Limiting Partial Molar Volumes of Tetra-*n*-alkylammonium Bromides in Dimethyl Sulfoxide + Water Mixtures at 298.15 K

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Partial molar volumes at infinite dilution, V_2^∞, are reported for tetra-*n*-alkylammonium bromides, R_4NBr (R = Me to Pen) in *x* dimethyl sulfoxide + (1 − *x*) water mixtures, up to *x* = 0.1587, at 298.15 K. A linear dependence between V_2^∞ of the electrolyte and the molecular weight of the tetraalkylammonium cation was found.

Introduction

In previous papers (Yanes et al., 1992; Garcia-Pañeda et al., 1992), limiting partial molar volumes, V_2^∞, of alkali-metal halides, $NaPh_4B$, and Ph_4AsCl were measured in binary mixtures of water with dimethyl sulfoxide (DMSO), covering the entire molar fraction range. The addition of DMSO produces a decrease in V_2^∞ values of the alkali-metal halides and extrema in the case of the two hydrophobic electrolytes.

In this paper, limiting partial molar volumes of five tetra-*n*-alkylammonium bromides, R_4NBr, in water-rich mixtures of DMSO are reported. Data from other authors are combined with these in order to obtain further insight into the influence of DMSO on limiting volume.

Experimental Section

Tetra-*n*-alkylammonium bromides, R_4NBr (R = Met, Et, Pr, Bu, Pen), from Fluka or Merck of the best quality available were purified and checked as described by Conway et al. (1966). Their purities were greater than 99.7%. They were kept in a vacuum desiccator with P_2O_5 prior to use.

Dimethyl sulfoxide (Merck, G.R., stated purity >99.5 mol%, H_2O <0.03%) was used as received and kept over thermally activated 4A molecular sieves prior to use. Water obtained from a Milli-Q water system (Millipore, $\kappa = 10^{-6}$ S cm^{-1}) and DMSO were degassed prior to use. Solvent and electrolyte solutions were prepared by mass with a precision of ±0.0001 g.

Measurements of densities were made using the apparatus and procedures described previously (Garcia-Pañeda et al., 1992). The temperature control was monitored to ±0.001 K inside the cell with a platinum resistance thermometer connected to an ASL model F250 resistance bridge, which was calibrated by Isotech (England). The precision was ±0.001 K, and the accuracy in absolute temperature was ±0.010 K (ITS-90). The whole system was placed in a room in which the temperature was kept constant within ±0.5 K. Densities have an uncertainty (95% confidence limits) of $\pm 9 \times 10^{-6}$ g cm^{-3}.

Results and Discussion

The experimental values of densities are used to calculate apparent molar volumes of R_4NBr, V_ϕ, by means of the equation

$$V_\phi = \frac{M_2}{\rho} + \frac{(\rho^\circ - \rho)}{m\rho^\circ\rho} \qquad (1)$$

where ρ° is the density of the *x* DMSO + (1 − *x*) water solvent (*x* is the mole fraction of DMSO), ρ is the density of the electrolyte solutions, and M_2 and *m* are the molar weight and the molality of the electrolyte, respectively. Values of ρ and V_ϕ are given in Table 1.

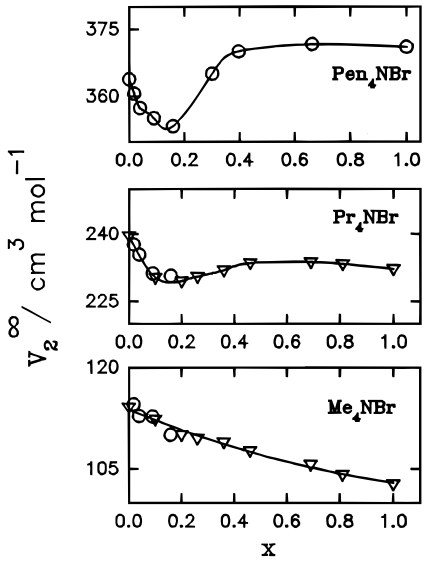

Figure 1. Variation of limiting partial molar volumes, V_2^∞, of R_4NBr with DMSO composition at 298.15 K: this work (○); Letellier et al. (1980) (▽).

The application of the Redlich−Meyer equation (Redlich and Meyer, 1964) was not possible to obtain limiting partial molar volumes, V_2^∞, owing to the lack of the values of the theoretical limiting slope, S_V, in these mixtures. Nevertheless, V_ϕ values were found to vary linearly with $m^{1/2}$ over the salt concentration range investigated (0 to 0.263) mol kg^{-1}. The limiting partial molar volumes, $V_2^\infty = V_\phi^\infty$, of the electrolytes were obtained by least-squares fitting of the results to the Masson equation

$$V_\phi = V_\phi^\infty + S_V^* m^{1/2} \qquad (2)$$

where S_V^* is the experimental slope. Table 2 shows values of V_2^∞ along with their 95% confidence limits (in parentheses), and we have also included values from other authors (Letellier et al., 1980).

The effect of DMSO on the V_2^∞ value is connected to the features of each R_4NBr salt, as is shown in Figure 1, where we have plotted V_2^∞ of Me_4NBr, Pr_4NBr, and Pen_4NBr against the molar fraction of DMSO. The corresponding plots for Et_4NBr and Bu_4NBr are similar to those of Me_4-

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Table 1. Molalities (m), Densities (ρ), and Apparent Molar Volumes (V_ϕ) for Tetra-*n*-alkylammonium Bromides in x DMSO + (1 − x) Water Mixures at 298.15 K

m/mol·kg^{-1}	ρ/g·cm^{-3}	V_ϕ/cm^3·mol^{-1}	m/mol·kg^{-1}	ρ/g·cm^{-3}	V_ϕ/cm^3·mol^{-1}	m/mol·kg^{-1}	ρ/g·cm^{-3}	V_ϕ/cm^3·mol^{-1}	m/mol·kg^{-1}	ρ/g·cm^{-3}	V_ϕ/cm^3·mol^{-1}
					$x = 0.0184$						
					Me_4NBr						
0.0	1.00648		0.1748	1.01320	114.35	0.0985	1.01030	114.35	0.2566	1.01626	114.33
0.0463	1.00828	114.49	0.1975	1.01405	114.37	0.1487	1.01221	114.38			
0.0746	1.00937	114.50	0.2356	1.01548	114.34						
					Et_4NBr						
0.0682	1.00891	173.22	0.1788	1.01292	172.15	0.1325	1.01128	172.22	0.2146	1.01423	171.83
0.1209	1.01082	172.63	0.1977	1.01358	172.14	0.1375	1.01248	172.42			
					Pr_4NBr						
0.0505	1.00789	236.66	0.1657	1.01112	235.83	0.1245	1.00996	236.15	0.2609	1.01375	235.35
0.1002	1.00928	236.31	0.2145	1.01245	235.68	0.1497	1.01066	236.01			
					Bu_4NBr						
0.0531	1.00771	297.07	0.1627	1.01027	296.19	0.1222	1.00932	296.53	0.2479	1.01223	295.72
0.0714	1.00815	296.72	0.1912	1.01093	296.02	0.1441	1.00983	296.37			
0.1001	1.00882	296.54	0.2172	1.01151	295.96						
					Pen_4NBr						
0.0465	1.00721	360.29	0.1404	1.00879	358.99	0.0920	1.00799	259.31	0.2438	1.01034	359.05
0.0706	1.00763	359.56	0.1870	1.00095	358.86	0.1186	1.00843	359.13	0.2541	1.01054	358.83
					$x = 0.0391$						
					Me_4NBr						
0.0	1.01655		0.1594	1.02275	113.22	0.0980	1.02040	113.11	0.2413	1.02587	113.14
0.0462	1.01837	113.23	0.1805	1.02357	113.13	0.1289	1.02159	113.15	0.2611	1.02658	113.26
0.0695	1.01931	112.82	0.2075	1.02459	113.16						
					Et_4NBr						
0.0528	1.01849	170.86	0.1661	1.02257	170.66	0.1158	1.02077	170.76	0.2465	1.02548	170.19
0.0773	1.01939	170.71	0.1703	1.02277	170.35	0.1443	1.02175	170.99			
0.1001	1.02022	170.64	0.2021	1.02391	170.26						
					Pr_4NBr						
0.0524	1.01802	234.45	0.1481	1.02075	233.53	0.0992	1.01936	233.88	0.2013	1.02222	233.38
0.0732	1.01861	234.23	0.1703	1.02132	233.73	0.1209	1.01997	233.77	0.2468	1.02360	232.68
					Bu_4NBr						
0.0511	1.01771	294.83	0.1592	1.02022	293.76	0.1014	1.01890	294.02	0.2228	1.02162	293.65
0.0789	1.01837	294.28	0.1954	1.02102	293.70	0.1263	1.01945	294.07	0.2512	1.02225	293.53
					Pen_4NBr						
0.0474	1.01726	357.58	0.1304	1.01855	356.78	0.0897	1.01794	356.84	0.2285	1.01990	356.96
0.0708	1.01764	357.05	0.1754	1.01920	356.78	0.1167	1.01833	356.94	0.2459	1.02013	356.98
					$x = 0.0899$						
					Me_4NBr						
0.0	1.03859		0.1567	1.04457	112.31	0.1045	1.04259	112.42	0.2186	1.04687	112.33
0.0753	1.04147	112.57	0.1822	1.04551	112.38	0.1370	1.04383	112.31	0.2482	1.04798	112.25
					Et_4NBr						
0.0480	1.04028	168.46	0.1642	1.04453	167.85	0.0934	1.04197	168.25	0.2085	1.04598	168.30
0.0717	1.04116	168.70	0.1969	1.04566	167.92	0.1361	1.04352	167.97	0.2394	1.04714	167.86
					Pr_4NBr						
0.0545	1.04002	231.73	0.1654	1.04305	230.39	0.1201	1.04183	230.65	0.2501	1.04528	230.10
0.0697	1.04046	231.09	0.1920	1.04375	230.32	0.1462	1.04253	230.52			
0.0925	1.04108	230.87	0.2148	1.04434	230.28						
					Bu_4NBr						
0.0528	1.03961	292.21	0.1693	1.04187	291.52	0.1266	1.04106	291.62	0.2348	1.04303	291.62
0.0746	1.04004	291.97	0.1776	1.04209	291.15	0.1485	1.04148	291.55			
0.1122	1.04078	291.69	0.2108	1.04265	291.41						
					Pen_4NBr						
0.0708	1.03920	356.23	0.2265	1.04035	356.62	0.1256	1.03968	356.01	0.2551	1.04049	356.87
0.0874	1.03934	356.21	0.2439	1.04044	356.76	0.1507	1.03987	356.11			
					$x = 0.1587$						
					Me_4NBr						
0.0	1.06157		0.1485	1.06726	110.53	0.1032	1.06556	110.40	0.2259	1.07011	110.64
0.0507	1.06354	110.44	0.1887	1.06875	110.61	0.1408	1.06698	110.47	0.2622	1.07143	110.73
0.0789	1.06462	110.50	0.2020	1.06924	110.63						
					Et_4NBr						
0.0502	1.06326	167.83	0.1653	1.06723	166.70	0.1220	1.06574	166.98	0.2472	1.06992	166.69
0.0726	1.06405	167.27	0.1908	1.06807	166.72	0.1475	1.06661	166.86			
0.0943	1.06478	167.26	0.2212	1.06908	166.66						
					Pr_4NBr						
0.0577	1.06288	230.40	0.1601	1.06515	230.21	0.1144	1.06414	230.33	0.2510	1.06711	230.04
0.0742	1.06325	230.37	0.1702	1.06537	230.17	0.1331	1.06458	230.11			
0.0883	1.06356	230.40	0.1895	1.06579	230.15						
					Bu_4NBr						
0.0588	1.06234	291.85	0.1563	1.06353	292.02	0.1133	1.06301	292.01	0.2270	1.06425	292.47
0.0775	1.06260	291.61	0.1913	1.06395	291.99	0.1399	1.06339	291.64	0.2410	1.06439	292.52
					Pen_4NBr						
0.0447	1.06161	355.73	0.1262	1.06141	357.74	0.0674	1.06157	356.54	0.2226	1.06107	358.70
0.0535	1.06159	356.20	0.1580	1.06133	357.97	0.0783	1.06156	356.65	0.2437	1.06094	359.05

Table 1. Continued

m/mol·kg^{-1}	ρ/g·cm^{-3}	V_ϕ/cm^3·mol^{-1}	m/mol·kg^{-1}	ρ/g·cm^{-3}	V_ϕ/cm^3·mol^{-1}	m/mol·kg^{-1}	ρ/g·cm^{-3}	V_ϕ/cm^3·mol^{-1}	m/mol·kg^{-1}	ρ/g·cm^{-3}	V_ϕ/cm^3·mol^{-1}
					$x = 0.3008$						
					Pen_4NBr						
0.0	1.08839		0.1200	1.08580	366.84	0.0747	1.08679	366.37	0.1755	1.08461	367.21
0.0571	1.08716	366.35	0.1502	1.08515	367.05	0.0937	1.08637	366.63	0.2107	1.08388	367.34
					$x = 0.3970$						
					Pen_4NBr						
0.0	1.09624		0.1263	1.09267	370.01	0.0918	1.09357	370.40	0.1880	1.09099	370.29
0.0594	1.09451	370.14	0.1333	1.09245	370.23	0.0989	1.09340	370.15	0.2081	1.09046	370.34
0.0827	1.09384	370.26	0.1593	1.09176	370.20						
					x=0.6625						
					Pen_4NBr						
0.0	1.09875		0.1374	1.09437	372.33	0.0955	1.09567	372.19	0.2140	1.09209	372.49
0.0543	1.09696	372.31	0.1585	1.09374	372.33	0.1164	1.09503	372.17	0.2380	1.09142	372.45
0.0751	1.09631	372.16	0.1844	1.09297	372.37						
					$x = 1.0$						
					Pen_4NBr						
0.0	1.09553		0.1266	1.09178	371.44	0.0889	1.09286	371.42	0.1799	1.09030	371.48
0.0526	1.09393	371.37	0.1449	1.09127	371.43	0.1072	1.09232	371.52	0.2099	1.08947	371.60
0.0763	1.09324	371.27	0.1624	1.09075	371.63						

Table 2. Limiting Partial Molar Volumes, V_2^∞, for Tetra-*n*-alkylammonium Bromides in *x* DMSO + (1 − *x*) Water Mixtures at 298.15 K

	V_2^∞/cm^3·mol^{-1}				
x	Me_4 NBr	Et_4 NBr	Pr_4 NBr	Bu_4 NBr	Pen_4 NBr
0.0	114.2[a]	174.3[a]	239.6[a]	301.0[a]	363.9[a]
0.0184	114.6(0.3)	174.7(0.9)	237.7(0.2)	298.1(0.2)	360.7(0.9)
0.0391	112.9(0.4)	171.5(0.7)	235.4(0.7)	295.6(0.5)	357.5(0.8)
0.0899	112.8(0.3)	169.1(0.8)	231.2(0.5)	292.8(0.7)	355.3(0.9)
0.1000	112.4[b]	167.6[b]	230.3[b]	291.5[b]	
0.1587	110.1(0.4)	168.5(0.5)	231.2(0.5)	290.9(0.9)	353.5(0.6)
0.2000	110.1[b]	165.5[b]	229.5[b]	292.4[b]	
0.2600	109.6[b]	165.3[b]	230.5[b]	295.4[b]	
0.3008					365.1(0.3)
0.3600	109.0[b]	165.4[b]	231.9[b]	298.5[b]	
0.3970					370.1(0.4)
0.4600	107.7[b]	165.1[b]	233.5[b]	300.5[b]	
0.6625					371.7(0.3)
0.6900	105.7[b]	163.9[b]	233.7[b]	301.2[b]	
0.8100	104.2[b]	163.1[b]	233.3[b]	300.9[b]	
1.0	102.8[b]	161.4[b]	232.2[b]	300.2[b]	371.1(0.3)

[a] Millero (1972). [b] Letellier et al. (1980). [c] Values in parentheses are 95% confidence limits.

NBr and Pen_4NBr, respectively, and they have been omitted for the sake of clarity. A perusal of Figure 1 reveals a regular decrease of V_2^∞ of Me_4NBr with the increasing composition of DMSO, a minimum in the case of Pen_4NBr in the water-rich region and a behavior midway between the lowest members and the highest one in the series for the Pr_4NBr salt.

It is interesting to note that in all mixtures studied a good linear dependence between V_2^∞ of R_4NBr and the molecular weight of the R_4N^+ cation, M_C, is found. In the case of $x = 1.0$ the values from Letellier et al. (1980) were used, excepting those of tetrapentylammoniun bromide that corresponds to this work. The following expressions have been obtained using a least-squares fit:

$$x = 0.0184;\ V_2^\infty = 1.097M_C + 32.69;\ \sigma(V_2^\infty) = 0.7$$

$$x = 0.0391;\ V_2^\infty = 1.093M_C + 30.86;\ \sigma(V_2^\infty) = 1.1$$

$$x = 0.0899;\ V_2^\infty = 1.084M_C + 30.05;\ \sigma(V_2^\infty) = 1.8$$

$$x = 0.1587;\ V_2^\infty = 1.086M_C + 28.48;\ \sigma(V_2^\infty) = 1.0$$

$$x = 1.0;\ V_2^\infty = 1.204M_C + 9.19;\ \sigma(V_2^\infty) = 3.5$$

where x is mole fraction of DMSO in the mixture and $\sigma(V_2^\infty)$ denotes the standard deviation.

It is difficult to decide whether the variation of V_2^∞ with DMSO content for a given salt is mainly due to the tetraalkylammonium ion or the bromide ion or both because of treating the electrolyte as a whole. However, it seems reasonable to think that the differences observed in the pattern of Figure 1 on going from methyl to pentyl must be chiefly connected to the features of each R_4N^+ ion, because all these electrolytes have the same anion.

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