International Journal of Thermophysics, Vol. 16, No. 1, 1995

Temperature Dependence of the Surface Tension for Binary Mixtures of *n*-Butanenitrile + *n*-Alkanes[1]

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The differential capillary-rise method was used to determine the orthobaric surface tension of binary liquid mixtures of *n*-butanenitrile mixed with *n*-pentane, *n*-hexane, and *n*-heptane, throughout the composition range, at 293.15, 303.15, 313.15, 323.15, 333.15, and 343.15 K. Furthermore, the system with *n*-hexane was also studied at 263.15 K, i.e., 19 K above its upper critical solution temperature, over the whole composition range. For each binary system the surface tension changes regularly with both temperature and composition between the values of the pure components. The results are discussed in terms of deviations from surface ideality and related to the large positive deviations observed for bulk properties of the same systems.

KEY WORDS: alkanes; butanenitrile; capillary rise; mixtures; orthobaric; surface tension.

1. INTRODUCTION

Liquid mixtures of an alkanenitrile with an alkane present large positive deviations from ideality. These deviations give rise, in bulk properties, to large positive values of H^E ($>1000\ \mathrm{J \cdot mol^{-1}}$) [1], G^E ($>800\ \mathrm{J \cdot mol^{-1}}$) [2, 3], and V^E [4-6], positive absolute azeotropy [7-9], and liquid-liquid immiscibility [10-13]. It is generally accepted that the aforementioned behavior is the result of weak characteristic energy of interaction between the unlike molecules in the mixtures compared with the Berthelot geometric-mean rule. In order to continue our studies on the thermodynamics of alkanenitrile + alkane binary liquid mixtures, we have now performed some

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[1] Paper presented at the Twelfth Symposium on Thermophysical Properties, June 19-24, 1994, Boulder, Colorado, U.S.A.

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0195-928X/95/0100-0045$07.50/0

experiments to determine the general features of the surface tension of several mixtures and to study any possible relationship between the latter and bulk properties such as the occurrence of azeotropy.

Measurements of the orthobaric surface tension of pure components are abundant as may be verified in the well-known review by Jasper [14] and other works reported in the literature [15], however, data for the single phase region of mixtures over a wide range of temperature are scarce for systems of chain molecules in which one of the components is strongly polar. Experimental information on the surface tension of mixtures is needed to improve our understanding of the thermodynamics of surface phenomena such as adsorption. Hence, we carried out a study of the orthobaric surface tension of three binary systems, as a function of composition, composed of *n*-butanenitrile as the common component mixed with *n*-pentane, *n*-hexane, and *n*-heptane, at 293.15, 303.15, 313.15, 323.15, 333.15, and 343.15 K. The upper critical solution temperatures (UCST) of these mixtures are 237.2, 244.2, and 252.3 K [13], respectively. In order to carry out measurements closer to an UCST we additionally studied the system with *n*-hexane at 263.15 K, i.e., 19 K above its UCST, also in the whole composition range.

2. APPARATUS

The well-known capillary-rise method, considered to be one of the most accurate absolute methods to study surface tension [16, 17], was used in an all-glass closed cell with three calibrated precision-bore capillaries of different diameters in order to apply the differential capillary-rise method introduced by Sugden [18]. A schematic diagram of the experimental apparatus [19–21] is shown in Fig. 1. The measuring cell has three capillaries, A, B, and C, whose constant diameter was determined by weighing an accurately known length of mercury contained at a constant temperature inside each piece of capillary tube, with an analytical balance to ±0.0001 g. The diameters obtained were 0.5000, 0.7900, and 1.0000 mm, respectively.

The mixing chamber D houses a Teflon-coated magnetic bar which is used to ensure thermal equilibrium of the 5-cm^3 sample of either a pure liquid or a mixture of known composition, before being transferred to chamber E. A glass plunger, attached to the body of a Vineland Teflon vacuum-tight valve, helps to displace the sample into the capillaries and to ensure zero contact angle by raising and lowering the level of the sample in the capillaries just before taking measurements of the relative meniscus heights. This is done by means of a 1-m Gaertner cathetometer with an accuracy of ±0.01 mm. The selected temperature of the thermal bath was

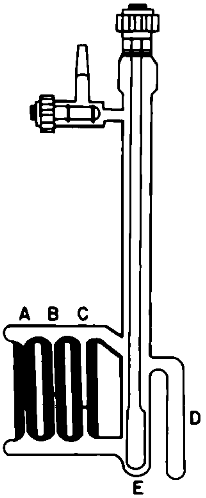

Fig. 1. All-glass surface tension cell. A C, calibrated capillaries; D, mixing chamber; E, chamber with plunger.

stabilized within ±0.002 K of the reported value by means of a precision Bayley controller, as measured with a digital thermometer, Systemteknik S1220, with a platinum resistance sensor. All the experiments were carried out with the cell wholly immersed in a thermostat [21].

3. DATA REDUCTION

The surface tension data γ under orthobaric conditions were obtained with the following relationship:

$$\gamma = r_i r_j \rho g[3\Delta h_{ij} - (r_j - r_i)]/6(r_j - r_i) \qquad (1)$$

where Δh_{ij} is the experimentally determined height difference of the menisci in the capillaries of radius r_i and r_j, ρ is the density of the liquid phase, and g is the acceleration of free fall in our laboratory, determined by the Geophysics Laboratory of the National University to be 9.7795 m s $^{-2}$.

Mixtures were prepared by weight and the density of both the pure components and their mixtures, throughout the composition range, was deterined in previous work [4–6] with a vibrating-tube densitometer.

All liquid samples used for the experiments were obtained from Aldrich, with a reported purity of >99.5 %, and are the same as those used in other studies reported by our laboratory [3, 6]. No further purification was attempted other than storing the alkanes over sodium and butanenitrile over a molecular sieve in order to eliminate any possible trace of water. The density and refractive indices of the pure samples at different temperatures agreed well with reported literature values.

4. RESULTS

The results of our measurements of γ for the four pure components and the three sets of binary mixtures in the temperature range 293 to 343 K at intervals of 10 K for seven compositions are given in Tables I–III. The results of the 263.15 K isotherm for the binary with hexane are also included in Table II. The γ values of the pure components agree very well with literature values [14] within an average percentage relative error of 0.3. Figure 2 illustrates the different isotherms for butanenitrile + hexane as a function of alkane composition.

In order to discuss some general features of the γ results we will make use of the mole fraction surface ideality, namely, $\gamma(\text{ideal}) = x_1\gamma_1 + x_2\gamma_2$.

Although it is clear that the results of the different binaries are rather regular with changes in both temperature and composition (see Fig. 2), considering the above convention for surface ideality, the 293, 303, 313, and 323 K isotherms for pentane show small negative deviations throughout the composition range, although larger the lower the temperature of the measurement; whereas the other two isotherms present small negative deviations from the low composition region of pentane up to approximately 0.75 mole fraction of pentane and small positive deviations in the rich concentration region of the alkane, i.e., there is a change in curvature in

Table I. Experimental Results of the Surface Tension γ for x_1 n-C_5H_{12} + $(1 - x_1)$ n-C_4H_7N as a Function of Temperature

	T(K)					
x_1	293.15	303.15	313.15	323.15	333.15	343.15
1	16.17	14.98	13.91	12.73	11.71	10.53
0.8961	16.45	15.60	14.53	13.94	13.05	12.28
0.7997	16.85	16.12	15.35	14.31	13.69	12.75
0.6026	17.18	16.55	15.95	15.57	14.92	14.09
0.5015	18.50	17.90	17.37	16.53	15.89	15.16
0.2995	20.82	19.87	19.11	18.40	17.89	16.84
0.2046	22.37	21.86	21.19	20.24	19.96	19.19
0.1022	24.28	23.75	23.12	22.59	21.82	20.98
0	27.48	26.43	25.19	24.39	23.39	22.26

Table II. Experimental Results of the Surface Tension γ for x_1 n-C_6H_{14} + $(1 - x_1)$ n-C_4H_7N as a Function of Temperature

x_1	T(K), 263.15	x_1	T(K)					
			293.15	303.15	313.15	323.15	333.15	343.15
1	21.84	1	18.50	17.52	16.46	15.43	14.46	13.33
0.9405	21.97	0.9131	19.34	18.56	17.68	17.08	16.22	15.30
0.8980	22.00	0.8252	19.56	18.65	17.98	17.12	16.50	15.67
0.8000	22.22	0.6427	20.31	19.50	18.70	17.95	16.93	16.27
0.6985	22.70	0.5449	21.08	20.40	19.32	18.40	17.56	16.61
0.6052	22.70	0.3379	21.84	21.03	20.26	19.74	19.04	18.19
0.4999	22.77	0.2286	23.26	22.57	21.82	21.17	20.40	19.58
0.3990	23.34	0.1145	24.84	24.17	23.49	22.83	22.26	21.44
0.2993	23.51	0	27.48	26.43	25.19	24.39	23.29	22.26
0.1995	24.02							
0.1000	27.45							
0	30.80							

the γ vs x function of the aforementioned isotherms. Furthermore, from a low mole fraction of pentane up to the middle of the mole fraction range, γ varies rapidly with composition, the slope being greater the lower the temperature of the data.

For the binaries with hexane, Fig. 2, the lowest isotherm, which is relatively close to an UCST, presents a sharp decrease in γ in the low-concentration region of the alkane, i.e., from 0 to 0.3 mole fraction, followed by a slight decrease with a nearly constant slope over the rest of the composition range. The data for this isotherm present negative deviations

Table III. Experimental Results of the Surface Tension γ for x_1 n-C_7H_{16} + $(1 - x_1)$ n-C_4H_7N as a Function of Temperature

x_1	T(K)					
	293.15	303.15	313.15	323.15	333.15	343.15
1	20.34	19.37	18.25	17.35	16.36	15.37
0.8950	20.51	19.55	18.52	17.47	16.46	15.48
0.8009	20.76	19.69	18.63	17.75	16.96	15.90
0.5993	21.26	20.02	19.23	18.23	17.23	16.22
0.4989	21.49	20.24	19.35	18.53	17.48	16.51
0.3000	22.46	21.32	20.41	19.48	18.58	17.61
0.1993	23.16	22.37	21.56	20.60	19.67	18.65
0.1001	25.01	24.20	23.21	22.13	21.07	19.93
0	27.48	26.43	25.19	24.39	23.39	22.26

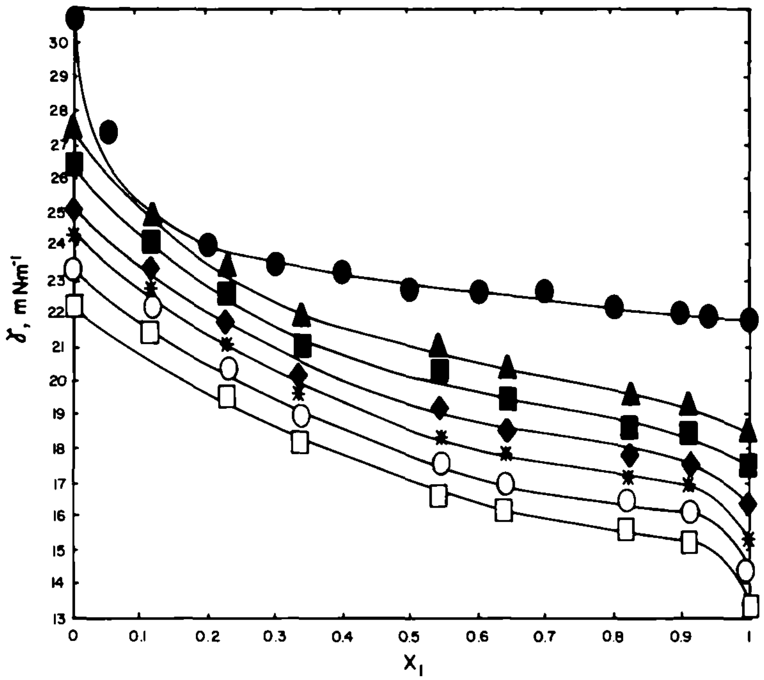

Fig. 2. Surface tension γ for x_1 n-C_6H_{14} + $(1-x_1)$ n-C_4H_7N at different temperatures. Experimental points are (●) 263.15 K, (▲) 293.15 K, (■) 303.15 K, (◆) 313.15 K, (∗) 323.15 K, ( ) 333.15 K, and (□) 343.15 K.

throughout the composition range with respect to the ideal surface defined above. Overall, the values of γ decrease monotonically from that of pure butanenitrile to that of pure hexane without an inflection point. The other six isotherms show, as in the binaries with pentane, small negative deviations from ideality in the low-alkane concentration region up to 0.75 mole fraction and small positive deviations in the high-concentration region of hexane, i.e., a monotonic decrease from the γ of butanenitrile to that of hexane with inflection point. The magnitude of the negative deviations decreases as the temperature increases, whereas the positive deviations increase with temperature. These isotherms show, in the low-mole fraction region of hexane, a significantly smaller change of γ with composition than that for the 263 K isotherm.

According to Khosla and Widom [20], at the UCST the orthobaric surface tension as a function of composition of a mixture has a horizontal tangent and an inflection at the critical composition, i.e., it takes the shape of a typical critical isotherm of a pure substance. From our results it is observed that although the isotherms that we report here for butanenitrile with pentane and hexane are far from the corresponding UCST, some of them (see Fig. 2) show a vanishing slope and inflection at $x \cong 0.75$, thus, verifying the prediction [20].

The main features of the results of the binaries with heptane are their regularity with both composition and temperature and the negative deviations from surface ideality of all the isotherms throughout the composition range. The behavior of the six isotherms of this system closely resembles that of the lowest isotherm with hexane.

The above surface behavior for the three sets of binaries can be compared with the bulk thermodynamics of the same systems in order to support the view that weak unlike molecular energies of interaction that give rise to positive deviations from bulk ideality according to Raoult's law are accompanied by negative deviations from surface ideality. The experimental evidence obtained in our laboratory for the binaries studied here present large bulk positive deviations from ideality [22], hence, they exhibit positive azeotropy. Consequently, the negative deviations from surface ideality are consistent with this behavior, however, the small regions of positive deviations for some of the mixtures with pentane and hexane are not. The absence of minimum surface tension points, with respect to γ of the pure components, in any of the isotherms of the three systems studied indicates that there is no mutual incidence of surface (aneotropy) and bulk azeotropy as has been found in other binary systems [19, 23].

5. CONCLUSIONS

Our experimental results on the orthobaric surface tension of binary mixtures of butanenitrile with alkanes show that the deviations from ideality are consistent with the bulk positive deviations from ideality and both are in turn consistent with a weak energy of interaction between the unlike molecules in the mixtures. Since the binaries considered in this study show marked positive azeotropy, we originally expected to observe aneotropy, however, this was not so. We propose to continue this study at temperatures closer to an UCST in order to observe the mentioned phenomenon, since the proximity of a UCST is a necessary condition [23], and to test Widom's predictions.

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