Refined Electrolyte-NRTL Model: Activity Coefficient Expressions for Application to Multi-Electrolyte Systems

G. M. Bollas
Process Systems Engineering Laboratory, Dept. of Chemical Engineering,
Massachusetts Institute of Technology, Cambridge, MA 02139

C. C. Chen
Aspen Technology Inc., 10 Canal Park, Cambridge, MA 02141

P. I. Barton
Process Systems Engineering Laboratory, Dept. of Chemical Engineering,
Massachusetts Institute of Technology, Cambridge, MA 02139

DOI 10.1002/aic.11485

The influence of simplifying assumptions of the electrolyte-nonrandom two-liquid (NRTL) model in the derivation of activity coefficient expressions as applied to multi-electrolyte systems is critically examined. A rigorous and thermodynamically consistent formulation for the activity coefficients is developed, in which the simplifying assumption of holding ionic-charge fraction quantities constant in the derivation of activity coefficient expressions is removed. The refined activity coefficient formulation possesses stronger theoretical properties and practical superiority that is demonstrated through a case study representing the thermodynamic properties and speciation of dilute to concentrated aqueous sulfuric acid solutions at ambient conditions. In this case study phenomena, such as hydration, ion pairing, and partial dissociation are all taken into account. The overall result of this study is a consistent, analytically derived, short-range interaction contribution formulation for the electrolyte-NRTL activity coefficients and a very accurate representation of aqueous sulfuric acid solutions at ambient conditions at concentrations up to 50 molal. © 2008 American Institute of Chemical Engineers *AIChE J*, 54: 1608–1624, 2008

Keywords: electrolyte thermodynamics, electrolyte-NRTL, ionic activity coefficients, multi-electrolyte solutions, mixing of electrolytes, aqueous sulfuric acid

Introduction

The electrolyte-nonrandom two-liquid (NRTL) model[1] has been extensively applied to represent thermodynamic properties of various electrolyte systems. Examples include mean ionic activity coefficients of aqueous strong electrolytes[1,2] and aqueous organic electrolytes,[3] phase behavior of weak electrolytes,[1] strong acids,[4] mixed-solvent electrolytes,[5] and so forth. The main reasons for its wide acceptance and application are the incorporation of semi-fundamental chemical theories such as the NRTL model for the simulation of local

---

Correspondence concerning this article should be addressed to G. M. Bollas at bollas@mit.edu.

neighborhoods in a solution, applicability to a large variety of systems without any restrictions on the number of electrolytes and solvents or on the molality range, the ability to predict the effect of temperature on the solution behavior and algebraic simplicity. The electrolyte-NRTL model provides a solid thermodynamic framework for computing various electrolyte thermodynamic properties, including mean ionic activity coefficients, osmotic coefficients, and solute and solvent fugacities. The rigorous and accurate computation of electrolyte thermodynamic properties forms a sound foundation for phase equilibrium calculations (that is, vapor-liquid equilibrium, liquid–liquid equilibrium and salt solubilities) and for the simulation of chemical processes involving electrolytes.

Nowadays, with the advent of novel electrolyte processes such as thermochemical cycles for hydrogen production,[6] the demand for accurate electrolyte models is higher than ever. Specifically, models are needed for the description of electrolyte systems at extremely high temperatures and concentrations, while the prediction of speciation has become more prominent. In view of these challenges it becomes important to critically examine the accuracy of the electrolyte-NRTL model and its assumptions when applied to multi-electrolyte, mixed-solvent systems. Furthermore, the effects of hydration and complex formation, which play an important role in the predictive accuracy of local composition models, such as the electrolyte-NRTL model, have to be comprehensively studied and appropriately incorporated in the model. Hydration chemistry, and its incorporation into the Gibbs free energy function and into the derived activity coefficients, has been demonstrated years ago.[7,8] Typically in these studies, hydration of the proton is considered and an average-constant hydration number is usually assumed. In more recent work,[9] hydration equilibria were studied and a new remarkably simple equation was proposed to represent the relation of cationic hydration with the water-cations short-range interactions. It is generally accepted[7–12] that the inclusion of hydration equilibria will increase both the accuracy and the fundamental nature of electrolyte models.

In the electrolyte-NRTL model, the existence of different ions of the same charge sign is accounted for with the choice of reference states and the use of mixing rules for binary parameters of the functions describing short-range interactions. The exact influence of these modeling assumptions is not always transparent, because ultimately the model is fitted against experimental data. But, when the accurate prediction of detailed speciation is important, these modeling assumptions can become of higher significance. In this study, the electrolyte-NRTL model is refined by considering the dependence on composition of the ionic fraction quantities, which are used to compute the reference state of the ions and to convert the salt-specific binary parameters to ion-specific quantities, during the differentiation of the NRTL Gibbs free energy term. This adds to the consistency and accuracy of the model. Moreover, the influence of hydration equilibria on the predictive accuracy of the model is examined. The results are in agreement with previous work[2] for low molalities, where an average hydration number of 3 (per mole of electrolyte) was found to represent many electrolyte systems accurately. On the other hand, the decline of the hydration number with increasing molality, because of the decrease in water activity, is also shown to be important. This study has resulted in a new versatile model, in which two options can be used for cationic hydration: depending on the concentration range of interest, either the hydration number can be considered constant, or the stepwise hydration equilibrium method can be applied for the calculation of the decline of hydration with increasing electrolyte concentration.

As a demonstration of this new model, results for the aqueous solution of sulfuric acid are presented. The aqueous sulfuric acid system, even at ambient conditions, poses great challenges for the existing electrolyte models. Reasons include the partial dissociation of the bisulfate ion, the hydronium and bisulfate complex formation, the different extents of proton hydration (with respect to the initial H_2SO_4 molality) and the partial dissociation of sulfuric acid at high concentrations (because of the elimination of free water). Attempts to model the sulfuric acid system have led to accurate thermodynamic representations of the system,[13–17] but these are deficient in the prediction of speciation. Considering the complexity of the aqueous sulfuric acid system and the large number of proton hydrates that can exist in this solution,[18] it is indeed an intriguing problem to predict the speciation. At low electrolyte concentrations, hydration can be considered of constant extent, but with increasing concentration the decreasing extent of hydration can be the dominating factor in the accuracy of model predictions. Furthermore, the sulfuric acid water mixture (although a binary system) is in fact a multi-electrolyte (because of the coexistence of the bisulfate and sulfate anions) and mixed-solvent (because of the partial dissociation of the sulfuric acid at high concentrations) system.

In conclusion, the combination of a representative chemistry model and thermodynamically consistent activity coefficient expressions with the virtues of the electrolyte-NRTL model lead to a very accurate representation of the sulfuric acid system. Furthermore, the proposed representation possesses better extrapolation capabilities when concentrated electrolyte solutions are examined.

Refinement of the Electrolyte-NRTL Model

The electrolyte-NRTL model utilizes the theory of the nonrandom two-liquid approach for the simulation of short-range interactions between species[19] and the Pitzer–Debye–Hückel (PDH) formula[20] for the long-range electrostatic interactions. In the case of mixed-solvent solutions, the Born equation[21] is utilized to account for the Gibbs free energy of transfer of the ionic species from the infinite dilution state in a mixed solvent to the infinite dilution state in the aqueous phase. Using the above formalism, the expression for the excess Gibbs free energy in the electrolyte-NRTL model is[22]

$$G^{*,\mathrm{ex}} = G^{*,\mathrm{SR}} + G^{*,\mathrm{LR}} + \Delta G^{*,\mathrm{Born}}.$$

Short-range (NRTL) contribution

The short-range interactions are modeled on the basis of the local composition concept. To account for the short-range interactions three types of local neighborhoods are considered: the immediate neighborhoods of cations, anions, and molecular species. The assumptions adopted regarding the liquid lattice structure of electrolyte systems in the development of the electrolyte-NRTL model, besides the simplification of disregarding the nonideal entropy of mixing (considering that it is negligible compared with the heat of mixing) of the NRTL approach, are local electroneutrality and like ion repulsion. Under these assumptions, the full expression of the electrolyte-NRTL molar excess Gibbs free energy short-range term, expressed in the symmetrical scale, is

$$\frac{\underline{G}^{\mathrm{SR}}}{\Re T} = \sum_m X_m \frac{\sum_j X_j G_{jm}\tau_{jm}}{\sum_j X_j G_{jm}} + \sum_c X_c \sum_a \left(\frac{X_a}{\sum_{a'} X_{a'}}\right) \frac{\sum_j X_j G_{jc.ac}\tau_{jc.ac}}{\sum_j X_j G_{jc.ac}} + \sum_a X_a \sum_c \left(\frac{X_c}{\sum_{c'} X_{c'}}\right) \frac{\sum_j X_j G_{ja.ca}\tau_{jc.ca}}{\sum_j X_j G_{ja.ca}}, \quad (1)$$

where τ is the difference between the Gibbs free energy of interactions between species, G denotes the NRTL binary parameters for the energy of interactions, the summations over j are for all species, m denotes molecular species, a and a' denote anionic species, and c and c' denote cationic species. By definition, the contribution of short-range interactions to the nonideality of the mixture expressed in terms of the rational activity coefficient of species j is given by the partial derivative of the excess Gibbs free energy function

$$\ln \gamma_j^{\mathrm{SR}}(T, P, \mathrm{x}) \equiv \frac{1}{\Re T} \overline{G}_j^{\mathrm{SR}} = \frac{1}{\Re T} \left(\frac{\partial G^{\mathrm{SR}}}{\partial N_j}\right)_{T,P,N_{k \neq j}}.$$

At constant temperature (T) and pressure (P) differentiation with respect to $N_{c,a}$ (cationic or anionic moles) of the excess Gibbs free energy resulting from short-range interactions (Eq. 1) gives:

$$\left(\frac{\partial\left(\sum_j N_j \underline{G}^{\mathrm{SR}}\right)}{\partial N_{c,a}}\right)_{T,P,N_m,N_{ca \neq c,a}} = \frac{\partial\left(\sum_m Z_m N_m \frac{\sum_j Z_j N_j G_{jm}\tau_{jm}}{\sum_k Z_j N_j G_{jm}}\right)}{\partial N_{c,a}} + \frac{\partial\left(\sum_c Z_c N_c \sum_a \frac{Z_a N_a}{\sum_{a'} Z_{a'} N_{a'}} \frac{\sum_j Z_j N_j G_{jc.ac}\tau_{jc.ac}}{\sum_j Z_j N_j G_{jc.ac}}\right)}{\partial N_{c,a}} + \frac{\partial\left(\sum_a Z_a N_a \sum_c \frac{Z_c N_c}{\sum_{c'} Z_{c'} N_{c'}} \frac{\sum_j Z_j N_j G_{ja.ca}\tau_{ja.ca}}{\sum_j Z_j N_j G_{ja.ca}}\right)}{\partial N_{c,a}}. \quad (2)$$

The sum of anionic fractions in the second term of the right hand side in Eqs. 1 and 2 comes from the assumption for the reference state of the ions, that is, the hypothetical homogeneously mixed, completely dissociated liquid electrolyte, in which each central cationic species is surrounded only by anionic species. Similarly, the sum of cationic fractions in the third term of the right hand side in Eqs. 1 and 2 is the result of the assumption that at the hypothetical pure electrolyte reference state each central anionic species is surrounded only by cationic species.

In the original[1] and the generalized[22] electrolyte-NRTL models these quantities were defined as

$$Y_a \equiv \frac{X_a}{\sum_{a'} X_{a'}}, \quad Y_c \equiv \frac{X_c}{\sum_{c'} X_{c'}}. \quad (3)$$

The ionic fraction quantities of Eq. 3, Y_a and Y_c, were held constant during the differentiation of the NRTL excess Gibbs energy term. In addition, the same simplifying assumption was made for the dependence assumed for the interaction parameters (τ_{ij}) and the energies of interaction (G_{ij}) on the ionic fraction quantities shown in Eqs. 4 and 5. Specifically, the derivatives of the terms G_{cm}, G_{am} and τ_{cm}, τ_{am}, and consequently of the terms $G_{ma.ca}$, $G_{mc.ac}$ and $\tau_{ma.ca}$, $\tau_{mc.ac}$ with respect to N_c or N_a were considered zero.

$$G_{cm} = \sum_a \frac{X_a G_{ca.m}}{\sum_{a'} X_{a'}}, \quad \tau_{cm} = -\frac{\ln G_{cm}}{\alpha_{ca.m}},$$
$$\tau_{mc.ac} = \tau_{cm} - \tau_{ca.m} + \tau_{m.ca}, \quad G_{mc.ac} = \exp(-\alpha_{ca.m}\tau_{mc.ac}), \quad (4)$$

$$G_{am} = \sum_c \frac{X_c G_{ca.m}}{\sum_{c'} X_{c'}}, \quad \tau_{am} = -\frac{\ln G_{am}}{\alpha_{ca.m}},$$
$$\tau_{ma.ca} = \tau_{am} - \tau_{ca.m} + \tau_{m.ca}, \quad G_{ma.ca} = \exp(-\alpha_{ca.m}\tau_{ma.ca}). \quad (5)$$

With the cationic and anionic fraction quantities (Y_a and Y_c) held constant during the derivation of the NRTL terms of the activity coefficients, the NRTL excess Gibbs free energy differentiation is straightforward and it results in simple and easily usable expressions with a minimum number of adjustable parameters. However, holding Y_a and Y_c constant during the derivation of the activity coefficient expressions does introduce an inconsistency between the excess Gibbs free energy that describes the short-range interactions, and the corresponding activity coefficients. To illustrate the inconsistency referred to in this article, the reader can verify that minimization of the Gibbs free energy based on Eq. 1 does not yield the same result as the so-called equilibrium constant method using the derived activity coefficients in the case of partially dissociated multi-electrolyte systems. Therefore, it appears imperative to re-examine this simplifying assumption and consider the ionic fraction quantities Y_a and Y_c composition dependent during the differentiation of the NRTL excess Gibbs free energy function (Eq. 2). The analytical differentiation of the excess Gibbs free energy yields the following expression for the symmetrical activity coefficients of the cations

$$\frac{1}{Z_c}\ln\gamma_c^{\mathrm{SR}} = \sum_a \frac{X_a}{\sum_{a'} X_{a'}} \frac{\sum_j X_j G_{jc.ac}\tau_{jc.ac}}{\sum_j X_j G_{jc.ac}} + \sum_m \frac{X_m}{\sum_j X_j G_{jm}} \left[\begin{array}{l} G_{cm}\left(\tau_{cm} - \frac{\sum_j X_j G_{jm}\tau_{jm}}{\sum_j X_j G_{jm}}\right) \\ +\sum_a \frac{X_a}{\sum_{c'} X_{c'}}(G_{ca.m} - G_{cm})\left(\frac{\alpha_{ca.m}\tau_{cm}-1}{\alpha_{ca.m}} - \frac{\sum_j X_j G_{jm}\tau_{jm}}{\sum_j X_j G_{jm}}\right) \end{array}\right]$$

$$+\sum_a X_a \left\{\begin{array}{l} \sum_{c'} \frac{X_{c'}}{\sum_{c''} X_{c''}} \frac{1}{\sum_j X_j G_{ja.c'a}} \left[G_{ca.c'a}\left(\tau_{ca.c'a} - \frac{\sum_j X_j G_{ja.c'a}\tau_{ja.c'a}}{\sum_j X_j G_{ja.c'a}}\right)\right. \\ \left. +\sum_m \frac{X_m}{\sum_{c''} X_{c''}} G_{ma.c'a} \frac{G_{ca.m}-G_{am}}{G_{am}} \left(\frac{\alpha_{ca.m}\tau_{ma.c'a}-1}{\alpha_{ca.m}} - \frac{\sum_j X_j G_{ja.c'a}\tau_{ja.c'a}}{\sum_j X_j G_{ja.c'a}}\right)\right] \\ +\frac{1}{\sum_{c''} X_{c''}} \left(\frac{\sum_j X_j G_{ja.ca}\tau_{ja.ac}}{\sum_j X_j G_{ja.ca}} - \sum_{c'} \frac{X_{c'}}{\sum_{c''} X_{c''}} \frac{\sum_j X_j G_{ja.c'a}\tau_{ja.c'a}}{\sum_j X_j G_{ja.c'a}}\right) \end{array}\right\}. \quad (6)$$

The final expression for the activity coefficients of anions in the symmetrical scale is

$$\frac{1}{Z_a}\ln\gamma_a^{\mathrm{SR}} = \sum\nolimits_c \frac{X_c}{\sum_{c'} X_{c'}} \frac{\sum_j X_j G_{ja.ca}\tau_{ja.ca}}{\sum_j X_j G_{ja.ca}} + \sum_m \frac{X_m}{\sum_j X_j G_{jm}} \left[\begin{array}{l} G_{am}\left(\tau_{am} - \frac{\sum_j X_j G_{jm}\tau_{jm}}{\sum_j X_j G_{jm}}\right) \\ +\sum_c \frac{X_c}{\sum_{a'} X_{a'}}(G_{ca.m} - G_{cm})\left(\frac{\alpha_{ca.m}\tau_{cm}-1}{\alpha_{ca.m}} - \frac{\sum_j X_j G_{jm}\tau_{jm}}{\sum_j X_j G_{jm}}\right) \end{array}\right]$$

$$+\sum_c X_c \left\{\begin{array}{l} \sum_{a'} \frac{X_{a'}}{\sum_{a''} X_{a''}} \frac{1}{\sum_j X_j G_{jc.a'c}} \left[G_{ac.a'c}\left(\tau_{ac.a'c} - \frac{\sum_j X_j G_{jc.a'c}\tau_{jc.a'c}}{\sum_j X_j G_{jc.a'c}}\right)\right. \\ \left. +\sum\nolimits_m \frac{X_m}{\sum_{a''} X_{a''}} G_{mc.a'c} \frac{G_{ca.m}-G_{cm}}{G_{cm}} \left(\frac{\alpha_{ca.m}\tau_{ma.a'c}-1}{\alpha_{ca.m}} - \frac{\sum_j X_j G_{jc.a'c}\tau_{jc.a'c}}{\sum_j X_j G_{jc.a'c}}\right)\right] \\ +\frac{1}{\sum_{a''} X_{a''}} \left(\frac{\sum_j X_j G_{jc.ac}\tau_{jc.ac}}{\sum_j X_j G_{jc.ac}} - \sum\nolimits_{a'} \frac{X_{a'}}{\sum_{a''} X_{a''}} \frac{\sum_j X_j G_{jc.a'c}\tau_{jc.a'c}}{\sum_j X_j G_{jc.a'c}}\right) \end{array}\right\}. \quad (7)$$

The activity coefficients of the uncharged species remain the same as in the original electrolyte-NRTL formulation

$$\ln\gamma_m^{\mathrm{SR}} = \frac{\sum_j X_j G_{jm}\tau_{jm}}{\sum_j X_j G_{jm}} + \sum_{m'} \frac{X_{m'} G_{mm'}}{\sum_j X_j G_{jm'}} \left(\tau_{mm'} - \frac{\sum_j X_j G_{jm'}\tau_{jm'}}{\sum_j X_j G_{jm'}}\right)$$
$$+\sum_c \sum_a \frac{X_a}{\sum_{a'} X_{a'}} \frac{X_c G_{mc.ac}}{\sum_j x_j G_{jc.ac}} \left(\tau_{mc.ac} - \frac{\sum_j X_j G_{jc.ac}\tau_{jc.ac}}{\sum_j X_j G_{jc.ac}}\right)$$
$$+\sum_a \sum_c \frac{X_c}{\sum_{c'} X_{c'}} \frac{X_a G_{ma.ca}}{\sum_j X_j G_{ja.ca}} \left(\tau_{ma.ca} - \frac{\sum_j X_j G_{ja.ca}\tau_{ja.ca}}{\sum_j X_j G_{ja.ca}}\right). \quad (8)$$

It should be noted that in Eqs. 6–8 and in the following analysis the nonrandomness factors ($\alpha_{ca.m}$, $\alpha_{m.ca}$, $\alpha_{ca.ca'}$) of all the electrolytes in the solution were considered equal (typically,[1,5] being assigned the value of $\alpha_{ca.m} = \alpha_{m.ca} = \alpha_{ca.ca'} = 0.2$ for salt-solvent, salt-salt interactions and $\alpha_{mm'} = 0.3$ for solvent-solvent interactions). The consideration of different nonrandomness factors would yield additional terms in Eqs. 6 and 7. The analytical expressions for the case of different nonrandomness factors for each electrolyte are given in Appendix I.

To normalize the activity coefficients to the unsymmetrical scale the corresponding activity coefficients at the infinite dilution limit of the aqueous solution have to be calculated:

$$\frac{\ln\gamma_c^{\mathrm{SR},\infty}}{Z_c} = \sum_a \frac{X_a}{\sum_{a'} X_{a'}} \tau_{wc.ac} + G_{cw}\tau_{cw} + \sum_a \frac{X_a}{\sum_{c'} X_{c'}} (G_{ca.w} - G_{aw})$$
$$\times \frac{\alpha_{ca.w}\tau_{aw} - 1}{\alpha_{ca.w}} - \sum_a X_a \left[\begin{array}{l} \sum_{c'} \frac{X_{c'}}{\sum_{c''} X_{c''}} \frac{1}{\sum_{c''} X_{c''}} \frac{(G_{ca.w} - G_{aw})}{\alpha_{ca.w} G_{aw}} \\ -\frac{1}{\sum_{c''} X_{c''}} \left(\tau_{wa.ca} - \sum_{c'} \frac{X_{c'}}{\sum_{c''} X_{c''}} \tau_{wa.c'a}\right) \end{array}\right], \quad (9)$$

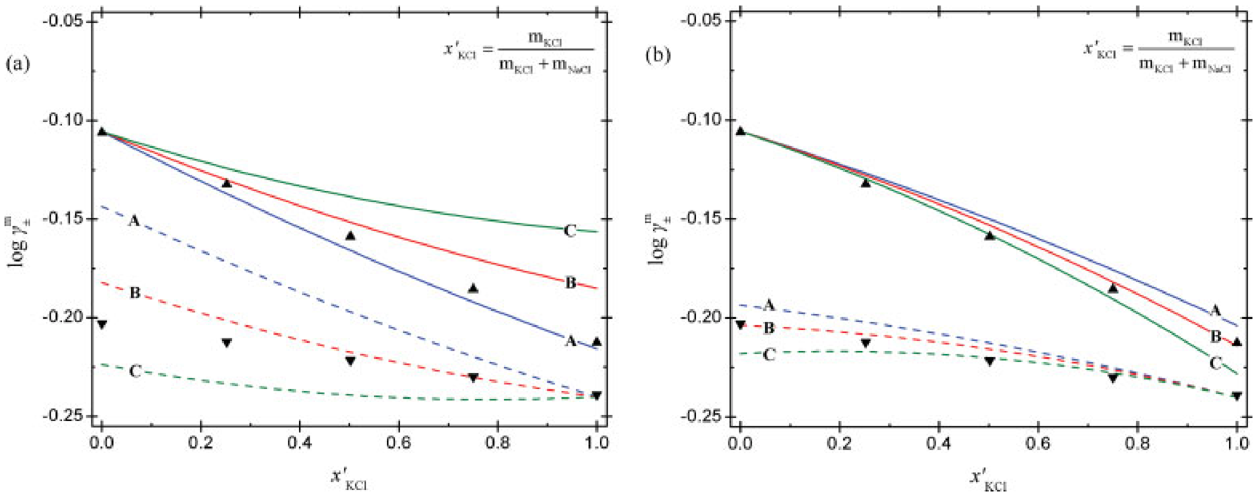

Figure 1. Harned's rule plot of mean ionic activity coefficient of the NaCl-KCl-H$_2$O solution at constant total molality of 4 (a) original eNRTL and (b) refined eNRTL (solid lines represent the mean activity coefficient of NaCl, dashed lines represent the mean activity coefficient of KCl; A: $\tau_{\mathrm{NaCl \cdot KCl}} = 0.00$; B: $\tau_{\mathrm{NaCl \cdot KCl}} = 0.25$; C: $\tau_{\mathrm{NaCl \cdot KCl}} = 0.50$; the data points are the respective values proposed by Robinson[23]: ▲ NaCl, ▼ KCl).

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

$$\begin{aligned}\frac{\ln\gamma_a^{\mathrm{SR},\infty}}{Z_a} &= \sum_c \frac{X_c}{\sum_{c'} X_{c'}}\tau_{wa.ca} + G_{aw}\tau_{aw} \\ &\quad + \sum_c \frac{X_c}{\sum_{a'} X_{a'}} \frac{(G_{ca.w}-G_{cw})(\alpha_{ca.w}\tau_{cw}-1)}{\alpha_{ca.w}} \\ &\quad - \sum_c X_c \left[\begin{array}{l} \sum_{a'} \frac{X_{a'}}{\sum_{a''}X_{a'}} \frac{1}{\sum_{a''}X_{a''}} \frac{(G_{ca.w}-G_{cw})}{\alpha_{ca.w}G_{cw}} \\ -\frac{1}{\sum_{a''}X_{a''}}\left(\tau_{wc.ac} - \sum_{a'}\frac{X_{a'}}{\sum_{a''}X_{a''}}\tau_{wc.a'c}\right)\end{array}\right]. \end{aligned} \tag{10}$$

The refined activity coefficient formulations presented in Eqs. 6–10 are considerably more complex than those of the original electrolyte-NRTL model (e.g., only the first two terms of the activity coefficients at infinite dilution exist in the original formulation). Its advantage is thermodynamic consistency. Moreover, the formulation presented in Eqs. 6–10 provides stronger predictive capability for multi-electrolyte solutions. A simple example of the latter is given in Figure 1, where the effect of mixing sodium chloride with potassium chloride in aqueous solutions of constant total molality is shown. The mean activity coefficient of each salt as predicted by the two models (the original electrolyte-NRTL–Figure 1a and the new formulation denoted as "refined eNRTL"–Figure 1b) for various salt-salt interaction parameters are compared with the respective values proposed by Robinson.[23,24] In this case study, the values of $\tau_{\mathrm{NaCl \cdot H_2O}} = -4.5916$, $\tau_{\mathrm{H_2O \cdot NaCl}} = 9.0234$, $\tau_{\mathrm{KCl \cdot H_2O}} = -4.1341$, $\tau_{\mathrm{H_2O \cdot KCl}} = 8.1354$, and $\alpha_{w.ca} = \alpha_{ca.w} = 0.2$ given in Ref. 1 were used for both models. Comparison of the Figures 1a and b shows that the new activity coefficient formulation provides more reliable extrapolation capability for the mixing of the electrolytes, while both models broadly follow the basic principle of the Harned's rule, i.e., the mean ionic activity coefficient of one electrolyte in an aqueous mixture of electrolytes of constant total molality is directly proportional to the molality of the other electrolyte.[8] A much more comprehensive comparison of the predictive accuracy of the two models is given in Section 4 of this article based on a study of the aqueous sulfuric acid system.

Long-range (PDH) contribution

Because of its empirical effectiveness, the PDH expression is chosen to describe the long-range electrostatic interactions in the electrolyte-NRTL model. It has been shown that the PDH formula is able to represent the long-range electrostatic interactions between ions in aqueous electrolyte solutions from infinite dilution to the fused salt limit.[1,25] In the PDH formula, the electrostatic contribution to the excess Gibbs free energy of an aqueous solution is calculated by Eq. 11:

$$\frac{G^{*,\mathrm{LR}}}{\Re T} = -\sum_j x_j \left(\frac{4A_\phi I_x}{\rho}\right) \ln(1 + \rho I_x^{1/2}), \tag{11}$$

where I_x is the ionic strength of the solution and A_ϕ is the so-called Debye–Hückel parameter, given by Eqs. 12 and 13, respectively:

$$I_x = \sum_i \frac{1}{2} x_i z_i^2, \tag{12}$$

$$A_\phi = \frac{1}{3}(2\pi N_A d_s)^{1/2}\left(\frac{Q_e^2}{\varepsilon_s kT}\right)^{3/2}. \tag{13}$$

The PDH formula is based on a primitive model in the McMillan-Mayer ensemble.[26] The simple addition of the two contributions from long- and short-range interactions is not a consistent way to combine the McMillan–Mayer (MM) ensemble with the customary framework of Lewis and Randal

(LR). The conversion between the MM and LR formalisms has been addressed in the work of Cardoso and O'Connell.[27] Later, Lee[28] summarized the problems and approaches for converting the thermodynamic quantities from the LR framework to the MM one. Similar studies were published recently by Simonin[29] and Breil and Mollerup.[30] According to Cardoso and O'Connell,[27] the PDH formula, and correspondingly the equation presented by Pitzer,[20] for the excess Gibbs free energy of electrostatic interactions is indeed an excess Helmholtz energy, which must be converted to excess Gibbs free energy. The difference is not very significant for the free energy and it is practically negligible for single-solvent solutions, but it becomes more important in the case of mixed-solvent solutions. The reason for this is that when differentiating the excess Gibbs free energy function of Eq. 11 the composition dependent average density and dielectric constant should be differentiated as well. But, since the PDH formula was not derived from an excess Gibbs free energy model, the additional terms that appear in the final expressions for the activity coefficients are spurious and incorrect.

The reference state in the Debye–Hückel theory is the infinite dilution of ionic species in the actual solvent media, which is considered as a dielectric continuum. For mixed-solvent systems the reference state, for which the Debye–Hückel theory is valid, is infinite dilution in a hypothetical medium of mixed-solvent composition. The properties of the mixed-solvent medium, namely the average density and dielectric constant can be calculated with the use of simple composition averaged mixing rules. As mentioned, this gives rise to an inconsistency between the derived activity coefficients and the Gibbs free energy of the solution. Practically, the excess free energy given by Eq. 11 should not be used in a Gibbs free energy minimization approach, as this would lead to salting out of the solvent with the highest dielectric constant. However, in this article the equilibrium constant method is used for the simulation of chemical equilibria in electrolyte solutions, hence this issue is not of primary importance. Nonetheless, this inconsistency is usually accepted to exist as a small error in the electrolyte model, which is not evident, because of the fitting of the parameters that describe short-range interactions. This approach is adopted in this work, that is, the averaged properties of the mixed solvent are computed from the ion-free concentrations and the properties of water and solvents, using Eqs. 14 and 15:

$$\frac{1}{d_s} = \sum_m \frac{x_m}{\sum_{m'} x_{m'}} \frac{1}{d_m}, \tag{14}$$

$$\varepsilon_s = \sum_m \frac{x_m M_m}{\sum_{m'} x_{m'} M_{m'}} \varepsilon_m. \tag{15}$$

Wang and Anderko[31] have proposed a more detailed semi-fundamental formulation to represent dielectric constants of mixed-solvent electrolyte solutions. However, the use of weight averaged values for the dielectric constant of the solvent has been found satisfactory in this and other works.[9,22] The inclusion of a detailed model for the description of the solution averaged properties, as well as the examination of the effect of the MM to LR conversion on the electrolyte-NRTL model will be addressed in a future article. The contribution of the long-range electrostatic interactions to the activity coefficients can be calculated by the original PDH formula, in which the mixing rules of Eqs. 14 and 15 can be applied for the calculation of the Debye–Hückel parameter (A_ϕ):

$$\ln \gamma_j^{*,\mathrm{LR}} = -A_\phi \left[\frac{2z_j^2}{\rho} \ln\left(1 + \rho I_x^{1/2}\right) + \frac{z_j^2 I_x^{1/2} - 2 I_x^{3/2}}{1 + \rho I_x^{1/2}} \right].$$

Born term correction

In the case of mixed-solvent systems the reference state for the short-range interactions term in the Gibbs free energy function is the infinitely diluted aqueous solution, whereas the reference state for the long-range interactions term is infinite dilution in the mixed-solvent medium. To correct this inconsistency the Born equation[21] is used to account for the energy needed to transfer the ionic species from the infinitely diluted mixed-solvent medium to the infinitely diluted aqueous solution. The Born correction applies to the unsymmetrical PDH expressions for the excess Gibbs free energy

$$\frac{\Delta \underline{G}^{*,\mathrm{Born}}}{\Re T} = \frac{Q_e^2}{2kT} \left(\frac{1}{\varepsilon_s} - \frac{1}{\varepsilon_w} \right) \sum_i \frac{x_i z_i^2}{r_i} 10^{-2} \tag{16}$$

and to the activity coefficients of the ions (with $z_j = 0$ for molecular species)

$$\Delta \ln \gamma_j^{*,\mathrm{Born}} = \frac{Q_e^2}{2kT} \left(\frac{1}{\varepsilon_s} - \frac{1}{\varepsilon_w} \right) \frac{z_j^2}{r_j} 10^{-2}.$$

It should be noted that the inconsistency due to the difference between the MM and LR scales is also present in Eq. 16. Nevertheless, Eqs. 11 and 16 are presented in this article in their original form for reasons of consistency with the literature.

Hydration and Association

The electrolyte-NRTL model was modified by Chen et al.[2] to account for hydration, partial electrolyte's dissociation and ions association. The hydration, dissociation and association chemistry used follows the analysis of Robinson and Stokes.[8] For strong electrolytes the mean molal stoichiometric activity coefficient ($\ln \gamma_\pm^{\mathrm{m}}$) at the experimentalist's level (E) is calculated from its respective value for a hydrated solution at the model level (M) with the following equation

$$\ln \gamma_\pm^{m(E)} = \ln \gamma_\pm^{(M)} - \frac{h}{v} \ln(a_w) - \ln\left(1 + \frac{v - h}{S}\right),$$

where v is the sum of stoichiometric coefficients of the cation and the anion in the electrolyte, h is the total hydration number of the electrolyte, a_w is the activity of water, $\gamma_\pm^{(M)}$ is the mean rational stoichiometric activity coefficient at the model level, and S is the number of moles of solvent per mole of electrolyte, taken as anhydrous, in the solution.

At high concentrations or in solutions of weak electrolytes, partial dissociation of the electrolyte ($N_s^{(M)}$) and ions association to form ionic pairs ($N_p^{(M)}$) cannot be neglected. In this case the mean molal stoichiometric activity coefficient of the electrolyte is

$$\begin{aligned}\ln \gamma_{\pm}^{m(E)} = \ln \gamma_{\pm}^{(M)} - \frac{h}{v} \ln a_w - \ln \Bigg\{ 1 + S^{-1}. \Bigg[v - h. \\ + \frac{N_p^{(M)}}{m} \left(1 - v_{c,p}^{(M)} - v_{a,p}^{(M)} + v_{c,p}^{(M)} h_c + v_{a,p}^{(M)} h_a \right) \\ + \frac{N_s^{(M)}}{m} \left(1 - v_{c,s}^{(M)} - v_{a,s}^{(M)} + v_{c,s}^{(M)} h_c + v_{a,s}^{(M)} h_a \right) \Bigg] \Bigg\} \\ + \frac{1}{v} \Bigg[v_c \ln \left(1 - \frac{v_{c,p}^{(M)}}{v_c} \frac{N_p^{(M)}}{m} - \frac{v_{c,s}^{(M)}}{v_c} \frac{N_s^{(M)}}{m} \right) \\ + v_a \ln \left(1 - \frac{v_{a,p}^{(M)}}{v_a} \frac{N_p^{(M)}}{m} - \frac{v_{a,s}^{(M)}}{v_a} \frac{N_s^{(M)}}{m} \right) \Bigg]. \qquad (17)\end{aligned}$$

The derivation of Eq. 17 and the assumptions used in the hydration and association theory of Robinson and Stokes[8] are discussed in Appendix II.

In the approach of Robinson and Stokes[8] it is implicitly assumed that the hydration number of an electrolyte is constant and independent of the electrolyte concentration in the solution. This assumption holds for narrow concentration ranges, but when large concentration ranges are considered the assumption loses its physical meaning.[32] It is reasonable to suppose that as the molality of the electrolyte increases, the "free" water (that does not participate in any hydration reaction) decreases, hence the probability of an ion being hydrated declines as well. A thorough analysis of the chemical potentials of H_2O molecules participating in hydration and solvent envelopes was presented by Nesbitt.[33] Recently, Simonin et al.[9] presented a stepwise solvation-equilibrium method for modeling hydration equilibria of cations. In their analysis the water molecule is assumed to interact with an anion in a similar manner to its interaction with other water molecules, hence the hydration of anions can be neglected. This assumption is generally consistent and valid and was adopted in the application of the electrolyte-NRTL model that follows. Using statistical considerations, Simonin et al.[9] were able to extend the relation given by Schönert[34] to electrolyte solutions. They proposed the following remarkably simple equation for the description of the average hydration number of the solution:

$$h_c = n \frac{k_h x_w \ln \gamma_w^{\mathrm{SR}}}{1 + k_h x_w \gamma_w^{\mathrm{SR}}}, \qquad (18)$$

where n is the number of "sites" on a cation available for water binding and k_h is the equilibrium constant for the attachment of a water molecule to a cationic site. For solutions of acids, it follows by the known chemistry of water-acids interaction[35] that the minimum hydration number of the hydrogen cation is 1 (i.e., the hydronium ion represents the state of minimum hydration). The consideration of a non-constant hydration number in the NRTL model gives rise to the issue of whether the interaction parameters of the different forms of a hydrated ion should be considered equal. Simonin et al.[9] presented satisfactory results using this assumption, i.e., that all the hydrates are energetically equivalent. It is possible to relax this hypothesis by introducing phenomenological relations to describe the interaction parameters as functions of hydration, but with the simplifying assumption of negligible effect of hydration on the energetic character of the hydrates the number of parameters in the thermodynamic model of the solution remains minimal.

Application to the Aqueous Sulfuric Acid Solution at Ambient Conditions

The solution of aqueous sulfuric acid is of high interest in industry mainly because of its many applications and economic importance. Furthermore, it poses great challenges to electrolyte thermodynamic models, mainly because of the uncertainty in its dissociation products (hydrogen cations, hydronium ions or higher-order hydrated protons, bisulfate and sulfate anions and complexes of all these ions with water molecules) and the complexity that is added to the electrolyte model by the corresponding dissociation and association equilibria. Because of its high importance the aqueous sulfuric acid solution has been extensively studied experimentally during the last century. These works can be categorized as vapor pressure, osmotic coefficient and activity coefficient measurements,[8,36–41] speciation measurements[8,18,35,39,42–59] and thermal properties measurements.[44,60–63]

Experimental data and previous work

The vapor pressures over sulfuric acid solutions reported in the literature are in good agreement. A summary of the total vapor pressure and partial pressures of H_2O, SO_3, and H_2SO_4 as calculated by Vermeulen et al.[64] based on experimental VLE data over the whole concentration range of sulfuric acid was included in Perry's Chemical Engineers' Handbook.[65] On the other hand, the experimental results on speciation are less consistent. Although the presented general trends and curves are in agreement, there is a large deviation in the absolute values of concentrations, which is mainly due to different interpretations of the spectroscopy measurements. Young and Blatz[39] reported a decrease in the dissociation of H_2SO_4 with increasing sulfuric acid concentration. Later, Young et al.[52] showed that the first dissociation of sulfuric acid in water is essentially complete at molalities up to 40. Hood and Reilly[43] confirmed the results of Young et al., but they discussed the asymptotic decrease of undissociated H_2SO_4 at molalities lower than 40. Myhre et al.[50] presented similar but not identical experimental results, by assuming complete dissociation of H_2SO_4. Chen and Irish[42] discussed the existence of $H_3O^+ \cdot h(H_2O) \cdot HSO_4^-$ complexes, whereas a series of articles published by Zarakhani et al.[53–56] and Maiorov and Librovich[45–47] considered complexes of $H_2SO_4 \cdot H_2O$ or $H_2SO_4 \cdot 2H_2O$ and $H_5O_2{}^+$, H_3O^+ hydrates, existing in the solution at concentrations significantly below the H_2SO_4–H_2O equimolar point. The factor analysis of Raman spectroscopic data by Malinowski et al.[48] confirms the increase of undissociated H_2SO_4 with increasing initial sulfuric acid concentration. The extent of hydration of the proton in aqueous sulfuric acid solutions was extensively studied by Robertson and Dunford[35] who presented hydration numbers up to 10 at low molalities. The large deviation of the experimental data presented in the literature is shown graphically in Figure 2. Despite the scatter in the literature

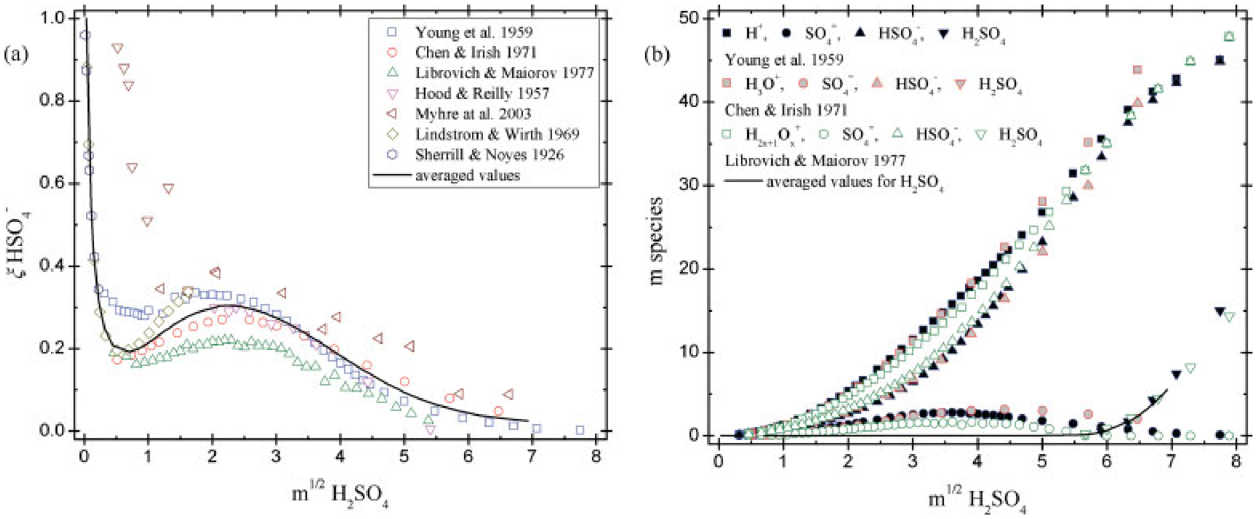

Figure 2. Experimental measurements of the speciation in aqueous sulfuric solution at ambient conditions vs. square root of the initial molality of sulfuric acid, (a) degree of HSO_4^- dissociation and (b) molalities of species (in the data of Librovich and Maiorov[45] the moles of $H_3O^+ \cdot HSO_4^-$ were added to those of HSO_4^- and H_3O^+ for the sake of comparison).

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

data, it is evident that the simplifying assumptions of complete dissociation of sulfuric acid in its aqueous solution, and negligible hydration extent that are usually adopted for the simulation of the H_2SO_4–H_2O system, are not in agreement with the experimental evidence.

Many different approaches have been proposed for the representation of aqueous sulfuric acid at ambient conditions. Pitzer et al.[66] simulated sulfuric acid solutions of concentrations up to 6 molal. Later, Clegg et al.[15] used the Pitzer model to derive a more accurate simulation of the H_2SO_4 solution in the temperature range of 273.15–328.15 K at low molalities. Clegg and Brimblecombe[14] used the mole fraction version of the Pitzer model to represent concentrated (up to 40 m) solutions. Staples[38] developed a model for the representation of sulfuric acid using a much simpler model. Zeleznik[40] proposed another simple model for the representation of the system. Although the results of all the above works are in good agreement, they are deficient in (or do not deal with) the prediction of the solution speciation. Moreover, they are limited to concentration ranges in which H_2SO_4 dissociation can be considered complete, thus resulting in models with a small number of fitted parameters, but incapable of extrapolating. Finally, the existence of hydrates and complexes is disregarded in these approaches.

Many studies have recognized the importance of accurately predicting the speciation of the solution. One of the first approaches was the work of Sanders[67] who adopted the assumption of Zarakhani[53] that neutral forms of H_2SO_4 exist in its aqueous solution at molalities lower than 40, mainly in the form of associated $H_3O^+ \cdot HSO_4^-$ pairs. Sanders considered that all the forms of associated ions can be considered as undissociated H_2SO_4 and presented a model based on the Bromley–Zemaitis electrolyte model[68,69] for the entire concentration range. However, the hydration of the ion complexes affects the mass balance equations (i.e., the elemental balances are different when H_2SO_4 or $H_2SO_4 \cdot H_2O$ are considered), which is not recognized by the assumption of Sanders. Later, Cherif et al.[13] extended the H_2SO_4 model of Pitzer et al.[15,66] by including detailed speciation data in the experimental database used to fit the Pitzer model parameters. They fitted their model to the Raman spectroscopic measurements of Young et al.[52] and Chen and Irish[42] and to the osmotic coefficient data of Robinson and Stokes,[8] Zeleznik[40] and Rard et al.[37] They simulated the aqueous sulfuric acid solution up to 27 molal, but did not consider hydrates, H_2SO_4 dissociation equilibria and ions-water complex formation. Wang et al.[16,70] presented a speciation based version of the UNIQUAC model,[71] which they fitted to the vapor partial pressure data of Gmitro and Vermeulen[36] and heat capacity data of Zaytsev and Aseyev.[60] In their model they used appropriate mixing rules for the estimation of the dielectric constant and density of the mixed-solvent solution and considered the partial dissociation of H_2SO_4. They pointed out the importance of considering an appropriate chemistry model (i.e., the solvation of hydrogen cations to form hydronium ions) especially for highly concentrated solutions, in which hydration affects the chemical equilibria and mass balance, but did not recognize the fact that the average hydration number should be higher than 1 (at least at low concentrations). Another approach for including hydration chemistry in an electrolyte model for the representation of the aqueous sulfuric acid solution up to 6 molal was presented by Simonin et al.,[10] using the MSA-NRTL model.[72] In their approach the bisulfate anion was considered as the ionic pair of a hydrogen cation and a sulfate anion, while hydration was considered for both the hydrogen and sulfate ions. They represented the osmotic coefficient and mean activity coefficient data of Rard et al.,[37] but failed to represent the speciation data of Chen and Irish,[42] Knopf et al.[44] and Myhre et al.[50] It is noteworthy that they fitted a very large number of parameters (the hydration numbers of the ions, the NRTL interaction parameters and the equilibrium constant of the bisulfate dissociation) and noted that thermodynamic quantities, such as the osmotic coefficient and the speciation data, are very sensitive to the model parameters.

Model application–results

The approach followed in this work makes use of the experimental observations of extended cationic hydration at low concentrations and H_2SO_4 partial dissociation at high concentrations of the aqueous sulfuric acid solution. Specifically, the hydration of the hydrogen cation is considered important and the equilibrium of the H_2SO_4 dissociation is taken into account in order to produce a fully descriptive model, capable of extrapolating to higher concentrations. The minimum cationic hydrate was considered to be the hydronium ion, therefore the dissociation equilibria considered and the overall hydration reaction are

$$\begin{aligned}
&H_2SO_4 + H_2O \rightarrow H_3O^+ + HSO_4^-\\
&HSO_4^- + H_2O \rightarrow H_3O^+ + SO_4^=\\
&H_3O^+ + (h_c - 1)\ H_2O \Rightarrow H(h_cH_2O)^+,
\end{aligned}$$

where the last reaction expresses the formation of the average hydrogen cation hydrate (i.e., it describes the overall result of all the possible hydration equilibria).

Two options were considered for the average (with respect to hydration reactions) hydration number of the hydrogen cation (h_c). Namely, it was considered to be constant or to be a function of the short-range water activity as proposed by Simonin et al.[9] and described by Eq. 18. In the hydration model of Robinson and Stokes[8] the assumption of constant hydration extent is supposed to be valid for electrolyte molalities up to $1000/M_w/h$ (see Appendix II). Hence, the model with the constant hydration number was fitted and is considered accurate for solution concentrations up to 20 m. The value of this constant-average hydration number was calculated by fitting the model to the experimental data. For the case study in which the hydration number was treated as a function of the short-range water activity the number of cationic "sites" $n = 4$, proposed by Simonin et al. was used to describe the maximum number of H_2O molecules bound to the hydrogen cation, whereas the average hydration equilibrium constant k_h was fitted to the experimental data. The equilibrium constants of the two dissociation reactions are

$$K_{H_2SO_4} = \exp\left(-\frac{\sum_j v_j \underline{G}_j^{O}}{\Re T}\right) = \frac{a_{H_3O^+}a_{HSO_4^-}}{a_{H_2SO_4}a_{H_2O}}, \tag{19}$$

$$K_{HSO_4^-} = \exp\left(-\frac{\sum_j v_j \underline{G}_j^{O}}{\Re T}\right) = \frac{a_{H_3O^+}a_{SO_4^=}}{a_{HSO_4^-}a_{H_2O}}. \tag{20}$$

Moreover, from the hydration equilibria it follows that[8]

$$a_{H_3O^+} = a_{H(h_cH_2O)^+}a_{H_2O}^{-(h_c-1)}. \tag{21}$$

Substituting in Eqs. 19 and 20, the activity of the hydronium ion by its respective activity after hydration (Eq. 21) results in a multiple dissociation equilibria problem, in which the species considered are the "free" water, the undissociated sulfuric acid, the average hydrated hydrogen cation and the bisulfate and sulfate anions. The corresponding parameter estimation problem results in 8 adjustable binary interaction parameters for the description of "salt"-solvent interactions ($\tau_{H(h_cH_2O)^+\cdot HSO_4^- \leftrightarrow H_2O}$, $\tau_{H(h_cH_2O)^+\cdot SO_4^= \leftrightarrow H_2O}$ and $\tau_{H(h_cH_2O)^+\cdot HSO_4^- \leftrightarrow H_2SO_4}$, $\tau_{H(h_cH_2O)^+\cdot SO_4^= \leftrightarrow H_2SO_4}$), and 1 for the description of "salt"-"salt" interactions ($\tau_{H(h_cH_2O)^+\cdot HSO_4^- \leftrightarrow H(h_cH_2O)^+\cdot SO_4^=}$). Adding to those the hydration number h_c or the hydration equilibrium constant k_h (depending on the model used) the overall result is 10 parameters fitted to the experimental data. The value of 0.2 was assigned to the nonrandomness factors describing the "salt"-solvent and "salt"-"salt" interactions. The equilibrium constants were calculated from the reference chemical potentials taken from the ASPEN Properties database[73] and are given in Table 1.

Table 1. Parameters Used in all the Aqueous Sulfuric Acid Models Examined

	Parameter*
$K_{HSO_4^-}$	1.8925×10^{-4}
$K_{H_2SO_4}$	1.2873×10^{-7}
$r_{H(h_cH_2O)^+}$ (Å)	3.00
$r_{HSO_4^-}$ (Å)	3.00
$r_{SO_4^=}$ (Å)	2.58
ε_{H_2O}	78.54
$\varepsilon_{H_2SO_4}$	101
d_{H_2O} (g cm^{-3})	0.997
$d_{H_2SO_4}$ (g cm^{-3})	1.8305

*The value of $K_{HSO_4^-}$ was taken from Clegg and Brimblecombe,[14] $K_{H_2SO_4}$ was calculated from the standard chemical potentials given in ASPEN Properties Plus database,[73] the average value of 3 Å was assumed for the hydrated protons and bisulfate Born radii, whereas the respective value for the $SO_4^=$ was taken from Babu and Lim.[74] The values of densities and dielectric constants at ambient conditions were retrieved from the ASPEN Properties Plus database.[73]

The experimental database used, consists of the smoothed stoichiometric osmotic coefficient data of Zeleznik,[40] Rard et al.,[37] Staples[38] and Vermeulen et al.[65] and the averaged values for the degree of HSO_4^- dissociation and for the concentration of the undissociated H_2SO_4 shown in Figure 2. To derive these averaged values lower weights were given to the measurements of Librovich and Maiorov,[45] because of their different treatment of their spectroscopy measurements, while the measurements of Hood and Reilly[43] at concentrations below 2 m were removed from the database, as they do not agree with the other available experimental data.[15] Finally, the mean molal stoichiometric activity coefficients proposed by Zeleznik,[40] Rard et al.[37] and Staples[38] were used to examine the validity of the application of the hydration theory of Robinson and Stokes as expressed by Eq. 17. It should be noted that, unlike the comment of Simonin et al.,[10] in this work it was found that the regression over the parallel equilibria of the two dissociation reactions with such a large number of fitting parameters results in an intriguing optimization problem. The so-called feasibility problem (i.e., the solution of the equations to find an initial point) is difficult to solve, which results in initialization problems for the regression program. It was shown in this work that the Gibbs free energy minimization approach implemented into a suitable mathematical programming framework would surely increase the robustness of the fitting algorithm. However, the aforementioned inconsistency of the excess Gibbs free energy

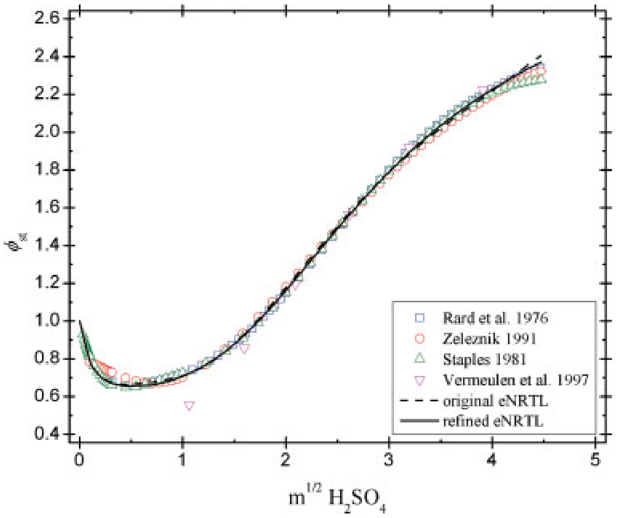

Figure 3. Model predictions and experimental measurements of the stoichiometric osmotic coefficient of aqueous sulfuric acid solutions vs. square root of the initial molality of sulfuric acid at ambient conditions and concentrations up to 20 molal, using a constant hydration number (data of Velrmeulen et al.[65] are at 20°C).

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

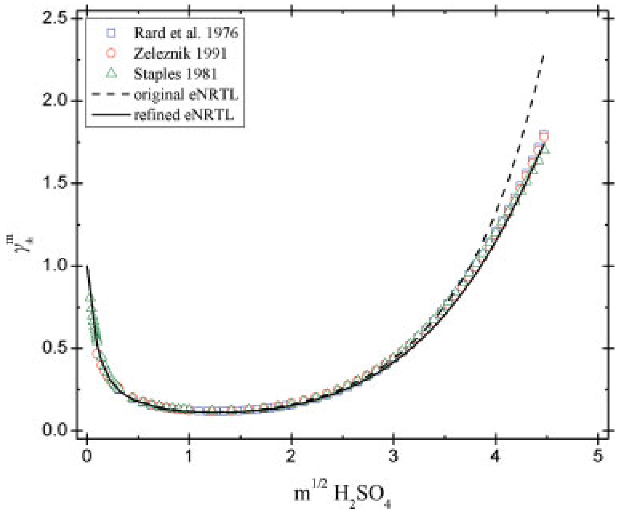

Figure 4. Model predictions and experimental measurements of the mean molal stoichiometric activity coefficient of aqueous sulfuric acid solutions vs. square root of the initial molality of sulfuric acid at ambient conditions and concentrations up to 20 molal (using a constant hydration number and Eq. 17).

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

(due to the difference between the MM and LR scales) that describes the long-range interactions does not allow the use of the more sophisticated Gibbs free energy minimization approach in the simulation of mixed-solvent solutions.

To show the significance of removing the simplifying assumptions associated with activity coefficient expressions from the short-range interaction excess Gibbs free energy term, both the original electrolyte-NRTL and the refined formulation presented in Eqs. 6–10 were fitted against the same experimental database. For this demonstration the constant hydration model was used and consequently both models were fitted to the experimental database restricted to initial H_2SO_4 concentrations up to 20 m. Up to this concentration level the hydration theory of Robinson and Stokes holds, thus Eq. 17 was used for the calculation of the mean molal stoichiometric activity coefficient. The results of the best fit of both models are presented in Figures 3–5. It is evident that the original electrolyte-NRTL model does not satisfactorily predict together the osmotic coefficient of the solution and the degree of dissociation of the bisulfate. On the other hand, the new formulation (denoted in all plots as "refined eNRTL") simulates the system accurately.

As a second step, the capability of the new formulation to extrapolate to higher concentrations using Eq. 18 for the estimation of the hydration number was examined. It has been commented elsewhere[9] that the simplifying assumption that all cation hydrates are energetically equivalent (same NRTL interaction parameters) should constrain the applicability of the model to low concentration ranges. However, it was found in this work that the extrapolation to concentrated solutions, although of empirical character, is indeed possible and yields satisfactory results. Nonetheless, because the hydration number changes from the infinite dilution limit to the actual concentration simulated, the mean molal stoichiometric activity coefficient was calculated from the predicted osmotic coefficients by utilizing the Gibbs–Duhem equation (see Appendix II). To examine the capability of the model to

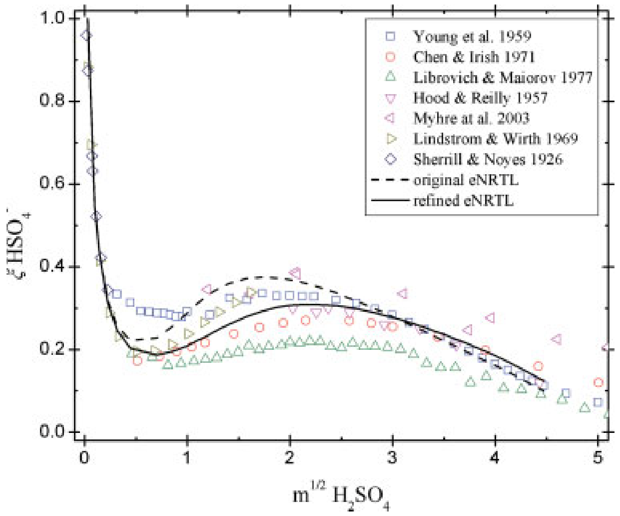

Figure 5. Model predictions and experimental measurements of the degree of dissociation of the bisulfate ion in aqueous sulfuric acid solutions vs. square root of the initial molality of sulfuric acid at ambient conditions and concentrations up to 20 molal (using a constant hydration number).

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

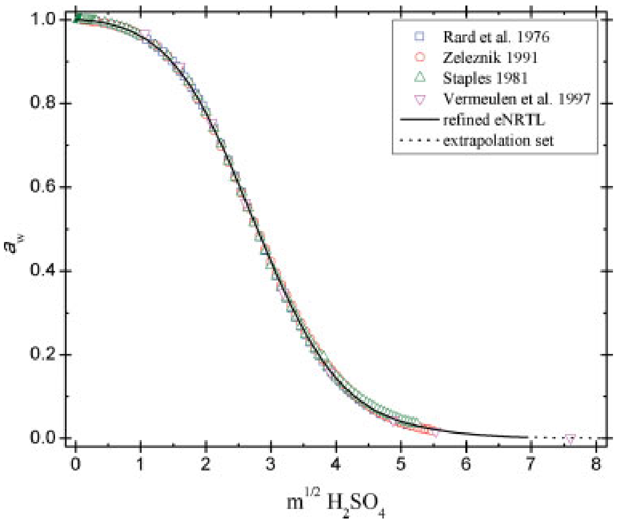

Figure 6. Model predictions and experimental measurements of the activity of water in aqueous sulfuric acid solutions vs. square root of the initial molality of sulfuric acid at ambient conditions and concentrations up to 65 molal (model predictions above 50 molal were not included in the fitting database – they show the extrapolation ability of the model).

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

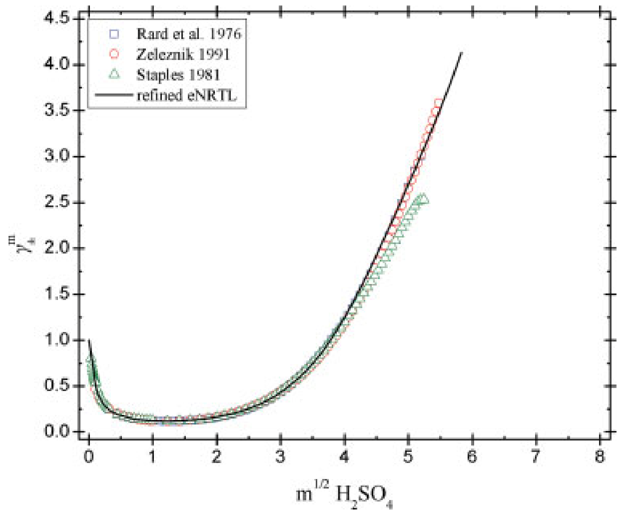

Figure 8. Model predictions and experimental measurements of the mean molal stoichiometric activity coefficient of aqueous sulfuric acid solutions vs. square root of the initial molality of sulfuric acid at ambient conditions and concentrations up to 35 molal.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

extrapolate, the model was fitted to experimental data up to 50 m and then used to predict the speciation and water activity of the solution up to 65 m. Above this concentration the SO_3 concentration and vapor partial pressure become important[65] and a more detailed chemistry model is needed for the system description. The results of the fit and extrapolation of the model are presented in Figures 6–10. It is evident that

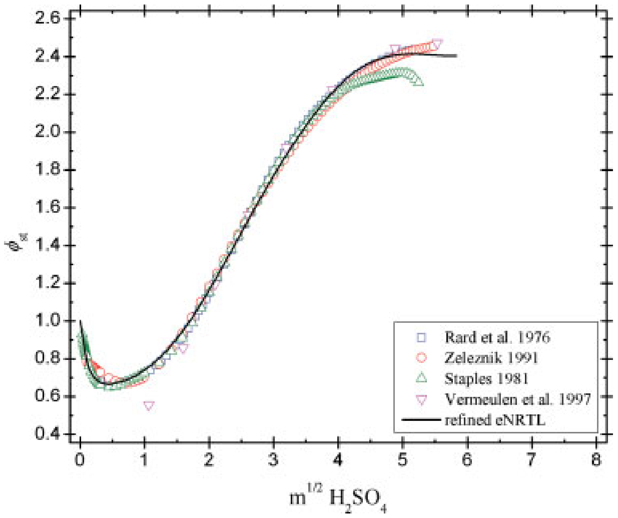

Figure 7. Model predictions and experimental measurements of the stoichiometric osmotic coefficient of aqueous sulfuric acid solutions vs. square root of the initial molality of sulfuric acid at ambient conditions and concentrations up to 35 molal (above 35 molal the stoichiometric osmotic coefficient cannot be defined, because of the existence of undissociated H_2SO_4).

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

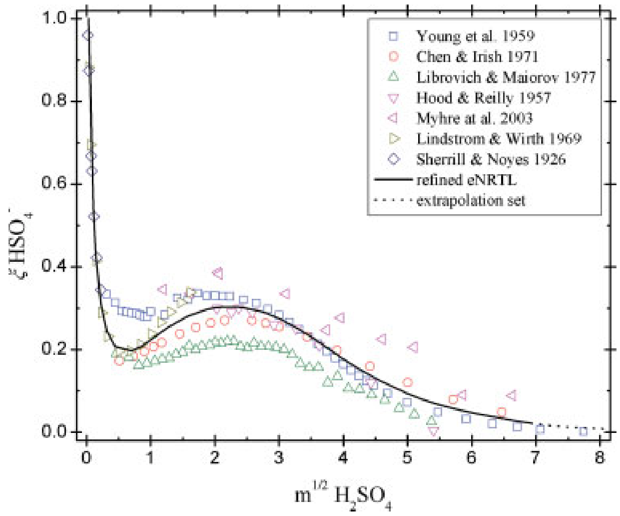

Figure 9. Model predictions and experimental measurements of the degree of dissociation of the bisulfate ion in aqueous sulfuric acid solutions vs. square root of the initial molality of sulfuric acid at ambient conditions and concentrations up to 65 molal (model predictions above 50 molal were not included in the fitting database—they show the extrapolation ability of the model).

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

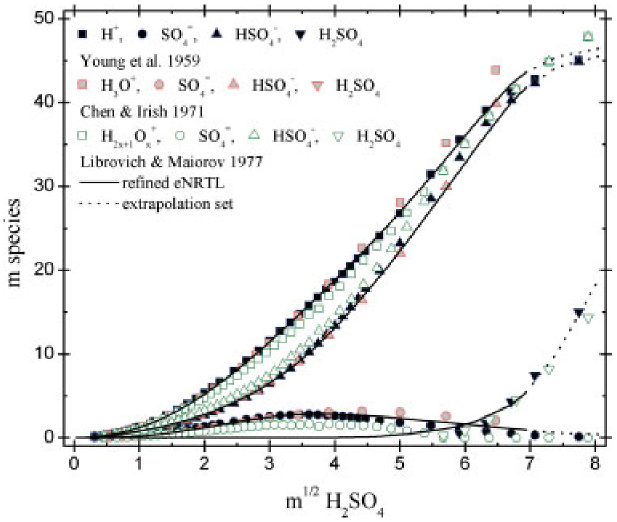

Figure 10. Model predictions and experimental measurements of the detailed speciation in aqueous sulfuric acid solutions vs. square root of the initial molality of sulfuric acid at ambient conditions and concentrations up to 65 molal (model predictions above 50 molal were not included in the fitting database—they show the extrapolation ability of the model).

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the new formulation for the electrolyte-NRTL model is able to satisfactorily describe and predict the dissociation equilibria in sulfuric acid solutions, even at very high concentrations. The prediction of speciation presented in Figure 10 demonstrates that the model is capable of capturing the actual chemistry of the system and, therefore, it can be used for kinetic studies of the system.

The NRTL binary interaction parameters, the hydration number (for the case of constant hydration extent) and the equilibrium constant of the attachment of water molecules to cationic sites (for the case of hydration equilibria) of the best fit of the models are given in Tables 2 and 3. As it has been observed in previous work,[2] the inclusion of hydration leads to the calculation of smaller values for the interaction parameters. This is consistent with the physical notion of the NRTL interaction parameters and the rationale that hydrated ions, while maintaining the same charge number, become larger in size and consequently weaker in interaction energetics. These are the only conclusions that can be drawn by the values of Table 2, as the binary interaction parameters do not have a sufficiently precise physical meaning. Another comment that can be made is that the values calculated for k_h in this work are much higher than the values calculated by Simonin et al.[9] mainly because much larger concentration ranges were considered, compared to the 0–6 molality range examined in the work of Simonin et al.[9] The hydration number of the hydronium was found to vary from 2 at infinite dilution to practically 0 at the limit of the concentration simulated, showing a relative constancy at low concentrations, which justifies the use of a constant hydration number for the simulation of moderately concentrated electrolytes. The overall results of the three models examined, namely the original and refined eNRTL with constant hydration and the refined eNRTL with the inclusion of Eq. 18 for the description of hydration equilibria are summarized in Table 3. It is evident from the average absolute relative errors (AARD%) presented that the new formulation is significantly better than the original electrolyte-NRTL.

Conclusions

A refined activity coefficient formulation for the electrolyte-NRTL model was presented. The refinement involves removal of the simplifying assumption of constant ionic charge composition fraction quantities from the short-range terms of the original electrolyte-NRTL model, in order to provide a rigorous framework for the simulation of multi-electrolyte solutions. This concept possesses virtues as far as both the consistency and the predictive capabilities of the electrolyte-NRTL model are concerned, when it is applied to multi-electrolyte solutions. The effect of the different treatment of the ionic charge composition fraction quantities was examined for the system of aqueous solution of potassium chloride with sodium chloride, showing that the refined set of equa-

Table 2. NRTL Binary Interactions Parameters of the Models Examined*

	Model Examined		
Interaction Pair	Original eNRTL[1]	Refined eNRTL[1]	Refined eNRTL[2]
H_2O–$H(h_cH_2O)^+ \cdot HSO_4^-$	8.136	9.641	7.576
$H(h_cH_2O)^+ \cdot HSO_4^- - H_2O$	−4.814	−5.076	−4.440
H_2SO_4–$H(h_cH_2O)^+ \cdot HSO_4^-$	11.251	9.889	7.151
$H(h_cH_2O)^+ \cdot HSO_4^- - H_2SO_4$	−4.562	−6.492	−5.959
$H_2O - H(h_2H_2O)^+ \cdot SO_4^=$	4.307	8.663	7.408
$H(h_cH_2O)^+ \cdot SO_4^= - H_2O$	−2.527	−4.170	−3.860
$H_2SO_4 - H(h_cH_2O)^+ \cdot SO_4^=$	3.024	7.993	5.778
$H(h_cH_2O)^+ \cdot SO_4^= - H_2SO_4$	−2.839	−4.839	−6.809
$H(h_cH_2O)^+ \cdot SO_4^= - H(h_cH_2O)^+ \cdot HSO_4^-$	−2.493	2.982	4.790
$H(h_cH_2O)^+ \cdot HSO_4^- - H(h_cH_2O)^+ \cdot SO_4^=$	2.493	−2.982	−4.790

*In all the models the value of 0.2 was assigned to the nonrandomness factors $\alpha_{ca \cdot m}$, $\alpha_{m \cdot ca}$, $\alpha_{ca \cdot ca'}$.

[1] Model considering a constant average hydration number.

[2] Model considering hydration equilibria.

Table 3. Effective Range, Hydration Parameters and Accuracy of the Models Examined

Model Examined	Molality Range (mol kg^{-1})	h_c	k_h	AARD%* ϕ_{st}	AARD%* $a\mathrm{HSO}_4^-$
Original eNRTL[1]	0–20	1.971	–	1.02%	14.83%
Refined eNRTL[1]	0–20	1.729	–	0.65%	1.82%
Refined eNRTL[2]	0–50 (−65)	–	25.366	1.00%	1.85%

*AARD% = $\left(\sum_n \left|y^{(M)} - y^{(E)}\right|/y^{(E)}\right)/n \times 100$, y property examined, n number of data points.

[1] Model considering a constant average hydration number.

[2] Model considering hydration equilibria.

tions predicts more accurately the contribution to the nonideality by the mixing of electrolytes. The superiority of the refined model was further demonstrated in a case study of simulating diluted to concentrated aqueous sulfuric acid solutions. In this analysis partial dissociation of the acid, formation of aggregates (intermediate charged ionic pairs) and cationic hydration were taken into account and were shown to provide the ability for the model to predict osmotic coefficients, activity coefficients and the speciation of the system. It was evident that application of the stepwise hydration equilibria theory, although it complicates the model, allows for extrapolating the electrolyte-NRTL model up to very high concentrations. The issue to be addressed in the future is the integration of short-range and long-range contributions into a consistent thermodynamic framework for mixed-solvent solutions.

Acknowledgments

This article is based upon work supported by the Department of Energy Nuclear Energy Research Initiative under Award Number DEFC07-06ID14751.1F

Notation

a = species activity
A_ϕ = Debye-Hückel parameter
d_s = molar density of solvent (mole cm^{-3})
f = species fugacity (atm)
G_{ij} = NRTL binary parameters for the energy of interactions of species i with species j
G = Gibbs free energy of solution (J)
h = average hydration number per mole of electrolyte ($h \equiv v_c h_c + v_a h_a$)
h_c = average hydration number of a cation per mole of the cation
I_x = ionic strength of solution
k = Boltzmann constant (1.38054 × 10^{-16} erg K^{-1})
K_{eq} = equilibrium constant
k_h = equilibrium constant describing hydration
M = molecular weight (kg mole^{-1})
N = moles of species (mole)
n = number of "sites" on a cation
N_A = Avogadro's Number (6.002251 × 10^{23} mol^{-1})
P = solution pressure (atm)
Q_e = absolute electronic charge (4.80298 esu)
r_i = Born radius of ions (Å)
$\Re$ = ideal gas constant (8.31447 J K^{-1} mol^{-1})
S = number of moles of solvent per mole of electrolyte
T = solution temperature (K)
X = effective mole fraction of species ($X_j = Z_j x_j$)
x = mole fractions of species
Z = absolute value of charge of species used in the NRTL equations (1 for molecular species)
z = absolute value of charge of species used in the PDH formula (0 for molecular species)

Greek letters

α = non-randomness factor
γ = rational activity coefficient (mole fraction basis)
γ^m = activity coefficient (molality basis)
ε_s = dielectric constant of solvent
v = stoichiometric coefficient
ξ = reaction extent (degree of dissociation)
ρ = closest approach parameter (14.9)
τ = NRTL binary interaction parameter

Subscripts and superscripts

(E) = property expressed at the experimentalist's level
(M) = property expressed at the model level
a = anionic species index
Born = Born term correction to the unsymmetric Pitzer-Debye-Hückel formula
c = cationic species index
ca = index for electrolyte constituted by c and a
j = index for all species (molecular and ionic)
LR = long-range interactions
m = molecular species index
s = solvent index
SR = short-range interactions
w = water index

Special Notation

_ = (underscore) property per mole
‾ = (overbar) partial molar property
* = property expressed in the unsymmetrical scale
± = mean stoichiometric property
∞ = property of a species infinitely diluted in water

Literature Cited

1. Chen CC, Evans LB. A local composition model for the excess Gibbs energy of aqueous-electrolyte systems. *AIChE. J.* 1986;32: 444–454.
2. Chen CC, Mathias PM, Orbey H. Use of hydration and dissociation chemistries with the electrolyte-NRTL model. *AIChE. J.* 1999;45: 1576–1586.
3. Chen CC, Bokis CP, Mathias P. Segment-based excess Gibbs energy model for aqueous organic electrolytes. *AIChE J.* 2001;47:2593–2602.
4. Chen CC. Some recent developments in process simulation for reactive chemical-systems. *Pure Appl. Chem.* 1987;59:1177–1188.
5. Mock B, Evans LB, Chen CC. Thermodynamic representation of phase-equilibria of mixed-solvent electrolyte systems. *AIChE. J.* 1986;32:1655–1664.
6. Brown LC, Funk JE, Showalter SK. Initial screening of thermochemical water-splitting cycles for high efficiency generation of hydrogen fuels using nuclear power. Technical report general atomics PROJECT 3. 2000.

7. Conway BE. Ionic hydration in chemistry and biophysics. Amsterdam: Elsevier Scientific Pub. Co., 1981.
8. Robinson RA, Stokes RH. *Electrolyte Solutions, 2nd ed.* London: Butterworth, 1959.
9. Simonin JP, Bernard O, Krebs S, Kunz W. Modelling of the thermodynamic properties of ionic solutions using a stepwise solvation-equilibrium model. *Fluid Phase Equil.* 2006;242:176–188.
10. Simonin JP, Krebs S, Kunz W. Inclusion of ionic hydration and association in the MSA-NRTL model for a description of the thermodynamic properties of aqueous ionic solutions: application to solutions of associating acids. *Ind. Eng. Chem. Res.* 2006;45:4345–4354.
11. Balomenos E, Panias D, Paspaliaris I. A semi-empirical hydration model (SEHM) for describing aqueous electrolyte solutions. II. Mixing rules for multiple electrolyte systems at 25 degrees C. *Fluid Phase Equil.* 2006;247:1–7.
12. Balomenos E, Panias D, Paspaliaris L. A semi-empirical hydration model (SEHM) for describing aqueous electrolyte solutions I. Single strong electrolytes at 25 degrees C. *Fluid Phase Equil.* 2006; 243:29–37.
13. Cherif M, Mgaidi A, Ammar MN, Abderrabba M, Furst W. Representation of VLE and liquid phase composition with an electrolyte model: application to H_3PO_4-H_2O and H_2SO_4-H_2O. *Fluid Phase Equil.* 2002;194:729–738.
14. Clegg SL, Brimblecombe P. Application of a multicomponent thermodynamic model to activities and thermal-properties of 0-40 mol kg^{-1} aqueous sulfuric-acid from <200 to 328 K. *J. Chem. Eng. Data* 1995;40:43–64.
15. Clegg SL, Rard JA, Pitzer KS. Thermodynamic properties of 0-6 mol kg^{-1} aqueous sulfuric-acid from 273.15 to 328.15 K. *J. Chem. Soc.-Faraday Trans.* 1994;90:1875–1894.
16. Wang P, Anderko A, Springer RD, Young RD. Modeling phase equilibria and speciation in mixed-solvent electrolyte systems: II. Liquid-liquid equilibria and properties of associating electrolyte solutions. *J. Mol. Liq.* 2006;125:37–44.
17. Haghtalab A, Papangelakis VG, Zhu X. The electrolyte NRTL model and speciation approach as applied to multicomponent aqueous solutions of H2SO4, Fe2(SO4)3, MgSO4 and Al2(SO4)3 at 230–270 °C *Fluid Phase Equil.* 2004;220:199–209.
18. Walrafen GE, Yang WH, Chu YC. High-temperature Raman investigation of concentrated sulfuric acid mixtures: measurement of H-Bond ΔH values between H_3O^+ or $H_5O_2^+$ and HSO_4^-. *J. Phys. Chem. A.* 2002;106:10162–10173.
19. Chen CC, Britt HI, Boston JF, Evans LB. Local composition model for excess Gibbs energy of electrolyte systems. 1. Single solvent, single completely dissociated electrolyte systems. *AIChE. J.* 1982; 28:588–596.
20. Pitzer KS. Electrolytes - from dilute-solutions to fused-salts. *J. Am. Chem. Soc.* 1980;102:2902–2906.
21. Rashin AA, Honig B. Reevaluation of the born model of ion hydration. *J. Phys. Chem.* 1985;89:5588–5593.
22. Chen CC, Song YH. Generalized electrolyte-NRTL model for mixed-solvent electrolyte systems. *AIChE. J.* 2004;50:1928–1941.
23. Robinson RA. Activity coefficients of sodium chloride and potassium chloride in mixed aqueous solutions at 25°C. *J. Phys. Chem.* 1961;65:662–667.
24. Harned HS, Robinson RA. *Multicomponent Electrolyte Solutions.* New York: Pergamon Press, 1968.
25. Pitzer KS, Simonson JM. Thermodynamics of multicomponent, miscible, ionic systems - theory and equations *J. Phys. Chem.* 1986; 90:3005–3009.
26. McMillan WG, Mayer JE. The statistical thermodynamics of multicomponent systems. *J. Chem. Phys.* 1945;13:276–305.
27. Cardoso M, O'Connell JP. Activity-coefficients in mixed-solvent electrolyte-solutions. *Fluid Phase Equil.* 1987;33:315–326.
28. Lee LL. Thermodynamic consistency and erence scale conversion in multisolvent electrolyte solutions. *J. Mol. Liq.* 2000;87:129–147.
29. Simonin JP. Thermodynamic properties of aqueous solutions of organic nonelectrolytes: use of a simple molecular model at the MacMillan-Mayer level. *Fluid Phase Equil.* 1999;165:41–58.
30. Breil MP, Mollerup JM. The McMillan-Mayer framework and the theory of electrolyte solutions. *Fluid Phase Equil.* 2006;242:129–135.
31. Wang PM, Anderko A. Computation of dielectric constants of solvent mixtures and electrolyte solutions. *Fluid Phase Equil.* 2001; 186:103–122.
32. Stokes RH, Robinson RA. Solvation equilibria in very concentrated electrolyte solutions. *J. Solution Chem.* 1973;2:173–191.
33. Nesbitt HW. The Stokes and Robinson hydration theory - a modification with application to concentrated electrolyte-solutions. *J. Solution Chem.* 1982;11:415–422.
34. Schönert H. The thermodynamic model of stepwise hydration of hydrophilic solutes in aqueous-solutions. 1. General-considerations. *Zeitschrift Fur Physikalische Chemie Neue Folge.* 1986;150:163–179.
35. Robertson EB, Dunford HB. The state of the proton in aqueous sulfuric acid. *J. Am. Chem. Soc.* 1964;86:5080–5089.
36. Gmitro JI, Vermeulen T. Vapor-liquid equilibria for aqueous sulfuric acid. *AIChE. J.* 1964;10:740–746.
37. Rard JA, Habenschuss A, Spedding FH. Review of osmotic coefficients of aqueous H_2SO_4 at 25°C. *J. Chem. Eng. Data* 1976;21:374–379.
38. Staples BR. Activity and osmotic coefficients of aqueous sulfuric-acid at 298.15 K. *J. Phys. Chem. Ref. Data* 1981;10:779–798.
39. Young TF, Blatz LA. The variation of the properties of electrolytic solutions with degrees of dissociation. *Chem. Rev.* 1949;44:93–115.
40. Zeleznik FJ. Thermodynamic properties of the aqueous sulfuric-acid system to 350 K. *J. Phys. Chem. Ref. Data* 1991;20:1157–1200.
41. Bolsaitis P, Elliott JF. Thermodynamic activities and equilibrium partial pressures for aqueous sulfuric-acid-solutions. *J. Chem. Eng. Data* 1990;35:69–85.
42. Chen H, Irish DE. Raman spectral study of bisulfate-sulfate systems. II. Constitution, equilibriums, and ultrafast proton transfer in sulfuric acid. *J. Phys. Chem.* 1971;75:2672–2681.
43. Hood GC, Reilly CA. Ionization of strong electrolytes. V. Proton Magnetic Resonance in Sulfuric Acid. *J. Chem. Phys.* 1957; 27:1126–1128.
44. Knopf DA, Luo BP, Krieger UK, Koop T. Thermodynamic dissociation constant of the bisulfate ion from Raman and ion interaction modeling studies of aqueous sulfuric acid at low temperatures. *J. Phys. Chem. A.* 2003;107:4322–4332.
45. Librovich NB, Maiorov VD. Ionic-molecular composition of aqueous sulfuric-acid solutions at 25°. Bulletin of the academy of sciences of the USSR division of chemical science. 1977;26:621–623.
46. Maiorov VD, Librovich NB. Study of H_2SO_4-H_2O equilibrium in concentrated sulfuric-acid solutions by a method of disturbed complete internal reflection. *Zhurnal Fizicheskoi Khimii.* 1973;47:2298–2301.
47. Maiorov VD, Librovich NB, Vinnik MI. Investigation of proton solvation in aqueous sulfuric-acid solutions based on the 1700 cm^{-1} absorption-band in their IR-spectra. Bulletin of the academy of sciences of the USSR division of chemical science. 1979;28:257–260.
48. Malinowski ER, Cox RA, Haldna UL. Factor-analysis for isolation of the raman-spectra of aqueous sulfuric-acid components. *Anal. Chem.* 1984;56:778–781.
49. Marziano NC, Tomasin A, Tortato C, Isandelli P. The problem of acidity in concentrated aqueous solutions of sulfuric acid. *J. Chem. Soc.-Perkin Trans. 2.* 1998:2535–2540.
50. Myhre CEL, Christensen DH, Nicolaisen FM, Nielsen CJ. Spectroscopic study of aqueous H_2SO_4 at different temperatures and compositions: variations in dissociation and optical properties. *J. Phys. Chem. A.* 2003;107:1979–1991.
51. Wu YC, Feng D. The 2nd dissociation-constant of sulfuric-acid at various temperatures by the conductometric method. *J. Solution Chem.* 1995;24:133–144.
52. Young TF, Maranville LF, Smith HM. *The Structure of Electrolytic Solutions.* New York: Wiley, 1959.
53. Zarakhani NG. Homogeneous catalytically active solutions. 10. The equilibrium-constant for the formation of the hydrogen sulfate-hydronium ion pair ($HSO_4^-.H_3O^+$) in aqueous sulfuric-acid solutions. *Zhurnal Fizicheskoi Khimii.* 1976;50:1023–1025.
54. Zarakhani NG. Homogeneous catalytically-active solutions. 11. Raman-spectra of sulfuric-acid aqueous-solutions at 15, 35 and 45°C. *Zhurnal Fizicheskoi Khimii.* 1978;52:1954–1956.
55. Zarakhani NG, Markin VS, Zaikov GE. Homogeneous catalytically-active solutions. 12. Equilibrium composition of sulfuric acid water system at 15°C. *Zhurnal Fizicheskoi Khimii.* 1979;53:2289–2293.

56. Zarakhani NG, Markin VS, Zaikov GE. Homogeneous catalytically-active solutions. 13. Equilibrium composition of sulfuric-acid - water system at 35°C. *Zhurnal Fizicheskoi Khimii.* 1979;53:2294–2296.
57. Luts P, Vanhees J, Yperman J, Mullens J, Vanpoucke LC. The determination of the 2nd dissociation-constant of sulfuric-acid. *J. Solution Chem.* 1994;23:75–80.
58. Lindstrom RE, Wirth HE. Estimation of the bisulfate ion dissociation in solutions of sulfuric acid and sodium bisulfate. *J. Phys. Chem.* 1969;73:218–223.
59. Sherrill MS, Noyes AA. The Inter-ionic attraction theory of ionized solutes VI. The ionization and ionization constants of moderately ionized acids. *J. Am. Chem. Soc.* 1926;48:1861–1873.
60. Zaytsev ID, Aseyev GG. *Properties of Aqueous Solutions of Electrolytes.* Boca Raton FL: CRC Press, 1992.
61. Wu YC, Young TF. Enthalpies of dilution of aqueous-electrolytes - sulfuric-acid, hydrochloric-Acid, and lithium-chloride. *J. Res. Natl. Bureau Standards* 1980;85:11–17.
62. Kim SK, Roth M. Enthalpies of dilution and excess molar enthalpies of an aqueous solution of sulfuric acid. *J. Chem. Eng. Data* 2001; 46:138–143.
63. Giauque WF, Hornung EW, Kunzler JE, Rubin TR. The thermodynamic properties of aqueous sulfuric acid solutions and hydrates from 15 to 300K. *J. Am. Chem. Soc.* 1960;82:62–70.
64. Vermeulen T, Dong J, Robinson S, Nguyen T. Vapor-liquid equilibrium of the sulfuric acid-water system. AIChE. Meeting. 1982; Anaheim, CA.
65. Liley PE, Thomson GH, Friend DG, Daubert TE, Buck E. Physical and chemical data. In: Perry RH, Green DW, Maloney JO. *Perry's Chemical Engineers' Handbook 7th ed.* New York: McGraw-Hill, 1997:2:78–2.83.
66. Pitzer KS, Roy RN, Silvester LF. Thermodynamics of electrolytes. 7. sulfuric-acid. *J. Am. Chem. Soc.* 1977;99:4930–4936.
67. Sanders SJ. Modeling organics in aqueous sulfuric-acid solutions. *Ind. Eng. Chem. Process Des. Dev.* 1985;24:942–948.
68. Bromley LA. Thermodynamic properties of strong electrolytes in aqueous-solutions. *AIChE. J.* 1973;19:313–320.
69. Zemaitis JF Jr, Clark DM, Rafal M, Scrivner NC. *Handbook of Aqueous Electrolyte Thermodynamics. Theory & Application.* New York: American Institute of Chemical Engineers, Inc., 1986.
70. Wang PM, Anderko A, Young RD. A speciation-based model for mixed-solvent electrolyte systems. *Fluid Phase Equil.* 2002;203: 141–176.
71. Abrams DS, Prausnitz JM. Statistical thermodynamics of liquid-mixtures - new expression for excess Gibbs energy of partly or completely miscible systems. *AIChE. J.* 1975;21:116–128.
72. Papaiconomou N, Simonin JP, Bernard O, Kunz W. MSA-NRTL model for the description of the thermodynamic properties of electrolyte solutions. *Phys. Chem. Chem. Phys.* 2002;4:4435–4443.
73. ASPEN Technology Inc. *ASPEN PLUS Electrolyte Manual.* Cambridge, MA, 2006.
74. Babu CS, Lim C. Theory of ionic hydration: insights from molecular dynamics simulations and experiment. *J. Phys. Chem. B.* 1999;103: 7958–7968.

Appendix I: Analytical Expressions for the Case of Different Nonrandomness Factors for each Electrolyte

In the case where the interactions of each electrolyte with the solvents are described by different nonrandomness factors the following mixing rules were proposed by Chen and Song[22]:

$$\alpha_{cm} = \sum_a \frac{X_a \alpha_{ca.m}}{\sum_{a'} X_{a'}}, \quad \tau_{cm} = -\frac{\ln G_{cm}}{\alpha_{cm}}, \quad \alpha_{mc.ac} = \alpha_{cm},$$

$$\tau_{mc.ac} = \tau_{cm} - \frac{\alpha_{ca.m}}{\alpha_{mc.ac}}(\tau_{ca.m} - \tau_{m.ca}) \quad \text{(A1)}$$

$$\alpha_{am} = \sum_c \frac{X_c \alpha_{ca.m}}{\sum_{c'} X_{c'}}, \quad \tau_{am} = -\frac{\ln G_{am}}{\alpha_{am}}, \quad \alpha_{ma.ca} = \alpha_{am},$$

$$\tau_{ma.ca} = \tau_{am} - \frac{\alpha_{ca.m}}{\alpha_{ma.ca}}(\tau_{ca.m} - \tau_{m.ca}). \quad \text{(A2)}$$

Using Eqs. A1 and A2, the analytical expression of the short-range terms of the activity coefficients of the cations becomes

$$\frac{1}{Z_c}\ln\gamma_c^{\mathrm{SR}} = \sum_a \frac{X_a}{\sum_{a'} X_{a'}} \frac{\sum_j X_j G_{jc.ac}\tau_{jc.ac}}{\sum_j X_j G_{jc.ac}} + \sum_m \frac{X_m}{\sum_j X_j G_{jm}} \left[\begin{array}{l} G_{cm}\left(\tau_{cm} - \frac{\sum_j X_j G_{jm}\tau_{jm}}{\sum_j X_j G_{jm}}\right) \\ + \sum_a \frac{X_a}{\sum_{c'} X_{c'}} \frac{(\alpha_{am}G_{ca.m} - \alpha_{ca.m}G_{am})\tau_{am} - (G_{ca.m} - G_{am})}{\alpha_{am}} \\ - \frac{\sum_j X_j G_{jm}\tau_{jm}}{\sum_j X_j G_{jm}} \sum_a \frac{X_a}{\sum_{c'} X_{c'}} (G_{ca.m} - G_{am}) \end{array} \right]$$

$$+ \sum_a X_a \left\{ \begin{array}{l} \sum_{c'} \frac{X_{c'}}{\sum_{c''} X_{c''}} \frac{1}{\sum_j X_j G_{ja.c'a}} \left[G_{ca.c'a}\left(\tau_{ca.c'a} - \frac{\sum_j X_j G_{ja.c'a}\tau_{ja.c'a}}{\sum_j X_j G_{ja.c'a}}\right) \right. \\ + \sum_m \frac{X_m}{\sum_{c''} X_{c''}} G_{ma.c'a} \frac{(\alpha_{am}G_{ca.m} - \alpha_{ca.m}G_{am})\tau_{ma.c'a} - (G_{ca.m} - G_{am})}{\alpha_{am}G_{am}} \\ - \frac{\sum_j X_j G_{ja.c'a}\tau_{ja.c'a}}{\sum_j X_j G_{ja.c'a}} \sum_m \frac{X_m}{\sum_{c''} X_{c''}} G_{ma.c'a} \frac{G_{ca.m} - G_{am}}{G_{am}} + \\ \frac{1}{\sum_{c''} X_{c''}} \left(\frac{\sum_j X_j G_{ja.ca}\tau_{ja.ca}}{\sum_j X_j G_{ja.ca}} - \sum_{c'} \frac{X_{c'}}{\sum_{c''} X_{c''}} \frac{\sum_j X_j G_{ja.c'a}\tau_{ja.c'a}}{\sum_j X_j G_{ja.c'a}} \right) \end{array} \right\}$$

and the respective expression for the anions is

$$\frac{1}{Z_a}\ln\gamma_a^{\mathrm{SR}} = \sum_c \frac{X_c}{\sum_{c'} X_{c'}} \frac{\sum_j X_j G_{ja.ca}\tau_{ja.ca}}{\sum_j X_j G_{ja.ca}} + \sum_m \frac{X_m}{\sum_j X_j G_{jm}} \left[\begin{array}{l} G_{am}\left(\tau_{am} - \frac{\sum_j X_j G_{jm}\tau_{jm}}{\sum_j X_j G_{jm}}\right) \\ + \sum_c \frac{X_c}{\sum_{a'} X_{a'}} \frac{(\alpha_{cm}G_{ca.m} - \alpha_{ca.m}G_{cm})\tau_{cm} - (G_{ca.m} - G_{cm})}{\alpha_{cm}} \\ - \frac{\sum_j X_j G_{jm}\tau_{jm}}{\sum_j X_j G_{jm}} \sum_c \frac{X_c}{\sum_{a'} X_{a'}} (G_{ca.m} - G_{cm}) \end{array}\right]$$

$$+ \sum_c X_c \left\{\begin{array}{l} \sum_{a'} \frac{X_{a'}}{\sum_{a''} X_{a''}} \frac{1}{\sum_j X_j G_{jc.a'c}} \left[G_{ac.a'c}\left(\tau_{ac.a'c} - \frac{\sum_j X_j G_{jc.a'c}\tau_{jc.a'c}}{\sum_j X_j G_{jc.a'c}}\right)\right. \\ + \sum_m \frac{X_m}{\sum_{a''} X_{a''}} G_{mc.a'c} \frac{(\alpha_{cm}G_{ca.m} - \alpha_{ca.m}G_{cm})\tau_{mc.a'c} - (G_{ca.m} - G_{cm})}{\alpha_{cm}G_{cm}} \\ \left. - \frac{\sum_j X_j G_{jc.a'c}\tau_{jc.a'c}}{\sum_j X_j G_{jc.a'c}} \sum_m \frac{X_m}{\sum_{a''} X_{a''}} G_{mc.a'c} \frac{G_{ca.m} - G_{cm}}{G_{cm}}\right] \\ + \frac{1}{\sum_{a''} X_{a''}} \left(\frac{\sum_j X_j G_{jc.ac}\tau_{jc.ac}}{\sum_j X_j G_{jc.ac}} - \sum_{a'} \frac{X_{a'}}{\sum_{a''} X_{a''}} \frac{\sum_j X_j G_{jc.a'c}\tau_{jc.a'c}}{\sum_j X_j G_{jc.a'c}}\right) \end{array}\right\}.$$

At the limit of infinite dilution the activity coefficients of the cations are

$$\frac{1}{Z_c}\ln\gamma_c^{\mathrm{SR},\infty} = \sum_a \frac{X_a}{\sum_{a'} X_{a'}}\tau_{wc.ac} + G_{cw}\tau_{cw}$$
$$+ \sum_a \frac{X_a}{\sum_{c'} X_{c'}} \frac{(\alpha_{aw}G_{ca.w} - \alpha_{ca.w}G_{aw})\tau_{aw} - (G_{ca.w} - G_{aw})}{\alpha_{aw}}$$
$$+ \sum_a X_a \left[\begin{array}{l} \sum_{c'} \frac{X_{c'}}{\sum_{c''} X_{c''}} \frac{1}{\sum_{c''} X_{c''}} \frac{(\alpha_{aw} - \alpha_{ca.w})\tau_{wa.c'a} - (G_{ca.w} - G_{aw})}{\alpha_{aw}G_{aw}} \\ + \frac{1}{\sum_{c''} X_{c''}} \left(\tau_{wa.ca} - \sum_{c'} \frac{X_{c'}}{\sum_{c''} X_{c''}}\tau_{wa.c'a}\right) \end{array}\right]$$

and of the anions

$$\ln\gamma_a^{\mathrm{SR},\infty} = \sum_c \frac{X_c}{\sum_{c'} X_{c'}}\tau_{wa.ca} + G_{aw}\tau_{aw}$$
$$+ \sum_c \frac{X_c}{\sum_{a'} X_{a'}} \frac{(\alpha_{cw}G_{ca.w} - \alpha_{ca.w}G_{cw})\tau_{cw} - (G_{ca.w} - G_{cw})}{\alpha_{cw}}$$
$$+ \sum_c X_c \left[\begin{array}{l} \sum_{a'} \frac{X_{a'}}{\sum_{a''} X_{a''}} \frac{1}{\sum_{a'} X_{a''}} \frac{(\alpha_{cw} - \alpha_{ca.w})\tau_{wc.a'c} - (G_{ca.w} - G_{cw})}{\alpha_{cw}G_{cw}} \\ + \frac{1}{\sum_{a''} X_{a''}} \left(\tau_{wc.ac} - \sum_{a'} \frac{X_{a'}}{\sum_{a''} X_{a''}}\tau_{wc.a'c}\right) \end{array}\right].$$

Appendix II: Conversion from Model Level to the Level of Experimentalists

An issue that raises difficulty is the conversion of mean molal activity coefficients of an electrolyte solution that is treated as completely dissociated and anhydrous by one school of thought (i.e., the experimentalist) and partially dissociated, forming aggregates and consisting of hydrated ions from another point of view. This issue has been addressed originally by Robinson and Stokes[8] and more recently by Chen et al.[2] and Simonin et al.[10] The basic idea behind the method of converting the mean activity of a solution from the experimentalist's level to the model level and vice versa is that the total Gibbs free energy of the solution is the same, regardless of the method used for expressing its composition. An example of this method is given below for the case of the aqueous sulfuric acid solution.

At the model level sulfuric acid is considered partially dissociated, forming the bisulfate aggregate and hydrated cations. The corresponding set of variables at this level is

$$\mathbf{S}^{(M)} = \left\{N_w^{(M)}, N_c^{(M)}, N_a^{(M)}, N_p^{(M)}, N_s^{(M)}\right\},$$

where $N_w^{(M)}$ is the number of moles of "free" water, $N_c^{(M)}$ the number of moles of "free" hydrated hydrogen cations, $N_a^{(M)}$ the number of moles of "free" sulfate anions, $N_p^{(M)}$ the number of moles of bisulfate ions and $N_s^{(M)}$ the number of moles of undissociated sulfuric acid. On the other hand, at the experimentalist's level the total moles of water ($N_w^{(E)}$) and the completely dissociated and unhydrated hydrogen ($N_c^{(E)}$) and sulfate ($N_a^{(E)}$) ions are considered:

$$\mathbf{S}^{(E)} = \left\{N_w^{(E)}, N_c^{(E)}, N_a^{(E)}\right\}.$$

The chemical potentials at the experimentalist's level can be expressed at the model level by taking into account hydration and association of ions to from ion pairs (charged or neutral). For the sulfuric acid case this translates to the solvation of hydrogen cations, the association of sulfate and hydrogen to form the bisulfate ion and the association of bisulfate and hydrogen to form sulfuric acid. The mole fractions at the two levels can be expressed

$$x_j^{(M)} \equiv \frac{N_j^{(M)}}{N_w^{(M)} + N_c^{(M)} + N_a^{(M)} + N_p^{(M)} + N_s^{(M)}}, \tag{B1}$$

$$x_j^{(E)} \equiv \frac{N_j^{(E)}}{N_w^{(E)} + N_c^{(E)} + N_a^{(E)}}. \tag{B2}$$

By identifying the respective terms in the Gibbs free energy functions at the two levels, taking into account that the aggregates ($N_p^{(M)}$ and $N_s^{(M)}$) are in equilibrium with the ions ($N_c^{(M)}$ and $N_a^{(M)}$) and taking the limit of infinite dilution it can be shown[10] that the relationship between the activity coefficients of the two levels is

$$\gamma_i^{(E)} = \frac{x_i^{(M)}}{x_i^{(E)} a_w^{h_1}} \gamma_i^{(M)}. \tag{B3}$$

Using Eqs. B1–B3 with the definition of the mean stoichiometric activity coefficient and the relation between rational and molal activity coefficients it can be shown that the mean molal stoichiometric coefficient of the actual solution (at the model level) expressed at the experimentalist's level is

$$\begin{aligned} \ln \gamma_{\pm}^{m(E)} = \ln \gamma_{\pm}^{(M)} - \frac{h}{v} \ln a_w - \ln \Bigg\{ 1 + S^{-1} \Bigg[v - h + \frac{N_p^{(M)}}{m} \\ \left(1 - v_{c,p}^{(M)} - v_{a,p}^{(M)} + v_{c,p}^{(M)} h_c + v_{a,p}^{(M)} h_a \right) \\ + \frac{N_s^{(M)}}{m} \left(1 - v_{c,s}^{(M)} - v_{a,s}^{(M)} + v_{c,s}^{(M)} h_c + v_{a,s}^{(M)} h_a \right) \Bigg] \Bigg\} \\ + \frac{1}{v} \Bigg[v_c \ln \left(1 - \frac{v_{c,p}^{(M)}}{v_c} \frac{N_p^{(M)}}{m} - \frac{v_{c,s}^{(M)}}{v_c} \frac{N_s^{(M)}}{m} \right) \\ + v_a \ln \left(1 - \frac{v_{a,p}^{(M)}}{v_a} \frac{N_p^{(M)}}{m} - \frac{v_{a,s}^{(M)}}{v_a} \frac{N_s^{(M)}}{m} \right) \Bigg]. \end{aligned} \tag{B4}$$

In Eq. B4 $S = 1000/M_w/m,\ v(=3), v_c(=2), v_a(=1)$ are the total, cations and anions stoichiometric coefficients of the electrolyte's dissociation reaction at the experimentalist's level, $v_{c,p}^{(M)}(=1), v_{a,p}^{(M)}(=1), v_{c,s}^{(M)}(=2), v_{a,s}^{(M)}(=1)$ are the stoichiometric coefficients of the ions association to form the aggregate (bisulfate) and the electrolyte (sulfuric acid), h is the total hydration number (per mole of electrolyte) and h_c and h_a are the hydration numbers of cations and anions (zero for the case of the sulfate), respectively, whereas no hydration was considered for the aggregates (sulfuric acid and bisulfate). The implicit extra-thermodynamic assumption of this treatment, which is based on the work of Simonin et al.[10] and oriented by the hydration theory of Robinson and Stokes,[8] is that the hydration number remains constant from the limit of infinite dilution up to the actual electrolyte molality. For this reason this treatment is valid up to the level where enough "free" water molecules exist to hydrate an ion, which approximately is $1000/M_{\mathrm{w}}/h$.[8] Nevertheless, if the thermodynamic model obeys the Gibbs-Duhem equation the mean molal stoichiometric activity coefficient can be found by the classical equation

$$\ln\gamma_{\pm}^{\mathrm{m}(E)} = \phi_{st} - 1 + \int_0^m (\phi_{st} - 1) d \ln m.$$

Manuscript received Sept. 18, 2007, and revision received Feb. 18, 2008.