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Surface Tensions of Dilute Solutions of Cycloheptanol in Ethylene Glycol

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Surface properties (surface entropy, surface enthalpy, and surface composition) of dilute solutions of cycloheptanol in ethylene glycol were obtained by using of surface tension measurements at various temperatures. Surface excess values and surface mole fractions were obtained from the Gibbs equation and the extended Langmuir model, respectively. The results show that cycloheptanol is surface-active in ethylene glycol. The lyophobicity of cycloheptanol decreases with increasing temperature.

Introduction

The surface tension of a liquid depends on the thermodynamic state of the fluid (e.g., temperature and pressure) and on its physical properties (e.g., intermolecular forces). Surface tension is an important property in mass and heat transfer, but the literature data for nonaqueous systems are scanty.

The literature dealing with the surface tension of aqueous binary mixtures is extensive, but the systems that involve alcohols are interesting[1−5] because of their inherent nature of forming associations in the form of hydrogen bonds within themselves or with other components. Recently, the surface tension of binary mixtures of linear-chain alcohols with ethylene glycol was investigated by us[4] (ethanol + ethylene glycol) and Jimenez et al.[5] (1-propanol + ethylene glycol and 1-butanol + ethylene glycol). We also studied the surface tension of binary mixtures of ethylene glycol with cyclic alcohols (ethylene glycol + cyclohexanol and cyclopentanol over the whole composition range,[6] ethylene glycol + methylcyclohexanols over the whole composition range,[7] and dilute solutions of cyclohexanol and cyclopentanol in ethylene glycol[8] and benzyl alcohol + ethylene glycol[9]).

In continuing our previous work on the surface properties of alkanols + ethylene glycol,[4,6−9] the present work reports surface properties of cycloheptanol in ethylene glycol. The surface tension of binary mixtures was investigated for dilute solutions of cycloheptanol in ethylene glycol because most of the surface tension changes in nonelectrolyte systems occur at very low solute concentrations, whereas surface parameters remain almost unchanged at high concentration. Our special interest was the temperature dependence of the surface tension.

Experimental Section

Ethylene glycol (99.5%) and cycloheptanol (>98%) were Merck products and were used as received. All mixtures of cycloheptanol + ethylene glycol were prepared by mass with a balance precision of $\pm 1 \times 10^{-4}$ g.

The surface tension of the samples was measured by a ring-detachment method using a Sigma 70 automated tensiometer with a precision of ±0.01 mN/m. The platinum ring was thoroughly cleaned and flame dried before each measurement. All solutions were thermostated with a precision of ±0.1 K using a Multi Temp III thermostat, and the temperature intervals between (20 and 50) °C were 5 °C. Each value reported 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 densitimeter (model DMA 4500) operated in static mode and calibrated with doubly distilled water. The values of the densities, ρ, and surface tensions, σ, for pure liquids are reported in Table 1 and compared with literature values.

Table 1. Comparison of Experimental Surface Tensions 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	48.55	48.40[a] 49.15[b]	1.11334	1.1135[a] 1.11323[b]
25.0	48.11	47.99[a]	1.10987	1.1100[a] 1.10950[b]
30.0	47.58	48.68[b] 47.54[a]	1.10636	1.10546[b]
35.0	47.14	47.10[a]	1.10282	1.10250[b] 1.10535[c]
40.0	46.79	46.65[a]	1.09839	1.09835[b]
45.0	46.29	46.21[a]	1.09572	
50.0	45.99	45.76[a]	1.09105	
		Cycloheptanol		
20.0	29.68		0.9582	0.958−0.960[d]
25.0	28.76		0.9544	
30.0	27.86		0.9504	
35.0	26.88		0.9465	
40.0	25.99		0.9428	
45.0	25.18		0.9388	
50.0	24.26		0.9348	

[a] Reference 29. [b] Reference 30. [c] Reference 31. [d] Reference 32.

Results and Discussion

The measured surface tensions (σ) of dilute solutions of cycloheptanol in ethylene glycol at various temperatures are listed in Table 1. Figure 1 shows the variation of surface tension with increasing quantities of cycloheptanol at various temperatures. For a given temperature, the surface tension of mixtures investigated here decreased with increasing cycloheptanol mole fraction. This trend is nonlinear, with the change in surface tension caused by a given change in the cycloheptanol mole fraction being larger at low mole fractions than at high mole fractions. The

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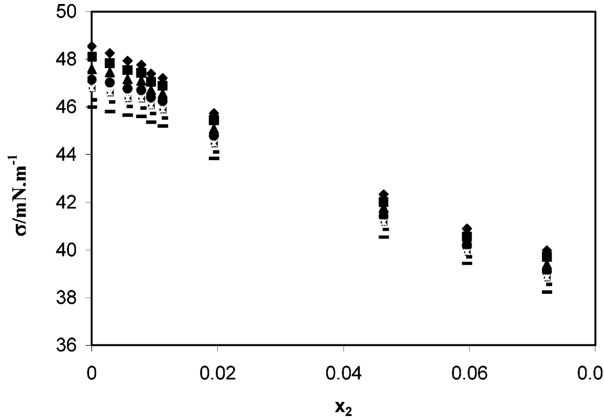

Figure 1. Surface tension vs mole fraction of cycloheptanol at various temperatures: ◆, t = 20 °C; ■, t = 25 °C; ▲, t = 30 °C; ●, t = 35 °C; □, t = 40 °C; -, $-t$ = 45 °C; —, $-t$ = 50 °C.

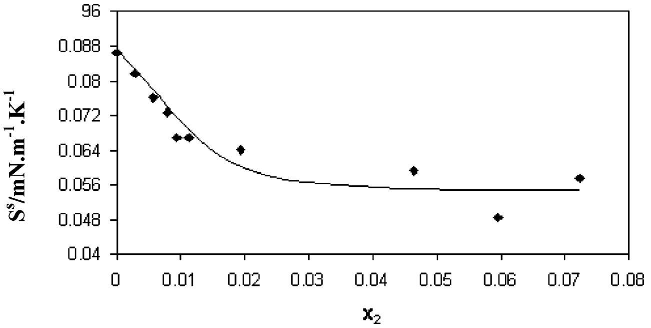

Figure 2. Surface entropy vs mole fraction of cycloheptanol, x_2.

observed rapid decrease in surface tension with mole fraction of solute is typical of aqueous systems with surface-active solutes.

The variation of the surface tensions of mixtures of cycloheptanol + ethylene glycol with temperature is linear in the temperature range of (20 to 50) °C. Thermodynamic properties of the surface of these solutions are obtained by the following equations. The excess surface entropy per unit area[10] or specific surface entropy[11] or variation of entropy per unit area due to interface formation[12,13] is

$$S^S = -\frac{d\sigma}{dT} \tag{1}$$

and the surface enthalpy is

$$H^S = \sigma - T\left(\frac{d\sigma}{dT}\right) \tag{2}$$

These equations were extensively used by Glinski et al.[14−22] to investigate the surface thermodynamics of various binary mixtures.

The surface entropies and the enthalpies of the cycloheptanol + ethylene glycol mixture were calculated from eqs 1 and 2 and drawn in Figures 2 and 3 versus the cycloheptanol mole fraction. The trend in surface entropy presented in Figure 2 shows that the surface entropy decrease sharply until $x_2 \approx 0.01$ and then decrease slowly. Figure 3 shows the trend in surface enthalpy with increasing cycloheptanol concentration, which is decreasing and means that the energy required for interface formation decreases at higher concentrations of cycloheptanol.

The deviation of surface tension from additivity (or excess surface tension) is

$$\sigma^E = \sigma - (x_1\sigma_1 + x_2\sigma_2) \tag{3}$$

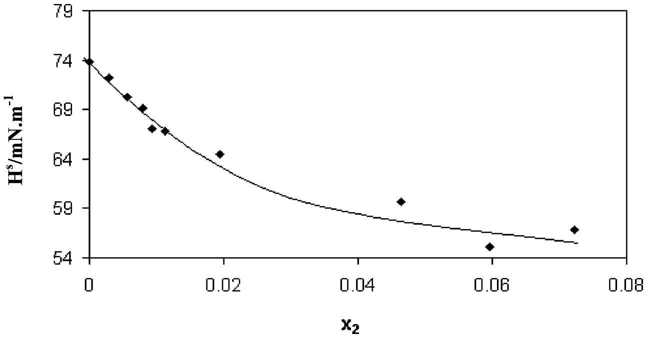

Figure 3. Surface enthalpy vs mole fraction of cycloheptanol, x_2.

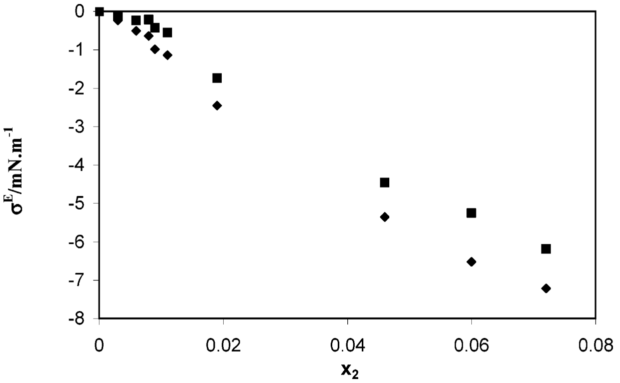

Figure 4. Excess surface tension (or deviation from additivity) vs mole fraction of cycloheptanol, x_2, at two temperature: ◆, t = 20 °C and ■, t = 50 °C.

In the present system, the experimental surface tension data show a negative deviation from additivity, indicating an enrichment of one component (component with lower surface tension) in the liquid−vapor interface. These data were presented in Figure 4 at two different temperatures. A quantitative description of this phenomenon can be achieved by the Gibbs adsorption isotherm for an ideal mixture[23,24]

$$\Gamma_2 = -\frac{x_2}{RT}\left(\frac{\partial\sigma}{\partial x_2}\right)_{T,P} \tag{4}$$

where Γ_2 is the excess number of moles of solute per unit interfacial area.

For nonideal mixtures, eq 4 converts to[23,24]

$$\Gamma_2 = -\frac{a_2}{RT}\left(\frac{\partial\sigma}{\partial a_2}\right)_{T,P} \tag{5}$$

where a_2 is the activity of the solute ($a_2 = \gamma\ _2x_2$). The activity coefficients for the solute (γ_2) were obtained from the mobil order−disorder theory (MOD).[25,26]

The Γ_2 values for cycloheptanol were calculated by eq 5 and plotted versus its mole fraction (x_2) in Figure 5 at two temperatures. As shown in this Figure, Γ_2 is always positive, and we conclude that cycloheptanol is more surface-active than ethylene glycol molecules and therefore the surface is enriched by cycloheptanol. Figure 5 shows a maximum (for Γ_2) that is similar to the aqueous solutions of 1,2-pentanediol[21] and also to dilute solutions of cyclopentanol and cyclohexanol in ethylene glycol.[8]

A new model (extended Langmuir model) that describes the surface tension of binary liquid mixtures as a function of the bulk composition was reported recently.[27] This model was applied to the analysis of the surface tension of some liquid binary mixtures.[8,9,28] In this model, the surface is

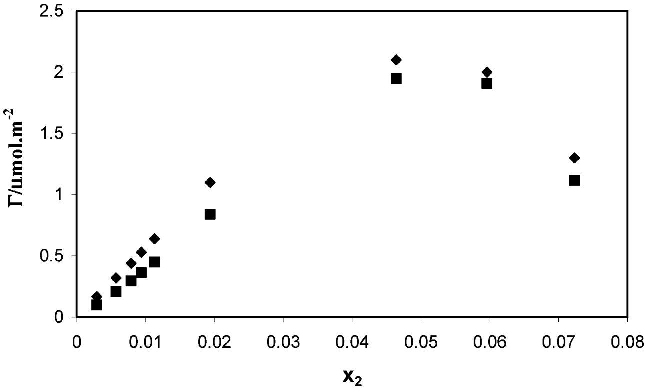

Figure 5. Surface excess of cycloheptanol vs its bulk mole fraction, x_2: ◆, t = 20 °C and ■, t = 50 °C.

considered to be a thin layer of finite depth, and the volume fraction of solute in this layer is denoted by ϕ_2^s when its bulk volume fraction is ϕ_2. At equilibrium, the relationship between ϕ_2^s and ϕ_2 is

$$\phi_2^s = \frac{\beta\phi_2}{1 + (\beta - 1)\phi_2} \tag{6}$$

or

$$\phi_2^s = \frac{\beta(\phi_2/\phi_1)}{1 + \beta(\phi_2/\phi_1)} \tag{7}$$

where β is a measure of the lyophobicity of component 2 relative to that of component 1, ϕ_1 is the bulk volume fraction of component 1, and $(\phi_2/\phi_1) = (x_2v_2/x_1v_1)$ is the ratio of occupations. v_2 and v_1 are the molar volumes of the pure components. In this model, the surface tension of nonideal binary mixtures is given by

$$\sigma = \phi_1^s\sigma_1 + \phi_2^s\sigma_2 - \lambda\phi_1^s\,\phi_2^s\Pi^0 \tag{8}$$

where σ_1 and σ_2 are the surface tensions of the pure components, λ represents the effect of unlike-pair interactions on the surface tension of the mixture, and Π^0 is the surface tension difference between pure components ($\sigma_1 - \sigma_2$). It was shown that when the interaction effect causes insignificant structural changes ($\lambda = 0$)

$$\frac{(\sigma - \sigma_1)}{(\sigma_2 - \sigma)} = \beta\frac{\phi_2}{\phi_1} \tag{9}$$

Equation 9 indicates that when the plot of $(\sigma-\sigma_1)/(\sigma_2-\sigma)$ versus ϕ_2/ϕ_1 (or ln − ln plot) is linear we may conclude that $\lambda = 0$; therefore, for these systems eq 8 simplifies to

$$\sigma = \phi_1^s\sigma_1 + \phi_2^s\sigma_2 \tag{10}$$

We obtained the molar volumes of the pure components from their measured densities and then calculated ϕ_2 and ϕ_1 from the following equations:

$$\phi_2 = \frac{x_2v_2}{x_1v_1 + x_2v_2} \tag{11}$$

$$\phi_1 = 1 - \phi_2 \tag{12}$$

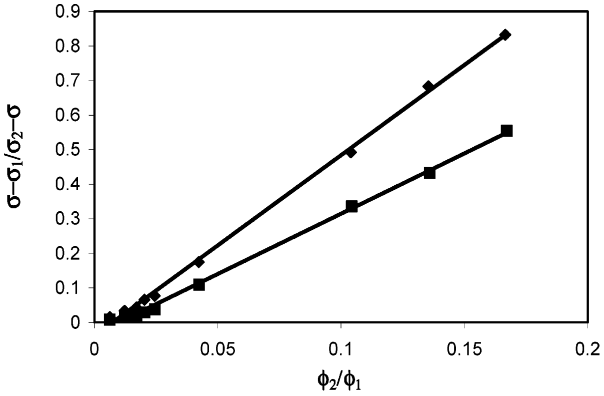

Figure 6. Plot of $\sigma - \sigma_1/\sigma_2 - \sigma$ vs ϕ_2/ϕ_1 for cycloheptanol: ◆, t = 20 °C and ■, t = 50 °C.

Table 2. Surface Tension of Ethylene Glycol + Cycloheptanol (x_2) at Various Temperatures with the Uncertainty in All Measured Surface Tensions Being (±0.01)

	t/°C						
x_2	20.0	25.0	30.0	35.0	40.0	45.0	50.0
	σ/mN·m^{-1}						
0.000	48.55	48.11	47.58	47.14	46.79	46.29	45.99
0.003	48.26	47.83	47.44	47.02	46.60	46.20	45.81
0.006	47.93	47.54	47.16	46.77	46.36	46.03	45.63
0.008	47.76	47.42	47.09	46.70	46.34	45.95	45.60
0.009	47.39	47.06	46.70	46.40	46.05	45.72	45.37
0.011	47.20	46.89	46.54	46.24	45.89	44.53	45.20
0.019	45.74	45.44	45.07	44.79	44.46	44.11	43.84
0.046	42.33	42.01	41.75	41.42	41.16	40.86	40.53
0.060	40.89	40.55	40.41	40.16	39.91	39.70	39.43
0.072	39.98	39.70	39.39	39.10	38.84	38.55	38.24
1.000	29.68	28.76	27.86	26.88	25.99	25.18	24.26

Table 3. Values of the Lyophobicity (β) of Cycloheptanol at Various Temperatures

t/°C	β
20.0	5.22
25.0	4.87
30.0	4.49
35.0	4.17
40.0	3.90
45.0	3.67
50.0	3.49

Figure 6 shows that the plots of $(\sigma - \sigma_1)/(\sigma_2 - \sigma)$ versus ϕ_2/ϕ_1 at various temperatures are linear for cycloheptanol + ethylene glycol and have slopes equal to β. The values of β at various temperatures were obtained from such plots and are listed in Table 3. These values of β show that with increasing temperature the lyophobicity of cycloheptanol relative to that of ethylene glycol decreases.

Because the plots in Figure 5 are linear, we conclude that for cycloheptanol + ethylene glycol at various temperatures $\lambda = 0$ (of course only at dilute concentrations is $\lambda = 0$); therefore, the surface tension of the mixtures obeys eq 10. By combining eqs 10 and 12 and rearranging, one obtains

$$\phi_2^s = \frac{(\sigma - \sigma_1)}{(\sigma_2 - \sigma_1)} \tag{13}$$

which relates the surface tension of the mixture to the surface volume fraction of solute. We calculated the surface volume fractions of solute (cycloheptanol) from eq 13 and then converted them to the surface mole fraction x_2^s by the following equation:

$$\phi_2^s = \frac{x_2^sv_2}{x_1^sv_1 + x_2^sv_2} \tag{14}$$

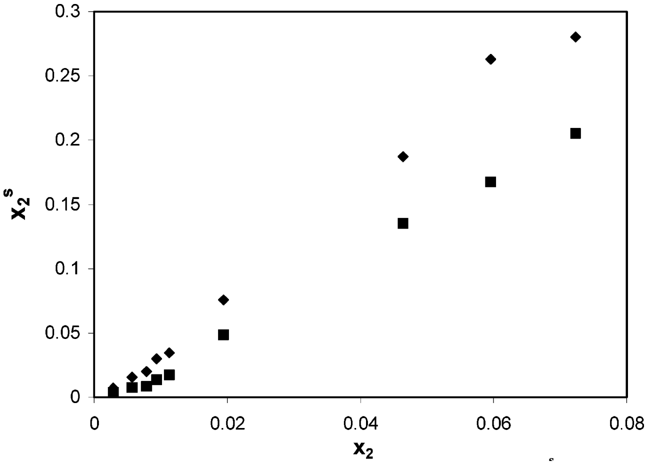

Figure 7. Surface mole fraction of cycloheptanol (x_2^s) vs its bulk mole fraction (x_2): ◆, t = 20 °C and ■, t = 50 °C.

The obtained values for the surface mole fractions of solute (x_2^s) were plotted versus their bulk mole fractions (x_2) at two temperatures in Figure 7. This diagram shows that the surface is enriched with solute (cycloheptanol) relative to its bulk composition. The calculated results show that the surface composition of cycloheptanol is more than three and four times its bulk composition at 50 and 20 °C, respectively.

Conclusions

We have measured the surface tension of dilute solutions of cycloheptanol in ethylene glycol at various temperatures. The experimental results show that by adding cycloheptanol the surface tension decreases (nonlinear) but by increasing the temperature (at constant concentration) the surface tension decreases (linear). Calculating surface excess values using the Gibbs equation and also the mole fraction of solute at the surface using the extended Langmuir model shows that the surface is enriched in cycloheptanol, which is in complete agreement with the negative deviation of the surface tension with additivity.

The surface entropy and enthalpy decrease with increasing cycloheptanol mole fraction. The lyophobicity values decrease with increasing temperature.

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