Surface Tension of Nonideal Binary Liquid Mixtures as a Function of Composition

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The composition dependence of the surface tension of highly nonideal organic–organic and aqueous–organic nonelectrolyte solutions is described, based on the assumption that the surface layer can be treated as a separate phase located between vapor and bulk liquid phases. The Wilson, NRTL, and UNIFAC methods are used for activity coefficients of surface and bulk phases and three techniques for calculation of molar surface areas, based on Paquette areas, Rasmussen areas, and a Langmuir-type approach are tested. Comparisons of the calculated surface tensions with experimental data yield mean absolute errors, in the best case, of less than 2.5% for the systems studied, all of which exhibit highly nonideal behavior. The surface tension predictions are found to be extremely sensitive to the values of the molar surface areas used in the computation. A Langmuir-type adsorption model is formulated to determine the surface mole fractions from a knowledge of the mixture surface tension as a function of bulk composition. A novel procedure is developed to obtain the partial molar surface area of the larger organic component as a function of composition in binary aqueous–organic systems, assuming that the two components are very dissimilar in size, and that deviations in the partial molar surface area of the smaller component (water) from its pure component molar surface area contribute negligibly to the total molar surface area of the mixture. This removes the approximation of equality of partial and pure component molar surface areas for the larger organic component. Use of the Langmuir-type approach with partial molar surface areas improves surface tension predictions of highly nonideal aqueous–organic mixtures by 20% over use of pure component molar surface areas. It is an important first step in the development of a thermodynamically consistent theory of surfaces for liquid mixtures based on an accurate determination of the composition dependence of partial molar surface areas for all components.

Key Words: Surface; surface tension; solution; mixture; liquid; nonideal; composition; thermodynamics; adsorption; surface area; partial molar surface area; activity coefficient; excess surface tension.

INTRODUCTION

The surface tension of liquid mixtures is an important transport property that reveals information on the structure and energetics of the surface region between two phases and exerts a considerable influence on the transfer of mass and energy across interfaces. An estimate of this surface property is required in many fields including separation processes and environmental engineering. It is an important quantity in cavity theories of molecular association (1–3) and a reliable predictor of solvent strength in liquid chromatography (4). Further, the surface tension is often very sensitive to small changes in composition of the mixture. As a result, it is essential to have a knowledge of the surface tension of mixtures over the entire composition range. Surface tension data for liquid mixtures over a wide range of composition and temperature are scarce and estimation methods are therefore required. Existing methods have limited application or accuracy or require parameters that are difficult to obtain. Further, few methods satisfactorily account for highly nonideal behavior. Nonideal behavior can, in fact, have a significant effect on surface tension (5–7) and it is useful to establish a practical method for quantitatively predicting the surface tension of nonideal liquid mixtures as a function of composition.

The surface tension of liquid mixtures has been investigated by several workers (6–16). The assumptions made in these works include ideal solution behavior in both bulk and surface phases (9, 10), surface concentrations that exhibit small deviations from the bulk concentration (11) and the use of regular solution theory (12, 13) (which applies only to mixtures having zero excess volume and entropy) to determine surface tension. Generally, none of these assumptions are valid for liquid mixtures, especially aqueous–organic systems which behave in an extremely nonideal way, their surface tensions revealing large surface excesses of the organic component.

In this paper we describe the composition dependence of the surface tension of binary organic–organic and aqueous–organic mixtures. The Wilson, NRTL, and UNIFAC equations have been used for computing activity coefficients of surface and bulk phases for both Paquette and Rasmussen pure component molar surface areas (16). Comparisons of the calculated surface tension with experimental data are carried out. A Langmuir-type adsorption model is employed to determine the surface mole fractions from a knowledge of the bulk mole fractions and a novel procedure is developed to obtain the
partial molar surface area of the more volatile component as a function of composition. This removes the approximation of equality of partial and pure component molar surface areas made in every work so far. Interpretation in terms of excess surface tension curves using our model provides insight into the nature of nonideal behavior.

THEORETICAL

Relations for the surface tension of nonelectrolyte solutions can be obtained based on the assumption that the surface layer can be treated thermodynamically as a phase separate from the bulk liquid phase.

The chemical potential, $\mu_i$, of a component $i$ in the bulk phase (B) of a nonelectrolyte solution is given by the relation

$$\mu_{i,B} = \mu_{i,B}^0 + RT \ln \bar{a}_{i,B}, \quad [1]$$

where $\mu_{i,B}^0$ is the standard state chemical potential of component $i$ in the bulk phase and $\bar{a}_{i,B}$ is the activity of $i$ in the bulk phase. $R$ and $T$ are the gas constant and absolute temperature, respectively. In the surface phase (S), the chemical potential of a component can be similarly written as

$$\mu_{i,S} = \mu_{i,S}^0 + RT \ln \bar{a}_{i,S} - \sigma A_i, \quad [2]$$

where $\sigma$ is the surface tension of the solution, $\bar{a}_{i,S}$ the activity of $i$ in the surface phase, and $A_i$ the partial molar surface area of component $i$ in the solution. For a pure component having surface tension $\sigma_i$ and molar surface area $A_i$,

$$\mu_{i,S}^0 - \mu_{i,B}^0 = \sigma_i A_i. \quad [3]$$

At equilibrium, the chemical potentials of component $i$ in the bulk and surface phases are equal; i.e.,

$$\mu_{i,S} = \mu_{i,B}. \quad [4]$$

Combining Eqs. [1]–[4] leads to

$$\sigma A_i = \sigma_i A_i + RT \ln \frac{\bar{a}_{i,S}}{\bar{a}_{i,B}}. \quad [5]$$

The activities $\bar{a}_i$ in Eq. [5] can be written in terms of activity coefficients, $\gamma_i$, as

$$\sigma A_i = \sigma_i A_i + RT \ln \frac{x_{i,S} \gamma_{i,S}}{x_{i,B} \gamma_{i,B}}, \quad [6]$$

where $x_{i,B}$ and $x_{i,S}$ are the mole fractions and $\gamma_{i,B}$ and $\gamma_{i,S}$ the activity coefficients in the bulk and surface liquid phases, respectively.

It is assumed in previous works (8–16) (this approximation will be removed later in this work) that

$$\bar{A}_i = A_i, \quad [7]$$

which reduces Eq. [6] to

$$\sigma = \sigma_i + \frac{RT}{A_i} \ln \frac{x_{i,S} \gamma_{i,S}}{x_{i,B} \gamma_{i,B}}. \quad [8]$$

Further, the sum of the mole fractions over all components in the solution for both bulk and surface liquid phases is unity:

$$\sum_i x_{i,B} = 1, \quad \sum_i x_{i,S} = 1. \quad [9]$$

For an $N$-component nonelectrolyte solution (i.e., known composition), Eq. [8] forms a system of $N$ equations in $N$ unknowns ($N - 1$ independent mole fractions $x_{i,S}$ and $\sigma$). This set of equations is solved iteratively by the Newton–Raphson technique. A calculated guess for $x_{i,S}$ and the criterion for convergence is shown in the Appendix. Pure component surface tensions (Table 1) may be obtained from tables of experimental data (16, 18) or estimated using group contribution methods (19). The excess surface tension is given by

$$\sigma^E = \sigma - \sum_i \sigma_i x_{i,B}. \quad [10]$$

Activity coefficients are calculated using Wilson, NRTL, and UNIFAC equations (17). Rasmussen molar surface areas have been estimated from experimental surface tension data (16). The equation for Paquette molar surface area is based on the assumption that molecules are spherical and that the appropriate geometrical area presented at the surface is the cross-sectional area of the molecule.

$$A_j = \pi \left( \frac{3}{4 \pi} \right)^{2/3} N^{2/3} V_i^{2/3} = 1.02 \times 10^9 V_i^{2/3}. \quad [11]$$
where \( N \) is Avogadro's number. The molar surface volume \( V_{i,S} \) is represented by an equation derived from an anisotropic surface model (10):

\[
V_{i,S} = V_{i,C}^{3/5} V_{i,B}^{2/5}.
\]  

[12]

Here \( V_{i,C} \) is the critical molar volume and \( V_{i,B} \) the bulk liquid molar volume of the \( i \)th component. Combining Eqs. [11] and [12] leads finally to the relation for Paquette areas:

\[
A_i = 1.02 \times 10^8 V_{i,C}^{6/15} V_{i,B}^{4/15}.
\]  

[13]

The description of the Langmuir-type model employed and the development of the partial molar surface area approach will be given in the next section. For the method of derivation of the Rasmussen areas, the reader is referred to the original source (16). The surface tension of aqueous-organic mixtures was measured by the capillary rise method using accurate temperature control to within 0.02°C (22).

### RESULTS AND DISCUSSION

Pure component surface tensions and pure component molar surface areas are shown in Table 1, while the Wilson and NRTL parameters used for calculation of activity coefficients are tabulated in Table 2. References to the experimental vapor-liquid equilibrium data on which the parameters are based have also been noted in Table 2. Using these values, the surface tension of acetone–water mixtures was measured by the capillary rise method using accurate temperature control to within 0.02°C (22).

![Graph](image)

**FIG. 1.** Surface tension as a function of composition for the system acetone (1)–water (2) at 25°C using the Wilson equation. (■) Experimental data. Dashed line represents calculations based on pure component Paquette areas. Bold line obtained for calculations based on pure component Rasmussen areas.
aqueous–organic system, the contribution of the deviation (\( n \)) components differ by a factor of thirteen (Table 1). Hence, for an pure component Rasmussen molar areas of the two compo-
at the surface than water. For acetone–water, for instance, the organic component (being the larger molecule in an aqueous–
oranic system) presents a much larger Rasmussen molar area
portant observation that the Paquette areas are larger than the
similar behavior is also found for the acetone–water mixture. We also make the im-
free and bound. In terms of mole fractions, we can write
x_{1,S} = x_{1,B} + x_{1,S}^b. \tag{14} 
Using the Langmuir isotherm to quantify the binding of com-
component 1 to the surface, we have 
\[ \theta = \frac{Kx_{1,S}^f}{1 + Kx_{1,S}^f}. \tag{15} \]
where \( \theta \) is the fraction of binding sites on the surface occupied by component 1 and \( K \) is the binding constant. The number of surface binding sites may be taken to be proportional to the number of molecules of component 2 at the surface (3–7), leading to the equation

<table>
<thead>
<tr>
<th>( x_{1,B} )</th>
<th>( \sigma_{exp} )</th>
<th>( \sigma_{calc,P} )</th>
<th>Error(_P) (%)</th>
<th>( \sigma_{calc,R} )</th>
<th>Error(_R) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0009</td>
<td>69.83</td>
<td>69.707</td>
<td>0.177</td>
<td>70.287</td>
<td>0.654</td>
</tr>
<tr>
<td>0.0046</td>
<td>65.64</td>
<td>61.248</td>
<td>6.691</td>
<td>65.279</td>
<td>0.550</td>
</tr>
<tr>
<td>0.0099</td>
<td>62.45</td>
<td>55.410</td>
<td>11.273</td>
<td>60.716</td>
<td>2.776</td>
</tr>
<tr>
<td>0.0250</td>
<td>56.90</td>
<td>48.483</td>
<td>14.793</td>
<td>53.513</td>
<td>5.952</td>
</tr>
<tr>
<td>0.0490</td>
<td>51.57</td>
<td>43.831</td>
<td>15.007</td>
<td>47.796</td>
<td>7.319</td>
</tr>
<tr>
<td>0.1000</td>
<td>45.30</td>
<td>39.598</td>
<td>12.588</td>
<td>42.121</td>
<td>7.017</td>
</tr>
<tr>
<td>0.2000</td>
<td>39.27</td>
<td>36.533</td>
<td>6.968</td>
<td>37.668</td>
<td>4.080</td>
</tr>
<tr>
<td>0.3000</td>
<td>36.95</td>
<td>35.315</td>
<td>4.425</td>
<td>35.745</td>
<td>3.261</td>
</tr>
<tr>
<td>0.4000</td>
<td>35.80</td>
<td>34.696</td>
<td>3.085</td>
<td>34.738</td>
<td>2.967</td>
</tr>
<tr>
<td>0.5000</td>
<td>35.00</td>
<td>34.328</td>
<td>1.921</td>
<td>34.154</td>
<td>2.416</td>
</tr>
<tr>
<td>0.6980</td>
<td>33.95</td>
<td>33.858</td>
<td>0.271</td>
<td>33.502</td>
<td>1.139</td>
</tr>
<tr>
<td>0.8163</td>
<td>33.60</td>
<td>33.579</td>
<td>0.064</td>
<td>33.217</td>
<td>1.140</td>
</tr>
<tr>
<td>0.8956</td>
<td>33.10</td>
<td>33.328</td>
<td>0.688</td>
<td>33.034</td>
<td>0.199</td>
</tr>
</tbody>
</table>

FIG. 2. Surface tension as a function of composition for the acetone (1)–water (2) liquid mixture at 25°C using pure component Rasmussen areas. Experimental data. Calculations using the Wilson equation and the NRTL equation superimpose to give the bold line while use of the UNIFAC equation yields the dashed line.
For the acetone–water system, the values of the slope and intercept of the straight line based on Eq. [21]. of component 1 can be obtained as component 1 at the surface and the partial molar surface area respectively. An increase in area results from the adsorption of for the 1,4-dioxane–water system work out to be 0.95 and 0.91, to measure 0.98 and 0.84, respectively. The values of the parameters with the reduced surface tension, component 1, and the weighted mean assumption) made in arriving at Eq. [21].

Further, we expect the relationship to hold because we do not anticipate any difference between the bulk phase and the nonbound molecules of the surface phase: they ought to behave in an equivalent way.

Combining Eqs. [14]–[17] and using Eq. [9] gives us the relationship

\[ x_{1,S}^b = k \theta x_{2,S} \]  \[ x_{1,S}^f = x_{1,B} \]  \[ x_{1,S} = \left[ 1 + \frac{bx_{2,B}}{1 - ax_{2,B}} \right] x_{1,B} \]

where

\[ a = \frac{K}{1 + K} \]  \[ b = \frac{K x_{2}\overline{S}/x_{2,B}}{1 + K} \]

Assuming the surface tension of the mixture to be the mean of the pure component surface tensions weighted by the surface compositions of the components (3), we have

\[ \frac{x_{1,B}x_{2,B}}{\sigma - x_{1,B}} = \frac{1}{b} - \frac{ax_{2,B}}{b} \]

with the reduced surface tension, \( \sigma \) given by \((\sigma_2 - \sigma)/(\sigma_2 - \sigma_1)\). Note carefully the main assumptions (Eqs. [16], [17], and the weighted mean assumption) made in arriving at Eq. [21]. The values of the parameters \( a \) and \( b \) can be determined from the slope and intercept of the straight line based on Eq. [21].

The acetone–water system, the values of \( a \) and \( b \) are found to measure 0.98 and 0.84, respectively. The values of \( a \) and \( b \) for the 1,4-dioxane–water system work out to be 0.95 and 0.91, respectively. An increase in area results from the adsorption of component 1 at the surface and the partial molar surface area of component 1 can be obtained as

\[ A_{1,S} = A_{1,B} + \left( \frac{dx_{1,S}}{dx_{1,B}} \right) \Delta x_{1,B} \]

Here, \( n \) refers to the step number and \( \Delta \) to the increment in \( x_{1,B} \). Starting from the Rasmussen area at \( x_{1,B} = 0 \), Eqs. [21] and [22] permit calculation of the partial molar surface area as a function of composition.

Table 4 summarizes the results of the above calculations. In all the cases studied, the use of Rasmussen areas results in superior predictions of the surface tension than use of Paquette areas, as clearly seen from the mean absolute errors. For the aqueous–organic systems studied, use of the Langmuir-type model and partial molar areas leads to a further 20% improvement in the surface tension predictions over use of the pure component Rasmussen areas (Table 4). Moreover, the Langmuir model–partial molar area approach yields better results at every value of the bulk composition compared to use of the pure component Rasmussen areas. In general, use of the ideal solution model leads to inferior predictions compared to use of Rasmussen areas in nonideal models of the surface (Table 4). However, exceptions to this should be noted in Table 4, for instance in the case of the 1,4-dioxane–water system, where the ideal solution with pure component Rasmussen areas performs better than any of the nonideal models used in conjunction with the pure component Rasmussen areas. Similarly, for the acetone–water mixture, the ideal solution model predicts the surface tension more accurately than nonideal solution models when pure component Paquette areas are employed in the computations (Table 4). These “discrepancies” do not arise from the method of comparison, which is the same for each model, i.e., the percentage error in prediction of surface tension is calculated as 100(\( \sigma_{\text{expt}} - \sigma_{\text{theory}} \)/\( \sigma_{\text{expt}} \) in each case; in fact they indicate that the values of the molar surface areas used in any computation to date in this field deviate from the actual areas these components exhibit in solution and help point the way forward for future research. The nonideal models will lead to superior predictions over the ideal solution model only if the correct molar surface areas are used at each composition of the mixture. No attempt is made to fill the two blank spaces for the Langmuir-type model in Table 4 corresponding to the two organic–organic mixtures because the sizes of both species are of comparable magnitude (unlike the >13-fold difference in areas between species in aqueous–organic mixtures that are instrumen-

\[
\begin{array}{|c|c|c|c|c|c|c|c|c|c|c|c|}
\hline
\text{System} & T \,(^\circ \text{C}) & \text{Mol \% of} & \text{Ideal solution} & \text{UNIFAC} & \text{Wilson} & \text{NRTL} & \text{Langmuir-type} \\
\hline
\text{Acetone–water} & 25 & 1.6–85.5 & 4.94 & 3.29 & 16.70 & 5.50 & 13.80 & 2.94 & 14.00 & 2.96 & 2.20 \\
\text{1,4-Dioxane–water} & 25 & 0.09–89.5 & 6.45 & 1.93 & 11.90 & 8.90 & 5.99 & 3.05 & 5.46 & 2.97 & 2.71 \\
\text{Ethanol–acetonitrile} & 20 & 18.1–88.1 & 3.59 & 2.85 & 3.75 & 4.30 & 2.22 & 2.86 & 3.28 & 2.76 & \\
\text{Methanol–benzene} & 30 & 30.1–88.1 & 6.73 & 3.61 & 0.58 & 2.28 & 5.28 & 1.00 & 6.66 & 1.57 & \\
\hline
\end{array}
\]

Table 4: Mean Absolute Percentage Error in the Calculation of Surface Tension of Nonideal Binary Liquid Mixtures
nal to the model developed here) and the deviations of partial molar surface areas from pure component molar surface areas as a function of composition need to be taken into account for both species. These aspirations must await the development of a more rigorous, thermodynamically consistent model of the surface.

Figures 3 and 4 depict the excess surface tension curves for acetone–water and 1,4-dioxane–water mixtures. For these highly nonideal aqueous–organic mixtures, the excess surface tension calculations were made from results using the Langmuir-type model as well as with the Paquette pure component areas. The large negative excess surface tensions indicate the deviation of the system from ideality. For both systems, the Langmuir-type model describes the nonideality in a superior fashion. Use of the Paquette areas leads to errors in excess surface tension values as high as 77% for both acetone–water and 1,4-dioxane–water systems at low mole fractions of the organic component (Figs. 3 and 4). These errors reduce to less than a tenth of the above errors when the Langmuir-type model is employed. Moreover, the Langmuir-type model correctly predicts the composition at which the minima in excess surface tension occurs; the Paquette model greatly underestimates the composition of the minima for both acetone–water and 1,4-dioxane–water systems (Figs. 3 and 4). Finally, the nonideality should not be correlated to the pure component surface tensions, \( \sigma_i \) or to the pure component surface tension difference (\( \sigma_2 - \sigma_1 \)), as done previously (9, 10, 16). The excess surface tension is a better, more fundamental parameter to characterize the nonideal surface phenomena involved.

**CONCLUSIONS**

The surface tension–composition behavior of highly nonideal binary organic–organic and aqueous–organic liquid mixtures was predicted using three techniques to estimate the activity coefficients and three methods for evaluation of molar surface areas. The computations were found to be very sensitive to the values of the molar surface areas used. Comparisons of the calculated surface tensions with the experimental data yielded mean absolute errors of less than 2.5% for the systems studied. The use of a Langmuir-type adsorption model and partial molar surface areas lead to superior surface tension predictions than use of pure component molar areas. The model presented here should help in the development of a general, thermodynamically consistent theory of surfaces based on partial molar surface areas.

**APPENDIX**

Convergence Criterion and the Initial Choice of Surface Mole Fractions

To ensure convergence of the Newton–Raphson iterative solution (see Eqs. [8] and [9]) a suitable initial choice for surface mole fraction needs to be found. This is done by taking all molar surface areas to be equal and both surface and bulk phase activity coefficients to be unity. With these assumptions, Eq. [8] becomes

\[
\sigma_i = \sigma_i + \frac{RT}{A} \ln \frac{x_i}{x_i,B} = \sigma_j + \frac{RT}{A} \ln \frac{x_j}{x_j,B} \quad [A1]
\]

for components \( i \) and \( j \).

**FIG. 3.** Excess surface tension as a function of composition for the acetone (1)–water (2) system at 25°C. (■) Experimental data. The bold line represents calculations using the Langmuir-type model with partial molar surface areas and the Wilson equation while the dashed line shows the results using the pure component Paquette areas and the Wilson equation.

**FIG. 4.** Excess surface tension as a function of composition for the 1,4-dioxane (1)–water (2) mixture at 25°C. (●) Experimental data. The bold line represents calculations using the Langmuir-type model with partial molar surface areas and the Wilson equation while the dashed line shows the results using the pure component Paquette areas and the Wilson equation.
For a two-component system, using Eqs. [9] and [A1] leads, after some algebraic manipulation, to an initial choice for \( x_{1,S} \):

\[
x_{1,S} = 1/\left[ 1 + \exp\left( -\frac{A}{RT} \left( \sigma_2 - \sigma_1 + \frac{RT}{A} \ln \frac{x_{1,B}}{x_{2,B}} \right) \right) \right], \quad [A2]
\]

where \( A \) can be taken as \( (A_1 + A_2)/2 \).

The iterations are performed until convergence. The convergence criterion employed was

\[
\frac{(x_{1,S})_{n+1} - (x_{1,S})_n}{(x_{1,S})_n} < 1 \times 10^{-5}, \quad [A3]
\]

where subscript \( n \) refers to the \( n \)th iteration.

REFERENCES