

# Surface Tension and Surface Properties of Binary Mixtures of 1,4-Dioxane or *N,N*-Dimethyl Formamide with *n*-Alkyl Acetates

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Surface tension of binary mixtures of (1,4-dioxane or DMF + *n*-alkyl acetate) were measured experimentally using the ring method and the results compared with those predicted by using the Sprow and Prausnitz method. The  $\sigma$  values decreased with an increase of the *n*-alkyl acetate mole fraction for its binary mixtures with 1,4-dioxane or DMF. Bulk mole fractions, surface molar area, and surface tension of pure components are necessary inputs for this equation. Also, the UNIFAC group contribution method is applied to account for the nonideality of the bulk liquid as well as that of the surface layer. The mean relative standard deviation values for six binary mixtures are less than 1 %. Surface mole fractions and surface excess concentration values show that the surface is enriched with *n*-alkyl acetate molecules relative to bulk composition.

## Introduction

Among thermodynamic properties, surface tension is an important physical property that shows information about surface and exerts a considerable influence on the transfer of mass and energy across interface. Surface tension of mixtures is often very sensitive to small changes in composition of the mixtures, and a detailed knowledge of this dependency is important for many fields including separation processes, emulsion, atomization of fuels,<sup>1</sup> environmental engineering, reaction catalysis, and biomembranes. Therefore, there is a need for relating the surface tension of mixtures to bulk-phase compositions. Different approaches have been used to predict the surface tension and its variation with composition: classical thermodynamic method,<sup>2–7</sup> perturbation theory,<sup>8</sup> parachor method,<sup>9</sup> molecular dynamic method,<sup>10</sup> and corresponding states model.<sup>11</sup> These methods have limited application or accuracy and require parameters that are normally difficult to obtain or sometimes furnish parameters with an unclear physical meaning. Here, we report experimental surface tensions for binary mixtures of a homologues series of *n*-alkyl acetates with 1,4-dioxane or DMF, using the ring method. Component and pair selections were based on some factors:

(I) The components are commonly used in flavoring, perfumery, artificial essences, and cosmetics, and also the selected solvents become one of the industrially important classes of liquids.

(II) The homologous suit allows a systematic analysis of solute structure on resulting interfacial behavior.

A comparison between the measured surface tension and predicted surface tension from the Sprow and Prausnitz<sup>12</sup> equation is made out. Among the classical thermodynamics-based equations, the Sprow and Prausnitz equation is widely accepted. The UNIFAC theory<sup>13</sup> was used to calculate the activity coefficients for the components in both the bulk and interface. Thermodynamic properties of pure fluids and of mixtures can be predicted with the help of the UNIFAC group contribution method. Some other parameters such as surface

**Table 1. Surface Tensions,  $\sigma$ , and Densities,  $\rho$ , of the Pure Compounds at 298.15 K and the Corresponding Reported Data**

liquid	$\sigma/(\text{mN}\cdot\text{m}^{-1})$		$\rho/(\text{g}\cdot\text{cm}^{-3})$	
	exp.	lit.	exp.	lit.
1,4-dioxane	32.71	32.75 <sup>14</sup>	1.02782	1.02797 <sup>15</sup>
DMF	36.98	37.20 <sup>16</sup>	0.94381	0.94387 <sup>15</sup>
butyl acetate	24.85	24.88 <sup>14</sup>	0.87638	0.87633 <sup>17</sup>
pentyl acetate	25.21	25.17 <sup>14</sup>	0.87017	0.87070 <sup>18</sup>
hexyl acetate	26.08	26.00 <sup>19</sup>	0.86852	0.86810 <sup>18</sup>

mole fraction, relative Gibbs adsorption value, and surface tension deviations were also calculated.

## Experimental Section

1,4-Dioxane (> 99 %), *N,N*-dimethyl formamide (> 99 %), and *n*-alkyl acetate ( $n = 4$  to 6) (> 99 %) were provided by Merck and used without further purification.

The surface tensions of the pure liquids and their mixtures were determined using the ring method with a KSV (Sigma 70, Finland) tensiometer. The uncertainty of the surface tension measurement is  $0.0002 \text{ N}\cdot\text{m}^{-1}$  of the final value of surface tension, and the corresponding reproducibility is  $\pm 0.01 \text{ mN}\cdot\text{m}^{-1}$ . Density values for the pure materials were determined by an Anton-Paar digital precision densitometer (model DMA 4500) operated in static mode with the uncertainty  $0.005 \text{ kg}\cdot\text{m}^{-3}$  and calibrated with double distilled water. The temperature was kept constant within  $\pm 0.1 \text{ K}$  by a water bath circulator (Pharmacia) and with the uncertainty  $0.1 \text{ K}$ . For each binary system, mixtures were prepared by mass in glass stoppered flasks with the uncertainty  $\pm 0.0001 \text{ g}$ . The uncertainty of the mole fractions was estimated to be within  $\pm 0.0001$ . Surface tension and density values of pure liquids are reported in Table 1 and compared with the literature values.

## Results and Discussion

The surface tensions of the binary mixtures at the specified temperatures are given in Tables 2 and 3. As shown in Figures 1 and 2, the surface tension,  $\sigma$ , for all binary mixtures of 1,4-dioxane or DMF with *n*-alkyl acetate decreased with increasing *n*-alkyl acetate mole fraction. This trend is nonlinear, and surface

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**Table 2.** Calculation and Experimental Surface Tension,  $\sigma$ , of 1,4-Dioxane (1) + *n*-Alkyl Acetate (2) Mixed at Various Mole Fractions of *n*-Alkyl Acetate ( $x_2$ )

$x_2$	$\sigma_{\text{exp}}$	$\sigma_{\text{cal}}$	$x_2$	$\sigma_{\text{exp}}$	$\sigma_{\text{cal}}$	100·MRSD
	mN·m <sup>-1</sup>	mN·m <sup>-1</sup>		mN·m <sup>-1</sup>	mN·m <sup>-1</sup>	
1,4-Dioxane (1) + Butyl Acetate (2)						
0.0500	31.19	31.09	0.5486	26.93	26.66	0.90
0.0975	30.51	30.23	0.5920	26.69	26.48	
0.1457	29.87	29.55	0.6429	26.45	26.28	
0.1995	29.32	28.93	0.6933	26.20	26.10	
0.2485	28.88	28.47	0.7466	25.97	25.92	
0.2883	28.55	28.14	0.7954	25.80	25.76	
0.3445	28.13	27.74	0.8438	25.56	25.58	
0.3932	27.79	27.44	0.8901	25.36	25.38	
0.4475	27.47	27.14	0.9419	25.16	25.18	
0.4929	27.21	26.91				
1,4-Dioxane (1) + Pentyl Acetate (2)						
0.0500	32.03	31.98	0.5614	27.22	27.39	0.73
0.1026	31.29	31.28	0.6136	26.94	27.09	
0.1516	30.66	30.70	0.6558	26.70	26.85	
0.2062	30.10	30.11	0.7043	26.51	26.59	
0.2562	29.60	29.63	0.7538	26.27	26.34	
0.3110	29.01	29.15	0.8033	26.05	26.10	
0.3637	28.52	28.73	0.8511	25.79	25.87	
0.4209	28.07	28.31	0.8956	25.65	25.66	
0.4616	27.81	28.03	0.9449	25.50	25.45	
0.5112	27.50	27.70				
1,4-Dioxane (1) + Hexyl Acetate (2)						
0.0463	32.33	32.08	0.5105	28.04	28.24	0.54
0.0884	31.85	31.57	0.5616	27.83	27.97	
0.1343	31.34	31.06	0.6155	27.59	27.69	
0.1737	30.89	30.67	0.6681	27.32	27.43	
0.2254	30.47	30.20	0.7222	27.15	27.19	
0.2756	29.95	29.78	0.7793	26.99	26.94	
0.3177	29.41	29.47	0.8345	26.76	26.71	
0.3600	29.07	29.17	0.8907	26.60	26.49	
0.4112	28.64	28.83	0.9444	26.39	26.28	
0.4587	28.35	28.54				

tension decreased rapidly by an increase of *n*-alkyl acetate mole fraction. A plot of  $\sigma$  vs *n*-alkyl acetate mole fraction shows a concave curve shape. This behavior is due to a difference in the distribution of molecules between the surface and the bulk of liquid.<sup>20</sup> In a characteristic case, the compound having a lower surface tension is expelled from the bulk to the liquid–vapor interface due to the attractive forces between solvent molecules. As has been observed in Figures 1 and 2, it can be found that the addition of butyl acetate to a solution of 1,4-dioxane or DMF decreases the surface tension more than that for pentyl acetate and hexyl acetate.

As composition, structure, and intermolecular interaction in surface and bulk of liquid mixtures are different, it can be assumed that the surface can be treated thermodynamically as a separate homogeneous phase from the bulk phase.

The assumptions that bulk and surface phases are in equilibrium and the partial molar area of component *i* is the same as the molar area of *i* lead to the Sprow and Prausnitz<sup>12</sup> equation for prediction of surface tension

$$\sigma = \sigma_i + \frac{RT}{A_i} \ln \frac{x_{i,s} \gamma_{i,s}}{x_{i,B} \gamma_{i,B}} \quad (1)$$

We have used the Sprow and Prausnitz method too, for surface area calculations from the molar liquid volumes,  $V_i$ , of pure components

$$A_i = V_i^{2/3} N_A^{1/3} \quad (2)$$

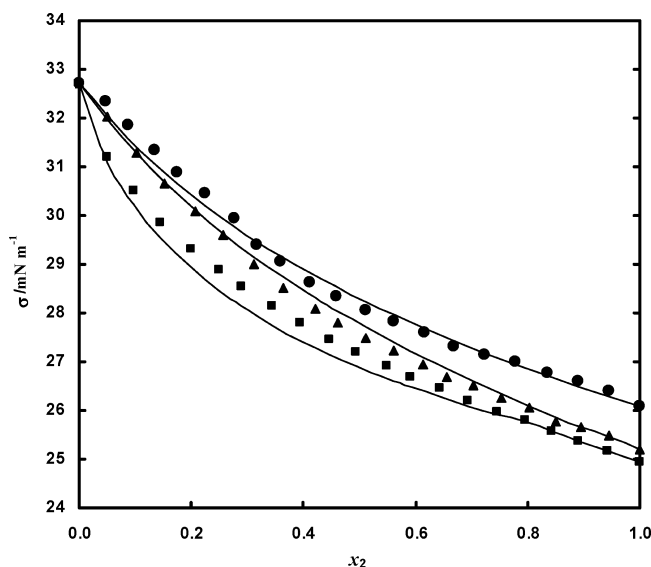
For an *N*-component nonelectrolyte solution (*i* = 1 to *N*) with known composition (i.e., known  $x_{i,B}$ ), eq 1 forms a set of *N*

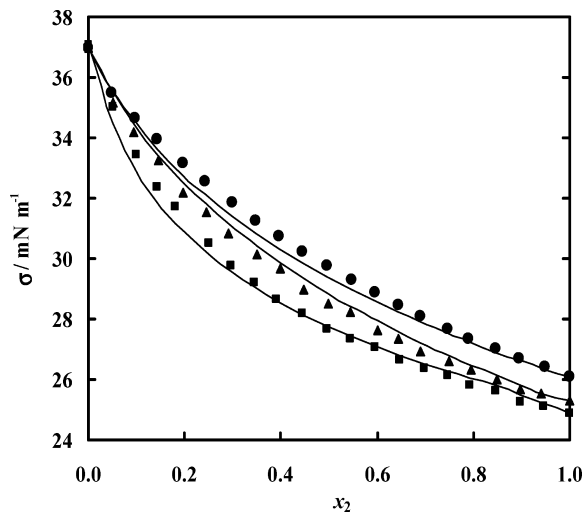
**Table 3.** Calculation and Experimental Surface Tension,  $\sigma$ , of DMF (1) + *n*-Alkyl Acetate (2) Mixed at Various Mole Fractions of *n*-Alkyl Acetate ( $x_2$ )

$x_2$	$\sigma_{\text{exp}}$	$\sigma_{\text{cal}}$	$x_2$	$\sigma_{\text{exp}}$	$\sigma_{\text{cal}}$	100·MRSD
	mN·m <sup>-1</sup>	mN·m <sup>-1</sup>		mN·m <sup>-1</sup>	mN·m <sup>-1</sup>	
DMF (1) + Butyl Acetate (2)						
0.0508	35.02	34.47	0.5443	27.35	27.44	0.92
0.0995	33.45	32.90	0.5956	27.07	27.11	
0.1441	32.35	31.86	0.6480	26.66	26.80	
0.1809	31.70	31.17	0.6993	26.36	26.52	
0.2500	30.50	30.13	0.7466	26.16	26.28	
0.2962	29.75	29.57	0.7935	25.81	26.06	
0.3447	29.19	29.05	0.8467	25.65	25.82	
0.3904	28.66	28.62	0.8983	25.27	25.48	
0.4455	28.19	28.16	0.9464	25.10	25.20	
0.4954	27.69	27.78				
DMF (1) + Pentyl Acetate (2)						
0.0500	35.14	35.54	0.5453	28.21	28.42	0.89
0.0941	34.21	34.48	0.5998	27.64	27.95	
0.1466	33.26	33.41	0.6445	27.34	27.58	
0.1980	32.18	32.51	0.6901	26.93	27.23	
0.2452	31.55	31.79	0.7499	26.60	26.79	
0.2909	30.81	31.16	0.7958	26.32	26.47	
0.3496	30.14	30.43	0.8477	25.98	26.13	
0.3978	29.68	29.88	0.8965	25.68	25.82	
0.4481	28.99	29.35	0.9397	25.52	25.56	
0.4998	28.52	28.84				
DMF (1) + Hexyl Acetate (2)						
0.0495	35.50	35.60	0.5461	29.29	28.97	0.68
0.0964	34.67	34.54	0.5945	28.86	28.58	
0.1435	33.96	33.65	0.6434	28.47	28.22	
0.1980	33.17	32.76	0.6908	28.10	27.89	
0.2432	32.56	32.12	0.7457	27.68	27.52	
0.2990	31.85	31.41	0.7896	27.36	27.24	
0.3490	31.26	30.83	0.8466	27.02	26.90	
0.3970	30.72	30.33	0.8951	26.68	26.63	
0.4440	30.25	29.87	0.9494	26.41	26.34	
0.4969	29.77	29.38				

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<sup>21</sup> technique, and the values of  $\gamma_{i,s}$  and  $\gamma_{i,B}$  can be estimated by the UNIFAC group contribution model.

In the present work, the surface tension values of six binary organic systems are predicted by this method and compared

**Figure 1.** Plot of the experimental surface tension (symbols) and theoretical surface tension (lines) vs  $x_2$  for the binary systems of 1,4-dioxane (1) + alkyl acetate (2): ■, butyl acetate; ▲, pentyl acetate; ●, hexyl acetate at 298.15 K.



**Figure 2.** Plot of the experimental surface tension (symbols) and theoretical surface tension (lines) vs  $x_2$  for the binary systems of DMF (1) + alkyl acetate (2): ■, butyl acetate; ▲, pentyl acetate; ●, hexyl acetate at 298.15 K.

with experimental values (see Figures 1 and 2). Also, the mean relative standard deviations (MRSD) have been calculated using the following equation for the six binary systems and have been tabulated in Tables 2 and 3.

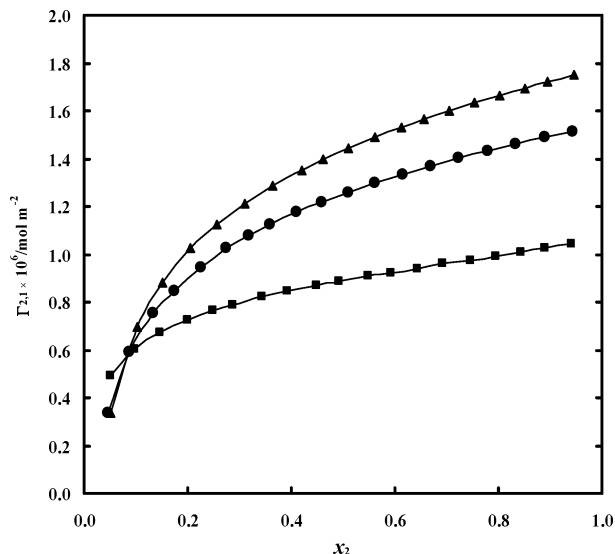
$$\text{MRSD} = \left[ \frac{1}{N} \sum_i \left( \frac{\sigma_{i,\text{exp}} - \sigma_{i,\text{cal}}}{\sigma_{i,\text{exp}}} \right)^2 \right]^{1/2} \quad (3)$$

The values of MRSD show a good consistency between predicted and experimental values. An analysis indicates that when the components of a binary system have the same chemical nature and molecular structure the prediction of surface tension shows a lower deviation of experimental surface tension, and it may be due to the following arguments: (a) As the exact solution was not possible, the approximation method should be used. (b) Due to the lack of values for surface molar area ( $A$ ) for mixtures, we assume some value of  $A$  for both pure and mixtures, and also the value of  $A$  for bulk and surface has been considered the same value, which causes deviation.<sup>22</sup> On the whole, by taking into account the above approximations, our obtained value for  $\sigma$  shows the least deviation compared to others reported, so this prediction has been reliable to determine surface tension of mixed solutions.

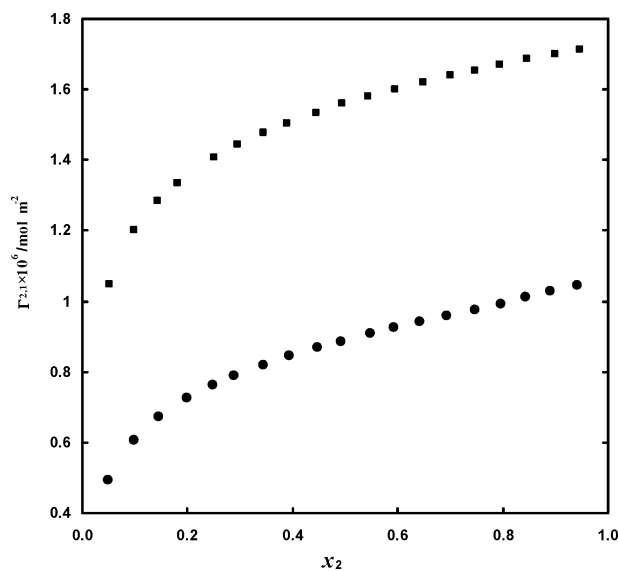
Useful information in the study of surface behavior is adsorption of component in the surface. Adsorption of a component at the phase boundary of a system is due to a different concentration in the interfacial layer and in the adjoining bulk phases. Quantitative information about the enrichment of the surface of the mixture of one component is given by the surface excess concentration,  $\Gamma_{2,1}$ . From the Gibbs suggestion, relative adsorption,  $\Gamma_{2,1}$ , was calculated according to the expression

$$\Gamma_{2,1} = - \left( \frac{\partial \sigma}{\partial \mu_2} \right)_{T,p} = - \frac{\left( \frac{\partial \sigma}{\partial a_2} \right)_{T,p}}{\left( \frac{\partial \mu_2}{\partial a_2} \right)_{T,p}} \quad (4)$$

where  $\mu_2$  and  $a_2$  are the chemical potential and activity of component 2 in the mixture, respectively. The values of  $a_2$  were obtained using the UNIFAC model. The calculated  $\Gamma_{2,1}$  are plotted against  $x_2$  in Figure 3. A positive value of  $\Gamma_{2,1}$  indicates that the  $n$ -alkyl acetate molecule is more surface active than



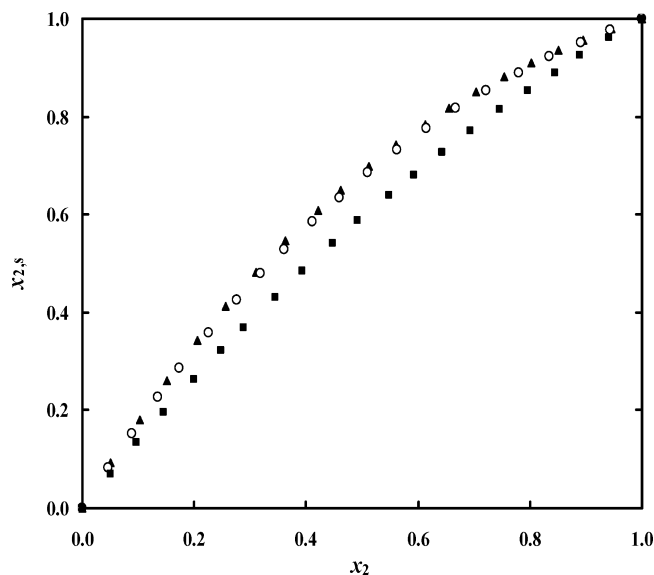
**Figure 3.** Typical plot of the values of  $\Gamma_{2,1}$  vs  $x_2$  for binary systems of 1,4-dioxane (1) + alkyl acetate (2): ■, butyl acetate; ▲, pentyl acetate; ●, hexyl acetate.



**Figure 4.** Variation of  $\Gamma_{2,1}$  with  $x_2$  for binary systems of ●, 1,4-dioxane (1) + butyl acetate (2); and ■, DMF (1) + butyl acetate (2).

the 1,4-dioxane and DMF molecules, and addition of the  $n$ -alkyl acetate to solution causes a decreasing effect in surface tension of solution. For (DMF or 1,4-dioxane +  $n$ -alkyl acetate) binary mixtures, there are two principal factors which conduct the 1,4-dioxane or DMF molecules to principally avoid the interface: the lower surface tension of the  $n$ -alkyl acetate and the fact that the polar interaction between 1,4-dioxane or DMF molecules can be accomplished more efficiently in the bulk liquid phase instead of the interface. Therefore, the  $n$ -alkyl acetate molecules are expelled from the bulk to the liquid–vapor interface due to the attractive force between 1,4-dioxane or DMF molecules.

Also the calculated relative adsorption values of  $n$ -alkyl acetate in Figure 3 show that  $\Gamma_{2,1}$  rises with  $x_2$  for dilute mixtures and passes through a maximum, which seems to correspond to the saturation limit for these compounds in the surface. It is interesting that  $\Gamma_{2,1}$  for mixtures containing DMF/ $n$ -alkyl acetate are more than those for mixtures containing 1,4-dioxane due to higher polarity of DMF molecules than 1,4-dioxane and stronger dipolar interactions between DMF molecules (see Figure 4, typically).



**Figure 5.** Calculated concentration of alkyl acetate at the liquid–vapor interface ( $x_{2,s}$ ) as a function of ( $x_2$ ) for a typical binary system 1,4-dioxane (1) + alkyl acetate (2): ■, butyl acetate; ▲, pentyl acetate; ○, hexyl acetate at 298.15 K.

**Table 4.**  $\alpha$  and  $\beta$  Parameters Obtained by Fitting Equation 8 to Surface Tension Data

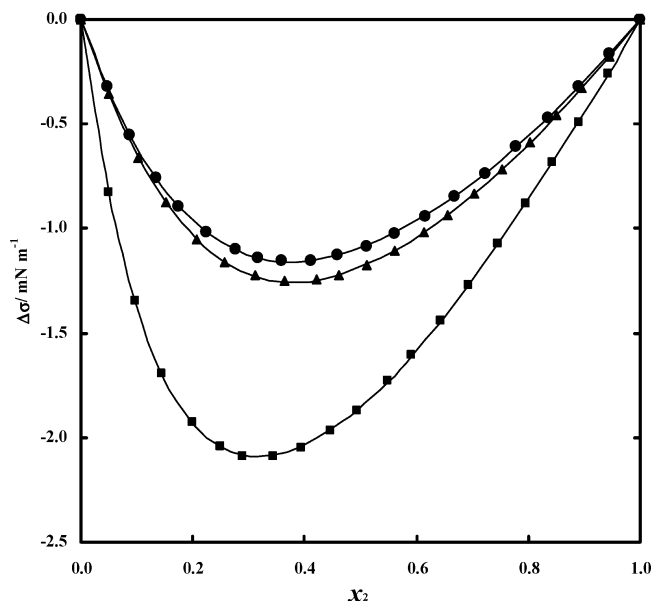
	butyl acetate		pentyl acetate		hexyl acetate	
	$\alpha$	$\beta$	$\alpha$	$\beta$	$\alpha$	$\beta$
1,4-dioxane	1.06	1.28	1.00	1.18	1.00	1.20
DMF	1.00	2.29	1.00	1.80	1.00	1.20

**Table 5.** Redlich–Kister Equation Parameters,  $A_k$ , and Their Standard Deviations

	$A_0$	$A_1$	$A_2$	$A_3$	$A_4$	SD
Butyl Acetate						
1,4-dioxane	-7.4279	-4.4886	-2.8670	-3.0790	-2.0688	0.40
DMF	-13.7022	-7.8078	-4.3024	-12.3449	-11.7993	0.37
Pentyl Acetate						
1,4-dioxane	-4.7368	-2.2277	-1.1381	-0.0820	0.3090	0.24
DMF	-7.9660	-3.8637	-2.4184	-1.7802	-0.7957	0.48
Hexyl Acetate						
1,4-dioxane	-4.3709	-2.0029	-1.1244	-0.3110	0.1591	0.21
DMF	-7.7413	-3.6955	-2.2155	-2.0019	-1.2167	0.20

It is well recognized that surface tension and surface composition play an important role in processes which involve mass transfer between liquid and vapor phases. According to what we have observed from the surface layer concentration curves, this property is a consequence of the preferential migration of molecules of the different components of a given mixture to the surface layer and eventually to the vapor phase. In the present work, we calculated surface mole fractions of components using eq 1 to investigate the relationship between surface layer concentrations and surface tensions. The variation of  $x_{2,s}$  versus  $x_2$  for 1,4-dioxane/*n*-alkyl acetate mixtures is given in Figure 5 typically. This figure shows that the mole fraction of *n*-alkyl acetate at the surface is greater than its mole fraction in the bulk at all concentration ranges.

Recently, a new semiempirical model (i.e., EL model) has been presented in detail elsewhere and was applied to analysis of surface tension for some systems.<sup>23–25</sup> Briefly, this equation considers the surface of a binary liquid mixture as a thin but finite layer and starts by developing the following expression



**Figure 6.** Surface tension deviation ( $\Delta\sigma$ ) for 1,4-dioxane (1) + alkyl acetate (2): ■, butyl acetate; ▲, pentyl acetate; ●, hexyl acetate at 298.15 K.

for the relationship between the volume fractions of component B in the surface and the bulk,  $\phi_B^s$  and  $\phi_B$ , respectively

$$\phi_B^s = \frac{\beta\phi_B}{1 + (\beta - 1)\phi_B} \quad (5)$$

where the parameter  $\beta = (\phi_B^s/\phi_B)/(\phi_A^s/\phi_A)$  is a measure of the lyophobicity of B relative to A. In this model, the surface tension of nonideal binary mixtures is given by

$$\sigma = \phi_A^s\sigma_A + \phi_B^s\sigma_B - \lambda\phi_A^s\phi_B^s\pi^\circ \quad (6)$$

where  $\sigma_A$  and  $\sigma_B$  are the surface tensions of the pure components A and B, respectively;  $\pi^\circ$  is the positive difference between them  $|\sigma_A - \sigma_B|$ ; and  $\lambda$  is a parameter that represents the effect of unlike-pair interactions on the surface tension of the mixture. Also, we continue to regard A as the component with higher surface tension. From eq 6, the surface pressure,  $\pi = \sigma_A - \sigma$ , can be written as

$$\pi = \pi^\circ\phi_B^s(\alpha\phi_A^s + \phi_B^s) \quad (7)$$

where  $\alpha = \lambda + 1$ . By substituting for  $\phi_B^s$  and  $\phi_A^s (= 1 - \phi_B^s)$  from eq 5 in eq 7

$$\pi = \frac{\pi^\circ\beta[\beta + \alpha(\phi_A/\phi_B)]}{[\beta + (\phi_A/\phi_B)]^2} \quad (8)$$

Table 4 lists the values of the adjustable parameters  $\alpha$  and  $\beta$  obtained by fitting eq 8. For all binary studied systems, values of  $\alpha = 1$  ( $\lambda = 0$ ) and  $\beta > 1$  imply that the interactions do not affect significantly the surface tension of the solution, and deviation of surface tension from ideal behavior is attributable exclusively to lyophobicity differences.

Finally, surface tension deviations,  $\Delta\sigma$ , were calculated from our measurements according to the following equation

$$\Delta\sigma = \sigma - \sum_{i=1}^2 x_i\sigma_i \quad (9)$$

where  $x_i$  and  $\sigma_i$  are the mole fraction and surface tension of component  $i$ , respectively. The values of surface tension



deviations were correlated by means of the Redlich–Kister<sup>26</sup> equation as follows

$$\Delta\sigma = x_i x_j \sum_k A_k (x_i - x_j)^k \quad k = 0, 1, 2, \dots, n \quad (10)$$

where  $A_k$  are adjustable parameters determined by the method of least-squares. The values of these parameters as well as the standard deviations are given in Table 5. Figure 6 shows the surface tension deviation ( $\Delta\sigma$ ) for 1,4-dioxane/alkyl acetate binary systems at  $T = 298.15$  K. The surface behavior of studied mixtures is similar. Surface tension deviations are negative over the whole composition range, and they show minimum values around  $x_2 \approx 0.3$  to 0.4. Also, the behaviors of alkyl acetate are very similar, although the mixtures containing  $n$ -butyl acetate with the lower surface tension show the lowest absolute  $\Delta\sigma$  values. This equation provides a simple tool for interpolation of surface tension in these mixtures with an accuracy that is within the experimental uncertainty.

## Conclusion

In this work, we attained the Sprow and Prausnitz equation for predicting the surface tension for binary mixtures of 1,4-dioxane and DMF with alkyl acetate. The overall MRSDs between experimental and calculated surface tensions show surface tension predictions can be considered to be in good agreement with experimental values, and this method is applicable to a long variety of systems. Also it is shown that this method can give knowledge about the surface structure of studied binary mixtures.

Calculated surface mole fraction and relative Gibbs adsorption values with this method show that the surface is enriched with  $n$ -alkyl acetate molecules relative to bulk composition.

Finally, experimental surface tensions were correlated with means of the Redlich–Kister equation and provided a series of adjustable parameters for prediction of surface tension of such mixed systems. Next, we are going to develop the equation by inserting additional parameters such as molecular structure, dipole moment of molecules, permittivity constants, molecular orientations, etc., to get a more accurate value with respect to experimental data and so one can apply the equation to other compounds.

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