Surface Tension of Dilute Solutions of Linear Alcohols in Benzyl Alcohol

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The surface tensions of binary mixtures of 1-propanol, 2-propanol, 1-butanol, 2-butanol, 1-pentanol, and 2-pentanol in benzyl alcohol were measured over the temperature range of (20 to 50) °C using a platinum ring method. The surface entropies and surface enthalpies of the mixtures were obtained. The surface tension of the binary mixtures decreases with increasing linear alcohol content. The surface tension of the mixtures was fitted by a polynomial equation, and fitting parameters are presented.

Introduction

Surface tension not only determines the quality of many of the products resulting from different industries, such as those producing coatings, paints, detergents, cosmetics, and agrochemicals, but also affects some important steps in the production process, such as catalysis, adsorption, distillation, and extraction.

The literature dealing with the surface tension of binary mixtures is extensive, but the systems that involve alcohols are interesting¹⁻⁸ because of their inherent nature of forming associations in the form of hydrogen bonds within themselves or with other components. Studies of the adsorption of organic compounds at the surface of nonaqueous solvents are scanty. This work reports a number of new data in the field. Recently, the surface tension of binary mixtures of linear chain alcohols with ethylene glycol was investigated by us⁴ (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 glycol⁸).

In the present work, the surface tension of binary mixtures was investigated for dilute solutions of 1-propanol, 2-propanol, 1-butanol, 2-butanol, 1-pentanol, and 2-pentanol in benzyl alcohol. Most surface tension changes in nonelectrolyte systems occur at very low solute concentrations.

Experimental Section

Benzyl alcohol (99%), 1-propanol (99%), 2-propanol (99%), 1-butanol (99.5%), 2-butanol (99.7%), 1-pentanol (>98%), and 2-pentanol (>98%) were Merck products and were used as received. All alcohol + benzyl alcohol mixtures 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 $\pm 0.01 \text{ mN} \cdot \text{m}^{-1}$. The platinum ring was thoroughly cleaned and flame dried before

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

	$\sigma(\text{exptl})/$	$\sigma(ref)/$	$\rho(\text{exptl})/$	$\rho(\text{ref})/$
t/°C	$\mathrm{mN}\cdot\mathrm{m}^{-1}$	${ m mN}{ m \cdot}{ m m}^{-1}$	g·cm ⁻³	g•cm ⁻³
		Dongral Alester	-	-
90.0	20.05	Denzyi Aicono	10459	
20.0	39.00	39.40°	1.0402	
05.0	90 50	39.00	1.0414	1.0410%
25.0	38.98	38.9	1.0414	1.0419^{a}
15.0	00.00	38.54	1.0050	
45.0	36.63	36.9	1.0258	-
		36.70		
		1-Propanol		
20.0	22.73	$23.7 \hat{0}^b$	0.8031	0.8038^{d}
25.0	23.30	23.31^{b}	0.7993	0.7996^{d}
45.0	21.68	21.76^{b}	0.7832	
		9 Propagal		
20.0	91 20	2-1 10panoi	0 7951	
20.0	21.50	21.32*	0.7601	
25.0 45.0	20.95	20.95° 10.95b	0.7609	
45.0	19.47	19.55*	0.7655	
		1-Butanol		
20.0	24.16	24.53^{b}	0.8104	
25.0	23.70	23.97^{b}	0.8065	0.8060^{e}
45.0	21.99	21.73^{b}	0.7909	0.7907^{e}
		2-Butanol		
20.0	23.18		0.8071	
25.0	22.74		0.8029	0.8026^{e}
45.0	21.11		0.7855	0.7854^{e}
		1 Dente : 1		
00.0	05 00	1-Pentanol	0.0159	0.01504
20.0	25.69	25.79°	0.8153	0.8150^{a}
25.0	25.29	25.36	0.8116	
45.0	23.67	23.610	0.7966	
		2-Pentanol		
20.0	23.70	23.95^{b}	0.8098	0.8090^{a}
25.0	23.28	23.45^{b}	0.8057	
45.0	21.60	21.44^{b}	0.7888	

 a Reference 23. b Reference 24. c Reference 25. d Reference 26. e Reference 27.

each measurement. All solutions were thermostated with a precision of ± 0.1 K using a Multi Temp III thermostat, and the temperature interval between (20 and 50) °C was 5 K. Each value reported was an average of 8 to 10 measurements with a standard deviation of ± 0.02 mN·m⁻¹. 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 densities, ρ , and surface tensions, σ ,

Table 2.	Surface	Tension (σ) of	1-Propanol	(2) +	Benzy	l Alcohol	(1) a	t Various	Temperatures ^a
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				t/°C			
x_2	20.0	25.0	30.0	35.0	40.0	45.0	50.0
			$\sigma/2$	$mN \cdot m^{-1}$			
0.0000	$39.05(\pm 0.01)$	$38.58(\pm 0.01)$	$38.12(\pm 0.01)$	$37.63(\pm 0.01)$	$37.16(\pm 0.01)$	$36.63(\pm 0.01)$	$36.18(\pm 0.01)$
0.0030	$37.57(\pm 0.01)$	$37.07(\pm 0.01)$	$36.60(\pm 0.01)$	$36.15(\pm 0.02)$	$35.64(\pm 0.01)$	$35.19(\pm 0.01)$	$34.73(\pm 0.01)$
0.0062	$37.01(\pm 0.01)$	$36.62(\pm 0.01)$	$36.23(\pm 0.01)$	$35.84(\pm 0.01)$	$35.44(\pm 0.01)$	$35.07(\pm 0.01)$	$34.68(\pm 0.01)$
0.0077	$36.88(\pm 0.01)$	$36.48(\pm 0.01)$	$36.12(\pm 0.01)$	$35.74(\pm 0.01)$	$35.36(\pm 0.01)$	$35.00(\pm 0.01)$	$34.64(\pm 0.01)$
0.0116	$36.75(\pm 0.01)$	$36.36(\pm 0.01)$	$36.00(\pm 0.01)$	$35.63(\pm 0.01)$	$35.20(\pm 0.01)$	$34.85(\pm 0.01)$	$34.44(\pm 0.01)$
0.0212	$36.35(\pm 0.01)$	$35.98(\pm 0.01)$	$35.62(\pm 0.01)$	$35.23(\pm 0.01)$	$34.83(\pm 0.01)$	$34.50(\pm 0.01)$	$34.13(\pm 0.01)$
0.0326	$35.95(\pm 0.01)$	$35.60(\pm 0.01)$	$35.30(\pm 0.01)$	$34.98(\pm 0.01)$	$34.67(\pm 0.01)$	$34.38(\pm 0.01)$	$34.03(\pm 0.01)$
0.0498	$35.62(\pm 0.01)$	$35.22(\pm 0.01)$	$34.86(\pm 0.02)$	$34.48(\pm 0.01)$	$34.14(\pm 0.02)$	$33.76(\pm 0.02)$	$33.41(\pm 0.02)$
1.0000	$23.73(\pm 0.01)$	$23.30(\pm 0.01)$	$22.90(\pm 0.01)$	$22.52(\pm 0.01)$	$22.10(\pm 0.01)$	$21.68(\pm 0.01)$	$21.27(\pm 0.01)$

^a The numbers in parentheses show the uncertainty of the measurements.

Table	3. Surface	e Tension (σ) of	2-Pro	panol (2) +	Benzy	l Alcoho	l (1) at	Various	Temperatures ^a
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				t/°C			
x_2	20.0	25.0	30.0	35.0	40.0	45.0	50.0
			σ/	$mN \cdot m^{-1}$			
0.0000	$39.05(\pm 0.01)$	$38.58(\pm 0.01)$	$38.12(\pm 0.01)$	$37.63(\pm 0.01)$	$37.16(\pm 0.01)$	$36.63(\pm 0.01)$	$36.18(\pm 0.01)$
0.0029	$37.69(\pm 0.01)$	$37.30(\pm 0.01)$	$36.95(\pm 0.01)$	$36.62(\pm 0.01)$	$36.29(\pm 0.01)$	$35.89(\pm 0.01)$	$35.55(\pm 0.01)$
0.0050	$37.53(\pm 0.02)$	$37.09(\pm 0.01)$	$36.68(\pm 0.01)$	$36.32(\pm 0.01)$	$35.92(\pm 0.01)$	$35.48(\pm 0.01)$	$35.04(\pm 0.01)$
0.0076	$37.21(\pm 0.01)$	$36.80(\pm 0.01)$	$36.43(\pm 0.01)$	$36.05(\pm 0.01)$	$35.68(\pm 0.01)$	$35.27(\pm 0.01)$	$34.92(\pm 0.01)$
0.0117	$36.95(\pm 0.02)$	$36.53(\pm 0.01)$	$36.13(\pm 0.01)$	$35.75(\pm 0.01)$	$35.39(\pm 0.01)$	$35.04(\pm 0.01)$	$34.64(\pm 0.01)$
0.0207	$36.79(\pm 0.01)$	$36.37(\pm 0.01)$	$35.97(\pm 0.01)$	$35.55(\pm 0.01)$	$35.14(\pm 0.01)$	$34.73(\pm 0.01)$	$34.29(\pm 0.01)$
0.0329	$36.56(\pm 0.01)$	$36.15(\pm 0.04)$	$35.78(\pm 0.01)$	$35.41(\pm 0.02)$	$35.04(\pm 0.02)$	$34.62(\pm 0.02)$	$34.22(\pm 0.02)$
0.0494	$36.06(\pm 0.02)$	$35.53(\pm 0.01)$	$35.09(\pm 0.01)$	$34.61(\pm 0.01)$	$34.11(\pm 0.01)$	$33.63(\pm 0.01)$	$33.22(\pm 0.01)$
1.0000	$21.30(\pm 0.01)$	$20.95 (\pm 0.01)$	$20.55(\pm 0.01)$	$20.20(\pm 0.01)$	$19.83(\pm 0.01)$	$19.47(\pm 0.01)$	$19.09 (\pm 0.01)$

^{*a*} The numbers in parentheses show the uncertainty of the measurements.

fable 4.	Surface	Tension (σ)) of	1-Butanol	. (2) -	+ B	enzyl	Alcohol	(1)) at	Various	Temperat	uresa
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				t∕°C			
x_2	20.0	25.0	30.0	35.0	40.0	45.0	50.0
			$\sigma/2$	$mN \cdot m^{-1}$			
0.0000	$39.05(\pm 0.01)$	$38.58(\pm 0.01)$	$38.12(\pm 0.01)$	$37.63(\pm 0.01)$	$37.16(\pm 0.01)$	$36.63(\pm 0.01)$	$36.18(\pm 0.01)$
0.0034	$37.89(\pm 0.01)$	$37.43(\pm 0.01)$	$36.95(\pm 0.01)$	$36.50(\pm 0.01)$	$36.06(\pm 0.01)$	$35.63(\pm 0.01)$	$35.24(\pm 0.01)$
0.0044	$37.67(\pm 0.01)$	$37.23(\pm 0.01)$	$36.79(\pm 0.01)$	$36.36(\pm 0.01)$	$35.93(\pm 0.01)$	$35.51(\pm 0.01)$	$35.08(\pm 0.01)$
0.0071	$37.12(\pm 0.01)$	$36.67(\pm 0.01)$	$36.22(\pm 0.01)$	$35.77(\pm 0.01)$	$35.33(\pm 0.01)$	$34.84(\pm 0.01)$	$34.44(\pm 0.01)$
0.0117	$36.88(\pm 0.01)$	$36.48(\pm 0.01)$	$36.03(\pm 0.01)$	$35.60(\pm 0.01)$	$35.10(\pm 0.01)$	$34.66(\pm 0.01)$	$34.18(\pm 0.01)$
0.0213	$36.62(\pm 0.01)$	$36.17(\pm 0.01)$	$35.68(\pm 0.01)$	$35.18(\pm 0.01)$	$34.74(\pm 0.01)$	$34.27(\pm 0.01)$	$33.84(\pm 0.01)$
0.0303	$36.46(\pm 0.01)$	$35.99(\pm 0.01)$	$35.52(\pm 0.01)$	$35.02(\pm 0.01)$	$34.57(\pm 0.01)$	$34.02(\pm 0.01)$	$33.59(\pm 0.01)$
0.0492	$35.94(\pm 0.01)$	$35.49(\pm 0.01)$	$35.06(\pm 0.01)$	$34.64(\pm 0.01)$	$34.16(\pm 0.01)$	$33.74(\pm 0.01)$	$33.35(\pm 0.01)$
1.0000	$24.16(\pm 0.01)$	$23.70(\pm 0.01)$	$23.26(\pm 0.01)$	$22.78(\pm 0.01)$	$22.39(\pm 0.01)$	$21.99 (\pm 0.01)$	$21.53(\pm 0.01)$

^{*a*} The numbers in parentheses show the uncertainty of the measurements.

Fable 5.	Surface	Tension (σ)) of	2-Butano	l (2)	$+ \mathbf{B}$	enzyl	Alcohol	(1)) at	Various	Tempera	ntures ^a
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				t/°C			
x_2	20.0	25.0	30.0	35.0	40.0	45.0	50.0
			σ	$mN \cdot m^{-1}$			
0.0000	$39.05(\pm 0.01)$	$38.58(\pm 0.01)$	$38.12(\pm 0.01)$	$37.63(\pm 0.01)$	$37.16(\pm 0.01)$	$36.63(\pm 0.01)$	$36.18(\pm 0.01)$
0.0026	$37.50(\pm 0.01)$	$37.08(\pm 0.01)$	$36.63(\pm 0.01)$	$36.20(\pm 0.01)$	$35.75(\pm 0.01)$	$35.35(\pm 0.01)$	$34.95(\pm 0.01)$
0.0056	$37.14(\pm 0.01)$	$36.75(\pm 0.01)$	$36.31(\pm 0.01)$	$35.97(\pm 0.01)$	$35.55(\pm 0.01)$	$35.17(\pm 0.01)$	$34.80(\pm 0.01)$
0.0078	$36.95(\pm 0.01)$	$36.52(\pm 0.01)$	$36.12(\pm 0.01)$	$35.71(\pm 0.01)$	$35.31(\pm 0.01)$	$34.90(\pm 0.01)$	$34.49(\pm 0.01)$
0.0107	$36.40(\pm 0.01)$	$36.05(\pm 0.01)$	$35.72(\pm 0.01)$	$35.39(\pm 0.01)$	$35.03(\pm 0.01)$	$34.67(\pm 0.01)$	$34.34(\pm 0.01)$
0.0246	$36.07(\pm 0.01)$	$35.64(\pm 0.01)$	$35.18(\pm 0.01)$	$34.77(\pm 0.01)$	$34.37(\pm 0.01)$	$33.95(\pm 0.01)$	$33.50(\pm 0.01)$
0.0366	$35.65(\pm 0.01)$	$35.25(\pm 0.01)$	$34.83(\pm 0.01)$	$34.46(\pm 0.01)$	$34.03(\pm 0.01)$	$33.62(\pm 0.01)$	$33.24(\pm 0.01)$
0.0512	$35.32(\pm 0.01)$	$34.88(\pm 0.01)$	$34.40(\pm 0.01)$	$34.00(\pm 0.01)$	$33.54(\pm 0.01)$	$33.07(\pm 0.01)$	$32.70(\pm 0.01)$
1.0000	$23.18(\pm 0.01)$	$22.74(\pm 0.01)$	$22.38(\pm 0.01)$	$21.94(\pm 0.01)$	$21.56(\pm 0.01)$	$21.11(\pm 0.01)$	$20.76(\pm 0.01)$

^a The numbers in parentheses show the uncertainty of the measurements.

for pure liquids are reported in Table 1 and compared with literature values.

Results and Discussion

Tables 2 to 7 list the measured surface tensions, σ , of dilute solutions of 1-propanol, 2-propanol, 1-butanol, 2-butanol, 1-pentanol, and 2-pentanol in benzyl alcohol. For a given temperature, the surface tension of all mixtures

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

Table 6. Surface Tension (σ) of 1-Pentanol (2) + Benzyl Alcohol (1) at Various Temperatures^{*a*}

				t/°C			
x_2	20.0	25.0	30.0	35.0	40.0	45.0	50.0
			$\sigma/2$	$mN \cdot m^{-1}$			
0.0000	$39.05(\pm 0.01)$	$38.58(\pm 0.01)$	$38.12(\pm 0.01)$	$37.63(\pm 0.01)$	$37.16(\pm 0.01)$	$36.63(\pm 0.01)$	$36.18(\pm 0.01)$
0.0037	$36.88(\pm 0.01)$	$36.41(\pm 0.01)$	$36.05(\pm 0.01)$	$35.64(\pm 0.01)$	$35.26(\pm 0.01)$	$34.86(\pm 0.01)$	$34.47(\pm 0.01)$
0.0052	$36.73(\pm 0.01)$	$36.34(\pm 0.01)$	$35.92(\pm 0.01)$	$35.51(\pm 0.01)$	$35.10(\pm 0.01)$	$34.70(\pm 0.01)$	$34.31(\pm 0.01)$
0.0083	$36.56(\pm 0.01)$	$36.12(\pm 0.01)$	$35.73(\pm 0.01)$	$35.28(\pm 0.01)$	$34.86(\pm 0.01)$	$34.47(\pm 0.01)$	$34.03(\pm 0.01)$
0.0117	$36.35(\pm 0.01)$	$35.93(\pm 0.01)$	$35.50(\pm 0.01)$	$35.10(\pm 0.01)$	$34.69(\pm 0.01)$	$34.29(\pm 0.01)$	$33.89(\pm 0.01)$
0.0213	$35.93(\pm 0.01)$	$35.50(\pm 0.01)$	$35.05(\pm 0.01)$	$34.64(\pm 0.01)$	$34.24(\pm 0.01)$	$33.82(\pm 0.01)$	$33.40(\pm 0.01)$
0.0336	$35.63(\pm 0.01)$	$35.21(\pm 0.01)$	$34.79(\pm 0.01)$	$34.35(\pm 0.01)$	$33.95(\pm 0.01)$	$33.52(\pm 0.01)$	$33.08(\pm 0.01)$
0.0536	$35.22(\pm 0.01)$	$34.76(\pm 0.01)$	$34.31(\pm 0.01)$	$33.80(\pm 0.01)$	$33.34(\pm 0.01)$	$32.95(\pm 0.01)$	$32.43(\pm 0.01)$
1.0000	$25.69(\pm 0.01)$	$25.29(\pm 0.01)$	$24.86(\pm 0.01)$	$24.49(\pm 0.01)$	$24.06(\pm 0.01)$	$23.67(\pm 0.01)$	$23.30(\pm 0.01)$

^{*a*} The numbers in parentheses show the uncertainty of the measurements.

Table 7. Surface Tension (σ) of 2-Pentanol (2) + Benzyl Alcohol (1) at Various Temperatures^{*a*}

				t/°C			
x_2	20.0	25.0	30.0	35.0	40.0	45.0	50.0
			σ/r	nN•m ^{−1}			
0.0000	$39.05(\pm 0.01)$	$38.58(\pm 0.01)$	$38.12(\pm 0.01)$	$37.63(\pm 0.01)$	$37.16(\pm 0.01)$	$36.63(\pm 0.01)$	$36.18(\pm 0.01)$
0.0026	$36.98(\pm 0.01)$	$36.48(\pm 0.01)$	$35.95(\pm 0.01)$	$35.46(\pm 0.01)$	$34.97(\pm 0.02)$	$34.44(\pm 0.01)$	$33.91(\pm 0.02)$
0.0055	$36.71(\pm 0.01)$	$36.22(\pm 0.03)$	$35.70(\pm 0.03)$	$35.18(\pm 0.02)$	$34.73(\pm 0.03)$	$34.18(\pm 0.03)$	$33.65(\pm 0.03)$
0.0093	$36.43(\pm 0.01)$	$35.95(\pm 0.02)$	$35.53(\pm 0.02)$	$35.00(\pm 0.03)$	$34.54(\pm 0.02)$	$34.07(\pm 0.01)$	$33.56(\pm 0.02)$
0.0129	$35.99(\pm 0.01)$	$35.54(\pm 0.02)$	$35.15(\pm 0.02)$	$34.73(\pm 0.01)$	$34.33(\pm 0.02)$	$33.91(\pm 0.03)$	$33.55(\pm 0.02)$
0.0238	$35.72(\pm 0.01)$	$35.32(\pm 0.01)$	$34.90(\pm 0.02)$	$34.49(\pm 0.02)$	$34.05(\pm 0.03)$	$33.63(\pm 0.01)$	$33.28(\pm 0.01)$
0.0344	$35.49(\pm 0.02)$	$35.08(\pm 0.01)$	$34.71(\pm 0.02)$	$34.32(\pm 0.02)$	$33.93(\pm 0.02)$	$33.49(\pm 0.01)$	$33.11(\pm 0.02)$
0.0542	$35.08(\pm 0.02)$	$34.61(\pm 0.02)$	$34.10(\pm 0.01)$	$33.61(\pm 0.02)$	$33.10(\pm 0.02)$	$32.69(\pm 0.02)$	$32.19(\pm 0.02)$
1.0000	$23.70(\pm 0.01)$	$23.28(\pm 0.01)$	$22.0.87(\pm 0.01)$	$22.43(\pm 0.01)$	$22.04(\pm 0.01)$	$21.6(\pm 0.01)$	$21.16(\pm 0.01)$

^a The numbers in parentheses show the uncertainty of the measurements.



Figure 1. Surface tension vs mole fraction of 1-propanonal at various temperatures for the benzyl alcohol + 1-propanol mixture: \blacklozenge , t = 20 °C; \blacksquare , t = 25 °C; \blacktriangle , t = 30 °C; \blacklozenge , t = 35 °C; \neg , t = 40 °C; \neg , t = 45 °C; \blacksquare , t = 50 °C.

The variation of the surface tensions of all mixtures (investigated here) with temperature is linear in the temperature range of (20 to 50) °C. Figure 2 shows this trend for 1-propanol in benzyl alcohol as a typical example. Thermodynamic properties of the surface of these solutions are obtained by the following equations. Excess surface entropy per unit area⁹ or specific surface entropy¹⁰ or variation of entropy per unit area due to interface formation^{11,12} is

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

and the surface enthalpy is

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



Figure 2. Surface tension of the 1-propanol + benzyl alcohol mixture vs temperature at various mole fractions: \bullet , $x_2 = 0.0498$; *, $x_2 = 0.0326$; -, $x_2 = 0.0212$; ·, $x_2 = 0.0116$; \bullet , $x_2 = 0.0077$; \triangle , $x_2 = 0.0062$; \Box , 0.0030.

These equations were extensively used by Glinski et al.^{13–21} to investigate the surface thermodynamics of various binary mixtures. The surface entropies and the enthalpies of alcohols + benzyl alcohol mixtures calculated from eqs 1 and 2 are listed in Tables 8 and 9, respectively. For all systems, the behavior of the surface entropy is very complicated. The surface enthalpies for all systems decrease at first and remain nearly constant.

In all systems, the experimental surface tension data show a negative deviation from additivity, indicating an enrichment of one component (the component with a lower surface tension, which in this work is linear alcohols) in the liquid-vapor interface.

Table 8. Surface Entropy (mN·m⁻¹·K⁻¹) Values at Various Mole Fractions of Alkanols

1-propanol		2-propanol		1-butanol		2-butanol		1-pentanol		2-pentanol	
x_2	$S^{ m s}$	x_2	$S^{ m s}$	x_2	$S^{ m s}$	x_2	$S^{ m s}$	x_2	$S^{ m s}$	x_2	S^{s}
0.0000	0.0964	0.0000	0.0964	0.0000	0.0964	0.0000	0.0964	0.0000	0.0964	0.0000	0.0964
0.0030	0.0946	0.0029	0.0707	0.0034	0.0862	0.0026	0.0856	0.0037	0.0795	0.0028	0.1016
0.0062	0.0777	0.0050	0.0818	0.0044	0.0862	0.0056	0.0782	0.0052	0.0812	0.0055	0.1016
0.0077	0.0745	0.0076	0.0762	0.0071	0.0899	0.0078	0.0816	0.0083	0.0839	0.0093	0.0954
0.0116	0.0767	0.0117	0.0762	0.0117	0.0906	0.0107	0.0688	0.0117	0.0819	0.0129	0.0813
0.0212	0.0743	0.0207	0.0828	0.0213	0.0934	0.0246	0.0850	0.0213	0.0841	0.0238	0.0826
0.0326	0.0631	0.0329	0.0773	0.0303	0.0964	0.0366	0.0806	0.0336	0.0848	0.0344	0.0794
0.0498	0.0734	0.0494	0.0950	0.0492	0.0869	0.0512	0.0883	0.0536	0.0926	0.0524	0.0966

Table 9. Surface Enthalpy (mN·m⁻¹) Values at Various Mole Fractions of Alkanols

1-propanol		2-propanol		1-butanol		2-butanol		1-pentanol		2-pentanol	
x_2	$H^{ m s}$	x_2	$H^{ m s}$	x_2	$H^{ m s}$	x_2	$H^{ m s}$	x_2	$H^{ m s}$	x_2	$H^{ m s}$
0.0000	67.32	0.0000	67.32	0.0000	67.32	0.0000	67.32	0.0000	67.32	0.0000	67.32
0.0030	65.29	0.0029	58.39	0.0034	63.93	0.0026	62.60	0.0037	60.15	0.0028	66.76
0.0062	59.79	0.0050	61.49	0.0044	62.92	0.0056	60.06	0.0052	60.53	0.0055	66.50
0.0077	58.70	0.0076	59.53	0.0071	63.48	0.0078	60.86	0.0083	61.16	0.0093	64.41
0.0116	59.23	0.0117	59.25	0.0117	63.48	0.0107	56.57	0.0117	60.35	0.0129	59.79
0.0212	58.14	0.0207	61.09	0.0213	63.47	0.0246	60.99	0.0213	60.56	0.0238	59.93
0.0326	54.42	0.0329	59.21	0.0303	64.01	0.0366	59.27	0.0336	60.50	0.0344	59.76
0.0498	57.12	0.0494	63.88	0.0492	61.39	0.0512	61.20	0.0536	62.37	0.0524	63.40

Table 10. Parameter Used in Equation 4 at Various Temperatures^a

	1-propanol	2-propanol	1-butanol	2-butanol	1-pentanol	2-pentanol
t/°C	В	В	В	В	В	В
20.0	$-36.10(\pm 0.92)$	$-36.77(\pm 0.62)$	$-36.50(\pm 0.88)$	$-35.84(\pm 1.08)$	$-35.59(\pm 0.95)$	$-35.71(\pm 0.79)$
25.0	$-35.71(\pm 0.88)$	$-36.23(\pm 0.73)$	$-35.97(\pm 0.95)$	$-35.46(\pm 1.06)$	$-35.34(\pm 0.80)$	$-35.21(\pm 0.82)$
30.0	$-35.46(\pm 0.75)$	$-35.84(\pm 0.74)$	$-35.59(\pm 0.88)$	$-34.97(\pm 1.13)$	$-34.72(\pm 0.99)$	$-34.72(\pm 0.84)$
35.0	$-35.09(\pm 0.73)$	$-35.34(\pm 0.87)$	$-35.21(\pm 0.82)$	$-34.60(\pm 1.11)$	$-34.24(\pm 1.04)$	$-34.25(\pm 0.84)$
40.0	$-34.72(\pm 0.68)$	$-34.84(\pm 0.99)$	$-34.72(\pm 0.85)$	$-34.13(\pm 1.16)$	$-33.78(\pm 1.10)$	$-33.78(\pm 0.85)$
45.0	$-34.36(\pm 0.66)$	$-34.36(\pm 1.0.5)$	$-35.25(\pm 0.88)$	$-33.67(\pm 1.30)$	$-33.44(\pm 1.04)$	$-33.33(\pm 0.82)$
50.0	$-34.01(\pm 0.62)$	$-34.01(\pm 1.02)$	$-33.90(\pm 0.82)$	$-33.22(\pm 1.35)$	$-32.89(\pm 1.17)$	$-32.90(\pm 0.80)$

^a The numbers in parentheses show the standard deviation in calculated surface tension in mN·m⁻¹.

The experimental surface tension of linear alcohols + benzyl alcohol were fitted to the following equation²² at various temperatures.

$$\sigma/\mathbf{N} \cdot \mathbf{m}^{-1} = x_2 \sigma_2 - \frac{x_1 x_2 B}{1 + x_1 A}$$
(3)

where σ and σ_2 are the surface tensions of mixtures and the solute, respectively, x_1 and x_2 are the mole fractions of the solvent and solute, and *A* and *B* are fitting constants. To find the *A* and *B* values, eq 3 can be rearranged to

$$\frac{x_2}{\sigma - x_2 \sigma_2} = -\frac{A}{B} - \frac{1}{Bx_1} \tag{4}$$

so that the plot of $x_2/\sigma - x_2\sigma_2$ versus $1/x_1$ gives a straight line with -A/B and -1/B as the intercept and slope, respectively. This plot is shown in Figure 3 for 1-propanol + benzyl alcohol at (20 and 50) °C. For other systems, such plots were drawn, and the *B* and *A* values were obtained from their slopes and intercepts, respectively. The fitting regression is very good for all systems($R^2 \ge 0.9998$). The *B* values are reported in Table 10 at various temperatures. For all systems, the *B* values decrease with increasing temperature. The obtained *A* values for all systems are equal to -1.

Conclusions

The surface tensions of binary mixtures of linear alcohols + benzyl alcohol were measured over a wide temperature range using a ring method at seven mole fractions (dilute region). The experimental data show that by the addition



Figure 3. Plot of $x_2/(\sigma - \sigma_2 x_2)$ vs $1/x_1$ for 1-propanol at two temperatures: $\diamond, t = 20$ °C; $\Box, t = 50$ °C.

of linear alcohols to benzyl alcohol the surface tension decreases nonlinearly. The negative deviation of the surface tension of mixtures from additively shows that the component with a lower surface tension (linear alcohols) tends to migrate to the surface and therefore its surface concentration is higher than its bulk concentration.

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