Thermodynamic Representation of Phase Equilibria of Mixed-Solvent Electrolyte Systems

The electrolyte nonrandom two-liquid model proposed by Chen and Evans provides a thermodynamically consistent framework for representation of the phase equilibria of mixed-solvent electrolyte systems. Using only binary adjustable parameters, the model satisfactorily correlates the vapor-liquid equilibrium and liquid-liquid equilibrium of mixed-solvent electrolyte systems over the entire range of temperature and concentrations.

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SCOPE

The addition of salts alters the phase equilibrium behavior of systems containing one or more molecular solvents. Examples of such salt-induced effects include vapor-pressure depression for single-solvent electrolyte systems, and alteration of relative volatilities (salting-in or salting-out) and liquid-phase stability for mixed-solvent electrolyte systems. Because the salt effect can often shift phase equilibrium toward more effective separation of selective components, there is a potential for using salts to enhance separation processes (Furter, 1972).

The observed salt effects on the phase equilibrium behavior of mixed-solvent electrolyte systems are determined by the interactions between ionic and solvent species present in the electrolyte system. A critical examination of existing models for representing salt effects on the phase equilibrium of mixed-solvent electrolyte systems reveals the following common deficiencies:

- Inconsistent thermodynamic framework
- Model parameters highly dependent on solvent and salt compositions
- Inability to represent liquid-liquid equilibrium

Recently, an excess Gibbs energy model based on the local composition concept of nonrandom two-liquid (NRTL) theory was developed for aqueous electrolyte systems (Chen et al., 1982; Chen and Evans, 1986). The model has been shown to be very successful in representing the phase equilibrium of aqueous electrolyte systems. The objective of this work was to extend the aqueous electrolyte NRTL model to represent the phase equilibrium of mixed-solvent electrolyte systems.

CONCLUSIONS AND SIGNIFICANCE

The development of the electrolyte NRTL model provides an accurate and thermodynamically consistent framework for representation of the phase equilibrium of mixed-solvent electrolyte systems. The model explicitly accounts for solvent-solvent, ion-ion, and ion-solvent interactions in the liquid phase. The model offers significant advantages over previously proposed models, including the ability to represent *the entire* salt/solvent composition range with a single set of binary parameters, and the ability to model liquid-liquid equilibrium.

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Correlation of experimental data for 47 single-solvent electrolyte systems and 33 mixed-solvent electrolyte systems demonstrates that the electrolyte NRTL model gives excellent representation of vapor-liquid equilibrium and liquid-liquid equilibrium of mixed-solvent electrolyte systems. Average errors of $\Delta P = 1$ kPa, $\Delta T = 0.1$ K, $\Delta y = 0.01$ in correlating vapor-liquid equilibrium data at atmospheric conditions, and $\Delta x = 0.01$ in correlating liquid-liquid equilibrium data are typical.

Previous Methods

In the late 1960's and the 1970's, several semiempirical models for representing the excess Gibbs energy of nonelectrolyte liquid solutions were developed with the local composition concept. Examples are the Wilson (1964) model, the NRTL model (Renon and Prausnitz, 1968), and the UNIQUAC model (Abrams and Prausnitz, 1975). These models are able to represent, with a reasonable number of binary adjustable parameters, the phase equilibrium of highly nonideal nonelectrolyte systems.

In contrast to the more systematic approaches used for nonelectrolyte systems, methods for representing the phase equilibrium of mixed-solvent electrolyte systems have primarily taken the approach of regarding the presence of salts implicitly, in terms of a correction to the phase equilibrium behavior of salt-free systems.

Johnson and Furter (1960) proposed the first quantitative correlation of salt effect on the vapor-liquid equilibrium of two-solvent, one-salt electrolyte systems:

$$\ln(\alpha_s/\alpha_o) = k_o x_{\text{salt}} \tag{1}$$

The quantity α_s is the relative volatility in the electrolyte solution; α_o is the relative volatility in a salt-free solution with the same solvent composition; k_o is the salt effect parameter; x_{salt} is the salt concentration, expressed as mol salt/(mol salt + mol solvent).

While Eq. 1 is attractive because of its simplicity, the salt effect parameter has been shown to be dependent on salt and solvent compositions and the range of applicability is limited (Meranda and Furter, 1972; Burns and Furter, 1979).

Ohe (1976) proposed a model in which the salt forms a preferential solvate with one of the solvents in a two-solvent system. The equilibrium composition of the vapor phase is calculated from the liquid phase composition by assuming that solvated species can not participate in vapor-liquid equilibrium. Therefore, the solvent that forms the preferential solvate is diminished in the vapor phase (salted-in), while the other solvent is salted-out.

To be used quantitatively, the Ohe model requires the determination of the solvation number, which is the ratio of the number of solvent molecules to salt in the preferential solvate.

Results of applying the solvation model to vapor-liquid equilibrium data for two-solvent, one-salt systems indicate that the solvation number, like the salt effect parameter, is a strong function of both solvent and salt compositions. The dependency of solvation number on composition is not surprising, considering that the formation of solvate should be dependent upon the availability of both solvent molecules and salts. The inability of a single solvation number to represent vapor-liquid equilibrium behavior over the entire salt/solvent composition range is a major drawback of the solvation method. A further objection to the assumptions of the solvation method concerns systems where the solvate formation may not be restricted to a single solvent in the liquid mixture.

Rousseau et al. (1972, 1978) adapted the nonelectrolyte excess Gibbs energy models to the problem of two-solvent, one-salt electrolyte systems using the so-called pseudobinary approach. In this approach, the liquid phase is considered to consist of two components, component 1* being the salted-out component, and component 2* being composed of the mixture of the salted-in solvent and the salt. The association of the salt effect with only one solvent is comparable to the preferential solvation assumption in the solvation approach.

Jaques and Furter (1972a) proposed a similar approach for saturated salt systems. In their method, pseudocomponent 1* is the first solvent saturated with the salt, and pseudocomponent 2* is the second solvent saturated with the salt.

In either approach, one of the nonelectrolyte excess Gibbs energy models is applied to the pseudobinary mixture, and vapor-liquid equilibrium data are correlated in the same manner as would be done for a binary nonelectrolyte system, with the binary adjustable parameters associated with the composition-dependent pseudocomponents.

A complication of these approaches is that the reference fugacity for the pseudocomponents must be calculated as a function of salt concentration. Therefore, changes in the salt concentration would necessitate redefinition of the pseudocomponent reference states.

Another drawback of these approaches is the inability to represent liquid-liquid equilibrium in electrolyte systems. The two liquid phases must necessarily have different salt concentrations; therefore, according to the pseudobinary approach, the two phases would be made of totally different pseudocomponents, prohibiting the expression of liquid-liquid phase equilibrium relationships.

Excess Gibbs Energy of Mixed-Solvent Electrolyte Systems

As a result of dissociation of salts into ions in the liquid phase, the solvent-solvent, ion-solvent, and ion-ion interactions present in an electrolyte system determine the thermodynamic properties of the system. Specifically, solvent-solvent and ion-solvent interactions dictate the thermodynamic properties of solvent species, while ion-solvent and ion-ion interactions dictate the thermodynamic properties of ionic species.

The dispersion, induction, and electrostatic interactions between species of solvent-solvent pairs and ion-solvent pairs are short-range in nature; they are similar in magnitude and nature to interactions that occur in nonelectrolyte systems. The electrostatic interactions between ions are long-range in nature, although the electrostatic potential diminishes rapidly with the distance of the two interacting ions.

Nonelectrolyte excess Gibbs energy models that were developed from the local composition concept, such as the Wilson, NRTL, or UNIQUAC models, postulate local compositions at the immediate neighborhood of any species. These local compositions are different from the system composition and they reflect the local solvent-solvent short-range interactions that contribute to the excess Gibbs energy. In applying the local composition concept to electrolyte systems, one postulates these local compositions to be governed by the local solvent-solvent short-range interaction, the ion-solvent short-range interaction, and the ion-ion long-range interaction that exist at the immediate neighborhood of a central species. As proposed by Chen et al. (1982), the excess Gibbs energy of electrolyte systems can then be treated as the sum of two terms, one related to the local short-range and long-range interactions that exist at the immediate neighborhood of any central species, and the other related to the long-range ion-ion interactions that exist beyond the immediate neighborhood of a central ionic species. Although it is the long-range nature of the ion-ion electrostatic interaction that characterizes electrolyte systems, the excess Gibbs energy of electrolyte systems is dominated by the local interactions that govern the local compositions.

Electrolyte NRTL Model

The electrolyte nonrandom, two-liquid (NRTL) model was first proposed to represent the excess Gibbs energy of aqueous electrolyte systems (Chen et al., 1982; Chen and Evans, 1986). The model postulated two fundamental assumptions about the liquid lattice structure of electrolyte systems:

1. The local composition of cations (anions) around a central cation (anion) is zero.
2. The distribution of cations and anions around a central molecule is such that the net local ionic charge is zero.

The model also proposed the excess Gibbs energy to be the sum of two expressions. One expression is derived from the NRTL equation (Renon and Prausnitz, 1968), which accounts for the local interaction contribution resulting from all short-range and long-range interactions that occur between all neighboring species. The other expression is the Pitzer-Debye-Hückel equation (Pitzer, 1980), which accounts for the long-range interaction contribution resulting from the long-range ion-ion electrostatic interactions beyond the immediate neighborhood of a central ion.

In adapting the electrolyte NRTL model for mixed-solvent electrolyte systems, the main consideration was the ability to represent the phase equilibrium behavior of solvent species. The long-range interaction contribution of the Pitzer-Debye-Hückel expression, although essential in computing aqueous phase ionic activity coefficients, was found to have little effect on the phase equilibrium behavior of water. Therefore, only the local interaction contribution term of the electrolyte NRTL model is used in this study and the long-range interaction contribution term is dropped.

The local interaction contribution of the electrolyte NRTL model for a multicomponent electrolyte system is expressed below:

$$\frac{g^{ex}}{RT} = \sum_m X_m \frac{\sum_j X_j G_{jm} \tau_{jm}}{\sum_k X_k G_{km}} + \sum_c X_c \sum_{a'} \frac{X_{a'}}{\sum_{a''} X_{a''}} \frac{\sum_j X_j G_{jc,a'c} \tau_{jc,a'c}}{\sum_k X_k G_{kc,a'c}} + \sum_a X_a \sum_{c'} \frac{X_{c'}}{\sum_{c''} X_{c''}} \frac{\sum_j X_j G_{ja,c'a} \tau_{ja,c'a}}{\sum_k X_k G_{ka,c'a}} \tag{2}$$

Where:

$$X_j = x_j C_j \ (C_j = Z_j \text{ for ions and } C_j = \text{unity for molecules} \tag{3}$$

$$G_{ji} = \exp(-\alpha_{ji} \tau_{ji}) \tag{4}$$

$$G_{ji,ki} = \exp(-\alpha_{ji,ki} \tau_{ji,ki}) \tag{5}$$

The expressions for the activity coefficient of solvent species can be obtained from Eq. 2:

$$\ln \gamma_m = \frac{\sum_j X_j G_{jm} \tau_{jm}}{\sum_k X_k G_{km}} + \sum_{m'} \frac{X_{m'} G_{mm'}}{\sum_k X_k G_{km'}} \left(\tau_{mm'} - \frac{\sum_k X_k G_{km'} \tau_{km'}}{\sum_k X_k G_{km'}} \right) + \sum_c \sum_{a'} \frac{X_{a'}}{\sum_{a''} X_{a''}} \frac{X_c G_{mc,a'c}}{\sum_k X_k G_{kc,a'c}} \cdot \left(\tau_{mc,a'c} - \frac{\sum_k X_k G_{kc,a'c} \tau_{kc,a'c}}{\sum_k X_k G_{kc,a'c}} \right) + \sum_a \sum_{c'} \frac{X_{c'}}{\sum_{c''} X_{c''}} \frac{X_a G_{ma,c'a}}{\sum_k X_k G_{ka,c'a}} \cdot \left(\tau_{ma,c'a} - \frac{\sum_k X_k G_{ka,c'a} \tau_{ka,c'a}}{\sum_k X_k G_{ka,c'a}} \right) \tag{6}$$

Note that in the absence of salts ($x_a = x_c = 0$), Eq. 2 reduces to the original NRTL expression for nonelectrolyte systems.

Parameter Requirements

The model binary adjustable parameters are associated with the solvent-solvent pairs, solvent-salt pairs, and salt-salt pairs.

They include: the nonrandomness factors, $\alpha_{ca,m}$, $\alpha_{ca,ca'}$, $\alpha_{ca,c'a}$, 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 $\tau_{m'm}$. The α's and τ's of Eqs. 3 to 6 are composition-dependent parameters. They are functions of the model binary adjustable parameters and ionic compositions.

$$\alpha_{cm} = \frac{\sum_a X_a \alpha_{ca,m}}{\sum_{a'} X_{a'}} \tag{7}$$

$$\alpha_{am} = \frac{\sum_c X_c \alpha_{ca,m}}{\sum_{c'} X_{c'}} \tag{8}$$

$$G_{cm} = \frac{\sum_a X_a G_{ca,m}}{\sum_{a'} X_{a'}} \tag{9}$$

$$G_{am} = \frac{\sum_c X_c G_{ca,m}}{\sum_{c'} X_{c'}} \tag{10}$$

$$\tau_{ma,ca} = \tau_{am} - \tau_{ca,m} + \tau_{m,ca} \tag{11}$$

$$\tau_{mc,ac} = \tau_{cm} - \tau_{ca,m} + \tau_{m,ca} \tag{12}$$

For a system with two solvents, *m* and *w*, and one salt, *ca*, there are nine adjustable binary parameters: $\tau_{ca,m}$, $\tau_{m,ca}$, $\tau_{ca,w}$, $\tau_{w,ca}$, τ_{mw}, τ_{wm}, $\alpha_{ca,m}$, $\alpha_{ca,w}$, α_{mw}. This is equivalent to the number of binary adjustable parameters needed to model a ternary nonelectrolyte system with the NRTL model. The parameter requirements for a two-solvent, one-salt system are illustrated in Figure 1.

Data Regression

The ability of the electrolyte NRTL model to represent phase equilibrium of mixed-solvent electrolyte systems was demonstrated through the regression of the following types of data:

- Vapor pressure depression data of single-solvent electrolyte systems
- Vapor-liquid equilibrium data of mixed-solvent electrolyte systems
- Liquid-liquid equilibrium data of mixed-solvent electrolyte systems

Data from the literature for 47 single-solvent electrolyte systems and 33 mixed-solvent electrolyte systems were examined. The majority of the mixed-solvent electrolyte systems contain water as one of the solvents, with the other solvents being either aliphatic alcohols or other organic solvents. The list of the mixed-solvent electrolyte systems examined in this work is given in Table 1.

The data regression system (DRS) of the ASPEN PLUS® process simulator (Aspen Technology, 1984) was used to perform the data regression carried out in this work. The DRS uses the maximum likelihood principle of Britt and Luecke (1973). The minimization objective function is:

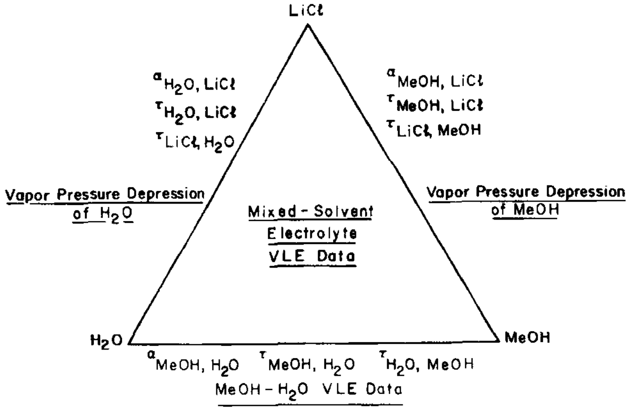

Figure 1. Binary parameter requirements for methanol-water-LiCl system.

Table 1. Summary of Regressed Mixed-Solvent Electrolyte Systems

Mixed Solvent	Salt
Vapor-liquid equilibrium	
Ethanol-water	KCl
	LiCl
	NH_4CL
	NaBr
	NaCl
	$CaCl_2$
Ethanol-water	KCl
	KI
	LiCl
	NH_4Br
	NH_4CL
	NaBr
	NaCl
	NaI
	$BaCl_2$
	$CaCl_2$
Isopropanol-water	LiBr
	LiCl
	$CaCl_2$
1,4-Dioxan–water	$LiClO_3$
	$NaClO_3$
n-Propanol–*i*-propanol	$CaCl_2$
Methanol–*n*-propanol–water	LiCl
Ethanol–*n*-propanol–water	LiCl
Liquid-Liquid Equilibrium	
Acetonitrile-water	KAc
	KBr
	LiAc
	NaBr
	$NaNO_3$
	NH_4NO_3
Methylethyl ketone-water	$CaCl_2$
Ethyl acetate-ethanol-water	KAc
	NaAc

$$f = \sum_{k=1}^{n} W_{U_k}(U_k - \bar{U}_k)^2/\sigma^2_{U_k} \tag{13}$$

The measurable variables, U_k, are the state variables (i.e., T, P, x^a, y).

The objective function is minimized by adjustment of the measurable variables and the model parameters, subject to the following constraints and bounds.

Vapor-liquid equilibrium constraints:

$$P_{y_i} = \gamma_i(\theta) P_i^s x_i \tag{14}$$

Liquid-liquid equilibrium constraints:

$$[\gamma_i(\theta)x_i]^{\mathrm{I}} = [\gamma_i(\theta)x_i]^{\mathrm{II}} \tag{15}$$

Parameter bounds:

$$\theta_{lb} \leq \theta \leq \theta_{ub} \tag{16}$$

Values used for the standard error of measurements, σ_{U_k}, are listed in Table 2.

Single-Solvent Electrolyte Systems

In correlating the data for vapor pressure depression of single solvent m by salt ca, values for the binary adjustable parameters $\alpha_{ca,m}$, $\tau_{ca,m}$, and $\tau_{m,ca}$ are to be determined. Regression attempts indicated that it was not always possible to obtain statistically meaningful values for all three parameters from vapor pressure depression data alone. Therefore, the salt-solvent nonrandomness parameter was set to an arbitrary value of $\alpha_{ca,m} = 0.2$, following Chen and Evans (1986), for all correlations of single-solvent electrolyte systems. The two parameters $\tau_{ca,m}$ and $\tau_{m,ca}$ were left to be adjusted to provide the best fit for the vapor pressure depression data. Results for the 47 systems tested are shown in Table 3.

The electrolyte NRTL model gave an excellent fit for vapor pressure depression data of single-solvent electrolyte systems, with average pressure deviations on the order of less than 0.1 kPa.

Mixed-Solvent Electrolyte Systems

In order to represent the phase equilibrium of mixed-solvent electrolyte systems, it is necessary to determine the binary adjustable parameters for each solvent-solvent, solvent-salt, and salt-salt pairs in the system. For example, in a two-solvent, one-salt system, nine binary adjustable parameters for three pairs must be determined. To make the parameter determination tractable for multicomponent systems, binary solvent-solvent parameters were first determined from phase equilibrium data of solvent-solvent binary systems, and binary salt-water parameters were determined independently from vapor pressure depression data of binary aqueous electrolyte systems. In this manner, because of the common availability of these two types of data, it is possible to reduce the data regression problem for mixed-solvent electrolyte systems to the determination of binary salt-nonaqueous solvent parameters only. Thus, for a two-solvent, one-salt system, for example, only the three parameters $\alpha_{ca,m}$, $\tau_{ca,m}$, and $\tau_{m,ca}$ need to be determined from data for mixed-solvent electrolyte systems.

Results of data correlation for vapor-liquid equilibrium and liquid-liquid equilibrium of mixed-solvent electrolyte systems are presented in Table 4. Binary solvent-solvent and solvent-salt parameters are given in Table 5. Phase equilibrium diagrams for some systems are shown in Figures 2 to 4.

With a single set of binary parameters, the phase equilibrium data were represented satisfactorily for the entire salt/solvent composition range. For vapor-liquid equilibrium data, typical mean average deviations obtained for temperature, pressure, and vapor phase mole fractions are 0.1 K, 1 kPa, and 0.01, respectively. For liquid-liquid equilibrium data, the mean average deviation in liquid-phase mole fractions was 0.01. These results are comparable to those obtained for nonelectrolyte systems.

Vapor-liquid equilibrium data for a few mixed-solvent electrolyte systems, notably the ethanol-water-(KI, NaBr, NaI) data of Meranda and Furter (1972), gave poor correlations. However, the accuracy of this particular data has been subject to question (Jaques and Furter, 1972b).

Solvent-Salt Nonrandomness Factor

In regressing data of single-solvent electrolyte systems, an arbitrary value of 0.2 was satisfactory for solvent-salt nonrandomness factors. However, in regressing data of mixed-solvent electrolyte systems, the relative values of the nonrandomness factor were found to be critical in representing the phase equilibrium of mixed-solvent electrolyte systems.

For the data correlation done in this study, the nonrandomness factor for the most salted-in solvent (usually water) was set arbitrarily to 0.2. Values for all other parameters were determined through data regression. Using this scheme, the solvent-

Table 2. Estimated Variances in State Variables for Maximum Likelihood Parameter Estimation

System Type	Data Type	Standard Error of Measurements
Solvent vapor pressure depression	TPx	$\sigma_T = 0.0$ $\sigma_p = 0.1$ kPa $\sigma_x = 0.0$
Vapor-liquid equilibrium of mixed-solvent nonelectrolyte systems	$TPxy$	$\sigma_T = 0.1$ K $\sigma_p = 0.3$ kPa $\sigma_x = 0.0001$ $\sigma_y = 0.005$
Vapor-liquid equilibrium of mixed-solvent electrolyte systems	$TPxy$	$\sigma_T = 0.1$ K $\sigma_p = 0.5$ kPa $\sigma_x = 0.0001$ $\sigma_y = 0.005$
Liquid-liquid equilibrium of mixed-solvent nonelectrolyte systems	Txx	$\sigma_T = 0.0$ $\sigma_x = 0.001$
Liquid-liquid equilibrium of mixed-solvent electrolyte systems	Txx	$\sigma_T = 0.0$ $\sigma_x = 0.001$

Table 3. Results of Fitting of Vapor Pressure Depression Data

Salt	Temp. K	Max. Salt Conc. mol. salt / kg solvent	$\tau_{ca,m}$	$\tau_{m,ca}$	ΔP kPa	Reference
		Solvent: Water				
KAc	298	3.5	−4.868	9.769	0.001	Robinson & Stokes (1970)*
KBr	298	5.0	−4.318	8.981	0.001	Robinson & Stokes (1970)*
KF	298	4.0	−4.671	9.660	0.001	Robinson & Stokes (1970)*
LiAc	298	4.0	−4.616	9.395	0.001	Robinson & Stokes (1970)*
LiCl	298	6.0	−5.902	13.592	0.027	Robinson & Stokes (1970)*
$LiClO_3$	298	10.3	−5.075	10.330	0.013	Campbell & Oliver (1969)
NaBr	298	4.0	−4.770	9.790	0.001	Robinson & Stokes (1970)*
NaCl	298	6.0	−4.678	9.693	0.001	Robinson & Stokes (1970)*
NaAc	298	3.5	−4.780	9.621	0.001	Robinson & Stokes (1970)*
$NaClO_3$	298	9.4	−3.917	8.144	0.003	Campbell & Oliver (1969)
$NaNO_3$	298	6.0	−3.807	8.179	0.003	Robinson & Stokes (1970)*
NH_4NO_3	298	6.0	−3.181	6.939	0.005	Robinson & Stokes (1970)*
LiBr	348	13.9	−5.740	13.045	0.250	Sada et al. (1975)
LiCl	348	9.8	−5.493	12.496	0.305	Sada et al. (1975)
KCl	373	6.0	−4.465	9.573	0.032	CRC (1972)
KI	373	10.0	−4.332	8.837	0.015	CRC (1972)
LiBr	373	10.0	−5.401	11.875	0.079	CRC (1972)
LiCl	373	8.0	−5.161	11.074	0.047	CRC (1972)
NaBr	373	6.0	−4.734	9.744	0.010	CRC (1972)
NaCl	373	10.0	−4.666	9.866	0.027	CRC (1972)
NaI	373	10.0	−5.001	10.315	0.020	CRC (1972)
$NaNO_3$	373	10.0	−3.655	7.649	0.031	CRC (1972)
NH_4Br	373	10.0	−3.923	8.088	0.020	CRC (1972)
NH_4Cl	373	10.0	−4.098	8.825	0.077	CRC (1972)
$CaCl_2$	298	6.0	−6.379	14.810	0.012	Robinson & Stokes (1970)*
$BaCl_2$	373	2.0	−5.202	10.054	0.015	CRC (1972)
$Ba(NO_3)_2$	373	1.0	−5.752	11.745	0.000	CRC (1972)
$CaCl_2$	373	5.0	−5.848	11.623	0.037	CRC (1972)
$Ca(NO_3)_2$	373	5.0	−4.892	9.159	0.075	CRC (1972)
Na_2SO_4	373	3.0	−4.754	9.728	0.200	CRC (1972)
$Sr(NO_3)_2$	373	4.0	−4.736	9.260	0.016	CRC (1972)
		Solvent: Methanol				
KI	298	1.1	−5.199	11.474	0.027	Bixon et al. (1979)
LiCl	298	5.4	−5.394	11.611	0.216	Bixon et al. (1979)
NaBr	298	1.6	−5.187	11.310	0.017	Bixon et al. (1979)
NaI	298	4.5	−5.043	9.769	0.108	Bixon et al. (1979)
NaOH	298	5.9	−5.455	10.073	0.172	Bixon et al. (1979)
$CaCl_2$	298	2.6	−5.343	10.414	0.117	Bixon et al. (1979)
$CuCl_2$	298	4.0	−4.522	9.285	0.088	Bixon et al. (1979)
		Solvent: Ethanol				
NaI	278	2.8	−5.077	10.740	0.008	Subbotinna & Mischenko (1966)
NaI	283	2.8	−5.061	10.782	0.015	Subbotinna & Mischenko (1966)
NaI	288	2.8	−5.014	10.539	0.025	Subbotinna & Mischenko (1966)
NaI	293	2.8	−5.014	10.755	0.024	Subbotinna & Mischenko (1966)
NaI	298	2.8	−5.022	10.996	0.037	Subbotinna & Mischenko (1966)
NaI	308	2.8	−4.980	10.904	0.055	Subbotinna & Mischenko (1966)
NaI	318	2.8	−4.929	10.869	0.096	Subbotinna & Mischenko (1966)
		Solvent: Isopropanol				
LiBr	348	2.0	−4.390	10.782	0.060	Sada et al. (1975)
LiCl	348	1.5	−5.057	13.176	1.02	Sada et al. (1975)

*Vapor pressure depression data converted from osmotic coefficient.

Table 4. Results of Fitting Mixed-Solvent Electrolyte Data

	Vapor-Liquid Equilibrium							
Mixed Solvent	Salt	Temp./ Pres.	Salt Conc.	ΔT K	ΔP kPa	Δy_{m1}	Δy_{m2}	Reference
Methanol(1)-water(2)	—	298 K	—	0.02	0.04	0.002	—	Ciparis No. 29 (1966)
	LiCl	298 K	1M	0.07	0.08	0.019	—	Ciparis No. 22 (1966)
	NaBr	298 K	1–7M	0.09	0.08	0.006	—	Ciparis No. 29 (1966)
	$CaCl_2$	298 K	Sat.	0.05	0.34	0.005	—	Nishi (1975)
Methanol(1)-water(2)	—	101.3 kPa	—	0.03	0.15	0.002	—	Dechema I/1a p. 53 (1977)
	KCl	101.3 kPa	Sat.	0.08	0.91	0.003	—	Johnson & Furter (1960)
	LiCl	101.3 kPa	1–4M	0.12	1.40	0.013	—	Boone et al. (1976)
	NH_4Cl	100.6 kPa	Sat.	0.09	1.14	0.006	—	Furter (1958)
	NaBr	101.3 kPa	1–4M	0.26	0.99	0.013	—	Boone et al. (1976)
	NaCl	101.6 kPa	Sat.	0.05	0.55	0.004	—	Johnson & Furter (1960)
	$CaCl_2$	101.6 kPa	16.7wt.%	0.08	0.93	0.015	—	Nishi (1975)
Ethanol(1)-water(2)	—	298 K	—	0.02	0.09	0.006	—	Dechema I/1a p. 125 (1977)
	LiCl	298 K	1–4M	0.02	0.21	0.006	—	Butler & Thomson (1933)
Ethanol(1)-water(2)	—	93.3 kPa	—	0.05	0.23	0.003	—	Dechema I p. 183 (1977)
	KCl	93.3 kPa	Sat.	0.17	0.89	0.013	—	Rius et al. (1957)
	LiCl	93.3 kPa	Sat.	0.07	1.57	0.011	—	Rius et al. (1957)
	NaCl	93.3 kPa	Sat.	0.04	0.92	0.013	—	Rius et al. (1957)
	$BaCl_2$	93.3 kPa	Sat.	0.02	0.26	0.004	—	Rius et al. (1960)
Ethanol(1)-water(2)	—	101.3 kPa	—	0.04	0.16	0.002	—	Dechema I p. 104–6 (1977)
	KI	101.0 kPa	Sat.	0.04	0.70	0.006	—	Burns & Furter (1979)
	KI	100.1 kPa	Sat.	0.15	3.10	0.022	—	Meranda & Furter (1972)
	NH_4Br	101.2 kPa	Sat.	0.07	1.34	0.015	—	Burns & Furter (1979)
	NH_4Cl	100.5 kPa	Sat.	0.08	1.60	0.021	—	Furter (1958)
	NaBr	100.6 kPa	Sat.	0.33	3.83	0.036	—	Meranda & Furter (1972)
	NaCl	100.6 kPa	Sat.	0.07	1.34	0.011	—	Johnson & Furter (1960)
	NaI	100.5 kPa	Sat.	1.75	17.8	0.056	—	Meranda & Furter (1972)
	$CaCl_2$	101.3 kPa	16.7wt.%	0.13	2.39	0.024	—	Nishi (1975)
i-Propanol(1)-water(2)	—	348 K	—	0.09	0.48	0.008	—	Sada & Morisue (1975)
	LiBr	348 K	0-Sat.	0.09	0.77	0.010	—	Sada et al. (1975)
	LiCl	348 K	0-Sat.	0.20	0.47	0.006	—	Sada et al. (1975)
	$CaCl_2$	348 K	0–0.5M	0.15	0.52	0.013	—	Sada et al. (1975)
1,4-Dioxan(1)-water(2)	—	298 K	—	0.03	0.15	0.007	—	Dechema I, p. 379 (1977)
	$LiClO_3$	298 K	1–10M	0.05	0.09	0.007	—	Campbell & Oliver (1969)
	$NaClO_3$	298 K	4–9M	0.12	0.17	0.015	—	Campbell & Oliver (1969)
Propanol(1)-isopropanol(2)	—	101.3 kPa	—	—	0.31	0.005	—	Dechema I/2a p. 531 (1977)
	$CaCl_2$	101.3 kPa	16.7wt%	0.12	2.00	0.010	—	Nishi (1975)
Methanol(1)-propanol(2)-water(3)	—	101.3 kPa	—	0.17	0.70	0.013	0.008	Dechema I, pp. 571–2 (1977)
	LiCl	101.3 kPa	1–4M	0.15	0.76	0.011	0.015	Rousseau & Boone (1978)
Ethanol(1)-propanol(2)-water(3)	—	101.3 kPa	—	0.12	0.21	0.010	0.007	Dechema I, p. 605 (1977)
	LiCl	101.3 kPa	1–4M	0.36	0.65	0.008	0.008	Rousseau & Boone (1978)

	Liquid-Liquid Equilibrium						
Mixed Solvent	Salt	Temp.	Δx^{I}_{m1}	Δx^{I}_{m2}	Δx^{II}_{m1}	Δx^{II}_{m2}	
Acetonitrile(1)-water(2)	KAc	298 K	0.007	—	0.007	—	Renard & Heichelheim (1967)
	KBr	298 K	0.046	—	0.015	—	Renard & Oberg (1965)
	LiAc	298 K	0.016	—	0.009	—	Renard & Heichelheim (1967)
	NaBr	298 K	0.015	—	0.003	—	Renard & Heichelheim (1968)
	$NaNO_3$	298 K	0.017	—	0.007	—	Renard & Heichelheim (1968)
	NH_4NO_3	298 K	0.012	—	0.017	—	Renard & Heichelheim (1968)
Methylethyl ketone(1)-water(2)	$CaCl_2$	290 K	0.012	—	0.005	—	Meissner & Stokes (1944)
Ethyl acetate(1)-ethanol(2)-water(3)	KAc	303 K	0.003	0.006	0.005	0.006	Pai & Rao (1966)
	NaAc	303 K	0.004	0.022	0.007	0.006	Pai & Rao (1966)

Table 5. Binary Parameters for Mixed-Solvent Electrolyte Systems

Solvent	Electrolyte, *ca*	$\alpha_{ca,m1}$	$\tau_{ca,m1}$	$\tau_{m1,ca}$	$\alpha_{ca,m2}$	$\tau_{ca,m2}$	$\tau_{m2,ca}$
Methanol (1)-water (2)	$T = 298$ K; $\alpha_{m1,m2} = 0.3$; $\tau_{m1,m2} = -0.2249$; $\tau_{m2,m1} = 0.8621$						
	LiCl	0.065	−13.002	25.704	0.2	−5.902	13.592
	NaBr	0.076	−9.569	19.040	0.2	−4.770	9.790
	$CaCl_2$	0.077	−13.317	26.624	0.2	−6.379	14.810
Methanol (1)-water (2)	$P = 101.3$ kPa; $\alpha_{m1,m2} = 0.3$; $\tau_{m1,m2} = -0.3544$; $\tau_{m2,m1} = 1.2860$						
	KCl	0.104	−4.076	8.678	0.2	−4.465	9.573
	LiCl	0.099	−7.101	13.539	0.2	−5.161	11.074
	NH_4Cl	0.083	−6.831	13.263	0.2	−4.098	8.825
	NaBr	0.060	−10.500	19.059	0.2	−4.734	9.744
	NaCl	0.106	−4.728	9.396	0.2	−4.666	9.866
	$CaCl_2$	0.090	−9.946	18.098	0.2	−5.848	11.623
Ethanol (1)-water (2)	$T = 298$ K; $\alpha_{m1,m2} = 0.3$; $\tau_{m1,m2} = 0.4472$; $\tau_{m2,m1} = 1.4623$						
	LiCl	0.053	−13.548	24.659	0.2	−5.902	13.592
Ethanol (1)-water (2)	$P = 93.3$ kPa; $\alpha_{m1,m2} = 0.3$; $\tau_{m1,m2} = -0.1893$; $\tau_{m2,m1} = 1.9329$						
	KCl	0.040	−13.972	26.088	0.2	−4.465	9.573
	LiCl	0.060	−11.614	20.785	0.2	−5.161	11.074
	NaCl	0.052	−9.760	18.398	0.2	−4.666	9.866
	$BaCl_2$	0.053	−12.226	20.279	0.2	−5.202	10.054
Ethanol (1)-water (2)	$P = 101.3$ kPa; $\alpha_{m1,m2} = 0.3$; $\tau_{m1,m2} = -0.1341$; $\tau_{m2,m1} = 1.8224$						
	KI	0.069	−7.906	15.672	0.2	−4.332	8.837
	NH_4Br	0.067	−6.442	12.356	0.2	−3.923	8.088
	NH_4Cl	0.060	−8.028	15.214	0.2	−4.098	8.825
	NaBr	0.047	−12.560	23.916	0.2	−4.734	9.744
	NaCl	0.054	−8.778	16.757	0.2	−4.666	9.866
	NaI	0.020	−8.315	16.189	0.2	−5.001	10.315
	$CaCl_2$	0.060	−13.928	25.032	0.2	−5.848	11.623
Isopropanol (1)-water (2)	$T = 348$ K; $\alpha_{m1,m2} = 0.3$; $\tau_{m1,m2} = -0.1305$; $\tau_{m2,m1} = 2.5874$						
	LiBr	0.034	−21.334	43.306	0.2	−5.740	13.045
	LiCl	0.031	−23.090	46.899	0.2	−5.493	12.496
	$CaCl_2$	0.037	−21.468	39.208	0.2	−5.848	11.623
1,4-Dioxan (1)-water (2)	$T = 298$ K; $\alpha_{m1,m2} = 0.3$; $\tau_{m1,m2} = 1.1607$; $\tau_{m2,m1} = 0.8177$						
	$LiClO_3$	0.10	−6.627	19.265	0.2	−5.075	10.330
	$NaClO_3$	0.10	−4.504	13.503	0.2	−3.917	8.144
Acetonitrile (1)-water (2)	$T = 298$ K; $\alpha_{m1,m2} = 0.3$; $\tau_{m1,m2} = 1.2871$; $\tau_{m2,m1} = 1.3840$						
	KAc	0.05	−10.628	32.081	0.2	−4.868	9.769
	KBr	0.05	−10.936	26.005	0.2	−4.318	8.981
	LiAc	0.05	−8.864	21.417	0.2	−4.616	9.395
	NaBr	0.05	−11.872	28.317	0.2	−4.770	9.790
	$NaNO_3$	0.05	−10.011	23.138	0.2	−3.807	8.179
	NH_4NO_3	0.05	−10.043	23.477	0.2	−3.181	6.939
Methylethyl ketone (1)-water (2)	$T = 298$ K; $\alpha_{m1,m2} = 0.3$; $\tau_{m1,m2} = 0.6348$; $\tau_{m2,m1} = 2.6057$						
	$CaCl_2$	0.07	−10.282	25.250	0.2	−6.379	14.810
Propanol (1)-Isopropanol (2)	$P = 101.3$ kPa; $\alpha_{m1,m2} = 0.3$; $\tau_{m1,m2} = 1.2836$; $\tau_{m2,m1} = -0.9057$						
	$CaCl_2$	0.206	−3.639	7.353	0.2	−3.719	7.812

Solvent	Electrolyte, *ca*	$\alpha_{ca,m1}$	$\tau_{ca,m1}$	$\tau_{m1,ca}$	$\alpha_{ca,m2}$	$\tau_{ca,m2}$	$\tau_{m2,ca}$	$\alpha_{ca,m3}$	$\tau_{ca,m3}$	$\tau_{m3,ca}$
Ethanol (1)-propanol (2)-water (3)	$P = 101.3$ kPa $\alpha_{m1,m2} = 0.3$ $\tau_{m1,m2} = -0.5375$ $\tau_{m2,m1} = 0.5542$ $\alpha_{m1,m3} = 0.3$ $\tau_{m1,m3} = -0.1341$ $\tau_{m3,m1} = 1.8220$ $\alpha_{m2,m3} = 0.3$ $\tau_{m2,m3} = -0.0858$ $\tau_{m3,m2} = 3.1758$									
	LiCl	0.06	−11.093	23.516	0.04	−13.740	25.532	0.2	−5.161	11.074
Methanol (1)-propanol (2)-water (3)	$P = 101.3$ kPa $\alpha_{m1,m2} = 0.3$ $\tau_{m1,m2} = 0.3000$ $\tau_{m2,m1} = -0.1676$ $\alpha_{m1,m3} = 0.3$ $\tau_{m1,m3} = -0.3544$ $\tau_{m3,m1} = 1.2860$ $\alpha_{m2,m3} = 0.3$ $\tau_{m2,m3} = -0.0387$ $\tau_{m3,m2} = 2.8118$									
	LiCl	0.099	−7.101	13.539	0.031	−18.631	33.683	0.2	−5.161	11.074
Ethyl acetate (1)-ethanol (2)-water (3)	$T = 303$ K $\alpha_{m1,m2} = 0.3$ $\tau_{m1,m2} = 2.9037$ $\tau_{m2,m1} = -1.0476$ $\alpha_{m1,m3} = 0.3$ $\tau_{m1,m3} = 1.4169$ $\tau_{m3,m1} = 3.7410$ $\alpha_{m2,m3} = 0.3$ $\tau_{m2,m3} = 0.0447$ $\tau_{m3,m2} = 1.4620$									
	KAc	0.03	−16.833	38.640	0.07	−5.912	7.443	0.2	−4.868	9.769
	NaAc	0.02	−19.240	46.222	0.05	−6.957	8.925	0.2	−4.780	9.621

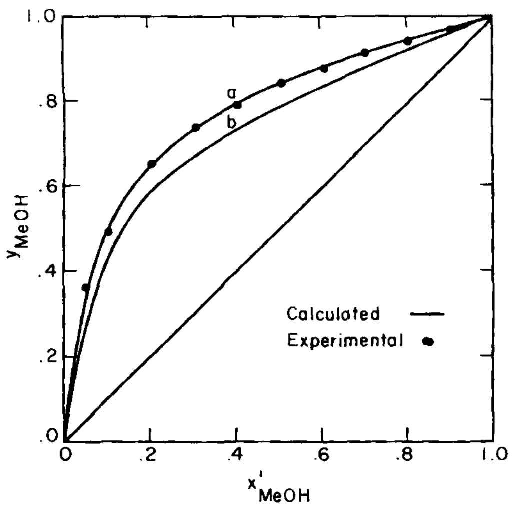

Figure 2. Vapor-liquid equilibrium data for methanol-water-$CaCl_2$ system at 101.3 kPa (Nishi, 1975).
Liquid mole fraction is on a salt-free basis.
a: 16.7 wt. % $CaCl_2$; b: salt-free

salt nonrandomness factor for salted-out solvents was always found to be less than 0.2.

Average values determined for the nonrandomness factor are listed in Table 6 for a number of water-alcohol solvent pairs. The nonrandomness factor $\alpha_{ca,m2}$ seems to have a direct dependency on the solvent pair, with slight variations from the average value, depending on the particular salt added.

As the solvents in the pair become structurally and chemically more different, the differences in the values of the nonrandomness factor increase. Note from Table 6 that the nonrandomness factor for isopropanol and water, the most dissimilar solvents, are very different, while the parameters for propanol and isopropanol are quite similar. The solvent-dependent nature of $\alpha_{ca,m}$ reflects the dependency of solvent-ion interactions on solvent dielectric constant, density, and other solvent characteristics.

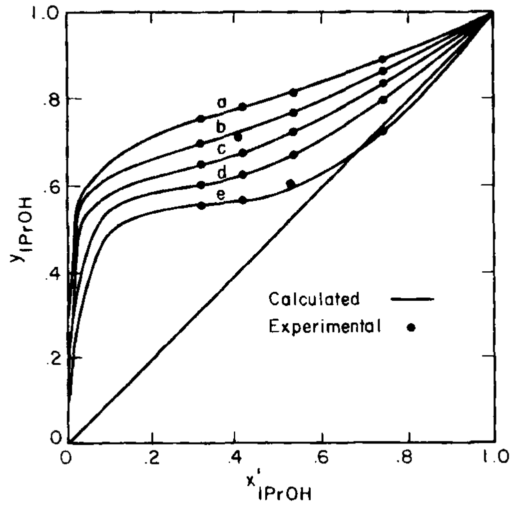

Figure 3. Vapor-liquid equilibrium data for isopropanol-water-LiCl system at 348 K (Sada & Morisue, 1975; Sada et al., 1975).
Liquid mole-fraction is on a salt-free basis.
a: $x_{ions} = 0.20$; b: $x_{ions} = 0.14$; c: $x_{ions} = 0.10$; d: $x_{ions} = 0.06$; e: $x_{ions} = 0$

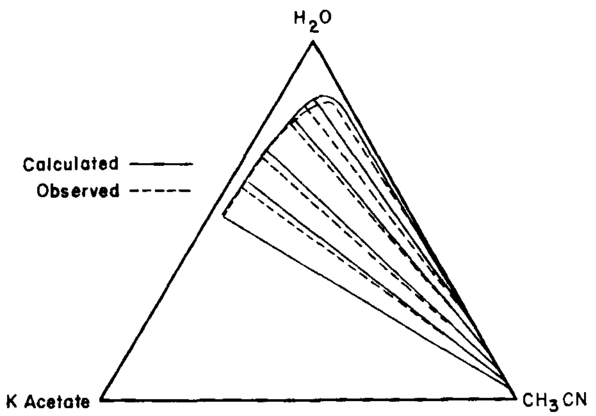

Figure 4. Liquid-liquid equilibrium data for acetonitrile-water-KAc system at 303 K (Renard and Heichelheim, 1967).

Ionic Activity Coefficients

The electrolyte NRTL model does not fully account for the long-range interaction contribution that is essential in accurately computing ionic activity coefficients. Ionic activity coefficients are needed to study, among others, the following phenomena:

- Partial dissociation of weak electrolytes
- Ionic equilibrium and complex formation
- Salt distribution in two-liquid phase electrolyte systems
- Salt solubility

The development of an appropriate expression to fully represent the long-range ion-ion interaction contribution for the excess Gibbs energy of mixed-solvent electrolyte systems would facilitate the computation of ionic activity coefficients. The Pitzer-Debye-Hückel expression has been successfully adapted by Chen and Evans (1986) as the long-range interaction contribution expression in computing the aqueous phase ionic activity coefficients for aqueous electrolyte systems. A similar expression that takes into account the changes in density and dielectric constant as a function of the mixed-solvent composition should be developed for the long-range interaction contribution of mixed-solvent electrolyte systems. However, it is beyond the scope of this work to develop and to examine the behavior of such an expression for the ionic activity coefficients of mixed-solvent electrolyte systems.

Table 6. Average Values of $\alpha_{ca,m}$ for Water-Alcohol Systems

Solvent Pair ($m1$-$m2$)	$\alpha_{ca,m1}$	$\alpha_{ca,m2}$	No. of Systems
Water-methanol	0.20	0.090 ± 0.015	5
Water-ethanol	0.20	0.057 ± 0.007	7
Water-isopropanol	0.20	0.032 ± 0.002	3
Water-propanol	0.20	0.035 ± 0.005	2
Propanol-isopropanol	0.20	0.206	1

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Notation

g^{ex} = molar excess Gibbs free energy
k_o = salt effect parameter, Eq. 1
M = molarity, mol/L solution
n = number of experimental determinations
P = pressure, kPa
p^s = saturation vapor pressure
R = gas constant
T = temperature, K
$\underline{U}$ = measurable variable, experimental value
$\bar{U}$ = measurable variable, calculated value
W = weighting factor
X = effective liquid phase mole fraction
x = true liquid phase mole fraction based on all species, molecular and ionic
x^a = apparent liquid phase mole fraction based on undissociated species, molecular and salt
y = vapor phase mole fraction
Z = absolute value of ionic charge

Greek letters

α = NRTL nonrandomness factor
α_o = relative volatility in absence of salt
α_s = relative volatility in presence of salt, calculated using liquid compositions on a salt-free basis
γ = activity coefficient
θ = binary adjustable parameters in data regression
σ = standard error of measurements
τ = NRTL binary interaction energy parameter
Δ = mean average deviation for regressed data

Subscripts

a, a', a'' = anion
c, c', c'' = cation
i, j, k = any species
m, m' = molecular species
w = water
ca = salt with cation c and anion a
lb = lower bound
ub = upper bound

Superscripts

I = first liquid phase
II = second liquid phase

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