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Table I. BTCA Contents and Densities ρ of Saturated Aqueous Solutions of BTCA and Its Salts at 25 °C

BTCA salt	mass % BTCA	ρ/(g cm^{-3})
After Equilibration for 15 min		
free acid	20.00[a]	1.074[a]
K	24.62 ± 0.04	1.138 ± 0.008
After Equilibration for 5 h		
free acid	18.30 ± 0.10	1.067[a]
NH_4	21.19 ± 0.11	1.087[a]
$(NH_4)_2$	5.99 ± 0.05	1.035[a]
$(NH_4)_3$	16.01 ± 0.18	1.083 ± 0.000[b]
$(NH_4)_4$	25.35 ± 0.41	1.138 ± 0.003
K	22.46 ± 0.78	1.092 ± 0.004
K_2	3.72 ± 0.00	1.019 ± 0.005
K_3	3.17 ± 0.02	1.179 ± 0.002
K_4	>32.05[a]	
Na	24.59 ± 0.04	1.128 ± 0.000[c]
Na_2	10.00 ± 0.04	1.070 ± 0.000[b]
Na_3	16.23 ± 0.42	1.191 ± 0.006[d]
Na_4	21.56 ± 0.02	1.227 ± 0.001[d]
KNa	7.90 ± 0.08	1.050 ± 0.001[b]
After Equilibration for 16 h		
free acid	18.28 ± 0.02	1.067 ± 0.000[b]

[a] No replication. [b] Density at 26 °C. [c] Density at 24 °C. [d] Density at 23 °C.

The weighed aliquot of tetrasodium salt solution, obtained as described for the other sodium salts, was dried in an oven at temperatures no higher than 40 °C and then kept in a vacuum desiccator until its weight became constant. The tetrasodium salt's solubility was calculated from the weight of this residue and its Karl-Fischer water content.

Except as otherwise noted, reported values are means of data from 2-4 replications.

Results and Discussion

The results of solubility determinations at 25 °C, expressed as mass percent BTCA (free acid) in the saturated solutions, are presented in Table I. The solubility data and the accompanying density data are given as means plus/minus standard errors. Because no solid remained in the tetrapotassium salt mixture after equilibration, only a minimum value for the solubility of this salt was calculated.

As discussed elsewhere (*7*), at this temperature the BTCA content of a saturated aqueous solution prepared from the anhydrous compound decreased from 20 mass % to less than 19 mass % within 3 h, remained almost constant for a time, and then decreased again. An equilibration time of 5 h, within the period of constant BTCA solubility, was selected for the comparison of BTCA's solubility with the solubilities of its salts. Thus, the solubility reported for BTCA is not that of the form that is thermodynamically stable at 25 °C, and it is possible that this is true of the salts also. The observed decrease in the solubility of the monopotassium salt within 5 h is evidence that it, like the free acid, can undergo a transformation to a less soluble crystal form. The reported solubilities are minimums that can be expected within the given time. Therefore, they can serve as a basis for selecting salts to be tried as substitutes for the free acid in applications requiring a high solubility in water. Only the monobasic and the tetrabasic salts are more soluble than the free acid in terms of BTCA content in the saturated solutions.

The solubility of BTCA in water at 5 °C was found to be 7.50 ± 0.46 mass % after equilibration for 1 h and 7.20 ± 0.23 mass % after equilibration for 5 h. This decrease in solubility with time was not significant even at the 50% confidence level.

The solubility reported for BTCA at 19 °C by Auwers and Jacob (*4*) was substantially higher than would be expected from the data presented here; the reason for this difference is not evident. The low solubility for BTCA indicated in the reports by Rowland et al. (*5*, *6*) may have been due to impurities in the commercial product they used and/or to the presence of BTCA monohydrate (*7*) in their solid phase.

Acknowledgment

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Registry No. BTCA, 4534-68-3; NH_4BTCA, 141411-71-4; $(NH_4)_2$BTCA, 141411-72-5; $(NH_4)_3$BTCA, 141411-73-6; $(NH_4)_4$BTCA, 141411-74-7; KBTCA, 141411-75-8; K_2BTCA, 141437-75-4; K_3BTCA, 141411-76-9; K_4BTCA, 141411-77-0; NaBTCA, 141411-78-1; Na_2BTCA, 141411-79-2; Na_3BTCA, 141411-80-5; Na_4BTCA, 141411-81-6; KNaBTCA, 141411-82-7.

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Surface Tensions of Propylene Glycol + Water

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Surface tensions of propylene glycol + water have been measured using the maximum bubble pressure method from ambient temperature to the mixture boiling point at 1 atm of pressure. A correlation of the surface tensions as a function of temperature and composition is given.

Introduction

In an earlier paper by Hoke and Chen (*1*), surface tensions for mixtures of 2-propanol + water and ethylene glycol + water are reported. The maximum bubble pressure method described by Sugden (*2*) was used to measure the surface tension as a function of temperature and composition. In this paper, surface tension results for propylene glycol + water are reported. Propylene glycol, as received from Fisher Scientific, was used. A description of the experimental approach, apparatus, and

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Table I. Surface Tension σ for Water (A) + Propylene Glycol (B)

t/°C	σ/(mN m^{-1})	t/°C	σ/(mN m^{-1})	t/°C	σ/(mN m^{-1})
		x_B = 0.048			
25.0	56.7	55.0	52.8	85.0	49.3
30.0	56.8	60.0	52.2	90.0	48.7
35.0	55.3	65.0	51.6	95.0	47.8
40.0	54.5	70.0	51.0	100.0	46.9
45.0	54.1	75.0	50.5		
50.0	53.4	80.0	49.8		
		x_B = 0.10			
25.0	51.0	55.0	47.4	85.0	44.5
30.0	49.7	60.0	47.0	90.0	44.0
35.0	49.6	65.0	46.5	95.0	43.3
40.0	48.9	70.0	45.7	100.0	42.7
45.0	48.3	75.0	45.4		
50.0	47.7	80.0	45.1		
		x_B = 0.21			
25.0	45.8	55.0	42.3	85.0	39.7
30.0	45.3	60.0	41.8	95.0	38.7
35.0	44.6	65.0	41.4	100.0	37.9
40.0	44.1	70.0	40.9	105.0	37.0
45.0	44.1	75.0	40.5		
50.0	43.4	80.0	40.3		
		x_B = 0.32			
25.0	43.2	60.0	39.7	90.0	37.4
30.0	42.4	65.0	39.5	95.0	36.9
40.0	41.9	70.0	39.0	100.0	36.5
45.0	41.0	75.0	38.5	105.0	35.9
50.0	40.6	80.0	38.1		
55.0	40.2	85.0	37.8		
		x_B = 0.43			
30.0	41.0	60.0	38.2	90.0	35.8
35.0	40.4	65.0	37.9	95.0	35.3
40.0	39.9	70.0	37.4	100.0	34.8
45.0	39.3	75.0	36.9	105.0	34.3
50.0	39.0	80.0	36.6	110.0	33.5
55.0	38.6	85.0	36.0		
		x_B = 0.65			
20.0	39.4	55.0	36.7	95.0	33.3
25.0	39.3	65.0	35.7	100.0	32.8
30.0	38.7	70.0	35.6	105.0	32.6
35.0	38.5	75.0	35.1	110.0	32.1
40.0	38.0	80.0	34.8	115.0	31.6
45.0	37.6	85.0	34.2	120.0	31.0
50.0	37.2	90.0	33.9	125.0	30.4
		x_B = 0.81			
25.0	38.5	70.0	34.7	110.0	31.4
30.0	37.9	75.0	34.3	115.0	30.9
35.0	37.6	80.0	33.9	120.0	30.4
40.0	37.2	85.0	33.6	125.0	30.0
50.0	36.4	90.0	33.1	130.0	29.5
55.0	35.9	95.0	32.8	135.0	29.1
60.0	35.6	100.0	32.2	140.0	28.6
65.0	35.1	105.0	31.9		
		x_B = 1.0			
22.4	36.6	80.0	32.3	150.0	26.5
25.0	35.8	90.0	31.4	150.0	26.5
30.0	35.7	100.0	30.8	160.0	25.6
40.0	35.0	100.0	30.9	170.0	24.5
50.0	34.2	110.0	29.8	180.0	23.1
50.0	34.1	120.0	29.1	185.0	23.0
60.0	33.5	130.0	28.3		
70.0	33.0	140.0	27.4		

procedure has been given previously (*1*). The accuracy in the temperature was ±0.1 K, and the accuracy of the surface tension was ±0.4%.

Results and Discussion

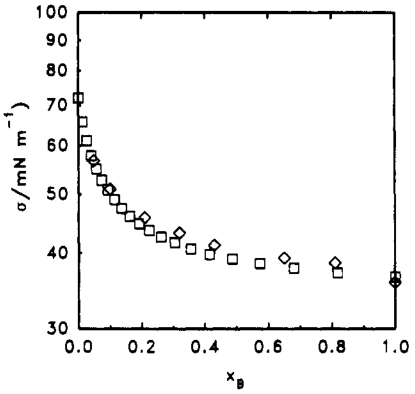

Figure 1. Surface tensions σ of water (A) + propylene glycol (B) at 25 °C: ◇, this work; □, Jones and Tamplin (*3*).

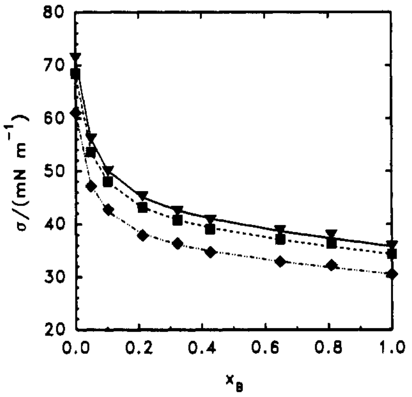

Figure 2. Surface tensions of propylene glycol + water: ▼, 30 °C; ■, 50 °C; ◆, 100 °C.

Table II. Surface Tension Parameters α and β for Water (A) + Propylene Glycol (B)

x_B	α	β	av % dev[a]
0.048	90.91	0.7624	0.33
0.10	76.85	0.6773	0.32
0.21	73.80	0.7668	0.48
0.32	65.13	0.6659	0.29
0.43	63.51	0.6857	0.27
0.65	60.97	0.6920	0.29
0.81	59.54	0.6819	0.18
1.0	55.35	0.6535	0.73

[a] \|predicted − experimental\|/experimental.

Surface tensions for the propylene glycol + water mixtures are given in Table I. The table lists the composition, temperature, and the corresponding surface tension. Jones and Tamplin (*3*) report surface tensions of propylene glycol and its aqueous solutions at 25 °C. These values are compared graphically to measured values in Figure 1.

At each mole fraction the surface tensions are correlated using the equation

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

where T_r' is the reduced temperature based on a pseudocritical temperature. The pseudocritical temperature for mixtures with mole fractions x_A and x_B is defined by

$$T_c' = x_A T_{c,A} + x_B T_{c,B} \qquad (2)$$

where $T_{c,A}$ and $T_{c,B}$ are the critical temperatures for components A and B. Nonlinear least-squares regression of the data provided α and β. Results of the regressions are given in Table II. Average deviations between the correlation and experimental values for the surface tension are seen to be less than 1.0%.

Using the correlations for surface tension as a function of temperature for each composition, the effect of composition on the surface tension was investigated. The surface tension for water was obtained from the correlation by Jasper (*4*) as $\sigma/(\mathrm{mN\ m^{-1}}) = 75.83 - 0.1477(t/°\mathrm{C})$. Figure 2 shows the surface tensions for propylene glycol + water against mole fraction interpolated for temperatures of 30, 50, and 100 °C.

Connors and Wright (*5*) propose the equation

$$\sigma = \sigma_A - \left\{1 + \frac{bx_A}{1 - ax_A}\right\} x_B(\sigma_A - \sigma_B) \qquad (3)$$

where σ_A is the surface tension of water and σ_B the surface tension of the organic component to describe the effect of composition on the mixture surface tension. Hoke and Chen (*1*) showed that the surface tension parameters *a* and *b* are temperature dependent.

On the basis of the results given in Table II, the values for the surface tension parameters *a* and *b* are found from a nonlinear least-squares fit. Parameters are best described by

$$a = 0.9509 + 4.711 \times 10^{-6}(t/°\mathrm{C}) + 3.929 \times 10^{-7}(t/°\mathrm{C})^2$$

$$b = 0.7920 + 2.926 \times 10^{-6}(t/°\mathrm{C}) + 1.001 \times 10^{-7}(t/°\mathrm{C})^2$$

for temperatures between 10 °C and the normal boiling point of the propylene glycol + water mixture. The average deviation for *a* and *b* is less than 0.01%. Propylene glycol + water surface tensions at any temperature between 10 °C and the normal boiling point can be calculated using the pure component surface tension correlations and eq 3.

Acknowledgment

We thank Professor John C. Chen for providing the experimental equipment.

Nomenclature

a = surface tension parameter defined in eq 3
b = surface tension parameter defined in eq 3
t = temperature
T_c = critical temperature
T_c' = pseudocritical temperature defined in eq 2
T_r' = reduced temperature, T/T_c'
x = mole fraction

Greek Letters

α = surface tension parameter defined in eq 1
β = surface tension parameter defined in eq 1
σ = surface tension

Subscripts

A = water
B = propylene glycol

Registry No. Propylene glycol, 57-55-6.

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Partial Molar Volumes of Transfer at Infinite Dilution of Some Electrolytes in Dimethyl Sulfoxide–Water Mixtures at 298.15 K

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Limiting partial molar volumes, V_2^∞, of LiCl, NaCl, KCl, NaBr, KBr, KI, $NaPh_4B$, and Ph_4AsCl have been determined in dimethyl sulfoxide (DMSO)–water mixtures at 298.15 K with a vibrating tube digital densimeter. V_2^∞ values for alkali-metal halides with a common cation or anion increase with the increasing size of the counterion and decrease with the increase of the DMSO composition. This last effect is also shown in the case of $NaPh_4B$ and Ph_4AsCl. Partial molar volumes of transfer from water to DMSO–water mixtures, $\Delta_t V_2^\infty$, have been calculated in order to obtain a measure of the difference in electrolyte–solvent interactions between water and the different mixtures. Observed effects show a decrease in $\Delta_t V_2^\infty$ with the DMSO composition for all electrolytes studied, but whereas $\Delta_t V_2^\infty$ values for Ph_4AsCl are negative, those for $NaPh_4B$ are positive at all DMSO compositions.

Introduction

The partial molar volume at infinite dilution, V_2^∞, is an appropriate thermodynamic quantity for elucidating the nature of solute–solvent interactions. While extensive data have been obtained for V_2^∞ of electrolytes in water (*1*) and nonaqueous solvent (*2–9*), less attention has been paid to mixed aqueous solvents (*10–13*). Possibly, due to the large quantity of experimental work necessary, proof that some of the work on mixed aqueous solvents has been done at only one electrolyte concentration (*12*, *13*). This paper reports limiting partial volumes of some electrolytes in dimethyl sulfoxide (DMSO)–water mixtures at 298.15 K. DMSO was chosen because of its extensive application in chemistry, pharmacy, and industry.

Experimental Section

Dimethyl sulfoxide (Merck, G.R., stated purity >99.5 mol %, H_2O <0.03%) was kept over thermally activated 4-Å molecular sieves prior to use. Nonane (Fluka, 74252, >99 mol %) was used as received. The salts LiCl, NaCl, KCl, NaBr, and KI were reagents (Merck) and were used after drying overnight at 393.15 K. $NaPh_4B$ (Merck, G.R.) was dried at 353.15 K in a vacuum desiccator for 48 h. $Ph_4AsCl{\cdot}H_2O$ (Merck, G.R.) was prepared as an anhydrous salt according to the literature recommended method (*15*). Water was obtained from a Milli-RO and Milli-Q water system (Millipore, $\sigma \approx 10^{-6}$ S m^{-1}). Both DMSO and water were degassed prior to making solutions by weight.

The solution densities were measured at 298.15 K with an Anton Paar (DMA 60/602) vibrating tube densimeter with precision of $\pm 3 \times 10^{-3}$ kg m^{-3}. The temperature in the measuring cell was regulated through a cascade water bath apparatus (Heto). This system permits stability within ±0.01 K for a period of several days as checked by a digital precision thermometer

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