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Surface Properties of Dilute Solutions of Alkanes in Benzyl Alcohol

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Surface tensions of dilute solutions of cyclohexane, hexane, heptane, and nonane in benzyl alcohol were measured at various temperatures. Surface mole fractions were obtained from an extended Langmuir model. The results show that all of alkanes are surface active in benzyl alcohol and that their surface mole fractions are higher than their bulk mole fractions. The lyophobicity of solutes decreases with increasing temperature.

Introduction

A knowledge of surface and interfacial tension of liquid mixtures is very important because these properties play an important role in interphase heat and mass transfer. These quantities also contain information on the structure and energetics of the surface region.

The dependence of surface tension on state parameters can provide some information including surface entropy from the temperature dependency of surface tension and also surface composition from the dependence of surface tension on bulk composition.

The literature dealing with surface tension of aqueous binary mixtures is extensive, but for nonaqueous binary mixtures it is scanty. Recently, we have investigated the surface tension of nonaqueous binary mixtures.[1−6] In the present work, benzyl alcohol was chosen as the solvent, and cyclohexane, hexane, heptane, and nonane were chosen as the solute. The surface tension of binary mixtures was investigated at low concentration of alkanes because most of the surface tension changes in nonelectrolyte systems occur at very low concentration of the solutes, while surface parameters remain almost unchanged for high concentration. Our special interest was the temperature dependence of the surface tension.

Experimental Section

Benzyl alcohol (99 %), cyclohexane (99 %), hexane (99 %), heptane (99 %), and nonane (99 %) were Merck products and were used as received. All mixtures of alkanes + benzyl alcohol were prepared by mass with the 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 $\pm$ 0.01 $\mathrm{mN{\cdot}m^{-1}}$. The platinum ring was thoroughly cleaned and flame-dried before each measurement. All solutions were thermostated with the 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. Densities of pure components were measured with an Anton-Paar digital precision densitimeter (model DMA 4500) operated in static mode and calibrated with bidistilled water. The values of densities (ρ) and surface tension (σ) for pure liquids are reported in Table 1 and compared with literature values.

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

t / °C	σ(exptl) / $\mathrm{mN{\cdot}m^{-1}}$ (±0.01)	σ(ref) / $\mathrm{mN{\cdot}m^{-1}}$	ρ(exptl) / $\mathrm{g{\cdot}cm^{-3}}$ (±0.0002)	ρ(ref) / $\mathrm{g{\cdot}cm^{-3}}$
		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	1.0419[a]
40.0	37.16	37.4[d] 37.06[a]	1.0298	
		Hexane		
20.0	18.56	18.34[b]	0.6602	0.659[a]
25.0	18.03	17.83[b]	0.6554	
40.0	16.38	16.30[b]	0.6414	
		Heptane		
20.0	20.05	20.14[b]	0.6960	0.684[a]
25.0	19.54	19.65[b]	0.6919	
40.0	18.08	18.18[b]	0.6800	
		Nonane		
20.0	23.04		0.7177	0.718[a]
25.0	22.49	22.37[c]	0.7139	
40.0	20.47		0.6942	
		Cyclohexane		
20.0	25.06	24.95[b]	0.7786	0.779[a]
25.0	24.45	24.34[b]	0.7739	
40.0	22.71	22.53[b]	0.7596	

[a] Ref 22. [b] Ref 23. [c] Ref 21. [d] Ref 24.

Table 2. Surface Tension (σ/mN·m^{-1}) of Hexane (x_2) + Benzyl Alcohol at Various Temperatures[a]

	σ/mN·m^{-1} at t/°C				
x_2	20.0	25.0	30.0	35.0	40.0
0.0000	39.05	38.58	38.12	37.63	37.16
0.0068	37.39	37.10	36.84	36.53	36.30
0.0085	37.24	36.85	36.41	36.01	35.60
0.0198	34.45	34.74	35.03	35.35	35.63
0.0215	33.73	34.04	34.38	34.69	34.99
0.0264	33.22	33.56	33.86	34.25	34.59
0.0493	30.61	31.06	31.54	31.92	32.35
0.0700	27.46	27.96	28.72	29.29	29.90
1.0000	18.56	18.03	17.44	16.92	16.38

[a] In all cases the standard deviation in surface tensions is ± 0.01 mN·m^{-1}.

Results and Discussion

The measured surface tensions (σ) of dilute solutions of hexane, heptane, nonane, and cyclohexane in benzyl alcohol at various temperatures are reported in Tables 2 to 5. For a given

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Table 3. Surface Tension (σ/mN·m^{-1}) of Heptane (x_2) + Benzyl Alcohol at Various Temperatures[a]

	σ/mN·m^{-1} at t/°C						
x_2	20.0	25.0	30.0	35.0	40.0	45.0	50.0
0.0000	39.05	38.58	38.12	37.63	37.16	36.63	36.18
0.0065	37.77	37.47	37.10	36.78	36.49	36.18	35.92
0.0090	37.07	36.87	36.62	36.41	36.16	35.95	35.74
0.0112	34.43	34.69	35.02	35.28	35.53	35.83	36.11
0.0238	33.61	33.83	34.05	34.27	34.48	34.70	34.95
0.0306	32.37	32.58	32.82	33.04	33.24	33.46	33.68
0.0445	28.84	29.16	29.43	29.68	30.00	30.30	30.61
0.0670	26.09	26.47	26.89	27.27	27.70	28.08	28.46
1.0000	20.05	19.54	19.10	18.58	18.08	17.60	17.06

[a] In all cases the standard deviation in surface tensions is ± 0.01 mN·m^{-1}.

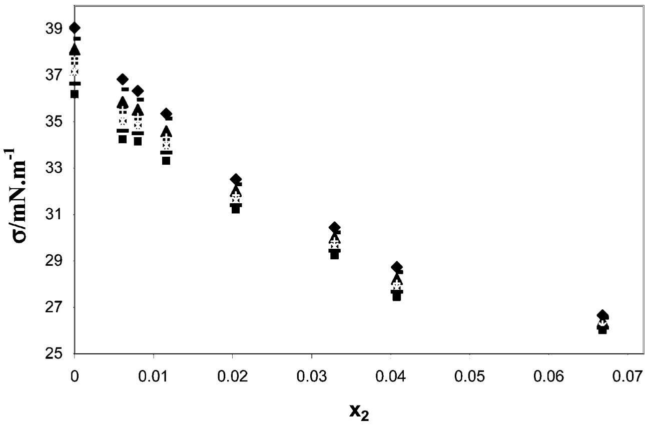

Figure 1. Surface tension vs mole fraction of nonane at various temperatures: ◆, t = 20 °C; =, t = 25 °C; ▲, t = 30 °C; ::, t = 35 °C; • •, t = 40 °C; —, t = 45 °C; ■, t = 50 °C.

temperature the surface tension of all mixtures investigated here decreased with an increase of alkanes mole fraction. This trend is nonlinear, with the change in surface tension caused by a given change in alkanes mole fraction being larger at low mole fractions than at high mole fractions. Figure 1 shows this trend for benzyl alcohol + nonane as an example. The observed rapid decrease in surface tension with the mole fraction of solute is typical of aqueous systems with surface active solutes.

The variation of the surface tensions of all the mixtures 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. Excess surface entropy per unit area[7] or specific surface entropy[8] or variation of entropy per unit area due to an interface formation[9,10] is

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

The surface entropy has units of mN·m^{-1}·K^{-1}. The surface enthalpy (mN·m^{-1}) is

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

These equations were extensively used by Glinski et al.[11−19] to investigate the surface thermodynamics of various binary mixtures.

The surface entropies and the enthalpies of alkanes + benzyl alcohol mixtures are calculated from eqs 1 and 2 and shown in Figures 2 and 3 as a function of solute mole fractions. For all systems (except of heptane) the surface entropy decreases with increasing alkane mole fraction.

In all systems the experimental surface tension data show negative deviation from additivity ($\sigma = x_1\sigma_1 + x_2\sigma_2$), indicating an enrichment of one component (component with lower surface tension) in liquid−vapor interface. So, it is concluded that, in all systems studied here, the surface of mixture was enriched with alkanes.

A new model (extended Langmuir model) was reported recently that describes the surface tension of binary liquid mixtures as a function of the bulk composition.[20] This

Table 4. Surface Tension (σ/nN·m^{-1}) of Nonane (x_2) + Benzyl Alcohol at Various Temperatures[a]

	σ/mN·m^{-1} at t/°C						
x_2	20.0	25.0	30.0	35.0	40.0	45.0	50.0
0.0000	39.05 (± 0.01)	38.58 (± 0.01)	38.12 (± 0.01)	37.63 (± 0.01)	37.16 (± 0.01)	36.63 (± 0.01)	36.18 (± 0.01)
0.0061	36.83 (± 0.01)	36.40 (± 0.01)	35.85 (± 0.01)	35.51 (± 0.01)	35.03 (± 0.02)	34.61 (± 0.01)	34.25 (± 0.01)
0.0080	36.33 (± 0.02)	35.95 (± 0.01)	35.52 (± 0.01)	35.21 (± 0.01)	34.84 (± 0.01)	34.50 (± 0.03)	34.16 (± 0.02)
0.0116	35.34 (± 0.02)	35.13 (± 0.01)	34.59 (± 0.02)	34.33 (± 0.01)	33.98 (± 0.01)	33.67 (± 0.01)	33.32 (± 0.01)
0.0204	32.52 (± 0.01)	32.31 (± 0.02)	32.02 (± 0.02)	31.83 (± 0.01)	31.61 (± 0.03)	31.41 (± 0.02)	31.22 (± 0.02)
0.0329	30.44 (± 0.01)	30.23 (± 0.01)	30.00 (± 0.02)	29.85 (± 0.01)	29.62 (± 0.01)	29.44 (± 0.01)	29.25 (± 0.01)
0.0408	28.73 (± 0.01)	28.52 (± 0.02)	28.22 (± 0.02)	28.03 (± 0.01)	27.82 (± 0.02)	27.67 (± 0.03)	27.46 (± 0.01)
0.0668	26.66 (± 0.02)	26.56 (± 0.02)	26.38 (± 0.02)	26.28 (± 0.01)	26.19 (± 0.03)	26.12 (± 0.01)	26.02 (± 0.01)
1.0000	23.04 (± 0.01)	22.49 (± 0.01)	22.04 (± 0.01)	21.49 (± 0.01)	20.94 (± 0.01)	20.47 (± 0.01)	19.98 (± 0.01)

[a] The numbers in parentheses show the standard deviation in surface tensions in mN·m^{-1}.

Table 5. Surface Tension (σ/mN·m^{-1}) of Cyclohexane (x_2) + Benzyl Alcohol at Various Temperatures[a]

	σ/mN·m^{-1} at t/°C						
x_2	20.0	25.0	30.0	35.0	40.0	45.0	50.0
0.0000	39.05 (± 0.01)	38.58 (± 0.01)	38.12 (± 0.01)	37.63 (± 0.01)	37.16 (± 0.01)	36.63 (± 0.01)	36.18 (± 0.01)
0.0068	37.88 (± 0.02)	37.43 (± 0.02)	37.06 (± 0.02)	36.66 (± 0.02)	36.29 (± 0.02)	35.84 (± 0.02)	35.50 (± 0.01)
0.0079	37.73 (± 0.02)	37.39 (± 0.02)	36.93 (± 0.02)	36.54 (± 0.02)	36.12 (± 0.03)	35.74 (± 0.02)	35.32 (± 0.01)
0.0107	37.48 (± 0.01)	37.15 (± 0.02)	36.74 (± 0.02)	36.38 (± 0.02)	35.99 (± 0.01)	35.66 (± 0.01)	35.25 (± 0.01)
0.0202	37.07 (± 0.01)	36.68 (± 0.02)	36.32 (± 0.02)	35.92 (± 0.02)	35.58 (± 0.02)	35.24 (± 0.02)	34.86 (± 0.01)
0.0312	36.53 (± 0.01)	36.25 (± 0.02)	35.98 (± 0.02)	35.73 (± 0.02)	35.47 (± 0.02)	35.22 (± 0.02)	34.96 (± 0.01)
0.0409	35.88 (± 0.02)	35.66 (± 0.02)	35.41 (± 0.02)	35.22 (± 0.02)	34.96 (± 0.01)	34.77 (± 0.02)	34.53 (± 0.01)
0.0655	34.14 (± 0.02)	34.04 (± 0.02)	33.94 (± 0.02)	33.82 (± 0.02)	33.72 (± 0.01)	33.61 (± 0.01)	33.50 (± 0.01)
1.0000	25.06 (± 0.01)	24.45 (± 0.01)	23.87 (± 0.01)	23.21 (± 0.01)	22.71 (± 0.01)	22.05 (± 0.01)	21.45 (± 0.01)

[a] The numbers in parentheses show the standard deviation in surface tensions in mN·m^{-1}.

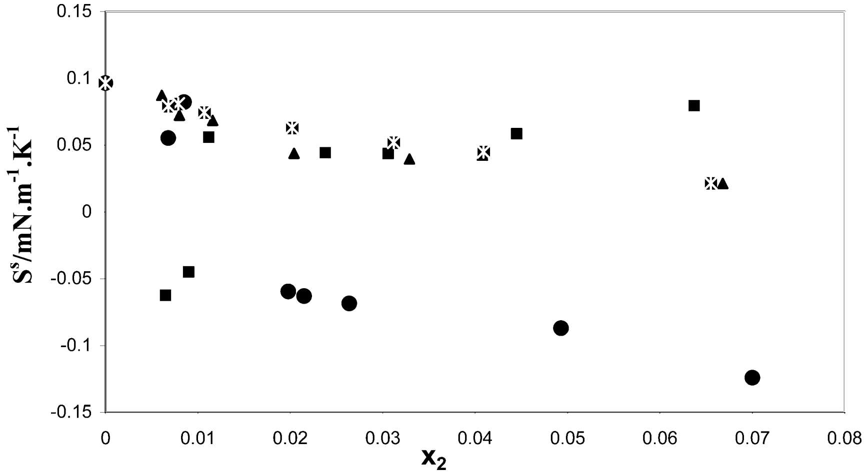

Figure 2. Surface entropy vs mole fraction of alkanes: ●, hexane; ■, heptane; ▲, nonane; white X in solid circle, cyclohexane.

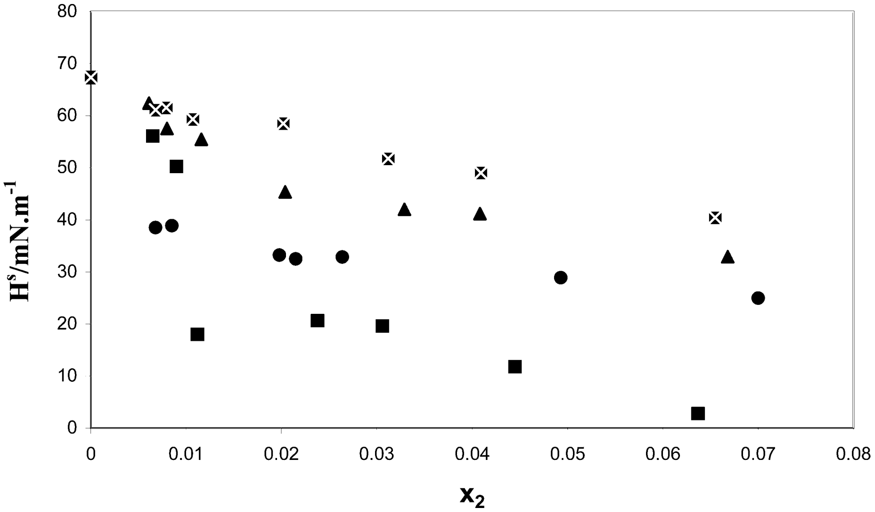

Figure 3. Surface enthalpy vs mole fraction of alkanes: ●, hexane; ■, heptane; ▲, nonane; white X in solid circle, cyclohexane.

model has been applied for analysis of surface tension of some nonaqueous binary mixtures.[4,5,6,21] In this model, the surface is considered as a thin layer of finite depth, and the volume fraction of solute in this layer denoted by ϕ_2^s when its bulk volume fraction is ϕ_2. In this model a relationship between ϕ_2^s and ϕ_2 is presented.[20] There is an equation that relates surface tension to ϕ_i; a complete review and a brief review on this equation are in refs 20 and 6, respectively.

On the basis of extended Langmuir model, if the plot of $(\sigma - \sigma_1)/(\sigma_2 - \sigma)$ versus ϕ_2/ϕ_1 (or ln − ln plot) is linear, then its slope gives β, which is a measure of lyophobicity of component 2 relative to component 1. Lyophobicity shows the interaction of component 2 with interface or, in other words, the tendency of component 2 for migration from bulk to surface.

Figure 4 (as a typical example) shows that the plot of $(\sigma - \sigma_1)/(\sigma_2 - \sigma)$ versus ϕ_2/ϕ_1 is linear for nonane + benzyl alcohol at various temperatures, where its slope is β. The values of β for all systems at various temperatures were obtained from such plots and listed in Table 6. These values of β show that for all systems by increasing of temperature the lyophobicity of alkanes relative to benzyl alcohol decreases. Comparison of β values for alkanes show that in all temperatures the trend of lyophobicity is nonane> heptane > hexane > cyclohexane.

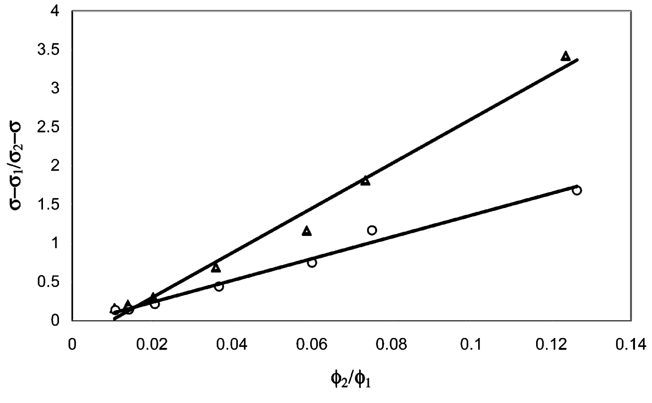

Figure 4. Plot of $(\sigma - \sigma_1)/(\sigma_2 - \sigma)$ vs ϕ_2/ϕ_1 for nonane at two temperatures: Δ, nonane at 20 °C; ○, nonane at 50 °C.

It is possible to calculate the surface mole fraction of components by this theory (eqs 8 and 9 of ref 6); the values for surface mole fractions of solute (x_2^s) were calculated (and only for nonane were plotted vs its bulk mole fraction (x_2) at two temperatures in Figure 5). This diagram and also the calculated surface mole fractions show that in all systems the surface is enriched with solutes (alkanes) relative to their bulk composition. This result is in complete agreement with negative deviation of mixture surface tension from additivity, which means that the comment with lower surface tension should accumulate at surface.

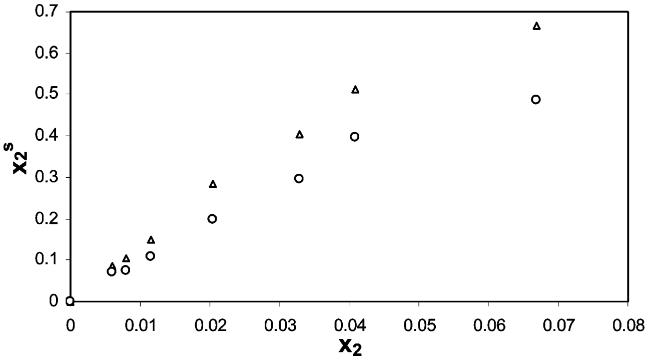

Figure 5. Surface mole fraction vs bulk mole fraction of nonane at two temperatures: △, t = 20 °C; ○, t = 50 °C.

Table 6. Values of Lyophobicity (β) of Alkanes in Benzyl Alcohol (as Solvent) at Various Temperatures

	β			
t/°C	hexane	heptane	nonane	cyclohexane
20.0	13.42	21.96	28.84	6.46
25.0	10.94	17.96	24.97	5.59
30.0	8.46	14.94	22.81	4.79
35.0	6.84	12.50	20.03	4.08
40.0	5.44	10.43	17.46	3.49
45.0		8.84	15.52	2.89
50.0		7.51	14.08	2.38

Conclusion

This work reports a number of data to the adsorption of organic compounds at the surface of nonaqueous solutions. We have measured the surface tension of dilute solutions of alkanes in benzyl alcohol at various temperatures. The experimental results show that by addition of alkanes the surface tension decrease nonlinearly but that by increasing the temperature (at constant concentration) the surface tension changes linearly. Calculation of the mole fraction of solute at surface using the extended Langmuir model shows that the surface is enriched by alkanes (i.e., all of these solutes are surface active). The negative deviation of surface tensions from additivity confirms that alkanes are surface active in benzyl alcohol. Comparison of lyophobicity values (β) for solutes shows that the trend of this parameter for solutes is nonane > heptane > hexane> cyclohexane and that by increasing temperature the β values decrease for all systems.

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