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 area 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

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

[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

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

[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 \( A_i \),

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

[3]

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

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

[4]

Combining Eqs. [1]–[4] leads to

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

[5]

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

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

[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 (8–10) (this approximation will be removed later in this work) that

\[
\bar{A}_i = A_i,
\]

[7]

which reduces Eq. [6] to

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

[8]

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

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

[9]

For an \( N \)-component nonelectrolyte solution (\( i = 1 \) to \( N \)) of known composition (i.e., known \( x_{i,B} \)), 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

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

[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.

\[
A_i = \frac{3}{4\pi} \frac{N^{1/3} \gamma_{i,b}^{2/3}}{2K_{Lb}^{1/3}} = 1.02 \times 10^6 \frac{1}{\gamma_{i,b}^{2/3}}.
\]

[11]
TABLE 2
Values of Wilson and NRTL Parameters for Activity Coefficient Calculations

<table>
<thead>
<tr>
<th>System</th>
<th>Wilson</th>
<th>NRTL</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T$ (°C)</td>
<td>$a_{12}$ (cal/mol)</td>
</tr>
<tr>
<td>Acetone–water (21)</td>
<td>25</td>
<td>$-93.7097$</td>
</tr>
<tr>
<td>1,4-Dioxane–water (22)</td>
<td>25</td>
<td>$-296.3764$</td>
</tr>
<tr>
<td>Ethanol–acetoneitrile (23)</td>
<td>20</td>
<td>$892.5958$</td>
</tr>
<tr>
<td>Methanol–benzene (20)</td>
<td>30</td>
<td>$1041.3975$</td>
</tr>
</tbody>
</table>

where $N$ is Avogadro’s number. The molar surface volume $V_{AB}$ is represented by an equation derived from an anisotropic surface model (10):

$$V_{AB} = V_{AC}^{53/12}V_{CB}^{53/12}. \quad [12]$$

Here $V_{IC}$ is the critical molar volume and $V_{IJ}$ the bulk liquid molar volume of the $i$th component. Combining Eqs. [11] and [12] leads finally to the relation for Paquette areas:

$$A_i = 1.02 \times 10^9 V_{IC}^{53}V_{IC}^{53} \quad [13]$$

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 as a function of composition is shown in Fig. 1. The plots were generated for both Paquette and Rasmussen areas using the Wilson equation for activity coefficients. Use of Paquette areas underestimated the surface tension by as high as 23% in the dilute region (bulk mole fractions of acetone between 0 and 0.1) (Fig. 1). Even in the intermediate mole fraction region ($x_{1,B} = 0.2$–0.5), the predicted surface tension values using Paquette areas were more than 8% lower on the average than the experimentally measured surface tensions. Use of Rasmussen areas resulted in a vastly improved fit to the experimental data (Fig. 1). The maximum error in the low acetone mole fraction region ($x_{1,B} = 0$–0.1) measured less than 2.8% while the mean error in this range worked out to be less than 1.8% for this system. In the region of $x_{1,B}$ between 0.2 and 0.5, the maximum error measured less than 4.8%. This is a good result, considering the fact that acetone–water is a highly nonideal aqueous–organic system (acetone and water differ considerably in size and nature of species, for example, in polarity and hydrophobicity and the mixture exhibits a high surface excess of acetone). Similar results were obtained for methanol–benzene, ethanol–acetoneotrile, and 1,4-dioxane–water systems. Thus, in the region where the surface tension is extremely sensitive to changes in composition, i.e., for mole fraction of the organic component less than 0.2, the Rasmussen areas lead to far superior surface tension predictions compared to use of Paquette areas.

Figure 2 shows the experimental and predicted surface tension as a function of composition for the acetone–water system using Rasmussen areas. The predicted surface tension values are not significantly affected by the method of activity coefficient evaluation; the curves using Wilson and NRTL methods superimpose into one curve (Fig. 2). Either of these methods with experimentally determined parameters yield superior results compared to use of the UNIFAC computational method. The latter leads to a maximum error of greater than 12% with Rasmussen areas (and a maximum error of almost 30% with Paquette areas) in the dilute range for the acetone-water system.

![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.](image-url)
Similar results are obtained with other liquid mixtures. Use of the UNIFAC (16) method of activity coefficient determination for acetone–water gave identical results to that depicted in Fig. 2. It can therefore be concluded that, for both Paquette and Rasmussen areas, the mean percentage errors in surface tension work out to be the same irrespective of the method (based on experimentally determined parameters) used to calculate the activity coefficients. However, the computations are very sensitive to the values of the molar surface areas used.

The dependence of the predicted surface tension on the choice of pure component molar surface areas is clearly seen in Table 3 for the 1,4-dioxane–water mixture using the Wilson equation for determination of activity coefficients. For low and intermediate mole fractions of the organic component (x_{1,B} \approx 0.4), the surface tension predictions based on Rasmussen areas are far superior to those based on Paquette areas. In this composition range for 1,4-dioxane–water, the mean percentage error measures only 3.84% for Rasmussen areas compared to 8.34% for Paquette areas, an improvement of over 115% when Rasmussen areas are used (Table 3). Moreover, the percentage error incurred by use of Rasmussen areas is significantly lower at almost every mole fraction in this range (compared to use of Paquette areas) (Table 3). Consideration of the surface tension predictions at high mole fractions of 1,4-dioxane (x_{1,B} \approx 0.5) shows the opposite trend; now the Paquette areas lead to superior results (a mean error of 0.74% for Paquette areas against 1.27% for Rasmussen areas). Similar behavior is also found for the acetone–water mixture. We also make the important observation that the Paquette areas are larger than the Rasmussen areas for every component (Table 1); further, the organic component (being the larger molecule in an aqueous–organic system) presents a much larger Rasmussen molar area at the surface than water. For acetone–water, for instance, the pure component Rasmussen molar areas of the two components differ by a factor of thirteen (Table 1). Hence, for an aqueous–organic system, the contribution of the deviation (A_i - A_0) of water to the total molar surface area, A (cm²/mol), of the mixture is small, compared to the contribution of the corresponding deviation for the organic component. We may therefore anticipate superior results if we consider the partial molar surface area of the organic component (keeping water fixed at its pure component Rasmussen area) and use the complete equation (Eq. [6]) for surface tension predictions. This partial molar surface area of the organic component will possess the following physical characteristics in the aqueous–organic mixture: (i) it will be small at low values of the mole fraction of the organic and approach the pure component Rasmussen molar surface area given in Table 1 at infinite dilution; (ii) it will increase with increase in the mole fraction of the organic; and (iii) it will asymptote to a value of the pure component area that is larger than the Rasmussen area (and perhaps even approach the Paquette area) as x_{1,B} tends to 1.

To determine how the surface molar fraction x_{1,B} and the partial molar surface area A_i increases with x_{1,B}, we employ a Langmuir-type adsorption model at the surface. The more volatile component 1 occurs in two states in the surface phase: free and bound. In terms of mole fractions, we can write

\[ x_{1,S} = x_{1,S}^f + x_{1,S}^b. \]  

Using the Langmuir isotherm to quantify the binding of component 1 to the surface, we have

\[ \theta = \frac{K x_{1,S}^f}{1 + K x_{1,S}^f}. \]  

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 3**

Surface Tension as a Function of Composition for the 1,4-Dioxane–Water System at 25°C Using the Wilson Equation and Paquette and Rasmussen Areas

<table>
<thead>
<tr>
<th>x_{1,B}</th>
<th>σ_{exp}</th>
<th>σ_{calc,p}</th>
<th>Error_p (%)</th>
<th>σ_{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>66.64</td>
<td>66.248</td>
<td>0.691</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>14.795</td>
<td>53.513</td>
<td>5.952</td>
</tr>
<tr>
<td>0.0400</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>4.880</td>
</tr>
<tr>
<td>0.3000</td>
<td>36.95</td>
<td>35.315</td>
<td>4.253</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>34.789</td>
<td>2.967</td>
</tr>
<tr>
<td>0.5000</td>
<td>33.50</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>1.319</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>
Mean Absolute Percentage Error in the Calculation of Surface Tension of Nonideal Binary Liquid Mixtures

<table>
<thead>
<tr>
<th>System</th>
<th>$T$ (°C)</th>
<th>Mol % of 1 (°C)</th>
<th>Ideal solution</th>
<th>UNIFAC</th>
<th>Wilson</th>
<th>NRTL</th>
<th>Langmuir-type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone–water</td>
<td>25</td>
<td>1.6–85.5</td>
<td>4.94</td>
<td>16.70</td>
<td>13.80</td>
<td>14.00</td>
<td>2.20</td>
</tr>
<tr>
<td>1,4-Dioxane–water</td>
<td>25</td>
<td>0.09–89.5</td>
<td>6.45</td>
<td>11.90</td>
<td>5.99</td>
<td>5.46</td>
<td>2.71</td>
</tr>
<tr>
<td>Ethanol–acetonitrile</td>
<td>20</td>
<td>18.1–88.1</td>
<td>3.59</td>
<td>3.75</td>
<td>2.22</td>
<td>3.28</td>
<td>2.76</td>
</tr>
<tr>
<td>Methanol–benzene</td>
<td>30</td>
<td>30.1–88.1</td>
<td>6.73</td>
<td>0.58</td>
<td>5.28</td>
<td>6.66</td>
<td>1.57</td>
</tr>
</tbody>
</table>

Further, we expect the relationship

$$x_{1,5}^b = k0x_{2,5}$$

[16]

to hold because we do not anticipate any difference between the bulk phase and the nonbond 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

$$x_{1,5} = \left(1 + \frac{bx_{1,5}}{1 - ax_{2,5}}\right)x_{1,5}$$

[18]

where

$$a = \frac{K}{1 + K}$$

[19]

$$b = \frac{Kx_{2,5}}{1 + K}$$

[20]

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

$$\sigma_s = \frac{x_{1,5}^b x_{2,5}}{\sigma_2 - \sigma_1} = \frac{1}{b} - \frac{ax_{2,5}}{b}$$

[21]

with the reduced surface tension, $\sigma_s$ 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]. For 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

$$\Delta A_{1,n} = A_{1,n-1} - \int \left(1 + \frac{dx_{1,5}}{dx_{1,5}^b}\right) \Delta x_{1,5}$$

[22]

Here, $n$ refers to the step number and $\Delta$ to the increment in $x_{1,5}$. Starting from the Rasmussen area at $x_{1,5} = 0$, 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 $100(\sigma_{\text{exp}} - \sigma_{\text{theor}})/\sigma_{\text{exp}}$ 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-
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

$$
\sigma = \sigma_i + \frac{RT}{A} \ln \frac{x_{iS}}{x_{iB}} = \sigma_j + \frac{RT}{A} \ln \frac{x_{jS}}{x_{jB}} \quad [A1]
$$

for components $i$ and $j$.

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 \( x_{1,b} \):

\[
x_{1,b} = \frac{1}{1 + \exp \left( \frac{A}{RT} \left[ (\sigma_2 - \sigma_1) + \frac{RT}{A} \ln \frac{x_{1,b}}{x_{2,b}} \right] \right)}.
\]

[A2]

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

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

\[
\frac{(x_{1,b})_{n+1} - (x_{1,b})_n}{(x_{1,b})_n} \leq 1 \times 10^{-5},
\]

[A3]

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

REFERENCES