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Binary Aqueous–Organic Surface Tension Temperature Dependence

Bryan C. Hoke, Jr. and John C. Chen*

Department of Chemical Engineering, Lehigh University, Bethlehem, Pennsylvania 18015-4791

Surface tensions of binary mixtures of 2-propanol–water and ethylene glycol–water have been measured by using the maximum bubble pressure method. Temperature was varied from ambient to the mixture boiling point at a pressure of 1 atm. Theoretically based correlations are provided that are useful for interpolating the data as a function of temperature and composition.

The surface tension of mixtures is an important physical property for many chemical processes, including distillation, gas absorption, liquid–liquid extraction, and condensation. Surface tension affects the hydrodynamics and transfer rates of such systems, particularly multiphase systems where a gas–liquid interface exists. A falling liquid film evaporator is an example of a system where surface tension is very important. Surface tension gradients, the so-called Marangoni effect, provide a fluid diversion mechanism whereby films may breakdown. Film breakdown is the condition where the evaporator surface is not completely wetted by the fluid. Breakdown provides a system deficiency because the entire evaporator surface is not utilized, and thus it provides an operating limit for the system.

The objective of this work is to measure and correlate mixture surface tensions as a function of temperature and composition. The maximum bubble pressure method described by Sugden (*1*) was used to measure the surface tension of mixtures of ethylene glycol–water and 2-propanol–water. The duNouy or "ring" method, using a Fisher surface tensiomat, was tried first, but repeatable readings for the mixtures were not obtained. It is believed that the surface layer concentration changed over time, leading to erratic results. The maximum bubble pressure technique, however, provided consistent, repeatable results, perhaps because a fresh surface is formed for each measurement. Mixture surface tensions are correlated by using a mole fraction mixing rule proposed by Connors and Wright (*2*). The current work shows that the surface tension parameters in the model are temperature-dependent. Both systems are described well by this mixing rule, provided the temperature dependence of the surface tension parameters is included.

Experiment

A schematic of the maximum bubble pressure (MBP) tensiomat used in this study is shown in Figure 1. Kalbassi and Biddulph (*3*) describe an apparatus that is very similar to the one described here. The apparatus consists of fitted glassware with a side-arm condenser, large and fine capillary tubes with radii of about 0.9 and 0.2 mm, respectively, and a variable heating element. The tensiomat is instrumented with a type K thermocouple and two pressure transducers. The pressure transducers are connected to a data acquisition system. Calibration of the pressure transducers provided a linear relationship between pressure and the output voltage signal. A regulated nitrogen source provides bubbles that are blown through the capillary tubes at a very slow rate.

The maximum bubble pressure method for measuring surface tension is based on the differences in capillary pressure produced by forcing a bubble through capillary tubes of different radii. The total pressure measured for each tube is due to surface tension and fluid static head forces according to the equation

$$P_i = \frac{2\sigma}{r_i} + \rho g h_i \qquad (1)$$

where r_i is the radius of curvature at the base of the bubble in tube i. Initially, as the bubble forms, the radius of the bubble is large. Pressure rises as the radius decreases. The minimum radius corresponds roughly to the radius of the tube and provides the maximum pressure, P_i.

Subtracting eq 1 from itself for tubes 1 and 2 yields

$$P_1 - P_2 = \rho g(h_1 - h_2) + 2\sigma\left(\frac{1}{r_1} - \frac{1}{r_2}\right) \qquad (2)$$

Fixing the tubes to the same elevation causes the static head terms to be equal, and eq 2 reduces to

$$P_1 - P_2 = 2\sigma\left(\frac{1}{r_1} - \frac{1}{r_2}\right) \qquad (3)$$

Therefore, given the tube radii and the maximum pressures, the surface tension can be calculated.

Adam (*4*) gives an empirical formula to calculate the surface tension, using the maximum bubble pressure method that accounts for the distortion of the bubble.

$$\sigma = A(P_1 - P_2)\left(1 + 0.69 r_2 \frac{g\rho}{P_1 - P_2}\right) \qquad (4)$$

This formula is applicable if the radius of the larger tube is less than 2 mm and the radius of the smaller tube is about 0.1 mm. The value of A is a constant for the apparatus and is determined by measuring the maximum bubble pressures of fluids with known surface tensions and back-calculating the value of A by using eq 4. Note that this formula is given incorrectly by Kalbassi and Biddulph (*3*).

Calibration of the apparatus was accomplished by using two fluids: certified ACS 2-propanol and purified ethylene glycol. Surface tensions at 25 °C were measured with a Fisher tensiomat, and the maximum bubble pressures were measured with the MBP tensiomat. With use of these values, A is calculated to be 1.267×10^{-4} and 1.256×10^{-4} m for 2-propanol and ethylene glycol, respectively. A value of 1.262×10^{-4} m was accepted for calculating surface tensions using the MBP surface tensiomat. There is a ±0.4% uncertainty in the calibration of the apparatus.

The procedure for measuring the mixture surface tensions follows. Glassware was first carefully cleaned, rinsed in acetone, and baked in an oven. A sample was introduced to the tensiomat and placed on the heating element. The nitrogen flow rate was adjusted to maintain the bubble period between 4 and 8 s, as compared to Kalbassi and Biddulph who maintained a gas flow rate to produce a period of about 5 s. There was no apparent change in the maximum bubble pressures for nitrogen flow rate adjustments between the extremes of this range, indicating that a bubble period in this range is a long enough time for the gas–liquid interface to reach equilibrium conditions. Dynamic surface tensions could also be measured by this apparatus. This was done by Miller and Meyer (*5*) using a similar technique. Bubble frequencies for their dynamic measurements ranged from 1–10 bubbles/s.

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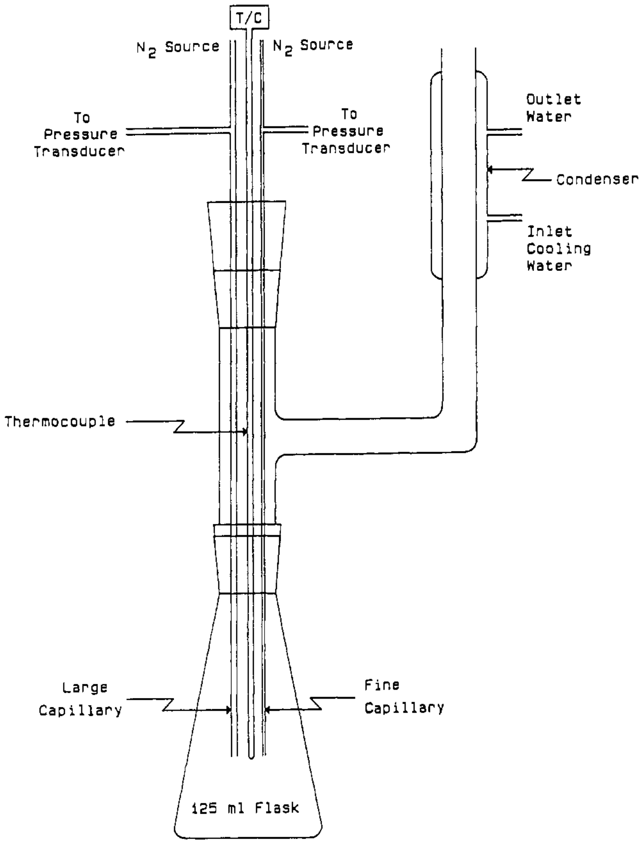

Figure 1. Experimental apparatus.

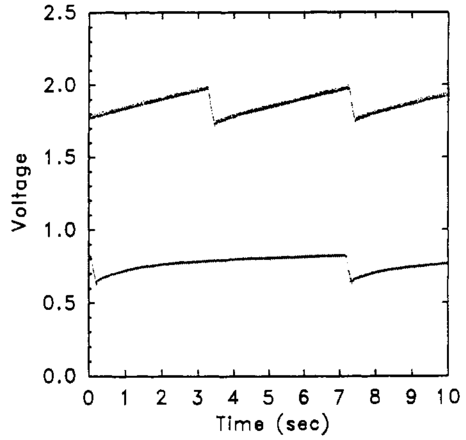

Figure 2. Voltage profile from pressure transducer.

When the sample was at the desired temperature, the pressure was scanned for 10 s by using the data acquisition system. A typical voltage profile from a sample case is shown in Figure 2. The upper curve corresponds to the fine capillary tube and the lower curve to the large capillary tube; a smaller bubble radius provides a higher pressure. Note how the pressure increases as the bubble radius decreases and the pressure drops when the bubble releases. The maximum voltage for each transducer was recorded with the corresponding temperature.

The sample was then elevated to the next desired temperature, and the maximum voltages were recorded. This was repeated until the boiling point was reached. This procedure constitutes one sample run.

A small sample of fluid was extracted before and after each sample run. Compositions of the mixtures were measured to verify that the concentrations did not change significantly during the surface tension measurements. The concentrations of the ethylene glycol-water mixtures were checked with a refractometer and the 2-propanol-water mixtures with a GC. The mole fraction of each sample was seen to vary by less than 1 mol % from its original composition.

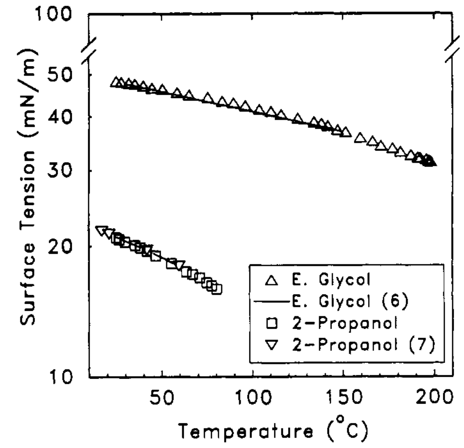

Figure 3. Surface tensions of ethylene glycol and 2-propanol.

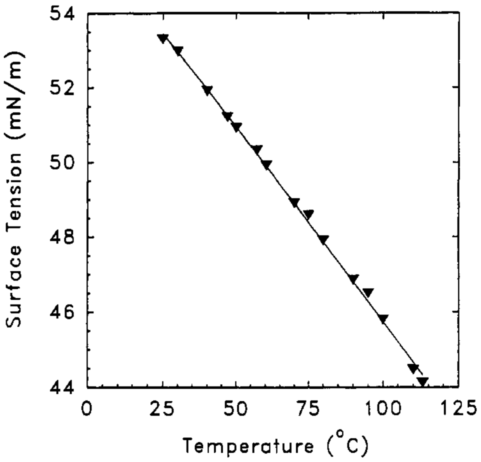

Figure 4. Surface tensions of a 0.41 mole fraction ethylene glycol-water mixture.

Results and Discussion

Transducer voltages were converted to pressures and the surface tensions calculated by using eq 4. Surface tensions for the ethylene glycol-water and 2-propanol-water mixtures are given in Tables I and II, respectively. The tables list the composition, temperature, and the corresponding surface tension.

A comparison between the measured surface tensions and previously published data for ethylene glycol (*6*) and 2-propanol (*7*) is shown in Figure 3. Ethylene glycol's surface tension as a function of temperature is given by the authors in equation form. The temperature range of the data used to generate this descriptive equation is 30-150 °C. This equation is plotted for this temperature range along with the measured data. Previously published 2-propanol data is tabulated and is plotted along with the measured data. We see that the current data does not deviate significantly from the previously published data.

The surface tension of a 0.41 mole fraction ethylene glycol-water mixture versus temperature is shown in Figure 4. The surface tensions for each mixture are correlated by using an equation of the form

$$\sigma/(\mathrm{mN\ m^{-1}}) = \alpha(1 - T_r')^{\beta} \quad (5)$$

where T_r' is the reduced temperature based on a pseudocritical

Table I. Ethylene Glycol–Water Mixture Surface Tensions

mole fraction organic	T/°C	σ/(mN/m)	mole fraction organic	T/°C	σ/(mN/m)	mole fraction organic	T/°C	σ/(mN/m)	mole fraction organic	T/°C	σ/(mN/m)
0.047	24.7	66.0	0.20	71.0	52.2	0.51	40.1	50.8	0.81	70.0	45.2
	25.2	65.9		74.9	51.8		45.2	50.2		80.1	44.9
	29.0	65.5		80.0	51.4		48.1	49.9		90.1	43.8
	32.2	65.0		86.5	50.5		49.9	49.8		100.0	43.0
	41.4	63.8		89.8	49.9		53.5	49.4		110.0	41.8
	44.0	63.3		95.2	49.2		55.0	49.4		120.0	40.7
	50.5	62.5		100.2	48.4		60.0	48.9		130.0	39.6
	53.7	62.2		102.8	48.2		65.0	48.4		140.0	38.6
	61.0	61.0	0.30	24.4	55.3		70.0	47.9		150.0	37.4
	63.9	60.4		30.1	54.8		75.2	47.4		152.0	37.1
	62.8	60.7		35.0	54.3		80.3	46.9	1.00	25.0	48.2
	69.7	59.6		40.0	53.8		85.0	46.6		27.8	48.0
	73.0	59.1		45.0	53.4		89.8	46.2		31.9	47.8
	79.8	58.1		50.0	52.8		95.0	45.5		35.2	47.5
	81.5	57.8		55.0	52.5		99.9	45.0		39.8	47.1
	92.2	56.2		60.0	51.8		105.0	44.3		44.6	46.4
	97.5	55.3		65.0	51.2		110.2	43.7		50.3	46.3
	99.2	54.8		70.0	50.8		115.0	43.5		58.4	45.4
0.10	22.2	62.3		75.0	50.3		120.0	42.6		65.0	44.8
	24.0	62.4		80.0	49.9	0.61	25.0	50.8		75.4	44.2
	25.4	62.1		85.0	49.1		30.0	50.4		83.4	43.3
	29.3	61.7		90.0	48.6		35.0	49.8		89.6	42.9
	35.8	60.7		95.0	47.9		40.0	49.5		96.0	42.3
	40.7	60.2		100.0	47.4		44.9	49.2		103.8	41.4
	44.1	59.7		104.8	46.5		50.0	48.5		110.2	41.0
	49.7	59.2		111.0	45.9		55.0	48.0		115.8	40.4
	57.3	58.4	0.41	25.0	53.3		60.1	47.8		125.0	39.5
	66.8	56.9		30.0	53.0		64.9	47.1		133.9	38.8
	70.3	56.6		40.0	51.9		70.1	46.8		138.0	38.5
	80.0	55.1		47.0	51.2		75.0	46.2		141.5	38.0
	82.0	54.8		50.0	50.9		80.0	45.8		146.9	37.2
	85.9	54.4		57.1	50.3		84.9	45.3		151.4	36.9
	91.4	53.5		60.3	49.9		90.0	44.8		159.4	35.7
	93.0	53.2		70.0	48.9		100.0	43.7		166.2	35.1
	103.2	51.5		75.0	48.6		110.0	42.7		170.8	34.2
	102.7	51.5		80.0	47.9		120.0	41.7		177.2	33.7
0.20	24.6	57.2		90.0	46.9		127.3	40.6		181.5	33.1
	38.0	55.8		95.0	46.5	0.81	23.5	48.9		187.2	32.5
	40.0	55.7		100.0	45.8		25.0	48.7		190.9	32.0
	45.2	55.1		110.0	44.5		30.0	48.6		192.3	32.0
	49.6	54.6		113.1	44.1		40.0	47.8		195.7	31.8
	55.1	54.0	0.51	24.0	52.0		50.0	47.0		197.0	31.5
	60.0	53.4		30.0	51.6		60.0	46.2		198.0	31.4
	65.0	52.9		35.0	51.0						

temperature. The pseudocritical temperature for mixtures with mole fractions y_A and y_B is defined by

$$T_c' = y_A T_{c,A} + y_B T_{c,B} \tag{6}$$

where $T_{c,A}$ and $T_{c,B}$ are the critical temperatures (K) for components A and B. Nonlinear regression of the data was done by using SigmaPlot on an 80286 machine with a math coprocessor.

Results of the regressions are given in Table III for ethylene glycol–water and 2-propanol–water mixtures. Average percent deviations between the correlation and experimental data are seen to be less than 1.0%.

Dörfler (*8*) measured ethylene glycol–water mixture surface tensions at 20 °C. Figure 5 shows values read from Dörfler's published graph along with current values extrapolated to 20 °C by using eq 5. The minimum temperature for the measured surface tensions is about 25 °C, thus requiring a slight extrapolation for comparison purposes. There is good agreement between these values.

With use of the correlations for surface tension as a function of temperature for each composition, the effect of composition on the surface tension was investigated. Surface tension data for water is widely available, and the best available data is correlated and is given by Jasper (*9*) as σ/(mN m^{-1}) = 75.83 − 0.1477 (t/°C). Figure 6 shows a plot of the surface tension for mixtures of 2-propanol–water versus composition interpolated for temperatures of 30, 50, and 70 °C. The surface tensions of the mixtures lie between those of the pure components.

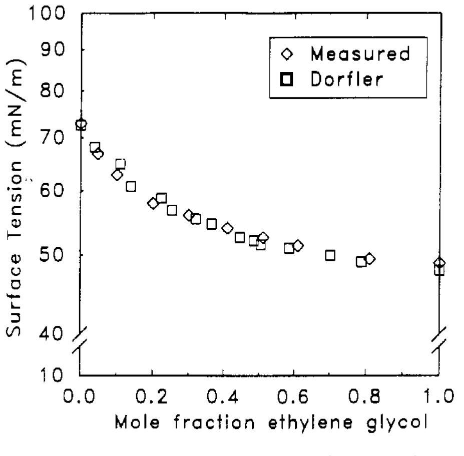

Figure 5. Ethylene glycol–water mixture surface tensions at 20 °C.

Connors and Wright (*2*) propose an equation of the form

$$\sigma = \sigma_A - \left[1 + \frac{b y_A}{1 - a y_A}\right] y_B(\sigma_A - \sigma_B) \tag{7}$$

Table II. 2-Propanol-Water Mixture Surface Tensions

mole fraction organic	T/°C	σ/(mN/m)	mole fraction organic	T/°C	σ/(mN/m)
0.055	24.1	33.4	0.58	25.0	22.3
	25.0	33.3		30.0	21.8
	30.0	32.4		40.0	21.1
	40.0	30.9		50.0	20.4
	50.0	29.5		60.0	19.6
0.10	25.0	26.6		65.0	19.3
	30.0	26.3		70.0	18.8
	40.0	25.6		80.0	17.7
	50.0	24.8	0.81	23.2	21.5
	60.0	24.1		25.2	21.2
	70.0	23.3		30.0	21.3
	80.0	22.7		40.0	20.5
	83.0	22.3		50.0	19.6
0.19	23.0	24.7		60.0	18.7
	25.0	24.6		70.0	17.7
	30.0	24.4		80.0	16.6
	40.0	23.6	1.00	25.0	20.9
	45.0	23.5		26.6	20.7
	50.0	23.3		29.8	20.5
	60.0	22.6		35.4	20.1
	70.0	21.9		38.2	19.8
	80.0	21.2		41.8	19.5
0.37	23.0	23.3		46.7	19.0
	25.0	23.2		55.4	18.2
	30.0	22.9		63.6	17.4
	40.0	22.3		67.0	17.2
	50.0	21.6		71.0	16.9
	60.0	21.0		74.8	16.5
	70.0	20.2		77.5	16.2
	76.0	19.6		80.3	15.9
	79.0	19.4			

Table III. Surface Tension Parameters α and β for Aqueous-Organic Mixtures

organic component	mole fraction organic	α	β	av % dev[a]
ethylene glycol	0.047	105.7	0.7613	0.17
	0.10	97.17	0.7218	0.27
	0.20	87.06	0.6772	0.22
	0.30	82.94	0.6536	0.24
	0.41	79.55	0.6457	0.19
	0.51	76.07	0.6153	0.21
	0.61	75.25	0.6352	0.22
	0.81	70.86	0.5978	0.53
	1.0	71.52	0.6334	0.61
2-propanol	0.055	92.23	1.626	0.14
	0.10	47.99	0.9242	0.18
	0.19	41.34	0.7869	0.31
	0.37	42.57	0.8627	0.38
	0.58	45.47	0.9466	0.50
	0.81	46.27	0.9451	0.95
	1.00	45.82	0.8866	0.26

[a] |predicted − experimental|/experimental, as %.

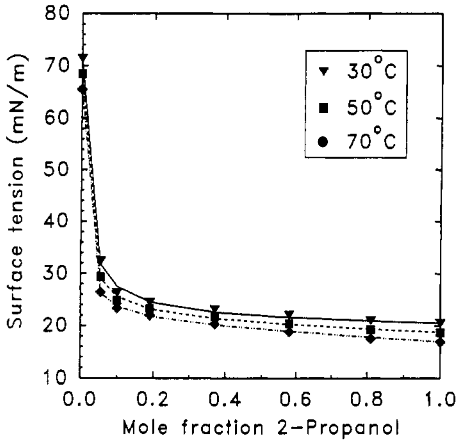

Figure 6. Surface tensions of 2-propanol-water mixtures.

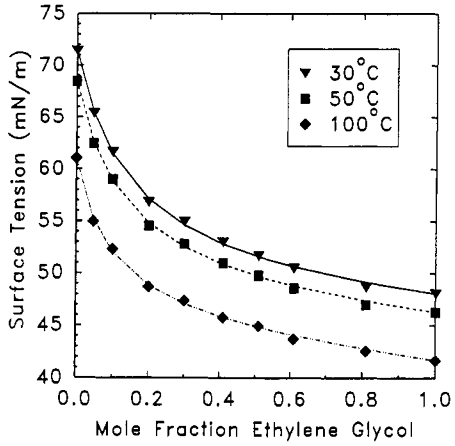

Figure 7. Surface tensions of ethylene glycol-water mixtures.

where σ_A is the water surface tension and σ_B the organic component surface tension, to describe the effect of composition on the mixture surface tension. They provide values for the surface tension parameters, *a* and *b*, for several mixtures at 25 °C. Connors and Wright do not discuss the temperature dependence of *a* and *b*.

The present analysis shows that these surface tension parameters, *a* and *b*, are temperature-dependent. The temperature dependence for the 2-propanol-water mixture surface tension parameters is linear for the temperature range 10–100 °C and can be described by

$$a = 0.9804 + 1.615 \times 10^{-4}(t/°\mathrm{C})$$

$$b = 0.9985 - 1.311 \times 10^{-3}(t/°\mathrm{C})$$

with an average deviation of ±0.01% and ±0.03% for *a* and *b*, respectively.

Figure 7 shows ethylene glycol-water mixture surface tensions versus composition interpolated for temperatures of 30, 50, and 100 °C. This mixture exhibits behavior similar to that of the 2-propanol-water mixture, where the surface tensions of the mixtures lie between that of the pure components. The temperature dependence for the ethylene glycol-water mixture surface tension parameters is also linear and is best described by the following first-order equations for the temperature range of 10–100 °C:

$$a = 0.8557 + 5.741 \times 10^{-4}(t/°\mathrm{C})$$

$$b = 0.8006 - 7.870 \times 10^{-4}(t/°\mathrm{C})$$

The average deviations for *a* and *b* are 0.09% and 0.05%.

Conclusion

This investigation provides surface tension data for mixtures of 2-propanol-water and ethylene glycol-water over ranges of temperature and composition. The maximum bubble pressure method for determining surface tension was used The temperature dependence on surface tension for a given composition is described well by eq 5.

The effect of composition on surface tension was also investigated. Surface tensions are correlated as a function of composition by using the equation proposed by Connors and Wright (*2*). The current work shows that the surface tension parameters, *a* and *b*, are temperature-dependent. The surface tension mixture rule works well for both the 2-propanol-water and ethylene glycol-water mixtures, provided a temperature correction is made for the surface tension parameters.

Glossary

a	surface tension parameter defined in eq 7
A	constant of MBP apparatus
b	surface tension parameter defined in eq 7
g	gravitational constant
h	tube immersion depth
P_i	pressure in tube i
P	maximum pressure in tube
r	radius of tube
t	temperature
T_c	critical temperature
T_c'	pseudocritical temperature defined in eq 6
T_r'	reduced temperature, T/T_c'
y	mole fraction

Greek Letters

α	surface tension parameter defined in eq 5
β	surface tension parameter defined in eq 5
ρ	density
σ	surface tension

Subscripts

1	fine capillary tube
2	larger capillary tube
A	aqueous component
B	organic component

Registry No. 2-Propanol, 67-63-0; ethylene glycol, 107-21-1.

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Excess Volume, Excess Enthalpy, and Excess Heat Capacity of the Binary Liquid Systems Ethanenitrile or 2-Butanone + 2,2,4-Trimethylpentane

H. Kalali, F. Kohler, and P. Svejda*

Ruhr-Universität Bochum, Institut für Thermo- und Fluiddynamik, P.O. Box 102148, D-4630 Bochum 1, Germany

The excess volumes (at 293.15 and 313.15 K) of the binary liquid mixtures of ethanenitrile (acetonitrile) or 2-butanone (ethyl methyl ketone) + 2,2,4-trimethylpentane (isooctane) have been determined from density measurements at atmospheric pressure. The excess enthalpies (at 293.15 K) and the isobaric heat capacities (at 293.15 and 313.15 K) of the same mixtures have been measured by means of Picker calorimeters at atmospheric pressure. The excess Gibbs energy of ethanenitrile + 2,2,4-trimethylpentane (at the upper critical solution temperature, T_c = 354.55 K) has been estimated from the liquid–liquid equilibrium curve.

Introduction

Data on mixtures containing polar liquids are needed in chemical engineering. We also used these data to develop a classification scheme for these types of systems (*1*) and to test a recently developed equation of state that incorporates information on molecular shape (*2*, *3*).

The thermodynamic excess properties of ethanenitrile or 2-butanone + 2,2,4-trimethylpentane presented here are part of our study on mixtures of polar liquids with a common nonpolar component. In the frame of this study, we have investigated 2,2′-dichlorodiethyl ether + 2,2,4-trimethylpentane (*4*) and ethanenitrile or 2-butanone + 2,4,4-trimethyl-1-pentene or + 2,4,4-trimethyl-2-pentene (*5*, *6*). Moreover, we have surveyed the properties of mixtures of other polar compounds + hydrocarbons (*7*) and their dependence on the dipole moment μ of the polar component (*8*).

Ethanenitrile (μ = 3.91 D in the gas phase) exhibits a miscibility gap in the system with 2,2,4-trimethylpentane at temperatures below 354.55 K and atmospheric pressure, while 2-butanone (μ = 2.88 D) is less polar and completely miscible at the temperatures used in this work.

Experimental Section

Ethanenitrile (J. T. Baker Chemicals, analytical reagent) with a purity of 99.95 mol % and 2-butanone (Merck, p.a.) with a purity of 99.89 mol %, both checked by GLC, were dried over potassium carbonate (Baker, analytical reagent). 2,2,4-Trimethylpentane (Fluka, puriss., or Phillips, research grade), with purities of 99.97 or 99.98 mol %, respectively, by GLC, was stored over Na–Pb (Merck, p.a.). The substances were used without further purification. They were carefully degassed by several pump/thaw cycles prior to each measurement. Relative atomic masses according to IUPAC (1987) (*9*) were used.

The molar excess volumes V^E were calculated from precise density measurements of the liquids with use of a vibrating glass tube densimeter (Model DMA 02 D, Paar) at 293.15 and 313.15 K and atmospheric pressure. The precision of the densities is estimated as 3 × 10^{-6} g cm^{-3}, and the accuracies are 1 × 10^{-5} g cm^{-3} at 293.15 K and 1 × 10^{-4} g cm^{-3} at 313.15 K. Mixtures were prepared from the degassed samples by weighing them into air-tight screw-capped tubes; the masses were corrected for the gas phase. This led to accuracies in the mole fraction x_i of 3 × 10^{-5} (*10*). V^E is accurate to 0.003 cm^3 mol^{-1} at about equimolar composition but less so at low and high concentration ranges in the partially miscible ethanenitrile + 2,2,4-trimethylpentane system.

The molar excess enthalpies H^E were measured in a dynamic flow microcalorimeter of Picker type (Setaram) at 293.15 K and atmospheric pressure, as described in detail previously (*11*). Here, x_i has an accuracy of 1 × 10^{-4}. H^E could be measured with a relative error of better than 2.5% at equimolar composition, but again this precision was reduced at the edges

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