Generalized Electrolyte-NRTL Model for Mixed-Solvent Electrolyte Systems

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DOI 10.1002/aic.10151

A generalized electrolyte Non-Random Two-Liquid (eNRTL) model proposed by Chen and coworkers is presented as a comprehensive excess Gibbs energy expression to represent the liquid-phase nonideality for aqueous and mixed-solvent electrolyte systems over the entire concentration range from pure solvents to saturated solutions or fused salts. The eNRTL model is used to correlate mean ionic activity coefficients of mixed-solvent electrolyte systems. The segment interaction concept provides the framework necessary to represent the attractive interaction of ions with the hydrophilic segments of organic solvents and the repulsive interaction of ions with the hydrophobic segments of organic solvents. The ability to explicitly account for such distinctly different ion–segment interactions is shown to be the key for quantitative correlation of mean ionic activity coefficients in mixed-solvent electrolyte systems. © 2004 American Institute of Chemical Engineers *AIChE J,* 50: 1928–1941, 2004

Keywords: electrolyte thermodynamics, NRTL, mean ionic activity coefficients, mixed solvents, excess Gibbs energy

Introduction

The process industry is concerned with the modeling and simulation of wide varieties of chemical products and processes that involve electrolyte systems in aqueous or mixed-solvent solutions. Example electrolyte systems include water–organics–salt mixtures, water–strong acid (such as nitric acid) mixtures, aqueous organic amines for gas treating, brines with organic additives, and extraction or crystallization of organic salts, to name a few of the foremost systems. Rigorous and accurate representation of the thermodynamic properties of these electrolyte systems is essential for successful modeling and simulation of such chemical products and processes (Chen and Mathias, 2002).

In the last few decades, numerous semiempirical excess Gibbs energy expressions have been proposed for electrolyte systems (for example, Chen et al., 1982, 1986, 2001; Iliuta et al., 2002; Papaiconomou et al., 2002; Pitzer, 1973). These semiempirical models often consist of two contribution terms, one long-range and one short-range. The long-range term is typically represented by variations or equivalents of the Debye–Hückel theory, which accounts for the long-range interaction contributions attributed to the electrostatic forces between ions. The short-range term is represented by modified versions of well-proven expressions for nonelectrolyte systems that account for the contributions arising from the short-range local interactions of various kinds. Among these excess Gibbs energy expressions, the model of Pitzer (1973) and the electrolyte NRTL model of Chen et al. (1982, 1986, 2001) have received wide acceptance in industrial practice of thermodynamic modeling of electrolyte systems. Whereas the use of the Pitzer model has been limited to dilute aqueous electrolyte solutions, the use of the electrolyte NRTL model covers wide varieties of aqueous and mixed-solvent electrolyte systems over the entire concentration range from pure solvents to saturated solutions or fused salts. These excess Gibbs energy models provide rigorous thermodynamic frameworks for computing various electrolyte thermodynamic properties, including mean ionic activity coefficients, osmotic coefficients, and solute and solvent fugacities, for example. The rigorous and accurate computation

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of electrolyte thermodynamic properties forms a sound foundation for phase equilibrium calculations (that is, vapor–liquid equilibrium, liquid–liquid equilibrium, and salt solubilities) and modeling and simulation for chemical processes involving electrolytes.

The eNRTL model has been extensively applied to represent thermodynamic properties of various electrolyte systems. Examples include mean ionic activity coefficients of aqueous strong electrolytes (Chen and Evans, 1986; Chen et al., 1999) and aqueous organic electrolytes (Chen et al., 2001); phase behavior of weak electrolytes (Chen and Evans, 1986), strong acids (Chen, 1987), and mixed-solvent electrolytes (Mock et al., 1986); solubilities of zwitterions (Chen et al., 1989), and so forth. In this article, we present a generalized segment-based eNRTL model for electrolyte systems and examine its use for correlating mean ionic activity coefficients of mixed-solvent electrolyte systems.

Electrolyte NRTL Model

Segment interaction concepts

The eNRTL model evolved over many years. Recently Chen et al. (2001) incorporated the segment interaction concept of the polymer NRTL model (Chen, 1993) and successfully applied the model to represent the phase behavior of aqueous organic electrolytes. We generalize the segment interaction concept in this work. Under such a generalization, any component, electrolyte or solvent, can be defined as an oligomer consisting of various segment species. For instance, an organic electrolyte component can be defined as an oligomer consisting of cationic segments, anionic segments, and molecular segments. An organic solvent can also be defined as an oligomer consisting of multiple molecular segments of different nature. This generalized segment interaction concept is particularly advantageous when one must explicitly account for the drastically different interaction characteristics that may be attributed to different parts of large, complex molecules.

The generalized eNRTL model contains two contributions: one from local interactions that exist at the immediate neighborhood of any species, and the other from the long-range ion–ion interactions that exist beyond the immediate neighborhood of an ionic species. To account for the local interactions, the model uses the segment-based NRTL expression (Chen, 1993). To account for the long-range interactions, the model uses the unsymmetric Pitzer–Debye–Hückel (PDH) formula (Pitzer, 1980). The following equation is the basis of the eNRTL model for the excess Gibbs energy of electrolyte systems

$$G_m^{*ex} = G_m^{*ex,lc} + G_m^{*ex,PDH} \tag{1}$$

where the notation "*" denotes the unsymmetric convention, G_m^{ex} is the excess Gibbs energy of electrolyte systems, $G_m^{ex,lc}$ is the contribution from the local composition interactions, and $G_m^{ex,PDH}$ is the contribution arising from long-range ion–ion interactions. The excess Gibbs energy G_m^{ex} is defined as follows

$$G_m^{ex} = G_m - G_m^{id} \tag{2}$$

where G_m is the Gibbs energy of electrolyte systems and G_m^{id} is the Gibbs energy of an ideal solution at the same conditions of temperature, pressure, and composition (Prausnitz et al., 1986). Accordingly, Eqs. 1 and 2 lead to the following expression for the activity coefficient

$$\begin{aligned}\ln \gamma_I^* &= \frac{1}{RT}\left(\frac{\partial G_m^{*,ex}}{\partial n_I}\right)_{T,P,n_{J\neq I}} \\ &= \frac{1}{RT}\left(\frac{\partial G_m^{*ex,lc}}{\partial n_I}\right)_{T,P,n_{J\neq I}} + \frac{1}{RT}\left(\frac{\partial G_m^{*ex,PDH}}{\partial n_I}\right)_{T,P,n_{J\neq I}}\end{aligned} \tag{3}$$

or

$$\ln \gamma_I^* = \ln \gamma_I^{*,lc} + \ln \gamma_I^{*,PDH} \tag{4}$$

where γ_I is the activity coefficient of the component I in the mixture, R is the gas constant, T is the temperature, P is the pressure, and n_I is the mole number of the component I in the mixture. The unsymmetric PDH formula, $G_m^{*ex,PDH}$, is obtained by normalization to mole fractions of unity for solvents and zero for electrolytes (Pitzer, 1973); the details are given in a later section. The local interaction NRTL model, $G_m^{ex,lc}$, is developed as a symmetric model (Chen et al., 1993, 2001), based on the *symmetric* reference state so that the derived activity coefficient, $\gamma_I^{lc} = 1$ as $x_I \to 1$ for any component (species). The model is then normalized by the *unsymmetric* reference state (that is, the infinite-dilution activity coefficient in an aqueous or mixed-solvent solution) to obtain the unsymmetric model, $G_m^{*ex,lc}$. Accordingly, the unsymmetric convention activity coefficient is calculated as follows

$$\ln \gamma_I^{*lc} = \ln \gamma_I^{lc} - \ln \gamma_I^{\infty lc} \tag{5}$$

$$\ln \gamma_I^{lc} = \frac{1}{RT}\left(\frac{\partial G_m^{ex,lc}}{\partial n_I}\right)_{T,P,n_{J\neq I}} \tag{6}$$

where γ_I^{∞} is the infinite-dilution activity coefficient of the ionic component I in an aqueous or mixed-solvent solution as calculated by Eq. 6; it is defined as the *unsymmetric* reference state in the unsymmetric convention and the details are given in the next section.

NRTL term for local interaction contribution

The model development for the NRTL local interaction contribution has been described in detail by Chen et al. (1982, 1986, 2001). Only the basic ideas and general expressions for multicomponent electrolyte systems related to the segment interaction concepts outlined above are discussed and represented here.

In an electrolyte system, after accounting for the segment interaction concept, all segment-based species can be categorized as one of three types: molecular species (segments and solvents), m; cationic species (cations and cationic segments), c; and anionic species (anions and anionic segments), a. The model assumes that there are three types of local composition interactions. The first type consists of a central molecular species with other molecular species, cationic species, and anionic species in the immediate neighborhood. Here, local electroneutrality is maintained. The other two types are based on the like-ion repulsion assumption and have either a cationic or anionic species as the central species. They also have an immediate neighborhood consisting of molecular species and oppositely charged ionic species. Accordingly, the excess Gibbs energy from local interactions for an electrolyte system can be written as follows

$$\frac{G_m^{ex,lc}}{RT} = \sum_I \sum_m r_{m,I} n_I \left(\frac{\sum_j X_j G_{jm} \tau_{jm}}{\sum_k X_k G_{km}} \right) + \sum_I \sum_c z_c r_{c,I} n_I \left(\sum_a Y_a \frac{\sum_j X_j G_{jc,ac} \tau_{jc,ac}}{\sum_k X_k G_{kc,ac}} \right) + \sum_I \sum_a z_a r_{a,I} n_I \left(\sum_c Y_c \frac{\sum_j X_j G_{ja,ca} \tau_{ja,ca}}{\sum_k X_k G_{ka,ca}} \right) \tag{7}$$

with

$$X_j = C_j x_j \tag{8}$$

$$x_j = \frac{\sum_J x_J r_{j,J}}{\sum_I \sum_i x_I r_{i,I}} \tag{9}$$

where the first term is the contribution when a molecular species is at the center, the second is the contribution when a cationic species is at the center, and the third term is the contribution when an anionic species is at the center. In Eqs. 7–9, i, j, and k denote segment-based species index. I and J denote component index. n_I is the mole number of component I, $C_j = z_j$ (charge number) for ionic species, and $C_j = 1$ for molecular species. x_j is the segment-based mole fraction of segment species j, and x_J is the mole fraction of component J. Also in Eqs. 7–9, $r_{m,I}$, $r_{c,I}$, and $r_{a,I}$ are number of molecular segment species m, number of cationic segment species c, and number of anionic segment species a, in component I, respectively. In Eq. 7, the summation over anionic species, $\sum_a Y_a \cdots$, comes from the assumption that a central cationic species is surrounded only by molecular species and anionic species; Y_a is an anionic charge composition fraction quantity, unspecified at the moment. Similarly, the summation over cationic species, $\sum_c Y_c \cdots$, comes from the assumption that a central anionic species is surrounded only by molecular species and cationic species; Y_c is a cationic charge composition fraction quantity, unspecified at the moment. Finally, in Eq. 7, G and τ are local binary quantities related to each other by the NRTL nonrandom factor parameter α

$$G = \exp(-\alpha\tau) \tag{10}$$

The details on how to calculate these binary quantities are given in the next subsection.

To compute the local composition term for the activity coefficients of components, we first compute local composition contributions for each segment. For this purpose, we rewrite Eq. 7 as follows

$$\frac{G_m^{ex,lc}}{RT} = \sum_m n_m \left(\frac{\sum_j X_j G_{jm} \tau_{jm}}{\sum_k X_k G_{km}} \right) + \sum_c z_c n_c \left(\sum_a Y_a \frac{\sum_j X_j G_{jc,ac} \tau_{jc,ac}}{\sum_k X_k G_{kc,ac}} \right) + \sum_a z_a n_a \left(\sum_c Y_c \frac{\sum_j X_j G_{ja,ca} \tau_{ja,ca}}{\sum_k X_k G_{ka,ca}} \right) \tag{11}$$

with

$$n_j = \sum_I n_I r_{j,I} \qquad j = m, c, a \tag{12}$$

$$X_j = C_j x_j \qquad j = m, c, a \tag{13}$$

$$x_j = \frac{n_j}{\sum_i n_i} \qquad j = m, c, a \tag{14}$$

where n_j is the total number of the segment species j in the mixture and x_j is the segment fraction of the segment species j in the mixture. Accordingly, the segment activity coefficient can be calculated as follows

$$\ln \gamma_j^{lc} = \frac{1}{RT} \left(\frac{\partial G_m^{ex,lc}}{\partial n_j} \right)_{T,P,n_{i \neq j}} \qquad i, j = m, c, a \tag{15}$$

Specifically, the segment contributions to the activity coefficients from molecular segments, cationic segments, and anionic segments can be carried out from Eqs. 11 and 15; the results are given in Appendix A. The local composition term for the logarithm of activity coefficient of component I is then computed as the sum of the individual segment contributions.

$$\begin{aligned} \ln \gamma_I^{lc} &= \sum_i r_{i,I} \ln \gamma_i^{lc} \qquad i = m, c, a \\ &= \sum_m r_{m,I} \ln \gamma_m^{lc} + \sum_c r_{c,I} \ln \gamma_c^{lc} + \sum_a r_{a,I} \ln \gamma_a^{lc} \end{aligned} \tag{16}$$

However, the activity coefficient by Eq. 16 needs to be further normalized so that $\gamma_I^{lc} = 1$ as $x_I \rightarrow 1$ for any component (species); this is the so-called *symmetric* reference state. The normalization can be done as follows

$$\begin{aligned} \ln \gamma_I^{lc} &= \sum_i r_{i,I} (\ln \gamma_i^{lc} - \ln \gamma_i^{lc,I}) \qquad i = m, c, a \\ &= \sum_m r_{m,I} (\ln \gamma_m^{lc} - \ln \gamma_m^{lc,I}) + \sum_c r_{c,I} (\ln \gamma_c^{lc} - \ln \gamma_c^{lc,I}) \\ &\quad + \sum_a r_{a,I} (\ln \gamma_a^{lc} - \ln \gamma_a^{lc,I}) \end{aligned} \tag{17}$$

where $\gamma_i^{lc,I}$ is the activity coefficient of the segment species i contained in the *symmetric* reference state of component I, which can be calculated from Eqs. A1–A3 for molecular segments, cationic segments, and anionic segments, respectively, and the results are also given in Appendix A.

Activity coefficients of nonelectrolyte components

Equation 17 is a general form for the local composition interaction contribution to activity coefficients of components in an electrolyte system. For nonelectrolyte monomers (or solvents) and oligomers (or polymers), Eq. 17 can be simplified and reduced to the classical NRTL model (Renon and Prausnitz, 1968) and to the polymer NRTL model (Chen, 1993), respectively. For instance, Eq. 17 can be rewritten as follows for nonelectrolyte systems with monomeric solvents (*S*)

$$\ln \gamma_{I=S}^{lc} = \frac{\sum_j X_j G_{jS} \tau_{jS}}{\sum_k X_k G_{kS}} + \sum_m \frac{X_m G_{Sm}}{\sum_k X_k G_{km}} \left(\tau_{Sm} - \frac{\sum_k X_k G_{km} \tau_{km}}{\sum_k X_k G_{km}} \right) \tag{18}$$

$$\ln \gamma_{I=S}^{lc,S} = 0 \tag{19}$$

Equation 18 is the same as the classical NRTL model (Renon and Prausnitz, 1968).

Similarly, for nonelectrolyte oligomeric/polymeric components, Eq. 17 can be rewritten as follows

$$\ln \gamma_{I=P}^{lc} = \sum_m r_{m,P} (\ln \gamma_m^{lc} - \ln \gamma_m^{lc,P}) \tag{20}$$

with

$$\ln \gamma_m^{lc} = \frac{\sum_j X_j G_{jm} \tau_{jm}}{\sum_k X_k G_{km}} + \sum_{m'} \frac{X_{m'} G_{mm'}}{\sum_k X_k G_{km'}} \left(\tau_{mm'} - \frac{\sum_k X_k G_{km'} \tau_{km'}}{\sum_k X_k G_{km'}} \right) \tag{21}$$

$$\ln \gamma_m^{lc,P} = \frac{\sum_j x_{j,P} G_{jm} \tau_{jm}}{\sum_k x_{k,P} G_{km}} + \sum_{m'} \frac{x_{m',P} G_{mm'}}{\sum_k x_{k,P} G_{km'}} \left(\tau_{mm'} - \frac{\sum_k x_{k,P} G_{km'} \tau_{km'}}{\sum_k x_{k,P} G_{km'}} \right) \tag{22}$$

$$x_{i,P} = \frac{r_{i,P}}{\sum_j r_{j,P}} \tag{23}$$

where $x_{i,P}$ is the segment mole fraction of segment species *i* in oligomeric/polymeric component *P*. Equation 21 is the same as the result given by the polymer NRTL model (Chen, 1993) for an oligomeric/polymeric component.

Binary parameters

There are three types of model adjustable binary parameters: molecular–molecular binary parameters, molecule–electrolyte binary parameters, and electrolyte–electrolyte binary parameters. Here "electrolyte" is meant to represent an ion pair composed of a cationic species and an anionic species. The model-adjustable binary parameters include the symmetric nonrandom factor parameters, α, and the asymmetric binary interaction energy parameters, τ. In short, the adjustable binary parameters include

$$\alpha_{mm'} = \alpha_{m'm} \qquad \alpha_{m,ca} = \alpha_{ca,m} \qquad \alpha_{ca,ca'} = \alpha_{ca',ca} \qquad \alpha_{ca,c'a} = \alpha_{c'a,ca} \tag{24}$$

$$\tau_{mm'} \qquad \tau_{m'm} \qquad \tau_{m,ca} \qquad \tau_{ca,m} \qquad \tau_{ca,ca'} \qquad \tau_{ca',ca} \qquad \tau_{ca,c'a} \qquad \tau_{c'a,ca} \tag{25}$$

As an example, for a system with two molecular species, *m* and *w*, and one electrolyte, *ca*, there are nine adjustable binary parameters: α_{mw}, $\alpha_{m,ca}$, $\alpha_{w,ca}$, τ_{mw}, $\tau_{m,ca}$, $\tau_{w,ca}$, τ_{wm}, $\tau_{ca,m}$, and $\tau_{ca,w}$. In practice, α values are often fixed as constants (that is, 0.2 or 0.3), whereas τ values are adjusted.

However, from Eqs. A1–A3, we also need the following binary parameters

$$\alpha_{cm} \qquad \alpha_{am} \qquad \alpha_{mc,ac} \qquad \alpha_{ma,ca} \tag{26}$$

$$\tau_{cm} \qquad \tau_{am} \qquad \tau_{mc,ac} \qquad \tau_{ma,ca} \tag{27}$$

These binary parameters are calculated from the model-adjustable binary parameters. A molal average mixing rule is adopted to calculate α_{cm} and α_{am}

$$\alpha_{cm} = \sum_a Y_a \alpha_{m,ca} \tag{28}$$

$$\alpha_{am} = \sum_c Y_c \alpha_{m,ca} \tag{29}$$

The anionic charge composition fraction, Y_a, and the cationic charge composition fraction, Y_c, are calculated as follows

$$Y_a = \frac{X_a}{\sum_{a'} X_{a'}} \tag{30}$$

$$Y_c = \frac{X_c}{\sum_{c'} X_{c'}} \tag{31}$$

It should be pointed out that Y_a and Y_c remained constants in Eqs. 7 and 11 when deriving the activity coefficients as given by Eqs. A1–A3. The molal average mixing rule is also applied to calculate G_{cm} and G_{am}

$$G_{cm} = \sum_a Y_a G_{ca,m} \tag{32}$$

$$G_{am} = \sum_c Y_c G_{ca,m} \tag{33}$$

The binary parameters τ_{cm} and τ_{am} are then calculated from Eq. 10

$$\tau_{cm} = -\frac{\ln(G_{cm})}{\alpha_{cm}} \tag{34}$$

$$\tau_{am} = -\frac{\ln(G_{am})}{\alpha_{am}} \tag{35}$$

The following relationships are further assumed for $\alpha_{mc,ac}$, $\alpha_{ma,ca}$, $\tau_{mc,ac}$, and $\tau_{ma,ca}$, respectively

$$\alpha_{mc,ac} = \alpha_{cm} \tag{36}$$

$$\alpha_{ma,ca} = \alpha_{am} \tag{37}$$

$$\tau_{mc,ac} = \tau_{cm} - \frac{\alpha_{ca,m}}{\alpha_{mc,ac}}(\tau_{ca,m} - \tau_{m,ca}) \tag{38}$$

$$\tau_{ma,ca} = \tau_{am} - \frac{\alpha_{ca,m}}{\alpha_{ma,ca}}(\tau_{ca,m} - \tau_{m,ca}) \tag{39}$$

$G_{mc,ac}$ and $G_{ma,ca}$ are thus calculated from Eq. 10 as follows:

$$G_{mc,ac} = \exp(-\alpha_{mc,ac}\tau_{mc,ac}) = \exp(-\alpha_{cm}\tau_{mc,ac}) \tag{40}$$

$$G_{ma,ca} = \exp(-\alpha_{ma,ca}\tau_{ma,ca}) = \exp(-\alpha_{am}\tau_{ma,ca}) \tag{41}$$

Infinite-dilution activity coefficients as unsymmetric reference states

For ionic species, we are interested in unsymmetric convention activity coefficients as given by Eq. 5. Therefore, we need to compute "infinite-dilution activity coefficients" in the symmetric normalization convention from Eq. 17

$$\begin{aligned}\ln \gamma_I^{\infty lc} &= \sum_i r_{i,I}(\ln \gamma_i^{\infty lc} - \ln \gamma_i^{lc,I}) \qquad i = m, c, a \\ &= \sum_m r_{m,I}(\ln \gamma_m^{\infty lc} - \ln \gamma_m^{lc,I}) + \sum_c r_{c,I}(\ln \gamma_c^{\infty lc} \\ &\quad - \ln \gamma_c^{lc,I}) + \sum_a r_{a,I}(\ln \gamma_a^{\infty lc} - \ln \gamma_a^{lc,I})\end{aligned} \tag{42}$$

The calculated infinite-dilution activity coefficients are then used as the *unsymmetric* reference states, in Eq. 5, to compute the unsymmetric activity coefficients for ionic components

$$\begin{aligned}\ln \gamma_I^{*lc} &= \ln \gamma_I^{lc} - \ln \gamma_I^{\infty lc} \\ &= \sum_i r_{i,I}(\ln \gamma_i^{lc} - \ln \gamma_i^{\infty lc}) \qquad i = m, c, a \\ &= \sum_m r_{m,I}(\ln \gamma_m^{lc} - \ln \gamma_m^{\infty lc}) + \sum_c r_{c,I}(\ln \gamma_c^{lc} - \ln \gamma_c^{\infty lc}) \\ &\quad + \sum_a r_{a,I}(\ln \gamma_a^{lc} - \ln \gamma_a^{\infty lc})\end{aligned} \tag{43}$$

The condition of an infinite-dilution solution for ionic segments can be written as follows

$$x_a = x_c = 0 \tag{44}$$

However, the definition of an *unsymmetric* reference state depends on the composition of electrolyte-free solvent mixtures. In other words, there are two choices for solvents in the infinite-dilution solutions: infinite-dilution aqueous solutions or infinite-dilution mixed-solvent solutions. If we choose the infinite-dilution activity coefficients in aqueous solutions [that is, water (w)] as the *unsymmetric* reference state, that is

$$x_w = 1 \tag{45}$$

we can then obtain the following from Eqs. A1–A3

$$\ln \gamma_m^{\infty lc} = \tau_{wm} + G_{mw}\tau_{mw} \tag{46}$$

$$\frac{1}{z_c}\ln \gamma_c^{\infty lc} = \sum_a Y_a \tau_{wc,ac} + G_{cw}\tau_{cw} \tag{47}$$

$$\frac{1}{z_a}\ln \gamma_a^{\infty lc} = \sum_c Y_c \tau_{wa,ca} + G_{aw}\tau_{aw} \tag{48}$$

If we choose the infinite-dilution activity coefficients in mixed-solvent solutions as the *unsymmetric* reference state, that is

$$\sum_s x_s' = 1 \tag{49}$$

where x_s' is the mole fraction of solvent species s in electrolyte-free solvent mixtures

$$x_s' = \frac{x_s}{\sum_s x_s} \tag{50}$$

we can then obtain the following from Eqs. A1–A3

$$\ln \gamma_m^{\infty lc} = \frac{\sum_s x_s' G_{sm}\tau_{sm}}{\sum_s x_s' G_{sm}} + \sum_s \frac{x_s' G_{ms}}{\sum_k x_k' G_{ks}}\left(\tau_{ms} - \frac{\sum_k x_k' G_{ks}\tau_{ks}}{\sum_k x_k' G_{ks}}\right) \tag{51}$$

$$\begin{aligned}\frac{1}{z_c}\ln \gamma_c^{\infty lc} &= \sum_a Y_a \frac{\sum_s x_s' G_{sc,ac}\tau_{sc,ac}}{\sum_s x_s' G_{sc,ac}} \\ &\quad + \sum_s \frac{x_s' G_{cs}}{\sum_k x_k' G_{ks}}\left(\tau_{cs} - \frac{\sum_k x_k' G_{ks}\tau_{ks}}{\sum_k x_k' G_{ks}}\right)\end{aligned} \tag{52}$$

$$\begin{aligned}\frac{1}{z_a}\ln \gamma_a^{\infty lc} &= \sum_c Y_c \frac{\sum_s x_s' G_{sa,ca}\tau_{sa,ca}}{\sum_s x_s' G_{sa,ca}} \\ &\quad + \sum_s \frac{x_s' G_{as}}{\sum_k x_k' G_{ks}}\left(\tau_{as} - \frac{\sum_k x_k' G_{ks}\tau_{ks}}{\sum_k x_k' G_{ks}}\right)\end{aligned} \tag{53}$$

with

$$x_k' = \frac{x_k}{\sum_s x_s} \tag{54}$$

Here again k is the segment species index derived from solvent components (that is, monomeric solvents and oligomeric solvents) in the mixture.

Long-range interaction contribution from PDH model

To account for the long-range ion–ion interactions, the model uses the unsymmetric PDH formula (Pitzer, 1980):

$$\frac{G^{*ex,PDH}}{RT} = -N\left(\frac{1000}{M_s}\right)^{1/2}\left(\frac{4A_\varphi I_x}{\rho}\right)\ln(1+\rho I_x^{1/2}) \tag{55}$$

with

$$N = \sum_I n_I \sum_i r_{i,I} = \sum_i \left(\sum_I n_I r_{i,I}\right) = \sum_i n_i \qquad i = m,\, c,\, a \tag{56}$$

$$A_\varphi = \frac{1}{3}\left(\frac{2\pi N_A d_s}{1000}\right)^{1/2}\left(\frac{Q_e^2}{\varepsilon_s kT}\right)^{3/2} \tag{57}$$

$$I_x = \frac{1}{2}\sum_i x_i z_i^2 = \frac{1}{2}\frac{\sum_i n_i z_i^2}{N} \tag{58}$$

where A_φ is the Debye–Hückel parameter; I_x is the ionic strength (segment mole fraction scale); M_s is the molecular weight of the solvent s; ρ is the closest approach parameter; N_A is Avogadro's number; d_s is the density of the solvent; Q_e is the electron charge; ϵ_s is the dielectric constant of the solvent; k is the Boltzmann constant; and z_i is the charge number of segment-based species i.

The activity coefficient of segment species i can be derived as follows

$$\begin{aligned}\ln \gamma_i^{*PDH} &= \frac{1}{RT}\left(\frac{\partial G^{*ex,PDH}}{\partial n_i}\right)_{T,P,n_{j\neq i}} \qquad i, j = m,\, c,\, a \\ &= -\left(\frac{1000}{M_s}\right)^{1/2} A_\varphi\left[\left(\frac{2z_i^2}{\rho}\right)\ln(1+\rho I_x^{1/2}) + \frac{z_i^2 I_x^{1/2} - 2I_x^{1/2}}{1+\rho I_x^{1/2}}\right]\end{aligned} \tag{59}$$

For an oligomeric ion component I, the logarithm of activity coefficient is the sum of contributions from its various segments

$$\ln \gamma_I^{*PDH} = \sum_m r_{m,I} \ln \gamma_m^{*PDH} + \sum_c r_{c,I} \ln \gamma_c^{*PDH} + \sum_a r_{a,I} \ln \gamma_a^{*PDH} \tag{60}$$

The Debye–Hückel theory is based on the infinite-dilution reference state for ionic species in the actual solvent media. For systems with water as the only solvent, the reference state is the infinite-dilution aqueous solution. For mixed-solvent systems, the reference state for which the Debye–Hückel theory remains valid is the infinite-dilution solution with the corresponding mixed-solvent composition. However, these quantities for the single solvent need to be extended for mixed solvents; simple composition average mixing rules are adequate to calculate them as follows

$$M_s = \sum_S x'_S M_S \tag{61}$$

$$\frac{1}{d_s} = \sum_S \frac{x'_S}{d_S} \tag{62}$$

$$\varepsilon_s = \sum_S w'_S \varepsilon_S \tag{63}$$

with

$$x'_S = \frac{x_S}{\sum_S x_S} \tag{64}$$

$$w'_S = \frac{M_S x_S}{\sum_S M_S x_S} \tag{65}$$

where S is a solvent component in the mixture, and M_S is the molecular weight of the solvent S. It should be pointed out that Eqs. 61–65 should be used only in Eq. 59 and M_S, d_s, and ϵ_s were already assumed as constants in Eqs. 55 and 57 when deriving Eq. 59 for mixed-solvent systems.

Born term correction to activity coefficient

If the infinite-dilution aqueous solution is chosen as the reference state, we need to correct the change of the reference state from the mixed-solvent composition to aqueous solution for the Debye–Hückel term. The Born term (Rashin and Honig, 1985; Robinson and Stokes, 1970) is used for this purpose

$$\frac{\Delta G^{Born}}{RT} = \frac{NQ_e^2}{2kT}\left(\frac{1}{\varepsilon_s} - \frac{1}{\varepsilon_w}\right)\sum_i \frac{x_i z_i^2}{r_i} 10^{-2} \tag{66}$$

ΔG^{Born} is the Born term correction to the unsymmetric PDH formula, $G_m^{*\,ex,PDH}$; ϵ_w is the dielectric constant of water; and r_i is the Born radius of segment species i. The expression for the activity coefficient of segment species i can be derived from Eq. 66

$$\begin{aligned}\Delta \ln \gamma_i^{Born} &= \frac{1}{RT}\left(\frac{\partial \Delta G^{Born}}{\partial n_i}\right)_{T,P,n_{j\neq i}} \\ &= \frac{Q_e^2}{2kT}\left(\frac{1}{\varepsilon_s} - \frac{1}{\varepsilon_w}\right)\frac{z_i^2}{r_i} 10^{-2} \qquad i = c,\, a\end{aligned} \tag{67}$$

For an oligomeric ion component I, this correction term on the logarithm of activity coefficient is the sum of contributions from its various segments

$$\Delta \ln \gamma_I^{Born} = \sum_c r_{c,I} \Delta \ln \gamma_c^{Born} + \sum_a r_{a,I} \Delta \ln \gamma_a^{Born} \tag{68}$$

Mean ionic activity coefficients and molality scale mean ionic activity coefficients

The mean ionic activity coefficients, $\gamma_{\pm}^{*}$, is related to individual ionic activity coefficients as follows

$$\ln \gamma_{\pm}^{*} = \frac{1}{\upsilon}(\upsilon_c \ln \gamma_c^{*} + \upsilon_a \ln \gamma_a^{*}) \tag{69}$$

where υ_c is the cationic stoichiometric coefficient and υ_a is the anionic stoichiometric coefficient, where $\upsilon = \upsilon_c + \upsilon_a$ (one mole of salt releases υ moles of ions in solution). They are given by the chemical equation describing the dissociation of the electrolyte

$$CA \rightarrow \upsilon_c C^{z_c+} + \upsilon_a A^{z_a-} \tag{70}$$

Equation 69 gives the mean ionic activity coefficient on the mole fraction scale and it should be converted to the molality scale for comparison with experimental data

$$\gamma_{\pm m}^{*} = \gamma_{\pm}^{*} x_S \tag{71}$$

where $\gamma_{\pm m}^{*}$ is the mean ionic activity coefficient on the molality scale, and x_S is the mole fraction of the solvent in the system; for an electrolyte system containing a single solvent and a single salt, x_S is related to the molality of the salt as follows

$$x_S = 1/(1 + \upsilon m M_s/1000) \tag{72}$$

or

$$m = \left(\frac{1}{x_S} - 1\right)\frac{1000}{\upsilon M_s} \tag{73}$$

where m is the molality of the salt (mol/kg solvent), and M_s is the molecular weight of the solvent (g/mol). The natural logarithm of the mean ionic activity coefficient can be written as follows

$$\ln \gamma_{\pm m}^{*} = \ln \gamma_{\pm}^{*} - \ln(1 + \upsilon m M_s/1000) \tag{74}$$

Modeling Mixed-Solvent Electrolyte Systems

Applying the eNRTL model to correlate the mean ionic activity coefficient data is a stringent test on the model's capability to represent ionic species in mixed-solvent electrolyte systems. There are varieties of mixed-solvent electrolyte systems. Example mixed-solvent systems of industrial significance include water–organics–salt mixtures, water–strong acid (such as nitric acid) mixtures, aqueous organic amines for gas treating, brines with organic additives, and extraction or crystallization of organic salts. In this study, we focus on systems with polar organic solvents such as methanol and ethanol because of the availability of mean ionic activity coefficient data. The polar nature of these alcohols makes it possible to dissolve them in water with high organic solvent contents. We use the data of Akerlof (1930), who reported mean ionic activity coefficients of sodium, potassium, and lithium chlorides and hydrochloric acid at infinite dilution in various water–methanol mixtures. Additional data for water–methanol system and water–ethanol system from Malahias and Popovych (1982) and Esteso et al. (1989) are also correlated. The Born term ionic cavity radii are taken from Rashin and Honig (1985). All calculations in this study are carried out with the commercial physical property system Aspen Properties™ with Polymers Plus® release 12.1, and all model parameters (except reported herein) needed for calculations are retrieved from Aspen Properties. The model parameters are summarized in Table 1.

Table 1. Some Parameters Used for Water–Methanol–Electrolyte and Water–Ethanol–Electrolyte Systems

Born Radius of Ionic Species*

Ionic species	Born radius (10^{-10} m)
K^+	2.172
Na^+	1.680
Li^+	1.316
H^+	1.316
Cl^-	1.937

Dielectric Constant of Solvents**

Solvent	A	B	C
Water	78.52	31989.4	298.15
Methanol	32.6146	12805.8	298.15
Ethanol	24.1113	12601.6	298.15

NRTL Parameters for Water–methanol and Water–Ethanol Mixtures†

	Water–Methanol	Water–Ethanol
a_{ij}	4.824	3.622
a_{ji}	−2.626	−0.922
b_{ij}	−1329.544	−636.726
b_{ji}	828.387	284.286
α	0.3	0.3

*These values (except for H^+) are taken from Rashin and Honig (1985). The value for H^+ is set to the value of Li^+.

**These values are retrieved from Aspen Properties® release 12.1. The temperature dependency of the dielectric constant is written as: $\varepsilon = A + B(1/T - 1/C)$, where T is the system temperature.

†These values are retrieved from Aspen Properties release 12.1. The nonrandomness factor α is fixed at the value of 0.3. The energy parameter τ is treated as temperature-dependent: $\tau_{ij} = a_{ij} + b_{ij}/T$, where T is the system temperature.

Some literature articles reported mean ionic activity coefficient data with aqueous phase infinite dilution as the reference state, whereas others reported mean ionic activity coefficient data with mixed solvent infinite dilution as the reference state. These two types of data can be converted from one to the other with adjustment based on the difference between the infinite-dilution activity coefficients at the two reference states.

Infinite-dilution mean ionic activity coefficients

We first apply the eNRTL model to correlate the infinite-dilution mean ionic activity coefficient data of Akerlof (1930). Figure 1a shows the four types of different cells suggested by the eNRTL model when we treat the ions and solvent molecules as interacting species. Figure 2 shows the experimental data of Akerlof (1930) and the best fit with the eNRTL model for the infinite-dilution mean ionic activity coefficients of sodium, potassium, and lithium chlorides and hydrochloric acid

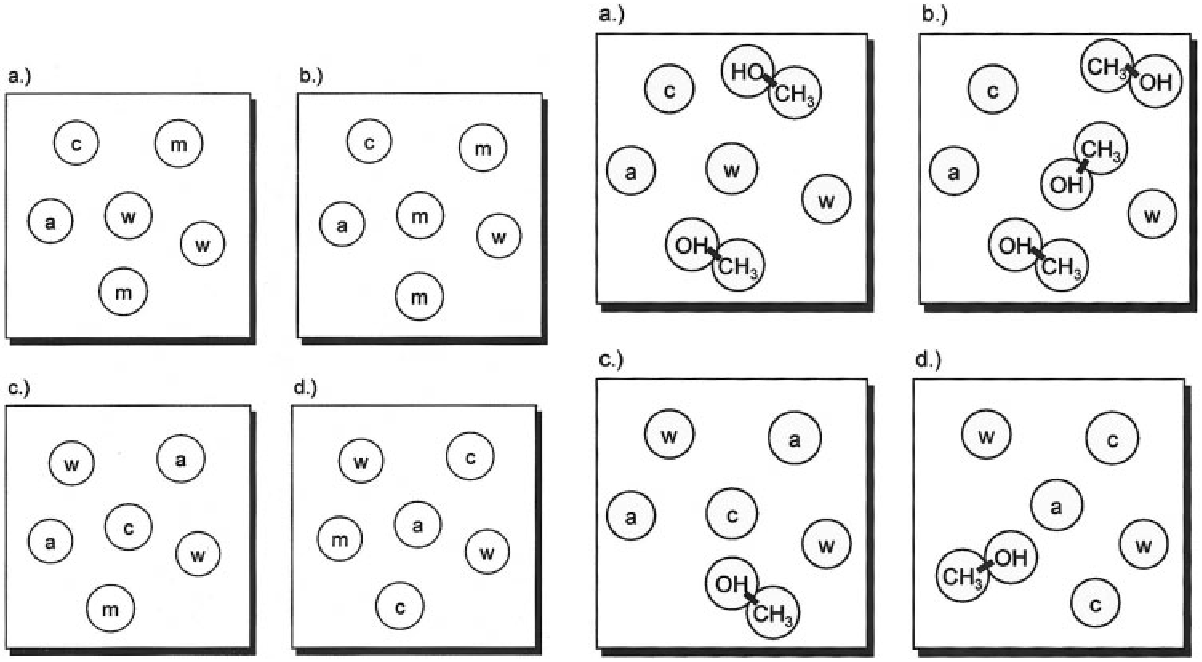

Figure 1. Four types of cells according to like-ion repulsion and local electroneutrality of the eNRTL model.

(a) a.) cell with water as central species; b.) cell with methanol as central species; c.) cell with cation as central species; d.) cell with anion as central species. (b) a.) cell with water as central species; b.) cell with methanol as central species (represented as two segments); c.) cell with cation as central species; d.) cell with anion as central species.

in water–methanol mixtures. The reference state is the infinite dilution in water. In this application, all species are treated as monomeric components. The NRTL parameters for electrolyte–water interactions are first determined from the activity coefficient data of Robinson and Stokes (1970) and the values are summarized in Table 2. The NRTL parameters for water–methanol interaction are retrieved from Aspen Properties. The NRTL parameters for electrolyte–methanol interaction are then determined by the best fit to the data and the results are summarized in Table 3. With two adjustable electrolyte-methanol interaction parameters, the residual root mean square errors, $[\sum_i^k (\ln \gamma_i^{*\exp} - \ln \gamma_i^{*cal})^2/k]^{1/2}$, are 0.192, 0361, 0.432, and 0.284, for potassium chloride, sodium chloride, lithium chloride, and hydrochloric acid, respectively.

The Akerlof data clearly show that the natural logarithm of the infinite-dilution mean ionic activity coefficient is a strong function of mixed-solvent compositions. Figure 2 shows that, although the eNRTL model qualitatively represents the infi-

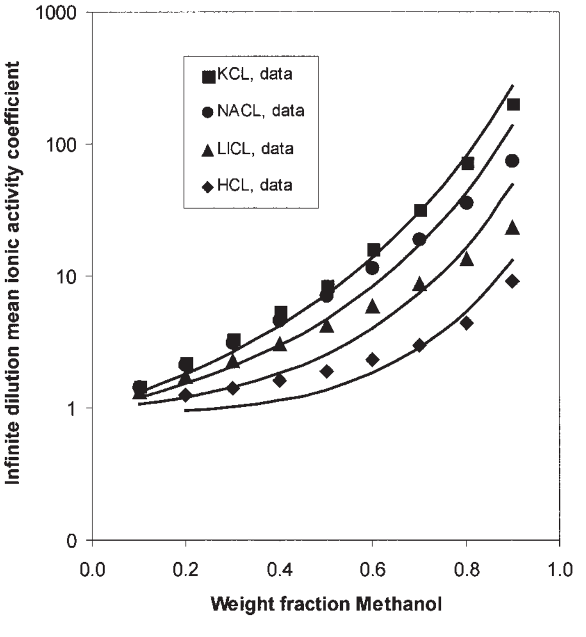

Figure 2. Best fit with the eNRTL model and the experimental data of Akerlof (1930) for the infinite-dilution mean ionic activity coefficients of sodium, potassium, and lithium chlorides, and hydrochloric acid in water–methanol mixtures.

Methanol is treated as a monomeric solvent in the correlation. Experimental data are taken from Akerlof (1930). (■) KCl, (●) NaCl, (▲) LiCl, (◆) HCl. (—) Calculated curves.

Table 2. Interaction Energy Parameters and Nonrandomness Factors for Aqueous Electrolyte Systems

Interaction Pair	τ*	α**
H_2O–K^+Cl^-	8.067	0.2
K^+Cl^-–H_2O	−4.108	0.2
H_2O–Na^+Cl^-	8.886	0.2
Na^+Cl^-–H_2O	−4.549	0.2
H_2O–Li^+Cl^-	10.031	0.2
Li^+Cl^-–H_2O	−5.154	0.2
H_2O–H^+Cl^-	10.090	0.2
H^+Cl^-–H_2O	−5.212	0.2

*The values of τ are determined by fitting the experimental data of Robinson and Stokes (1970).

**All values of α are fixed at 0.2.

Table 3. Interaction Energy Parameters and Nonrandomness Factors for Methanol–Ion Pairs when Methanol is Treated as a Monomeric Solvent in Water–Methanol–Electrolyte System

Interaction Pair	τ*	α**
$CH_3(OH)$–$K_\bullet^+Cl^-$	7.675	0.2
$K_\bullet^+Cl^-$–$CH_3(OH)$	−2.531	0.2
$CH_3(OH)$–$Na_\bullet^+Cl^-$	8.500	0.2
$Na_\bullet^+Cl^-$–$CH_3(OH)$	−3.546	0.2
$CH_3(OH)$–$Li_\bullet^+Cl^-$	9.659	0.2
$Li_\bullet^+Cl^-$–$CH_3(OH)$	−4.661	0.2
$CH_3(OH)$–$H_\bullet^+Cl^-$	9.713	0.2
$H_\bullet^+Cl^-$–$CH_3(OH)$	−5.019	0.2

Note: The *unsymmetric* reference state is the infinite-dilution solution in water.

*The values of τ are determined by fitting the experimental data of Akerlof (1930).

**All values of α are fixed at 0.2.

Table 4. Interaction Energy Parameters and Nonrandomness Factors for Hydrophobic Segment and Hydrophilic Segment Binary, and Hydrophobicity:Hydrophilicity Scale Factors for Alcohol Molecules

Interaction Pair	τ	α
C_2H_4–OH	6.562	0.3
OH–C_2H_4	3.364	0.3
Solvent	X	Z
$CH_3(OH)$	0.907	0.609
$C_2H_5(OH)$	1.811	0.609
$C_3H_7(OH)$	2.799	0.609
$C_4H_9(OH)$	3.188	0.609
$C_5H_{11}(OH)$	3.894	0.609
$C_6H_{13}(OH)$	4.452	0.609

nite-dilution mean ionic activity coefficient data, the model fails to quantitatively represent the data. The computed values for the infinite-dilution mean ionic activity coefficient are too low for low methanol content mixtures and too high for high methanol content mixtures. Figure 3 shows the contributions from the NRTL term and the Born term to the infinite-dilution mean activity coefficient of potassium chloride. The Born term has a significant but secondary contribution to the natural logarithm of the mean ionic activity coefficient. Furthermore, there are no adjustable parameters with the Born term given by Eqs. 66 and 67. This suggests that the NRTL term does not adequately account for the complex interactions between ions and various solvent molecules in the mixture.

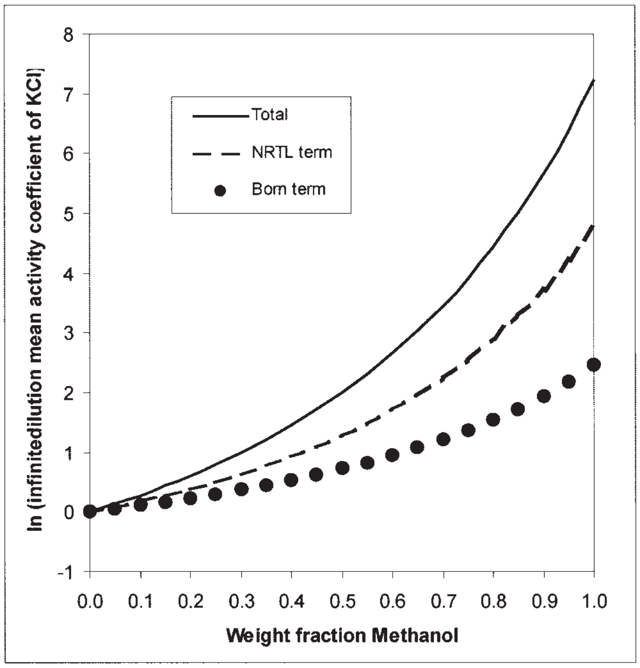

Figure 3. Relative contributions of the NRTL term and Born term in representing the infinite-dilution mean ionic activity coefficient of KCl in water–methanol mixtures.

Treating organic solvents as amphiphilic oligomers

In the previous section, we treated the ion–methanol interaction with the simplistic view that such interaction could be adequately captured with one characteristic set of binary electrolyte–solvent interaction parameters. We now consider methanol as an oligomer made up of hydrophobic segments and hydrophilic segments; this is one of the flexibilities in the current form of the eNRTL model. This treatment reflects the understanding that ions have interaction characteristics with hydrophobic segments that are distinctively different from the interaction characteristics between ions and hydrophilic segments. Figure 1b illustrates the difference in ion–molecule interactions in the two treatments. The interaction between ions and hydrophobic segments are repulsive in nature, whereas the interactions between ions and hydrophilic segments are attractive in nature. Consequently, at the neighborhood of ions, organic solvent molecules (methanol) are oriented in such a way that the hydrophilic segment (OH–) are positioned close to the ions, whereas the hydrophobic segments (CH_3–) are positioned away from the ions.

Specifically, for nonaqueous solvent molecules, we decompose the molecules to two types of conceptual segments: hydrophobic segment and hydrophilic segment. We identify equivalent numbers of hydrophobic segments and hydrophilic segments for each solvent molecule. The equivalent number of hydrophobic segment X represents the solvent hydrophobicity. The equivalent number of hydrophilic segment Z represents the solvent hydrophilicity.

We characterize hydrophobic segments with the –C_2H_4 group and hydrophilic segments with the –OH group. The NRTL binary parameters for the interaction between hydrophobic segment and hydrophilic segment are predetermined from the liquid–liquid equilibrium data of a water–hexane binary mixture. In this system, we fix the X:Z scale to 3:0 for the hexane molecule and 0:1 for the water molecule. Table 4 lists the binary interaction parameters between hydrophobic –C_2H_4 segment and hydrophilic –OH segment.

Treating organic solvents as amphiphilic oligomers is very suitable for polar–organic molecules such as methanol and ethanol. In general, alcohol molecules can be expressed as follows

$$C_nH_{2n+1}OH \rightarrow X(C_2H_4) + Z(OH) \qquad (75)$$

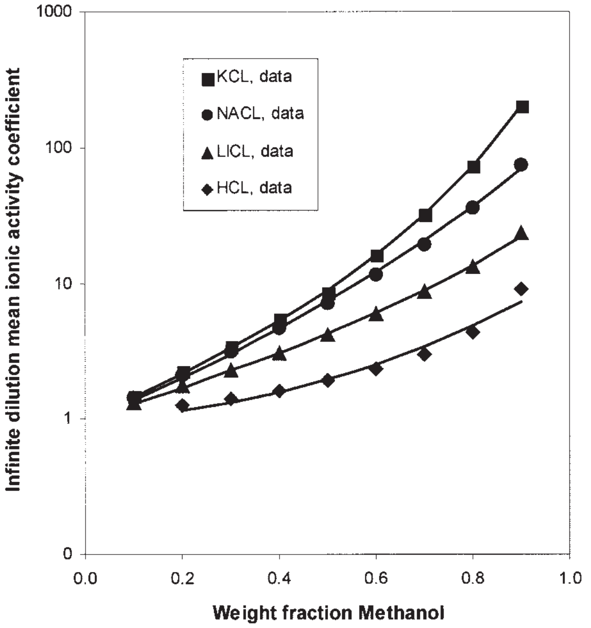

Figure 4. Best fit with the segment eNRTL model and the experimental data of Akerlof (1930) for the infinite-dilution mean ionic activity coefficients of sodium, potassium, and lithium chlorides in water–methanol mixtures.

Methanol is treated as an oligomer in the correlation. Experimental data are taken from Akerlof (1930). (■) KCl, (●) NaCl, (▲) LiCl, (◆) HCl. (—) Calculated curves.

where *n* is the carbon number. To determine the *X*:*Z* scale for alcohol molecules, we apply Eq. 75 to water–alcohol mixtures and treat the solution as a mixture of $–C_2H_4$ and –OH segments. We use the standard NRTL model to generate activity coefficients at 25°C and 1 atm as functions of composition. To obtain optimal fit to the generated activity coefficient "data," we adjust the *X*:*Z* scale for water in these mixtures from 0:1 to 0.2:0.8. We first determine the *X*:*Z* scale for methanol and then regress only *X* for other alcohol molecules by keeping the value of *Z* from methanol as a constant. The results are listed in Table 4.

Figure 4 shows the best fit with the segment-based eNRTL model and the experimental data of Akerlof (1930) for the infinite-dilution mean ionic activity coefficients of sodium, potassium, and lithium chlorides and hydrochloric acid in water–methanol mixtures. The only difference between the correlations shown in Figures 2 and 4 is that methanol is treated as a monomeric solvent in the former and as an oligomer in the latter. Except for potassium chloride, we set values for the interaction parameters between the ion pair and the hydrophilic segment to be same as that for the interaction parameter between the ion pair and water (see Table 2). We then treat the interaction parameters between the ion pair and the hydrophobic segment as the adjustable parameters. The resulting values for the two adjustable electrolyte–hydrophobic segment parameters, as shown in Table 5, are all positive values that are consistent with the repulsive nature of the ion–hydrophobic segment interactions. For potassium chloride in water–methanol mixtures, both the interaction parameters between the ion pair and the hydrophilic segment and between the ion pair and the hydrophobic segment need to be adjusted to achieve reasonable fit to the data. The residual root mean square errors are 0.024, 0.045, 0.030, and 0.107, for potassium chloride, sodium chloride, lithium chloride, and hydrochloric acid, respectively.

The excellent representation of the infinite-dilution mean ionic activity coefficient data with the treatment of methanol as a hydrophobic–hydrophilic oligomer highlights the importance of recognizing the selective interactions between ions and various segments and the resulting specific molecular orientation efforts. On the other hand, the poor representation of the mean ionic activity coefficient data in Figure 2 suggests that, without recognizing these organic solvents as hydrophobic–hydrophilic oligomers, the interactions between ions and organic solvents are not adequately described.

It should be noted that, in modeling mixed-solvent electrolyte systems, it is not necessary to treat all nonaqueous solvents as hydrophilic–hydrophobic amphiphilic oligomers. For example, hydrocarbon solvents such as hexane are totally hydrophobic. These solvents tend to have exceedingly low solubilities in water, and they do not form "mixed solvents" with water at any significant solvent concentration. For example, molecular hydrogen chloride is hydrophilic. We have been able to accurately represent the phase behavior of the water–hydrochloric acid system over the entire concentration range without the need to treat molecular hydrogen chloride as an oligomer (Aspen Technology, 1998).

Mean ionic activity coefficients in mixed-solvent mixtures

We now apply the eNRTL model to correlate the mean ionic activity coefficient data of potassium chloride (Mahalias and Popovych, 1982) and sodium chloride (Esteso et al., 1989) in water–methanol mixtures and water–ethanol mixtures, respectively. These data were reported with infinite dilution in mixed solvents as the reference state and covered the entire range of mixed-solvent compositions. In these applications, we still treat ionic species and water as monomeric components. However, both methanol and ethanol are treated as hydrophobic–hydrophilic oligomers according to Eq. 75. The NRTL parameters

Table 5. Interaction Energy Parameters and Nonrandomness Factors for Hydrophobic Segment–Ion Pairs and Hydrophilic Segment–Ion Pairs when Methanol is Treated as an Oligomer in Water–Methanol–Electrolyte System

Interaction Pair	τ*	α**
$C_2H_4–K^+Cl^-$	18.971	0.2
$K^+Cl^-–C_2H_4$	9.950	0.2
$OH–K^+Cl^-$	9.403	0.2
$K^+Cl^-–OH$	−3.924	0.2
$C_2H_4–Na^+Cl^-$	11.734	0.2
$Na^+Cl^-–C_2H_4$	5.301	0.2
$C_2H_4–Li^+Cl^-$	9.217	0.2
$Li^+Cl^-–C_2H_4$	8.338	0.2
$C_2H_4–H^+Cl^-$	7.600	0.2
$H^+Cl^-–C_2H_4$	4.242	0.2

Note: The *unsymmetric* reference state is the infinite-dilution solution in water.
*The values of τ are determined by fitting the experimental data of Akerlof (1930).
**All values of α are fixed at 0.2.

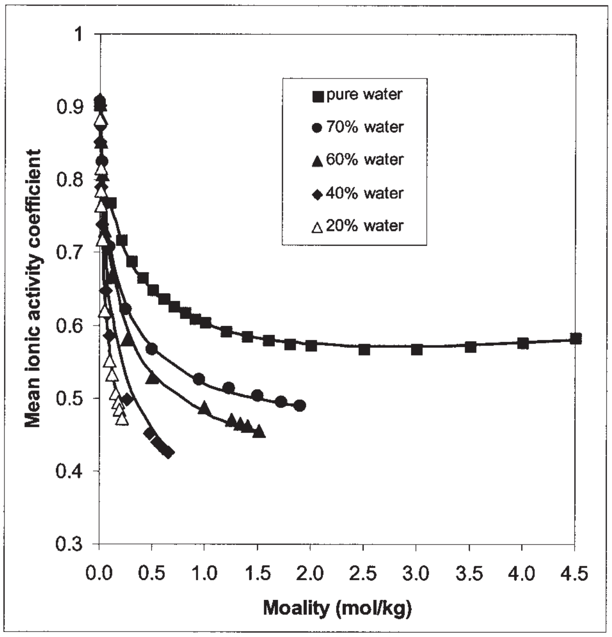

Figure 5. Best fit with the segment eNRTL model and the experimental data of Mahalias and Popovych (1982) for potassium chloride in methanol–water mixtures.

Methanol is treated as an oligomer. The interaction parameters for the ion pair and the hydrophilic segment are set to be the same as that between the ion pair and water. Only the interaction parameters between the ion pair and the hydrophobic segment are determined from a simultaneous fit of selected data. (■) Pure water, (●) 70% water, (▲) 60% water, (◆) 40% water, (△) 20% water. (—) Calculated curves.

for electrolyte–water interactions used are the same as those given in Table 2.

Figure 5 shows the best fit with the eNRTL model and experimental data of Mahalias and Popovych (1982) for potassium chloride in methanol–water mixtures. The mean ionic activity coefficient data are generated using the coefficients of polynomial curve-fitting to the experimental data reported by Mahalias and Popovych (1982). The data cover 0 to 100% of methanol by weight in methanol–water mixtures. The interaction parameters between the electrolyte and the hydrophilic segment are set to be the same as those between the electrolyte and water. Only the two interaction parameters between the electrolyte and the hydrophobic segment are determined from a simultaneous fit of selected data at 30, 40, 50, 60, 70, and 80% of methanol by weight in methanol–water mixtures. The data at 10% and 20% are not used in the regression because they appear to be inconsistent with the data of Robinson and Stokes (1970) for pure aqueous solutions. The data at 90 and 100% are also excluded because the electrolyte molalities for the data are too small to be meaningful for this study. The resulting NRTL parameters between the electrolyte and the hydrophobic segment are summarized in Table 6. With only two adjustable parameters, a satisfactory correlation was obtained with the residual root mean square error, $[\sum_i^k (\ln \gamma_i^{*\exp} - \ln \gamma_i^{*cal})^2/k]^{1/2}$, which is 0.024.

Table 6. Interaction Energy Parameters and Nonrandomness Factors for Hydrophobic Segment-K^+Cl^- and Hydrophilic Segment-K^+Cl^- when Methanol is Treated as an Oligomer in Water–Methanol–Potassium Chloride System

Interaction Pair	τ*	α**
C_2H_4–K^+Cl^-	16.139	0.2
K^+Cl^-–C_2H_4	1.475	0.2
OH–K^+Cl^-	8.067	0.2
K^+Cl^-–OH	−4.108	0.2

Note: The *unsymmetric* reference state is the infinite-dilution solution in water–methanol mixtures.

*The values of τ for OH–K^+Cl^- and K^+Cl^-–OH are set to be the same as that for H_2O–K^+Cl^- and K^+Cl^-–H_2O, respectively. The values of τ for C_2H_4–K^+Cl^- and K^+Cl^-–C_2H_4 are determined by fitting the experimental data of Mahalias and Popovych (1982).

**All values of α are fixed at 0.2.

Figure 6 shows the best fit with the segment eNRTL model and experimental data of Esteso et al. (1989) for sodium chloride in ethanol–water mixtures. The data cover 20, 40, 60, 70, 80, and 90% of ethanol by weight in ethanol–water mixtures. The pure aqueous solution data shown in the figure are taken from Robinson and Stokes (1970). Ethanol is treated as an oligomer. Once again, the interaction parameters between the electrolyte and the hydrophilic segment are set to be the same as those between the electrolyte and water (see Table 2). Only the two interaction parameters between the electrolyte and the hydrophobic segment are determined from a simultaneous fit of selected data at 20, 40, 60, and 70% of ethanol in ethanol–water mixtures. The data at 80 and 90% ethanol by weight were excluded because the electrolyte molalities for the

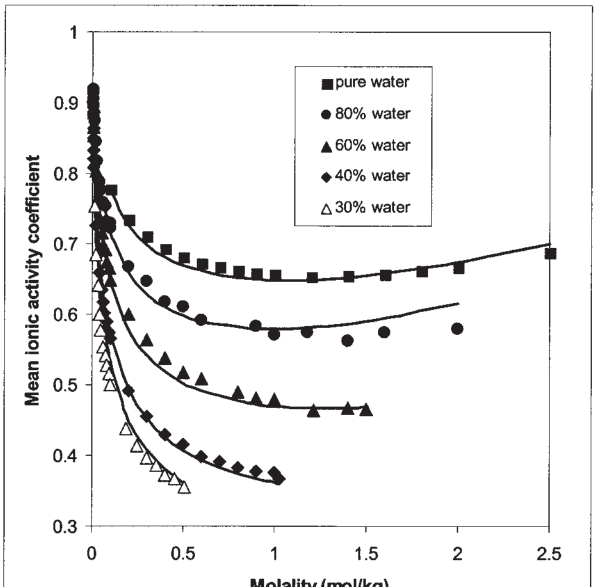

Figure 6. Best fit with the segment eNRTL model and the experimental data of Esteso et al. (1989) for sodium chloride in ethanol–water mixtures.

Ethanol is treated as an oligomer. The interaction parameters for the ion pair and the hydrophilic segment are set to be the same as that between the ion pair and water. Only the interaction parameters between the ion pair and the hydrophobic segment are determined from a simultaneous fit of selected data. (■) Pure water, (●) 80% water, (▲) 60% water, (◆) 40% water, (△) 30% water. (—) Calculated curves.

Table 7. Interaction Energy Parameters and Nonrandomness Factors for Hydrophobic Segment–$\mathrm{Na}^{+}_{\bullet}\mathrm{Cl}^{-}$ and Hydrophilic Segment–$\mathrm{Na}^{+}_{\bullet}\mathrm{Cl}^{-}$ when Ethanol is Treated as an Oligomer in Water–Ethanol–Sodium Chloride System

Interaction Pair	τ*	α**
C_2H_4–$\mathrm{Na}^{+}_{\bullet}\mathrm{Cl}^{-}$	15.526	0.2
$\mathrm{Na}^{+}_{\bullet}\mathrm{Cl}^{-}$–$C_2H_4$	0.759	0.2
OH–$\mathrm{Na}^{+}_{\bullet}\mathrm{Cl}^{-}$	8.886	0.2
$\mathrm{Na}^{+}_{\bullet}\mathrm{Cl}^{-}$–OH	−4.549	0.2

Note: The *unsymmetric* reference state is the infinite-dilution solution in water–ethanol mixtures.

*The values of τ for OH–$\mathrm{Na}^{+}_{\bullet}\mathrm{Cl}^{-}$ and $\mathrm{Na}^{+}_{\bullet}\mathrm{Cl}^{-}$–OH are set to be the same as that for H_2O–$\mathrm{Na}^{+}_{\bullet}\mathrm{Cl}^{-}$ and $\mathrm{Na}^{+}_{\bullet}\mathrm{Cl}^{-}$–$H_2O$, respectively. The values of τ for C_2H_4–$\mathrm{Na}^{+}_{\bullet}\mathrm{Cl}^{-}$ and $\mathrm{Na}^{+}_{\bullet}\mathrm{Cl}^{-}$–$C_2H_4$ are determined by fitting the experimental data of Esteso et al. (1989).

**The values of α are all fixed at 0.2.

data are too small to be meaningful for this correlation. The resulting NRTL parameters are summarized in Table 7. Excellent correlations were obtained for the data. Overall, the residual root mean square error is 0.026.

Conclusions

A generalized form of the electrolyte NRTL model of Chen et al. (1982, 1986, 2001) is successfully applied to correlate mean ionic activity coefficients of mixed-solvent electrolyte systems. The segment interaction concept provides the framework to explicitly account for the attractive interaction of ions with the hydrophilic segments of organic solvents and the repulsive interaction of ions with the hydrophobic segments of organic solvents. The ability to represent such distinctly different ion-segment interactions proves to be a key for quantitative correlation of mean ionic activity coefficients in mixed-solvent electrolyte systems. This eNRTL model provides a comprehensive excess Gibbs energy expression to represent the liquid-phase nonideality for aqueous and mixed-solvent electrolyte systems over the entire concentration range from pure solvents to saturated solutions or fused salts.

Notation

A_φ = Debye–Hückel parameter
C_i = z_i, for ionic species, and =1, for molecular species
d_s = density of solvent, g/cm^3
G_m^{ex} = excess Gibbs energy of electrolyte systems
$G_m^{ex,lc}$ = excess Gibbs energy from NRTL local interactions
$G^{*\mathrm{ex},PDH}$ = unsymmetric Pitzer–Debye–Hückel (PDH) formula
G_m^{id} = excess Gibbs energy of ideal solutions at the system temperature, pressure, and concentrations
G_m^{FH} = Flory–Huggins term attributed to nonideal entropy of mixing
I_x = ionic strength (segment mole fraction scale)
k = Boltzmann constant, 1.38054×10^{-16} erg/K
m = molality of salt, mol/kg solvent
m_I = number of segments in component I
M_s = molecular weight of solvent, g/mol
N_A = Avogadro's number, 6.02251×10^{23}/mol
n_i = segment number of segment species i
n_I = mole number of component I
Q_e = absolute electronic charge, 4.80298 e.s.u. (electro-static unit)
R = gas constant
r_i = Born radius of segment species i
$r_{i,I}$ = number of segment species i in component I
T = temperature
X = scale factor for hydrophobic segment, –C_2H_4 group
x_i = segment-based mole fraction of segment species i
x_I = mole fraction of component I
Y_a = anionic charge composition fraction in local interactions
Y_c = cationic charge composition fraction in local interactions
Z = scale factor for hydrophilic segment, –OH group
z_i = charge number for ionic species

Greek letters

γ_i = segment activity coefficient of segment species i
γ_i^{lc} = segment activity coefficient of segment species i
$\gamma_i^{lc,I}$ = segment activity coefficient of segment species i contained in component I
$\gamma_i^{\infty lc}$ = segment infinite-dilution activity coefficient of segment species i contained in ionic component I
γ_I = activity coefficient of component I
γ_I^{FH} = activity coefficient of component I attributed to Flory–Huggins term
γ_I^{lc} = local interaction activity coefficient of component I
$\gamma_I^{\infty FH}$ = infinite-dilution activity coefficient of component I attributed to Flory–Huggins term
$\gamma_I^{\infty lc}$ = infinite-dilution activity coefficient of ionic component I
$\gamma_\pm^*$ = mean ionic activity coefficient on mole fraction scale
$\gamma_{\pm m}^*$ = mean ionic activity coefficient on molality scale
α = symmetric nonrandom factor in NRTL model
τ = asymmetric binary interaction parameter in NRTL model
ϵ_s = dielectric constant of solvent
ϵ_w = dielectric constant of water
ρ = closest approach parameter, 14.9
ΔG^{Born} = Born term correction to the unsymmetric Pitzer–Debye–Hückel (PDH) formula
$\Delta \ln \gamma_I^{Born}$ = Born term correction to logarithm of activity coefficient of ionic component I
$\Delta \ln \gamma_i^{Born}$ = Born term correction to logarithm of segment activity coefficient of segment species i
ϕ_I = volume fraction of component I

Subscripts and superscripts

a = anionic segment species index
c = cationic segment species index
i, j, k = segment-based species index, m, c, a
I, J = component-based species index
m = molecular segment species index
P = pressure
w = water
lc = local composition
$*$ = unsymmetric convention for electrolyte systems

Acknowledgments

We thank Prof. John Prausnitz for comments and warm encouragement on this project.

Literature Cited

Akerlof, G., "Activity Coefficients of Sodium, Potassium and Lithium Chlorides and Hydrochloric Acid at Infinite Dilution in Water–Methyl Alcohol Mixtures," *J. Am. Chem. Soc.*, **52**, 2353 (1930).

Aspen Technology, Inc., *Aspen Plus Electrolyte Manual*, Cambridge, MA (1998).

Chen, C.-C., "Some Recent Developments in Process Simulation for Reactive Chemical Systems," *Pure Appl. Chem.*, **59**, 1177 (1987).

Chen, C.-C., "A Segment-Based Local Composition Model for the Gibbs Energy of Polymer Solutions," *Fluid Phase Equilib.*, **83**, 301 (1993).

Chen, C.-C., C. P. Bokis, and P. M. Mathias, "A Segment-Based Excess Gibbs Energy Model for Aqueous Organic Electrolyte Systems," *AIChE J.*, **47**, 2593 (2001).

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

Chen, C.-C., and L. B. Evans, "A Local Composition Model for the Excess

Gibbs Energy of Aqueous Electrolyte Systems," *AIChE J.*, **32**, 444 (1986).

Chen, C.-C., and P. M. Mathias, "Applied Thermodynamics for Process Modeling," *AIChE J.*, **48**, 194 (2002).

Chen, C.-C., P. M. Mathias, and H. Orbey, "Use of Hydration and Dissociation Chemistries with the Electrolyte-NRTL Model," *AIChE J.*, **45**, 1576 (1999).

Chen, C.-C., Y. Zhu, and L. B. Evans, "Phase Partitioning of Biomolecules: Solubilities of Amino Acids," *Biotechnol. Prog.*, **5**, 111 (1989).

Esteso, M. A., O. M. Gonzalez-Diaz, F. F. Hernandez-Luis, and L. Fernandez-Merida, "Activity Coefficients for NaCl in Ethanol–Water Mixtures at 25°C," *J. Solution Chem.*, **18**, 277 (1989).

Iliuta, M. C., K. Thomsen, and P. Rasmussen, "Modeling of Heavy Metal Salt Solubility Using the Extended UNIQUAC Model," *AIChE J.*, **48**, 2664 (2002).

Malahias, L., and O. Popovych, "Activity Coefficients and Transfer Free Energies of Potassium Chloride in Methanol–Water Solvents at 25°C," *J. Chem. Eng. Data*, **27**, 105 (1982).

Mock, B., L. B. Evans, and C.-C. Chen, "Thermodynamic Representation of Phase Equilibria in Multiple Solvent Electrolyte Systems," *AIChE J.*, **32**, 1655 (1986).

Papaiconomou, N., J.-P. Simonin, O. Bernard, and W. Kunz, "MSA-NRTL Model for the Description of the Thermodynamic Properties of Electrolyte Solutions," *Phys. Chem. Chem. Phys.*, **4**, 4435 (2002).

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

Pitzer, K. S., "Electrolytes: From Dilute Solutions to Fused Salts," *J. Am. Chem. Soc.*, **102**, 2902 (1980).

Prausnitz, J. M., R. N. Lichtenthaler, and E. Gomes de Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria*, 2nd Edition, Prentice-Hall, Englewood Cliffs, NJ (1986).

Rashin, A. A., and B. Honig, "Reevaluation of the Born Model of Ion Hydration," *J. Phys. Chem.*, **89**, 5588 (1985).

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

Robinson, R. A., and R. H. Stokes, *Electrolyte Solutions*, 2nd ed., Butterworth, Oxford, U.K. (1970).

Appendix

A. Segment activity coefficients from eNRTL model for local interactions

The segment contributions from local interactions to the activity coefficients for molecular segments, cationic segments, and anionic segments can be calculated from Eqs. 11 and 15. The derivation is straightforward and the results are given as follows

$$\begin{aligned}\ln \gamma_m^{lc} = {} & \frac{\sum_j X_j G_{jm}\tau_{jm}}{\sum_k X_k G_{km}} + \sum_{m'} \frac{X_{m'} G_{mm'}}{\sum_k X_k G_{km'}}\left(\tau_{mm'} - \frac{\sum_k X_k G_{km'}\tau_{km'}}{\sum_k X_k G_{km'}}\right) \\ & + \sum_c \sum_a \frac{Y_a X_c G_{mc,ac}}{\sum_k X_k G_{ka,ac}}\left(\tau_{mc,ac} - \frac{\sum_k X_k G_{kc,ac}\tau_{kc,ac}}{\sum_k X_k G_{kc,ac}}\right) \\ & + \sum_a \sum_c \frac{Y_c X_a G_{ma,ca}}{\sum_k X_k G_{ka,ca}}\left(\tau_{mc,ca} - \frac{\sum_k X_k G_{ka,ca}\tau_{ka,ca}}{\sum_k X_k G_{ka,ca}}\right)\end{aligned} \tag{A1}$$

$$\begin{aligned}\frac{1}{z_c}\ln \gamma_c^{lc} = {} & \sum_a Y_a \frac{\sum_k X_k G_{kc,ac}\tau_{kc,ac}}{\sum_k X_k G_{kc,ac}} \\ & + \sum_m \frac{X_m G_{cm}}{\sum_k X_k G_{km}}\left(\tau_{cm} - \frac{\sum_k X_k G_{km}\tau_{km}}{\sum_k X_k G_{km}}\right) \\ & + \sum_a \sum_{c'} \frac{Y_{c'} X_a G_{ca,c'a}}{\sum_k X_k G_{ka,c'a}}\left(\tau_{ca,c'a} - \frac{\sum_k X_k G_{ka,c'a}\tau_{ka,c'a}}{\sum_k X_k G_{ka,c'a}}\right)\end{aligned} \tag{A2}$$

$$\begin{aligned}\frac{1}{z_a}\ln \gamma_a^{lc} = {} & \sum_c Y_c \frac{\sum_k X_k G_{ka,ca}\tau_{ka,ca}}{\sum_k X_k G_{ka,ca}} \\ & + \sum_m \frac{X_m G_{am}}{\sum_k X_k G_{km}}\left(\tau_{am} - \frac{\sum_k X_k G_{km}\tau_{km}}{\sum_k X_k G_{km}}\right) \\ & + \sum_c \sum_{a'} \frac{Y_{a'} X_c G_{ac,a'c}}{\sum_k X_k G_{kc,a'c}}\left(\tau_{ac,a'c} - \frac{\sum_k X_k G_{ka,a'c}\tau_{kc,a'c}}{\sum_k X_k G_{kc,a'c}}\right)\end{aligned} \tag{A3}$$

with

$$j,\ k = m,\ c,\ a \tag{A4}$$

Accordingly, the *symmetric* reference state activity coefficient for each segment can be derived from Eqs. A1–A3 for molecular segments, cationic segments, and anionic segments, respectively

$$\begin{aligned}\ln \gamma_m^{lc,I} = {} & \frac{\sum_j X_{j,I} G_{jm}\tau_{jm}}{\sum_k X_{k,I} G_{km}} + \sum_{m'} \frac{X_{m',I} G_{mm'}}{X_{k,I} G_{km'}}\left(\tau_{mm'} - \frac{\sum_k X_{k,I} G_{km'}\tau_{km'}}{\sum_k X_{k,I} G_{km'}}\right) \\ & + \sum_c \sum_a \frac{Y_a X_{c,I} G_{mc,ac}}{\sum_k X_{k,I} G_{kc,ac}}\left(\tau_{mc,ac} - \frac{\sum_k X_{k,I} G_{kc,ac}\tau_{kc,ac}}{\sum_k X_{k,I} G_{kc,ac}}\right) \\ & + \sum_a \sum_c \frac{Y_c X_{a,I} G_{ma,ca}}{\sum_k X_{k,I} G_{ka,ca}}\left(\tau_{mc,ca} - \frac{\sum_k X_{k,I} G_{ka,ca}\tau_{ka,ca}}{\sum_k X_{k,I} G_{ka,ca}}\right)\end{aligned} \tag{A5}$$

$$\begin{aligned}\frac{1}{z_c}\ln \gamma_c^{lc,I} = {} & \sum_a Y_a \frac{\sum_k X_{k,I} G_{kc,ac}\tau_{kc,ac}}{\sum_k X_{k,I} G_{kc,ac}} \\ & + \sum_m \frac{X_{m,I} G_{cm}}{\sum_k X_{k,I} G_{km}}\left(\tau_{cm} - \frac{\sum_k X_{k,I} G_{km}\tau_{km}}{\sum_k X_{k,I} G_{km}}\right) \\ & + \sum_a \sum_{c'} \frac{Y_{c'} X_{a,I} G_{ca,c'a}}{\sum_k X_{k,I} G_{ka,c'a}}\left(\tau_{ca,c'a} - \frac{\sum_k X_{k,I} G_{ka,c'a}\tau_{ka,c'a}}{\sum_k X_{k,I} G_{ka,c'a}}\right)\end{aligned} \tag{A6}$$

$$\begin{aligned}\frac{1}{z_a}\ln \gamma_a^{lc,I} = {} & \sum_c Y_c \frac{\sum_k X_{k,I} G_{ka,ca}\tau_{ka,ca}}{\sum_k X_{k,I} G_{ka,ca}} \\ & + \sum_m \frac{X_{m,I} G_{am}}{\sum_k X_{k,I} G_{km}}\left(\tau_{am} - \frac{\sum_k X_{k,I} G_{km}\tau_{km}}{\sum_k X_{k,I} G_{km}}\right) \\ & + \sum_c \sum_{a'} \frac{Y_{a'} X_{c,I} G_{ac,a'c}}{\sum_k X_{k,I} G_{kc,a'c}}\left(\tau_{ac,a'c} - \frac{\sum_k X_{k,I} G_{ka,a'c}\tau_{kc,a'c}}{\sum_k X_{k,I} G_{kc,a'c}}\right)\end{aligned} \tag{A7}$$

with

$$X_{j,I} = C_j x_{j,I} \tag{A8}$$

$$x_{j,I} = \frac{r_{j,I}}{\sum_i r_{i,I}} \qquad i = m,\ c,\ a \tag{A9}$$

B. Flory–Huggins term for nonideal entropy of mixing

Although, in most common electrolyte systems, the nonideal entropy of mixing is much smaller than the heat of mixing, we may still want to include it in a general model. We follow the polymer NRTL model (Chen, 1993) and use the Flory–Huggins term to describe the nonideal entropy of mixing

$$\frac{G_m^{ex,FH}}{RT} = \sum_I n_I \ln\left(\frac{\phi_I}{x_I}\right) \tag{B1}$$

with

$$\phi_I = \frac{n_I m_I}{\sum_J n_J m_J} \tag{B2}$$

where $G_m^{ex,FH}$ is the Flory–Huggins term to the excess Gibbs energy G_m^{ex}, attributed to the nonideal entropy of mixing; ϕ_I is the volume fraction of component I; and m_I is the number of segments in component I

$$m_I = \sum_m r_{m,I} + \sum_c r_{c,I} + \sum_a r_{a,I} \tag{B3}$$

The activity coefficient of component I from the entropy of mixing can be derived from Eq. B1, as follows

$$\ln \gamma_I^{FH} = \ln\left(\frac{\phi_I}{x_I}\right) + 1 - m_I \sum_J \frac{\phi_J}{m_J} \tag{B4}$$

Using the condition given by Eq. 45, the infinite-dilution activity coefficient in water is

$$\ln \gamma_I^{\infty FH} = \ln m_I + 1 - m_I \tag{B5}$$

Similarly, using the condition given by Eq. 49, the infinite-dilution activity coefficient in mixed solvents is

$$\ln \gamma_I^{\infty FH} = \ln\left(\frac{m_I}{\sum_S x_S m_S}\right) + 1 - m_I\left(\frac{\sum_S x_S}{\sum_S x_S m_S}\right) \tag{B6}$$

We can then compute the unsymmetric activity coefficient from the Flory–Huggins term as follows

$$\ln \gamma_I^{*FH} = \ln \gamma_I^{FH} - \ln \gamma_I^{\infty FH} \tag{B7}$$

Manuscript received May 6, 2003, and revision received Oct. 24, 2003.