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Vapor–Liquid Equilibria and Salt Apparent Molar Volumes of the Water + 2-Propanol + Tetrabutylammonium Bromide System

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Vapor–liquid equilibrium and density measurements have been performed on 1.00–5.89 *m* tetrabutylammonium bromide (TBAB) in mixtures of 2-propanol and water. The VLE experiments were performed using a modified Othmer still at ambient pressure. The effect of salt on the relative volatility of 2-propanol was evaluated at molalities of 1.00, 1.79, and 5.89 over the full range of solvent composition. At each salt molality, as the alcohol concentration increased, salting-in and then salting-out behavior of the alcohol was observed. The azeotrope was shifted but apparently not eliminated for the salt concentrations studied. Density measurements at 25, 40, and 55 °C were taken using a vibrating tube densimeter at four salt molalities over the full range of solvent composition. As salt molality increases, the apparent molar volume of TBAB exhibits a minimum between 1 to 2 *m* TBAB in pure water, it is slightly larger and monotonically increases in pure 2-propanol, and it is larger yet, with a maximum at lower 2-propanol amounts, in the ternary mixture.

1. Introduction

Systems of mixed solvent electrolyte solutions, consisting of water, a nonelectrolyte, and a salt, have been the subject of many studies due both to their potential application to industrial unit operations (*1*, *2*) and to the frequent occurrence of these mixtures in natural systems. Correlation and prediction of the physical properties of these systems have proven to be difficult due to the complexity of the molecular interactions. This is particularly true for mixtures containing organic salts, because in addition to long-range electrostatic forces, they also have hydrophobic effects and, when the organic portions are large enough, conformational degrees of freedom. The resulting unusual behavior of these systems has prompted investigation of the conductance (*3*), density (*4*), vibrational spectroscopy (*5*), osmotic coefficient (*6*), and thermal diffusion (*9*, *10*) of aqueous and mixed solvent solutions of tetraalkylammonium halides (including tetrabutylammonium bromide (TBAB)) in an effort to probe the influence of molecular structure on the properties of these solutions.

The present study of tetrabutylammonium bromide in water and 2-propanol combines vapor–liquid equilibrium (VLE) experiments with density measurements in order to more fully characterize the effect of the organic salt on the solvent separability and of the solvent composition, temperature, and salt concentration on the effective size of the salt. The measurements are part of an ongoing project aimed at providing fundamental understanding of the thermophysical properties of mixed solvent electrolytes and, in particular, systems containing organic salts. The expectation is that complementary investigations of VLE via relative volatilities and volumetric behavior via V^{app} will suggest useful molecular interpretations.

2. Experimental Section

2.1. Materials. TBAB (99%) was obtained from Aldrich, and was used without further purification other than dehumidification as described below. HPLC grade 2-propanol (99.5%) was obtained from Fisher. Distilled, deionized (DD) water was used. Sodium chloride (>99.9%) was from Mallinckrodt.

2.2. VLE Experiments. 2.2.1. Apparatus and Methods. A modified Othmer still, used in all VLE experiments, was similar to that described by Johnson and Furter (*7*), but here, a two-way stopcock was fitted to the condensate chamber.

The experimental procedure was similar to that described elsewhere (*8*), with a few differences. The amount of solution charged to the still was determined by mass rather than by volume, to avoid effects of the high viscosity of the concentrated salt solutions. Initial charges to the still were diluted up to 4 times during an experimental run by introducing carefully a known mass of an equimolal TBAB solution of water or alcohol. Both the liquid and vapor were heated using a variable-power heating mantle and tape.

Each VLE experiment was repeated by at least two different researchers. In the results reported here, the system was initially open to the atmosphere and later pressure controlled at 1.013 ± 0.005 bar using a Cartesian diver manostat (Manostat Corp. Model 7A). In both cases, the pressure was monitored by a combination of an analog pressure meter (Curtin Matheson Model 68801-03) and a mercury barometer. The temperature was measured by a mercury-in-glass thermometer placed in the liquid phase. Fluctuations in the boiling often led to slight superheating of the liquid phase. As a result, the temperatures are not very reliable (±1 K).

In order to ensure accurate salt molalities, the TBAB was dried for at least 24 h at 97 °C and weighed under a dry nitrogen atmosphere. The still was operated at zero holdup for several minutes. Condensate samples of less than 1 mL were withdrawn by syringe via a sampling septum. Equilibrium was assumed when the analyses showed the same compositions.

The presence of the essentially nonvolatile salt in the liquid phase precluded direct solvent analysis via gas chromatography (GC) so the liquid composition was calculated by material balance. Since vapor loss from the system cannot be directly accounted for, ground-glass joints were sealed with Teflon tape to minimize leakage from the system. Salt-free experiments were performed in order to validate and define the limits of the experimental method. In these, the liquid

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Table 1. Experimental VLE Results

TBAB *m*	t/°C	x_a	y_a	α	t^b/°C	$x_a{}^b$	$y_a{}^b$	α^b
1.00	89.0	0.070	0.451	10.91	89.5	0.101	0.413	6.24
	86.4	0.134	0.485	6.09	89.5	0.130	0.445	5.39
	86.0	0.180	0.486	4.31	88.8	0.229	0.482	3.13
	85.0	0.229	0.511	3.52	88.0	0.310	0.505	2.27
	^{a}	0.304	0.548	2.78	86.6	0.374	0.503	1.69
	81.3	0.742	0.755	1.07	86.7	0.432	0.528	1.47
	82.5	0.797	0.794	0.98	86.5	0.589	0.651	1.30
	83.8	0.876	0.866	0.91	86.5	0.659	0.693	1.17
	82.8	0.927	0.913	0.83	86.5	0.727	0.739	1.06
					85.2	0.803	0.801	0.99
1.79	92.5	0.076	0.447	9.83	92.6	0.100	0.410	6.23
	91.0	0.127	0.430	5.19	93.0	0.129	0.456	5.64
	88.0	0.178	0.455	3.86	91.2	0.166	0.475	4.56
	86.5	0.225	0.466	3.01	89.5	0.230	0.519	3.60
	85.5	0.275	0.512	2.77	89.5	0.310	0.521	2.42
	83.7	0.615	0.677	1.31	88.0	0.375	0.533	2.00
	84.5	0.733	0.755	1.12	92.0	0.432	0.545	1.50
	84.5	0.805	0.812	1.05	91.8	0.498	0.573	1.36
	85.0	0.874	0.876	1.02	89.2	0.608	0.656	1.23
	84.6	0.899	0.896	0.97	89.8	0.669	0.706	1.19
					89.5	0.746	0.766	1.12
					86.4	0.827	0.838	1.08
					86.0	0.899	0.898	0.99
5.89	94.0	0.100	0.286	3.61	100.5	0.106	0.334	4.25
	92.0	0.149	0.399	3.79	99.8	0.129	0.353	3.69
	89.5	0.247	0.497	3.01	98.2	0.230	0.498	3.32
	91.0	0.296	0.489	2.28	95.8	0.312	0.525	2.44
	80.3	0.675	0.697	1.11	92.8	0.376	0.505	1.69
	92.0	0.734	0.747	1.07	103.8	0.430	0.520	1.44
	80.1	0.756	0.765	1.05	103.0	0.496	0.571	1.35
	94.0	0.800	0.801	1.01	104.0	0.607	0.669	1.31
	81.8	0.832	0.833	1.01	102.4	0.668	0.716	1.25
	90.0	0.868	0.844	0.82	102.7	0.746	0.781	1.22
	81.2	0.887	0.880	0.93	105.0	0.827	0.854	1.22
	94.5	0.898	0.870	0.76	103.8	0.899	0.914	1.20
	94.0	0.900	0.869	0.74				
	81.3	0.924	0.921	0.96				
	83.5	0.926	0.920	0.92				

[a] No data. [b] Reference 16, measurements taken at ambient pressure.

Table 2. Parameters for Eqs 1 and 6[a]

Eq 1

A_1	A_2	A_3	$\ln(\alpha_0)_{x_a=0}$	$\ln(\alpha_0)_{x_a=1}$
−1.1851	−4.6864	−0.4442	3.1214	−0.4999

Eq 6

t/°C	a_1	a_2	a_3	$V_w{}^\circ$/ (cm^3·mol^{-1})	$V_a{}^\circ$/ (cm^3·mol^{-1})
25.0	−7.3221	10.884	−7.1247	18.07	76.89
40.0	−6.6266	9.5392	−6.2148	18.16	78.09
55.2	−6.3287	9.5374	−6.3823	18.28	79.40

[a] Reference 17.

composition was calculated by material balance and compared to the liquid analysis to establish uncertainties in the data.

2.2.2. Sample Analysis. A Hewlett-Packard (model 5890) GC was used to determine the relative amounts of water and 2-propanol. The absolute error was estimated to be less than 0.002 in mole fraction. The carrier gas consisted of helium at a flow rate of 20–22 mL/min. The column was 1.3 m of Poropak T, the detection was by thermal conductivity at 180 °C, and the peak areas were determined with an HP 3392A integrator. In the analysis the column temperature was ramped from 140 °C at 10 °C·min^{-1}. Elution times were about 2.2 and 6.4 min for the water and 2-propanol, respectively.

2.3. Density Measurements. Density measurements of 0.25, 1, 2, and 4 *m* TBAB in pure and mixed water and 2-propanol were made at 25, 40, and 55 °C. A vibrating tube densimeter (Sodev Model 03D) was used. The temperature of the flow cell was regulated to within ±0.001 °C with an ethylene glycol + water bath circulated with a Sodev Model CT-L pump and thermostat, while an analog thermometer allowed the temperature to be monitored. DD water and aqueous solutions of NaCl served as standards. The density of pure water was interpolated from data given by Kell (*11*). The reference NaCl solution densities were calculated as a function of salt molality and temperature using correlations given by Connaughton et al. (*12*). As with the VLE experiments, TBAB was desiccated prior to use.

The 2-propanol was degassed under vacuum for 10 min. Prepared solutions were capped tightly, sealed with several layers of parafilm and stored at 10 °C. Samples were injected manually, with several flow cell volumes being introduced to ensure adequate washout of previous samples. After sample injection, 6 min was allowed for the sample and bath to reach thermal equilibrium, as evidenced by the constant (±0.0005) densimeter period. Then measurements were taken at fixed time intervals for 6 min, after which the period of DD water was remeasured to account for period drift. For each temperature regime, the densities of water, 2-propanol, and (salt-free) mixtures of 25, 50, and 75 mol % 2-propanol in water were determined to compare with literature values and calculate values at arbitrary compositions.

3. Results

3.1. Vapor–Liquid Equilibria. The VLE data have been reduced to relative volatilities of the alcohol, α, which allow a more reliable basis for comparison since this quantity is relatively insensitive to operating variables. Analysis of error accumulation due to analytical limitations yields uncertainty estimates in $\ln(\alpha)$ of ±0.002. From the total mass balance calculations we found that 1–5 mass % of the total charge to the still may be lost due to system leaks. Though these small leaks in the system do not affect the salt-free system results where the liquid is sampled directly, they become important when the liquid phase contains salt. Thus, although errors in the analytical methods are small, significant errors in the calculation of α may occur, especially in dilute mixtures. As a result, we believe that our data having a liquid mole fraction of alcohol (x_a) less than about 0.07 or greater than 0.93 are unreliable.

Table 1 presents experimental vapor and liquid compositions, relative volatilities,

$$\alpha \equiv \frac{y_a/x_a}{y_w/x_w}$$

and boiling temperatures for the salt-free and salt-containing systems. The salt-free data (not shown) were in good agreement with the literature (*13*). Salt-free values were also computed at infinite dilution from

$$(\alpha_0)_{x_a=0} = \frac{\gamma_a^\infty P_a^s}{P_w^s} \qquad (\alpha_0)_{x_a=1} = \frac{P_a^s}{\gamma_w^\infty P_w^s}$$

using γ^∞ values determined from the data of Kohoutova et al. (*14*) and vapor pressures (P_i^s) from a form of the Wagner equation (*15*). All of these α_0 values were fitted to

$$\ln(\alpha_0) = (1 - x_a)\ln(\alpha_0)_{x_a=0} + x_a \ln(\alpha_0)_{x_a=1} + A_1 x_a(1 - x_a) + A_2 x_a(1 - x_a)^2 + A_3 x_a{}^2(1 - x_a) \quad (1)$$

where the A_i are constants in the isobaric system. Table 2 gives the parameters of this fit. The effect of TBAB on the VLE is best shown by examining the quantity $\ln(\alpha_s/\alpha_0)$ vs x_a. This relationship was fitted to a straight line (r^2 = 0.82–

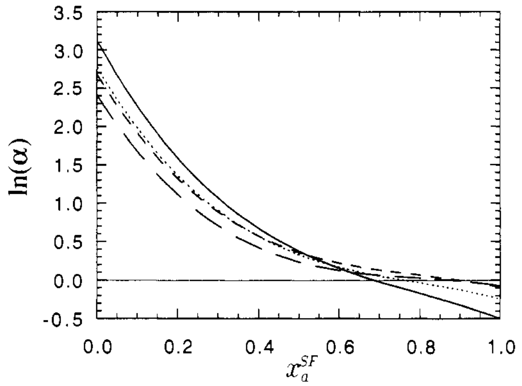

Figure 1. Natural log of the relative volatility of 2-propanol in the salt-free system (—), compared to mixtures of 1.00 (...), 1.79 (---), and 5.89 (- - -) *m* TBAB. The data are combined from experiments performed at both ambient pressure and a controlled pressure of 1.013 ± 0.005 bar.

Table 3. Apparent Molar Volumes (cm³·mol⁻¹) of TBAB as a Function of Salt Molality and Molar Fraction of 2-Propanol at 25, 40, and 55 °C

x_a^{SF}	m	V^{app}	x_a^{SF}	m	V^{app}	x_a^{SF}	m	V^{app}
				t = 25 °C				
0.00	0.25	299.8	0.10	0.25	301.6	0.25	0.25	301.4
0.00	0.99	295.8	0.10	0.99	303.7	0.25	1.00	304.5
0.00	1.90	295.6	0.10	2.00	304.3	0.25	1.88	305.7
0.00	2.49	296.2	0.10	3.97	305.5	0.25	2.49	305.6
0.00	3.24	297.1	0.10			0.25	3.25	305.5
0.00	3.99	297.9	0.10			0.25	3.99	305.4
0.50	0.25	299.5	0.75	0.25	299.4	1.00	0.25	297.6
0.50	1.03	303.7	0.75	1.00	302.4	1.00	0.50	299.1
0.50	2.50	305.1	0.75	1.90	303.5	1.00	1.00	299.9
0.50	3.25	305.2	0.75	2.50	303.8	1.00	1.43	300.5
0.50	4.00	305.2	0.75	3.25	304.2	1.00	1.90	301.4
						1.00	2.50	302.1
				t = 40 °C				
0.00	0.25	306.1	0.25	0.25	304.5	0.50	0.25	303.5
0.00	1.00	301.1	0.25	1.00	308.4	0.50	1.00	307.2
0.00	1.90	301.1	0.25	1.90	308.5	0.50	1.90	307.6
0.00	2.50	301.5	0.25	2.50	308.5	0.50	2.50	307.9
0.00	3.24	302.0	0.25	3.24	308.4	0.50	3.24	307.9
0.00	4.00	302.5	0.25	4.00	308.4	0.50	4.00	307.9
0.75	0.25	302.9	1.00	0.25	300.0			
0.75	1.00	304.4	1.00	1.00	300.9			
0.75	1.90	305.7	1.00	1.43	302.0			
0.75	2.50	306.0	1.00	1.89	303.0			
0.75	3.24	306.4	1.00	2.50	303.8			
0.75	4.00	306.6						
				t = 55 °C				
0.00	0.25	310.9	0.25	0.25	294.5	0.50	0.98	309.3
0.00	0.98	306.3	0.25	0.98	311.7	0.50	1.90	310.0
0.00	1.90	306.3	0.25	1.90	311.8	0.50	2.50	310.3
0.00	2.50	306.5	0.25	2.50	311.7	0.50	3.24	310.4
0.00	3.24	306.9	0.25	3.24	311.6	0.50	4.00	310.5
0.00	4.00	307.2	0.25	4.00	311.6			
0.75	0.98	306.6	1.00	0.98	302.6			
0.75	1.90	308.1	1.00	1.44	303.6			
0.75	2.50	308.5	1.00	1.90	305.1			
0.75	3.24	308.9	1.00	2.50	306.1			
0.75	4.00	309.2						

0.92), and these results were used to generate the smoothed data shown in Figure 1.

In dilute alcohol mixtures, the salt behaves as an organic solute, and consequently the alcohol is "salted-in", whereas with increasing alcohol concentration, the effect is reversed. In dilute water mixtures, the salt functions as do inorganic electrolytes, increasing the activity of the alcohol relative to that of the water. In the present case, the azeotrope does remain, even at the highest salt concentration. All of this is evident in Figure 1.

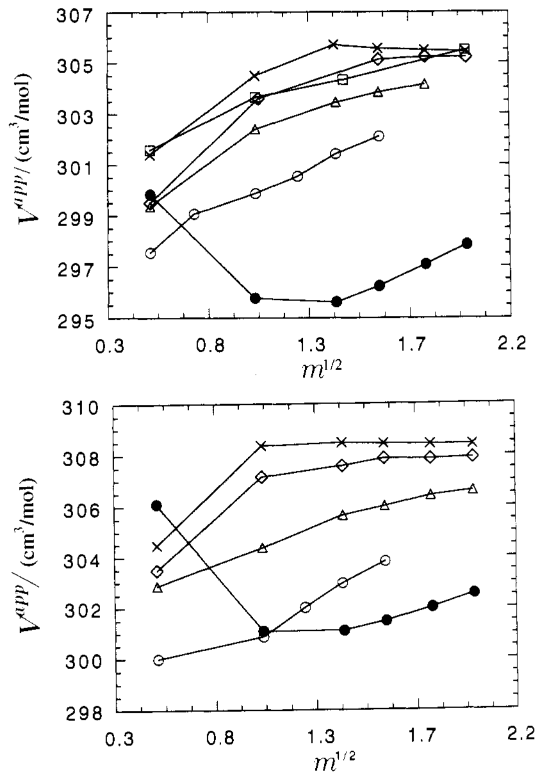

Figure 2. Apparent molar volume of TBAB as a function of $m^{1/2}$: (A, top) 25 °C, (B, bottom) 40 °C, (●) x_a^{SF} = 0.00, (□), x_a^{SF} = 0.10, (×) x_a^{SF} = 0.25, (◇) x_a^{SF} = 0.50, (△) x_a^{SF} = 0.75, (○) x_a^{SF} = 1.00.

3.2. Densities. The solution density, d_{sol}, is related to the densimeter vibrational period by

$$d_{sol} = B[(\tau_{sol})^2 - (\tau_{ref})^2] + d_{ref} \qquad (2)$$

where τ_{ref} and d_{ref} are the period and density of a reference fluid (in this case DD water) and B is a densimeter constant. In practice, B is a slight function of temperature, and even its isothermal value drifts slightly with time. As a result, it was redetermined for each series of experiments.

The desired quantity is the apparent molar volume of TBAB, given by

$$V^{app} = V^{app}(T,P,x_a,x_s) = [V - (1 - x_s)(V^{SF})]/x_s \qquad (3)$$

where $V = V(T,P,x_a,x_s)$ is the molar volume of the salt-containing solution and V^{SF} is the molar volume of the salt-free solution having the same mole fraction of alcohol on a salt-free basis. This property provides the most easily computed, sensitive indication of the effect of the solvent composition on the salt "size". In order to apply eq 3, we require the correlation of the excess volume of the salt-free system as a function of x_a so that V^{SF} can be calculated at arbitrary compositions. The excess volume of the binary alcohol + water system is defined by

$$V^{SF} = V^{SF}(T,P,x_a) = V^E + x_a V_a^\circ + x_w V_w^\circ \qquad (4)$$

where $V_i^\circ = V_i^\circ(T,P)$ are the molar volumes of the pure components and V^{SF} is computed via experimental salt-free densities, d^{SF}, as

$$V^{SF} = V^{SF}(T,P,x_a) = (x_a M_a + x_w M_w)/d^{SF} \qquad (5)$$

where M_a and M_w are the molecular weights of the pure solvents. The experimental excess volumes of the salt-free

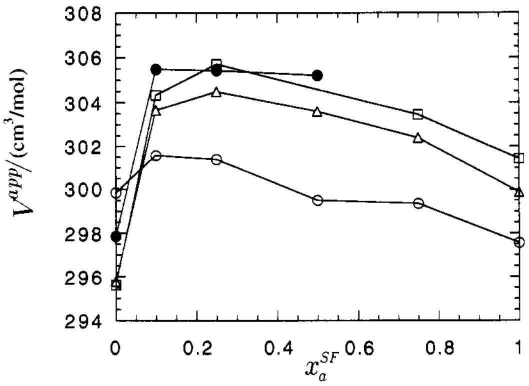

Figure 3. Apparent molar volume of TBAB at fixed salt molality as a function of solvent composition at 25 °C: (○) $m = 0.25$, (△) $m = 1.0$, (□) $m = 2.0$, (●) $m = 4.0$.

system calculated using eqs 4 and 5 may then be correlated by an equation of the form

$$V^{E}/(\text{cm}^3\cdot\text{mol}^{-1}) = a_1x_ax_w + a_2(x_a)^2x_w + a_3(x_a)^3x_w + ... \qquad (6)$$

where the a_i are parameters which, in the current system, depend only upon temperature. Truncation at the third term was adequate to fit our salt-free volumetric data within experimental error (*17*). The parameters for eq 6, along with the pure component molar volumes, are listed in Table 2. Finally, the calculation of V^{app} is made by using eqs 3, 4, and 6, with the alcohol and water mole fractions being the salt-free values, x_a^{SF} and x_w^{SF}.

Apparent molar volumes of TBAB in pure 2-propanol, pure water, and several alcohol + water compositions are presented in Table 3 (*17*). These can be used with the above equations and parameters to compute values of the density. The results for V^{app} in pure water at 25 °C closely match those given by Wen and Saito (*4*), and the current data extend the temperature range from 35 to 55 °C. An analysis of uncertainties in the balance and densimeter measurements leads to an overall uncertainty in the apparent molar volume of TBAB of about 0.2 cm^3·mol^{-1}. Values of V^{app} as a function of $m^{1/2}$ at 25 and 55 °C are shown in Figure 2. As can be seen, the effect of increased salt on V^{app} varies considerably with increased alcohol. For aqueous solutions, V^{app} goes through a minimum with increasing salt concentration, probably indicating a combination of hydrophobic conformational contractions with increasing salt and electrostatic effects that would be given by a variation of $m^{1/2}$. In pure 2-propanol, where the *n*-butyl chains are likely to be extended, V^{app} increases nearly linearly with $m^{1/2}$. Intermediate alcohol amounts show V^{app} increasing with $m^{1/2}$ and then gradually leveling off. The differences between parts A and B of Figure 2 show that the effect of increasing temperature is to increase V^{app}, particularly for the pure water solutions, while preserving the same general curve shape for the various alcohol amounts.

Figure 3 shows the effect of solvent composition on V^{app} at 25 °C when the salt molality is kept constant. The competing effects of salt dissociation and chain conformation lead to the maxima in V^{app} at $x_a \simeq 0.25$ seen for all salt molalities.

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