Vapor−Liquid Equilibrium and Density Measurements of Tetraalkylammonium Bromide + Propanol + Water Systems

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Isobaric vapor−liquid equilibrium (VLE) measurements at atmospheric pressure were made for 1.0−3.0 *m* tetrapropylammonium bromide (TPAB) and 3.0 *m* tetrabutylammonium bromide (TBAB) in mixtures of 2-propanol and water, and 3.0 *m* TPAB and 3.0 *m* TBAB in mixtures of 1-propanol and water. In addition, VLE measurements were made on 3.0 *m* TBAB in 2-propanol + water mixtures at 0.080 bar. The effects of the salt on the VLE in each system were assessed via relative volatilities. The effect of the solute was to salt-out at high alcohol concentrations and salt-in at low alcohol concentrations. A vibrating-tube densimeter was used to obtain solution densities at 25 °C from 0.1 to 4 *m* TBAB or TPAB in the pure solvent and in aqueous 1-propanol and 2-propanol solutions. Variations of the apparent molar volumes with salt molality in the mixed solvent differed markedly from those of the alcohol-free binary, while subtle distinctions were seen among the various salt and alcohol molecular structures.

1. Introduction

Electrolyte solutions have been the subject of a large number of experimental and theoretical studies aimed at prediction and correlation of the "salt effect" and its impact on fractional distillation (*1−3*). However, due to their complexity and the difficulty of modeling and predicting their thermodynamic properties, electrolyte solutions continue to represent an important and challenging area of theoretical interest as well. When the electrolyte species being studied contain apolar regions, such as hydrocarbon chains, their properties of solution show interesting behavior which can be attributed to a complex balance between long-ranged Coulombic and short-ranged intermolecular forces of the aqueous environment, and possibly conformational changes in the electrolyte. The tetraalkylammonium halide salts provide a convenient model system in which to study the interplay of these forces. The salt effect in these systems, unlike that of typical inorganic salts which always increase the volatility of ("salt-out") one of the solvent components over the other across the entire range of solvent composition (*4*), is to both salt-in and salt-out the alcohol, depending on the solvent composition. Volumetric measurements on the same mixtures show that there are interesting variations in the salt apparent molar volume with solvent composition and salt concentration. Some years ago, there were a number of experimental studies of the thermodynamic properties of solutions of these salts in various solvents (*5−11*). Recently, efforts have been made to understand the molecular behavior in aqueous solutions of these organic salts using the techniques of NMR (*12*), neutron diffraction (*13−16*), and computer simulation (*17*) to examine the hydrophobic hydration of the salt and its effect on the transient hydrogen-bond network in water. Some researchers have used small-angle neutron scattering (SANS) combined with thermodynamic measurements such as osmotic coefficients to obtain ion−ion pair correlation functions, which give clues as to the internal conformation of the salts and the extent of ion association in these systems (*18*, *19*).

Here we report vapor−liquid equilibrium (VLE) behavior and volumetric properties of ternary solutions consisting of either tetrapropylammonium bromide (TPAB) or tetrabutylammonium bromide (TBAB) in either aqueous 1-propanol or aqueous 2-propanol. The present work is part of an ongoing program of experiments (*4*, *20*) as well as theory and simulation studies (*21*) of mixed-solvent electrolyte solutions. The effect of the salt on the thermodynamic behavior of the solvent is seen through the salt effect on the VLE of water + propanol mixtures. We also examine the solvent effect on the properties of the salt, shown via density measurements, which yield the variations in salt apparent molar volume with solvent composition and salt concentration. The complementary investigations of VLE and volumetric behavior can then provide insight into the molecular behavior of these systems.

2. Experimental Section

2.1. Materials. TBAB (99%) and TPAB (98%) were purchased from Aldrich, and were used without further purification. The salts were dried for at least 24 h at 97 °C in order to ensure accurate salt concentrations.

HPLC grade 2-propanol (99.5%) and 1-propanol (99.5%) were obtained from Sigma. Distilled, deionized (DD) water was used. Sodium chloride (99%) was obtained from Mallinckrodt.

2.2. VLE. 2.2.1. Apparatus and Methods. The VLE results were measured with a modified Othmer still. The experimental procedure followed was similar to that described previously (*20*). In the present work, the pressure was controlled to either (1.013 ± 0.002) or (0.080 ± 0.005) bar using a Cartesian diver-type manostat (Manostat

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Corp.). Equilibrium temperatures were measured using a mercury-in-glass thermometer accurate to ±0.2 °C, which was placed in the liquid phase. For some of the experiments (noted below), the liquid phase composition was determined by mass balance, while in the remaining cases samples were directly analyzed.

2.2.2. Sample Analysis. The vapor phase mole fractions of alcohol were determined using Hewlett-Packard (models 5890 and 5890 II) gas chromatographs (GCs), with thermal conductivity detection at 180 °C. The 1.3 m columns were prepacked with Poropak T (Hewlett-Packard), and helium served as the carrier gas. The GCs were calibrated by injection of known volumes of standard mixtures of alcohol + water. Using a correlation for the excess volume (given as eq 8 below), a standard curve was constructed which fit the absolute amount (mol) of either component as a linear function of the peak area. These determinations are accurate to within ±0.002 in mole fraction. For the TBAB + 2-propanol and TPAB + 1-propanol systems, the liquid mole fraction of alcohol on a salt-free basis, x_a^{SF}, was also determined directly by GC. An inert glass insert at the column head protected the GC column from salt deposition. In the remaining experiments, x_a^{SF} was estimated using a material balance, as described previously (*22*, *20*). Errors in x_a^{SF} when calculated by material balance, particularly when one component is dilute, arise from small leaks from the still during equilibration. However, on the basis of our previous validation of the method (*22*), these errors should be negligible in the range of values of x_a^{SF} reported here. The uncertainty in x_a^{SF} in these systems is comparable to that of direct analysis of the samples, i.e., ±0.002.

2.3. Density Measurements. The densities of three ternary systems were measured at 25 °C, with the salt being either TPAB or TBAB and the alcohol either 1-propanol or 2-propanol. Densities of the TBAB + 2-propanol + water system were previously reported (*20*); those measurements were extended here. The salt concentration ranged from 0.1 to 4 *m*. A Sodev Model 03D vibrating-tube densimeter was used, with the flow cell regulated to ±0.001 °C. The specific details of the procedure have been described previously (*22*).

3. Results

3.1. Vapor–Liquid Equilibria. Salt-free VLE data for isobaric 2-propanol + water at a total pressure of 1.013 bar, 2-propanol + water at 0.080 bar, and 1-propanol + water at 1.013 bar served to validate the experimental procedure and to allow comparison of results from different systems. Tables 1 and 2 show the temperature, liquid mole fraction (on a salt-free basis), and vapor mole fraction at fixed pressures for various solutions. To show explicitly the effect of the salt on the solvents, the analysis used the relative volatility

$$\alpha = \frac{y_a/x_a^{SF}}{y_w/x_w^{SF}} \tag{1}$$

On the basis of previous VLE experiments with these water + alcohol mixtures (*4*), the vapor phase was assumed to be ideal, and so the fugacity coefficients and the Poynting correction were neglected. Thus, it was assumed that the fugacities of the vapor and liquid could be related via

$$y_i P = x_i \gamma_i(T,x_i)\, P_i^s(T) \beta_i \tag{2}$$

where β_i depends only on the salt molality and is unity for salt-free systems, $x_i = x_i^{SF}$ for ternary systems, and P_i^s is the vapor pressure of pure component *i* calculated using a form of the Wagner equation (*23*).

Table 1. Experimental VLE Results in 1-Propanol (a) + Water (w)

t/°C	x_a^{SF}	y_a	α	t/°C	x_a^{SF}	y_a	α
[TPAB] = 3.0 m, P = 1.013 bar							
99.8	0.045	0.191	5.06	96.0	0.503	0.483	0.92
98.8	0.123	0.314	3.28	97.2	0.617	0.548	0.75
96.0	0.150	0.335	2.87	98.5	0.636	0.563	0.74
95.2	0.206	0.357	2.14	100.5	0.733	0.643	0.65
95.0	0.291	0.389	1.55	102.0	0.830	0.738	0.58
95.0	0.309	0.392	1.44	105.5	0.954	0.915	0.52
95.4	0.393	0.430	1.16	105.9	0.980	0.966	0.57
95.0	0.488	0.475	0.95				
[TBAB] = 3.0 m, P = 1.013 bar							
96.2	0.078	0.216	3.26	95.0	0.582	0.505	0.73
94.9	0.136	0.244	2.05	*a*	0.690	0.588	0.64
94.2	0.186	0.282	1.72	97.8	0.709	0.611	0.64
93.8	0.231	0.303	1.45	99.8	0.808	0.712	0.59
93.8	0.262	0.324	1.35	100.0	0.837	0.753	0.59
93.5	0.289	0.341	1.27	101.5	0.873	0.793	0.56
94.8	0.391	0.398	1.03	100.8	0.885	0.819	0.59
95.0	0.512	0.459	0.81	102.1	0.914	0.857	0.56

[a] No data.

Table 2. Experimental VLE Results in 2-Propanol (a) + Water (w)

t/°C	x_a^{SF}	y_a	α	t/°C	x_a^{SF}	y_a	α
[TPAB] = 1.0 m, P = 1.013 bar							
94.6	0.016	0.176	13.1	82.5	0.490	0.622	1.71
91.8	0.037	0.338	13.3	83.1	0.523	0.635	1.59
91.3	0.052	0.370	10.7	80.2	0.606	0.679	1.38
87.1	0.094	0.452	7.95	81.7	0.622	0.691	1.36
84.1	0.224	0.524	3.81	81.1	0.716	0.747	1.17
81.5	0.226	0.539	4.00	80.4	0.815	0.818	1.02
83.1	0.293	0.554	3.00	80.1	0.905	0.892	0.86
83.0	0.409	0.589	2.07				
[TPAB] = 1.8 m, P = 1.013 bar							
88.0	0.091	0.432	7.60	80.0	0.682	0.741	1.33
86.8	0.133	0.486	6.16	83.1	0.686	0.739	1.30
84.5	0.186	0.516	4.67	80.5	0.777	0.803	1.17
82.0	0.235	0.536	3.76	83.6	0.829	0.843	1.11
84.0	0.263	0.546	3.37	82.5	0.877	0.887	1.10
83.8	0.287	0.557	3.12	84.0	0.891	0.897	1.07
83.3	0.392	0.604	2.37	83.9	0.924	0.918	0.92
83.0	0.505	0.647	1.80	84.1	0.925	0.921	0.95
83.4	0.614	0.719	1.61	83.5	0.951	0.944	0.87
[TPAB] = 3.0 m, P = 1.013 bar							
91.9	0.0660	0.405	9.63	86.1	0.460	0.629	1.99
89.1	0.0770	0.440	9.42	86.0	0.565	0.690	1.71
87.6	0.127	0.435	5.29	86.0	0.670	0.753	1.50
88.9	0.130	0.467	5.86	*a*	0.751	0.797	1.30
88.3	0.186	0.475	3.96	85.9	0.849	0.874	1.23
87.8	0.235	0.523	3.57	86.0	0.883	0.899	1.18
87.0	0.274	0.527	2.95	86.0	0.935	0.931	0.94
86.5	0.363	0.576	2.38				
[TBAB = 3.0 m, P = 1.013 bar							
96.5	0.042	0.197	5.62	88.0	0.547	0.621	1.36
93.0	0.093	0.310	4.40	88.0	0.676	0.710	1.18
91.5	0.146	0.367	3.40	88.9	0.767	0.781	1.08
89.8	0.208	0.409	2.64	90.1	0.874	0.874	1.00
88.8	0.319	0.489	2.05	89.0	0.933	0.931	0.96
88.8	0.448	0.564	1.59	90.1	0.960	0.960	1.00
[TBAB] = 3.0 m, P = 0.080 bar							
36.8	0.083	0.305	4.85	32.6	0.592	0.653	1.30
35.7	0.1216	0.329	3.56	33.3	0.608	0.659	1.25
34.0	0.225	0.438	2.69	33.6	0.729	0.754	1.14
33.8	0.270	0.460	2.30	33.9	0.823	0.836	1.10
32.8	0.378	0.520	1.78	34.6	0.895	0.905	1.12
32.4	0.481	0.584	1.52				

All three sets of binary propanol + water VLE data were fitted to a modified NRTL equation (*24*), where the activity

Table 3. Parameters for Eqs 2 and 3

P/bar	salt (3.0 m)	alcohol (1)	$g_{12} - g_{22}$[b]	$g_{21} - g_{11}$[b]	β_1	β_2
1.013	[a]	1-propanol	311.284	1811.01	1.0000	1.0000
1.013	[a]	2-propanol	235.126	1660.83	1.0000	1.0000
0.080	[a]	2-propanol	76.9524	1323.75	1.0000	1.0000
1.013	TPAB	1-propanol	−23.3627	1321.92	0.8783	0.8425
1.013	TPAB	2-propanol	−172.837	1768.61	0.9505	0.8000
1.013	TBAB	1-propanol	−249.045	1575.47	0.8946	0.9700
1.013	TBAB	2-propanol	−224.686	1307.40	0.7942	0.9030
0.080	TBAB	2-propanol	−219.458	1120.81	0.9382	0.9886

[a] Salt-free systems. [b] cal·mol^{-1}.

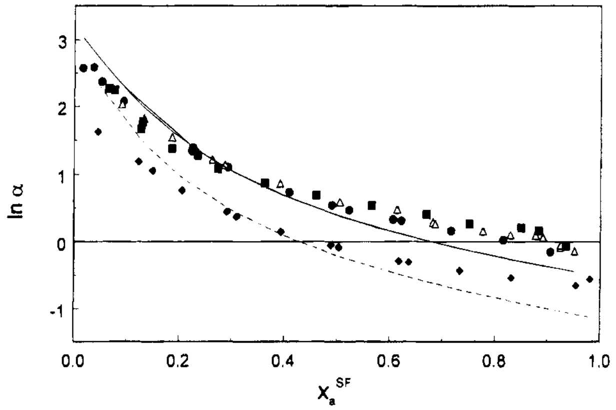

Figure 1. Relative volatilities for propanols to water with TPAB at ambient pressure. 2-Propanol systems: (●) 1.0 m; (△) 1.8 m; (■) 3.0 m. NPA system: (◆), 3.0 m. Lines calculated from fitted m-NRTL and vapor pressure reduction parameters: (—) salt-free 2-propanol; (- - -) salt-free 1-propanol.

coefficient of component i is given by

$$\ln \gamma_i = -\frac{x_j^2}{\alpha_{ij}}\left[\frac{G_{ji}^2 \ln G_{ji}}{(x_i + x_j G_{ji})^2} + \frac{G_{ij} \ln G_{ij}}{(x_j + x_i G_{ij})^2}\right] \tag{3}$$

where

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}), \quad \tau_{ij} = \frac{g_{ij} - g_{jj}}{RT}$$

and where the nonrandomness parameter, α_{ij}, is related to the other two parameters:

$$\alpha_{ij} = \frac{1}{2 + G_{ij}G_{ji}}$$

The 3.0 m salt + water + alcohol ternary VLE data were correlated using the same modified NRTL equation with the additional modifications of using the alcohol + salt and water + salt solutions (all at 3.0 m) as reference fugacities, and taking the liquid compositions on a salt-free (SF) basis. The data were fitted using a general least squares method described by Wooley and O'Connell (*25*), which utilizes the maximum likelihood technique (*26*) to estimate the model parameters $g_{ij} - g_{jj}$ (i, j = 1, 2; 1 = alcohol; 2 = water) and, for systems with salt, β_1. (The value of β_2 was obtained from the vapor pressure depression of pure water containing 3.0 m salt.) Both the salt-free and the 3.0 m salt-containing systems were correlated to within experimental error with the parameters shown in Table 3.

Figure 1 shows the relative volatility of the systems with TPAB. Several trends are evident from the figure. The primary result is that, unlike inorganic electrolytes, the effect of TPAB on VLE is a strong function of the solvent composition. It lowers the alcohol volatility (salts-in) at dilute alcohol, but at higher alcohol amounts it raises the alcohol volatility (salts-out), as do inorganic salts. The salt effect is stronger on the 1-propanol than on the 2-propanol, but the general effect is the same on both alcohol systems. Higher salt concentrations yield somewhat greater salting effects, but the crossover point for changing from salting-in to salting-out is not changed significantly. The azeotrope (where α = 1) is nearly broken for 2-propanol, though as pure alcohol is approached the influence of the salt decreases.

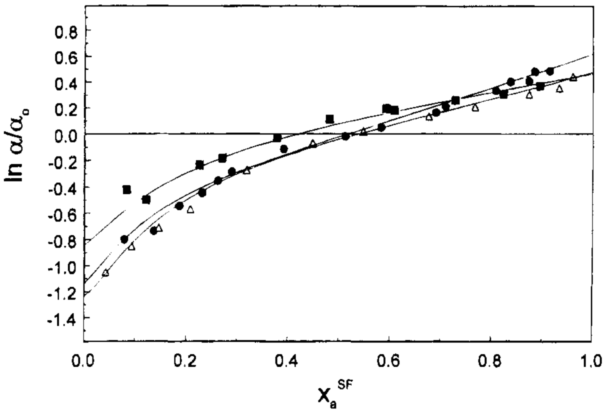

Figure 2. Enhancement factors of aqueous propanols of 3.0 m TBAB: (●) 1-propanol at 1.013 bar; (△) 2-propanol at 1.013 bar; (■) 2-propanol at 0.08 bar. Lines calculated from fitted m-NRTL and vapor pressure reduction parameters.

The effect of the salt on the VLE can be more easily seen via the enhancement factor, which is a ratio of relative volatilities:

$$\phi \equiv \ln\left(\frac{\alpha_s}{\alpha_0}\right) = \ln\left[\frac{\gamma_a(T_s, x_a^{SF})\, \gamma_w(T_o, x_a)}{\gamma_a(T_o, x_a)\, \gamma_w(T_s, x_a^{SF})}\right] + \ln\left[\frac{\beta_a P_a^s(T_s)\, P_w^s(T_o)}{\beta_w P_a^s(T_o)\, P_w^s(T_s)}\right] \tag{4}$$

where the subscripts s and o denote the salt-containing and salt-free systems, respectively. The second equality of eq 4 is from application of eq 2 for both cases. The values of γ_i are from eq 3.

Figure 2 shows ϕ as a function of x_a^{SF} for the systems containing TBAB at 3.0 m salt concentration. The experimental data are given by the symbols, with the lines being calculated using eq 4. Most of the scatter in these data is at high and low mole fractions of alcohol where the liquid phase compositions were obtained indirectly by material balance rather than directly by GC analysis. However, like TPAB, the effect of TBAB is similar for both alcohols, though somewhat stronger for 1-propanol. The effect of lowering the system pressure (lower temperature) is to augment salting-out, both moving the crossover to lower alcohol concentration and decreasing the deviation of ϕ from unity.

A comparison between the TPAB- and TBAB-containing solutions shows the effects of the two salts are slightly different. The crossover point from salting-in to salting-out is closer to the dilute alcohol region for TPAB. This is consistent with the results of Osborne (*27*), who found only salting-out behavior in the 2-propanol + water + tetramethylammonium bromide (TMAB) system. In addition, the enhancement factors for TPAB in 1-propanol are uniformly less than those for 2-propanol whereas for TBAB

Table 4. Apparent Molar Volumes of TPAB and TBAB in 1-Propanol (a) + Water (w)

x_a^{SF}	[TBAB]/(mol·kg^{-1})	d/(g·cm^{-3})	V^{app}	x_a^{SF}	[TPAB]/(mol·kg^{-1})	d/(g·cm^{-3})	V^{app}
0.000	0.000	0.997 07		0.000	0.000	0.997 07	
	0.102	0.999 37	299.91		0.105	0.999 95	238.94
	0.253	1.002 87	298.54		0.251	1.003 90	238.08
	0.500	1.008 44	297.05		0.500	1.010 68	236.43
	0.985	1.017 98	295.77		1.002	1.023 59	234.19
	1.896	1.030 58	295.62		1.981	1.045 01	231.57
	2.494	1.035 76	296.24		2.898	1.059 40	230.97
	3.245	1.040 26	297.08		4.027	1.071 40	231.24
	3.990	1.043 34	297.85				
0.099	0.000	0.953 74		0.100	0.000	0.953 34	
	0.105	0.956 85	304.54		0.101	0.957 72	230.49
	0.253	0.961 18	303.35		0.258	0.963 86	231.85
	0.500	0.967 76	302.74		0.440	0.970 46	232.30
	0.980	0.978 98	301.72		0.504	0.972 55	232.66
	1.018	0.979 75	301.70		0.998	0.987 78	232.91
	2.000	0.995 62	301.74		2.007	1.011 68	233.05
	2.016	0.996 61	302.06		2.999	1.028 48	233.34
	2.993	1.005 90	302.32		3.990	1.041 99	233.17
	4.001	1.013 61	302.57				
	4.000	1.014 14	302.27				
0.250	0.000	0.901 85					
	0.101	0.906 27	302.09				
	0.258	0.912 65	302.38				
	0.502	0.921 51	302.70				
	1.012	0.937 10	302.79				
	2.000	0.959 24	302.90				
	3.002	0.974 34	303.38				
	4.010	0.985 63	303.57				
0.510	0.000	0.850 07		0.500	0.000	0.851 48	
	0.102	0.855 76	299.93		0.100	0.857 27	231.32
	0.250	0.863 31	301.25		0.251	0.865 41	232.35
	0.500	0.974 78	302.05		0.502	0.877 93	232.82
	1.010	0.894 38	302.73		1.000	0.899 32	233.61
	2.006	0.922 50	303.41		1.999	0.932 87	234.17
	2.989	0.942 09	303.75		3.002	0.957 76	234.60
	3.946	0.957 00	303.55		4.004	0.977 15	234.77
0.750	0.000	0.822 76					
	0.100	0.828 93	298.40				
	0.250	0.837 44	299.73				
	0.580	0.854 03	300.75				
	1.001	0.871 85	301.38				
	1.999	0.903 22	302.75				
	3.005	0.926 03	303.02				
	4.017	0.942 69	303.48				
1.000	0.000	0.801 76		1.000	0.000	0.801 76	
	0.101	0.808 35	298.14		0.101	0.808 16	231.69
	0.250	0.817 41	298.89		0.250	0.817 08	232.32
	0.519	0.831 93	300.34		0.506	0.831 39	232.43
	1.000	0.854 39	300.48		0.500	0.831 08	232.40
	0.997	0.853 95	301.06		1.005	0.855 60	233.12
	1.980	0.888 30	301.55		1.000	0.855 11	233.54
	2.001	0.888 20	302.29		1.501	0.876 00	233.57
	2.992	0.911 96	303.12		1.999	0.893 60	233.85
	4.018	0.930 98	303.19		3.014	0.922 75	234.30
					3.650	0.936 88	234.92
					3.995	0.945 00	234.44

the effects on the alcohols are nearly indistinguishable except at the highest alcohol, where the values for 1-propanol are greater than those for 2-propanol.

3.2. Densities. Measured density data were used to calculate salt apparent molar volumes, a sensitive indication of changes in the salt "size" in various environments. This quantity is calculated with the expression

$$V^{app} = V^{app}(T,P,x_a,x_s) = [V - (1 - x_s)V_o]/x_s \qquad (5)$$

in which $V = V(T,P,x_a,x_s)$ is the molar volume of the salt-containing solution and V_o is the molar volume of the salt-free solution having the same mole fraction of alcohol on a salt-free basis. The salt-free volume was obtained from

$$V_o = V_o(T,P,x_a) \equiv V^E + x_a V_a^o + x_w V_w^o \qquad (6)$$

where $V_i^o = V_i^o(T,P)$ is the molar volume of pure component i and the excess volume, V^E, was obtained by correlating experimental density data

$$V^E\ (\text{cm}^3\text{·mol}^{-1}) = (x_a M_a + x_w M_w)/d_0 - x_a/d_a^o - x_w/d_w^o \qquad (7)$$

$$= x_a x_w \{a_1 + a_2 x_a + a_3 (x_a)^2 + ...\} \qquad (8)$$

where M_a, d_a^o, M_w, and d_w^o are the molecular weights and densities of the pure solvents, d_0 is the density of the salt-free solution, and the a_i are parameters depending only on temperature. Equations 5, 6, and 8 were used to obtain the values of V_{app} given in Tables 4 and 5. These tables include both new data and revised results for the TBAB + 2-propanol + water system tabulated previously (*20*). The parameters for eqs 8 and 9 are collected in Table 6.

Table 5. Apparent Molar Volumes of TPAB and TBAB in 2-Propanol (a) + Water (w)

x_a^{SF}	[TBAB]/(mol·kg^{-1})	d/(g·cm^{-3})	V^{app}	x_a^{SF}	[TPAB]/(mol·kg^{-1})	d/(g·cm^{-3})	V^{app}
0.000	0.102		299.91	0.000	0.105		238.94
	0.253		298.54		0.251		238.08
	0.500		297.05		0.500		236.43
	0.985		295.77		1.002		234.19
	1.896		295.62		1.981		231.57
	2.494		296.24		2.898		230.97
	3.245		297.08		4.027		231.24
	3.990		297.85				
0.100	0.000	0.950 43		0.100	0.000	0.950 43	
	0.100	0.953 54	303.76		0.101	0.954 61	233.24
	0.253	0.958 04	303.43		0.151	0.966 60	233.34
	0.504	0.964 64	303.42		0.249	0.960 31	233.77
	0.990	0.975 11	303.70		0.501	0.969 29	233.83
	2.000	0.990 36	304.30		1.001	0.984 70	233.82
	4.000	1.006 75	305.50		2.000	1.008 56	233.68
					3.001	1.025 87	233.77
					4.006	1.039 00	233.88
0.250	0.000	0.896 60					
	0.250	0.907 55	301.40				
	0.996	0.930 31	305.94				
	1.898	0.950 65	305.70				
	2.496	0.960 89	305.60				
	3.247	0.971 27	305.50				
	3.994	0.979 65	305.40				
0.500	0.000	0.838 80		0.510	0.000	0.837 09	
	0.101	0.844 55	301.39		0.100	0.842 90	233.62
	0.251	0.852 47	301.98		0.250	0.851 22	233.50
	0.500	0.864 04	303.46		0.501	0.863 99	233.94
	0.999	0.883 42	304.65		1.002	0.886 13	234.50
	2.002	0.912 89	304.82		2.001	0.920 46	235.20
	2.497	0.923 70	305.12		2.001	0.919 79	235.81
	3.253	0.937 62	305.20				
	4.001	0.948 84	305.20				
0.750	0.000	0.804 97		0.750	0.000	0.804 97	
	0.250	0.820 11	299.40		0.100	0.811 35	230.52
	0.996	0.856 15	302.40		0.253	0.820 54	231.34
	1.898	0.886 49	303.50		0.502	0.834 10	232.80
	2.497	0.901 14	303.80				
	3.249	0.917 03	304.20				
1.000	0.000	0.781 64		1.000	0.000	0.781 64	
	0.100	0.788 57	296.28		0.108	0.789 01	226.81
	0.250	0.798 21	297.60		0.253	0.798 17	228.87
	0.500	0.812 63	299.10		0.501	0.813 13	228.55
	0.998	0.837 26	299.87		1.002	0.838 81	230.41
	1.434	0.855 00	300.50		1.999	0.878 87	232.16
	1.897	0.870 58	301.40		2.998	0.908 97	233.15

Table 6. Parameters for Equations 8 and 9

Equation 8

alcohol	a_1	a_2	a_3	a_4	V_a°/(cm^3·mol^{-1})	V_w^{6}/(cm^3·mol^{-1})
1-propanol	−6.5265	18.387	−28.026	14.113	74.96	18.07
2-propanol	−7.3221	10.884	−7.1247		76.89	18.07

Equation 9

x_a^{SF}	V_o^{app}/(cm^3·mol^{-1})	S_v	c	x_a^{SF}	V_o^{app}/(cm^3·mol^{-1})	S_v	c
			TPAB + 1-Propanol + water				
0.00	243.1	−12.13	3.027	0.50	230.2	4.506	−1.120
0.10	229.4	5.310	−1.779	1.00	230.9	2.695	−0.452
			TBAB + 1-Propanol + Water				
0.00	303.3	−12.00	4.706	0.50	298.5	5.869	−1.558
0.10	306.0	−6.057	2.215	0.75	294.9	9.115	−2.482
0.25	302.3	0.2603	0.1877	1.00	299.0	2.403	−0.0974
			TPAB + 2-Propanol + Water				
0.10	233.1	1.054	−0.3605	1.00	221.5	10.27	−1.538
0.50	229.3	6.361	−1.672				
			TBAB + 2-Propanol + Water				
0.10	299.4	5.143	−1.053	0.50	293.8	13.50	−3.950
0.25	296.7	11.21	−3.465	1.00	295.3	5.340	−0.6814

[a] Reference 20.

Figures 3 (TPAB) and 4 (TBAB) show the variation of V_{app} with the square root of the salt molality for various mole fractions of both propanols (salt-free basis) at 25 °C. The lines result from fitting the data to a second-order

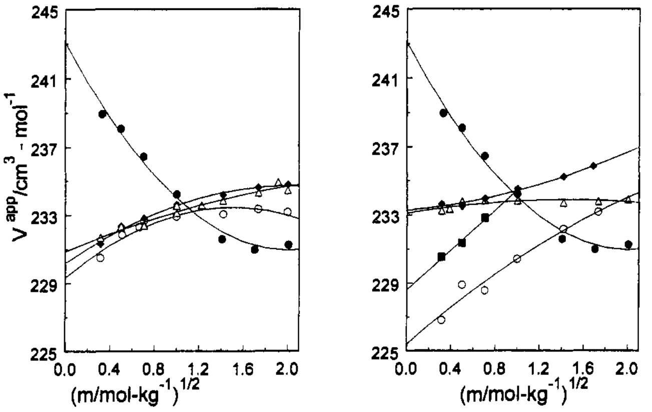

Figure 3. Apparent molar volumes of TPAB in 1-propanol (a) + water (w) and 2-propanol (a) + water (w) mixtures as a function of $m/(\text{mol}\cdot\text{kg}^{-1})^{1/2}$ at 25 °C: (●) $x_a^{SF} = 0.0$; (△) $x_a^{SF} = 0.1$; (◆) $x_a^{SF} = 0.5$; (■) $x_a^{SF} = 0.75$; (○) $x_a^{SF} = 1.0$.

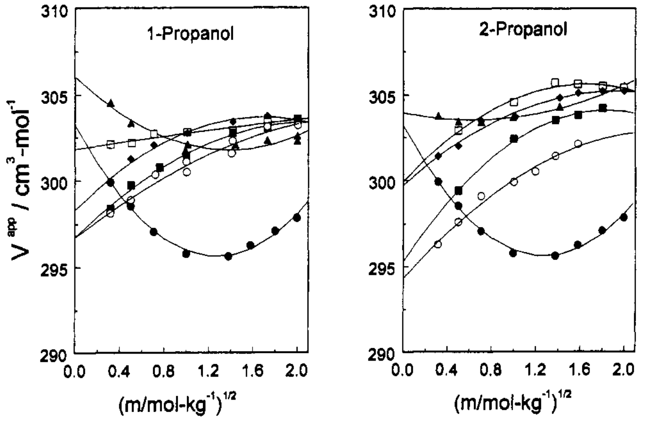

Figure 4. Apparent molar volumes of TBAB in 1-propanol (a) + water (w) and 2-propanol (a) + water (w) mixtures as a function of $m/(\text{mol}\cdot\text{kg}^{-1})^{1/2}$ at 25 °C: (●) $x_a^{SF} = 0.0$; (▲) $x_a^{SF} = 0.1$; (□) $x_a^{SF} = 0.25$; (◆) $x_a^{SF} = 0.5$; (■) $x_a^{SF} = 0.75$; (○) $x_a^{SF} = 1.0$.

polynomial in the square root of the salt molality:

$$V_{app} = V_o^{app} + S_v m^{1/2} + cm \qquad (9)$$

where V_o^{app} is the infinite dilution partial molar volume and, for small, strong electrolytes, S_v would be related to the theoretical value of the limiting slope from the Debye–Hückel theory (*28*).

The figures show that though the equation is an excellent fit of the data, the behavior is complex. In particular, the fitted curves for the alcohol-free systems have negative slopes with a minimum, which agree closely with the results found by Wen and Saito (*29*). The negative limiting slopes, in contrast to the positive theoretical slope of 1.87 predicted by the Debye–Hückel theory (*29*), are indicative of the hydrophobic nature of the alkylammonium salts. TBAB has a more pronounced minimum than does TPAB; Wen and Saito also showed that a minimum is not found in salts with shorter chains. The water-free systems all have positive slopes, with the increase being larger in 2-propanol than in 1-propanol. The theoretical limiting slopes in the pure alcohol and mixed solvents are not available due to the unknown values of the dielectric constant and its pressure dependence in these solutions. The behavior of the salts in the ternaries is more complex. In particular, TBAB shows a minimum when $x_a = 0.1$ though TPAB does not. The V_{app} values for TBAB at all salt levels increase as alcohol is added up to moderate amounts while those for TPAB generally decrease, especially at lower salt concentrations. The range of values taken on by TPAB is quite small in 1-propanol while all other combinations of salt and alcohol show significant variations with alcohol amount.

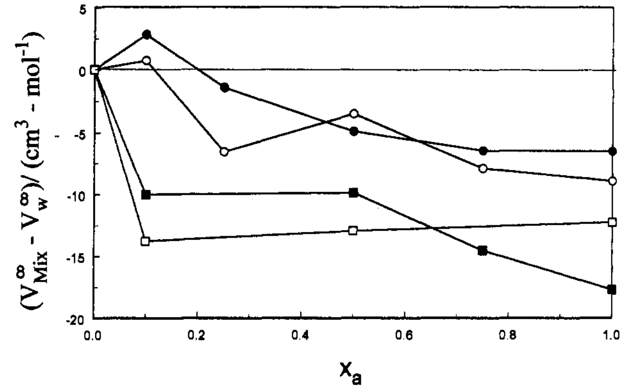

Figure 5. Infinite dilution apparent molar volume differences (see eq 10) at 25 °C as a function of solvent composition for TPAB in 1-propanol + water (□), TPAB in 2-propanol + water (■), TBAB in 1-propanol + water (●), and TBAB in 2-propanol + water (○).

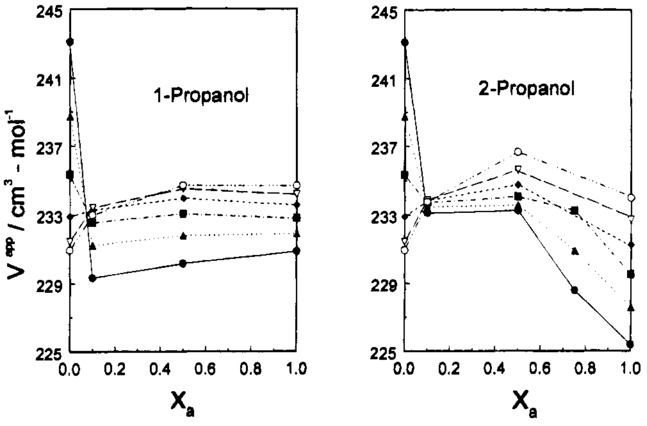

Figure 6. Calculated apparent molar volumes for TPAB in 1-propanol + water and 2-propanol + water at fixed salt concentrations as functions of solvent composition at 25 °C: (●) $m/(\text{mol}\cdot\text{kg}^{-1})^{1/2} = 0.0$; (▲) $m/(\text{mol}\cdot\text{kg}^{-1})^{1/2} = 0.4$; (■) $m/(\text{mol}\cdot\text{kg}^{-1})^{1/2} = 0.8$; (◆) $m/(\text{mol}\cdot\text{kg}^{-1})^{1/2} = 1.2$; (▽) $m/(\text{mol}\cdot\text{kg}^{-1})^{1/2} = 1.6$; (○) $m/(\text{mol}\cdot\text{kg}^{-1})^{1/2} = 2.0$.

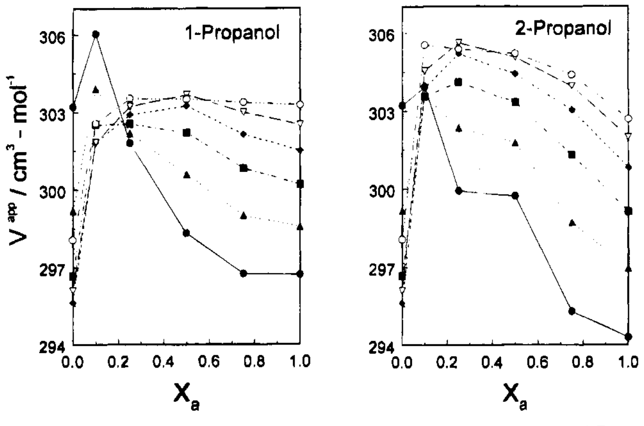

Figure 7. Calculated apparent molar volumes for TBAB in 1-propanol + water and 2-propanol + water mixtures at fixed salt concentrations as functions of solvent composition at 25 °C. (●) $m/(\text{mol}\cdot\text{kg}^{-1})^{1/2} = 0.0$; (▲) $m/(\text{mol}\cdot\text{kg}^{-1})^{1/2} = 0.4$; (■) $m/(\text{mol}\cdot\text{kg}^{-1})^{1/2} = 0.8$; (◆) $m/(\text{mol}\cdot\text{kg}^{-1})^{1/2} = 1.2$; (▽) $m/(\text{mol}\cdot\text{kg}^{-1})^{1/2} = 1.6$; (○) $m/(\text{mol}\cdot\text{kg}^{-1})^{1/2} = 2.0$.

The quantities V_o^{app}, found from fitting eq 9 to the V_{app} data, should isolate the effect of the solvent on the salts. To put all of the systems on a common basis, the value of

V_o^{app} in pure water can be subtracted out, yielding the quantity

$$\Delta V_o^{app} \equiv V_o^{app} - V_{o,w}^{app} \qquad (10)$$

This quantity is shown in Figure 5 for the four ternary systems. For a given salt, the differences between the alcohols are not dramatic. However, TBAB does not show the marked decrease with alcohol that TPAB does. Finally, at the finite salt concentrations shown in Figures 6 and 7, it can be seen that the values near 10% alcohol are nearly independent of salt concentration for all cases except TBAB in NPA where this convergence is nearer 20% alcohol.

4. Conclusions

Measurements have been made of vapor–liquid equilibria at low and ambient pressures and densities at 25 °C for solutions containing two large tetraalkylammonium bromide salts with aqueous propanols. In VLE, the systems show salting-in at low alcohol concentrations and salting-out at higher amounts; some differences are seen with salt and alcohol molecular structures. The addition of alcohol dramatically changes the behavior of the salt apparent molar volumes compared to those in water. Again, some distinctions are seen with different salt and alcohol molecular structures.

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