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Equilibrium Surface Tensions of Benzyl Alcohol + Ethylene Glycol Mixtures

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The paper presents the properties of mixtures of benzyl alcohol and ethylene glycol at the liquid/air interface. The properties were studied by surface tension measurements carried out at as a function of the mole fraction of benzyl alcohol at temperatures between (20 and 50) °C. It was shown that at constant temperature by the addition of benzyl alcohol the surface tension decreases and at constant composition by the increasing of temperature the surface tension decreases linearly. The surface entropies and enthalpies were calculated from experimental data. The surface composition of the mixture at a low concentration of benzyl alcohol was obtained from the extended Langmuir model. Values of the excess surface tension for mixtures were calculated and show a negative deviation from ideality.

Introduction

Surface tension is the fundamental parameter of surface chemistry that characterizes the free energy per unit area required for the formation of a liquid−air interface at constant temperature, pressure, and composition. Surface tension is an important characteristic of two-phase systems because it influences many physicochemical processes such as distillation, condensation, gas absorption, and liquid−liquid extraction.

Reports of surface tension are often given for aqueous solutions, and little work has been done on the experimental determination of the surface tension of binary organic mixtures. To contribute to the knowledge of surface phenomena in binary organic mixtures, the present work reports surface tension values of ethylene glycol + benzyl alcohol at various temperatures. This work is a continuation of our recent works on the surface properties of ethylene glycol + alcohols, including ethylene glycol + ethanol[1], ethylene glycol + cyclopentanol and cyclohexanol,[2,3] and ethylene glycol + methyl cyclohexanols.[4] Jimenez et al.[5] also reported the surface tension of ethylene glycol + 1-propanol and 1-butanol. The interest in investigating binary alcohol mixtures is due to their inherent nature of forming associations in the form of hydrogen bonds within themselves or with other components.

Table 1. Comparison of Experimental Surface Tension and Densities of Pure Liquids with Literature Values

t/°C	σ(exptl)/mN·m^{-1}	σ(ref)/mN·m^{-1}	ρ(exptl)/g·cm^{-3}	ρ(ref)/g·cm^{-3}
		Ethylene Glycol		
20.0	48.42	48.40[a] 49.15[b]	1.11334	1.1135[a] 1.11323[b]
25.0	48.03	47.99[a]	1.10987	1.1100[a] 1.10950[b]
30.0	47.57	48.68[b] 47.54[a]	1.10636	1.10546[b]
35.0	47.20	47.10[a]	1.10282	1.10250[b] 1.10535[c]
40.0	46.78	46.65[a]	1.09839	1.09835[b]
45.0	46.42	46.21[a]	1.09572	
50.0	46.02	45.76[a]	1.09105	
		Benzyl Alcohol		
20.0	39.05	39.4[d] 39.00[a]	1.0452	
25.0	38.58	38.9[d] 38.54[a]	1.0414	
30.0	38.12	38.4[d] 38.08[a]	1.0375	
35.0	37.63	37.9[d] 37.62[a]	1.0336	
40.0	37.16	37.4[d] 37.06[a]	1.0298	
45.0	36.63	36.9[d] 36.70[a]	1.0258	
50.0	36.18	36.4[d] 36.24[a]	1.0219	

[a] Reference 19. [b] Reference 20. [c] Reference 21. [d] Reference 22.

Experimental Section

Benzyl alcohol (>99%) and ethylene glycol (>99.5%) were Merck products and were used as received without further purification. All mixtures of ethylene glycol and benzyl alcohols were prepared by mass with a balance precision of ±1 × 10^{-4} g. The surface tension of samples was measured by a ring-detachment method using a Sigma 70 automated tensiometer with precision of ±0.01 mN/m. The platinum ring was thoroughly cleaned and flame dried before each measurement. The temperature of the system was controlled by a Multi Temp III thermostat with a precision of ±0.1 °C. The surface tension measurements were carried out at temperatures between 20 and 50 °C with a temperature interval of 5 °C. Each reported surface tension value was an average of at least eight measurements with a standard deviation of ±0.02 mN/m. The densities of the pure components were measured with an Anton Paar digital precision densitometer (model DMA 4500) that was calibrated with bidistilled water. Density, ρ, and surface tension, σ, values for pure liquids are reported in Table 1 and compared with literature values.

Results and Discussion

The measured surface tensions of pure and binary mixtures of ethylene glycol and benzyl alcohol at various temperatures are listed in Table 2. At all temperatures,

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Table 2. Surface Tension of Ethylene Glycol+ Benzyl Alcohol (x_2) at Various Temperatures

	t/°C						
x_2	20.0	25.0	30.0	35.0	40.0	45.0	50.0
	σ/mN·m^{-1}						
0.0000	48.42	48.03	47.57	47.20	46.78	46.42	46.02
0.0319	47.78	47.35	46.92	46.54	46.14	45.71	45.26
0.0535	47.45	47.01	46.53	46.07	45.66	45.24	44.79
0.0727	47.13	46.67	46.15	45.72	45.26	44.86	44.32
0.0854	46.69	46.19	45.76	45.31	44.85	44.41	43.91
0.1118	45.87	45.43	44.90	44.46	44.04	43.53	43.06
0.2060	44.07	43.61	43.08	42.60	42.12	41.67	41.16
0.2633	42.87	42.42	41.87	41.39	40.84	40.40	39.90
0.3883	41.53	41.07	40.61	40.14	39.70	39.24	38.76
0.5596	40.58	40.18	39.68	39.24	38.77	38.27	37.79
0.7394	39.44	38.95	38.45	37.94	37.51	36.99	36.53
0.9101	39.28	38.79	38.30	37.79	37.35	36.84	36.38
1.0000	39.05	38.58	38.12	37.63	37.16	36.63	36.18

Table 3. Surface Tension Parameters K_1 and K_2 for Ethylene Glycol + Benzyl Alcohol (x_2)

x_2	K_2/mN·m^{-1}·°C^{-1}	K_1/m·N·m^{-1}
0.0319	0.083	72.11
0.0535	0.088	49.20
0.0727	0.091	48.80
0.0854	0.092	48.51
0.1118	0.093	47.74
0.2060	0.097	46.01
0.2633	0.099	44.88
0.3883	0.092	43.37
0.5596	0.094	42.49
0.7394	0.097	41.37
0.9101	0.097	41.20

the surface tension of pure ethylene glycol is higher than that of benzyl alcohol. An analysis of the data in Table 2 shows that by adding benzyl alcohol to ethylene glycol at constant temperature the surface tension decreases nonlinearly. The surface tension changes rapidly at a low concentration of benzyl alcohol.

An analysis of the experimental data in Table 2 shows that the surface tension of mixtures decreases linearly with temperature. The linear variation of the surface tension with temperature has been shown by Jasper[7] to be

$$\sigma/\text{mN}\cdot\text{m}^{-1} = K_1 - K_2 t/°\text{C} \tag{1}$$

where σ is the surface tension, t is the temperature, and K_1 and K_2 are constants. The fitted values of K_1 and K_2 are given in Table 3.

Surface thermodynamic parameters are obtained from the following equations[8]

$$S^s = -\left(\frac{\partial\sigma}{\partial T}\right) \tag{2}$$

and

$$H^s = \sigma(t) - T\left(\frac{\partial\sigma}{\partial T}\right) \tag{3}$$

where S^s and H^s are the surface entropy and enthalpy, respectively. These equations were used extensively for various mixtures.[9–14] The surface entropy and surface enthalpy values at different concentrations are plotted in Figures 1 and 2. The trend in surface entropy presented in Figure 1 shows that by adding a little benzyl alcohol (until $x_2 \approx 0.2$) the surface entropy increases rapidly. This means that the surface become disordered by the addition of benzyl alcohol until $x_2 \approx 0.2$. By adding more benzyl alcohol ($x_2 > 0.2$), the surface entropy remains nearly constant.

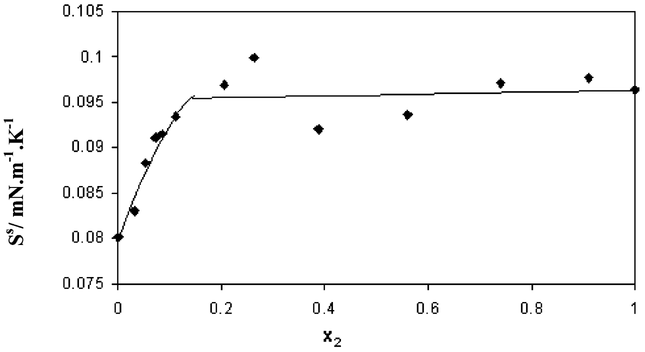

Figure 1. Surface entropy vs mole fraction of benzyl alcohol, x_2.

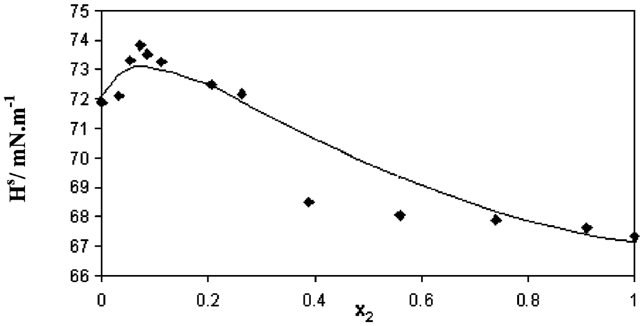

Figure 2. Surface entropy vs mole fraction of benzyl alcohol, x_2.

As shown in Figure 2, the trend in surface enthalpy with increasing benzyl alcohol concentration is nearly decreasing, which means that the energy required for interface formation decreases at higher concentrations of benzyl alcohol.

To describe the surface tension of binary liquid mixtures as a function of the bulk composition, a new model (extended Langmuir model) was reported recently.[15] This model was applied to an analysis of the surface tension of some binary mixtures more recently.[3,16] In this model, the relation between the surface and bulk volume fractions (ϕ_2^s and ϕ_2) is

$$\phi_2^s = \frac{\beta\phi_2}{1 + (\beta - 1)\phi_2} \tag{4}$$

where β is a measure of the lyophobicity of component 2 relative to that of component 1. In this model, it was shown that when the following relation

$$\frac{(\sigma - \sigma_1)}{(\sigma_2 - \sigma)} = \beta\frac{\phi_2}{\phi_1} \tag{5}$$

is valid the surface tension of binary mixtures obeys the following equation:

$$\sigma = \phi_1^s\sigma_1 + \phi_1^s\sigma_2 \tag{6}$$

In eqs 5 and 6, σ_1 and σ_2 are the surface tensions of the pure components, σ is the surface tension of the mixture, and ϕ_i and ϕ_i^s are the bulk and surface volume fractions of

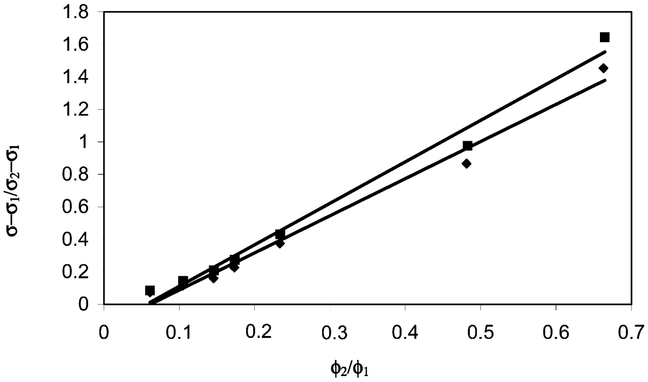

Figure 3. Plot of $\sigma-\sigma_1/\sigma_2-\sigma_1$ vs ϕ_2/ϕ_1 for benzyl alcohol at two different temperatures: ◆, t = 20 °C; ■, t = 50 °C.

Table 4. Lyophobicity Values (β) of Benzyl Alcohol at Various Temperatures

t/°C	β
20.0	2.46
25.0	2.44
30.0	2.49
35.0	2.50
40.0	2.50
45.0	2.46
50.0	2.51

component i, respectively. The bulk volume fraction is obtained from

$$\phi_2 = \frac{x_2 v_2}{x_1 v_1 + x_2 v_2} \tag{7}$$

where v_1 and v_2 are the molar volumes of components 1 and 2, respectively, from which we obtained the measured densities of the pure components. Figure 3 shows the diagram of $(\sigma - \sigma_1)/(\sigma_2 - \sigma)$ versus ϕ_2/ϕ_1 at (20 and 50) °C for dilute solutions of benzyl alcohol in ethylene glycol ($0 < x_2 < 0.3883$). Because this diagram is linear, it is concluded that for dilute solutions of benzyl alcohol in ethylene glycol eq 5 is valid and therefore the slope of the diagram is β. β values at different temperatures are listed in Table 4. Because of the validity of eq 5 in the dilute region, we conclude that the surface tension of mixtures obeys eq 6 (of course only in the dilute region, $x_2 < 0.39$). Rearranging eq 6 gives

$$\phi_2^{\mathrm{s}} = \frac{(\sigma - \sigma_1)}{(\sigma_2 - \sigma_1)} \tag{8}$$

which relates the surface tension of mixtures to the surface volume fraction of solute. The surface volume fractions of benzyl alcohol were calculated from eq 8 and then converted to the surface mole fraction by the equation

$$\phi_2^{\mathrm{s}} = \frac{x_2^{\mathrm{s}} v_2}{x_1^{\mathrm{s}} v_1 + x_2^{\mathrm{s}} v_2} \tag{9}$$

The obtained values for the surface mole fractions of benzyl alcohol (x_2^{s}) were plotted versus its bulk mole fractions (x_2) at (20 and 50) °C in Figure 4. This diagram shows that the surface concentrations of benzyl alcohol are about 1.5 times higher than its bulk concentrations, which means that benzyl alcohol has a higher tendency to migrate to the surface than ethylene glycol. As shown in this Figure, increasing temperature has a small effect on the surface composition.

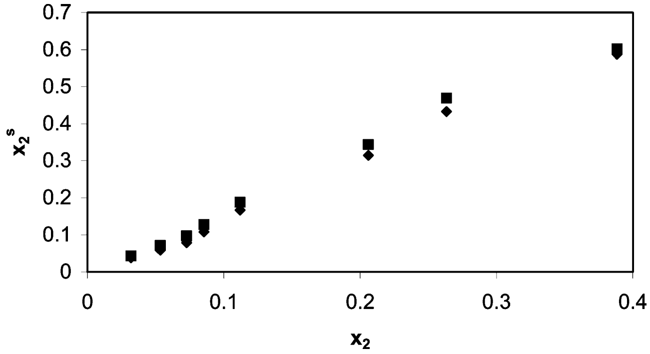

Figure 4. Surface mole fraction (x_2^{s}) vs bulk mole fraction of benzyl alcohol (x_2) at two different temperatures: ◆, t = 20 °C; ■, t = 50 °C.

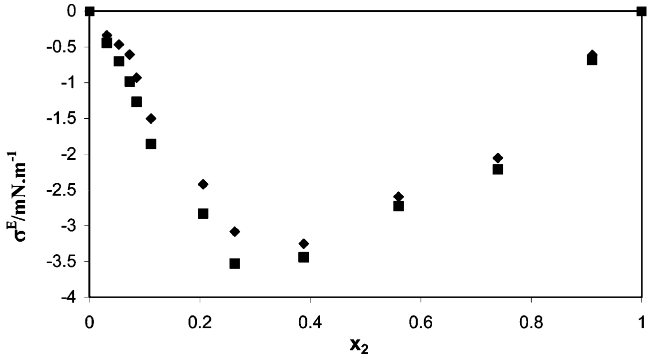

Figure 5. Plot of the excess surface tension vs mole fraction of benzyl alcohol: ◆, t = 20 °C; ■, t = 50 °C.

The surface tension of an ideal mixture is defined as[17]

$$\sigma^{\mathrm{id}} = [\sigma_1 x_1 + \sigma_2 x_2] \tag{10}$$

The excess surface tension, σ^{E}, is defined as[18]

$$\sigma^{\mathrm{E}} = \sigma - [\sigma_1 x_1 + \sigma_2 x_2] \tag{11}$$

or

$$\sigma^{\mathrm{E}} = \sigma - \sigma^{\mathrm{id}} \tag{12}$$

The values of σ^{E} for mixtures of ethylene glycol + benzyl alcohol are shown in Figure 5 at (20 and 50) °C. This system shows minima in σ^{E} values around 0.3 to 0.35 mole fraction of benzyl alcohol. At all concentration, the systems show a negative σ^{E}, which means that the system has a negative deviation from ideality at the mentioned temperatures. The results show that with increasing temperature the deviation from ideality increases slightly. The negative deviation from ideality means that the surface concentration of the component with higher surface tension (ethylene glycol in this system) is lower than its bulk concentration. Therefore, the surface tension of the mixture is lower than the expected ideal value (eq 10).

Conclusions

The results of the present study show that by adding benzyl alcohol to ethylene glycol the surface tension decreases nonlinearly and most surface tension changes occurred at a low concentration of benzyl alcohol. The surface tension of mixtures decreases with increasing temperature. The calculated results show that by the addition of benzyl alcohol to ethylene glycol the surface entropy increases and the surface enthalpy decreases. The results show that the surface mole fraction of benzyl alcohol is about 1.5 times higher than its bulk mole fraction, which means that benzyl alcohol is surface-active in ethylene glycol. The surface properties of the mixture of ethylene glycol + benzyl alcohol are not ideal, and the excess surface tension shows a negative deviation from ideality.

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