known. Several sets of ionic radii are available. The set used in this study is based on the work by Marcus (1983). The radius of H^+

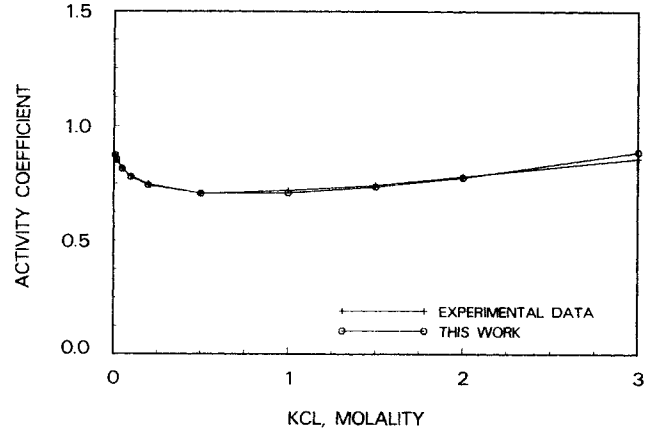

Figure 2. Activity coefficients of HCl in KCl at 298.15 K (HCl = 0.01 m).

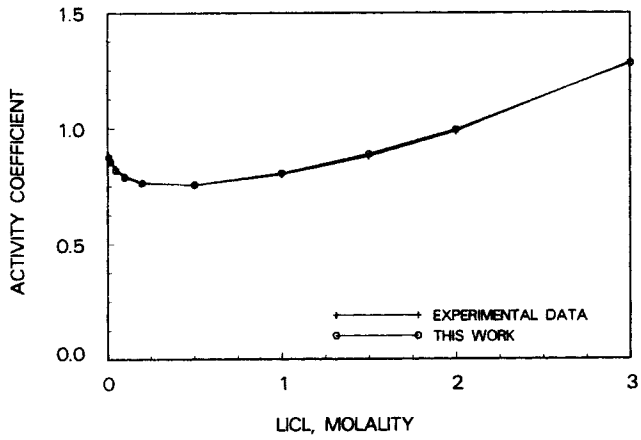

Figure 3. Activity coefficients of HCl in LiCl at 298.15 K (HCl = 0.01 m).

(r_{H^+} = 0.7 Å) is obtained from the fit of the activity coefficient data since its radius is not available. All coordination numbers are fixed as 6.

The correlation results are given in Tables 1 and 2. The size constants, λ, used were: 1.5 for cation, except for K^+ and NH_4^+ which were 1.1; 1.1 for anion except for Cl^- which was 1.5. It seemed that λ tended to have small values for large ions. The parameters corresponding to the cation-water interaction, $\tau_{ca,w}$, had negative values, while parameters corresponding to the anion-water interaction, $\tau'_{ca,w}$, had positive values. This trend was also observed from the correlation of the $H^+ - K^+ - Li^+ - Br^- - Cl^- - H_2O$ binary parameters by Liu et al. (1989b).

Multicomponent Solutions

The parameters for calculating multicomponent solutions activity coefficients are further defined as:

$$G_{c_i w,ww} = \sum_{a_j} x_{a_j} \exp\left(-\tau_{c_i a_j,w}\right) \Big/ \sum_{a_j} x_{a_j} \tag{13}$$

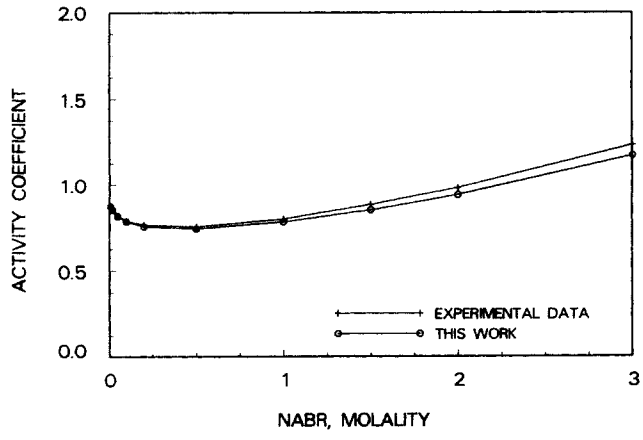

Figure 4. Activity coefficients of HBr in NaBr at 298.15 K (HBr = 0.01 m).

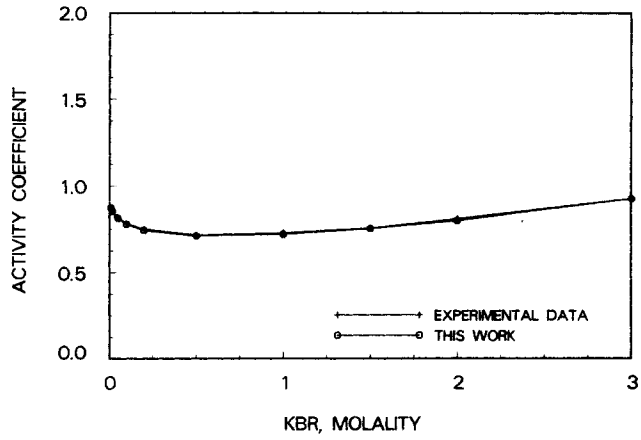

Figure 5. Activity coefficients of HBr in KBr at 298.15 K (HBr = 0.01 m).

$$G_{a_j w,ww} = \sum_{c_i} x_{c_i} \exp\left(-\tau'_{c_i a_j,w}\right) \Big/ \sum_{c_i} x_{c_i} \tag{14}$$

To characterize the mixture activity coefficients, the salt-salt interaction parameters are necessary. The salt-salt interaction parameters are $G_{c_i a_j,c_k a_j}$ and $G_{c_i a_j,c_i a_k}$, which can be directly calculated from the binary parameters.

If we assume $g_{ww} = 0$, then

$$G_{c_i a_j,c_k a_j} = \exp\left[-(g_{c_i a_j} - g_{c_k a_j})/RT\right]$$

$$= \exp\left[(\tau_{c_k a_j,w} - \tau_{w,c_k a_j}) - (\tau_{c_i a_j,w} - \tau_{w,c_i a_j})\right] \tag{15}$$

$$G_{c_i a_j,c_i a_k} = \exp\left[-(g_{c_i a_j} - g_{c_i a_k})/RT\right]$$

$$= \exp\left[(\tau_{c_i a_k,w} - \tau_{w,c_i a_k}) - (\tau_{c_i a_j,w} - \tau_{w,c_i a_j})\right] \tag{16}$$

The activity coefficients of HCl and HBr in halide solutions at 25°C were then calculated. The results were shown in Figures 1 to 5. The experimental data were taken from Harned and Owen (1958).

In summary, the modified Liu et al.'s NRTL model gives a practical method for correlating the model parameters from the available binary experimental data. The multicomponent activity coefficients could be calculated easily by using only the binary parameters.

It is worth pointing out that the model parameters, as well as the λ values given in this study, may not be the best ones because multiroots exist for highly nonlinear least square analysis. The best values should be selected in light of the multicomponent experimental data.

Notation

C = coordination number
D = dielectric constant
G = Gibbs free energy
$G_{ji,ki}$ = defined quantity
R = gas constant
T = temperature, K
e = protonic charge
g_{ji} = interaction energy parameter of j-i pair
k = Bolzmann constant
m = molality

n_i = number density of species i
r_c, r_a = ionic radius of cations and anions
x_i = true mole fraction of species i based on all species (ionic and molecular)
z_c, z_a = algebraic valences of cations and anions

Greek letters

α = defined quantity
γ = activity coefficient
λ = size constant
σ = standard deviation of the correlation
ν_c, ν_a = number of cations and anions produced by complete dissociation of one electrolyte molecule
τ, τ' = defined quantities

Superscripts

cal = calculated value
exptl = experiment value

Subscripts

a = anion
c = cation
ca = electrolyte ca
LR = long-range interaction
SR = short-range interaction
w = water

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