Asymmetric Framework for Predicting Liquid-Liquid Equilibrium of Ionic Liquid-Mixed Solvent Systems:

I. Theory, Phase Stability Analysis, and Parameter Estimation

Luke D. Simoni, Joan F. Brennecke and Mark A. Stadtherr*

Department of Chemical and Biomolecular Engineering
University of Notre Dame, Notre Dame, IN 46556, USA

March, 2009
(revised, May 2009)

*Author to whom all correspondence should be addressed. Phone (574) 631-9318; Fax (574) 631-8366; Email: markst@nd.edu

Abstract

A new approach for modeling liquid-liquid equilibrium in electrolyte/mixed-solvent systems is presented, with particular focus on systems involving a dilute aqueous solution of an ionic liquid (IL). This new approach involves an asymmetric framework in which different phases have different degrees of electrolyte dissociation, and are thus represented by different Gibbs free energy models. As a first case, we consider the situation in which the electrolyte is either completely dissociated or completely paired (molecular), with its state depending on the dielectric constant of the mixed solvent and on the concentration of the salt in the phase in question. The theory underlying this asymmetric framework is developed, and a rigorous approach for phase stability analysis is presented. It is explained how to formulate and solve the parameter estimation problem for determining model parameters from binary data, and this process is demonstrated using examples. An immediate goal is to use this approach to predict liquid-liquid equilibrium for ternary IL/solvent/water systems, using parameters obtained from binary and pure component data only.

Keywords: Liquid-liquid equilibrium; Ionic liquids; Electrolyte models; Phase stability; Parameter estimation

1. Introduction

Ionic liquids (ILs) are essentially nonvolatile at normal operating conditions. Thus, ILs have been widely discussed in the literature as possible "green" replacements for volatile organic compounds (VOCs) used as solvents and in other applications, with a number of research groups focusing on the replacement of volatile extraction and separation solvents with ILs. For example, ILs have been shown in some cases to be apt solvents for the selective extraction of alcohols from fermentation broths and for the recovery of amino acids from aqueous media.[1-4] The preliminary analysis and design of such separation processes require experimental multicomponent liquid-liquid equilibrium (LLE) data, or models capable of predicting the multicomponent LLE behavior. Since experimental LLE observations of all multicomponent IL systems of interest are infeasible, due in part to the sheer number of ILs one can potentially tailor and synthesize,[5] it is important that progress be made on predictive models for LLE in such systems.

The macroscopic modeling of LLE in multicomponent mixtures involving ILs has, to date, been done mostly through the correlation of multicomponent (ternary) LLE data with conventional excess Gibbs free energy models such as NRTL.[6-14] Previously, we have studied[15] the capability of such models, specifically NRTL, UNIQUAC and electrolyte-NRTL (eNRTL),[16] to predict ternary LLE from parameters fit only to *binary* LLE data. This showed that, when used in a symmetric framework (same model used to represent all phases), these models could predict some Type 1 and Type 2 ternary LLE systems reasonably well from parameters fit to binary data, but that there remained much potential for improvement. Other more purely predictive approaches have also been investigated for systems containing ILs. For example, COSMO-RS has been applied to predictions of binary LLE upper critical solution temperature (UCST) behavior and of a ternary LLE system, though not with satisfactory results.[17-19] More recently, COSMO-RS has been modified for LLE (COSMO_LL), yielding better ternary predictions involving ILs, but still with much room for improvement.[20] Another more purely predictive approach is the NRTL-SAC (NRTL Segment Activity Coefficient) model.[21] While this also shows promise for ternary LLE systems involving ILs, there are still cases in which its predictions are not qualitatively correct.[22] A very different approach is to not use thermodynamic models at all, but to use input/output models such as neural networks. Such an approach has been used[23] to correlate data for ternary LLE with ILs, and to predict (interpolate) tie lines not used in the training set.

ILs, like all electrolytes, ionize (dissociate) to varying degrees depending on the solution or phase in which they are dissolved. The degree of dissociation depends on the ability of the phase's components (mixed solvent) to screen the electrostatic forces of the ions.[24] This implies that the molecular state of the electrolyte depends on its concentration and on the dielectric constant of the mixed solvent. Thus, we introduce here a new framework for modeling LLE in which different phases are treated differently with regard to degree of dissociation. Since this may result in different models being used for different phases, this is an asymmetric framework. Although there is evidence that ILs in solution at high concentration may aggregate into clusters[25,26] and most likely only ionize partially,[27-29] as a first approximation we assume here that the IL is either completely dissociated or completely paired (molecular), with the state of the IL depending on the dielectric constant of the mixed solvent and on the concentration of IL in the phase in question. The assumption of complete dissociation is appropriate primarily in the case of an aqueous phase that is dilute in IL, as has been suggested in other studies.[30,31] Systems containing dilute aqueous phases arise in several applications of interest.[1-4]

In this first part of a two-part contribution, the asymmetric modeling framework is introduced, with different Gibbs free energy models used to represent different phases in modeling LLE in electrolyte (IL)/mixed-solvent systems. Since a particular phase is assumed to be either completely dissociated or not dissociated at all, there are two types of phases, each represented by a different model. While such an asymmetric approach has not been widely used, if at all, in modeling LLE, it is a common approach in modeling vapor-liquid equilibrium (VLE), when, for example, the liquid phase is modeled using an excess Gibbs free energy model and the vapor phase is modeled by the ideal gas law or other equation of state. The approach described here appears to be the first instance of an asymmetric framework for modeling LLE in mixed-salt/mixed-solvent systems. In Part I of this work, we concentrate first on the development of the underlying theory, including the form of the equal activity conditions for phase equilibrium and an approach for rigorous phase stability analysis in this context. We then show how to formulate and solve the parameter estimation problem for determining model parameters from binary data, and demonstrate this process using examples. In Part II, we then proceed to study the extent to which this approach is able to *predict* ternary LLE, using parameters obtained from binary and pure component data only. This will be done by making comparisons to experimental data representing various types of ternary LLE behavior.

2. Model Formulation

Consider the general case of a mixture of multiple salts (ILs) and multiple solvents, all of which are liquids as pure components at the system temperature *T* and pressure *P*. We formulate here a new asymmetric framework for modeling LLE in such systems. The basic idea in this framework is that there are different degrees of ionic dissociation in each phase, and that this can be accounted for by using different Gibbs free energy models in different phases. As discussed above, we will assume here, as a first approximation, that there are two types of phases: 1. A type in which the electrolytes are completely dissociated, generally a dilute aqueous phase or one in which the mixed solvent has a high average dielectric constant; 2. A type in which the electrolytes are completely associated as ion pairs (molecular), generally a liquid salt-rich phase or one in which the mixed solvent has a low average dielectric constant. In this section, we develop Gibbs free energy expressions for each of these two types of phases. For this purpose, the references states chosen are: 1. For solvent species, pure liquid at the system *T* and *P*; 2. For the electrolyte species, pure *dissociated* liquid at the system *T* and *P*. To distinguish Gibbs free energy expressions (and the corresponding chemical potentials and activity coefficients) of a phase in which electrolytes are completely dissociated (a "dissociated phase"), we will use a tilde; thus $\tilde{g}$ will indicate the molar Gibbs free energy of a dissociated phase and *g* the molar Gibbs free energy of a phase in which all components are molecular species (a "molecular phase").

2.1 Dissociated Phase

In a dissociated phase, the salt species are completely dissociated. Assume a mixture of n_i, $i \in \mathcal{S}$, moles of solvent species and n_i, $i \in \mathcal{E}$, moles of electrolyte species, where $\mathcal{S}$ indicates the set of all solvent component indices and $\mathcal{E}$ represents the set of all electrolyte (salt) component indices. Since there is complete dissociation of electrolytes, we have $n_{+,i} = \nu_{+,i} n_i$ moles of cations and $n_{-,i} = \nu_{-,i} n_i$ moles of anions for each salt $i \in \mathcal{E}$, where $\nu_{+,\mathrm{i}}$ and $\nu_{-,\mathrm{i}}$ are the stoichiometric coefficients on the ions of salt *i* in the dissociation reaction

$$\text{Salt}_i \rightarrow \nu_{+,i}(\text{Cation}_i)^{z_{+,i}} + \nu_{-,i}(\text{Anion}_i)^{z_{-,i}}, \quad i \in \mathcal{I}. \tag{1}$$

Here $z_{+,i}$ and $z_{-,i}$ are the ionic valencies. The total number of moles is then $N = \sum_{i\in\mathcal{I}}(n_{+,i} + n_{-,i}) + \sum_{i\in S} n_i$. The *actual* mole fractions of the species are indicated by $y_i = n_i / N$, $i \in S$, $y_{+,i} = n_{+,i}/N$, $i \in \mathcal{I}$, and $y_{-,i} = n_{-,i}/N$, $i \in \mathcal{I}$. Thus, $\sum_{i\in\mathcal{I}}(y_{+,i} + y_{-,i}) + \sum_{i\in S} y_i = 1$. Note that, for a ternary system containing a single IL, this means it is treated as involving four components, solvent, cosolvent, cation and anion. The *observable* mole fractions are indicated by $x_i = n_i / N_{\text{obs}}$, $i \in \{\mathcal{I}, S\}$, where $N_{\text{obs}} = \sum_{i\in\{\mathcal{I},S\}} n_i$.

Conventionally, excess Gibbs free energy models for electrolytes have used an unsymmetric reference state consisting of pure liquid solvent components and infinitely-dilute salt components. However, if a salt is an IL, it is liquid in its pure state, making it more appropriate to use a symmetric reference state in which all components are pure liquids. This explains the choice of reference states given above. For this case, and for any ionic valencies, the total molar Gibbs free energy $\tilde{g}$ (relative to the actual number of moles *N*) is given[15] by the Gibbs free energy of mixing function

$$\tilde{g} = \tilde{g}^{\text{M}} = \tilde{g}^{\text{id}} + \tilde{g}^{\text{E}} = RT \sum_{i\in\mathcal{I}} \frac{\nu_i y_{\pm,i}}{\nu_{\pm,i}} \ln \frac{\nu_i y_{\pm,i}}{\nu_{\pm,i}} + RT \sum_{i\in S} y_i \ln y_i + \tilde{g}^{\text{E}}. \tag{2}$$

Here, $\tilde{g}^{\text{id}}$ is the ideal molar Gibbs free energy of mixing, $\tilde{g}^{\text{E}}$ is the excess molar Gibbs free energy relative to the symmetric reference state used, *R* is the gas constant, and ± indicates a *mean-ionic* quantity. For salt *i*, and any generic quantity ζ_i associated with the salt, the corresponding mean-ionic quantity[24] is given by $\zeta_{\pm,i} = (\zeta_{+,i}^{\nu_{+,i}} \zeta_{-,i}^{\nu_{-,i}})^{1/\nu_i}$, with $\nu_i = \nu_{+,i} + \nu_{-,i}$. The actual mole fractions are related to the mean-ionic and observable mole fractions by

$$y_{+,i} = \frac{\nu_{+,i} y_{\pm,i}}{\nu_{\pm,i}}, \quad i \in \mathcal{I}, \tag{3}$$

$$y_{-,i} = \frac{\nu_{-,i} y_{\pm,i}}{\nu_{\pm,i}}, \quad i \in \mathcal{I}, \tag{4}$$

$$y_{\pm,i} = \frac{\nu_{\pm,i} x_i}{\sum_{i\in\mathcal{I}} \nu_i x_i + \sum_{i\in S} x_i}, \quad i \in \mathcal{I} \tag{5}$$

and

$$y_i = \frac{x_i}{\sum\limits_{i\in \mathcal{E}} \nu_i x_i + \sum\limits_{i\in S} x_i}, \quad i \in S\,. \tag{6}$$

Note that in the case of an IL(1)/solvent(2)/co-solvent(3) system, with the IL a 1:1 electrolyte ($\nu_1 = 2$ and $\nu_{\pm,1} = 1$), eq 2 reduces to

$$\frac{\tilde{g}}{RT} = 2y_{\pm,1}\ln\left(2y_{\pm,1}\right) + y_2 \ln y_2 + y_3 \ln y_3 + \frac{\tilde{g}^{\mathrm{E}}}{RT}\,. \tag{7}$$

For the excess molar Gibbs free energy $\tilde{g}^{\mathrm{E}}$ in eqs 2 and 7, any suitable electrolyte model based on complete dissociation may be considered. We will use the electrolyte-NRTL (eNRTL) model of Chen and Song,[32] as recently renormalized for the symmetric reference state by Simoni et al.[15,33] The renormalized model is given in Appendix A.

From electrical conductivity data of inorganic electrolytes in alcohols, it has been suggested that significant ionic dissociation exists only in solvents with large dielectric constants.[34] Furthermore, we would expect significant dissociation only in relatively dilute salt solutions.[31] Thus, a phase is considered dissociated if the total observable salt mole fraction $\sum_{i\in\mathcal{E}} x_i$ is less than some specified cut-off value x_{c}, and if the average mixed-solvent dielectric constant ε is greater than some specified cut-off value ε_{c}. For this purpose, we approximate the average mixed-solvent dielectric constant by[32]

$$\varepsilon = \sum_{i\in S}\left[\left(\frac{M_i y_i}{\sum\limits_{i'\in S} M_{i'} y_{i'}}\right)\varepsilon_i\right], \tag{8}$$

where M_i is the molecular weight of solvent component i. If either of these two criteria are not met, then the phase is treated as molecular. For the dielectric constant cut-off, we have arbitrarily chosen a value of roughly one-half the dielectric constant of water at room temperature, i.e., $\varepsilon_{\mathrm{c}} = 40$, and, for the salt mole fraction cut-off, we have arbitrarily chosen $x_{\mathrm{c}} = 0.10$.

2.2 Molecular Phase

In a molecular phase, the salt species are completely associated as ion pairs, and so can be treated as molecular species. Now the actual and observed mole fractions are the same for all species, and will be denoted by x_i, $i \in \{\mathcal{E}, \mathcal{S}\}$. For this case, the total molar Gibbs free energy g is given by the usual Gibbs free energy of mixing function

$$g = g^{\mathrm{M}} = g^{\mathrm{id}} + g^{\mathrm{E}} + \sum_{i \in \mathcal{E}} x_i \, g_i^{\circ} = RT \sum_{i \in \{\mathcal{E}, \mathcal{S}\}} x_i \, \ln x_i + g^{\mathrm{E}} + \sum_{i \in \mathcal{E}} x_i \, g_i^{\circ} \,, \tag{9}$$

where g_i° is the molar Gibbs free energy of pure liquid *associated* salt i relative to its standard (*dissociated*) state. To determine g_i°, we use the Coulombic potential energy between a mole of ion pairs of generic valence. Then we assume that the pairs of ions are brought from infinite separation (dissociation) to contact with a center-to-center distance of σ_i for a salt *i*. This obviously requires the coarse assumption that the cations and anions are spheres of equal size. With these assumptions, g_i° is given by[35]

$$\frac{g_i^{\circ}}{RT} \equiv -\frac{\left| z_{+,i} z_{-,i} \right| e^2}{8\pi\varepsilon_0 \varepsilon_i k_{\mathrm{B}} T \sigma_i}, \quad i \in \mathcal{E} \,, \tag{10}$$

where k_{B} is the Boltzmann constant, e is the elementary charge, ε_i is the dielectric constant of pure liquid salt *i*, and ε_0 is the permittivity of free space. For the excess molar Gibbs free energy g^{E} in eq 9, any appropriate molecular model may be considered. We will use the NRTL model,[36] details of which are stated in Appendix A.

3. Phase Equilibrium Conditions

In this section, we discuss the equipotential relationships for the asymmetric framework. These are necessary (but not sufficient) conditions for phase equilibrium at constant T and P, and are also used in the parameter estimation procedure described below.

In a molecular phase, the chemical potential (partial molar Gibbs free energy) is given by $\mu_i = \mu_i^{\circ} + RT \ln(\gamma_i \, x_i)$, where $\mu_i^{\circ} = 0$ for solvent species $i \in \mathcal{S}$ and $\mu_i^{\circ} = g_i^{\circ}$ for electrolyte species $i \in \mathcal{E}$. In both cases, the activity coefficient γ_i is obtained from the molecular g^{E}

model used (NRTL). In a dissociated phase, $\mu_i^\circ = 0$ for all species. Thus, for solvent species $i \in \mathcal{S}$, the chemical potential is given by $\tilde{\mu}_i = RT\ln(\tilde{\gamma}_i\, y_i)$, and, for electrolyte species $i \in \mathcal{E}$, the definition of chemical potential, with $\tilde{g}$ from eq 2, gives

$$\tilde{\mu}_i = \left(\frac{\partial\left(N\tilde{g}\right)}{\partial n_i} \right)_{n_{j\neq i},T,P} = RT\nu_i \ln(\nu_i \tilde{\gamma}_{\pm,i} y_{\pm,i}) , \tag{11}$$

where $\tilde{\gamma}_i$, $i \in \mathcal{S}$, and the mean ionic activity coefficient $\tilde{\gamma}_{\pm,i}$, $i \in \mathcal{E}$, are obtained from the electrolyte $\tilde{g}^{\mathrm{E}}$ model used (eNRTL).

For a biphasic situation with one molecular phase, denoted by α, and one dissociated phase, denoted by β, the resulting equipotential conditions for phase equilibrium are

$$\begin{aligned} &\nu_i \ln(\nu_i \tilde{\gamma}_{\pm,i}^{(\beta)} y_{\pm,i}^{(\beta)}) = \ln(\gamma_i^{(\alpha)} x_i^{(\alpha)}) + \frac{-\left|z_{+,i} z_{-,i}\right| e^2}{8\pi k_{\mathrm{B}} T \varepsilon_0 \varepsilon_i \sigma_i}, \quad i \in \mathcal{E}, \\ &\ln(\tilde{\gamma}_i^{(\beta)} y_i^{(\beta)}) = \ln(\gamma_i^{(\alpha)} x_i^{(\alpha)}), \quad i \in \mathcal{S}. \end{aligned} \tag{12}$$

For ILs that are 1:1 electrolytes, this becomes, for a mixed-IL, mixed-solvent system,

$$\begin{aligned} &2\ln(2\tilde{\gamma}_{\pm,i}^{(\beta)} y_{\pm,i}^{(\beta)}) = \ln(\gamma_i^{(\alpha)} x_i^{(\alpha)}) + \frac{-e^2}{8\pi k_{\mathrm{B}} T \varepsilon_0 \varepsilon_i \sigma_i} , \quad i \in \mathcal{E}, \\ &\ln(\tilde{\gamma}_i^{(\beta)} y_i^{(\beta)}) = \ln(\gamma_i^{(\alpha)} x_i^{(\alpha)}), \quad i \in \mathcal{S}. \end{aligned} \tag{13}$$

4. Stability Analysis

For LLE at constant *T* and *P,* the total Gibbs free energy must be at a global minimum with respect to the number of phases present and their amounts and composition. The equipotential relationships are a necessary but not sufficient condition for this minimum. To verify that a global minimum in the total Gibbs free energy has been found, global phase stability analysis is needed. For this purpose, we use the tangent plane analysis originally formulated by Baker et al.[37] and Michelsen[38] for the case of a symmetric thermodynamic framework with no dissociation, and extend it to the case of an asymmetric framework with dissociation, as described above. The basic idea in tangent plane analysis is to consider a test or "feed" phase and then to determine whether the Gibbs free energy of the system can be lowered by allowing this phase to split. For our asymmetric framework, details of the analysis depend on whether the test phase is molecular or dissociated, and on whether the new phase that appears in the split is molecular or dissociated. We will begin by considering the case of a molecular test phase.

4.1 Molecular Test Phase

Consider a test phase described by the component mole number vector $\boldsymbol{n}_0 = (n_{0i},\ i \in \mathcal{E}, \mathcal{S})$ and corresponding mole fraction vector $\boldsymbol{z} = (z_i,\ i \in \mathcal{E}, \mathcal{S})$, with $z_i = n_{0i} / N_0$ and $N_0 = \sum_{i\in\{\mathcal{E},\mathcal{S}\}} n_{0i}$. Assuming that $\sum_{i\in\mathcal{E}} z_i \geq x_\mathrm{c}$ and/or $\varepsilon(\boldsymbol{z}) \leq \varepsilon_\mathrm{c}$, then this is a molecular phase. The total Gibbs free energy of the test phase is $G_0 = G(\boldsymbol{n}_0)$. Now assume that there is a split of the test phase into: 1. A *molecular* incipient phase containing an infinitesimal number of moles δ with an arbitrary composition (mole fraction) vector $\boldsymbol{x}$ consistent with a molecular phase. This phase has a component mole number vector $\delta\boldsymbol{x}$ and total Gibbs free energy $G(\delta\boldsymbol{x})$. 2. A molecular residual phase now containing $N_0 - \delta$ moles and mole number vector $\boldsymbol{n}_0 - \delta\boldsymbol{x}$. This phase has a total Gibbs free energy $G(\boldsymbol{n}_0 - \delta\boldsymbol{x})$, which can be obtained from the first-order Taylor expansion

$$G(\boldsymbol{n}_0 - \delta\boldsymbol{x}) = G(\boldsymbol{n}_0) + \sum_{i\in\{\mathcal{E},\mathcal{S}\}} \left(\frac{\partial G}{\partial n_i}\right)_0 (-\delta x_i) = G(\boldsymbol{n}_0) - \delta \sum_{i\in\{\mathcal{E},\mathcal{S}\}} x_i \mu_{i0} \tag{14}$$

where $\mu_{i0} = \mu_i(\boldsymbol{z})$ is the chemical potential of species i evaluated at the feed phase composition. The change in total Gibbs free energy due to the phase split is then

$$\begin{aligned}\Delta G &= \left[G(\delta\boldsymbol{x}) + G(\boldsymbol{n}_0 - \delta\boldsymbol{x})\right] - G(\boldsymbol{n}_0) = G(\delta\boldsymbol{x}) - \delta \sum_{i\in\{\mathcal{E},\mathcal{S}\}} x_i \mu_i(\boldsymbol{z}) \\ &= \sum_{i\in\{\mathcal{E},\mathcal{S}\}} (\delta x_i)\mu_i(\boldsymbol{x}) - \delta \sum_{i\in\{\mathcal{E},\mathcal{S}\}} x_i \mu_i(\boldsymbol{z}) = \delta\left[\sum_{i\in\{\mathcal{E},\mathcal{S}\}} x_i(\mu_i(\boldsymbol{x}) - \mu_i(\boldsymbol{z}))\right].\end{aligned} \tag{15}$$

For the test phase to be at a stable equilibrium, G must be at a global minimum, so ΔG must not be negative. Thus, a necessary condition for phase stability is that

$$D(\boldsymbol{x}, \boldsymbol{z}) = \sum_{i\in\{\mathcal{E},\mathcal{S}\}} x_i(\mu_i(\boldsymbol{x}) - \mu_i(\boldsymbol{z})) \geq 0 \tag{16}$$

for all incipient phase mole fraction vectors $\boldsymbol{x}$ satisfying the logical constraint

$$\left(\sum_{i\in\mathcal{E}} x_i \geq x_\mathrm{c}\right) \vee \left(\varepsilon(\boldsymbol{x}) \leq \varepsilon_\mathrm{c}\right) = \text{'true'} \tag{17}$$

and with the chemical potentials μ_i determined as described in Section 3. The first term in eq 16 is the molar Gibbs free energy function

$$g(\boldsymbol{x}) = \frac{G(\boldsymbol{n})}{N} = \frac{1}{N}\sum_{i\in\{\mathcal{I},\mathcal{S}\}} n_i \mu_i(\boldsymbol{x}) = \sum_{i\in\{\mathcal{I},\mathcal{S}\}} x_i \mu_i(\boldsymbol{x}) \tag{18}$$

Also noting that the chemical potential can be written[39] in terms of mole fractions by $\mu_i(\boldsymbol{x}) = g(\boldsymbol{x}) + \left(\partial g / \partial x_i\right)_{T,P,x_{j\neq i}} - \sum_{k\in\{\mathcal{I},\mathcal{S}\}} x_k \left(\partial g / \partial x_k\right)_{T,P,x_{j\neq k}}$, the second term in eq 16 can be expressed as

$$\sum_{i\in\{\mathcal{I},\mathcal{S}\}} x_i \mu_i(\boldsymbol{z}) = g(\boldsymbol{z}) + \sum_{i\in\{\mathcal{I},\mathcal{S}\}} \left.\frac{\partial g}{\partial x_i}\right|_{\boldsymbol{z}} (x_i - z_i) = g_{\tan}(\boldsymbol{x},\boldsymbol{z}), \tag{19}$$

a (hyper)plane tangent to the molar Gibbs free energy function $g(\boldsymbol{x})$ at the test (feed) composition $\boldsymbol{z}$. Thus, $D(\boldsymbol{x},\boldsymbol{z}) = g(\boldsymbol{x}) - g_{\tan}(\boldsymbol{x},\boldsymbol{z})$, and we have the familiar tangent plane criterion for phase stability, stating that a phase of composition (mole fraction) $\boldsymbol{z}$ is stable if a plane tangent to the molar Gibbs free energy surface $g(\boldsymbol{x})$ at $\boldsymbol{x} = \boldsymbol{z}$ never crosses (goes above) $g(\boldsymbol{x})$. That is, for phase stability, the tangent plane distance function $D(\boldsymbol{x},\boldsymbol{z})$, as given in this case by eq 16, must have a global minimum of zero with respect to $\boldsymbol{x}$, subject to the logical constraint given by eq 17.

Now consider the case in which the incipient phase is *dissociated*, not molecular as in the discussion above. Assume that the incipient dissociated phase contains an infinitesimal *observable* number of moles δ, with an arbitrary composition (observable mole fraction) vector $\boldsymbol{x}$ consistent with a dissociated phase. This phase has a component mole number vector $\delta\boldsymbol{x}$ and total Gibbs free energy $\tilde{G}(\delta\boldsymbol{x}) = \delta \sum_{i\in\{\mathcal{I},\mathcal{S}\}} x_i \tilde{\mu}_i(\boldsymbol{x})$. Proceeding as above, it can be seen that, in this case, a necessary condition for phase stability is

$$D(\boldsymbol{x},\boldsymbol{z}) = \sum_{i\in\{\mathcal{I},\mathcal{S}\}} x_i (\tilde{\mu}_i(\boldsymbol{x}) - \mu_i(\boldsymbol{z})) \geq 0, \tag{20}$$

for all incipient phase mole fraction vectors $\boldsymbol{x}$ satisfying the logical constraint

$$\left(\sum_{i\in\mathcal{I}} x_i < x_{\mathrm{c}}\right) \wedge \left(\varepsilon(\boldsymbol{x}) > \varepsilon_{\mathrm{c}}\right) = \text{'true'} \tag{21}$$

and with the chemical potentials $\tilde{\mu}_i$ and μ_i determined as described in Section 3. The first term in eq 20 is related to the molar Gibbs free energy function $\tilde{g}(\boldsymbol{x})$ of the dissociated phase by

$$\tilde{g}(\boldsymbol{x}) = \frac{\tilde{G}(\boldsymbol{n})}{N} = \frac{N_{\mathrm{obs}}}{N}\frac{1}{N_{\mathrm{obs}}}\sum_{i\in\{\mathcal{I},\mathcal{S}\}} n_i \tilde{\mu}_i(\boldsymbol{x}) = \frac{N_{\mathrm{obs}}}{N}\sum_{i\in\{\mathcal{I},\mathcal{S}\}} x_i \tilde{\mu}_i(\boldsymbol{x}), \tag{22}$$

where the ratio of observable to actual moles in the dissociated phase N_{obs} / N is given by (see Appendix B)

$$\frac{N_{\mathrm{obs}}}{N} = \frac{1}{1+\sum_{i\in\mathcal{I}} x_i(\nu_i - 1)}. \tag{23}$$

Thus, the first term in eq 20 is

$$\tilde{g}_{\mathrm{a}}(\boldsymbol{x}) = \sum_{i\in\{\mathcal{I},\mathcal{S}\}} x_i \tilde{\mu}_i(\boldsymbol{x}) = \left[1+\sum_{i\in\mathcal{I}} x_i(\nu_i - 1)\right]\tilde{g}(\boldsymbol{x}) \tag{24}$$

an *adjusted* molar Gibbs free energy function for the dissociated phase that accounts for the difference between actual and observable moles. The second term in eq 20 is again given by the tangent plane specified by eq 19. Thus, $D(\boldsymbol{x},\boldsymbol{z}) = \tilde{g}_{\mathrm{a}}(\boldsymbol{x}) - g_{\tan}(\boldsymbol{x},\boldsymbol{z})$. So now the tangent plane criterion is that a molecular phase of composition $\boldsymbol{z}$ is stable, with respect to a dissociated phase, if a plane tangent to the molecular-phase molar Gibbs free energy surface $g(\boldsymbol{x})$ at $\boldsymbol{x} = \boldsymbol{z}$ never crosses (goes above) $\tilde{g}_{\mathrm{a}}(\boldsymbol{x})$, the adjusted dissociated-phase molar Gibbs free energy surface, subject to the logical constraint on $\boldsymbol{x}$ given by eq 21.

The results of the foregoing analysis are depicted graphically in Figs. 1 and 2 for a hypothetical binary IL(1)/solvent(2) system. Due to the assumption that only solvent species contribute to the dielectric continuum, the logical constraint (eq 21) for a dissociated phase requires that $x_1 < x_{\mathrm{c}} = 0.1$ and $\varepsilon_2 > \varepsilon_{\mathrm{c}} = 40$. Assuming the latter solvent property to be true, the composition constraint leads to the partition of the composition space into two domains, one dissociated ($x_1 < 0.1$) and one molecular ($x_1 \geq 0.1$). These are depicted in Figs. 1 and 2 by the white (dissociated) and shaded (molecular) areas. In the molecular domain, only the molecular Gibbs free energy curve (g) is relevant, and the curve for the dissociated state ($\tilde{g}_{\mathrm{a}}$) can be ignored. This is indicated by using a bolder curve for g in this domain. Conversely, in the dissociated domain, only the curve for the dissociated state ($\tilde{g}_{\mathrm{a}}$) is relevant, and the molecular curve (g) can be ignored, as indicated by a bolder $\tilde{g}_{\mathrm{a}}$ curve in this domain.

Fig. 1 shows the case of a feed composition in the molecular domain of $z_1 = 0.75$. In the molecular domain, the tangent plane distance D is the directed distance from $g_{\tan}$ to g and is always nonnegative. In the dissociated domain, D is the directed distance from $g_{\tan}$ to $\tilde{g}_{\mathrm{a}}$ and is also always nonnegative. Thus, since D is always nonnegative, the test phase is stable. Fig. 2

shows the case of a feed composition in the molecular domain of $z_1 = 0.5$. Now, D is always nonnegative in the molecular domain (note that the $\tilde{g}_\mathrm{a}$ curve is not relevant in this domain), but is negative in the dissociated domain (note that the g curve is not relevant in this domain). Thus, since D can be negative for an incipient dissociated phase, this test phase is not stable. For phase stability, the tangent line must lie on or below the relevant curves for all compositions in each domain. This is true for the case of $z_1 = 0.75$ in Fig. 1, but not for the case of $z_1 = 0.5$ in Fig. 2.

4.2 Dissociated Test Phase

Now consider the case of a dissociated test phase with component mole number vector $\boldsymbol{n}_0$ and corresponding observable mole fraction vector $\boldsymbol{z}$. This will be the case when $\sum_{i\in\mathcal{E}} z_i < x_\mathrm{c}$ and $\varepsilon(\boldsymbol{z}) > \varepsilon_\mathrm{c}$. The total Gibbs free energy of the test phase is then $G_0 = \tilde{G}(\boldsymbol{n}_0)$. Assume a split of the test phase into: 1. A molecular incipient phase containing an infinitesimal observable number of moles δ with an arbitrary composition (observable mole fraction) vector $\boldsymbol{x}$ consistent with a molecular phase. This phase has an observable component mole number vector $\delta\boldsymbol{x}$ and total Gibbs free energy $G(\delta\boldsymbol{x})$. 2. A dissociated residual phase now with mole number vector $\boldsymbol{n}_0 - \delta\boldsymbol{x}$. This phase has a total Gibbs free energy $\tilde{G}(\boldsymbol{n}_0 - \delta\boldsymbol{x})$. Proceeding as in the previous section, with $\tilde{G}(\boldsymbol{n}_0 - \delta\boldsymbol{x})$ obtained from a first-order Taylor expansion, and determination of the ΔG of the phase split, it is easily shown that a necessary condition for phase stability is that

$$D(\boldsymbol{x},\boldsymbol{z}) = \sum_{i\in\{\mathcal{E},\mathcal{S}\}} x_i(\mu_i(\boldsymbol{x}) - \tilde{\mu}_i(\boldsymbol{z})) \geq 0 \tag{25}$$

for all incipient phase mole fraction vectors $\boldsymbol{x}$ satisfying the logical constraint given by eq. 17. The first term in eq 25 is the molar Gibbs free energy function $g(\boldsymbol{x})$ for the molecular phase (see eq 18). Also noting that[39] $\tilde{\mu}_i(\boldsymbol{x}) = \tilde{g}_\mathrm{a}(\boldsymbol{x}) + \left(\partial\tilde{g}_\mathrm{a}/\partial x_i\right)_{T,P,x_{j\neq i}} - \sum_{k\in\{\mathcal{E},\mathcal{S}\}} x_k\left(\partial\tilde{g}_\mathrm{a}/\partial x_k\right)_{T,P,x_{j\neq k}}$, the second term in eq 25 can be expressed as

$$\sum_{i\in\{\mathcal{E},\mathcal{S}\}} x_i\tilde{\mu}_i(\boldsymbol{z}) = \tilde{g}_\mathrm{a}(\boldsymbol{z}) + \sum_{i\in\{\mathcal{E},\mathcal{S}\}} \left.\frac{\partial\tilde{g}_\mathrm{a}}{\partial x_i}\right|_{\boldsymbol{z}} (x_i - z_i) = \tilde{g}_\mathrm{a,tan}(\boldsymbol{x},\boldsymbol{z}), \tag{26}$$

a (hyper)plane tangent to the adjusted molar Gibbs free energy function $\tilde{g}_\mathrm{a}(\boldsymbol{x})$ for the dissociated test phase at observable composition $\boldsymbol{z}$. Thus, $D(\boldsymbol{x},\boldsymbol{z}) = g(\boldsymbol{x}) - \tilde{g}_\mathrm{a,tan}(\boldsymbol{x},\boldsymbol{z})$, indicating that a dissociated phase of observable composition $\boldsymbol{z}$ is stable, with respect to a molecular phase, if a plane tangent to the adjusted dissociated-phase molar Gibbs free energy surface $\tilde{g}_{\mathrm{a}}(\boldsymbol{x})$ at $\boldsymbol{x} = \boldsymbol{z}$ never crosses (goes above) the molecular-phase Gibbs free energy surface $g(\boldsymbol{x})$, subject to the logical constraint on $\boldsymbol{x}$ given by eq 17.

This analysis can be repeated for a dissociated incipient phase, showing that for this case, a necessary condition for phase stability is that

$$D(\boldsymbol{x},\boldsymbol{z}) = \sum_{i\in\{\mathcal{E},S\}} x_i(\tilde{\mu}_i(\boldsymbol{x}) - \tilde{\mu}_i(\boldsymbol{z})) \geq 0 \tag{27}$$

for all incipient phase mole fraction vectors $\boldsymbol{x}$ satisfying the logical constraint given by eq 21. From eqs 24 and 26, this is equivalent to $D(\boldsymbol{x},\boldsymbol{z}) = \tilde{g}_{\mathrm{a}}(\boldsymbol{x}) - \tilde{g}_{\mathrm{a,tan}}(\boldsymbol{x},\boldsymbol{z})$. So, for this case, the tangent plane criterion is that a dissociated phase of observable composition $\boldsymbol{z}$ is stable, with respect to a dissociated phase, if a plane tangent to the adjusted dissociated-phase molar Gibbs free energy surface $\tilde{g}_{\mathrm{a}}(\boldsymbol{x})$ at $\boldsymbol{x} = \boldsymbol{z}$ never crosses (goes above) $\tilde{g}_{\mathrm{a}}(\boldsymbol{x})$, subject to the logical constraint on $\boldsymbol{x}$ given by eq 21.

Consider again the same hypothetical binary IL(1)/solvent(2) system featured in Figs. 1 and 2, now considering test phases in the dissociated domain. Fig. 3 shows the case of a feed composition (observable mole fraction) $z_1 = 0.04$. Here the tangent line $\tilde{g}_{\mathrm{a,tan}}$ lies on or below the relevant Gibbs free energy curves for all compositions in each domain. Thus, this test phase is stable. Fig. 4 shows the case of a feed composition (observable mole fraction) $z_1 = 0.06$. Now $\tilde{g}_{\mathrm{a,tan}}$ lies above the relevant curve (g) in the molecular domain, indicating that this test phase is not stable with respect to formation of a molecular phase. Finally, Fig. 5 represents the case of a stable, biphasic system at equilibrium, with one molecular phase (α phase) of composition x_1^{α} and one dissociated phase (β phase) of composition x_1^{β}. Note that the equilibrium compositions correspond to the points of tangency and that $\tilde{g}_{\mathrm{a,tan}}$ and g_{tan} coincide.

4.3 Summary

We have extended the tangent plane analysis originally formulated by Baker et al.[37] and Michelsen[38] for the case of a symmetric thermodynamic framework with no dissociation to the new case of an asymmetric framework with dissociation. For a molecular test (feed) phase of composition (observable mole fraction) $\boldsymbol{z}$, phase stability must be determined relative to both molecular and dissociated phases. Thus, the global optimization problem that must be solved is

$$\min_{\boldsymbol{x}} D(\boldsymbol{x},\boldsymbol{z}) = \begin{cases} \sum\limits_{i\in\{\mathcal{I},S\}} x_i(\mu_i(\boldsymbol{x}) - \mu_i(\boldsymbol{z})) = g(\boldsymbol{x}) - g_{\tan}(\boldsymbol{x},\boldsymbol{z}), & \left(\sum_{i\in\mathcal{I}} x_i \geq x_{\mathrm{c}}\right) \vee \left(\varepsilon(\boldsymbol{x}) \leq \varepsilon_{\mathrm{c}}\right) = \text{'true'} \\ \sum\limits_{i\in\{\mathcal{I},S\}} x_i(\tilde{\mu}_i(\boldsymbol{x}) - \mu_i(\boldsymbol{z})) = \tilde{g}_{\mathrm{a}}(\boldsymbol{x}) - g_{\tan}(\boldsymbol{x},\boldsymbol{z}), & \left(\sum_{i\in\mathcal{I}} x_i < x_{\mathrm{c}}\right) \wedge \left(\varepsilon(\boldsymbol{x}) > \varepsilon_{\mathrm{c}}\right) = \text{'true'} \end{cases} \tag{28}$$

$$\text{subject to} \quad 1 - \sum_{i\in\{\mathcal{I},S\}} x_i = 0.$$

If the global minimum value of D is zero, then the test phase is stable. If the global minimum value of D is negative, then the test phase is not stable. Similarly, for a dissociated test (feed) phase of composition (observable mole fraction) $\boldsymbol{z}$, phase stability must be determined relative to both molecular and dissociated phases. Thus, the global optimization problem that must be solved is

$$\min_{\boldsymbol{x}} D(\boldsymbol{x},\boldsymbol{z}) = \begin{cases} \sum\limits_{i\in\{\mathcal{I},S\}} x_i(\mu_i(\boldsymbol{x}) - \tilde{\mu}_i(\boldsymbol{z})) = g(\boldsymbol{x}) - \tilde{g}_{a,\tan}(\boldsymbol{x},\boldsymbol{z}), & \left(\sum_{i\in\mathcal{I}} x_i \geq x_{\mathrm{c}}\right) \vee \left(\varepsilon(\boldsymbol{x}) \leq \varepsilon_{\mathrm{c}}\right) = \text{'true'} \\ \sum\limits_{i\in\{\mathcal{I},S\}} x_i(\tilde{\mu}_i(\boldsymbol{x}) - \tilde{\mu}_i(\boldsymbol{z})) = \tilde{g}_{\mathrm{a}}(\boldsymbol{x}) - \tilde{g}_{a,\tan}(\boldsymbol{x},\boldsymbol{z}), & \left(\sum_{i\in\mathcal{I}} x_i < x_{\mathrm{c}}\right) \wedge \left(\varepsilon(\boldsymbol{x}) > \varepsilon_{\mathrm{c}}\right) = \text{'true'} \end{cases} \tag{29}$$

$$\text{subject to} \quad 1 - \sum_{i\in\{\mathcal{I},S\}} x_i = 0.$$

Again, if the global minimum value of D is zero, then the test phase is stable, and if the global minimum value of D is negative, then the test phase is not stable.

5. Binary Parameter Estimation

In this section, we show how to formulate and solve the parameter estimation problem for determining model parameters from binary LLE data (mutual solubility). We assume that the Gibbs free energy models g (molecular phase) and $\tilde{g}$ (dissociated phase) each contain two energetic binary interaction parameters θ_{ij} and θ_{ji} (see Appendix A) for each pair of components $i \in \{\mathcal{I}, S\}$ and $j \in \{\mathcal{I}, S\}$, and that these are the only fully adjustable model parameters. Furthermore, we make the key assumption that these parameters are the same in g as in $\tilde{g}$. This follows from the assumption of Chen et al.,[16] based on local electroneutrality and the symmetry of interaction energies, that short-range cation-solvent and anion-solvent interaction energies are the same. We extend this assumption to make these cation-solvent and anion-solvent interaction energies the same as the short-range interaction energy for the corresponding molecular salt and solvent. With this assumption, we can maintain in the asymmetric framework the use of two fully adjustable parameters per binary.

For symmetric thermodynamic frameworks of LLE with molecular phases, it is well known[36,40,41] that values of the binary parameters can be determined directly from mutual solubility data at a given temperature. This is done using the equal activity conditions for LLE, which provide two equations that, given the experimental LLE phase compositions, can be solved simultaneously for the two binary parameter values needed, thereby providing an exact fit to the experimental results. Recently, Simoni et al.[33] extended this approach to the case of electrolyte models in a symmetric LLE framework with dissociated phases. Here we show that this approach can be further extended to the asymmetric modeling framework described here.

For a binary salt (1)/solvent (2) system, and assuming a 1:1 electrolyte, the equal activity conditions are (from eq 13)

$$\begin{aligned} 2\ln(2\tilde{\gamma}_{\pm,1}^{(\beta)} y_{\pm,1}^{(\beta)}) &= \ln(\gamma_1^{(\alpha)} x_1^{(\alpha)}) + \frac{-e^2}{8\pi k_\mathrm{B} T \varepsilon_0 \varepsilon_1 \sigma_1} \\ \ln(\tilde{\gamma}_2^{(\beta)} y_2^{(\beta)}) &= \ln(\gamma_2^{(\alpha)} x_2^{(\alpha)}), \end{aligned} \qquad (30)$$

where α denotes a molecular phase and β denotes a dissociated phase. Here the activity coefficients depend on the phase compositions and on the values of the binary interaction parameters θ_{12} and θ_{21}. Thus, if experimental values of $x_1^{(\alpha)}$, $x_2^{(\alpha)}$, $y_{\pm,1}^{(\beta)}$, and $y_2^{(\beta)}$ are substituted into eq 30, the result is a system of two nonlinear equations that can be solved for the two unknowns, θ_{12} and θ_{21}. A difficulty with this process, whether involving symmetric or asymmetric frameworks, is that the number of solutions (each a pair of parameter values) to this nonlinear equation system is unknown. There may be one solution, no solution or, for some models, multiple solutions. In the context of models used in symmetric frameworks, Simoni et al.[33] have shown that this difficulty can be resolved by using an interval-Newton technique,[42,43] which provides a mathematically and computationally rigorous approach, guaranteeing that all solutions to the equation system are found, or showing with certainty that there are none. We will use the same interval-Newton approach here for the case of the asymmetric framework. The initial search interval used for each parameter is $[-1\times10^6, 1\times10^6]$ J/mol.

Once parameter solution(s) are found, they must be tested for their suitability in subsequent phase equilibrium calculations. The key criteria are:[33]

1. Parameters must correspond to a stable solution of the equal activity condition. We use the methods introduced in Section 4 to test each solution for phase stability.
2. Parameters should not have excessive negative magnitude, say a value not below −20,000 J/mol. Note that since this cut-off value is arbitrary, we use a search interval that will allow finding parameter solutions below this value.
3. Parameters should not result in Gibbs free energy curves that exhibit multiple miscibility gaps.

If more than one parameter set satisfies the above criteria, the solution with the smallest parameter magnitudes is used.

In addition to the binary interaction parameters, the models used for g and $\tilde{g}$ contain a number of other parameters that we do not treat as fully adjustable. These are the NRTL nonrandomness parameters $\alpha_{ij} = \alpha_{ji}$, the Pitzer-Debye-Hückel closest approach parameter ρ (see eq A5), and the ion diameter parameter σ_i (see eq 10). Some standard values for these parameters are used in the binary parameter estimation examples presented below. In Part II of this contribution, we will describe a systematic method for setting these parameters in modeling ternary LLE.

6. Examples

In this section, we present two examples demonstrating the estimation of binary parameters in the asymmetric framework for modeling LLE. Examples demonstrating the use of the asymmetric framework in predicting ternary LLE, with comparison to experimental data and results obtained from other models, will be presented in detail in Part II of this contribution.

Each of the parameter estimation examples considered here is a system consisting of a strongly hydrophobic IL (component 1) and water (component 2) for which LLE data (mutual solubility) is available at $T = 297$ K. In all cases, the solvent-rich (aqueous) phase (denoted by β) meets the criteria ($x_1 < x_c = 0.1$ and $\varepsilon_2 > \varepsilon_c = 40$) for a phase in which complete salt dissociation is assumed, and the salt-rich (IL) phase (denoted by α) is assumed to be molecular. Fixed parameter values used for all of the example problems are $\alpha_{12} = \alpha_{21} = 0.2$ (NRTL and eNRTL) and ρ = 14.9 (eNRTL). For water,[44] ε_2 = 78.4 and calculation of the Debye-Hückel parameter (eq A9) gives $A_\phi = 0.55$. Other problem-specific parameters are given below.

6.1 [hmim][Tf$_2$N] and Water

The binary system 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([hmim][Tf$_2$N]) (component 1) and water (component 2) at T = 297 K exhibits a miscibility gap of[45] $x_1^{(\alpha)} = 0.7889$ and $x_1^{(\beta)} = 9.445\times10^{-5}$. Here we will use the asymmetric framework described above, with NRTL representing the molecular IL-rich phase (α) and eNRTL the aqueous, dissociated-IL phase (β). For this system, we assume $\sigma_1 = 1\times10^{-8}$ m and use ε_1 = 11.4. The latter value (dielectric constant of the IL) was obtained by extrapolating the IL dielectric constant data of Daguenet et al.[46] as a function of alkyl chain length. To determine the binary interaction parameters, the experimental phase compositions were substituted into eq 30, which was then solved for the binary interaction parameters θ_{12} and θ_{21}, using an interval-Newton method to obtain all parameter solutions. The results obtained are presented in Table 1. This shows that there are four possible parameter solutions, but that only one of them corresponds to stable phase equilibrium.

When parameter solution 1 is used, the resulting model curves are those shown in Fig. 6 (showing the entire composition range) and Fig. 7 (enlarging the range $0 \le x_1 \le 0.001$). Note the bitangent line g_{tan}, with points of tangency corresponding to the experimental equilibrium phase compositions. Since this line lies below the molecular Gibbs free energy curve g in the molecular domain $x_1 \ge 0.1$, and below the adjusted electrolyte Gibbs free energy curve $\tilde{g}_{\text{a}}$ in the electrolyte domain $x_1 < 0.1$, this represents stable phase equilibrium. In Fig. 7, g_{tan} goes above the molecular curve g; however, this is in the electrolyte domain, where the molecular curve is not relevant. In practice, phase stability would be determined by choosing either $x_1^{(\alpha)} = 0.7889$ or $x_1^{(\beta)} = 9.445\times10^{-5}$ as the test phase composition (z_1), and then solving the global optimization problem of eq 28 or eq 29 (depending on whether the test phase chosen is the molecular one or the dissociated one). In either case, it is clear that D will be nonnegative for all compositions, and will have a global minimum value of zero, demonstrating phase stability.

For the purpose of comparison, we have also plotted the Gibbs free energy curves and bitangent line for parameter solution 4, which does not correspond to a stable system. This is shown in Fig. 8 (entire composition range) and Fig. 9 (enlargement of the range $0.995 \leq x_1 \leq 1$). Again the bitangent line has points of tangency that correspond to the experimental equilibrium phase compositions. However, as emphasized in Fig. 9, in this case the molecular Gibbs free energy curve drops below the bitangent line in the molecular domain. Thus, the tangent plane distance function becomes negative, demonstrating that this parameter solution does not correspond to stable phase equilibrium.

6.2 [bmpy][Tf_2N] and Water

The binary system 1-butyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide ([bmpy][Tf_2N]) (component 1) and water (component 2) at 297 K has a miscibility gap of[45] $x_1^{(\alpha)} = 0.8138$ and $x_1^{(\beta)} = 0.0023$. Again we will use NRTL to represent the molecular IL-rich phase (α) and eNRTL to represent the aqueous, dissociated-IL phase (β). For this system, we assume $\sigma_1 = 5\times10^{-9}$ m and use $\varepsilon_1 = 11.9$ (Weingärtner[47]). Solving eq 30 with an interval-Newton method for the binary parameter values yields the four solutions given in Table 2. Of these, solutions 1, 2 and 3 do not represent stable phase equilibrium, but solution 4 does. The model curves corresponding to solution 4 are illustrated in Fig. 10, which also shows that this yields a stable biphasic equilibrium, since we observe that the directed distance from the tangent line to the relevant curve is never negative.

7. Concluding Remarks

We have described here a new asymmetric framework for modeling liquid-liquid equilibrium in electrolyte/mixed-solvent systems. In this approach, different phases may have different degrees of electrolyte dissociation and thus are characterized by different Gibbs free energy models. As an initial example of how this framework can be used, we have developed the case in which the electrolytes are either completely dissociated or completely paired (molecular), depending on the dielectric constant of the mixed solvent and on the total concentration of the electrolytes. However, this framework can also be used in cases involving partial dissociation, and we are currently developing and evaluating asymmetric frameworks of this type.

For the assumptions made here of either complete dissociation or no dissociation, the applications of interest are systems involving an aqueous phase that is dilute in IL. Examples[1-4] of such systems include the extraction of biofuels and biofeedstocks from fermentation broths and the recovery of amino acids from aqueous media. In Part II of this contribution, we demonstrate and evaluate the use of the asymmetric modeling framework described here to *predict* LLE for ternary IL/solvent/water systems, using parameters obtained from binary and pure component data only.

Acknowledgements

This work was supported in part by the Department of Energy under Grant DE-FG36-08GO88020. Additional support was provided by a University of Notre Dame Arthur J. Schmitt Presidential Fellowship (LDS).

Literature Cited

(1) Fadeev, A. G.; Meagher, M. M. Opportunities for Ionic Liquids in Recovery of Biofuels. *Chem. Commun.* **2001,** *3*, 295-296.

(2) Wang, J. J.; Pei, Y. C.; Zhao, Y.; Hu, Z. G. Recovery of amino acids by imidazolium based ionic liquids from aqueous media. *Green Chem.* **2005,** *7*, 196-202.

(3) Wang, J. J.; Pei, Y. C.; Zhao, Y.; Zhang, S. J. Selective extraction of bioproducts by ionic liquids. *Chin. J. Chem.* **2005,** *23*, 662-664.

(4) Chapeaux, A.; Simoni, L. D.; Ronan, T.; Stadtherr, M. A.; Brennecke, J. F. Extraction of alcohols from water with 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. *Green Chem.* **2008,** *10*, 1301-1306.

(5) Holbrey, J. D.; Seddon, K. R. Ionic liquids. *Clean Prod. Process* **1999,** *1*, 223-236.

(6) Banerjee, T.; Singh, M. K.; Sahoo, R. K.; Khanna, A. Volume, surface and UNIQUAC interaction parameters for imidazolium based ionic liquids via polarizable continuum model. *Fluid Phase Equilib.* **2005,** *234*, 64-76.

(7) Letcher, T. M.; Deenadayalu, N.; Soko, B.; Ramjugernath, D. Ternary liquid-liquid equilibria for mixtures of 1-methyl-3-octylimidazolium chloride + an alkanol + an alkane at 298.2 K and 1 bar. *J. Chem. Eng. Data* **2003,** *48*, 904-907.

(8) Letcher, T. M.; Deenadayalu, N. Ternary liquid-liquid equilibria for mixtures of 1-methyl-3-octylimidazolium chloride + benzene + an alkane at 298.2 K and 1 atm. *J. Chem. Thermodyn.* **2003,** *35*, 67-76.

(9) Letcher, T. M.; Reddy, P. Ternary liquid-liquid equilibria for mixtures of 1-hexyl-3-methylimidozolium (tetrafluoroborate or hexafluorophosphate) + ethanol + an alkene at T = 298.2K. *Fluid Phase Equilib.* **2004,** *219*, 107-112.

(10) Letcher, T. M.; Reddy, P. Ternary (liquid + liquid) equilibria for mixtures of 1-hexyl-3-methylimidazolium (tetrafluoroborate or hexafluorophosphate) + benzene + an alkane at T = 298.2 K and p = 0.1 MPa. *J. Chem. Thermodyn.* **2005,** *37*, 415-421.

(11) Selvan, M. S.; McKinley, M. D.; Dubois, R. H.; Atwood, J. L. Liquid-liquid equilibria for toluene + heptane + 1-ethyl-3-methylimidazolium triiodide and toluene + heptane + 1-butyl-3-methylimidazolium triiodide. *J. Chem. Eng. Data* **2000,** *45*, 841-845.

(12) Hu, X. S.; Yu, J.; Liu, H. Z. Liquid-liquid equilibria of the system 1-(2-hydroxyethyl)-3-methylimidozolium tetrafluoroborate or 1-(2-hydroxyethyl)-2,3-dimethylimidozolium tetrafluoroborate plus water plus 1-butanol at 293.15 K. *J. Chem. Eng. Data* **2006,** *51*, 691-695.

(13) Wang, R.; Wang, J.; Meng, H.; Li, C.; Wang, Z. Liquid-liquid equilibria for benzene plus cyclohexane 1-methyl-3-methylimidazolium dimethylphosphate or 1-ethyl-3-methylimidazolium diethylphosphate. *J. Chem. Eng. Data* **2008,** *53*, 1159-1162.

(14) Pereiro, A. B.; Rodríguez, A. Azeotrope-breaking using [BMIM] [MeSO4] ionic liquid in an extraction column. *Sep. Purif. Technol.* **2008,** *62*, 733-738.

(15) Simoni, L. D.; Lin, Y.; Brennecke, J. F.; Stadtherr, M. A. Modeling liquid-liquid equilibrium of ionic liquid systems with NRTL, electrolyte-NRTL, and UNIQUAC. *Ind. Eng. Chem. Res.* **2008,** *47*, 256-272.

(16) Chen, C.-C.; Britt, H. I.; Boston, J. F.; Evans, L. B. Local composition model for excess Gibbs energy of electrolyte solutions, part I: Single solvent, single completely dissociated electrolyte systems. *AIChE J.* **1982,** *28*, 588-596.

(17) Domańska, U.; Pobudkowska, A.; Eckert, F. Liquid-liquid equilibria in the binary systems (1,3-dimethylimidazolium, or 1-butyl-3-methylimidazolium methylsulfate plus hydrocarbons). *Green Chem.* **2006,** *8*, 268-276.

(18) Freire, M. G.; Santos, L. M. N. B. F.; Marrucho, I. M.; Coutinho, J. A. P. Evaluation of COSMO-RS for the prediction of LLE and VLE of alcohols + ionic liquids. *Fluid Phase Equilib.* **2007,** *255*, 167-178.

(19) Jork, C.; Kristen, C.; Pieraccini, D.; Stark, A.; Chiappe, C.; Beste, Y. A.; Arlt, W. Tailor-made ionic liquids. *J. Chem. Thermodyn.* **2005,** *37*, 537-558.

(20) Banerjee, T.; Verma, K. K.; Khanna, A. Liquid-liquid equilibrium for ionic liquid systems using COSMO-RS: Effect of cation and anion dissociation. *AIChE J.* **2008,** *54*, 1874-1885.

(21) Chen, C.-C.; Song, Y. Solubility modeling with a nonrandom two-liquid segment activity coefficient model. *Ind. Eng. Chem. Res.* **2004,** *43*, 8354-8362.

(22) Chen, C.-C.; Simoni, L. D.; Brennecke, J. F.; Stadtherr, M. A. Correlation and prediction of phase behavior of organic compounds in ionic liquids using the nonrandom two-liquid segment activity coefficient model. *Ind. Eng. Chem. Res.* **2008,** *47*, 7081-7093.

(23) Torrecilla, J. S.; Deetlefs, M.; Seddon, K. R.; Rodríguez, F. Estimation of ternary liquid-liquid equilibria for arene/alkane/ionic liquid mixtures using neural networks. *Phys. Chem. Chem. Phys.* **2008,** *10*, 5114-5120.

(24) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions;* Butterworths: London, UK, 1959.

(25) Singh, T.; Kumar, A. Aggregation behavior of ionic liquids in aqueous solutions: Effect of alkyl chain length, cations, and anions. *J. Phys. Chem. B* **2007,** *111*, 7843-7851.

(26) Wang, J.; Wang, H.; Zhang, S.; Zhang, H.; Zhao, Y. Conductivities, volumes, fluorescence, and aggregation behavior of ionic liquids [C_4mim][BF_4] and [$C_n$mim]Br (n = 4, 6, 8, 10, 12) in aqueous solutions. *J. Phys. Chem. B* **2007,** *111*, 6181-6188.

(27) Tokuda, H.; Tsuzuki, S.; Susan, M. A. B. H.; Hayamizu, K.; Watanabe, M. How ionic are room-temperature ionic liquids? An indicator of the physicochemical properties. *J. Phys. Chem. B* **2006,** *110*, 19593-19600.

(28) Jarosik, A.; Krajewski, S. R.; Lewandowski, A.; Radzimski, P. Conductivity of ionic liquids in mixtures. *J. Mol. Liq.* **2006,** *123*, 43-50.

(29) Zhang, L.; Zheng, X.; Wang, Y.; Li, H. Prediction of the solvation and structural properties of ionic liquids in water by two-dimensional correlation spectroscopy. *J. Phys. Chem. B* **2008,** *112*, 6411-6419.

(30) Katayanagi, H.; Nishikawa, K.; Shimozaki, H.; Miki, K.; Westh, P.; Koga, Y. Mixing schemes in ionic liquid-H2O systems: A thermodynamic study. *J. Phys. Chem. B* **2004,** *108*, 19451-19457.

(31) Kato, H.; Nishikawa, K.; Murai, H.; Morita, T.; Koga, Y. Chemical potentials in aqueous solutions of some ionic liquids with the 1-ethyl-3-methylimidazolium cation. *J. Phys. Chem. B* **2008,** *112*, 13344-13348.

(32) Chen, C.-C.; Song, Y. Generalized electrolyte-NRTL model for mixed-solvent electrolyte systems. *AIChE J.* **2004,** *50*, 1928-1941.

(33) Simoni, L. D.; Lin, Y.; Brennecke, J. F.; Stadtherr, M. A. Reliable computation of binary parameters in activity coefficient models for liquid-liquid equibrium. *Fluid Phase Equilib.* **2007,** *255*, 138-146.

(34) Sokol, V.; Tominić, I.; Tomaš, R.; Višić, M. Thermodynamics of the association reaction of Li+ and Br– Ions in 2-butanol + water mixtures from conductivity measurements. *Croatica Chemica Acta* **2005,** *78*, 43-37.

(35) Israelachvili, J. N. *Intermolecular and Surface Forces;* Academic Press Inc.: San Diego, CA, 1991.

(36) Renon, H.; Prausnitz, J. M. Local compositions in thermodynamic excess functions for liquid mixtures. *AIChE J.* **1968,** *14*, 135-144.

(37) Baker, L. E.; Pierce, A. C.; Luks, K. D. Gibbs energy analysis of phase equilibria. *Soc. Petrol. Engrs. J.* **1982,** *22*, 731-742.

(38) Michelsen, M. L. The isothermal flash problem. Part I: Stability. *Fluid Phase Equilib.* **1982,** *9*, 1-19.

(39) Van Ness, H. C.; Abbott, M. M. *Classical Thermodynamics of Nonelectrolyte Solutions: With Applications to Phase Equilibria;* McGraw-Hill, Inc.: 1982.

(40) Renon, H.; Prausnitz, J. Estimation of parameters for the NRTL equation for excess Gibbs energies of strongly nonideal liquid mixtures. *Ind. Eng. Chem. Proc. Des. Dev.* **1969,** *8*, 413-419.

(41) Sørensen, J. M.; Arlt, W. *Liquid-Liquid Equilibrium Data Collection;* DECHEMA: Frankfurt/Main, Germany, 1979-1980.

(42) Kearfott, R. B. *Rigorous Global Search: Continuous Problems;* Kluwer Academic Publishers: Dordrecht, The Netherlands, 1996.

(43) Neumaier, A. *Interval Methods for Systems of Equations;* Cambridge University Press: Cambridge, UK, 1990.

(44) Fernández, D. P.; Goodwin, A. R. H.; Lemmon, E. W.; Levelt Sengers, J. M. H.; Williams, R. C. A formulation for the static permittivity of water and steam at temperatures from 238 K to 873 K at pressures up to 1200 MPa, including derivatives and Debye-Hückel coefficients. *J. Phys. Chem. Ref. Data* **1997,** *26*, 1125-1166.

(45) Chapeaux, A.; Simoni, L. D.; Stadtherr, M. A.; Brennecke, J. F. Liquid phase behavior of ionic liquids with water and 1-octanol and modeling of 1-octanol/water partition coefficients. *J. Chem. Eng. Data* **2007,** *52*, 2462-2467.

(46) Daguenet, C.; Dyson, P. J.; Krossing, I.; Oleinikova, A.; Slattery, J.; Wakai, C.; Weingartner, H. Dielectric response of imidazolium-based room-temperature ionic liquids. *J. Phys. Chem. B* **2006,** *110*, 12682-12688.

(47) Weingärtner, H. The static dielectric constant of ionic liquids. *Z. Phys. Chem.* **2006,** *220*, 1395-1405.

(48) Pitzer, K. S. Electrolytes. From dilute solutions to fused salts. *J. Amer. Chem. Soc.* **1980,** *102*, 2902-2906.

Appendix A

In this Appendix, we present details of the excess Gibbs free energy models used for $\tilde{g}^{\mathrm{E}}$ in eq 2 (dissociated phase) and g^{E} in eq 9 (molecular phase). For g^{E} we will use the NRTL model[36] and for $\tilde{g}^{\mathrm{E}}$ we will use the electrolyte-NRTL (eNRTL) model.[32]

For the NRTL model,

$$\frac{g^{\mathrm{E}}}{RT} = \sum_{i=1}^{n} x_i \frac{\sum_{j=1}^{n} \tau_{ji} G_{ji} x_j}{\sum_{k=1}^{n} G_{ki} x_k}, \tag{A1}$$

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \tag{A2}$$

and

$$\tau_{ij} = \frac{g_{ij} - g_{jj}}{RT} = \frac{\Delta g_{ij}}{RT}. \tag{A3}$$

Here g_{ij} is an energy parameter characterizing the interaction of species *i* and *j*, and the parameter $\alpha_{ij} = \alpha_{ji}$ is related to the nonrandomness in the mixture. The binary interaction parameters $\theta_{ij} = \Delta g_{ij}$ are estimated from binary experimental data, as described in Section 5.

The eNRTL model[16] is an excess Gibbs free energy model for multiple electrolytes in mixed solvents, and is based on the assumption of complete dissociation. It consists of two terms, a Pitzer extended Debye-Hückel expression, $g_{\mathrm{PDH}}^{\mathrm{E}}$, for the long-range electrostatic contribution[48] and an NRTL-type local composition contribution, $g_{\mathrm{LC}}^{\mathrm{E}}$, for the short-range interactions, so that $\tilde{g}^{\mathrm{E}} = g_{\mathrm{PDH}}^{\mathrm{E}} + g_{\mathrm{LC}}^{\mathrm{E}}$. Since the reference state used here is symmetric (pure liquids of all components at system temperature and pressure), we need to use a symmetrically-referenced form of this model.

From Chen and Song,[32] the symmetrically-referenced expression for the local composition (LC) contribution is

$$
\begin{aligned}
\frac{g_{\mathrm{LC}}^{\mathrm{E}}}{RT} = {} & \sum_{i\in S} y_i \left(\frac{\sum\limits_{l\in\{+,-,S\}} z_l y_l G_{li}\tau_{li}}{\sum\limits_{k\in\{+,-,S\}} z_k y_k G_{ki}} \right) + \sum_{i\in\{+\}} z_i y_i \left\{ \sum_{j\in\{-\}} \left[\left(\frac{y_j}{\sum\limits_{j'\in\{-\}} y_{j'}} \right) \frac{\sum\limits_{l\in\{+,-,S\}} z_l y_l G_{li,ji}\tau_{li,ji}}{\sum\limits_{k\in\{+,-,S\}} z_k y_k G_{ki,ji}} \right] \right\} \\
& + \sum_{i\in\{-\}} z_i y_i \left\{ \sum_{j\in\{+\}} \left[\left(\frac{y_j}{\sum\limits_{j'\in\{+\}} y_{j'}} \right) \frac{\sum\limits_{l\in\{+,-,S\}} z_l y_l G_{li,ji}\tau_{li,ji}}{\sum\limits_{k\in\{+,-,S\}} z_k y_k G_{ki,ji}} \right] \right\} .
\end{aligned}
\tag{A4}
$$

Here G and τ refer to local binary parameters related by $G = \exp(-\alpha\tau)$ where α is the NRTL nonrandomness parameter. These binary parameters are discussed further below. The index sets $\{+\}$ and $\{-\}$ refer to the cation and anion indices, respectively. That is $\{+\} = \{(+,i) \mid i \in \mathcal{E}\}$ and $\{-\} = \{(-,i) \mid i \in \mathcal{E}\}$. Also note that, in eq A4, $z_i = 1$ for $i \in S$.

To obtain the symmetrically-referenced expression for the PDH contribution, Simoni et al.[15,33] renormalized Pitzer's expression[48] to be relative to the symmetric reference state, resulting in

$$
\begin{aligned}
\frac{g_{\mathrm{PDH}}^{\mathrm{E}}}{RT} = {} & -\sqrt{\frac{1000}{M}} \frac{4A_\phi I_y}{\rho} \ln\left(1+\rho\sqrt{I_y}\right) \\
& + A_\phi \sqrt{\frac{1000}{M}} \sum_{i\in\mathcal{E}} \left\{ y_{+,i} \left[\frac{2z_{+,i}^2}{\rho} \ln\left(1+\rho\sqrt{I_i^0}\right) + \Gamma_{+,i}^0 \right] \right\} \\
& + A_\phi \sqrt{\frac{1000}{M}} \sum_{i\in\mathcal{E}} \left\{ y_{-,i} \left[\frac{2z_{-,i}^2}{\rho} \ln\left(1+\rho\sqrt{I_i^0}\right) + \Gamma_{-,i}^0 \right] \right\},
\end{aligned}
\tag{A5}
$$

where I_y is the ionic strength

$$
I_y = \frac{1}{2}\sum_i \left(z_{+,i}^2 y_{+,i} + z_{-,i}^2 y_{-,i} \right),\ i \in \mathcal{E}\,, \tag{A6}
$$

with

$$
I_i^0 = \lim_{x_i \to 1} I_y,\ \ i \in \mathcal{E}\,, \tag{A7}
$$

and

$$
\Gamma_{j,i}^0 = \frac{z_{j,i}^2\sqrt{I_i^0} - 2(I_i^0)^{3/2}}{1+\rho\sqrt{I_i^0}},\ j = +,-. \tag{A8}
$$

A_ϕ is the Debye-Hückel parameter,[48] which depends on temperature and on the density and dielectric constant of the mixed solvent and is given by

$$A_\phi = \frac{1}{3}\sqrt{\frac{2\pi N_A d}{1000}}\left(\frac{e^2}{\varepsilon_0 \varepsilon kT}\right)^{3/2}, \tag{A9}$$

where N_A is Avogadro's number, d is the density of the mixed solvent in kg/m^3, e is the elementary charge, ε_0 is the permittivity of free space, ε is the dielectric constant (relative permittivity) of the mixed solvent, k is Boltzmann's constant, and T is the absolute temperature. The closest approach parameter ρ is a constant, whose value is discussed in Section 5. Mixing rules for the mixed solvent molecular weight M, density d, and dielectric constant ε are[32]

$$M = \sum_{i \in S}\left[\left(\frac{y_i}{\sum_{i' \in S} y_{i'}}\right) M_i\right], \tag{A10}$$

$$\frac{1}{d} = \sum_{i \in S}\left[\left(\frac{y_i}{\sum_{i' \in S} y_{i'}}\right)\frac{1}{d_i}\right] \tag{A11}$$

and

$$\varepsilon = \sum_{i \in S}\left[\left(\frac{M_i y_i}{\sum_{i' \in S} M_{i'} y_{i'}}\right)\varepsilon_i\right]. \tag{A12}$$

Here, eq A10 is exact and eqs A11 and A12 are approximations.

For the case of primary interest here, namely ternary IL(1)/solvent(2)/cosolvent(3) systems, application of eq A4 for the LC contribution generates the following binary interaction parameters: τ_{c2}, τ_{a2}, τ_{32}, τ_{c3}, τ_{a3}, τ_{23}, $\tau_{2c,ac}$, $\tau_{3c,ac}$, $\tau_{2a,ca}$, $\tau_{3a,ca}$, with the indices c = (+,1) and a = (−,1). Using the electroneutrality condition, together with the symmetry of the underlying interaction energies, it can be shown[16,32] that $\tau_{c2} = \tau_{a2} = \tau_{12}$, $\tau_{2c,ac} = \tau_{2a,ca} = \tau_{21}$, $\tau_{c3} = \tau_{a3} = \tau_{13}$, and $\tau_{3c,ac} = \tau_{3a,ca} = \tau_{31}$. Note also that $\tau_{cc,ac} = \tau_{ac,ac} = \tau_{ca,ca} = \tau_{aa,ca} = \tau_{11} = 0$ and $\tau_{22} = \tau_{33} = 0$. Thus we have the usual six binary interaction parameters for the ternary system, two for each of the three observable binary subsystems. The binary interaction parameters $\theta_{ij} = \Delta g_{ij} = RT\tau_{ij}$ are estimated from binary data, as discussed in Section 5.

Appendix B

In this Appendix, we develop the relationship (eq 23) between the number of actual moles N and number of observable moles N_{obs} in a generic dissociated phase. For this case, in a mixed-salt/mixed-solvent system,

$$N_{\text{obs}} = \sum_{i \in \mathcal{E}} n_i + \sum_{i \in S} n_i \quad . \tag{B1}$$

and

$$N = \sum_{i \in \mathcal{E}} \left(n_{+,i} + n_{-,i} \right) + \sum_{i \in S} n_i = \sum_{i \in \mathcal{E}} \left(\nu_{+,i} + \nu_{-,i} \right) n_i + \sum_{i \in S} n_i = \sum_{i \in \mathcal{E}} \nu_i n_i + \sum_{i \in S} n_i \quad . \tag{B2}$$

Subtracting eq B1 from eq B2 yields

$$N - N_{\text{obs}} = \sum_{i \in \mathcal{E}} \left(\nu_i - 1 \right) n_i \, . \tag{B3}$$

Dividing by N_{obs}, noting that $x_i = n_i / N_{\text{obs}}$ and rearranging, results in

$$\frac{N_{\text{obs}}}{N} = \frac{1}{1 + \sum_{i \in \mathcal{E}} x_i (\nu_i - 1)} , \tag{B4}$$

which is eq 23.

Table 1: NRTL/eNRTL parameter solutions for [hmim][Tf_2N]/water at 297 K.

Solution	θ_{12} (J/mol)	θ_{21} (J/mol)	Stable?
1	155.58	17420	Yes
2	9630.8	123160	No
3	18441	122730	No
4	55640	17239	No

Table 2: NRTL/eNRTL parameter solutions for [bmpy][Tf_2N]/ water at 297 K.

Solution	θ_{12} (J/mol)	θ_{21} (J/mol)	Stable?
1	44028	9576.5	No
2	20954	86692	No
3	9025.6	87935	No
4	824.23	9578.1	Yes

List of Figures

Figure 10: Model curves with parameter solution 4 for [bmpy][Tf$_2$N]/water at 297 K. The tangent line also has a point of tangency with the $\tilde{g}_{\mathrm{a}}$ (eNRTL) curve at $x_1^{(\beta)} = 0.0023$.

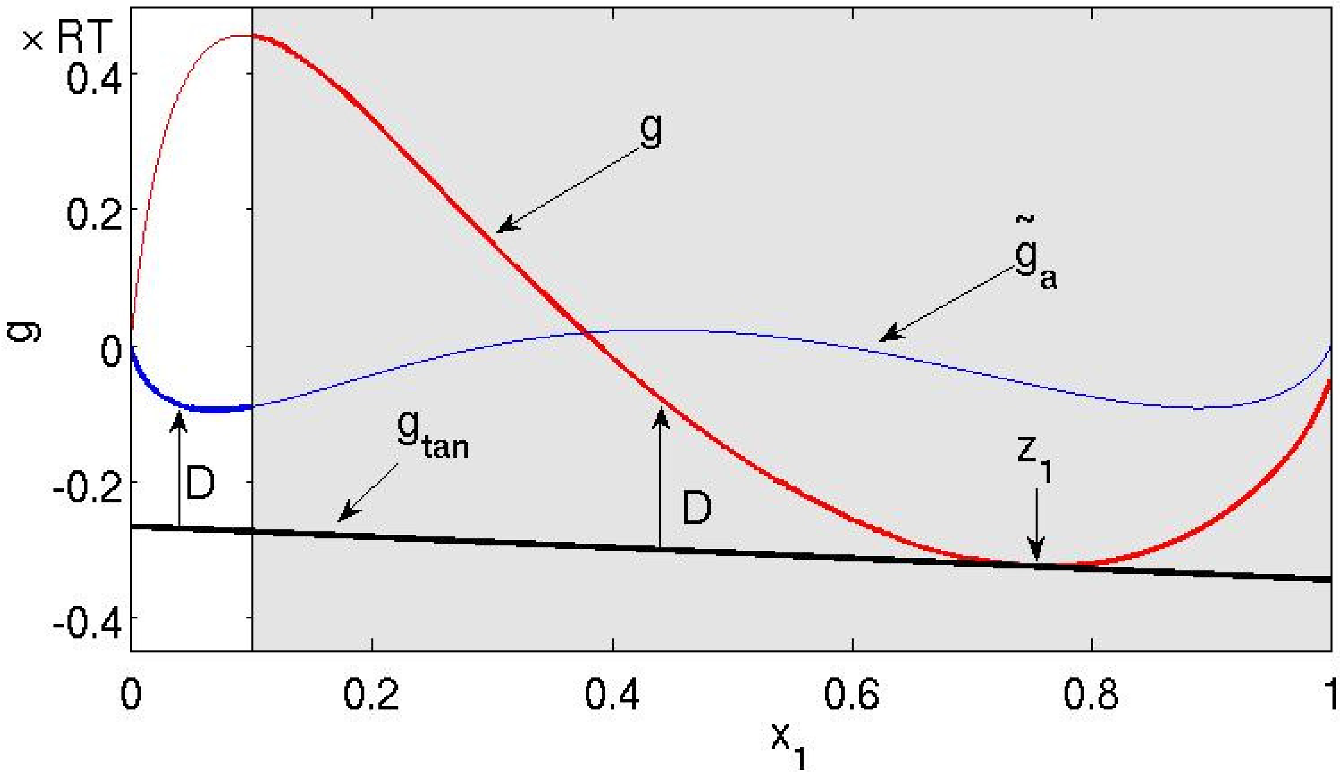

Figure 1: Phase stability analysis for a test (feed) phase of composition z_1 = 0.75 in a hypothetical binary salt(1)/solvent(2) system. This test phase is stable.

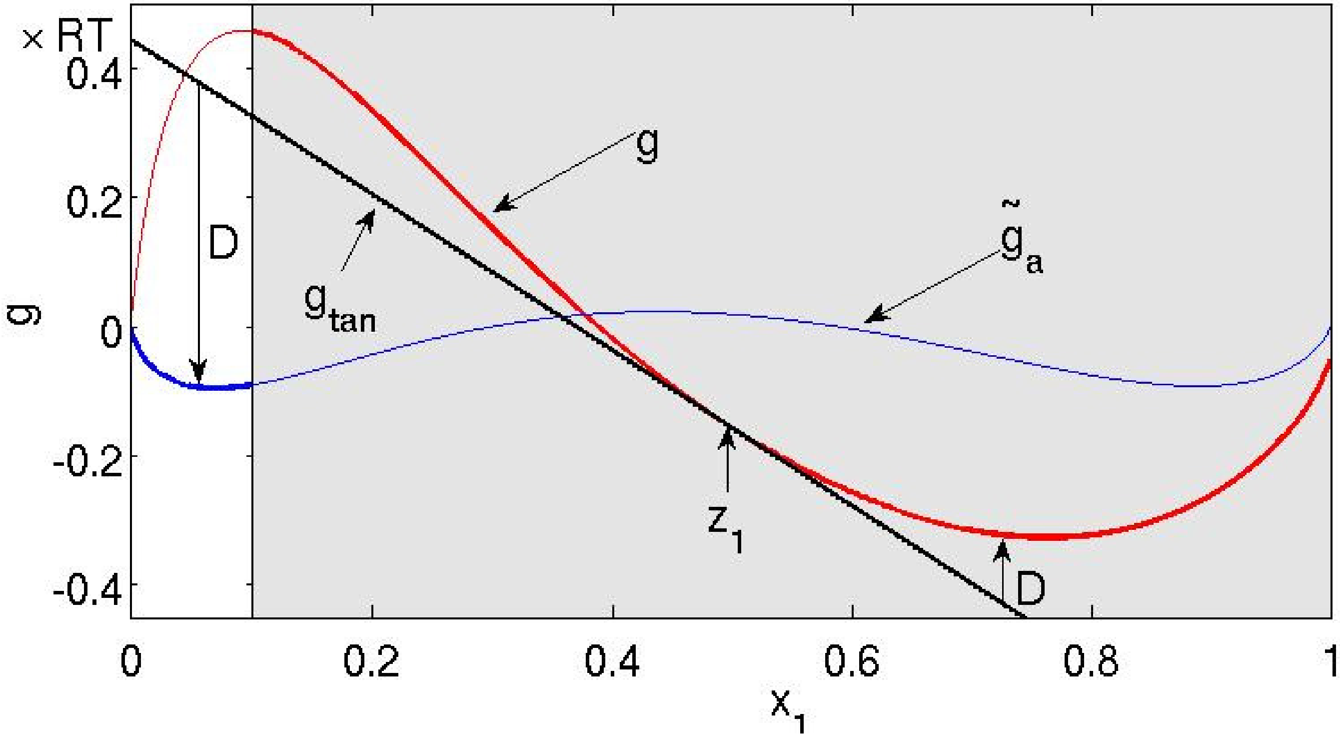

Figure 2: Phase stability analysis for a test (feed) phase of composition $z_1 = 0.5$ in a hypothetical binary salt(1)/solvent(2) system. This test phase is not stable.

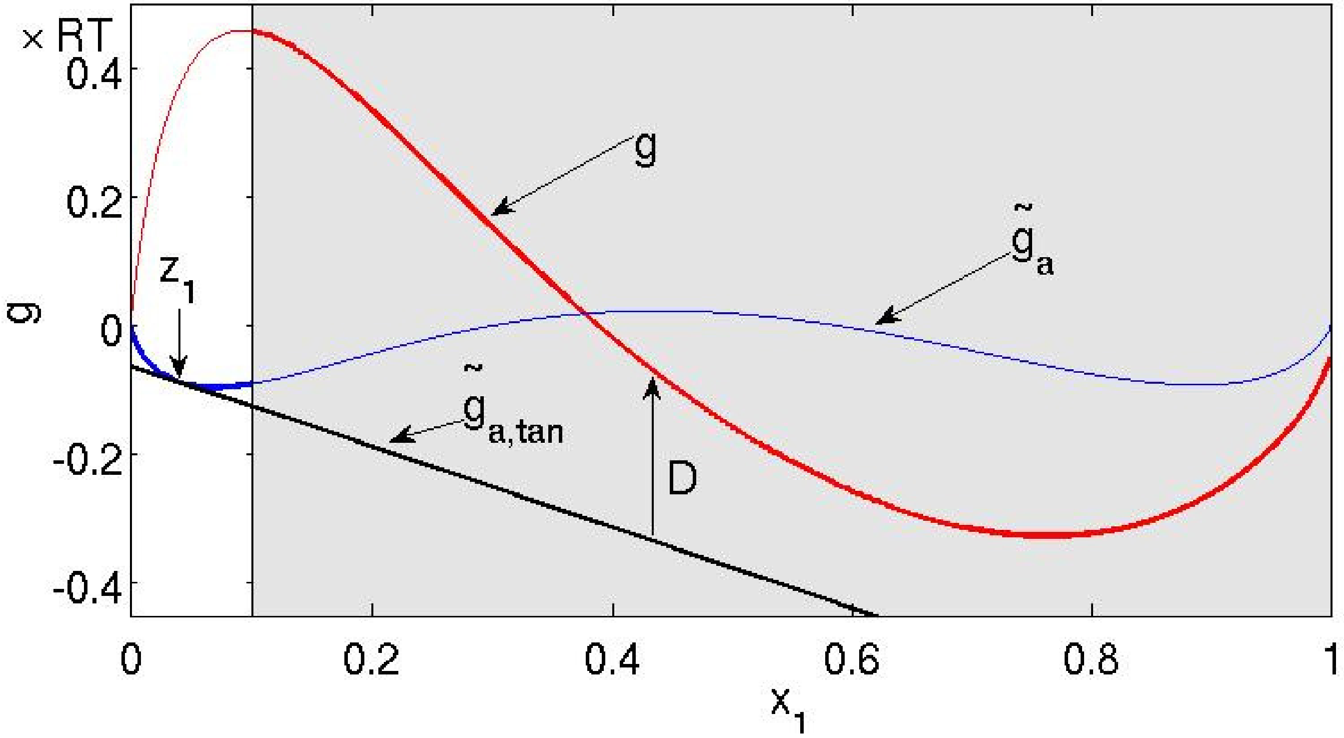

Figure 3: Phase stability analysis for a test (feed) phase of composition (observable mole fraction) $z_1 = 0.04$ in a hypothetical binary salt(1)/solvent(2) system. This test phase is stable.

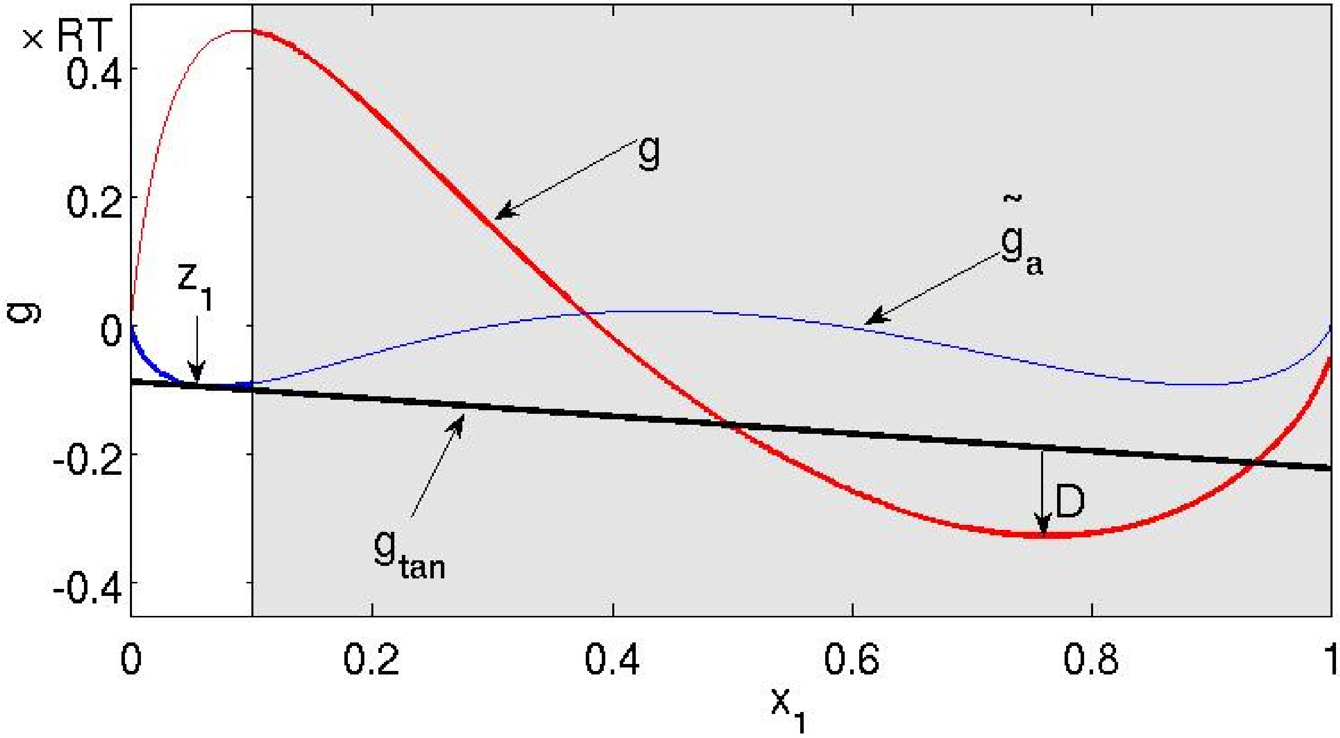

Figure 4: Phase stability analysis for a test (feed) phase of composition (observable mole fraction) z_1 = 0.06 in a hypothetical binary salt(1)/solvent(2) system. This test phase is not stable.

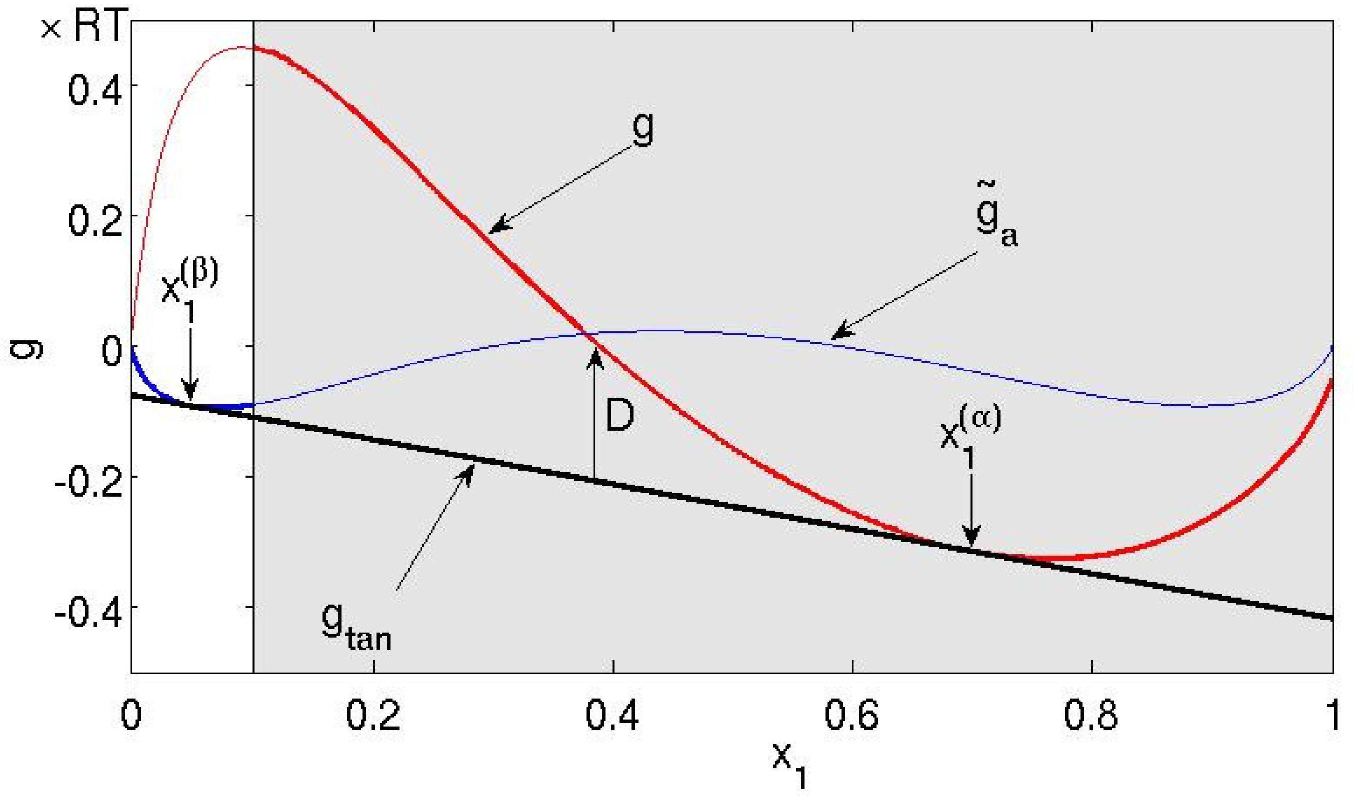

Figure 5: Stable, biphasic LLE, with one molecular phase (α phase) of composition $x_1^{(\alpha)}$ and one dissociated phase (β phase) of composition $x_1^{(\beta)}$.

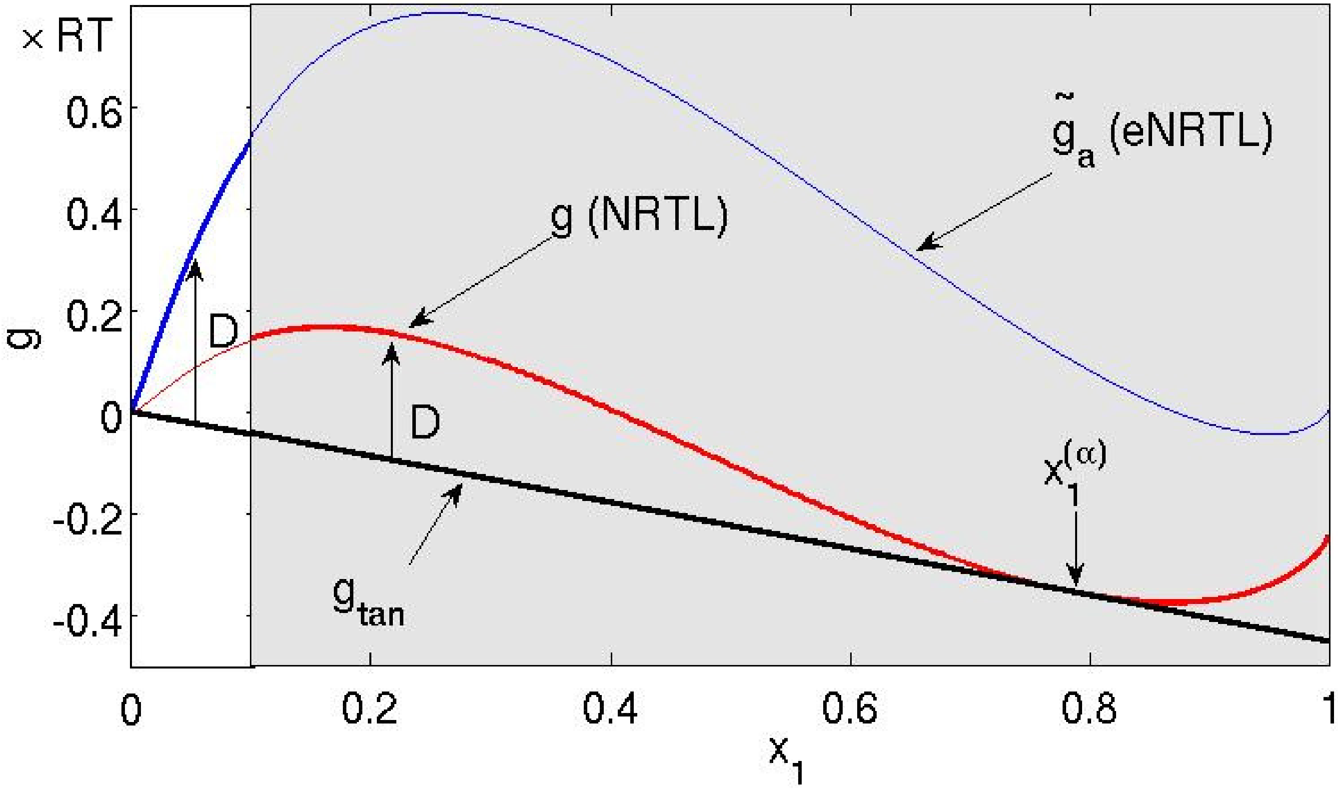

Figure 6: Model curves with parameter solution 1 for [hmim][Tf_2N]/water at 297 K over the entire composition range. See also Fig. 7.

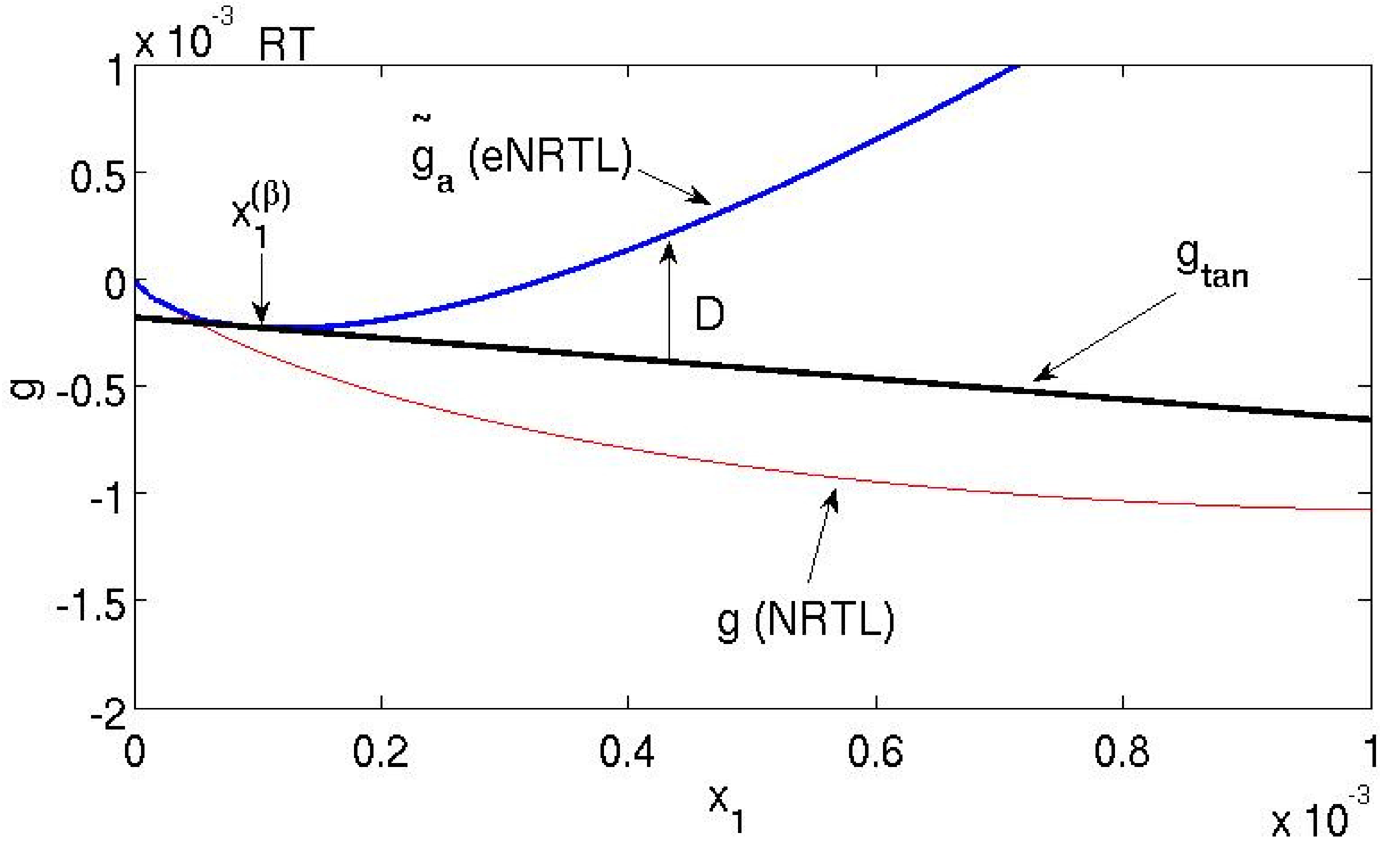

Figure 7: Model curves with parameter solution 1 for [hmim][Tf$_2$N]/water at 297 K over $0 \leq x_1 \leq 0.001$.

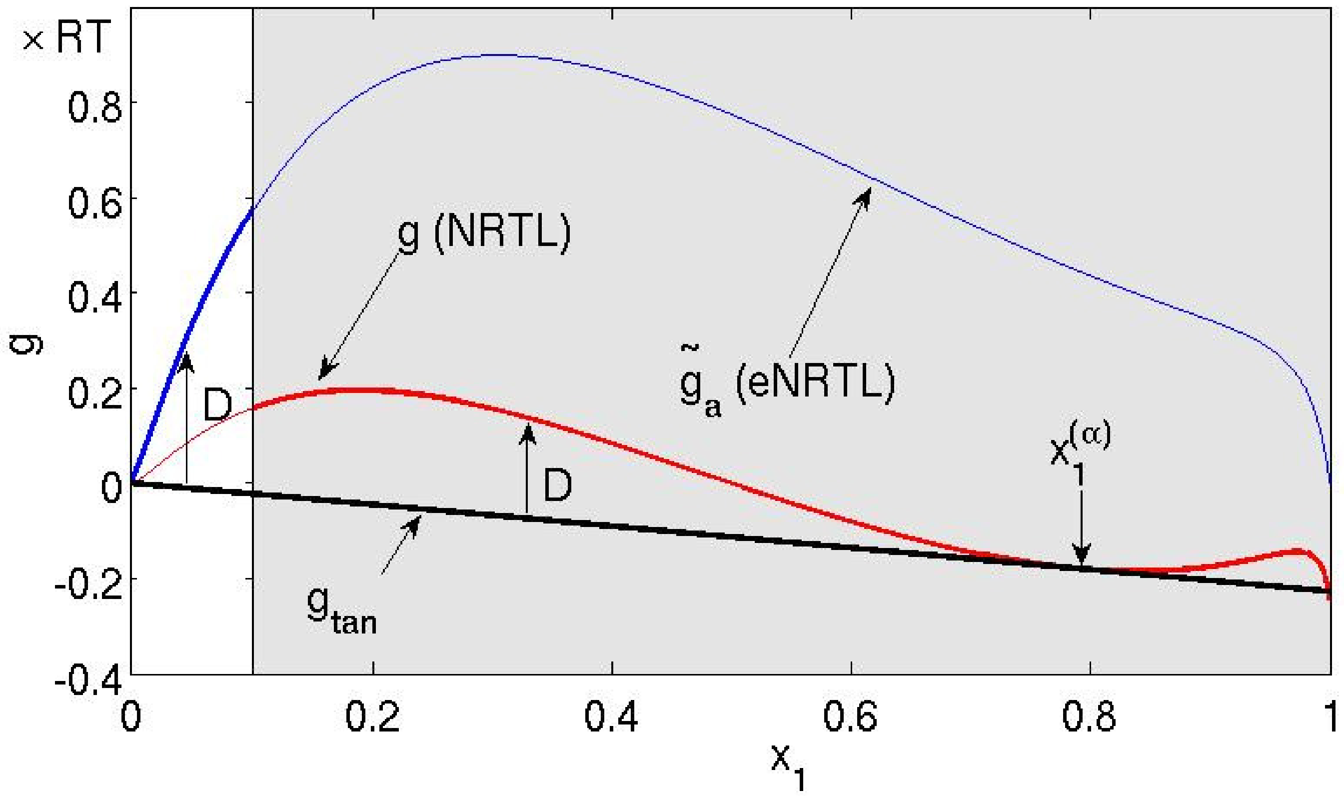

Figure 8: Model curves for parameter solution 4 for [hmim][Tf_2N]/water at 297 K. The tangent line also has a point of tangency with the $\tilde{g}_a$ (eNRTL) curve at $x_1^{(\beta)} = 9.445 \times 10^{-5}$. See also Fig. 9.

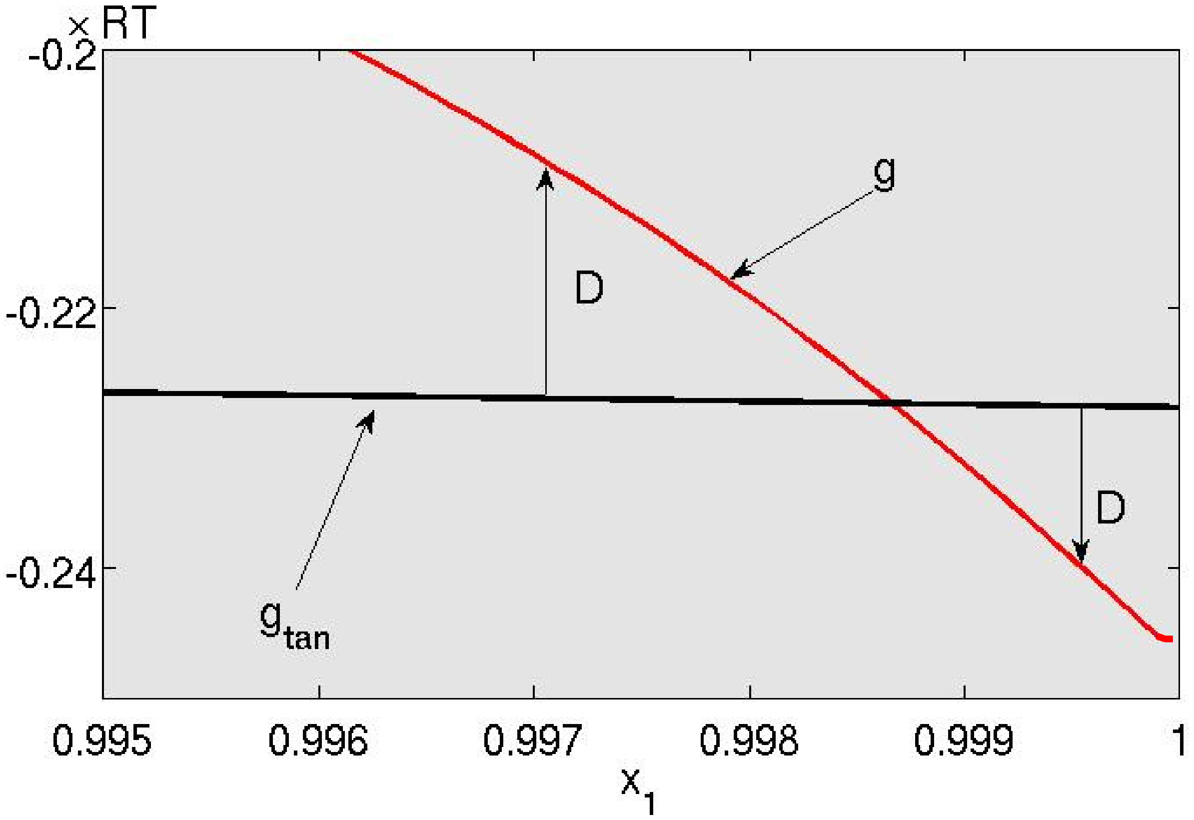

Figure 9: Model curves for parameter solution 4 for [hmim][Tf$_2$N]/water at 297 K over $0.995 \le x_1 \le 1$.

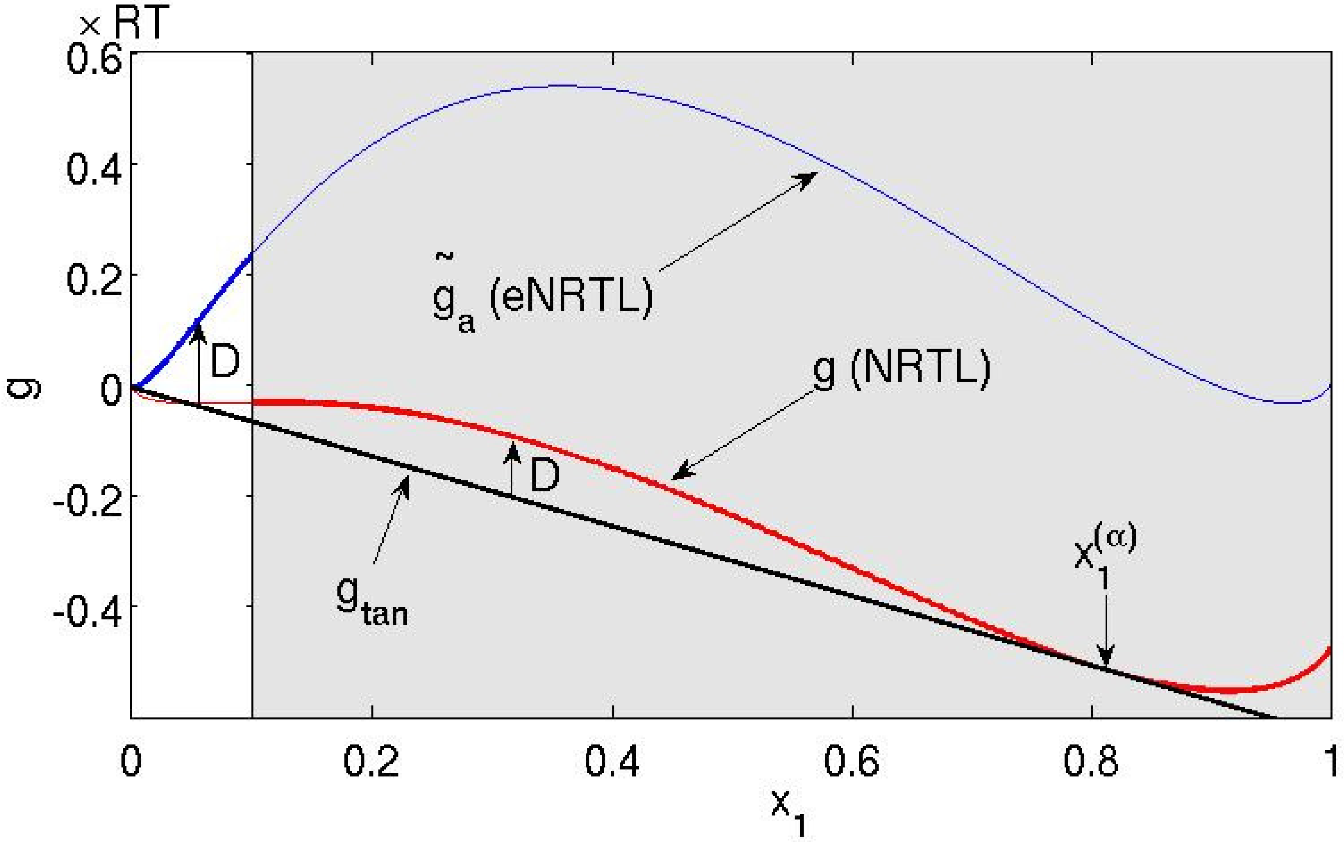

Figure 10: Model curves with parameter solution 4 for [bmpy][Tf$_2$N]/water at 297 K. The tangent line also has a point of tangency with the $\tilde{g}_a$ (eNRTL) curve at $x_1^{(\beta)} = 0.0023$.