Limiting Ionic Partial Molar Volumes of R_4N^+ and Br^- in Aqueous Acetonitrile at 298.15 K

Pandharinath S. Nikam* and Arun B. Sawant

P. G. Department of Physical Chemistry, M. S. G. College, Malegaon Camp, Pin 423 105, India

The densities of tetraalkylammonium bromide, R_4NBr (R = CH_3 through *n*-C_5H_{11}), solutions in (0, 10, 30, 50, 70, 90, and 100) mass % acetonitrile + water have been measured over the whole composition range at 298.15 K. From these densities, apparent and limiting partial molar volumes of the electrolytes and ions in these mixtures have been evaluated.

Introduction

The volumetric behavior of electrolytes has proved to be very useful in elucidating the nature of ion−solvent interactions occurring in aqueous and nonaqueous solutions (Millero, 1972). A knowledge of this property is very important in many practical problems concerning energy transport, mass transport, and fluid flow. In the present paper, we report ionic apparent and limiting partial molar volumes of some symmetrical tetraalkylammonium bromides in acetonitrile (ACN) + water mixtures at 298.15 K to determine the effect of variation of limiting ionic partial molar volumes, $V_\phi{}^{\circ\pm}$, with ACN content for a given salt. In addition, ionic partial molar volumes of transfer from water to ACN + water mixtures, $\Delta t V_\phi{}^{\circ+}$, have been calculated.

Experimental Section

Water was distilled in a quick-fit apparatus over alkaline $KMnO_4$, followed by further distillation over H_2SO_4. The electric conductance of distilled water varied between 7×10^{-7} and 9×10^{-7} Ω^{-1} cm^{-1}. Commercially available ACN (98% pure; E Merck) was distilled over P_2O_5 and then over anhydrous Na_2CO_3. Finally, a third distillation of ACN was carried out without any additive. ACN with conductivity of about 5×10^{-8} Ω^{-1} cm^{-1} or less was collected in air-tight amber-colored bottles. The purity of ACN was checked by comparing its observed density, 0.776 45 g cm^{-3}, with that of literature, 0.776 49 g cm^{-3}, (Riddick et al., 1986) at 298.15 K.

All R_4NBr were from Fluka, with a purity ranging between 98 and 99%. All these salts were recrystallized by the procedure adopted by Conway et al. (1966). The calibration of glasswares was done as described in the literature.

ACN + water mixtures of compositions (0, 10, 30, 50, 70, 90, and 100) mass % ACN were prepared by mixing known masses of water and ACN in glass-stoppered flasks. No attempt was made to monitor the relative humidity of the air to which the ACN was exposed for a short period of time during preparation. However, any effect of humidity on the composition of ACN was considered to be negligible. The recrystallized salts were dried at (100−110) °C in vacuum for 24 h prior to use. Due to the hygroscopic nature of the bromides, these salts were stored in a vacuum desiccator over calcium chloride. Accurately known masses of recrystallized salts were dissolved in a particular solvent to give a concentration of 0.05 M. This served as the stock solution. Further concentrations were obtained by using a mass dilution technique. Salt concentrations varied from (0.002 to 0.05) M. The exact concentration of the salt solution was obtained either from measurement of halide ion concentration using Volahdr's method or by gravimetric analysis (Bassett et al., 1978; Kreshkov, 1970). The gravimetric analysis for concentration determination of the salt was done by weighing small amounts of this solution into weighing bottles and drying them in an oven. The weighing bottle was then cooled in a desiccator and weighed to obtain the mass of the dry salt. The solutions were stored in dark-colored amber bottles which were kept in a drybox. Densities were determined by using a 15 cm^3 double-arm pycnometer as described earlier (Nikam and Mehdi, 1988; Nikam et al., 1995). The pycnometer was calibrated using conductivity water with 0.997 05 g cm^{-3} as its density at 298.15 K. The pycnometer filled with air-bubble-free experimental liquids was kept in a transparent-walled water bath (maintained constant to ±0.01 K) for 10 to 15 min to attain thermal equilibrium. The positions of the liquid levels in the two arms were recorded with the help of a traveling microscope which could be read to ±0.01 mm. The estimated accuracy of density measurements of solvent and salt solutions was ±0.000 01 g cm^{-3}.

Results and Discussion

The observed densities, *d*, of the solutions, which are the mean of three or four series of many measurements, of R_4NBr at 298.15 K are given in Table 1 along with the mass % values of ACN in the mixed solvent. The apparent molar volumes, V_ϕ, of the R_4NBr were calculated from the densities using the equation

$$V_\phi = M/d_0 - [1000(d - d_0)/cd_0] \qquad (1)$$

where d_0 is the density of ACN, water, or ACN + water solvent, *d* is the density of R_4NBr solutions, *M* is the molecular weight of the R_4NBr, and *c* is the concentration in moles per unit volume. The values of V_ϕ for each R_4NBr salt are given in Table 1. Since V_ϕ's varied linearly with $c^{1/2}$ over the concentration range studied, $V_\phi{}^\circ$, the limiting partial molar volume of the R_4NBr, was obtained by computerized least-squares fitting of the results to the Masson equation (1929)

$$V_\phi = V_\phi{}^\circ + S^*{}_v c^{1/2} \qquad (2)$$

where $S^*{}_v$ is the experimental slope. The values of $V_\phi{}^\circ$ and $S^*{}_v$ are presented in Table 2.

The $S^*{}_v$ values shown in Table 2 are positive for solutions of $(CH_3)_4NBr$ in water and their mixtures up to 70 mass %

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Table 1. Concentration (c), Densities (d), and Apparent Molar Volumes (V_ϕ) for Various Tetraalkylammonium Bromides in ACN + Water at 298.15 K

c/(mol dm^{-3})	d/(g cm^{-3})	V_ϕ/(cm^3 mol^{-1})	c/(mol dm^{-3})	d/(g cm^{-3})	V_ϕ/(cm^3 mol^{-1})	c/(mol dm^{-3})	d/(g cm^{-3})	V_ϕ/(cm^3 mol^{-1})	c/(mol dm^{-3})	d/(g cm^{-3})	V_ϕ/(cm^3 mol^{-1})
$(CH_3)_4NBr$ with 0 Mass % ACN						$(C_3H_7)_4NBr$ with 50 Mass % ACN					
0.0	0.99705		0.02545	0.99806	114.60	0.0	0.89073		0.02537	0.89227	230.77
0.00261	0.99715	114.54	0.03532	0.99846	114.62	0.00238	0.89088	230.93	0.03564	0.89288	230.73
0.00549	0.99727	114.55	0.04553	0.99886	114.63	0.00575	0.89107	230.89	0.04544	0.89348	230.70
0.01032	0.99746	114.57	0.05559	0.99927	114.65	0.01055	0.89137	230.85	0.05515	0.89406	230.67
0.01572	0.99768	114.58				0.01559	0.89167	230.82			
$(C_2H_5)_4NBr$ with 0 Mass % ACN						$(C_4H_9)_4NBr$ with 50 Mass % ACN					
0.0	0.99705		0.02515	0.99793	174.83	0.0	0.89073		0.02515	0.89227	292.15
0.00281	0.99715	175.27	0.03542	0.99829	174.70	0.00276	0.89096	292.65	0.03544	0.89291	292.01
0.00572	0.99725	175.18	0.04593	0.99866	174.60	0.00572	0.89108	292.54	0.04539	0.89352	291.89
0.01052	0.99742	175.06	0.05528	0.99899	174.51	0.01078	0.89139	292.41	0.05533	0.89413	291.79
0.01559	0.99760	175.97				0.01523	0.89166	292.32			
$(C_3H_7)_4NBr$ with 0 Mass % ACN						$(C_5H_{11})_4NBr$ with 50 Mass % ACN					
0.0	0.99705		0.02555	0.99768	238.93	0.0	0.89073		0.02564	0.89226	356.62
0.00211	0.99711	239.47	0.03544	0.99793	238.48	0.00257	0.89089	357.35	0.03519	0.89284	356.44
0.00552	0.99718	239.28	0.04525	0.99813	238.31	0.00539	0.89105	357.21	0.04532	0.89344	356.27
0.01093	0.99731	239.06	0.05577	0.99843	238.14	0.01066	0.89137	357.00	0.05576	0.89407	356.11
0.01532	0.99744	238.93				0.01571	0.89167	356.86			
$(C_4H_9)_4NBr$ with 0 Mass % ACN						$(CH_3)_4NBr$ with 70 Mass % ACN					
0.0	0.99705		0.02554	0.99768	297.03	0.0	0.84374		0.02576	0.84545	106.03
0.00216	0.99710	298.07	0.03574	0.99793	296.76	0.00264	0.84391	104.71	0.03542	0.84608	106.36
0.00538	0.99718	297.82	0.04538	0.99817	296.53	0.00529	0.84409	104.97	0.04511	0.84673	106.65
0.01062	0.99731	297.55	0.05561	0.99843	296.33	0.01092	0.84446	105.35	0.05499	0.84738	106.91
0.01573	0.99744	297.34				0.01517	0.84475	105.58			
$(C_5H_{11})_4NBr$ with 0 Mass % ACN						$(C_2H_5)_4NBr$ with 70 Mass % ACN					
0.0	0.99705		0.02304	0.99747	359.40	0.0	0.84374		0.02532	0.84367	158.48
0.00209	0.99709	360.58	0.03494	0.99770	359.00	0.00281	0.84373	157.14	0.03561	0.84365	158.66
0.00542	0.99715	360.27	0.04593	0.99790	358.70	0.00573	0.84372	157.82	0.04581	0.84362	158.82
0.01033	0.99724	360.96	0.05598	0.99808	358.44	0.01092	0.84371	157.96	0.05568	0.84359	158.96
0.01561	0.99734	359.70				0.01529	0.84370	158.26			
$(CH_3)_4NBr$ with 10 Mass % ACN						$(C_3H_7)_4NBr$ with 70 Mass % ACN					
0.0	0.98105		0.02594	0.98504	113.85	0.0	0.84374		0.02585	0.84572	225.18
0.00272	0.98147	113.68	0.03591	0.99658	113.90	0.00291	0.84396	224.92	0.03530	0.84644	225.25
0.00509	0.98184	113.71	0.04508	0.99800	113.93	0.00522	0.84414	224.97	0.04527	0.84719	225.30
0.01071	0.99270	113.76	0.05509	0.99952	113.97	0.01084	0.84457	225.04	0.05569	0.84801	225.36
0.01524	0.99339	113.79				0.01523	0.84490	225.09			
$(C_2H_5)_4NBr$ with 10 Mass % ACN						$(C_4H_9)_4NBr$ with 70 Mass % ACN					
0.0	0.98105		0.02581	0.98000	173.78	0.0	0.84374		0.02578	0.84576	288.82
0.00215	0.98096	174.15	0.03563	0.97960	173.69	0.00257	0.84420	289.01	0.03569	0.84654	288.77
0.00503	0.98085	174.07	0.04507	0.97792	173.62	0.00578	0.84460	288.97	0.04577	0.84733	288.73
0.01028	0.99063	173.97	0.05505	0.97878	173.54	0.01092	0.84460	288.92	0.05581	0.84812	288.69
0.01519	0.99043	174.90				0.01555	0.84496	288.88			
$(C_3H_7)_4NBr$ with 10 Mass % ACN						$(C_5H_{11})_4NBr$ with 70 Mass % ACN					
0.0	0.98105		0.02584	0.98188	237.53	0.0	0.84374		0.02522	0.84572	354.81
0.00261	0.98113	238.19	0.03533	0.98219	237.37	0.00239	0.84393	355.21	0.03561	0.84654	354.70
0.00584	0.98124	238.04	0.04592	0.98253	237.21	0.00523	0.84415	355.13	0.04519	0.84729	354.61
0.01045	0.98139	237.88	0.05591	0.98284	237.08	0.01083	0.84459	355.01	0.05590	0.84813	354.52
0.01555	0.98155	237.75				0.01592	0.84499	354.93			
$(C_4H_9)_4NBr$ with 10 Mass % ACN						$(C_2H_5)_4NBr$ with 90 Mass % ACN					
0.0	0.98105		0.02524	0.97371	296.46	0.0	0.79788		0.02565	0.79821	149.18
0.00266	0.98026	297.36	0.03522	0.97080	296.22	0.00222	0.79791	147.78	0.03568	0.79834	149.54
0.00528	0.97951	297.18	0.04511	0.96792	296.01	0.00533	0.79795	148.10	0.04582	0.79847	149.85
0.01055	0.97799	296.93	0.05555	0.99489	295.82	0.01039	0.79801	148.46	0.05586	0.79860	150.13
0.01592	0.97642	296.74				0.01554	0.79808	148.74			
$(C_5H_{11})_4NBr$ with 10 Mass % ACN						$(C_3H_7)_4NBr$ with 90 Mass % ACN					
0.0	0.98105		0.02523	0.98167	359.14	0.0	0.79788		0.02566	0.80029	217.28
0.00229	0.98110	360.30	0.03522	0.98191	358.84	0.00251	0.79811	216.40	0.03550	0.80121	217.50
0.00525	0.98118	360.05	0.04555	0.98217	358.58	0.00559	0.79841	216.59	0.04528	0.80213	217.70
0.01011	0.98130	359.75	0.05632	0.98243	358.33	0.01088	0.79890	216.83	0.05561	0.80310	217.88
0.01559	0.98143	359.50				0.01544	0.79933	216.99			
$(CH_3)_4NBr$ with 30 Mass % ACN						$(C_4H_9)_4NBr$ with 90 Mass % ACN					
0.0	0.93857		0.02521	0.93982	111.68	0.0	0.78788		0.02553	0.78033	284.04
0.00221	0.93868	111.27	0.03512	0.94032	111.79	0.00251	0.79812	283.74	0.03538	0.80128	284.12
0.00579	0.93886	111.38	0.04563	0.94034	111.89	0.00547	0.79841	283.80	0.04517	0.80222	284.19
0.01034	0.93908	111.47	0.05539	0.94133	111.97	0.01073	0.79891	283.88	0.05532	0.80319	284.25
0.01573	0.93982	111.56				0.01534	0.79935	283.94			
$(C_2H_5)_4NBr$ with 30 Mass % ACN						$(C_5H_{11})_4NBr$ with 90 Mass % ACN					
0.0	0.93857		0.02544	0.93783	169.82	0.0	0.78788		0.02559	0.80030	352.21
0.00274	0.93849	169.94	0.03584	0.93752	169.79	0.00234	0.79810	352.13	0.03531	0.80132	352.23
0.00537	0.93841	169.91	0.04566	0.93723	169.76	0.00553	0.79842	352.15	0.04555	0.80232	352.24
0.01021	0.93827	169.88	0.05901	0.93793	169.73	0.01071	0.79892	352.17	0.05528	0.80327	352.26
0.01520	0.93812	169.86				0.01522	0.79936	352.18			

Table 1 (Continued)

c/ (mol dm^{-3})	d/ (g cm^{-3})	V_ϕ/ (cm^3 mol^{-1})	c/ (mol dm^{-3})	d/ (g cm^{-3})	V_ϕ/ (cm^3 mol^{-1})	c/ (mol dm^{-3})	d/ (g cm^{-3})	V_ϕ/ (cm^3 mol^{-1})	c/ (mol dm^{-3})	d/ (g cm^{-3})	V_ϕ/ (cm^3 mol^{-1})
$(C_3H_7)_4NBr$ with 30 Mass % ACN						$(C_2H_5)_4NBr$ with 100 Mass % ACN					
0.0	0.93857		0.02514	0.93972	234.33	0.0	0.77645		0.02513	0.77716	142.52
0.00228	0.93868	234.79	0.03503	0.94017	234.21	0.00272	0.77668	140.76	0.03567	0.77739	143.03
0.00553	0.93882	234.68	0.04543	0.94165	234.10	0.00543	0.77674	141.11	0.04533	0.77760	143.43
0.01078	0.93906	234.56	0.05518	0.94106	234.01	0.01079	0.77685	141.62	0.05480	0.77781	143.79
0.01534	0.93927	234.48				0.01534	0.77695	141.95			
$(C_4H_9)_4NBr$ with 30 Mass % ACN						$(C_3H_7)_4NBr$ with 100 Mass % ACN					
0.0	0.93857		0.02591	0.93972	294.39	0.0	0.77645		0.02549	0.80029	212.26
0.00229	0.93867	295.16	0.03573	0.94018	294.19	0.00219	0.77685	210.87	0.03523	0.78024	212.60
0.00517	0.93880	295.00	0.04531	0.94061	294.03	0.00518	0.77716	211.18	0.04587	0.78135	212.93
0.01088	0.93906	294.77	0.05512	0.94105	293.88	0.01079	0.77773	211.57	0.05512	0.78229	213.18
0.01535	0.93926	294.64				0.01512	0.77817	211.81			
$(C_5H_{11})_4NBr$ with 30 Mass % ACN						$(C_4H_9)_4NBr$ with 100 Mass % ACN					
0.0	0.93857		0.02578	0.93863	358.87	0.0	0.77645		0.02503	0.77924	281.01
0.00248	0.93867	358.85	0.03532	0.94003	358.62	0.00224	0.77685	280.37	0.03519	0.78031	281.18
0.00538	0.93879	358.64	0.04576	0.94046	358.39	0.00507	0.77715	280.51	0.04553	0.78139	281.33
0.01042	0.93900	358.39	0.05613	0.94088	358.19	0.01027	0.77770	280.68	0.05503	0.78239	281.46
0.01579	0.93922	358.18				0.01557	0.77820	280.82			
$(CH_3)_4NBr$ with 50 Mass % ACN						$(C_5H_{11})_4NBr$ with 100 Mass % ACN					
0.0	0.89073		0.02534	0.89463	109.09	0.0	0.77645		0.02538	0.77933	350.48
0.00211	0.89105	108.31	0.03522	0.89615	109.29	0.00221	0.77685	350.07	0.03546	0.78041	350.59
0.00564	0.89159	108.51	0.04568	0.89777	109.47	0.00537	0.77720	350.17	0.04568	0.78150	350.69
0.01038	0.89233	108.70	0.05529	0.89925	109.62	0.01028	0.77772	350.27	0.05532	0.78250	350.76
0.01577	0.89316	108.86				0.01513	0.77823	350.35			
$(C_2H_5)_4NBr$ with 50 Mass % ACN											
0.0	0.89073		0.02585	0.99030	165.13						
0.00222	0.89069	164.89	0.03554	0.89014	165.19						
0.00511	0.89065	164.95	0.04501	0.88999	165.24						
0.01073	0.89055	165.01	0.05508	0.88982	165.29						
0.01591	0.89047	165.06									

ACN, indicating some ion−ion interactions in these solvent media (Sen, 1976). In the case of $(C_2H_5)_4NBr$ to $(C_5H_{11})_4NBr$, the slope is negative in the water-rich media and positive in ACN-rich media, suggesting ionic dissociation and association, respectively (Das and Hazra, 1991). Second, the S^*_v values decrease as the size of R_4NBr increases. It appears that the dielectric constant of the solvent medium and the size of the R_4N^+ ion play an important role in determining the nature of the slope.

$V_\phi°$ is regarded as a measure of solute−solvent interactions. The results of $V_\phi°$ shown in Table 2 of all R_4NBr agree well with those reported by earlier workers (Wen and Saito, 1964; Uosaki et al., 1972; Kumar et al., 1986).

Ionic limiting partial molar volumes have been calculated following the extrapolation method suggested by Conway and co-workers (1966). Following this procedure, the $V_\phi°$ values for the R_4NBr in water, ACN + water, and ACN were plotted against the molecular weight of the corresponding R_4N^+ ions using an equation of the form

$$V_\phi° = V_\phi°(Br^-) + b(\text{mol wt of } R_4N^+) \qquad (3)$$

where b is a constant and $V_\phi°(Br^-)$ is the limiting ionic partial molar volume of Br^- ion. Representative plots are shown in Figure 1. An excellent linear relationship was observed for all R_4NBr in all solvents with correlation coefficients greater than 0.999. Table 3 represents the values of $V_\phi°(Br^-)$ and b. The $V_\phi^{\circ+}$ values also show a systematic increase as the size of the R_4N^+ increases. When an ion is introduced into a solvent, the $V_\phi°$ can be expressed as (Hirata and Arakawa, 1973; Sen, 1976)

$$V_\phi^{\circ ion} = V_\phi^{\circ int} + \Delta V \qquad (4)$$

where $V_\phi^{\circ int}$ is the intrinsic volume of the ion and ΔV is the change in volume of the system due to ion−solvent interactions. It has been assumed by earlier authors (Sen, 1976; Nikam and Hiray, 1989) that, in electrolytic solu-

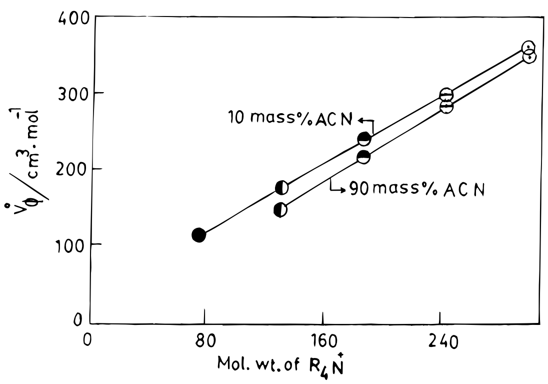

Figure 1. Plot of $V_\phi°$ versus mol wt of R_4N^+ in different mass % ACN at 298.15 K: (●) $(CH_3)_4NBr$, (◐) $(C_2H_5)_4NBr$, (◓) $(C_3H_7)_4NBr$, (⊖) $(C_4H_9)_4NBr$, (⊙) $(C_5H_{11})_4NBr$.

tions, the anion solvation can be considered as negligible. They argued that the solvation number at infinite dilution is really a measure of the extent to which the cation is solvated. Extending these arguments to solutions of R_4NBr in ACN + water mixtures, it can be assumed that, in the case of R_4NBr, the main contribution to solvation is due to that of the R_4N^+ ion. Therefore, eq 4 can be written as

$$V_\phi°(R_4N^+) = V_\phi^{\circ int}(R_4N^+) + \Delta V \qquad (5)$$

The term $V_\phi^{\circ int}(R_4N^+)$ was calculated with the help of an equation (Krumgalz, 1980)

$$V_\phi^{\circ int}(R_4N^+) = 2.52r^3(R_4N^+) \qquad (6)$$

where $r(R_4N^+)$ is the crystallographic radius of the R_4N^+ ion. The values of ΔV for all R_4N^+ ions in ACN + water mixtures are given in Table 4. It is seen that all ΔV values are negative, and the negative values, in general, show a tendency to increase in magnitude with the size of the R_4N^+

Table 2. Limiting Partial Molar Volumes (V_ϕ°) and Experimental Slopes (S^*_v) of R_4NBr in ACN + Water at 298.15 K

R_4NBr	mass % ACN	V_ϕ°/ cm^3 mol^{-1})	S^*_v/ (cm^3 L$^{1/2}$ mol$^{-3/2}$)
$(CH_3)_4NBr$	0	114.51	0.61
		114.8[a]	
		114[b]	
	10	113.59	1.64
	20	109[b]	
	30	111.10	3.70
	40	108[b]	
	50	108.01	6.89
	60	103[b]	
	70	104.10	12.00
	80	101[b]	
$(C_2H_5)_4NBr$	0	175.50	−4.21
		173.3[a]	−3.3[a]
		174[b]	
	10	174.29	−3.18
	20	169[b]	
	30	170.00	−1.09
	40	168[b]	
	50	164.80	2.08
	60	164[b]	
	70	157.50	6.18
	80	159[b]	
	90	147.19	12.40
	100	139.90	16.61
		140.8[c]	15.1[c]
$(C_3H_7)_4NBr$	0	239.80	−7.00
		240.8[a]	−6.0[a]
		240[b]	
	10	238.50	−5.99
	20	240[b]	
	30	235.00	−4.23
	40	235[b]	
	50	231.80	−1.39
	60	224[b]	
	70	224.80	2.42
	80	227[b]	
	90	215.99	8.01
	100	210.30	12.28
		214.7[c]	11.4[c]
$(C_4H_9)_4NBr$	0	298.49	−9.17
		302.9[a]	−8.4[a]
		300[b]	
	10	297.80	−8.39
	20	305[b]	
	30	295.60	−6.90
	40	306[b]	
	50	292.90	−4.69
	60	301[b]	
	70	289.10	−1.67
	80	300[b]	
	90	283.60	2.79
	100	288.10	5.83
		286.1[c]	4.6[c]
$(C_5H_{11})_4NBr$	0	361.10	−11.22
		365.6[a]	−8.3[a]
	10	360.80	−10.40
	30	359.30	−8.90
	50	357.7	−6.7
	70	355.40	−2.42
	90	352.1	0.7
	100	349.89	3.73

[a] Wen and Saito (1964). [b] Kumar et al. (1986). [c] Uosaki et al. (1972).

ions, suggesting a decrease in ion−solvent interaction with an increase in the size of the R_4N^+ ion.

A measure of the difference in ion−solvent interactions between water and ACN + water can be obtained by means of limiting partial molar volumes of transfer, ΔtV_ϕ°$^+$(mixed solvent → pure solvent). Using the value of V_ϕ° of R_4N^+'s in ACN + water mixtures, we calculated the ΔtV_ϕ°$^+$ from water to ACN + water mixtures from the equation

Table 3. Parameters of V_ϕ° Versus Molecular Weight of R_4N^+ with Standard Errors in ACN + Water Mixtures at 298.15 K

mass % ACN	V_ϕ°(Br^-)/(cm^3 mol^{-1})	b
0	33.22 ± 1.86	1.10
10	31.76 ± 1.64	1.10
30	27.61 ± 2.15	1.11
50	22.46 ± 3.63	1.11
70	15.53 ± 6.15	1.13
90	−11.02 ± 0.62	1.21
100	−22.37 ± 0.41	1.25

Table 4. ΔV Values for R_4N^+ Ions in ACN + Water Mixtures at 298.15 K and Different Mass % ACN

	ΔV/(cm^{-3} mol^{-1})						
R_4N^+	0	10	30	50	70	90	100
$[CH_3]_4N^+$	23.91	23.36	21.71	19.65	16.63		
$[C_2H_5]_4N^+$	19.00	18.75	18.89	18.94	19.31	3.07	0.99
$[C_3H_7]_4N^+$	26.13	25.97	25.32	24.17	23.44	5.70	0.04
$[C_4H_9]_4N^+$	38.52	37.75	35.80	33.35	30.22	9.17	6.68
$[C_5H_{11}]_4N^+$	45.17	44.01	41.36	37.81	33.18	9.94	0.79

Table 5. Ionic Partial Molar Volume of Transfer of R_4N^+ at Infinite Dilution (ΔtV_ϕ°$^+$) from Water to ACN + Water Solvent Mixtures at 298.15 K and Different Mass % ACN (Assumptions: $V_\phi° = V_\phi°(Br^-) + b$(mol wt of R_4N^+) and $\Delta V_\phi°^+ = V_\phi°^+$(ACN + Water) − $V_\phi°^+(H_2O)$)

	ΔtV_ϕ°$^+$/(cm^3 mol^{-1})						
R_4N^+	0	10	30	50	70	90	100
$[CH_3]_4N^+$	0	0.54	2.20	4.26	7.28		
$[C_2H_5]_4N^+$	0	0.67	0.11	0.06	−0.31	15.93	19.99
$[C_3H_7]_4N^+$	0	0.16	0.81	1.96	2.69	20.43	26.09
$[C_4H_9]_4N^+$	0	0.77	2.72	5.17	8.30	29.35	45.20
$[C_5H_{11}]_4N^+$	0	1.16	3.81	7.36	11.99	35.23	44.36

$$\Delta tV_\phi°^+ = V_\phi°^+(\text{ACN + water}) - V_\phi°^+(\text{water}) \quad (7)$$

where V_ϕ°$^+$(ACN + water) and V_ϕ°$^+$(water) are the limiting partial molar volume of R_4N^+ in ACN + water and water, respectively. The results are presented in Table 5. Perusal of Table 5 shows that comparatively small positive values of $\Delta tV\phi$°$^+$ suggest preferential solvation of R_4N^+ ions by ACN and this preference increases with an increase in ACN, thereby reducing the strong solvent−solvent interactions between water and ACN (Cox et al., 1979; Davis, 1983). Thus, the large R_4N^+ are scarcely solvated in these solvents.

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