J. Chem. Eng. Data 1988, 33, 473-476

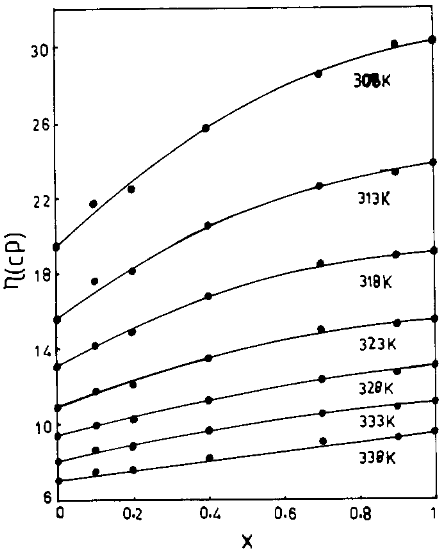

Figure 1. Variation of viscosity of $0.3[x\text{NaSCN} + (1 - x)\text{KSCN}] + 0.7\text{Na}_2\text{S}_2\text{O}_3\cdot5.1\text{H}_2\text{O}$ melt with composition.

ions studied to date. In binary melts also normally a negative deviation of η from additivity is observed (*9*).

It has been reported (*10*) recently that when Na^+ and K^+ ions are added to the molten sodium thiosulfate pentahydrate only the Na^+ ions compete for the water of hydration of the hydrate melt. Probably, this particular interaction between the Na^+ ions of the solute and the water of hydration of the molten solvent which is absent in other similar type of mixed alkali systems studied earlier may be causing in the present case the unusual positive deviation of η from additivity. A comparative study, however, reveals that positive deviations of η from additivity are noticed in binary mixtures containing organic salts (*11*, *12*). By looking into the nature of the dependences of A, B, and T_0 on x, it is realized that the B parameter seems to govern the variation of η with x. Finally, it may be commented that in the system under study, although x varies from 0 to 1, the mole fraction, $K^+/(Na^+ + K^+)$, varies from 0 to 0.18 only.

Registry No. NaSCN, 540-72-7; KSCN, 333-20-0; $Na_2S_2O_3\cdot5H_2O$, 10102-17-7.

Literature Cited

(1) Moynihan, C. T. *J. Electrochem. Soc.* **1979**, *126*, 2144.
(2) Easteal, A. J.; Emson, M. C. *J. Phys. Chem.* **1980**, *84*, 3330.
(3) Easteal, A. J. *Aust. J. Chem.* **1981**, *34*, 1853.
(4) Sangma, P.; Mahiuddin, S.; Ismail, K. *J. Phys. Chem.* **1984**, *88*, 2378.
(5) Ingram, M. D.; King, K.; Kranbuehl, D.; Adel-Hadadi, M. *J. Phys. Chem.* **1981**, *85*, 289.
(6) Isard, J. O. *J. Non-Cryst. Solids* **1969**, *1*, 235.
(7) Day, D. E. *J. Non-Cryst. Solids* **1976**, *21*, 343.
(8) Islam, N.; Ismail, K. *J. Phys. Chem.* **1975**, *79*, 2180.
(9) Janz, G. J.; Krebs, U.; Siegenthaler, H. F.; Tomkins, R. P. T. *J. Phys. Chem. Ref. Data* **1972**, *1*, 581.
(10) Islam, S. S.; Ismail, K. *Can. J. Chem.* **1988**, *66*, 242.
(11) Ewell, R. H. *J. Chem. Phys.* **1937**, *5*, 967.
(12) Woermann, D.; Sarholz, W. *Ber. Bunsen-Ges. Phys. Chem.* **1965**, *69*, 319.

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Surface Tensions of Mixtures at Their Boiling Points

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The surface tensions at the boiling points of four binary mixtures and one ternary system are reported. The mixtures studied were methanol/water, ethanol/water, 1-propanol/water, methanol/1-propanol, and methanol/1-propanol/water. The apparatus used in these experimental measurements is simple and easy to use in this application. It uses the principle of bubble detachment pressures from two capillaries in a boiling liquid. Good agreement with previous values for pure components was achieved, and surface tension/composition data for all five systems are reported. Correlations of the data from the four binary mixtures are given.

The measurements of surface tension described in this paper were made in connection with a project to study the effect of surface phenomena on distillation efficiencies.

The "Marangoni" effect has been attracting increased attention because of its influence on mass transfer in the field of distillation (*1*–*6*) humidification, absorption of gases, and liquid–liquid extraction (*7*). It has been shown to occur in many systems of commercial interest, affecting interfacial turbulence and droplet–droplet coalescence rates, froth formation and droplet size, thus altering the interfacial area available for mass transfer. Marangoni effects occur in mixtures when large surface tension differences exist between the components, and they are intensified by large mass-transfer driving forces. Examples of such systems are alcohol–water mixtures, and considerable efforts have been made in the past to develop suitable correlations to describe the surface tension behavior of these systems (*8*, *9*). Due to the highly nonlinear nature of these systems, arising from the complexity of the structure of the hydrogen bonding of water, the correlations have not been very successful. In the field of distillation the surface tension/composition relationship at the boiling point is of interest, and most of the measurement techniques, such as capillary rise, cannot be used. Sugden (*10*, *11*) gave details of a tensiometer which was reported by Adam (*12*) to "combine the advantages of speed, simplicity and accuracy to a greater extent than any other method". Although the apparatus was originally designed for room temperature determinations, with some modification it was used successfully for measurements at the boiling point by Catchpole (*13*) and Biddulph (*2*).

By use of this equipment the surface tensions of some binary and ternary alcohol–water mixtures were measured. In addition, the surface tension of the system MeOH/1-PrOH was also

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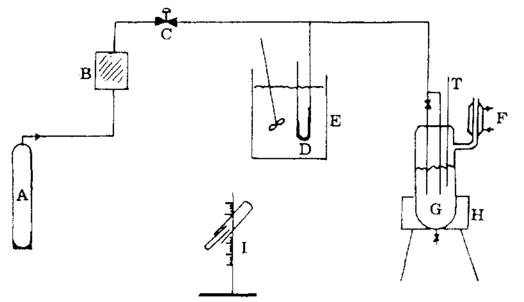

Figure 1. Surface tension apparatus.

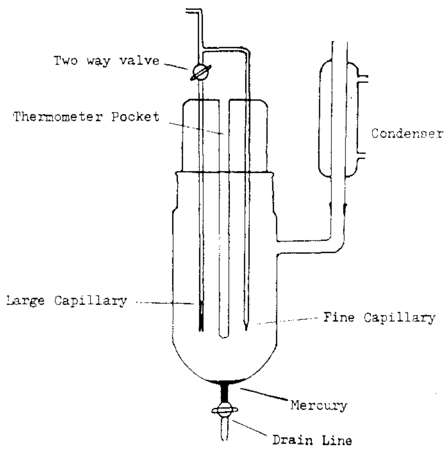

Figure 2. Tensiometer.

determined. Correlations are proposed for the binary systems which predict the surface tension at the boiling point. The apparatus described is also capable of measuring the surface tension at temperatures below the boiling point. Data obtained by using a similar apparatus for the system carbon tetrachloride/*n*-heptane have been reported previously (*2*).

Apparatus

The overall equipment is shown in Figure 1. The glass tensiometer (G) consists of a vessel provided with a variable electrical heating element (H), side condensers (F), and a drain line. Into the top of the vessel is fitted a B.40 general glass stopper through which are sealed two tubes and a thermometer pocket (Figure 2). One tube has a short length of precision bore capillary tube of 1.52 mm hole diameter; the other is drawn out until its diameter is about one-third of that of the capillary section. This diameter need not be known. The lengths of these tubes are identical, so their depth of immersion in the boiling liquid is the same. A two-way tap is used to divert the gas flow from one tube to the other.

Nitrogen from the gas cylinder (A) passes through a drying tower (B) containing calcium chloride, and then passes through a fine needle valve (C) and a manometer (D) immersed in a constant temperature water bath (E), to the tensiometer (G).

Procedure

A liquid mixture was introduced into the tensiometer vessel, and a small amount of mercury was introduced into the vessel to fill the drain arm, thus avoiding "dead-space" liquid. The heating mantle (H) was then switched on and the current varied to maintain a nonvigorous boiling of the liquid. The gas flow rate was adjusted to maintain a bubbling rate of about one bubble every 5 s. The manometer level fluctuated, registering a pressure difference corresponding the maximum pressure required for a bubble to break. The water bath temperature was kept at 30 °C. The mixture boiling temperature was measured by using a precalibrated thermocouple with an error of ±0.1 °C. The manometer pressure difference was measured by using a travelling microscope. The equipment had been carefully cleaned and was free from contamination, and all the tensiometer joints were seated with PTFE sleeving. The tensiometer fitted in the heating mantle was maintained upright by using a spirit level mounted in a circular, flat stainless steel disk. The pressure drops were taken as nitrogen bubbles left the capillaries. The procedure was repeated up to five times to check for reproducibility.

Table I. Summary of Tensiometer Calibration with Dried Distilled Toluene[a]

T, °C	δ,[b] mN/m	δ_m, mN/m	% error	A
26.1	27.80	27.76	0.14	0.035 24
28.6	27.50	27.70	0.69	0.034 95
35.3	26.70	26.75	0.19	0.035 12
37.6	26.43	26.56	0.49	0.035 02
41.7	25.94	25.32	2.40	0.036 05
47.9	25.21	25.89	2.71	0.035 64
50.3	24.92	24.64	1.11	0.035 59
53.4	24.55	24.59	0.15	0.035 14
56.2	24.22	24.28	0.26	0.035 10
59.0	23.88	23.88	0.00	0.035 19
63.1	23.39	23.53	0.67	0.035 00
69.4	22.65	22.86	0.95	0.034 85
74.4	22.05	22.27	0.99	0.034 85
80.3	21.35	21.69	1.59	0.034 64
84.6	20.84	21.55	3.41	0.034 04
89.3	20.28	20.01	1.33	0.035 66
110.00[c]	17.70	17.21	2.74	0.036 18

[a] A (average) = 0.03519. Deviation of the measured surface tension = ∓0.26 mN/m. [b] Jasper (*14*). [c] Boiling point.

Sugden Equation

The empirical equation developed by Sugden (*10*, *11*) and reported by Catchpole (*13*) has an accuracy of 0.1% for the surface tension and is

$$\delta_m = A\rho_m g(\Delta H_1 - \Delta H_2)\frac{1 + 0.69r_2\rho_{mix}}{\rho_m(\Delta H_1 - \Delta H_2)} \tag{1}$$

where A is a constant of apparatus, determined by calibration with dried distilled toluene; δ_m is the surface tension of the mixture (mN/m) or (dyn/cm); ΔH_1 is the manometer difference through the fine capillary (cm); ΔH_2 is the manometer difference through larger capillary (cm); r_2 is the radius of larger capillary = 0.076 (cm); ρ_{mix} is density of liquid (g/mL); ρ_m is density of manometer liquid = 0.784 (g/mL) (kerosene); g = 981 cm/s^2, gravitational constant.

Incorporating the values of g, ρ_m, and r_2, eq 1 reduces to

$$\delta_m = 769.104A(\Delta H_1 - \Delta H_2) + 51.44\rho_{mix} \tag{2}$$

Calibration

The calibration of the tensiometer was carried out using dried distilled toluene, over a range of temperatures up to and including the boiling point. The pure component surface tension data for this system were reported by Jasper (*14*) and the density data by Gallant (*15*). Table I summarizes all the measurements. The constant A was found to have an average value of 0.035 19, which produced a maximum error in surface tension evaluation of 3.4%. The percentage error was calculated from the equation

$$\%\ \text{error} = \frac{(\delta^* - \delta_m)100}{\delta^*} \tag{3}$$

With the average A value the surface tensions at the boiling points of water, methanol, and ethanol were determined and compared with the measurements reported by Jasper (*14*).

Table II. Deviation of Measured Surface Tension from Published Work

liquid	T, °C	δ,[a] mN/m	δ_m, mN/m	$\delta^b - \delta_m$, mN/m
ethanol	78.0[b]	17.56	17.69	0.13
methanol	65.0[b]	18.98	19.47	0.50
methanol	47.0	20.37	20.71	0.34
water	100.0[b]	58.85	59.21	0.3

[a] Jasper (*14*). [b] Boiling point.

Table III. Methanol/1-Propanol Surface Tension at the Boiling Point

test no.	x_1	δ_m, mN/m	T, °C
68	0.0428	19.72	66.0
69	0.1594	19.35	68.6
70	0.2971	19.82	72.5
71	0.5276	18.63	77.8
72	0.6579	18.85	82.0
73	0.7825	18.82	86.6
74	0.8640	18.15	90.5
75	0.935	18.18	93.1
76	0.9659	17.38	95.0

Table IV. Methanol/Water Boiling Point Surface Tension

test no.	x_1	δ_m, mN/m	T, °C
1	0.0218	49.23	96.6
2	0.04345	45.69	92.6
3	0.0384	49.69	92.2
4	0.0760	42.43	88.0
5	0.1696	37.14	82.6
6	0.1980	34.03	82.8
7	0.2667	32.53	79.1
8	0.2974	30.06	78.0
9	0.3630	27.85	76.0
10	0.6004	23.20	70.8
11	0.5026	24.40	73.0
12	0.7293	21.63	68.6
13	0.8162	20.40	67.8
14	0.8959	20.52	66.8
15	0.9480	20.31	66.0

Table V. Ethanol/Water Surface Tension at the Boiling Point

test no.	x_1	δ_m, mN/m	T, °C
34	0.0143	46.95	96.2
35	0.0206	45.17	94.8
36	0.0423	38.26	91.0
37	0.0576	34.15	88.7
38	0.1076	28.44	85.4
39	0.1347	28.58	84.4
40	0.17505	25.88	83.2
41	0.1830	24.96	82.0
42	0.3027	21.59	81.1
43	0.5269	20.58	79.3
44	0.7029	18.19	78.5
45	0.8982	18.10	78.0

This comparison is shown in Table II, and the agreement is good.

AR grade alcohols and deionized water were used throughout this work.

Analysis of the Samples

The analysis of the samples was carried out using gas liquid chromatography. The chromatograph was equipped with a thermal conductivity detector.

Table VI. 1-Propanol/Water Surface Tension at the Boiling Point

test no.	x_1	δ_m, mN/m	T, °C
16	0.00	59.21	99.8
17	0.0088	54.75	96.4
18	0.0194	38.32	90.7
19	0.0300	30.05	89.4
20	0.0495	26.66	88.0
21	0.0663	24.35	88.0
22	0.0830	23.84	88.0
23	0.0874	24.23	88.0
24	0.1136	26.30	87.7
25	0.1351	22.77	87.4
26	0.2306	22.55	87.3
27	0.4990	21.12	87.4
28	0.6621	21.08	88.6
29	0.8125	19.18	90.2
30	0.9033	19.10	92.4
31	0.2306	20.985	87.7
32	0.0851	22.66	88.3
33	0.078	28.39	88.7
33a	1.000	17.53	99.0

Table VII. Surface Tension of the Ternary System MeOH/1-PrOH/H_2O[a]

test no.	x_1	x_2	δ_m, mN/m	T, °C
46	0.8458	0.0053	19.77	68.00
47	0.7880	0.0720	19.50	69.00
48	0.7044	0.1272	19.06	72.0
49	0.1780	0.8015	17.40	89.0
50	0.1110	0.5433	19.07	87.7
52	0.3972	0.3445	19.99	77.9
53	0.4689	0.3023	18.57	76.8
54	0.5544	0.2522	19.61	74.3
55	0.4132	0.1979	21.31	77.5
56	0.2177	0.1116	26.18	81.0
57	0.1805	0.0979	24.45	82.0
58	0.1317	0.0718	24.08	83.2
59	0.0830	0.0458	28.08	85.0
60	0.0528	0.0293	31.16	88.0
61	0.0298	0.0152	37.32	90.5
63	0.3690	0.0184	34.55	89.0
64	0.1395	0.0129	34.50	84.00
65	0.2691	0.0100	30.56	78.4
66	0.3727	0.0079	28.45	73.2
67	0.4339	0.1155	23.23	76.2

[a] x_1 is the mole fraction of methanol. x_2 is the mole fraction of 1-propanol.

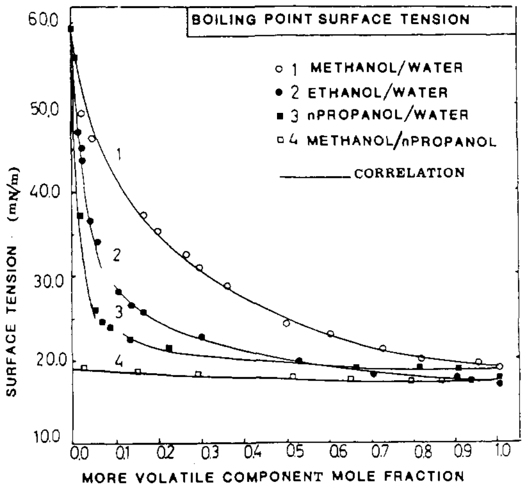

Figure 3. Binary surface tensions.

Results

The surface tensions of the binary systems MeOH/1-PrOH, MeOH/H_2O, and EtOH/H_2O and the ternary system MeOH/1-PrOH/H_2O were determined. These results are tabulated in Tables III–VII. The compositions (x_1) in these tables are given as the mole fraction of the more volatile component. The tables also include the bubble point temperatures of the test mixture, determined by the thermocouple. The results of the

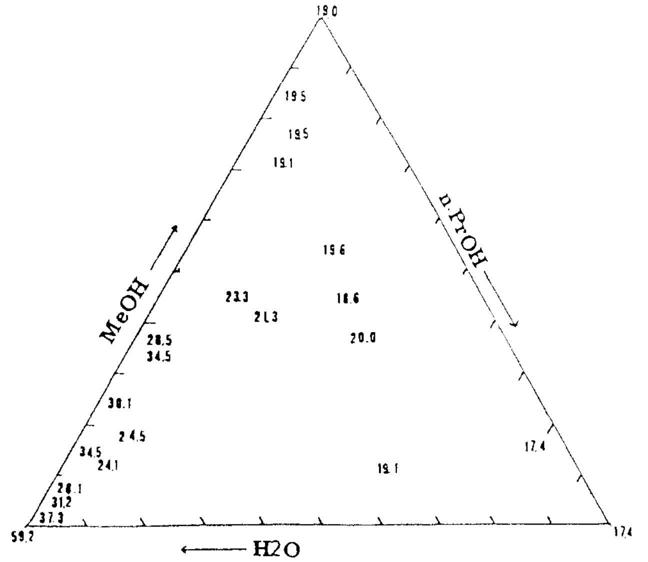

Figure 4. Surface tension (mN/m) of the MeOH/n-PrOH/H_2O system at boiling point.

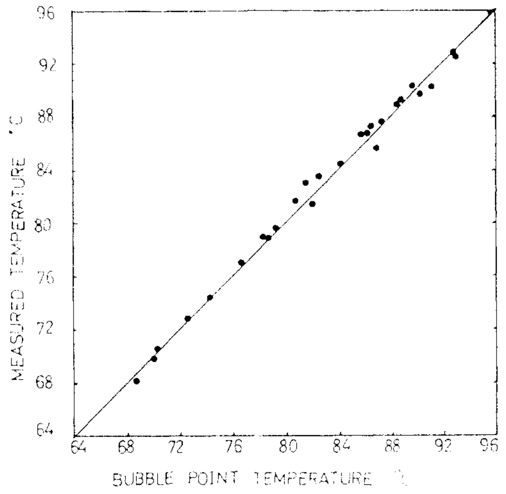

Figure 5. Comparison of measured and bubble temperatures.

binary surface tension determinations are plotted in Figure 3 and those for the ternary system in the triangular diagram, Figure 4. The bubble point temperature of the test mixture was also calculated, taking into account the nonidealities in the phases (*16*). These temperatures are plotted against the measurements by the thermocouple in Figure 5. It can be seen that the agreement is good.

Discussion

Boiling point surface tensions of the aqueous systems of interest were measured by using the tensiometer described. The use of this equipment is quick, easy, and precise. There have been a few attempts to measure the surface tension of the systems at boiling point under mass-transfer conditions in the past. Ling and Van Winkle (*17*) developed a method designed to bring the liquid and the vapor into equilibrium contact while measuring the surface tension, but the equipment was rather complicated. Aquilar et al. (*18*) measured the surface tensions of their mixtures, using the ring method, at lower temperatures and extrapolated them to the boiling point. Both authors measured the boiling point surface tension of the system 1-PrOH/H_2O, and a comparison of their measurements is shown in Figure 6 and compared with the measurements reported here. There is good agreement between these measurements. A very important feature of the measurements using the tensiometer described here is the ease of use under boiling conditions.

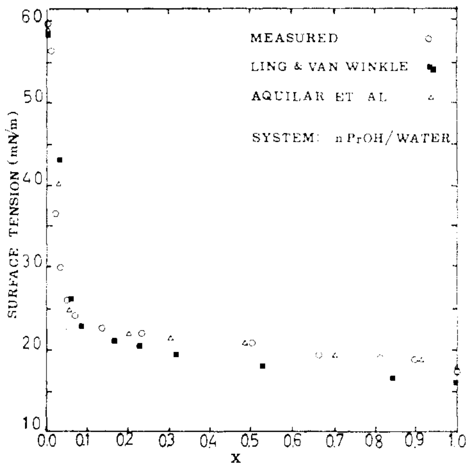

Figure 6. 1-Propanol/water surface tension.

Registry No. Methanol, 67-56-1; ethanol, 64-17-5; 1-propanol, 71-23-8; water, 7732-18-5.

Literature Cited

(1) Zuiderweg, F. J.; Harmens, A. *Chem. Eng. Sci.* **1958**, *9*, 89.
(2) Biddulph, M. W. Ph.D. Thesis, University of Birmingham, U.K., 1966.
(3) Boyes, A. P.; Ponter, A. B. *Ind. Eng. Chem. Fundam.* **1971**, *10*, 641.
(4) Fane, A. G.; Sawistowski, H. *Inst. Chem. Eng. Symp. Ser.* **1969**, *32*, 1:8.
(5) Bainbridge, G. S.; Sawistowski, H. *Chem. Eng. Sci.* **1964**, *19*, 992.
(6) Zuiderwag, F. J. *Chem. Eng. Res. Des.* **1983**, *61*, 388.
(7) Liddell, J. *Chem. Eng.* **1984** (April), 36.
(8) Winterfield, P. H.; Scriven, L. E.; Davis, H. T. *AIChE J.* **1978**, *24*, 1010.
(9) Tamura, M.; Kurata, M.; Hisashi, O. *Bull. Chem. Soc. Jpn.* **1955**, *28*, 83.
(10) Sugden, S. *J. Chem. Soc.* **1922**, *121*, 858.
(11) Sugden, S. *J. Chem. Soc.* **1924**, *27*, 125.
(12) Adam, N. K. *The Physics and Chemistry of Surfaces*, 3rd ed.; Oxford University Press: London, 1941; p 374.
(13) Catchpole, J. P. Ph.D. Thesis, University of Birmingham, U.K., 1962.
(14) Jasper, J. J. *J. Phys. Chem. Ref. Data* **1972**, *1*, 14.
(15) Gallant, R. W. *Physical Properties of Hydrocarbons*; Gulf: Houston, TX, 1968–1970; Vol. 2.
(16) Prausnitz, J. M.; Eckert, C. A.; Orye, R. V.; O'Connell, J. P.; *Computer Calculations for Multicomponent Vapour-liquid Equilibria*; Prentice-Hall: Englewood Cliffs, NJ, 1967.
(17) Ling, D.; van Winkle, M. *Ind. Eng. Chem.* **1958**, *3*, 82.
(18) Aquilar, A. M.; Rosello Segado, A.; Patino, J. M. R.; Hormigo Leon, A. *Ingenieria Quimico*; University of Seville, Department of Physical Chemistry: Seville, Spain, Jan 1983; p 127.

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