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Surface Tension of Dilute Solutions of Alkanes in Cyclohexanol at Different Temperatures

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Surface tension for binary mixtures of alkanes + cyclohexanol was measured over the dilute composition range of alkanes. The alkanes include hexane, heptane, nonane, dodecane, and cyclohexane. Measurements were made under atmospheric pressure in the temperature range between (293.15 and 323.15) K. The surface tension data were analyzed using the extended Langmuir model.

Introduction

Intermolecular interactions play an important role in the properties of binary liquid mixtures. To investigate the intermolecular interactions in liquids, there are different methods. Surface tension measurement is one of the important methods to investigate the intermolecular interactions. From a practical point of view, the surface tension of a liquid is a property which is important in mass transfer processes such as distillation, absorption, and extraction. For binary liquid mixtures, usually the surface is enriched with one of the components. For modeling of the distillation process it is necessary to find some information about surface enrichment of components. This can be done by measurement of the surface tension of liquid mixtures. There are a lot of data about surface tension of binary mixtures, but studies of the composition at the air/solution interface of nonaqueous liquid mixtures are much less numerous than those of water + organic solvent mixtures.

In recent years, we have studied the surface tension of several binary organic mixtures[1−8] and also aqueous solutions of surfactants.[9−11] Alkanes are one of the important classes of solvents, and therefore the surface tension of binary mixtures including alkanes is of interest to different researchers.[1,12−15]

The purpose of the present work is to investigate the surface tension of binary solutions of alkanes and cyclohexanol. Since most of the changes in surface tension of a binary mixture occur at very low concentration of the solute, our study focuses on the dilute solutions of alkanes in cyclohexanol.

Experimental Section

Cyclohexanol (99 %), hexane (99 %), heptane (99 %), nonane (99 %), dodecane (99 %), and cyclohexane (99 %) were supplied by Merck and were used as received without further purification. Mixtures of alkanes + cyclohexanol were prepared in all the cases by mass using a Mettler Toledo AB 204-M balance with the precision of $\pm\, 1 \cdot 10^{-4}$ g, but the uncertainty of the mole fraction is estimated to be about $\pm\, 1 \cdot 10^{-3}$. Surface tension was measured at 5 °C intervals between (20 and 50) °C, using a Sigma 70 automated tensiometer and with a platinum ring method. The platinum ring was thoroughly cleaned and flame dried before each measurement. The temperature of the system was controlled with a precision of ± 0.2 K, using a Multi Temp III thermostat. Each value of reported surface tension was an average of eight to ten measurements, where the maximum deviations from the average value were always less than 0.4 %. The uncertainty of the measurements was $\pm\, 0.02$ mN·m^{-1}. Densities of pure components were measured with an Anton-Paar DMA 4500 digital precision densitometer. The densitometer was calibrated with bidistilled water. The measured values of densities, ρ, and surface tensions, σ, of pure components are listed in Table 1 and compared with the literature values.

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

t / °C	σ(exp) / mN·m^{-1}	σ(ref) / mN·m^{-1}	ρ(exp) / g·cm^{-3}	ρ(ref) / g·cm^{-3}
		Cyclohexanol		
20.0	33.15	33.40[16]	0.9504	−
25.0	32.74	32.92[16]	0.9465	0.9489[18]
45.0	31.13	30.98[16]	0.9306	−
		Hexane		
20.0	18.56	18.34[16]	0.6602	0.659[18] 0.65942[19]
25.0	18.03	17.83[16] 17.93[15]	0.6554	0.65489[19]
45.0	15.85	15.79[16]	0.6367	0.63638[19]
		Heptane		
20.0	20.05	20.14[16]	0.6860	0.684[18] 0.68399[19]
25.0	19.54	19.65[16] 19.69[15]	0.6819	0.67975[19]
45.0	17.60	17.69[16]	0.6660	0.66252[19]
		Nonane		
20.0	23.04		0.7177	0.718[18]
25.0	22.49	22.37[17] 22.30[15]	0.7139	0.7141[20]
45.0	20.47		0.6902	−
		Dodecane		
20.0	25.35	25.35[16]	0.7488	0.749[18] 0.74883[21]
25.0	24.92	24.91[16]	0.7452	0.7449[20]
45.0	23.14	23.14[16]	0.7307	0.73118[22]
		Cyclohexane		
20.0	25.06	24.95[16]	0.7786	0.779[18]
25.0	24.45	24.34[16]	0.7739	0.7738[22]
45.0	22.05	21.92[16]	0.7548	0.7596[22a]

[a] At 40 °C.

Results and Discussions

The measured surface tensions of dilute solutions of alkanes in cyclohexanol at various concentrations at each temperature

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Table 2. Surface Tension, σ, of Hexane + Cyclohexanol at Various Temperatures and Mole Fractions of Hexane (x_2)

	t/°C				
x_2	20.0	25.0	30.0	35.0	40.0
	σ/mN·m^{-1}				
0.000	33.15	32.74	32.35	31.91	31.58
0.007	31.87	31.50	31.13	30.77	30.42
0.009	31.64	31.31	30.96	30.64	30.31
0.012	31.50	31.08	30.70	30.26	29.88
0.021	31.11	30.71	30.33	29.96	29.55
0.030	30.50	30.07	29.67	29.26	28.85
0.042	30.00	29.59	29.15	28.74	28.33
0.075	28.85	28.42	27.96	27.50	27.06
1.000	18.56	18.03	17.44	16.92	16.38

Table 3. Surface Tension, σ, of Heptane + Cyclohexanol at Various Temperatures and Mole Fractions of Heptane (x_2)

	t/°C						
x_2	20.0	25.0	30.0	35.0	40.0	45.0	50.0
	σ/mN·m^{-1}						
0.000	33.15	32.74	32.35	31.91	31.58	31.13	30.78
0.011	32.84	32.47	32.11	31.78	31.43	31.07	30.70
0.014	32.69	32.29	31.92	31.55	31.23	30.85	30.45
0.020	32.56	32.20	31.80	31.39	31.01	30.57	30.16
0.025	31.80	31.48	31.08	30.74	30.41	30.07	29.70
0.033	31.53	31.17	30.82	30.44	30.10	29.76	29.43
0.037	31.38	31.01	30.56	30.14	29.77	29.39	28.99
0.061	29.87	29.54	29.20	28.83	28.54	28.23	27.87
1.000	20.05	19.54	19.10	18.58	18.08	17.60	17.06

Table 4. Surface Tension, σ, of Nonane + Cyclohexanol at Various Temperatures and Mole Fractions of Nonane (x_2)

	t/°C						
x_2	20.0	25.0	30.0	35.0	40.0	45.0	50.0
	σ/mN·m^{-1}						
0.000	33.15	32.74	32.35	31.91	31.58	31.13	30.78
0.003	32.91	32.51	32.11	31.72	31.36	30.99	30.54
0.006	32.70	32.30	31.84	31.44	31.08	30.69	30.30
0.008	32.65	32.22	31.78	31.35	30.94	30.52	30.07
0.012	32.24	31.85	31.49	31.09	30.75	30.41	30.02
0.022	31.79	31.44	31.09	30.72	30.38	29.99	29.62
0.041	30.67	30.30	29.91	29.52	29.17	28.80	28.41
0.060	29.88	29.48	29.11	28.72	28.37	27.98	27.56
1.000	23.04	22.49	22.04	21.49	20.94	20.47	19.98

Table 5. Surface Tension, σ, of Dodecane + Cyclohexanol at Various Temperatures and Mole Fractions of Dodecane (x_2)

	t/°C						
x_2	20.0	25.0	30.0	35.0	40.0	45.0	50.0
	σ/mN·m^{-1}						
0.000	33.15	32.74	32.35	31.91	31.58	31.13	30.78
0.006	31.70	31.23	30.78	30.35	29.92	29.49	29.00
0.009	31.11	30.71	30.28	29.88	29.49	29.07	28.69
0.011	30.68	30.32	29.99	29.61	29.25	28.88	28.5
0.022	30.22	29.85	29.46	29.08	28.72	28.35	27.99
0.031	29.81	29.37	28.87	28.44	28.01	27.57	27.13
0.046	29.14	28.74	28.35	27.98	27.58	27.21	26.83
0.075	27.16	26.80	26.47	26.10	25.76	25.44	25.09
1.000	24.28	23.84	23.38	22.98	22.56	22.14	21.71

are listed in Tables 2, 3, 4, 5, and 6 for hexane, heptane, nonane, dodecane, and cyclohexane as solute, respectively. For all mixtures and at each composition, the variation of surface tension with temperature is linear and decreases with increasing temperature (in the temperature range investigated). For all systems except hexane + cyclohexanol, the temperature range was (20 to 50) °C. For a given temperature, the surface tension of all mixtures investigated here decreases with an increase of alkane mole fraction. Figure 1 shows the variation of surface tension with the bulk mole fraction of nonane at different temperatures, as a typical example.

Table 6. Surface Tension, σ, of Cyclohexane + Cyclohexanol at Various Temperatures and Mole Fractions of Cyclohexane (x_2)

	t/°C						
x_2	20.0	25.0	30.0	35.0	40.0	45.0	50.0
	σ/mN·m^{-1}						
0.000	33.15	32.74	32.35	31.91	31.58	31.13	30.78
0.005	31.44	31.00	30.55	30.12	29.73	29.26	28.88
0.009	30.93	30.54	30.17	29.77	29.40	29.00	28.63
0.013	30.73	30.32	29.88	29.49	29.06	28.67	28.30
0.023	30.42	29.99	29.57	29.15	28.76	28.34	27.91
0.031	30.26	29.80	29.38	28.93	28.48	28.07	27.66
0.044	30.12	29.62	29.16	28.65	28.26	27.78	27.35
0.070	29.62	29.15	28.65	28.18	27.75	27.27	26.82
1.000	25.06	24.45	23.87	23.21	22.71	22.05	21.45

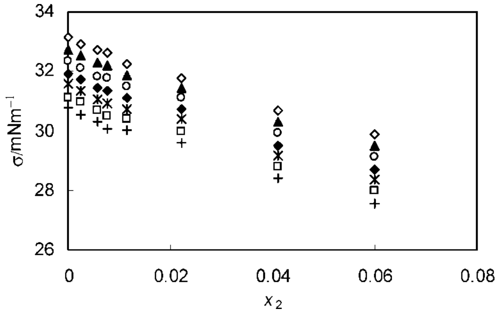

Figure 1. Surface tension vs mole fraction of nonane (x_2) in cyclohexanol at various temperatures. The symbols from top to bottom correspond to (20, 25, 30, 35, 40, 45, and 50) °C, respectively.

There are different theoretical investigations into the dependence of surface tension on solution composition.[24,25] One of the new models is the extended Langmuir model for binary liquid mixtures.[25] This model was applied to analysis of the surface tension of different binary liquid mixtures by us[1−4] and others[26−28] successfully. In this model, the surface is considered as a thin layer of finite depth. 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[25]

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

or

$$\phi_2^s = \frac{\beta\left(\dfrac{\phi_2}{\phi_1}\right)}{1+\beta\left(\dfrac{\phi_2}{\phi_1}\right)} \tag{2}$$

where β is a measure of lyophobicity of component 2 relative to component 1; ϕ_1 is bulk volume fraction of component 1; and $(\phi_2/\phi_1) = (x_2 v_2/x_1 v_1)$ is the ratio of occupations. v_2 and v_1 are the molar volume of pure components. In this model, the surface tension of nonideal binary mixtures is given by[25]

$$\sigma = \phi_1^s\sigma_1 + \phi_2^s\sigma_2 - \lambda\phi_1^s\phi_2^s\Pi^0 \tag{3}$$

where σ_1 and σ_2 are the surface tension of pure components; λ represents the effect of unlike-pair interactions on the surface tension of the mixture; and $\Pi°$ is the surface tension difference between pure components $(\sigma_1 - \sigma_2)$.[25] It was shown that when the interaction effect causes insignificant structural changes $(\lambda = 0)$

$$\frac{(\sigma-\sigma_1)}{(\sigma_2-\sigma)} = \beta\frac{\phi_2}{\phi_1} \tag{4}$$

Equation 4 shows that, if the plot of $(\sigma-\sigma_1)/(\sigma_2-\sigma)$ vs ϕ_2/ϕ_1 is linear, then it concluded that $\lambda = 0$ and therefore eq 3 simplifies to

$$\sigma = \phi_1^s \sigma_1 + \phi_2^s \sigma_2 \qquad (5)$$

For calculation of volume fraction of components, we obtained the molar volume of pure components from their measured densities.

Figure 2a shows the plot of $(\sigma - \sigma_1)/(\sigma_2 - \sigma)$ vs ϕ_2/ϕ_1 for the nonane + cyclohexanol system at two different temperatures as an example. Figure 2b shows the corresponding ln−ln plot for clarity. It is clear that the plots are linear, and therefore λ is close to zero. The β value can be obtained from the slope of Figure 2a or the intercept of Figure 2b. For all of the systems investigated here, the plots are linear. Thus, the values of β for all systems at various temperatures were obtained from such plots and listed in Table 7. These values of β show that for heptane, nonane, and dodecane systems by increasing the temperature the lyophobicity of alkanes relative to cyclohexanol decreases, while for hexane and cyclohexane systems, the lyophobicity increases with temperature. However, it should be noted that in all systems investigated here the variation of β with temperature is small. Comparison of β values for alkanes shows that, in all temperatures, the trend of lyophobicity is dodecane > cyclohexane > nonane > heptane > hexane.

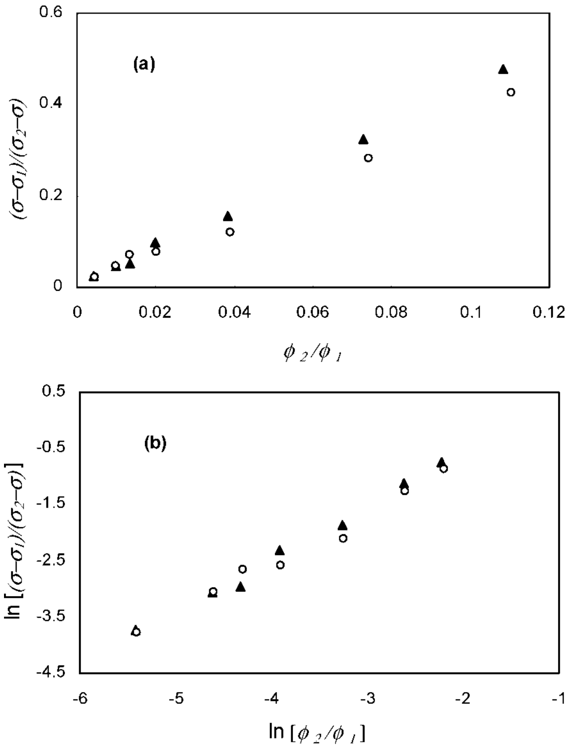

Figure 2. (a) Linear plot of $(\sigma - \sigma_1)/(\sigma_2 - \sigma)$ vs ϕ_2/ϕ_1 for nonane (2) + cyclohexanol (1) at two different temperatures. (b) As for (a), but using a ln−ln plot. Filled triangles are at 20 °C, and open circles are at 50 °C.

Table 7. Values of Lyophobicity (β) of Alkanes Relative to Cyclohexanol at Various Temperatures

	β				
t/°C	hexane	heptane	nonane	cyclohexane	dodecane
20.0	3.46	4.18	4.39	5.51	8.37
25.0	3.48	4.02	4.26	5.65	8.30
30.0	3.53	3.95	4.15	5.93	8.17
35.0	3.58	3.89	4.02	5.98	7.98
40.0	3.63	3.75	3.84	6.01	7.97
45.0	-	3.58	3.77	6.06	7.77
50.0	-	3.48	3.74	6.12	7.61

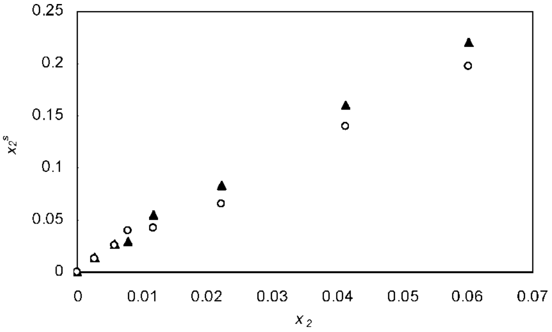

Figure 3. Surface mole fraction (x_2^s) vs bulk mole fraction (x_2) of nonane at 20 °C (filled triangles) and 50 °C (open circles).

The linearity of plots of $(\sigma - \sigma_1)/(\sigma_2 - \sigma)$ vs ϕ_2/ϕ_1 indicates that for these dilute solutions at various temperatures $\lambda \approx 0$, and therefore, the surface tension of mixtures obeys eq 5. Equation 5 can also be written as

$$\phi_2^s = \frac{(\sigma - \sigma_1)}{(\sigma_2 - \sigma_1)} \qquad (6)$$

which relates the surface tension of the mixture to the surface volume fraction of solute. The surface volume fractions of solutes (alkanes) can be calculated by eq 6 and then converted to the surface mole fractions x_2^s by the following equation

$$\phi_2^s = \frac{x_2^s v_2}{x_1^s v_1 + x_2^s v_2} \qquad (7)$$

As an example, the obtained values for surface mole fractions of nonane (x_2^s) were plotted vs its bulk mole fractions (x_2) at two temperatures in Figure 3. This diagram shows that the surface is enriched with solute (nonane); in other words, the surface composition of solute is higher than its bulk composition.

Conclusion

Surface tension values for dilute solutions of hexane, heptane, nonane, dodecane, and cyclohexane in cyclohexanol at various temperatures have been reported in this paper. The present data show that the surface tensions of all binary solutions decrease as a linear form with an increase of temperature. The decrease of surface tension of cyclohexanol solutions by addition of alkanes means that the alkanes are more surface active than cyclohexanol in these systems. In other words, for the alkane + cyclohexanol mixtures, the tendency of alkanes for migration to the surface is higher than cyclohexanol. The trend of lyophobicity for investigated alkanes in cyclohexanol is dodecane > cyclohexane > nonane > heptane > hexane.

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