

# Modeling Surface Tension of Concentrated and Mixed-Solvent Electrolyte Systems

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**ABSTRACT:** A comprehensive model has been developed for calculating the surface tension of aqueous, nonaqueous, and mixed-solvent electrolyte systems ranging from dilute solutions to fused salts. The model consists of a correlation for computing the surface tension of solvent mixtures and an expression for the effect of electrolyte concentration. The dependence of surface tension on electrolyte concentration has been derived from the Gibbs equation combined with a modified Langmuir adsorption isotherm for modeling the surface excess of species. The model extends the Langmuir adsorption formalism by introducing the effects of binary interactions between solute species (ions or molecules) on the surface. This extension is especially important for high electrolyte concentrations and in strongly speciated systems. The surface tension of mixed solvents is calculated by utilizing the surface tensions of the constituent pure components together with an effective surface concentration, which is defined for each component and takes into account interactions between solvent molecules. This procedure has been shown to reproduce experimental data for a variety of mixtures. In particular, it accurately predicts the surface tension of ternary solvent mixtures using parameters determined from only binary data. The surface tension model has been coupled with a previously developed thermodynamic equilibrium model to provide speciation and activity coefficients, which are necessary for electrolyte systems. This makes it possible to reproduce the effects of complexation or other reactions in solution. In all cases for which experimental data are available and have been tested, the new model has been shown to be accurate in reproducing surface tension over wide ranges of temperature and concentration. The average deviations between the calculated results and experimental data are 0.68% for binary solvent mixtures, 1.89% for ternary solvent mixtures, and 0.71% for salt solutions up to the solid saturation or pure solute limit.

## 1. INTRODUCTION

The surface tension of solutions has a considerable influence on the transfer of mass and energy across interfaces. It is a basic thermodynamic property that plays an important role in a multitude of processes including those encountered in adsorption, refrigeration, distillation, reservoir engineering, metasomatism, and pharmaceutical formulation. Because of their practical importance, studies of surface tension and surface chemistry have been an area of active research over the past century. Accurate determination of surface tension for various liquids and liquid mixtures is important to gain insight into interfacial processes. Over the past decades, a large amount of experimental surface tension data has been reported for liquids and liquid mixtures including electrolyte solutions. Also, the published data have been critically evaluated for pure liquids.<sup>1</sup> The experimental data that are available in the literature are sufficient for a comprehensive analysis of the factors that influence the surface tension of both electrolyte and nonelectrolyte systems.

Numerous approaches have been reported in the literature to model the surface tension of liquids and liquid mixtures. Reviews of some of the published models are available.<sup>2,3</sup> For nonelectrolyte mixtures, the most widely used approaches to the calculation of surface tension fall into two categories: those based on empirical relations such as the corresponding-states principle<sup>4</sup> or the parachor method,<sup>5</sup> and those derived from thermodynamic principles.<sup>6–11</sup> Models based on molecular dynamics simulation<sup>12</sup> and on the gradient theory<sup>13,14</sup> have also been reported. The classical thermodynamic treatment of surface tension generally requires estimates of surface areas for mixture

components and an activity coefficient model to determine the activity coefficients in the surface and bulk phases. Such treatment involves solving a set of nonlinear equations. Among the thermodynamic-based models, the model of Suarez et al.<sup>7</sup> has been recommended<sup>2</sup> owing to its generally good accuracy in representing the surface tension of both nonaqueous and aqueous mixtures. However, the complexity of the computational scheme and the inadequacy of the model near the mixture critical point have made the model of Suarez et al. less advantageous in certain circumstances.<sup>2</sup> Models of empirical nature require less involved calculations but can be limited to certain types of systems and are generally applied to mixtures in which pure component surface tensions do not differ greatly and in which deviations from ideal solution behavior are not large.<sup>2</sup>

For electrolyte solutions, it has long been known that adding salts to water generally increases the surface tension. In a well-known study, Onsager and Samaras<sup>15</sup> attributed such increases to the repulsion of ions from the surface by the electrostatic image force and derived, by integrating the electrostatic interaction theory with the Gibbs adsorption isotherm, an expression that gives a positive slope with respect to electrolyte concentration. However, the theory of Onsager and Samaras<sup>15</sup> assumes the same image repulsion for all ions with the same valence and cannot explain ionic specificity, thus failing to give the proper

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limiting slope in many electrolyte solutions.<sup>3</sup> Modified versions of the Onsager–Samaras expression have been proposed to improve the agreement with experimental results.<sup>16,17</sup> Other theories for calculating surface tension of electrolyte solutions have also been published.<sup>18–20</sup> Although these models constitute an advancement over the original model of Onsager and Samaras<sup>15</sup> and its modifications, they are generally limited to electrolyte concentrations of up to ~1 M.

Models for calculating surface tension at higher electrolyte concentrations have also been reported. One of such approaches originated from the thermodynamic treatment of Butler<sup>9</sup> in which the equilibrium between a hypothetical surface phase and a bulk phase is considered by equating the chemical potentials of the components in both phases and, subsequently, by introducing an activity coefficient model to calculate the components' activities.<sup>21–24</sup> A different approach has been proposed<sup>25–27</sup> to combine a thermodynamic treatment based on the Gibbs equation<sup>26</sup> with an adsorption isotherm that defines the surface concentrations of electrolyte components. The activities required in the Gibbs equation are then determined by introducing an activity coefficient model. The applicability range of both approaches is generally limited by that of the activity coefficient model that is incorporated in the computation of surface tension. For example, the Pitzer equation for activity coefficients has been used by Li and Lu<sup>27</sup> in their surface tension model and, therefore, the applicability range of the Li–Lu<sup>27</sup> model coincides with that of the Pitzer model, which is generally valid up to 6 *m* for most electrolyte systems. It should be noted that these models do not take into account the chemical speciation in electrolyte solutions, which can be significant for highly associated systems such as sulfuric acid. For example, it is noteworthy that surface tension in sulfuric acid solutions shows an abnormal behavior that can be difficult to represent using any of the existing surface tension models without taking into account the complex speciation patterns in this system.

In mixed-solvent electrolyte solutions, surface tension is determined not only by concentrations of electrolytes, but also by the composition of the solvent. The surface tension of solvent mixtures alone may change significantly with composition. In addition, in systems with strong ion association effects (e.g., in fully miscible acids or bases), surface tension—like most thermophysical properties—is influenced by concentrations of both ions and associated ion pairs. Thus, a comprehensive treatment of surface tension of mixed-solvent electrolyte systems requires taking into account not only the ion–solvent and ion–ion interactions that predominate in aqueous solutions, but also the solvent–solvent and ion pair–solvent interactions. This is possible only if a comprehensive, speciation-based model is used as a thermodynamic foundation for the surface tension model.

The objective of this work is to develop a comprehensive, engineering-oriented model for predicting surface tension of mixed-solvent electrolyte solutions in contact with a bulk vapor phase. In this study, the term “mixed solvent electrolytes” is used in the broadest possible sense to include (1) aqueous electrolyte solutions from the dilute region to the molten salt limit, (2) fully miscible acids or bases in water, (3) electrolytes in pure organic or mixed organic–water solvents. Further, the model is designed to account for speciation effects, such as complexation or ion association, when combined with a speciation-based thermodynamic model. The model developed in this study consists of two parts: (1) computation of surface tension of pure and mixed solvents as a function of temperature and solvent composition

and (2) computation of the dependence of surface tension on electrolyte concentration.

## 2. SURFACE TENSION OF SOLVENT MIXTURES

It is well-known that surface tension of a liquid mixture is not a simple function of pure component properties. On a fundamental level, it contains information on the structure and energetics of the surface region, which can depend, in a complex way, on the identity and concentrations of the components of the mixture (both in the bulk and at the surface). Although surface tension in a majority of mixtures is lower than a mole fraction average of the surface tensions of pure components, systems with positive deviations from the mole fraction average are also observed.<sup>2</sup> A general model needs to account for these phenomena in order to provide a basis for calculations when salts are introduced into mixed solvents.

In this study, we propose a simple mixing rule for calculating the surface tension of mixed solvents on the basis of the fundamental assumption that the surface phase, located between the bulk liquid and vapor phases, can be represented by a region of uniform composition, which is different from that in the bulk liquid. Thus, the surface tension of the mixture ( $\sigma_{ms}$ ) can be assumed to be an average of the surface tensions of pure components weighted by their surface concentrations; that is,

$$\sigma_{ms} = \sum_i^n x_{i,s} \sigma_i \quad (1)$$

where  $x_{i,s}$  is the mole fraction of component *i* at the surface and  $\sigma_i$  is the surface tension of the pure liquid component *i*.

In a typical situation, the surface composition is unknown, but must be related to that in the bulk phase. In modeling thermodynamic properties of nonelectrolyte mixtures, one of the most efficient empirical approaches is based on introducing local compositions to represent the effect of molecular interactions on the concentration of a component in the proximity of other neighboring molecules.<sup>2</sup> In the present study, a formalism based on the local composition concept<sup>28</sup> is proposed to represent the surface composition. As a starting point, the surface mole fractions must satisfy the equation:

$$\sum_i^n x_{i,s} = 1 \quad (2)$$

Following the local composition approach, the surface mole fraction of component *i*,  $x_{i,s}$ , is related to that in the bulk phase,  $x_i$ , by

$$x_{i,s} = x_i \cdot \sum_{j=1}^n \left( \frac{x_j \tau_{ji}}{\sum_k^n x_k \tau_{jk}} \right) \quad (i = 1, 2, \dots, n) \quad (3)$$

where  $\tau_{ij}$  ( $\tau_{ji} \neq \tau_{ij}$  and  $\tau_{ii} = \tau_{jj} = 1$ ) represent the binary interaction coefficients between the species *i* and *j* in the surface phase and are calculated as  $\tau_{ij} = \exp(a_{ij})$  to maintain a positive value, which is determined from experimental surface tension data by adjusting  $a_{ij}$  ( $a_{ji} \neq a_{ij}$ ,  $a_{ii} = a_{jj} = 0$ ). The dependence of the surface concentrations on molecular structural parameters such as the molecular surface area and size, although not explicitly expressed in eq 3, is implicitly incorporated in the interaction parameters. A general trend of the interaction parameters with molecular size will be discussed further in this study. The surface mole fractions deviate

from those in the bulk liquid due to stronger or weaker  $i$ – $j$  interactions relative to the  $i$ – $s$  and  $j$ – $s$  interactions (where  $s$  refers to the surface), as determined by the interaction parameters  $\tau_{ji}$  and  $\tau_{ij}$ . When all of the  $\tau_{ji}$  and  $\tau_{ij}$  parameters are equal to unity (or  $a_{ij}$  and  $a_{ji}$  are equal to zero), the surface concentrations of all components reduce to those in the bulk phase.

In mixtures with strong deviations from the mole fraction average, surface tension can exhibit a maximum or a minimum as a function of composition.<sup>29</sup> Such behavior has been found to be best represented when a modified average of the surface tension of components  $i$  and  $j$ ,  $\sigma_{ij}$ , is introduced as

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j)(1 + k_{ij}) \quad (4)$$

Then, eq 1 is rewritten using pairwise contributions; that is,

$$\sigma_{ms} = \sum_i^n \sum_j^n x_{i,s} x_{j,s} \sigma_{ij} \quad (5)$$

where  $k_{ij}$  is an adjustable parameter that represents the deviation from the arithmetic mean for components  $i$  and  $j$  and can be determined together with  $\tau_{ji}$  and  $\tau_{ij}$  from experimental surface tension data. It can be easily shown that when the  $k_{ij}$  coefficients for all  $i$ – $j$  pairs are zero, eq 5 reduces to eq 1.

In the calculations using eq 5, the values of pure-component surface tensions,  $\sigma_i$ , have been obtained from the compilation of Daubert and Danner<sup>1</sup> for organic solvents. The IAPWS formulation<sup>30</sup> has been used for water. The interaction parameters  $\tau_{ji}$  and  $\tau_{ij}$  can be determined from experimental surface tension data for binary mixtures of  $i$  and  $j$ .

### 3. DEPENDENCE OF SURFACE TENSION ON ELECTROLYTE CONCENTRATION

**3.1. The Gibbs Equation.** In this study, a thermodynamic-based approach has been adopted to take into account the effect of electrolyte concentration on the surface tension of the solution. In the classical thermodynamic treatment of the variation of surface tension with composition, a quantity denoted as “surface excess”,  $\Gamma_i^\sigma$ , is introduced to represent the excess (positive) or deficiency (negative) of any component  $i$ , per unit area, at the surface of a solution.<sup>26</sup> Thus, for a given system at constant temperature and pressure, the change in surface tension between the vapor and liquid phases can be expressed using the Gibbs equation:

$$d\sigma = - \sum_i \Gamma_i^\sigma d\mu_i \quad (6)$$

where  $\mu_i$  is the chemical potential of species  $i$ . It can be shown that the surface excess can be defined on the basis of an arbitrarily chosen dividing surface between the bulk phase and the surface region.<sup>26,31</sup> In the present work, we treat the solvent mixture as a uniform entity when applying the Gibbs equation and a dividing surface is chosen so that the surface excess of the solvent is zero, that is,  $\Gamma_{\text{solvent}} = 0$  and  $\Gamma_{\text{solvent}} d\mu_{\text{solvent}}^\sigma = 0$ . Such definition of the dividing surface is equivalent to selecting a mixed-solvent reference state in which any deviation from the surface tension of the solvent mixture is attributed to the effect of electrolyte concentration. This reference state can be equivalently represented by a dividing surface for which  $\sum_l^N \Gamma_l^\sigma d\mu_l = 0$ , where the sum is over all solvent components  $l$  and  $N_s$  is the number of solvents.

At equilibrium, the chemical potential of species  $i$  at the surface is equal to that in the bulk liquid phase; that is,

$$\mu_i = \mu_i^\sigma = \mu_i^L = \mu_i^{L0} + RT \ln a_i \quad (7a)$$

and

$$d\mu_i = RT d \ln a_i \quad (7b)$$

where  $a_i$  is the activity of species  $i$  in the solution. Substituting eq 7b into eq 6 yields

$$d\sigma = - RT \sum_i \Gamma_i^\sigma d \ln a_i \quad (8)$$

Owing to the selection of the Gibbs dividing surface, the sum in eq 8 includes only solute species.

**3.2. Modified Langmuir Adsorption Model.** To determine the surface excess in the Gibbs equation, it is necessary to introduce an adsorption isotherm. Among various adsorption isotherms discussed in the literature, the Langmuir isotherm is the simplest yet widely used model that has been applied to surface chemistry of various systems including aqueous and nonaqueous solutions.<sup>32</sup> Desnoyer et al.<sup>25</sup> and Li and Lu<sup>27,33</sup> introduced the Langmuir isotherm to describe the adsorption of electrolytes on the solution interface in their derivations of vapor–liquid and liquid–liquid interfacial tension models for aqueous electrolyte solutions. These approaches do not take into account the speciation of electrolyte systems and, thus, can be difficult to extend to multicomponent solutions over wide ionic concentration ranges.

In this study, we extend the methodology of Desnoyer et al.<sup>25</sup> and Li and Lu<sup>27,33</sup> by introducing a previously developed speciation-based thermodynamic model<sup>34</sup> into the Gibbs equation so that any change of surface tension due to chemical speciation can be explicitly represented as a function of electrolyte composition. The activities required for the calculation of surface tension are also determined from the thermodynamic model. The use of an extensively validated thermodynamic equilibrium model<sup>34</sup> makes it possible for the surface tension model to be applicable from dilute solutions to the limit of fused salts. The Langmuir adsorption isotherm is applied to all species, i.e., the ions, ion pairs, and neutral molecules that contribute to adsorption. Furthermore, the derivation of the surface tension expression from the Gibbs equation and the Langmuir isotherm needs to take into account the interactions between solute species at the solution surface.

According to the Langmuir model, and taking into consideration the competitive adsorption of multiple species, the adsorption equilibrium condition can be expressed by

$$k_{i,a}(1 - \sum_j \theta_j)a_i = k_{i,d}\theta_i \quad (9)$$

where  $k_{i,a}$  and  $k_{i,d}$  are the adsorption and desorption rate constants, respectively,  $\theta_i$  is the surface fraction occupied by the adsorbed species  $i$ , and  $a_i$  is the activity of species  $i$ . Equation 9 can be rearranged to give

$$\theta_i = \frac{K_i a_i}{1 + \sum_j K_j a_j} \quad (10)$$

where  $K_i = k_{i,a}/k_{i,d}$  is the adsorption equilibrium constant for species  $i$ . Assuming that the adsorption layer has a fixed capacity for a given species, the surface fraction  $\theta_i$  can be represented by eq 11 by introducing a maximum surface excess,  $\Gamma_i^{\sigma,0}$ ; <sup>25,27,33</sup>

Table 1. Parameters of Equations 1–4 for Selected Binary Solvent Mixtures

solvent mixture		parameters			<i>T</i> (°C)	no. points	AAD	ref
<i>i</i>	<i>j</i>	$\tau_{ij}$	$\tau_{ji}$	$k_{ij}$				
methanol	water	0.208568	7.86749	0	20–50	102	0.90	60,61
ethanol	water	0.085888	23.5079	0	20–96	123	1.31	60–62
1-propanol	water	0.008046	112.669	0	20–50	146	1.59	60,61,63–65
formic acid	water	0.306135	6.14804	0	20–50	119	0.66	42,43
acetic acid	water	0.277566	17.3809	0	25–50	133	0.98	42,43,53
propionic acid	water	0.103932	57.4632	0	20–50	98	0.44	43
ethylene glycol	water	0.299443	6.65849	0	–20–150	230	0.65	63,65–69
1,3-propanediol	water	0.416423	17.4328	0	30	16	0.40	68
glycerin	water	0.056452	4.02134	0	25	9	1.12	62
benzene	hexane	2.95018	0.469849	0	20–40	21	0.58	44,70,71
benzene	nitrobenzene	3.51192	0.458513	0	25	4	0.24	72
1-propanol	nitrobenzene	7.12327	0.398201	0	25	4	0.36	72
benzene	1-propanol	1	1	0	25	4	0.44	72
methanol	1-propanol	0.071043	0.000123	0	Tb	9	2.68	73
glycerin	ethanol	7.50723	0.280390	0	25	9	0.63	62
methanol	ethanol	0.750678	3.60028	0	20–60	33	0.38	71
ethylene glycol	1-propanol	0.263440	8.94000	0	20	4	0.99	65
cyclohexane	benzene	0.177762	2.31404	0	20–80	92	0.41	44,71,74,75
cyclohexane	hexane	1.93722	0.81182	0	20	6	0.47	44
<i>n</i> -butanol	ethyl acetate	1.92976	0.50139	0	25	9	0.07	76
<i>n</i> -butanol	toluene	1	1	0	25	9	0.28	76
ethyl acetate	toluene	0.79164	1.13407	0	25	9	0.16	76
methanol	acetone	0.264102	0.191972	0.03792	25	9	0.24	77
methanol	cyclohexane	2.511266	0.85234	–0.10785	46, 48	29	0.25	29

that is,

$$\theta_i = \frac{\Gamma_i^\sigma}{\Gamma_i^{\sigma,0}} \quad (11)$$

Combining eqs 11 and 10 leads to an expression for  $\Gamma_i^\sigma$ :

$$\Gamma_i^\sigma = \Gamma_i^{\sigma,0} \frac{K_i a_i}{1 + \sum_j K_j a_j} \quad (12)$$

By substituting eq 12 into eq 8 and integrating eq 8 from  $a_i = 0$  (for which the surface tension is equal to that of the pure or mixed solvent,  $\sigma_{ms}$ ) to the actual value of  $a_i$ , an expression for the effect of electrolyte concentration on surface tension is obtained:

$$\sigma - \sigma_{ms} = RT \sum_i \Gamma_i^{\sigma,0} \ln \left( 1 - \frac{K_i a_i}{1 + \sum_j K_j a_j} \right) \quad (13)$$

Equation 13 was previously obtained by Li and Lu<sup>27</sup> and successfully applied to calculating the surface tension of aqueous electrolyte solutions at (mostly) moderate concentrations.

In this study, we are concerned with the surface tension of electrolyte systems in the complete concentration range, that is, from infinite dilution to the pure solute limit. Therefore, a further extension of eq 13 is necessary. To propose an extended form of eq 13, we note that, for a multicomponent system, the surface excess of species *i* must be affected by the presence of

other species. Classical approaches, such as the Frumkin and related isotherms, exist to account for the effects of interactions between species in an adsorbed layer.<sup>35</sup> However, combining these isotherms with the Gibbs equation does not lead to an analytical, closed-form expression for the surface tension. Although it would be possible to use numerical integration in conjunction with more complex isotherms, such an approach would be very cumbersome, especially for process simulation applications, which require calculating thermophysical properties numerous times. Therefore, we seek a closed-form equation that would extend eq 13 by allowing for pairwise interactions. For this purpose, it is reasonable to assume that the surface excess  $\Gamma_i^\sigma$  can be decomposed into contributions that result from pairwise species–species interactions:

$$\Gamma_i^\sigma = \sum_k \Gamma_{ik}^\sigma \quad (14)$$

In analogy with eq 12,  $\Gamma_{ik}^\sigma$  can be written as a product of a maximum surface excess term and a function of the activities of species in the solution; that is,

$$\Gamma_{ik}^\sigma = \Gamma_{ik}^{\sigma,0} f_{ik}(\mathbf{a}) \quad (14a)$$

where  $\mathbf{a}$  is a vector of activities and  $f_{ik}$  is a function that is not known a priori. In particular, for the Langmuir isotherm,  $f_{ii}(\mathbf{a}) = K_i a_i / (1 + \sum_j K_j a_j)$ . Substituting eqs 14 and 14a into eq 8 and integrating eq 8 yields

$$\sigma - \sigma_{ms} = -RT \sum_i \sum_k \Gamma_{ik}^{\sigma,0} \int_0^{a_i} f_{ik}(\mathbf{a}) \, d \ln a_i \quad (15)$$



**Table 2.** Predicted Results for Ternary Mixtures Using the Binary Parameters from Table 1

solvent mixture			<i>T</i> (°C)	no. points	AAD	ref
<i>i</i>	<i>j</i>	<i>k</i>				
methanol	ethanol	water	5–60	252	2.48	78
ethanol	glycerin	water	25	36	1.39	62
1-propanol	ethylene glycol	water	20	59	3.46	65
methanol	1-propanol	water	Tb	19	3.80	73
benzene	cyclohexane	hexane	20	35	0.79	44
benzene	hexane	pentane	25	10	1.98	79
benzene	1-propanol	nitrobenzene	25	16	1.08	72
<i>n</i> -butanol	ethyl acetate	toluene	25	36	0.11	76

To develop a suitable closed-form expression for the integral  $\int_{0f_{ik}}^{a_{f_{ik}}} d \ln a_i$ , the following two requirements have to be satisfied:

1. The expression for  $\int_{0f_{ik}}^{a_{f_{ik}}} d \ln a_i$  needs to be written in terms of binary pairwise contributions rather than single-species terms. The simplest approach here is to define it in terms of binary averages  $a_{ik}$  of the activities of species *i* and *k*; that is,

$$a_{ik} = (a_i a_k)^{1/2} \quad (16)$$

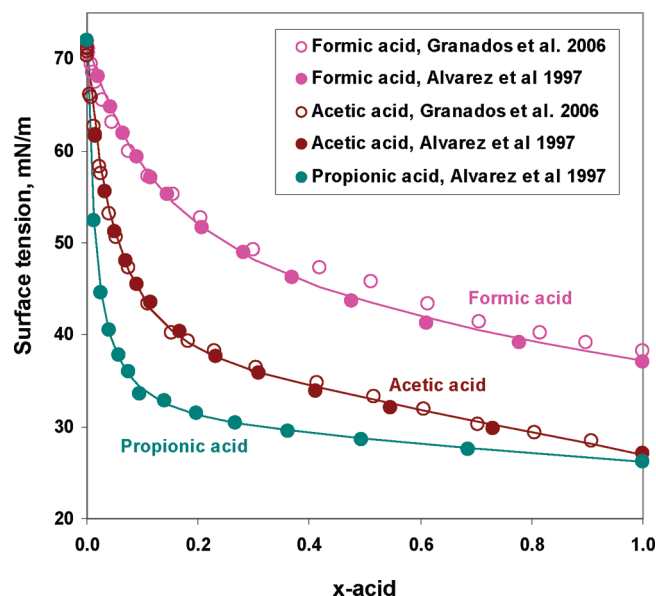
2. The expression needs to preserve the competitive nature of adsorption of different species, which, according to the Lagmuir isotherm, is reflected by the normalizing factor  $(1 + \sum K_j a_j)$  in the denominator of eq 12.

Considering these two requirements, we propose an expression for  $\int_{0f_{ik}}^{a_{f_{ik}}} d \ln a_i$  that is an empirical extension of eq 13 in which the single-species contributions  $K_i a_i$  are replaced by pairwise contributions  $K_{ik} a_{ik}$ :

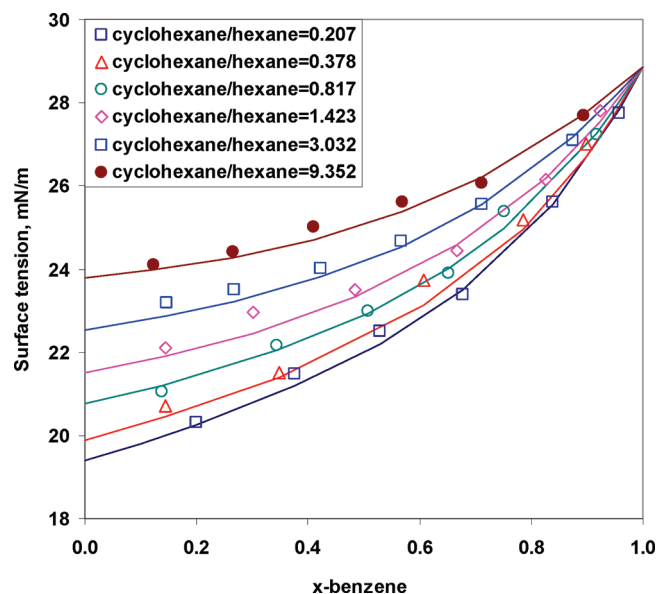
$$\sigma - \sigma_{ms} = RT \sum_i \sum_k \Gamma_{ik}^{\sigma,0} \ln \left( 1 - \frac{K_{ik} a_{ik}}{1 + \sum_j K_{jk} a_{jk}} \right) \quad (17)$$

Because of the selection of the Gibbs dividing surface in the present study, eq 17 does not explicitly reflect the effects of solvent composition on the change of the solution surface tension  $d\sigma$  when two or more solvent components are present. Although such a selection is consistent with the physical meaning of the Gibbs equation, the parameters of eq 17 (i.e.,  $\Gamma_{ik}^{\sigma,0}$  and  $K_{ik}$ ) are unavoidably dependent on the solvent environment in which the electrolyte components find themselves. If such a dependence was ignored, the surface tension increment due to the presence of electrolytes would be the same in all solvents at the same electrolyte activities. Therefore, eq 17 needs to be further extended to introduce the dependence of  $\Gamma_{ik}^{\sigma,0}$  and  $K_{ik}$  on solvent composition. This can be achieved by introducing a factor of  $(X'_m X'_n)^{1/2}$  into eq 17 and redefining the parameters  $\Gamma_{ik}^{\sigma,0}$  and  $K_{ik}$  as  $\Gamma_{ik,mm}^{\sigma,0}$  and  $K_{ik,mm}$  respectively, where *m* and *n* denote the solvent components:

$$\begin{aligned} \sigma - \sigma_{ms} \\ = RT \sum_m \sum_n (x'_m x'_n)^{1/2} \sum_i \sum_k \Gamma_{ik,mm}^{\sigma,0} \ln \left( 1 - \frac{K_{ik,mm} a_{ik}}{1 + \sum_j K_{jk,mm} a_{jk}} \right) \end{aligned} \quad (17a)$$



**Figure 1.** Experimental and calculated surface tensions for the mixtures of water with formic, acetic, and propionic acids at 25 °C. Experimental data were taken from Granados et al.<sup>42</sup> and Alvarez et al.<sup>43</sup>



**Figure 2.** Comparison of the predicted and experimental surface tensions for the ternary system benzene + cyclohexane + hexane at 20 °C at various ratios of cyclohexane/hexane. Experimental data were taken from Ridgway and Butler.<sup>44</sup>

where  $X'_m$  and  $X'_n$  are the salt-free mole fractions of the solvents *m* and *n*, respectively. The factor  $(X'_m X'_n)^{1/2}$  vanishes (i.e., becomes equal to one) if only one solvent is present, and then eq 17a reduces to eq 17 for single-solvent systems such as aqueous electrolyte solutions.

#### 4. PARAMETER EVALUATION

**Parameters  $\tau_{ij}$ ,  $\tau_{ji}$ , and  $k_{ij}$  in the Mixed-Solvent  $\sigma_{ms}$  Model.** The model for calculating the surface tension of a mixed solvent (eqs 1–5) includes three adjustable parameters,  $\tau_{ij}$ ,  $\tau_{ji}$ , and  $k_{ij}$ ,

Table 3. Interaction Parameters (eqs 17–19) for Modeling Surface Tension of Selected Systems<sup>a</sup>

system and conditions	parameters	no. points	AAD	ref
LiCl + methanol, $T = 25\text{ }^{\circ}\text{C}$ , $x_{\text{LiCl}}^{\text{max}} = 0.030$	$\Gamma_{\text{LiCl}/\text{MeOH},\text{MeOH}}^{01} = -0.582576 \times 10^{-3}$ $K_{\text{LiCl}/\text{MeOH},\text{MeOH}}^{(1)} = 5.94436$	9	0.07	57
LiCl + ethanol, $T = 21\text{ }^{\circ}\text{C}$ , $x_{\text{LiCl}}^{\text{max}} = 0.094$	$\Gamma_{\text{LiCl}/\text{EtOH},\text{EtOH}}^{01} = -0.422375 \times 10^{-3}$ $K_{\text{LiCl}/\text{EtOH},\text{EtOH}}^{(1)} = 0.659196$	5	0.12	50
LiCl + formic acid, $T = 14\text{ }^{\circ}\text{C}$ , $x_{\text{LiCl}}^{\text{max}} = 0.071$	$\Gamma_{\text{LiCl}/\text{HCOOH},\text{HCOOH}}^{01} = -0.746615 \times 10^{-3}$ $K_{\text{LiCl}/\text{HCOOH},\text{HCOOH}}^{(1)} = 43.6008$	5	0.99	50
LiCl + acetone, $T = 25\text{ }^{\circ}\text{C}$ , $x_{\text{LiCl}}^{\text{max}} = 0.0076$	$\Gamma_{\text{LiCl}/\text{acetone},\text{acetone}}^{01} = -0.101756 \times 10^{-2}$ $K_{\text{LiCl}/\text{acetone},\text{acetone}}^{(1)} = 7.26861$	7	0.03	57
LiCl + water, $T = 10\text{--}100\text{ }^{\circ}\text{C}$ , $x_{\text{LiCl}}^{\text{max}} = 0.27$	$\Gamma_{\text{LiCl}/\text{H}_2\text{O},\text{H}_2\text{O}}^{01} = -0.332206 \times 10^{-2}$ $\Gamma_{\text{LiCl}/\text{H}_2\text{O},\text{H}_2\text{O}}^{02} = 0.543814$ $K_{\text{LiCl}/\text{H}_2\text{O},\text{H}_2\text{O}}^{(1)} = 53.7578$	139	0.60	45,50,53
MgCl <sub>2</sub> + water, $T = 10\text{--}70\text{ }^{\circ}\text{C}$ , $x_{\text{MgCl}_2}^{\text{max}} = 0.068$	$\Gamma_{\text{MgCl}_2/\text{H}_2\text{O},\text{H}_2\text{O}}^{01} = 0.00136810$ $\Gamma_{\text{MgCl}_2/\text{H}_2\text{O},\text{H}_2\text{O}}^{02} = -0.634729$ $K_{\text{MgCl}_2/\text{H}_2\text{O},\text{H}_2\text{O}}^{(1)} = 334.084$	37	0.75	46–53
KOH + water, $T = 16\text{--}167\text{ }^{\circ}\text{C}$ , $x_{\text{KOH}}^{\text{max}} = 0.24$	$\Gamma_{\text{KOH}/\text{H}_2\text{O},\text{H}_2\text{O}}^{01} = -0.00352681$ $\Gamma_{\text{KOH}/\text{H}_2\text{O},\text{H}_2\text{O}}^{02} = 0.237849$ $K_{\text{KOH}/\text{H}_2\text{O},\text{H}_2\text{O}}^{(1)} = 35.5463$	87	0.93	53,54,80–82
H <sub>2</sub> SO <sub>4</sub> + water, $T = 0\text{--}250\text{ }^{\circ}\text{C}$ , $x_{\text{H}_2\text{SO}_4}^{\text{max}} = 1.0$	$\Gamma_{\text{H}_2\text{O},\text{H}_2\text{SO}_4/\text{H}_2\text{O},\text{H}_2\text{O}}^{01} = -0.187342 \times 10^{-2}$ $\Gamma_{\text{H}_2\text{O},\text{H}_2\text{SO}_4/\text{H}_2\text{O},\text{H}_2\text{O}}^{02} = 0.682542$ $K_{\text{H}_2\text{O},\text{H}_2\text{SO}_4/\text{H}_2\text{O},\text{H}_2\text{O}}^{(1)} = 5.92852$ $\Gamma_{\text{H}_2\text{O},\text{SO}_4/\text{H}_2\text{O},\text{H}_2\text{O}}^{01} = -0.388416 \times 10^{-2}$ $\Gamma_{\text{H}_2\text{O},\text{SO}_4/\text{H}_2\text{O},\text{H}_2\text{O}}^{02} = 0.970621$ $K_{\text{H}_2\text{O},\text{SO}_4/\text{H}_2\text{O},\text{H}_2\text{O}}^{(1)} = 550.762$ $\tau_{\text{H}_2\text{O},\text{H}_2\text{SO}_4} = 0.48330$ $\tau_{\text{H}_2\text{SO}_4,\text{H}_2\text{O}} = 1.58323$ $k_{\text{H}_2\text{SO}_4,\text{H}_2\text{O}} = 0.08790$	233	1.51	38–40,50,56,81,83
HNO <sub>3</sub> + water, $T = 0\text{--}80\text{ }^{\circ}\text{C}$ , $x_{\text{HNO}_3}^{\text{max}} = 1.0$	$\Gamma_{\text{H}_2\text{O},\text{HNO}_3/\text{H}_2\text{O},\text{H}_2\text{O}}^{01} = -1.56239$ $K_{\text{H}_2\text{O},\text{HNO}_3/\text{H}_2\text{O},\text{H}_2\text{O}}^{(1)} = 0.184223 \times 10^{-2}$ $\tau_{\text{H}_2\text{O},\text{HNO}_3} = 4.85917$ $\tau_{\text{HNO}_3,\text{H}_2\text{O}} = 0.70417$	147	1.43	46–51,53,84

<sup>a</sup> Temperature-dependent parameters not shown in this table are set equal to zero for the listed systems.

which can be determined using experimental data for binary mixtures. The variation of the surface tension of solvent mixtures with temperature is determined exclusively by the temperature dependence of the surface tensions of the constituent pure components,  $\sigma_i$ . No temperature-dependent binary parameters have been found necessary for the conditions tested in this study, which span a maximum temperature range of as much as 170 °C for one of the binary mixtures (i.e., the mixture of ethylene glycol with water). Further, for the majority of the binary systems, only two parameters,  $\tau_{ij}$  and  $\tau_{ji}$ , are needed. The parameter  $k_{ij}$  is only necessary for systems that exhibit a maximum or a minimum of  $\sigma$  as a function of  $x$ .

**The  $\Gamma_{ik}^{\sigma,0}$  and  $K_{ik}$  Parameters.** For the effects of electrolyte concentration on surface tension, it is necessary to introduce a temperature dependence for the interaction parameters,  $\Gamma_{ik}^{\sigma,0}$  and  $K_{ik}$  in eq 17a. The temperature dependence of these parameters is given by

$$\Gamma_{ik}^{\sigma,0} = \Gamma_{ik}^{\sigma,01} + \Gamma_{ik}^{\sigma,02}/T + \Gamma_{ik}^{\sigma,03} \cdot T \quad (18)$$

$$K_{ik} = K_{ik}^{(1)} + K_{ik}^{(2)}/T + K_{ik}^{(3)} \cdot T \quad (19)$$

It should be noted that these parameters are solvent-dependent. For example,  $\Gamma_{ik}^{\sigma,0}$  and  $K_{ik}$  for a given species pair in water can be

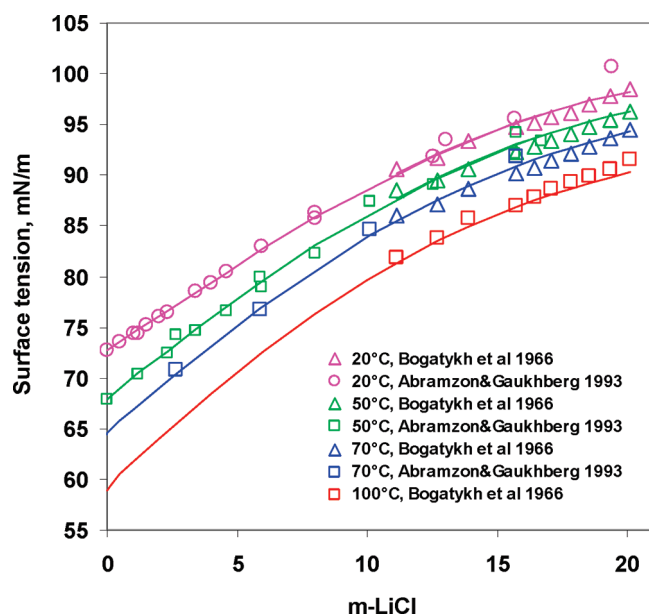
different from those in organic solvents. Solvent effects on these parameters will be discussed in the next section.

## 5. RESULTS AND DISCUSSIONS

**Surface Tension of Solvent Mixtures.** Experimental data for a number of binary, ternary, and quaternary solvent mixtures have been used for validating the mixing rule described in section 2. Table 1 lists the parameters  $\tau_{ij}$ ,  $\tau_{ji}$ , and  $k_{ij}$  for selected binary systems, together with the average percentage error, which is defined by

$$\text{AAD} = \left[ \sum_k^m 100 |\sigma_{\text{expt},k} - \sigma_{\text{cal},k}| / \sigma_{\text{expt},k} \right] / m \quad (20)$$

where  $m$  is the number of experimental data points. Literature data sources are also given in the table. Using the parameters determined from binary mixtures, the surface tension of ternary and quaternary systems can be predicted. Table 2 shows the predicted results for ternary mixtures using the binary parameters listed in Table 1. These results can be better visualized when  $\sigma$  is plotted with respect to the mole fraction of a selected component as demonstrated in Figures 1 and 2. In these figures, results are shown for binary mixtures of water with organic acids and for ternary mixtures of benzene, cyclohexane, and hexane. The results shown in these

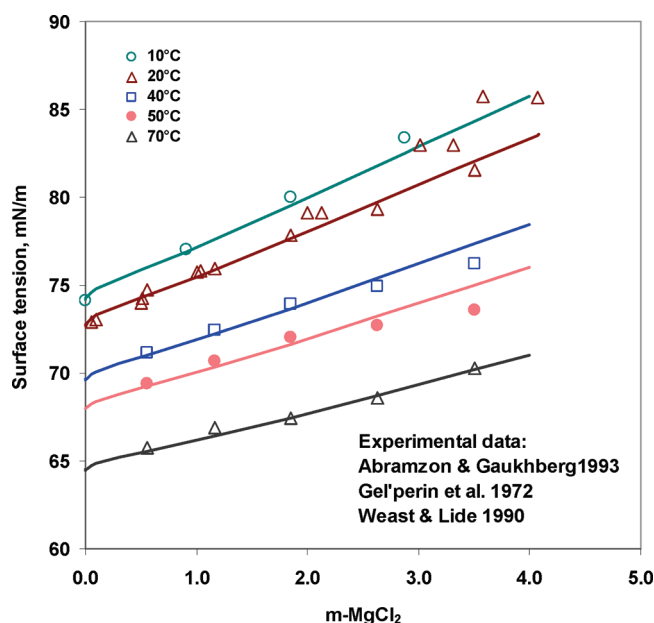


**Figure 3.** Surface tension of the LiCl + water solutions as a function of the molality of LiCl at various temperatures. The experimental data were taken from Bogatykh et al.<sup>45</sup> and Abramzon and Gaukhberg.<sup>46–51</sup>

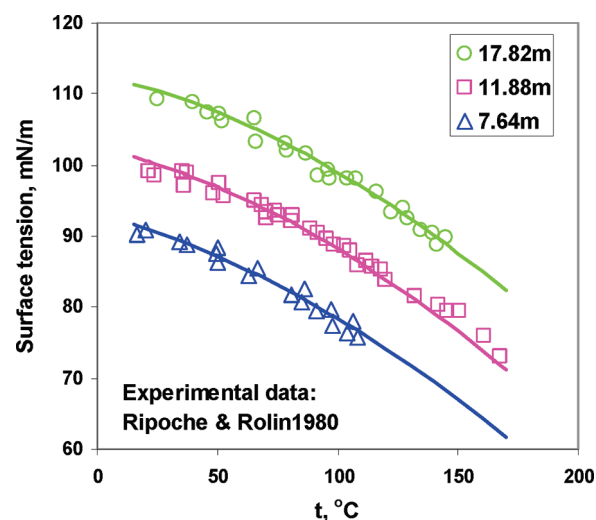
figures and in Tables 1 and 2 indicate that the model (eqs 1–5) can accurately reproduce experimental data for solvent mixtures of any composition and is capable of predicting surface tension in multicomponent mixtures using parameters obtained from data for binary subsystems. It is worth noting that the value of the parameter  $\tau_{ij}$ , which is proportional to the surface mole fraction of  $i$ , increases with the molecular size of component  $i$  for pairs with a fixed component  $j$ . This indicates a dependence of the surface concentrations on the molecular size, although molecular structural parameters such as the molecular area or size are not explicitly introduced in eq 3. This trend can be seen in the parameters listed in Table 1 for the alcohol–water and carboxylic acid–water systems. Exception to this trend may exist due to stronger or weaker interactions between the two components.

**Surface Tension of Electrolyte Solutions.** Application of the new surface tension model to electrolyte solutions has been focused on two classes of systems: (1) aqueous electrolyte systems (salts, acids, and bases) ranging from dilute solutions to fused salts or pure acids or bases and (2) electrolytes in organic and mixed solvents.

Experimental surface tension data for aqueous electrolyte systems are available from the compilations of Washburn and Aseyev<sup>36,37</sup> and from other literature sources. Unfortunately, the Aseyev compilation contains smoothed data that are often inconsistent with published original laboratory results. In our study, data from this compilation are used only for systems for which no other literature data have been found or when the smoothed data show trends that are consistent with those observed under other conditions (i.e., temperature and concentration) for the same system. Compared to aqueous solutions, much less surface tension data are available for nonaqueous electrolyte systems and the experimental coverage is even sparser for mixed-solvent electrolyte solutions. Nonetheless, the available literature data provide a sound basis for testing the new model. For all of the systems for which the surface tension model has been tested, thermodynamic model parameters<sup>34</sup> have been first developed to provide appropriate speciation and activity coefficient input for surface tension modeling.

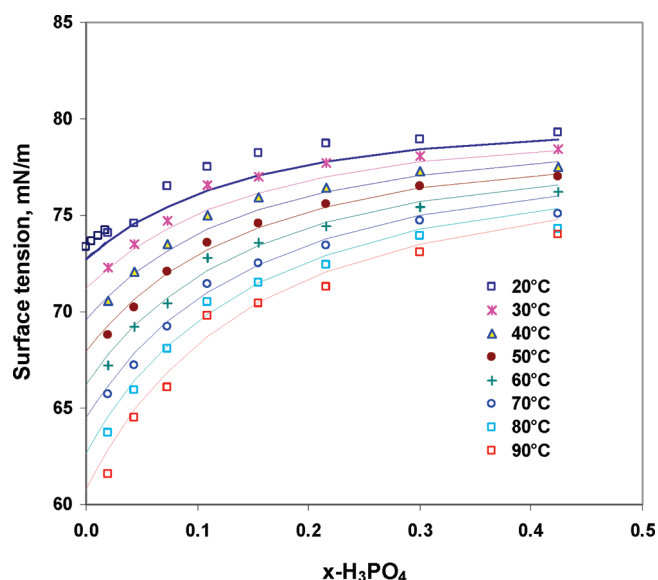


**Figure 4.** Surface tension of the MgCl<sub>2</sub> + water solutions as a function of the molality of MgCl<sub>2</sub> at various temperatures. The experimental data were taken from Abramzon and Gaukhberg,<sup>46–51</sup> Gel'perin et al.,<sup>52</sup> and Weast and Lide.<sup>53</sup>



**Figure 5.** Surface tension of the KOH + water solutions as a function of temperature at various molalities of KOH. The experimental data were taken from Ripoche and Rolin.<sup>54</sup>

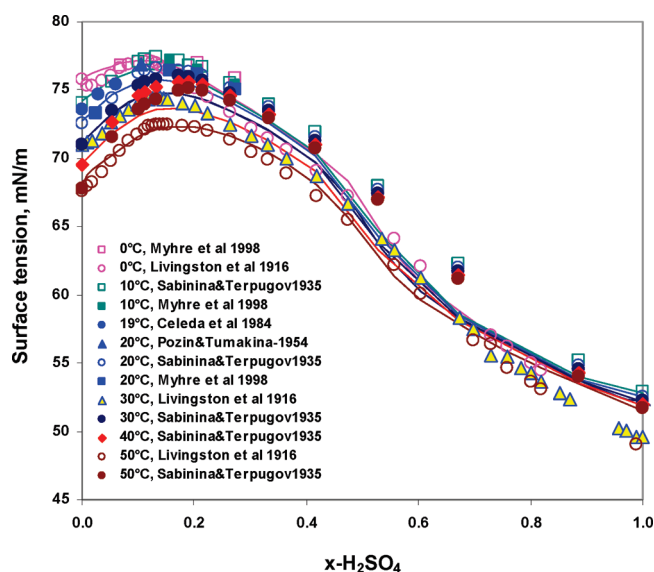
Table 3 lists the adjustable parameters in eqs 17–19 for selected aqueous and nonaqueous electrolyte systems, that is,  $\Gamma_{ik}^{\sigma,0}$  and  $K_{ik}$  including their temperature dependence and, if necessary, the parameters of eqs 1–5 (e.g., for sulfuric acid). The performance of the model for binary aqueous systems is illustrated in Figures 3–8. In these figures, literature data for systems containing water and LiCl, MgCl<sub>2</sub>, KOH, H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, and HNO<sub>3</sub> are compared with calculated results for various temperatures and electrolyte concentrations. In general, negative values of  $\Gamma_{ik}^{\sigma,0}$  are obtained for systems in which surface tension increases with electrolyte concentration, indicating a negative adsorption of the electrolyte on the solution surface.



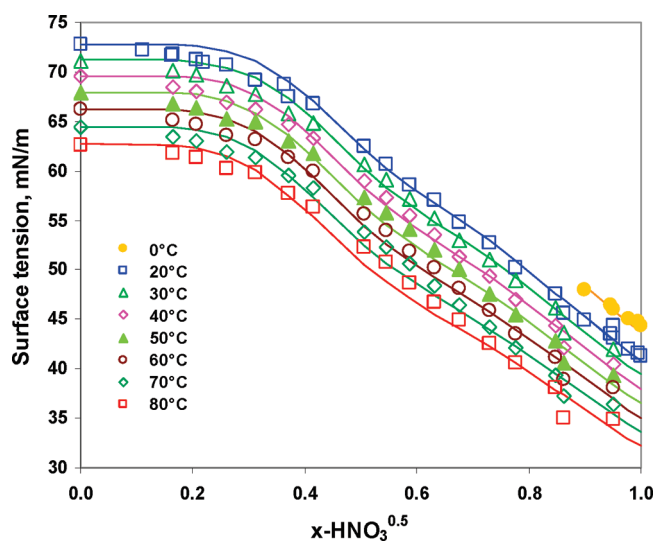
**Figure 6.** Surface tension of aqueous phosphoric acid solutions as a function of  $x_{\text{H}_3\text{PO}_4}$  at various temperatures. The experimental data were taken from Abramzon and Gaukhberg<sup>46–51</sup> and Celeda et al.<sup>55</sup>

Similarly, a positive  $\Gamma_{ik}^{\sigma,0}$  leads to a decrease in surface tension with electrolyte concentration.

In the case of most electrolytes that are strongly dissociated, surface tension increases with concentration as shown in Figures 3–5 for aqueous LiCl, MgCl<sub>2</sub>, and KOH. In contrast to the strongly dissociated salts, surface tension of fully miscible aqueous acids exhibits a more complex behavior. The surface tension of such systems may increase (e.g., for H<sub>3</sub>PO<sub>4</sub> + water), decrease (e.g., for HNO<sub>3</sub> + water and HCl + water), or show a complex behavior (e.g., for H<sub>2</sub>SO<sub>4</sub> + water) with changing electrolyte concentration. The increases or decreases with electrolyte concentration that are observed for different solutions are due to variations in the adsorption tendency of these electrolytes on the solution surface. Because of their strong association effects, the fully miscible acid systems provide not only good test cases, but also offer an excellent opportunity to examine the effect of speciation on surface tension. Figures 6–8 illustrate the surface tension results for these acids. For the aqueous solutions of HNO<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub>, the surface tension decreases or increases monotonically as the acid concentration increases (cf., Figures 6 and 8). In aqueous solutions of H<sub>2</sub>SO<sub>4</sub>, the surface tension increases with rising concentration and then decreases after a maximum is reached, as shown in Figure 7. Two of the data sources for the surface tension of aqueous of H<sub>2</sub>SO<sub>4</sub>, that is, those of Livingston et al.<sup>38</sup> and of Sabinina and Terpugov,<sup>39</sup> show significant deviations from each other over nearly the entire  $x_{\text{H}_2\text{SO}_4}$  range from 0 to 1, with the data of Livingston et al. being substantially lower than those of Sabinina and Terpugov. Myhre et al.<sup>40</sup> have discussed in detail the measurements reported by these authors and reported surface tension results that appear to be consistent with the data of Sabinina and Terpugov at their experimental conditions, which cover only the temperatures below 25 °C and  $x_{\text{H}_2\text{SO}_4}$  values below 0.27. In pure liquid H<sub>2</sub>SO<sub>4</sub>, the Sabinina and Terpugov data are consistent with the critically evaluated values from Daubert and Danner.<sup>1</sup> However, these authors did not provide sufficient information on the accuracy of solution concentrations used in their measurements, thus making it difficult to validate their data.<sup>40</sup> In the present study, we have included all of the reported experimental data in the



**Figure 7.** Surface tension of the H<sub>2</sub>SO<sub>4</sub> + water system as a function of  $x_{\text{H}_2\text{SO}_4}$  at various temperatures. The experimental data were taken from Livingston et al.,<sup>38</sup> Sabinina and Terpugov,<sup>39</sup> Celeda et al.,<sup>55</sup> Pozin and Tumakina,<sup>56</sup> and Myhre et al.<sup>40</sup>

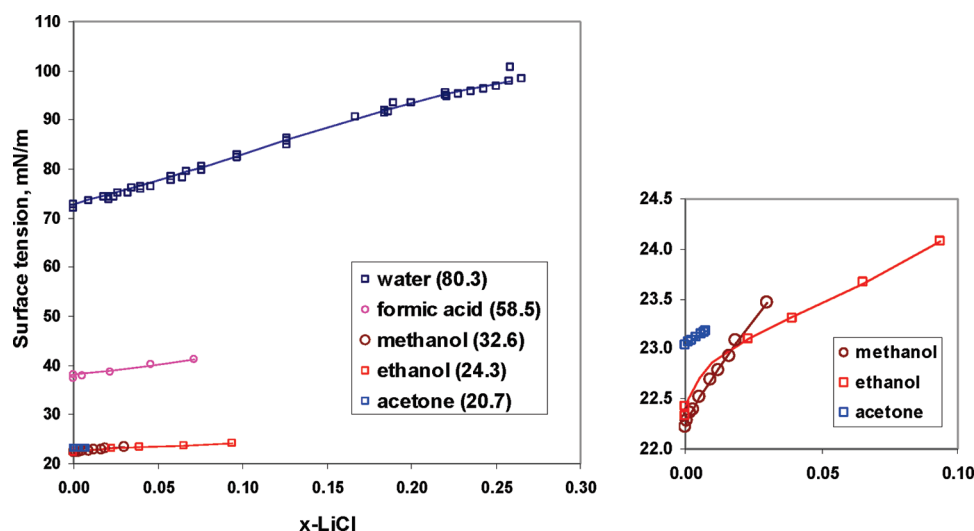


**Figure 8.** Surface tension of the HNO<sub>3</sub> + water system as a function of  $x_{\text{HNO}_3}^{0.5}$  at various temperatures. The experimental data were taken from Abramzon and Gaukhberg<sup>46–51</sup> and Weast and Lide.<sup>53</sup>

determination of model parameters. The obtained results are within the scattering of the published experimental data and are in good agreement with the pure liquid H<sub>2</sub>SO<sub>4</sub> data of Sabinina and Terpugov and Daubert and Danner (cf. Figure 7).

When modeling fully miscible acids, both water and the undissociated acid molecules (e.g., H<sub>2</sub>SO<sub>4</sub><sup>0</sup>, H<sub>3</sub>PO<sub>4</sub><sup>0</sup>, HNO<sub>3</sub><sup>0</sup>) have been treated as solvent components. In these systems, speciation can change dramatically as the acid concentration increases. In particular, a significant amount of neutral acid molecules appears as the acid concentration approaches a mole fraction of 1 and association becomes nearly complete in a pure acid.<sup>41</sup> The interaction parameters that are used in the model for this type of systems include the  $\Gamma_{ik}^{\sigma,0}$  and  $K_{ik}$  parameters between ionic species in eq 17a and the  $\tau_{ji}$ ,  $\tau_{ij}$ , and  $k_{ji}$  parameters between

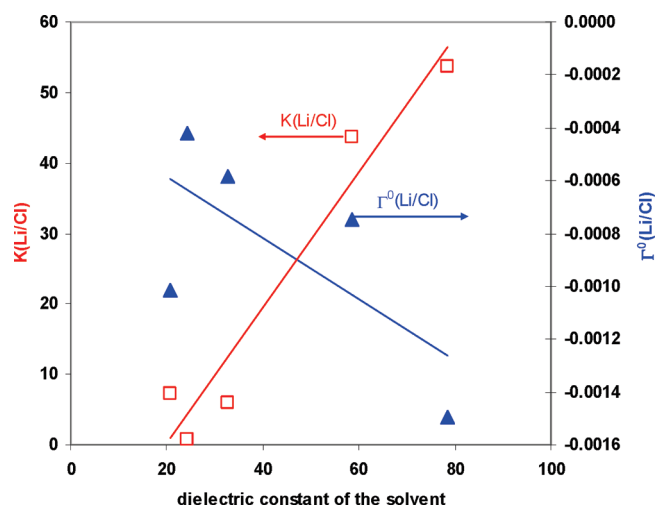




**Figure 9.** Surface tension of solutions of LiCl near room temperature in water (20 °C), methanol (25 °C), ethanol (21 °C), acetone (25 °C), and formic acid (15 °C) as a function of  $x_{\text{LiCl}}$ . The dielectric constants of the solvent at corresponding temperatures are shown in parentheses. The experimental data were taken from Stairs et al.<sup>57</sup> and Abramzon and Gaukhberg.<sup>46–51</sup> The results for LiCl solutions in methanol, ethanol, and acetone are rescaled in the smaller graph to the right for a better view.

solvent components (e.g.,  $\text{H}_2\text{O}$  and  $\text{HNO}_3^0$ ) in eqs 1–5. Here, it should be noted that neutral acid molecules take on the meaning of solvent species when they are present in high concentrations and, simultaneously, water is depleted in the solution. For example, the best fit for the  $\text{HNO}_3 + \text{H}_2\text{O}$  system was obtained when the parameters  $\Gamma_{\text{H}_3\text{O}^+, \text{NO}_3^-/\text{H}_2\text{O}, \text{H}_2\text{O}}^0$ ,  $K_{\text{H}_3\text{O}^+, \text{NO}_3^-/\text{H}_2\text{O}, \text{H}_2\text{O}}$ ,  $\tau_{\text{H}_2\text{O}, \text{HNO}_3}$ , and  $\tau_{\text{HNO}_3, \text{H}_2\text{O}}$  were introduced. In the  $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$  system, the interaction parameters  $\Gamma_{\text{H}_3\text{O}^+, \text{HSO}_4^-/\text{H}_2\text{O}, \text{H}_2\text{O}}^0$ ,  $K_{\text{H}_3\text{O}^+, \text{HSO}_4^-/\text{H}_2\text{O}, \text{H}_2\text{O}}$ ,  $\Gamma_{\text{H}_3\text{O}^+, \text{SO}_4^{2-}/\text{H}_2\text{O}, \text{H}_2\text{O}}^0$ ,  $K_{\text{H}_3\text{O}^+, \text{SO}_4^{2-}/\text{H}_2\text{O}, \text{H}_2\text{O}}$  as well as  $\tau_{\text{H}_2\text{O}, \text{H}_2\text{SO}_4}$ ,  $\tau_{\text{H}_2\text{SO}_4, \text{H}_2\text{O}}$ , and  $k_{\text{H}_2\text{SO}_4, \text{H}_2\text{O}}$  are used to reproduce the data ranging from dilute solutions to pure  $\text{H}_2\text{SO}_4$ . These parameters are listed in Table 3. Excellent agreement between experimental data and calculated results has been obtained for all of the investigated acids over wide ranges of temperature and concentration.

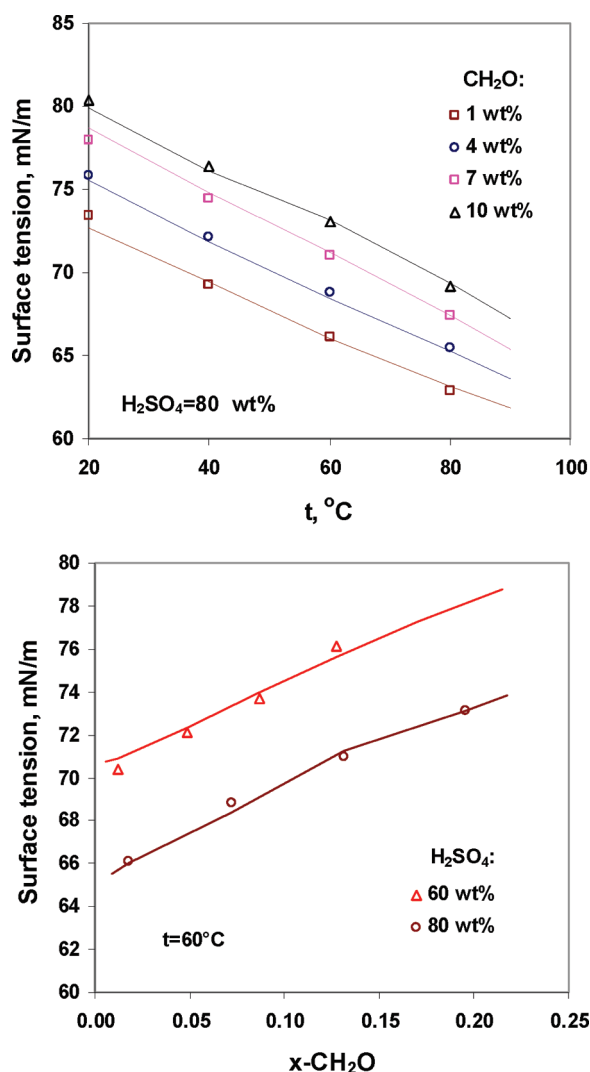
The behavior of surface tension in nonaqueous electrolyte systems can be demonstrated using the solutions of LiCl in various organic solvents as examples. In Figure 9, the surface tension is plotted as a function of the LiCl mole fraction in methanol, ethanol, acetone, and formic acid. For comparison, results for solutions in water are also shown. The model parameters that were used to generate the results shown in Figure 9 are given in Table 3. It is noteworthy that solvent properties have a more significant effect on surface tension than the electrolyte concentration. In general, the increase of the surface tension with electrolyte concentration is more pronounced for solvents with higher dielectric constants, or higher polarity. A plot of the model parameters,  $\Gamma_{\text{LiCl}}^0$  and  $K_{\text{LiCl}}$ , with respect to the dielectric constant of the solvent is shown in Figure 10. In general, the value of  $\Gamma_{\text{LiCl}}^0$  becomes more negative with an increase in the dielectric constant, thus indicating that solvents with stronger polarity (e.g., water) tend to increase the deficiency (or the negative adsorption) of the electrolyte on the surface compared to less polar solvents (e.g., acetone or alcohols). The large  $K_{\text{LiCl}}$  values obtained for the aqueous solution suggest that the variations of the surface tension in water environments are primarily due to the variations of electrolyte activities.<sup>25,27</sup> Consequently, the lower values of  $K_{\text{LiCl}}$  in



**Figure 10.** Variation of the surface tension model parameters,  $\Gamma_{\text{LiCl}}^0$  and  $K_{\text{LiCl}}$ , with the dielectric constant of the solvent, in which LiCl is dissolved.

organic solvents with lower dielectric constants indicate a weaker dependence of the surface tension on the electrolyte activity in such solvents.

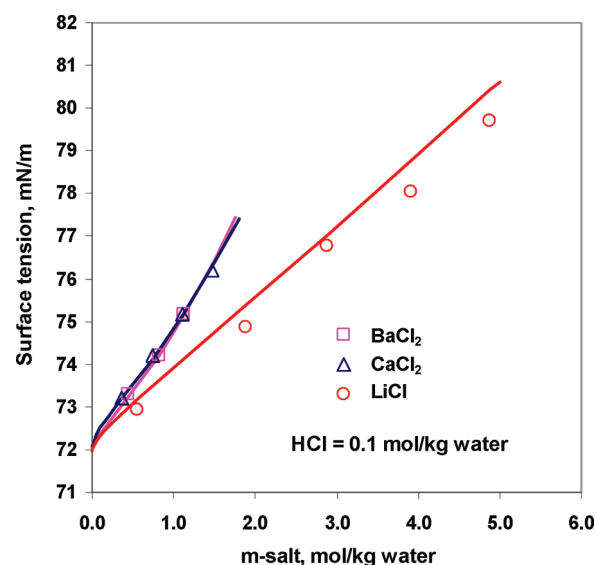
The surface tension data in mixed-solvent electrolytes are sparse. Thus, only the system formaldehyde +  $\text{H}_2\text{SO}_4$  + water has been tested using the new surface tension model. The results are shown in Figure 11 where the surface tension is plotted to show the trends as a function of formaldehyde composition and temperature. Because of the high reactivity of formaldehyde, the experimental data cover only a limited concentration range for this component. It has been found that a better fit to the experimental data can be obtained if formaldehyde is treated as a solute rather than a solvent. Thus, the model has been applied to a mixture that essentially contains a mixed solvent composed of water with undissociated  $\text{H}_2\text{SO}_4$  and solute species including the dissociated ions  $\text{H}^+$  and  $\text{HSO}_4^-$  as well as formaldehyde



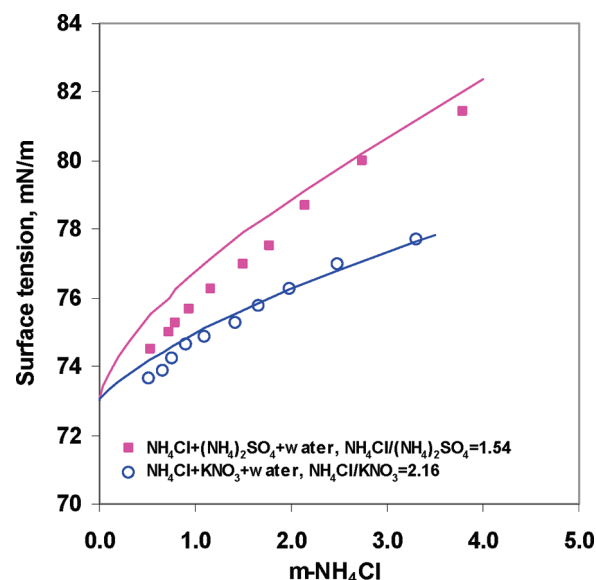
**Figure 11.** Surface tension results for formaldehyde +  $\text{H}_2\text{SO}_4$  + water mixtures (a) as a function of temperature at various formaldehyde weight percents (sulfuric acid concentration is fixed at 80 wt %) and (b) as a function of mole fraction of formaldehyde at 60 and 80 wt %  $\text{H}_2\text{SO}_4$  ( $t = 60\text{ }^\circ\text{C}$ ). Experimental data are from Kim et al.<sup>58</sup>

molecules. The binary parameters introduced for this mixture are  $\Gamma_{\text{H}_2\text{SO}_4, \text{CH}_2\text{O}}$ ,  $\Gamma_{\text{H}_2\text{O}, \text{CH}_2\text{O}}$ ,  $k_{\text{H}_2\text{SO}_4, \text{CH}_2\text{O}}$ , and  $k_{\text{H}_2\text{O}, \text{CH}_2\text{O}}$  in  $\text{H}_2\text{O}$  and in  $\text{H}_2\text{SO}_4$ . Good agreement has been obtained for this system between the calculated and experimental results.

The model's capability to predict surface tension in multi-component electrolyte solutions has also been tested and is illustrated in Figures 12 and 13 for the ternary systems  $\text{HCl} + \text{MCl}_n + \text{H}_2\text{O}$  (where  $\text{M} = \text{Ba}, \text{Ca}, \text{Li}, n = 1 \text{ or } 2$ ),  $\text{NH}_4\text{Cl} + (\text{NH}_4)_2\text{SO}_4 + \text{H}_2\text{O}$  and  $\text{NH}_4\text{Cl} + \text{KNO}_3 + \text{H}_2\text{O}$ . In each case,  $\sigma$  rises as the total electrolyte concentration increases. This behavior has been accurately reproduced. It should be noted that the results shown in these figures are predicted using interaction parameters determined solely from data for binary aqueous solutions. However, in some cases, especially for more concentrated multicomponent solutions, the predicted results may not be entirely satisfactory due to strong ionic interactions on the surface. It is then possible to improve the modeling results by introducing binary parameters between like ions (i.e., between two cations or two anions). Such parameters cannot be obtained

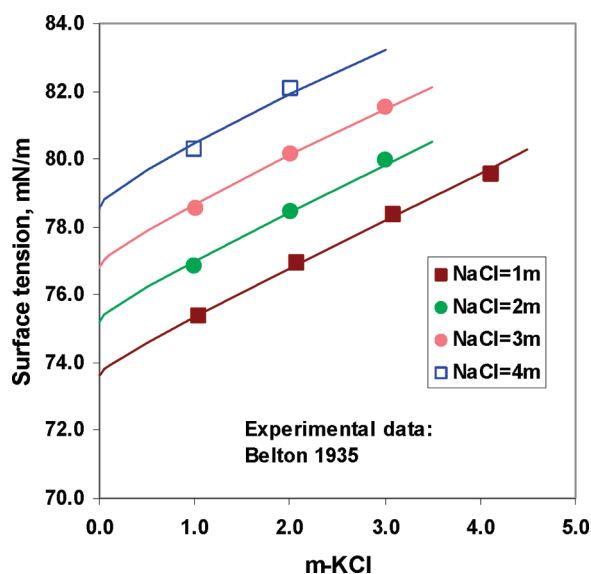


**Figure 12.** Surface tensions for solutions of  $\text{HCl} + \text{BaCl}_2 + \text{H}_2\text{O}$ ,  $\text{HCl} + \text{CaCl}_2 + \text{H}_2\text{O}$  and  $\text{HCl} + \text{LiCl} + \text{H}_2\text{O}$  at  $25\text{ }^\circ\text{C}$  with the  $\text{HCl}$  concentration of  $0.1\text{ mol/kg H}_2\text{O}^{-1}$ . The lines are the results predicted using binary parameters determined from data for binary aqueous electrolyte solutions. Experimental data were taken from Abramzon and Gaukhberg.<sup>46–51</sup> The average relative deviations for the predicted results are 0.06% for  $\text{HCl} + \text{BaCl}_2 + \text{H}_2\text{O}$ , 0.07% for  $\text{CaCl}_2 + \text{H}_2\text{O}$  and  $\text{HCl}$ , and 0.63% for  $\text{HCl} + \text{LiCl} + \text{H}_2\text{O}$ .



**Figure 13.** Surface tensions for solutions of  $\text{NH}_4\text{Cl} + (\text{NH}_4)_2\text{SO}_4 + \text{H}_2\text{O}$  and  $\text{NH}_4\text{Cl} + \text{KNO}_3 + \text{H}_2\text{O}$  at  $18\text{ }^\circ\text{C}$ . The lines are the results predicted using binary parameters determined from data for binary aqueous electrolyte solutions. Experimental data were taken from Abramzon and Gaukhberg.<sup>46–51</sup> The average relative deviations for the predicted results are 1.04% for  $\text{NH}_4\text{Cl} + (\text{NH}_4)_2\text{SO}_4 + \text{H}_2\text{O}$  and 0.34% for  $\text{NH}_4\text{Cl} + \text{KNO}_3 + \text{H}_2\text{O}$ .

from single-salt data and, therefore, their only source may be some selected ternary data. For example, in the  $\text{KCl} + \text{NaCl} + \text{H}_2\text{O}$  system, the predicted surface tensions have an average relative deviation of 1.79%. Although such deviations are acceptable for most practical applications, a further improvement is



**Figure 14.** Comparison of the calculated and experimental surface tensions for solutions of KCl + NaCl + H<sub>2</sub>O at 25 °C as a function of  $m_{\text{KCl}}$  at various fixed  $m_{\text{NaCl}}$ . Experimental data were taken from Belton.<sup>59</sup>

obtained when a binary interaction parameter is introduced between the Na<sup>+</sup> and K<sup>+</sup> ions. Then, the deviation is reduced to 0.13%. The results obtained with the Na<sup>+</sup>–K<sup>+</sup> parameter are shown in Figure 14.

It should be noted that the range of applicability of the current surface tension model is limited by that of the underlying thermodynamic speciation model,<sup>34</sup> which is based on a combination of an excess Gibbs energy model and the Helgeson–Kirkham–Flowers (HKF) equation<sup>85</sup> for standard-state properties. In general, models that are based on an explicit formulation for the excess Gibbs energy of the liquid phase are limited to temperatures that are reasonably lower than the critical temperature of the system. Such models can be generally used at temperatures that do not exceed roughly  $0.9T_c$ , where  $T_c$  is the critical temperature of a mixture. The standard-state properties, as calculated from the Helgeson–Kirkham–Flowers equation of state,<sup>85</sup> are based on the infinite dilution reference state in water, and, through a rigorous thermodynamic manipulation, are extended to nonaqueous or mixed solvents.<sup>34</sup> This standard-state property model is strongly affected by the temperature and pressure variations of pure water properties in the near-critical region. Thus, the application of the model to temperatures above ca. 300 °C in water-based systems may require using modified or alternative treatments of standard-state properties.<sup>86</sup>

## 6. CONCLUSION

A general model has been developed for calculating the surface tension of aqueous, nonaqueous, and mixed-solvent electrolyte solutions. The model consists of two main parts, i.e., a correlation for computing the surface tension of solvent mixtures as a function of temperature and solvent composition, and an expression for the effect of electrolyte concentration. The correlation for solvent mixtures utilizes the surface tensions of pure components as well as adjustable parameters for each binary pair, which are used to define the surface concentrations. The correlation has been shown to be very effective for representing experimental data for a variety of solvent mixtures. In particular,

the surface tension of ternary solvent mixtures can be accurately predicted using parameters determined from only binary data. The expression for the dependence of surface tension on electrolyte concentration has been derived from the Gibbs equation, combined with a modified Langmuir adsorption isotherm for modeling the surface excess of the species. The model extends the Langmuir adsorption equation to introduce contributions to the surface excess due to interactions between any two solute species, ions or molecules, in the solution. This is especially important at high electrolyte concentrations and in highly speciated systems. The surface tension model has been coupled with a previously developed thermodynamic equilibrium model<sup>34</sup> to provide the necessary speciation and activity coefficients. This makes it possible to account for the effects of complexation or other reactions in solution. In all cases in which experimental data are available, the new model has been shown to be accurate for reproducing surface tension over wide ranges of temperature and concentration.

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