A Local Composition Model for the Excess Gibbs Energy of Aqueous Electrolyte Systems

The electrolyte nonrandom two-liquid (NRTL) model proposed by Chen et al. (1982) is generalized to represent the excess Gibbs energy of aqueous multicomponent electrolyte systems. Using only binary parameters, the model correlates and predicts the deviation from ideality of aqueous multicomponent electrolyte systems over the entire range of temperature and concentration.

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SCOPE

Representation of the excess Gibbs energy and activity coefficients for aqueous electrolyte systems is a fundamental problem in the design and operation of many industrial processes. Recently, active research has led to several excess Gibbs energy models and activity coefficient models for aqueous electrolyte systems up to concentrations of 6 molal or higher. Among them are the models of Pitzer (1973), Meissner and Tester (1972), Bromley (1973), and Cruz and Renon (1978).

A local composition model was later proposed by Chen et al. (1982) to represent the excess Gibbs energy of single-solvent, single completely dissociated electrolyte systems over the entire range of temperature and concentration. The model proposed two fundamental assumptions about the liquid lattice structure of electrolyte systems:

1. The like-ion repulsion assumption states that the local composition of cations around cations is zero (and likewise for anions around anions). This implies that the repulsive forces between ions of like charge are relatively large. The like-ion repulsion was justified on the basis that repulsive forces between ions of the same sign are very strong for neighboring species.
2. The local electroneutrality assumption states that the distribution of cations and anions around a central molecule is such that the net local ionic charge is zero. Local electroneutrality has been observed for interstitial molecules in salt crystals.

The model further postulates the excess Gibbs energy to be the sum of two contributions, one resulting from long-range electrostatic forces between ions and the other from short-range forces between all the species. The Pitzer-Debye-Hückel equation (Pitzer, 1980) was applied to model the long-range contribution. The nonrandom two-liquid (NRTL) theory (Renon and Prausnitz, 1968) was adopted to account for the short-range contribution.

The model was applied to obtain good data correlation results on many single-solvent, single completely dissociated electrolyte systems over a wide range of concentration and temperature. The model represents a basic framework that provides a continuous connection among limiting electrolyte systems, such as infinitely dilute electrolyte systems (where the model reduces to the Debye-Huckel model), pure molecular systems (where the model reduces to the NRTL model), and pure fused salts.

The objectives of this work are to generalize this electrolyte NRTL model to represent the excess Gibbs energy of aqueous multicomponent electrolyte systems and to examine the behavior and performance of the

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model for industrial applications. Discussion of the basic assumptions of the model and the hypothesized physical significance of the model binary parameters have been presented (Chen et al., 1982) and are not addressed here.

CONCLUSIONS AND SIGNIFICANCE

The electrolyte NRTL model has been generalized to represent the excess Gibbs energy of aqueous multicomponent electrolyte systems. Using only binary parameters, the model can be applied to wide varieties of aqueous electrolyte systems, including both strong electrolyte systems and weak electrolyte systems.

The model has many desirable features that make it especially suitable for representing the excess Gibbs energy of aqueous multicomponent electrolyte systems. First, with proper account of ionic equilibrium, the model requires only binary parameters to represent satisfactorily the deviation from ideality of any aqueous electrolyte systems. No higher-order parameters are needed, even at high concentrations. Second, the binary parameters are weak but well-behaved functions of temperature. Third, with binary salt-salt parameters being zero, the mixing rule of the model performs much like the Guggenheim equation (Robinson and Stokes, 1979, p. 437) for predicting osmotic coefficients and Harned's rule (Robinson and Stokes, p. 438) for predicting mean ionic activity coefficients for aqueous multicomponent electrolyte systems. Furthermore, the binary parameters correlate the deviations from the "ideal" mixing behavior suggested by the Guggenheim equation and Harned's rule.

Successful data correlation of many aqueous multicomponent electrolyte systems demonstrates the versatility of the model.

Model Development

The unsymmetric Pitzer-Debye-Hückel model is used to represent the contribution of the long-range ion-ion interactions, and the nonrandom two-liquid theory is used to represent the short-range interactions. The short-range interaction contribution model is developed as a symmetric model, based on reference states of pure solvents and hypothetical, homogeneously mixed, completely dissociated liquid electrolytes. The model is then normalized by infinite dilution activity coefficients in order to obtain an unsymmetric model. This expression and the Pitzer-Debye-Hückel expression are added to give Eq. 1 for the excess Gibbs energy.

$$g^{ex*}/RT = g^{ex*,pdh}/RT + g^{ex*,lc}/RT \qquad (1)$$

This leads to

$$\ln \gamma_i = \ln \gamma_i^{pdh} + \ln \gamma_i^{lc} \qquad (2)$$

Long-range interaction contribution

The Pitzer-Debye-Hückel formula, normalized to mole fractions of unity for solvent and zero for electrolytes, is used to represent the long-range interaction contribution.

$$g^{ex*,pdh}/RT = -\left(\sum_k x_k\right)\left(\frac{1{,}000}{M_s}\right)^{1/2} (4A_\phi I_x/\rho) \ln (1 + \rho I_x^{1/2}) \qquad (3)$$

Taking the appropriate derivative of Eq. 3, an expression for the activity coefficient can then be derived.

$$\ln \gamma_i^{*pdh} = -\left(\frac{1{,}000}{M_s}\right)^{1/2} A_\phi \{(2Z_i^2/\rho) \ln (1 + \rho I_x^{1/2}) + (Z_i^2 I_x^{1/2} - 2I_x^{3/2})/(1 + \rho I_x^{1/2})\} \qquad (4)$$

Short-range interaction contribution

The short-range interaction contribution is accounted for by the nonrandom two-liquid theory. The basic assumption of the NRTL model is that the nonideal entropy of mixing is negligible compared to the heat of mixing. This model was adopted because of its algebraic simplicity. Furthermore, the model does not require specific volume or area data.

To introduce the NRTL theory for electrolyte systems, an argument similar to that presented for the nonelectrolyte NRTL equation by Renon and Prausnitz (1968) is followed. Due to a new formulation of effective mole fraction, X, the following derivation is slightly different from that of Chen et al. (1982). The difference affects treatment of non-uni-univalent electrolytes.

The effective local mole fractions X_{ji} and X_{ii} of species j and i, respectively, in the neighborhood of molecular species i are related by:

$$X_{ji}/X_{ii} = (X_j/X_i)\, G_{ji} \qquad (5)$$

where:

$X_j = x_j C_j$ ($C_j = Z_j$ for ions and C_j = unity for molecules)

$G_{ji} = \exp(-\alpha_{ji}\tau_{ji})$

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

α_{ji} = nonrandomness factor

g_{ji} and g_{ii} are energies of interaction between j-i and i-i species, respectively. Both g_{ji} and α_{ji} are inherently symmetric ($g_{ji} = g_{ij}$ and $\alpha_{ji} = \alpha_{ij}$).

Similarly, the effective local mole fractions X_{ji} and X_{ki} of species j and k, respectively, in the neighborhood of ionic species i are related by:

$$X_{ji}/X_{ki} = (X_j/X_k)\, G_{ji,ki} \qquad (6)$$

where:

$$G_{ji,ki} = \exp(-\alpha_{ji,ki}\,\tau_{ji,ki})$$

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

$$\alpha_{ji,ki} = \text{nonrandomness factor}$$

The derivations that follow are based on a simple system of one solvent, *m*, and one completely dissociated liquid electrolyte, *ca*, dissociated into its cations, *c*, and anions, *a*. In this system, three different types of cells exist. One type consists of a central solvent molecule with other solvent molecules, cations, and anions in its immediate neighborhood. This type of cell follows the assumption of local electroneutrality: the surrounding cations and anions are such that the neighborhood of the solvent is electrically neutral. The other types of cells consist of either a central cation or anion with solvent molecules and ions of opposite charge in its immediate neighborhood. These two types of cells follow the assumption of like-ion repulsion: no ions of like charge exist near each other.

The effective local mole fractions are related by the following expressions:

$$X_{cm} + X_{am} + X_{mm} = 1 \text{ (central solvent cells)} \tag{7}$$

$$X_{mc} + X_{ac} = 1 \text{ (central cation cells)} \tag{8}$$

$$X_{ma} + X_{ca} = 1 \text{ (central anion cells)} \tag{9}$$

Using Eqs. 7–9 and the notation introduced in Eqs. 5 and 6, expressions for the effective local mole fractions in terms of the effective mole fractions can be derived.

$$X_{im} = X_i G_{im}/(X_a G_{am} + X_c G_{cm} + X_m G_{mm}) \quad i = c,\ a, \text{ or } m \tag{10}$$

$$X_{ac} = X_a/(X_a + X_m G_{mc,ac}) \tag{11}$$

$$X_{ca} = X_c/(X_c + X_m G_{ma,ca}) \tag{12}$$

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

$$g^{(c)} = Z_c(X_{mc} g_{mc} + X_{ac} g_{ac}) \tag{13}$$

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

$$g^{(m)} = X_{am} g_{am} + X_{cm} g_{cm} + X_{mm} g_{mm} \tag{15}$$

The reference Gibbs energy is determined for the reference states of completely dissociated liquid electrolyte and of pure solvent. The reference Gibbs energies per mole are:

$$g^{(c)}_{\text{ref}} = Z_c g_{ac} \tag{16}$$

$$g^{(a)}_{\text{ref}} = Z_a g_{ca} \tag{17}$$

$$g^{(m)}_{\text{ref}} = g_{mm} \tag{18}$$

The molar excess Gibbs energy is found by summing all changes in residual Gibbs energy per mole that result when the electrolyte and solvent in their reference states are mixed to form the existing electrolyte system. The expression is:

$$g^{ex,lc} = x_m(g^{(m)} - g^{(m)}_{\text{ref}}) + x_c(g^{(c)} - g^{(c)}_{\text{ref}}) + x_a(g^{(a)} - g^{(a)}_{\text{ref}}) \tag{19}$$

Using the above relation for the excess Gibbs energy and the expressions for the residual and reference Gibbs energy (Eqs. 13–15 and 16–18), the following expression for the excess Gibbs energy is obtained:

$$\begin{aligned} g^{ex,lc}/RT = {} & X_m X_{cm} \tau_{cm} + X_m X_{am} \tau_{am} \\ & + X_c X_{mc} \tau_{mc,ac} + X_a X_{ma} \tau_{ma,ca} \end{aligned} \tag{20}$$

The assumption of local electroneutrality applied to cells with central molecule may be stated as follows:

$$X_{am} = X_{cm} \tag{21}$$

Combining this expression with the expression for the effective local mole fractions given in Eq. 5, the following equality is obtained:

$$G_{am} = G_{cm} \tag{22}$$

The following relationships are further assumed for nonrandomness factors:

$$\alpha_{am} = \alpha_{cm} = \alpha_{ca,m} \tag{23}$$

$$\alpha_{mc,ac} = \alpha_{ma,ca} = \alpha_{m,ca} \tag{24}$$

and,

$$\alpha_{ca,m} = \alpha_{m,ca} \tag{25}$$

It may be inferred from the equations above that

$$\tau_{am} = \tau_{cm} = \tau_{ca,m} \tag{26}$$

$$\tau_{mc,ac} = \tau_{ma,ca} = \tau_{m,ca} \tag{27}$$

The nonrandomness factor, $\alpha_{ca,m}$, and the energy parameters, $\tau_{ca,m}$ and $\tau_{m,ca}$, are the adjustable binary parameters for a binary system of a single electrolyte and a single solvent.

The excess Gibbs energy expression, Eq. 20, must be normalized to the infinite dilution reference state for ions as follows:

$$g^{ex*,lc}/RT = g^{ex,lc}/RT - x_c \ln \gamma_c^{\infty} - x_a \ln \gamma_a^{\infty} \tag{28}$$

This yields the unsymmetric expression:

$$\begin{aligned} g^{ex*,lc}/RT = {} & X_m(X_{cm} + X_{am})\,\tau_{ca,m} + X_c X_{mc} \tau_{m,ca} + X_a X_{ma} \tau_{m,ca} \\ & - X_c(\tau_{m,ca} + G_{cm}\tau_{ca,m}) - X_a(\tau_{m,ca} + G_{am}\tau_{ca,m}) \end{aligned} \tag{29}$$

Multicomponent Systems

The equations for binary electrolyte systems, presented above, are readily generalized to solutions containing any number of electrolytes. The local composition concept considered here takes into consideration only two-body interactions and therefore the generalization requires no additional assumptions.

The pure component state is adopted as the reference state for the reference Gibbs energy of molecules and the hypothetical homogeneously mixed, completely dissociated liquid electrolyte mixture is adopted as the reference state for electrolytes. The reference Gibbs energies per mole are then:

$$g_{\mathrm{ref}}^{(c)} = Z_c \sum_{a'} (X_{a'} g_{a'c}) \Big/ \sum_{a''} X_{a''} \tag{30}$$

$$g_{\mathrm{ref}}^{(a)} = Z_a \sum_{c'} (X_{c'} g_{c'a}) \Big/ \sum_{c''} X_{c''} \tag{31}$$

$$g_{\mathrm{ref}}^{(m)} = g_{mm} \tag{32}$$

With the same procedure as outlined above for binary electrolyte systems, the excess Gibbs energy expression for aqueous multicomponent electrolyte systems can be derived as follows:

$$\frac{g^{ex,lc}}{RT} = \sum_m X_m \frac{\sum_j X_j G_{jm} \tau_{jm}}{\sum_k X_k G_{km}} + \sum_c X_c \sum_{a'} \frac{X_{a'}}{\sum_{a''} X_{a''}} \frac{\sum_j X_j G_{jc,a'c} \tau_{jc,a'c}}{\sum_k X_k G_{kc,a'c}} + \sum_a X_a \sum_{c'} \frac{X_{c'}}{\sum_{c''} X_{c''}} \frac{\sum_j X_j G_{ja,c'a} \tau_{ja,c'a}}{\sum_k X_k G_{ka,c'a}} \tag{33}$$

By taking the appropriate derivatives of Eq. 33, expressions for the activity coefficients of all species may be obtained. The activity coefficient equation for molecular components is given by:

$$\begin{aligned} \ln \gamma_m^{lc} = {} & \frac{\sum_j X_j G_{jm} \tau_{jm}}{\sum_k X_k G_{km}} + \sum_{m'} \frac{X_{m'} G_{mm'}}{\sum_k X_k G_{km'}} \left(\tau_{mm'} - \frac{\sum_k X_k G_{km'} \tau_{km'}}{\sum_k X_k G_{km'}} \right) \\ & + \sum_c \sum_{a'} \frac{X_{a'}}{\sum_{a''} X_{a''}} \frac{X_c G_{mc,a'c}}{\sum_k X_k G_{kc,a'c}} \cdot \left(\tau_{mc,a'c} - \frac{\sum_k X_k G_{kc,a'c} \tau_{kc,a'c}}{\sum_k X_k G_{kc,a'c}} \right) \\ & + \sum_a \sum_{c'} \frac{X_{c'}}{\sum_{c''} X_{c''}} \frac{X_a G_{ma,c'a}}{\sum_k X_k G_{ka,c'a}} \cdot \left(\tau_{ma,c'a} - \frac{\sum_k X_k G_{ka,c'a} \tau_{ka,c'a}}{\sum_k X_k G_{ka,c'a}} \right) \end{aligned} \tag{34}$$

The activity coefficient equation for cations is given by:

$$\begin{aligned} \frac{1}{Z_c} \ln \gamma_c^{lc} = {} & \sum_{a'} \frac{X_{a'}}{\sum_{a''} X_{a''}} \frac{\sum_k X_k G_{kc,a'c} \tau_{kc,a'c}}{\sum_k X_k G_{kc,a'c}} + \sum_m \frac{X_m G_{cm}}{\sum_k X_k G_{km}} \left(\tau_{cm} - \frac{\sum_k X_k G_{km} \tau_{km}}{\sum_k X_k G_{km}} \right) \\ & + \sum_a \sum_{c'} \frac{X_{c'}}{\sum_{c''} X_{c''}} \frac{X_a G_{ca,c'a}}{\sum_k X_k G_{ka,c'a}} \cdot \left(\tau_{ca,c'a} - \frac{\sum_k X_k G_{ka,c'a} \tau_{ka,c'a}}{\sum_k X_k G_{ka,c'a}} \right) \end{aligned} \tag{35}$$

The activity coefficient equation for anions is given by:

$$\begin{aligned} \frac{1}{Z_a} \ln \gamma_a^{lc} = {} & \sum_{c'} \frac{X_{c'}}{\sum_{c''} X_{c''}} \frac{\sum_k X_k G_{ka,c'a} \tau_{ka,c'a}}{\sum_k X_k G_{ka,c'a}} + \sum_m \frac{X_m G_{am}}{\sum_k X_k G_{km}} \left(\tau_{am} - \frac{\sum_k X_k G_{km} \tau_{km}}{\sum_k X_k G_{km}} \right) \\ & + \sum_c \sum_{a'} \frac{X_{a'}}{\sum_{a''} X_{a''}} \frac{X_c G_{ac,a'c}}{\sum_k X_k G_{kc,a'c}} \cdot \left(\tau_{ac,a'c} - \frac{\sum_k X_k G_{kc,a'c} \tau_{kc,a'c}}{\sum_k X_k G_{kc,a'c}} \right) \end{aligned} \tag{36}$$

Applying the local electroneutrality assumption and the two-body interaction assumption of the local composition concept, the following relationships can then be derived:

$$G_{cm} = \frac{\sum_a X_a G_{ca,m}}{\sum_{a'} X_{a'}} \tag{37}$$

$$G_{am} = \frac{\sum_c X_c G_{ca,m}}{\sum_{c'} X_{c'}} \tag{38}$$

A molal average mixing rule is adopted for the nonrandomness factor as follows:

$$\alpha_{cm} = \frac{\sum_a X_a \alpha_{ca,m}}{\sum_{a'} X_{a'}} \tag{39}$$

$$\alpha_{am} = \frac{\sum_c X_c \alpha_{ca,m}}{\sum_{c'} X_{c'}} \tag{40}$$

The variable τ_{im} can then be computed accordingly from the G_{im}. Furthermore, the variables $\tau_{ma,ca}$ and $\tau_{mc,ac}$ can be computed from the τ_{im}.

$$\begin{aligned}\tau_{ma,ca} &= (g_{ma} - g_{ca})/RT \\ &= (g_{ma} - g_{mm})/RT + (g_{mm} - g_{ca})/RT \\ &= \tau_{am} - \tau_{ca,m} + \tau_{m,ca}\end{aligned} \tag{41}$$

and

$$\tau_{mc,ac} = \tau_{cm} - \tau_{ca,m} + \tau_{m,ca} \tag{42}$$

The nonrandomness factor, $\alpha_{ca,m}$, $\alpha_{ca,ca'}$, $\alpha_{ca,c'a}$, and $\alpha_{mm'}$, and the energy parameters, $\tau_{ca,m}$, $\tau_{m,ca}$, $\tau_{ca,ca'}$, $\tau_{ca',ca}$, $\tau_{ca,c'a}$, $\tau_{c'a,ca}$, $\tau_{mm'}$ and $\tau_{m'm}$, are the adjustable binary parameters for the model. In the following data correlation discussions, unless indicated otherwise, all nonrandomness factors are fixed at 0.2.

Note that $\tau_{ca,c'a}$ and $\tau_{c'a,ca}$ may further be correlated by the following relationship.

$$\begin{aligned}\tau_{ca,c'a} &= (g_{c'a} - g_{ca})/RT \\ &= -(g_{ca} - g_{c'a})/RT \\ &= -\tau_{c'a,ca}\end{aligned} \tag{43}$$

This is because both g_{ca} and $g_{c'a}$ are assumed to be pure electrolyte quantities. Indeed, it is found that Eq. 43 is a satisfactory relationship for many of the systems examined in this work. Similarily, $\tau_{ca,ca'}$ and $\tau_{ca',ca}$ may be correlated by the following relationship.

$$\tau_{ca,ca'} = -\tau_{ca',ca} \tag{44}$$

Binary parameters

An advantage of models based on the local composition concept is that binary parameters of a multicomponent system and binary parameters of its constituent binary systems are the same and no higher-order parameters are required. Therefore, binary parameters for solvent-salt pairs of a multicomponent system can be obtained from data correlations of binary solvent-salt systems. Table 1 shows values of energy parameters for 43 water-salt pairs determined from osmotic coefficient data of binary aqueous electrolyte systems at 298.15 K. As presented in Table 1 and in the previous paper (Chen et al., 1982) the model gives accurate representation of electrolyte thermodynamic properties. For some of the electrolyte systems that show relatively high values of root mean square errors in fitting the osmotic coefficient data in Table 1, the results reflect the inadequacy of the assumption of complete dissociation. Both osmotic coefficient data and mean ionic activity coefficient data are quantities that inherit the assumption of complete dissociation. In other words, for those electrolyte systems in which the complete dissociation assumption is not satisfactory or significant ionic reactions take place in aqueous phase, osmotic coefficient data and mean ionic activity coefficient data are lumped quantities of the reactive mixtures. True speciation of the system is not rigorously accounted for. For more meaningful data regression, the ionic equilibrium should be taken into account as discussed in the next section.

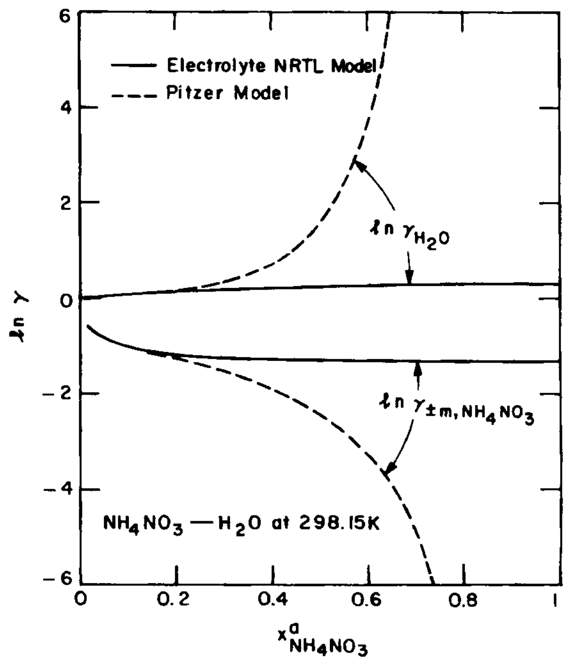

Figure 1. Prediction of water activity coefficient and NH_4NO_3 mean ionic activity coefficient of H_2O-NH_4NO_3 System.

With only binary parameters, the model is applicable to aqueous electrolyte systems with concentrations ranging from molecular liquid to fused salts (Chen et al., 1982). Figure 1 shows the predicted water activity coefficient and mean ionic activity coefficient of aqueous NH_4NO_3 solution over the entire concentration range using the binary parameters of Table 1, which were obtained from osmotic coefficient data at concentrations less than 6 molal. While the model predictions into higher concentration are smooth and are consistent with the experimental data of Othmer and Frohlich (1960), the prediction of the commonly used Pitzer model is not acceptable with reported virial coefficient parameters determined from osmotic coefficient data at concentrations less than 6 molal (Pytkowicz, 1979).

Also discussed in the previous paper, the energy parameters are weak but well-behaved functions of temperature. Using the following temperature function as suggested by Clarke and Glew (1966), the model has been used successfully to correlate excess enthalpy of mixing and excess heat capacity of mixing (Aspen Technology, 1984).

$$\tau = a + b\left(\frac{1}{T} - \frac{1}{\Theta}\right) + c\left\{\left(\frac{\Theta - T}{T}\right) + \ln\left(\frac{T}{\Theta}\right)\right\} \tag{45}$$

Since data are not available for salt-salt binary systems, the only way to estimate salt-salt binary parameters is through data correlation of solvent-salt$_1$-salt$_2$ ternary systems. These salt-salt binary parameters have significant effects on nonideality of ternary systems.

The effect of the salt-salt energy parameters on the solvent osmotic coefficient can be illustrated with Figure 2. The osmotic coefficient of a constant total molal NaCl-LiCl-H_2O system is compared at 2 molal with different mole fractions of LiCl in the salt mixture. Curve *A* of Figure 2 shows linear interpolation of

Table 1. Results of Fit for Osmotic Coefficients Data of Aqueous Electrolysis at 298.15 K with $\alpha = 0.2$*

Aqueous Solutions of Salts at 25°C	Maximum Molality	$\tau_{ca,w}$	$\tau_{w,ca}$	Root Mean Square Error $100\,\sigma_\phi$
NaCl	6	−4.5916	9.0234	1.2
NaBr	4	−4.6070	8.9288	0.6
NaI	3.5	−4.6920	8.9820	0.7
NaF	1	−3.7493	7.4322	0.02
$NaNO_3$	6	−3.6151	7.2886	0.2
KCl	4.8	−4.1341	8.1354	0.2
KBr	5.5	−4.1707	8.1699	0.3
KI	4.5	−4.1217	7.9408	0.2
LiCl	6	−5.1737	10.1242	2.4
$LiNO_3$	3.5	−4.6136	8.7565	0.4
$AgNO_3$	6	−3.1090	7.0619	0.7
KNO_3	3.5	−3.2747	7.2728	0.6
RbCl	5	−4.1358	8.2053	0.2
RbBr	5	−4.0399	8.0151	0.2
RbI	5	−4.0916	8.1419	0.1
CsCl	6	−4.3726	8.4238	0.4
NH_4Cl	6	−4.0121	7.8599	0.07
NH_4NO_3	6	−3.3162	6.8739	0.5
HCl	6	−5.2286	10.1728	1.9
HBr	3	−5.2194	9.9746	0.8
HI	3	−5.2039	9.7714	1.0
HNO_3	3	−4.3663	8.7223	0.5
LiBr	6	−5.3628	10.5393	2.8
LiI	3	−5.0883	9.5925	1.5
$HClO_4$	6	−5.4365	10.7078	3.3
NaOH	6	−4.7893	9.4200	2.3
KOH	6	−5.0644	9.2928	1.5
$CaCl_2$	6	−5.2549	10.5126	9.0
$CaCl_2$	2.5	−4.8618	9.3732	2.5
$CaBr_2$	6	−5.4801	11.0038	13.0
CaI_2	2	−5.1151	9.7214	2.4
$MgCl_2$	5	−5.3583	10.6681	9.0
$MgBr_2$	5	−5.5307	10.9725	9.0
MgI_2	5	−5.7064	11.3459	11.0
$SrCl_2$	4	−4.9537	9.7230	5.0
$BaCl_2$	1.8	−4.2068	7.9145	1.2
$Pb(ClO_4)_2$	6	−5.1308	10.1330	7.0
Na_2SO_4	4	−3.8760	7.9756	2.2
$(NH_4)_2SO_4$	5.5	−3.7871	7.7870	0.8
$MgSO_4$	3	−4.1796	8.2533	5.0
$AlCl_3$	1.8	−5.2306	10.0495	6.0
$LaCl_3$	2	−4.8883	9.3370	5.0
$CrCl_3$	1.2	−4.7759	8.7991	3.5

*From Robinson and Stokes (1970).

osmotic coefficients of the $NaCl$-H_2O system and $LiCl$-H_2O system, which represents the result of the Guggenheim treatment of mixed electrolyte solutions with a common ion (Robinson and Stokes, 1970). It is significant to note that Curve *B*, the osmotic coefficient curve with the NaCl-LiCl energy parameters set to zero, is very close to Curve *A*. In other words, the "ideal" mixing rule of the model is similar to that of the Guggenheim equation. Curves *C* and *D* represent osmotic coefficient with $\tau_{NaCl,LiCl} = -\tau_{LiCl,NaCl} = 1$ and 2, respectively. Table 2 shows good representation of osmotic coefficient data for many different $salt_1$-$salt_2$-H_2O systems with the $salt_1$-$salt_2$ energy parameters set to zero.

The effect of the salt-salt energy parameters on the mean ionic activity coefficient is illustrated with Figure 3. The mean ionic activity coefficients of a constant total molal $NaCl$-KCl-H_2O system (4 molal) are shown as functions of the mole fraction of KCl in the salt mixture. Curves *A*, *B*, and *C* represent mean ionic activity coefficients with $\tau_{NaCl,KCl} = -\tau_{KCl,NaCl} = 0$, 0.5, and 1, respectively. It is noteworthy that all curves are nearly linear and the model prediction resembles that of Harned's rule: the logarithm of the mean ionic activity coefficient of one electrolyte in a mixture of constant total molality is directly proportional to the molality of the other electrolyte (Robinson and Stokes, 1970).

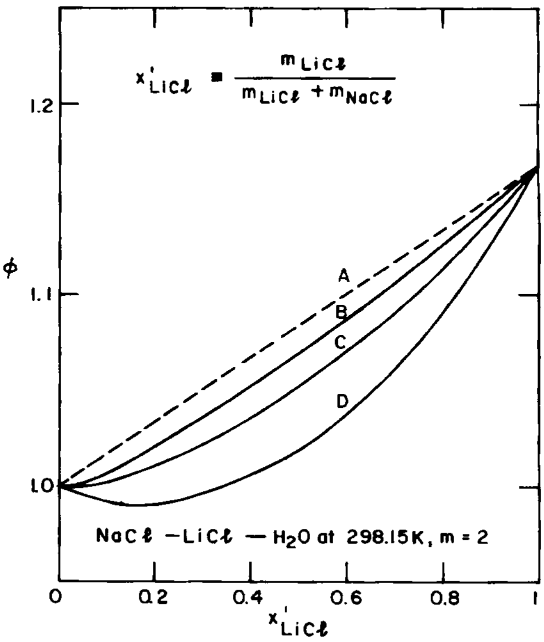

Figure 2. Prediction of osmotic coefficient of a constant total molal $NaCl$-$LiCl$-H_2O system with various salt-salt energy parameters.

A: $\phi = \phi^\circ_{LiCl}\, x'_{LiCl} + \phi^\circ_{NaCl}\, x'_{NaCl}$
B: $\tau_{NaCl,LiCl} = -\tau_{LiCl,NaCl} = 0$
C: $\tau_{NaCl,LiCl} = -\tau_{LiCl,NaCl} = 1$
D: $\tau_{NaCl,LiCl} = -\tau_{LiCl,NaCl} = 2$

Table 2. Results of Fit for Osmotic Coefficient Data of Aqueous Electrolytes at 298.15 K with $\alpha = 0.2$

Salts	$\sigma_\phi(\tau_{salt,salt} = 0)$	Data Source
NaCl-KCl	0.019	Covington et al. (1968)
NaCl-CsCl	0.013	Robinson (1952)
NaCl-NaBr	0.009	Covington et al. (1968)
NaCl-LiCl	0.017	Robinson et al. (1971)
$NaCl$-$NaNO_3$	0.015	Bezboruah et al. (1970)
NaBr-KBr	0.003	Covington et al. (1968)
$NaNO_3$-$LiNO_3$	0.018	Robinson et al. (1971)
$NaNO_3$-KNO_3	0.014	Bezboruah et al. (1970)
NaAc-LiAc	0.009	Robinson et al. (1971)
Na_2SO_4-K_2SO_4	0.021	Robinson et al. (1971)
$NaCl$-$MnCl_2$	0.027	Downes (1974)
KCl-KBr	0.006	Covington et al. (1968)
KCl-CsCl	0.005	Robinson (1953)
KCl-$SrCl_2$	0.054	Downes (1974)
KCl-KNO_3	0.011	Bezboruah et al. (1970)

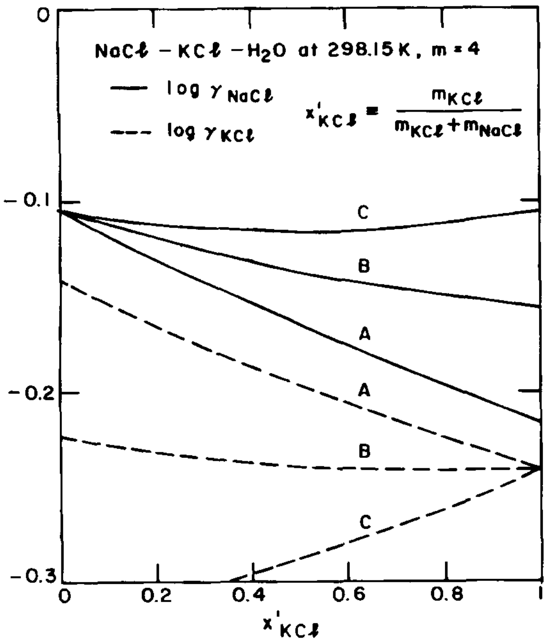

Figure 3. Prediction of mean ionic activity coefficient of a constant total molal NaCl-KCl-H_2O system with various salt-salt energy parameters.

A: $\tau_{NaCl,KCl} = -\tau_{KCl,NaCl} = 0$
B: $\tau_{NaCl,KCl} = -\tau_{KCl,NaCl} = 0.5$
C: $\tau_{NaCl,KCl} = -\tau_{KCl,NaCl} = 1$

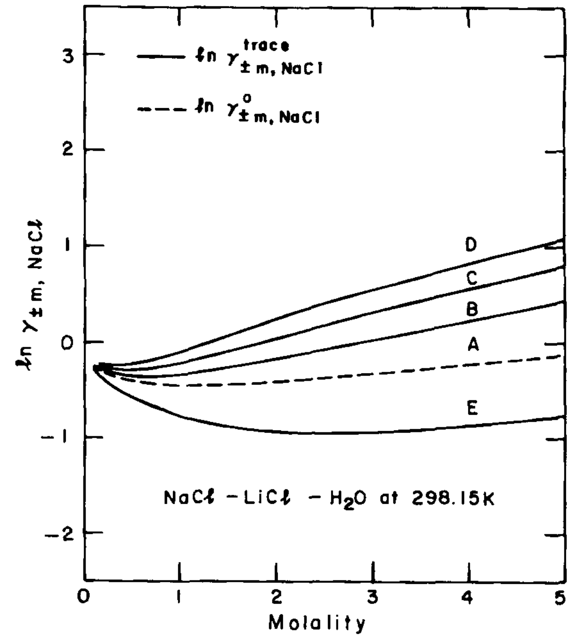

Figure 4. Prediction of trace mean ionic activity coefficient of a NaCl-LiCl-H_2O system with various salt-salt energy parameters.

A: Mean ionic activity coefficient
B–E: Trace mean ionic activity coefficient
B: $\tau_{NaCl,LiCl} = -\tau_{LiCl,NaCl} = 0$
C: $\tau_{NaCl,LiCl} = -\tau_{LiCl,NaCl} = 1$
D: $\tau_{NaCl,LiCl} = -\tau_{LiCl,NaCl} = 2$
E: $\tau_{NaCl,LiCl} = -\tau_{LiCl,NaCl} = -2$

Figure 4 illustrates further the effect of salt-salt energy parameters on the mean ionic activity coefficient at trace concentration. Curve *A* represents the mean ionic activity coefficient of NaCl in an NaCl-H_2O mixture, while curves *B–E* represent the mean ionic activity coefficient of NaCl in an NaCl-LiCl-H_2O system at trace concentration with $\tau_{NaCl,LiCl} = -\tau_{LiCl,NaCl} = 0, 1, 2,$ and -2, respectively. The curves are quite sensitive to values of the energy parameters.

Table 3 shows the results of data correlation of trace mean ionic activity coefficient of HCl and HBr in various aqueous electrolyte systems. The energy parameters for salt-salt pairs were adjusted and they were found to be relatively small compared with the energy parameters for salt-molecule pairs.

Ionic equilibrium

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

In the discussions above, complete dissociation of electrolytes has been assumed. The assumption of complete dissociation is not an inherent part of the model. Instead, it is introduced to simplify the treatment of data correlation and it often results in adequate representation of data. However, when ionic reaction among various species becomes significant, or dissociation is far from complete, the assumption of complete dissociation can lead to unsatisfactory results. Some examples of poor data correlation due to incomplete dissociation of electrolytes are the NaOH-H_2O system, the $CaBr_2$-H_2O system, and the HCl-H_2O system of Table 1.

Accounting for the formation of an ion pair of Na^+ and OH^- in an NaOH-H_2O system significantly improves the data correlation of solvent vapor pressure, as illustrated in Table 4.

$$NaOH_m \rightleftharpoons Na^+ + OH^- \qquad (46)$$

Two molecular species, water and molecular NaOH exist in the liquid phase in addition to cation Na^+ and anion OH^-. Addition of the chemical equilibrium constant of reaction 46 as an adjustable parameter significantly improves the goodness of fit, especially for high-concentration electrolyte systems. In this

Table 3. Results of Fit for Mean Ionic Activity Coefficients of HCl and HBr in Halide Solutions at 298.15 K with $\alpha = 0.2$*

Acid	Salt	$\tau_{salt,acid}$	$\sigma_{\ln\gamma_{acid}}$
HCl	KCl	−1.527	0.020
HCl	NaCl	−1.057	0.008
HCl	LiCl	−0.095	0.023
HCl	CsCl	−0.821	0.022
HCl	$SrCl_2$	−0.318	0.025
HCl	$AlCl_3$	0.001	0.057
HCl	$CeCl_3$	0.817	0.028
HBr	KBr	−1.300	0.008
HBr	NaBr	−1.056	0.007
HBr	LiBr	−0.294	0.028

*From Harned and Owen (1958).

Table 4. Results of Fit for Vapor Pressure of Caustic Solution*

T, K	τ_{NaOH,H_2O}	$\tau_{H_2O,NaOH}$	$\ln K_{NaOH_m}$	σ_P**	σ_p†
293.15	−28.282	57.521	21.500	0.007	0.027
313.15	−27.659	56.059	21.827	0.007	0.031
333.15	−27.087	54.716	21.534	0.007	0.031
353.15	−26.507	53.478	21.629	0.007	0.029
373.15	−26.000	52.327	21.413	0.008	0.027
393.15	−25.501	51.205	21.175	0.009	0.024

*From Perry and Chilton (1973).
**$\alpha_{NaOH,H_2O} = 0.03$, K_{NaOH_m} in molality scale.
†Ionic equilibrium not considered.

study, the energy parameters were set to zero except for those listed in Table 4. The maximum electrolyte concentration is 50 wt. % caustic.

Consideration of ionic equilibrium is essential in representing vapor-liquid equilibrium data of aqueous strong acids with the molecular thermodynamic framework. For example, molecular HCl exists in the aqueous phase as a result of partial dissociation of HCl.

$$HCl_m \rightleftharpoons H^+ + Cl^- \tag{47}$$

As shown in Table 5, vapor-liquid equilibrium data for the HCl-H_2O system were well-correlated by adjusting the energy parameters of the HCl-H_2O pair and the Henry's law constant of HCl_m in aqueous solution. Other parameters were set to zero. The maximum electrolyte concentration is 42 wt. % HCl. The sum of squares objective function used in data correlation was

$$S = \sum_{i=1}^{n} (y_{HCl,i}^{calc} - y_{HCl,i}^{exp})^2 + \sum_{i=1}^{n} \left(\frac{P_i^{calc} - P_i^{exp}}{P_i^{exp}} \right)^2 \tag{48}$$

Industrial Applications

The electrolyte NRTL model provides a general framework with which experimental data of industrial electrolyte systems can be satisfactorily represented with only binary parameters. It has been used successfully to model many important industrial electrolyte systems, among which are the hot carbonate CO_2 removal system, the sour water stripper system, and flue gas desulfurization (Aspen Technology, 1984; Taylor, 1984). Some typical applications are briefly discussed.

Table 5. Results of Fit for Vapor-Liquid Equilibrium of Aqueous HCl Solution*

T, K	τ_{HCl,H_2O}	$\tau_{H_2O,HCl}$	$\ln H_{HCl_m}$	σ_P**
273.15	−32.268	65.694	15.322	0.010
293.15	−32.681	64.568	15.352	0.017
298.15	−32.784	64.278	15.363	0.014
313.15	−32.604	63.036	15.934	0.012
333.15	−33.130	62.235	15.957	0.017
353.15	−34.861	62.610	15.214	0.016
373.15	−34.968	61.538	15.706	0.057

*From Perry and Chilton (1973).
**$\alpha_{HCl,H_2O} = 0.03$, $PK_{HCl_m} = -3.8$.

Salting-out effect

The effect of salts on the solubility of molecular solutes is often correlated using the Setschenow equation:

$$\ln \gamma_m^* = k_{s,m} m_s \tag{49}$$

However, the Setschenow equation is not a good approximation unless the solubility of molecular solutes is very small (Gordon, 1975). The relationship assumed by the Setschenow equation is often too simple to adequately describe the salting-out effect.

Table 6 reports the results of data correlation on the solubility of carbon dioxide in aqueous electrolyte solution at 298.15 K with salt-water energy parameters obtained from Table 1, carbon dioxide-water energy parameters obtained from data correlation of the binary nonelectrolyte system with data from Houghton et al. (1957), and adjusted salt-carbon dioxide energy parameters. The salting-out effect was represented successfully with the model while the Setschenow equation was found to be inadequate (Yasunishi and Yoshida, 1979).

Weak electrolyte vapor-liquid equilibrium

Data correlation of vapor-liquid equilibrium of the NH_3-H_2S-H_2O system has been examined by many previous investigators (Newman, 1980). In the vapor phase, ammonia, hydrogen sulfide, and water are present. In the liquid phase, hydrogen, hydroxide, ammonium, bisulfide, and sulfide ions are present in addition to ammonia and hydrogen sulfide molecular solutes and the solvent, water. The following reactions occur in the liquid phase

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \tag{50}$$

$$H_2S \rightleftharpoons H^+ + HS^- \tag{51}$$

$$HS^- \rightleftharpoons H^+ + S^= \tag{52}$$

$$H_2O \rightleftharpoons H^+ + OH^- \tag{53}$$

The high-concentration vapor-liquid equilibrium data of Miles and Wilson (1975) were successfully correlated with the model for the NH_3-H_2S-H_2O system. Vapor phase fugacity coefficients were calculated by the Redlich-Kwong-Soave equa-

Table 6. Results of Fit on Solubility of Carbon Dioxide in Aqueous Solution at 298.15 K with α = 0.2*

Salt	max. m	$\tau_{ca,m}$	$\tau_{m,ca}$	$\sigma_{\ln\gamma}$
NaCl	5.719	−2.500	5.139	0.011
KCl	4.710	−4.464	6.742	0.004
Na_2SO_4	2.370	0.0	6.091	0.030
KNO_3	1.749	−4.892	9.642	0.002
$(NH_4)_2SO_4$	4.386	−3.457	6.491	0.007
$NaNO_3$	9.644	−1.979	4.392	0.003
NH_4Cl	7.273	−5.330	8.016	0.004
$MgCl_2$	4.417	−3.708	5.418	0.047
$CaCl_2$	5.286	−4.076	6.020	0.023
K_2SO_4	0.463	−3.934	7.940	0.002
$MgSO_4$	2.342	0.0	5.120	0.025

*Yasunishi and Yoshida (1979).
$\tau_{CO_2,H_2O} = 10.0640 - 3{,}268.135/T$
$\tau_{H_2O,CO_2} = \tau_{CO_2,H_2O}$

Table 7. Physical Property Parameters for NH_3-H_2S-H_2O System

$$\ln K_{50} = 2.76 - 3335.7/T + 1.4971 \ln T - 0.0370566\mathrm{T}$$
$$\ln K_{51} = 218.599 - 12995.4/T - 33.5471 \ln T$$
$$\ln K_{52} = 136.91 - 13445.9/T - 22.4773 \ln T$$
$$\ln K_{53} = 140.932 - 13445.9/T - 22.47731 \ln T$$
$$(K \text{ in molality scale})$$

$$\ln H_{NH_3} = -133.463 - 157.552/T - 28.1001 \ln T - 0.049227T$$
$$\ln H_{H_2S} = 358.138 - 13236.8/T - 55.0551 \ln T + 0.0595651T$$
$$\tau_{NH_3,H_2O} = 0.7449 - 453.80/T$$
$$\tau_{H_2O,NH_3} = 1.6707 - 932.82/T$$
$$\tau_{H_2S,H_2O} = \tau_{H_2O,H_2S} = -3.674 + 1155.9/T$$

$$\tau_{H_2O,NH_4HS} = 20.05 - 4520.4/T$$
$$\tau_{NH_4HS,H_2O} = -9.152 + 1890.4/T$$
$$\tau_{NH_4HS,NH_3} = -4.719$$
$$\tau_{NH_4HS,H_2S} = -2.137$$

tion of state. The chemical equilibrium constants and Henry's law constants were obtained from Maurer (1980) and are reported in Table 7. Binary parameters for the NH_3-H_2O pair and the H_2S-H_2O pair were determined a priori from experimental data for these binary systems. Except for the parameters listed in Table 7, which were adjusted to fit the experimental data, all other parameters were set to −4.072 for salt-molecule

Table 8. Calculated and Experimental Results for NH_3-H_2S-H_2O System*

T	Molality		Partial Pressures			
			NH_3		H_2S	
K	NH_3	H_2S	Exp	Calc	Exp	Calc
353.15	0.960	0.971	12.1	11.0	2,389.0	2,360.0
353.15	1.063	1.452	4.4	4.2	8,556.0	10,077.0
353.15	2.332	1.151	136.0	140.0	319.0	309.0
353.15	5.112	1.143	575.0	494.0	94.8	96.3
353.15	5.538	5.305	72.6	71.2	12,140.0	11,806.0
353.15	9.245	7.935	209.0	197.0	9,506.0	9,000.0
353.15	10.201	5.983	597.0	547.0	1,916.0	1,745.0
353.15	22.627	5.561	2,285.0	2,332.0	241.0	291.0
393.15	0.0106	0.0005	2.14	3.13	0.65	0.20
393.15	0.442	0.181	81.2	87.9	333.0	302.0
393.15	0.526	0.109	177.0	135.0	82.5	86.4
393.15	0.534	0.712	23.7	24.1	6,410.0	7,282.0
393.15	0.992	0.493	183.0	175.0	916.0	883.0
393.15	1.131	0.998	95.4	97.4	4,632.0	4,906.0
393.15	2.031	0.433	569.0	539.0	280.0	259.0
393.15	10.081	2.114	3,179.0	2,995.0	973.0	914.0

*From Miles and Wilson (1975).

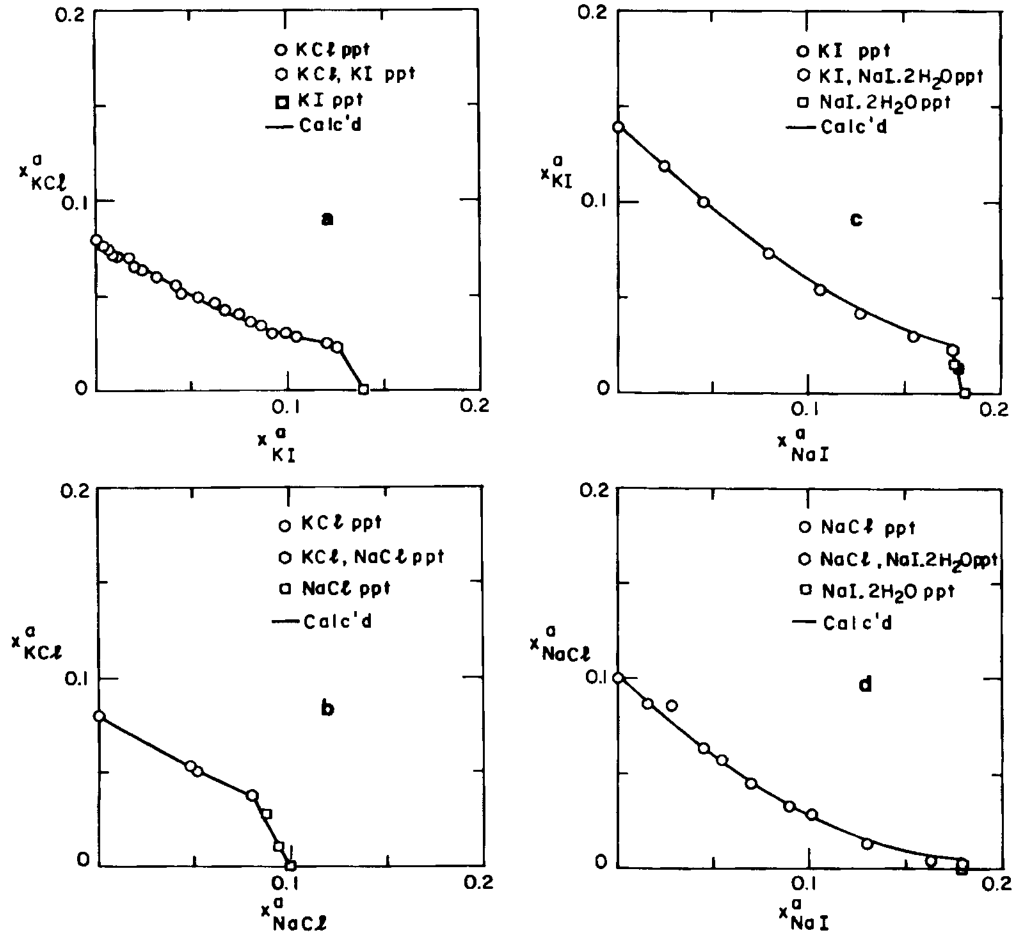

Figure 5. Measured and calculated solubilities at 298.15K.

a. KCl-KI-H_2O system
b. KCl-NaCl-H_2O system
c. KI-NaI-H_2O system
d. NaCl-NaI-H_2O system

Table 9. Regressed Values of Salt-Salt Energy Parameters and Solubility Product Constants for Aqueous $Na^+/K^+/Cl^-/I^-$ System at 298.15 K

$$
\begin{aligned}
\tau_{\mathrm{NaCl,NaI}} &= -0.895\\
\tau_{\mathrm{NaI,NaCl}} &= -2.733\\
\tau_{\mathrm{KCl,KI}} &= 0.109\\
\tau_{\mathrm{KI,KCl}} &= 0.124\\[6pt]
\tau_{\mathrm{NaCl,KCl}} &= 0.489\\
\tau_{\mathrm{KCl,NaCl}} &= -0.484\\
\tau_{\mathrm{NaI,KI}} &= 0.385\\
\tau_{\mathrm{KI,NaI}} &= -0.184\\[6pt]
K_{sp,\mathrm{NaCl}} &= -4.4620\\
K_{sp,\mathrm{KCl}} &= -5.9695\\
K_{sp,\mathrm{NaI\cdot 2H_2O}} &= -2.8192\\
K_{sp,\mathrm{KI}} &= -4.2346
\end{aligned}
$$

energy parameters and 8.045 for molecule-salt energy parameters. These represent average values of a wide variety of electrolyte systems with the nonrandomness factor being 0.2. Parameters for salt-salt pairs were set to zero. Calculated results and experimental data for the NH_3-H_2S-H_2O system are given in Table 8. The sum of squares objective function used in data correlation was

$$S = \sum_{i=1}^{n} (y^{\mathrm{calc}}_{\mathrm{NH_3},i} - y^{\mathrm{exp}}_{\mathrm{NH_3},i})^2 + \sum_{i=1}^{n} (y^{\mathrm{calc}}_{\mathrm{H_2S},i} - y^{\mathrm{exp}}_{\mathrm{H_2S},i})^2 + \sum_{i=1}^{n} \left(\frac{P_i^{\mathrm{calc}} - P_i^{\mathrm{exp}}}{P_i^{\mathrm{exp}}}\right)^2 \qquad (54)$$

Liquid-solid equilibrium

Liquid-solid equilibrium of aqueous electrolyte systems is characterized by wide electrolyte concentration and temperature ranges, common ion effect, ionic equilibrium complications, multiple hydrate formation, double salt formation, etc. It requires accurate prediction of activity coefficients of ions in aqueous phase. This is especially important when saturated concentration of one electrolyte becomes so small that the solubility is dominated by the mean ionic activity coefficient at trace concentration.

The aqueous electrolyte system of $Na^+/K^+/Cl^-/I^-$ ions is examined here primarily because ample liquid-solid equilibrium data are available in the literature (Linke, 1965). There are four electrolytes in the four ion system, i.e., NaCl, NaI, KCl, and KI. Water-salt energy parameters of these electrolytes are available in Table 1. Solid phases that may be saturated with the aqueous electrolyte system include $NaCl_{(s)}$, $NaI \cdot 2H_2O_{(s)}$, $KCl_{(s)}$, and $KI_{(s)}$. Solubility products of these solids can be written as follows:

$$K_{sp,\mathrm{NaCl}} = x_{\mathrm{Na^+}}\gamma^*_{\mathrm{Na^+}} \cdot x_{\mathrm{Cl^-}}\gamma^*_{\mathrm{Cl^-}} \qquad (55)$$

$$K_{sp,\mathrm{NaI\cdot 2H_2O}} = x_{\mathrm{Na^+}}\gamma^*_{\mathrm{Na^+}} \cdot x_{\mathrm{I^-}}\gamma^*_{\mathrm{I^-}} \cdot x^2_{\mathrm{H_2O}}\gamma^2_{\mathrm{H_2O}} \qquad (56)$$

$$K_{sp,\mathrm{KCl}} = x_{\mathrm{K^+}}\gamma^*_{\mathrm{K^+}} \cdot x_{\mathrm{Cl^-}}\gamma^*_{\mathrm{Cl^-}} \qquad (57)$$

$$K_{sp,\mathrm{KI}} = x_{\mathrm{K^+}}\gamma^*_{\mathrm{K^+}} \cdot x_{\mathrm{I^-}}\gamma^*_{\mathrm{I^-}} \qquad (58)$$

Solubility product constants and salt-salt energy parameters were successfully regressed from the liquid-solid equilibrium data. Figures 5a–d show that the data regression results. The regressed solubility product constants and binary salt-salt parameters are given in Table 9. The sum of squares objective function used in data correlation was

$$S = \sum_{i=1}^{n} (x^{a^{\mathrm{calc}}}_{\mathrm{NaCl},i} - x^{a^{\mathrm{exp}}}_{\mathrm{NaCl},i})^2 + \sum_{i=1}^{n} (x^{a^{\mathrm{calc}}}_{\mathrm{NaI},i} - x^{a^{\mathrm{exp}}}_{\mathrm{NaI},i})^2 + \sum_{i=1}^{n} (x^{a^{\mathrm{calc}}}_{\mathrm{KCl},i} - x^{a^{\mathrm{exp}}}_{\mathrm{KCl},i})^2 + \sum_{i=1}^{n} (x^{a^{\mathrm{calc}}}_{\mathrm{KI},i} - x^{a^{\mathrm{exp}}}_{\mathrm{KI},i})^2 \qquad (59)$$

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Notation

A_ϕ = Debye-Hückel constant for the osmotic coefficient
H = Henry's law constant, Pa/kmol
I_x = ionic strength in mole fraction scale
K_{sp} = solubility product constant
M_s = solvent molecular weight, kg/kmol
P = pressure, N/m^2
PK = cologarithm of dissociation constant
R = gas constant
T = temperature, K
X = effective liquid phase mole fraction
Z = absolute value of ionic charge
g^{ex} = molar excess Gibbs energy
$k_{s,m}$ = Setschenow constant
m = molality, gmol/kg solvent
n = number of experimental determinations
x = true liquid phase mole fraction based on all species; molecular and ionic
x^a = apparent liquid phase mole fraction
y = vapor phase mole fraction

Greek letters

α = NRTL nonrandomness factor
γ = activity coefficient
Θ = reference temperature, 298.15 K
ρ = the closest approach parameter of the Pitzer-Debye-Hückel equation, =14.9
σ = root mean square error
σ_p = root mean square relative error on pressure
σ_ϕ = root mean square relative error on osmotic coefficient
$\sigma_{\ln\gamma}$ = root mean square relative error on logarithm of activity coefficient
τ = NRTL binary interaction energy parameter
ϕ = osmotic coefficient

Superscripts

o = single electrolyte system
$*$ = unsymmetric convention
∞ = infinite dilution
pdh = long range contribution, represented by the Pitzer-Debye-Hückel equation
lc = short range contribution, represented by the local composition model
calc = calculated value
exp = experimental value
trace = trace concentration

Subscripts

a, a', a'' = anion
c, c', c'' = cation
ca = salt ca
i, j, k = any species
m = molecular species

ppt = solid precipitation
ref = reference
s = salt
w = water

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