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Viscometric Behavior of Some Symmetrical Tetraalkylammonium Bromides in Acetonitrile + Water Mixtures at 303.15 K

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The viscosity measurements for some symmetrical tetraalkyl ammonium bromide (R_4NBr, $R = CH_3$ to C_5H_{11}) KCl, and KBr solutions in acetonitrile (ACN) + water mixtures containing 0, 10, 30, 50, 70, 90, and 100 mass% of ACN at 303.15 K have been performed. The Jones–Dole equation was used for the analysis of viscosity data of these salts. The viscosity B-coefficients in the entire range of ACN + water mixtures were obtained from the computerized least-squares method. The experimental criterion $B(K^+) = B(Cl^-) = (1/2)B(KCl)$ was applied in order to obtain the ionic B-coefficients. The $B_\pm$ coefficients are interpreted in terms of solvent structure and ion-solvent interactions in the solvents.

Measurements of viscosity in solutions provide an excellent method for obtaining data on ion–ion and ion–solvent interactions.[1,2] Hydrophobic (structure making) and hydrophilic (structure breaking) characters of the solute i.e. H-bonding formation and disruption properties are correlated to changes in the viscosity. Recently,[3] we have investigated the nature of ion–solvent interactions of some salts solutions from the measurements of some thermodynamic and transport properties. Although a number of extensive viscometric studies have been made in various solvents involving simple salts, the literature provides very little information regarding the viscometric studies of the mixtures. This led us to undertake the present investigation.

Experimental

Water was distilled in a pyrex glass apparatus over alkaline $KMnO_4$, followed by further distillation over H_2SO_4. 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. The purity of ACN was checked by comparing its observed density, 0.77122 g cm^{-3}, with that in the literature,[4] 0.77125 g cm^{-3}, at 303.15 K. All R_4NBr salts were from Fluka with a purity ranging between 98 and 99%. All these salts were recrystallized by the procedure described by Conway et al.[5] ACN + water mixtures of compositions (0, 10, 30, 50, 70, 90, and 100) mass% ACN corresponding to (0, 0.0466, 0.1586, 0.3054, 0.5064, 0.7983, and 1) mole fraction of ACN were prepared by mixing known masses of water and ACN in a glass-stoppered flask. 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 °C in vacuum for 24 h prior to use. Owing 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 (1 M = 1 mol dm^{-3}). The uncertainty in the mass measurement was less than 0.02%. 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 Volhard's method or by gravimetric analysis.[6,7] The mass of the solution and dried salts were determined with an analytical balance accurate to 0.01 mg. The solutions were stored in dark-colored amber bottles that were kept in a dry box.

Densities of solvent mixtures and salt solutions were determined using a 15 cm^3 double arm pycnometer as reported earlier.[8] The estimated accuracy of density measurements of solutions was ±0.00003 g cm^{-3}.

The viscosity measurements were made using a commercial capillary viscometer of an Ostwald–Sprengel type.[9] The viscometer was clamped vertically in the bath, and 20 cm^3 of the solution was added from a graduated pipet. The viscometer was calibrated with water using the viscosity and density values reported by the Stokes and Mills.[2] Viscosity values were determined using the relation (Wright[10]; Mulcahy[11])

$$\eta = d(Kt - L/t), \tag{1}$$

where η is the viscosity, d is the density of liquid, t is the flow time, and K and L are the constants for a given viscometer. The flow time was measured with an electronic stopwatch with an accuracy of ±0.01 s. The maximum and minimum flow times were about 800 and 150 s, respectively. At least three repetitions of each data

Table 1. Solvent Properties at 303.15 K

Mass% ACN	Density (g cm^{-3})	Viscosity (mPa s)
0	0.99565	0.7973
10	0.97862	0.7964
30	0.93485	0.7665
50	0.88645	0.6845
70	0.83890	0.5398
90	0.79256	0.3593
100	0.77122	0.3142

Table 2. Concentration (c), Density (d), and Viscosity (η) for Various Electrolytes in Different Mass Fractions (w) of Acetonitrile (A) + Water (B) at 303.15 K

c mol dm^{-3}	d g cm^{-3}	η mPa s	d g cm^{-3}	η mPa s	c mol dm^{-3}	d g cm^{-3}	η mPa s	d g cm^{-3}	η mPa s
		KCl			0.0055	0.93532	0.7677	0.77177	0.3161
	$w_A = 0\%$		$w_A = 70\%$		0.0103	0.93572	0.7683	0.77224	0.3175
0.0024	0.99576	0.7975	0.83905	0.5413	0.0153	0.93614	0.7688	0.77268	0.3188
0.0053	0.99590	0.7976	0.83922	0.5424	0.0253	0.93699	0.7698	0.77366	0.3216
0.0104	0.99614	0.7977	0.83947	0.5439	0.0353	0.93784	0.7708	0.77453	0.3240
0.0153	0.99638	0.7978	0.83975	0.5456	0.0453	0.93868	0.7717	0.77553	0.3268
0.0257	0.99687	0.7980	0.84029	0.5486	0.0551	0.93951	0.7725	0.77646	0.3294
0.0358	0.99775	0.7981	0.84085	0.5516		$w_A = 50\%$			
0.0456	0.99781	0.7982	0.84135	0.5542	0.0024	0.89666	0.6854		
0.0551	0.99827	0.7982	0.84190	0.5570	0.0054	0.89692	0.6861		
	$w_A = 10\%$		$w_A = 90\%$		0.0104	0.88735	0.6872		
0.0029	0.97876	0.7969	0.79269	0.3603	0.0156	0.88781	0.6883		
0.0058	0.97890	0.7972	0.79287	0.3613	0.0254	0.88866	0.6902		
0.0105	0.97913	0.7974	0.79316	0.3628	0.0354	0.88953	0.6920		
0.0157	0.97938	0.7976	0.79345	0.3644	0.0452	0.89038	0.6938		
0.0252	0.97984	0.7980	0.79400	0.3671	0.0556	0.89128	0.6957		
0.0357	0.98035	0.7983	0.79458	0.3700					
0.0459	0.98084	0.7985	0.79514	0.3727			$[CH_3]_4NBr$		
0.0558	0.98132	0.7988	0.79572	0.3755		$w_A = 0\%$		$w_A = 70\%$	
	$w_A = 30\%$		$w_A = 100\%$		0.0026	0.99575	0.7976	0.83906	0.5408
0.0022	0.93496	0.7674	0.77136	0.3152	0.0055	0.99587	0.7979	0.83924	0.5417
0.0051	0.93511	0.7679	0.77153	0.3161	0.0103	0.99606	0.7984	0.83959	0.5433
0.0102	0.93536	0.7688	0.77182	0.3175	0.0157	0.99628	0.7988	0.83986	0.5446
0.0154	0.93562	0.7695	0.77210	0.3189	0.0254	0.99667	0.7996	0.84053	0.5475
0.0253	0.93612	0.7708	0.77268	0.3216	0.0353	0.99706	0.8005	0.84114	0.5501
0.0354	0.93662	0.7720	0.77328	0.3245	0.0455	0.99747	0.8013	0.84176	0.5527
0.0452	0.93711	0.7731	0.77386	0.3272	0.0556	0.99788	0.8021	0.84239	0.5554
0.0554	0.93762	0.7742	0.77444	0.3298		$w_A = 10\%$			
	$w_A = 50\%$				0.0027	0.97873	0.7969		
0.0028	0.88659	0.6858			0.0051	0.97884	0.7972		
0.0053	0.88672	0.6865			0.0107	0.97907	0.7978		
0.0109	0.88701	0.6880			0.0152	0.97926	0.7983		
0.0157	0.88726	0.6892			0.0259	0.97971	0.7994		
0.0258	0.88778	0.6915			0.0359	0.98013	0.8003		
0.0356	0.88829	0.6937			0.0451	0.98052	0.8012		
0.0458	0.88881	0.6960			0.0550	0.98094	0.8021		
0.0559	0.88933	0.6982				$w_A = 30\%$			
					0.0022	0.93496	0.7671		
		KBr			0.0058	0.93513	0.7678		
	$w_A = 0\%$		$w_A = 70\%$		0.0103	0.93535	0.7685		
0.0025	0.99585	0.7974	0.83910	0.5407	0.0157	0.93560	0.7694		
0.0053	0.99608	0.7974	0.83937	0.5415	0.0252	0.93606	0.7709		
0.0105	0.99650	0.7973	0.83985	0.5429	0.0351	0.93654	0.7724		
0.0153	0.99689	0.7973	0.84028	0.5440	0.0456	0.93704	0.7740		
0.0253	0.99771	0.7971	0.84117	0.5463	0.0554	0.93751	0.7755		
0.0353	0.99852	0.7968	0.84206	0.5486		$w_A = 50\%$			
0.0455	0.99935	0.7966	0.84295	0.5508	0.0021	0.88657	0.6852		
0.0552	1.00014	0.7963	0.84390	0.5531	0.0056	0.88676	0.6860		
	$w_A = 10\%$		$w_A = 90\%$		0.0104	0.88703	0.6871		
0.0023	0.97881	0.7967	0.79276	0.3601	0.0158	0.88734	0.6883		
0.0053	0.97906	0.7969	0.79307	0.3610	0.0253	0.88787	0.6904		
0.0104	0.97948	0.7970	0.79350	0.3623	0.0352	0.88843	0.6925		
0.0154	0.97989	0.7970	0.79398	0.3636	0.0457	0.88902	0.6947		
0.0255	0.98073	0.7971	0.79492	0.3661	0.0553	0.88956	0.6967		
0.0355	0.98156	0.7971	0.79584	0.3686					
0.0454	0.98238	0.7971	0.79676	0.3710			$[C_2H_5]_4NBr$		
0.0554	0.98321	0.7970	0.79772	0.3735		$w_A = 0\%$		$w_A = 70\%$	
	$w_A = 30\%$		$w_A = 100\%$		0.0028	0.99574	0.7982	0.83890	0.5410
0.0025	0.93506	0.7672	0.77146	0.3151	0.0057	0.99583	0.7991	0.83889	0.5420

Table 2. (Continued)

c	d	η	d	η
mol dm^{-3}	g cm^{-3}	mPa s	g cm^{-3}	mPa s
0.0105	0.99598	0.8005	0.83889	0.5435
0.0156	0.99614	0.8019	0.83889	0.5447
0.0251	0.99643	0.8045	0.83888	0.5474
0.0354	0.99675	0.8073	0.83887	0.5501
0.0459	0.99708	0.8102	0.83886	0.5528
0.0553	0.99737	0.8127	0.83885	0.5553
	$w_A = 10\%$		$w_A = 90\%$	
0.0021	0.97853	0.7972	0.79259	0.3601
0.0050	0.97841	0.7980	0.79264	0.3609
0.0103	0.97819	0.7995	0.79271	0.3621
0.0152	0.97798	0.8009	0.79279	0.3633
0.0258	0.97753	0.8038	0.79294	0.3655
0.0356	0.97712	0.8065	0.79309	0.3677
0.0451	0.97672	0.8090	0.79324	0.3698
0.0557	0.97628	0.8119	0.79339	0.3719
	$w_A = 30\%$		$w_A = 100\%$	
0.0027	0.93477	0.7675	0.77129	0.3151
0.0054	0.93469	0.7683	0.77135	0.3158
0.0102	0.93455	0.7697	0.77148	0.3171
0.0152	0.93440	0.7711	0.77159	0.3182
0.0254	0.93409	0.7738	0.77183	0.3204
0.0358	0.93378	0.7765	0.77208	0.3228
0.0457	0.93349	0.7791	0.77231	0.3249
0.0559	0.93318	0.7818	0.77255	0.3271
	$w_A = 50\%$			
0.0022	0.88642	0.6855		
0.0051	0.88637	0.6865		
0.0107	0.88629	0.6882		
0.0159	0.88621	0.6897		
0.0258	0.88606	0.6924		
0.0355	0.88592	0.6950		
0.0450	0.88578	0.6975		
0.0551	0.88563	0.7001		
		$[C_3H_7]_4NBr$		
	$w_A = 0\%$		$w_A = 70\%$	
0.0021	0.99570	0.7986	0.83835	0.5410
0.0055	0.99577	0.8008	0.83792	0.5418
0.0109	0.99589	0.8041	0.83686	0.5436
0.0153	0.99601	0.8069	0.83603	0.5450
0.0255	0.99624	0.8133	0.83403	0.5483
0.0354	0.99647	0.8194	0.83223	0.5512
0.0452	0.99670	0.8255	0.83040	0.5542
0.0558	0.99693	0.8321	0.82838	0.5574
	$w_A = 10\%$		$w_A = 90\%$	
0.0026	0.97870	0.7982	0.79280	0.3602
0.0058	0.97880	0.8000	0.79310	0.3610
0.0104	0.97895	0.8025	0.79362	0.3624
0.0155	0.97895	0.8052	0.79405	0.3635
0.0258	0.97911	0.8107	0.79505	0.3661
0.0353	0.97943	0.8156	0.79600	0.3685
0.0459	0.98006	0.8211	0.79695	0.3706
0.0554	0.98035	0.8259	0.79795	0.3733
	$w_A = 30\%$		$w_A = 100\%$	
0.0023	0.93496	0.7678	0.77146	0.3150
0.0055	0.93511	0.7692	0.77178	0.3158
0.0108	0.93536	0.7715	0.77238	0.3173
0.0153	0.93557	0.7733	0.77284	0.3184
0.0251	0.93602	0.7772	0.77396	0.3211
0.0350	0.93649	0.7811	0.77500	0.3235
0.0454	0.93697	0.7851	0.77615	0.3262

c	d	η	d	η
mol dm^{-3}	g cm^{-3}	mPa s	g cm^{-3}	mPa s
0.0552	0.93743	0.7889	0.77714	0.3285
	$w_A = 50\%$			
0.0024	0.88660	0.6857		
0.0057	0.88681	0.6869		
0.0105	0.88711	0.6887		
0.0156	0.88742	0.6905		
0.0254	0.88803	0.6938		
0.0356	0.88867	0.6973		
0.0454	0.88928	0.7005		
0.0551	0.88989	0.7037		
		$[C_4H_9]_4NBr$		
	$w_A = 0\%$		$w_A = 70\%$	
0.0021	0.99570	0.7993	0.83911	0.5412
0.0054	0.99577	0.8024	0.83937	0.5426
0.0106	0.99589	0.8072	0.83979	0.5448
0.0157	0.99601	0.8119	0.84017	0.5467
0.0255	0.99624	0.8208	0.84101	0.5508
0.0357	0.99647	0.8301	0.84182	0.5548
0.0454	0.99670	0.8389	0.84265	0.5587
0.0556	0.99693	0.8482	0.84347	0.5627
	$w_A = 10\%$		$w_A = 90\%$	
0.0027	0.97783	0.7718	0.79281	0.3603
0.0053	0.97708	0.7739	0.79311	0.3613
0.0105	0.97556	0.7780	0.79363	0.3629
0.0159	0.97399	0.7821	0.79409	0.3643
0.0252	0.97129	0.7891	0.79511	0.3672
0.0352	0.96838	0.7966	0.79610	0.3701
0.0451	0.96549	0.8040	0.79708	0.3729
0.0555	0.96247	0.8118	0.79809	0.3757
	$w_A = 30\%$		$w_A = 100\%$	
0.0023	0.93496	0.7684	0.77146	0.3151
0.0052	0.93510	0.7703	0.77179	0.3161
0.0109	0.93537	0.7740	0.77236	0.3178
0.0153	0.93558	0.7767	0.77295	0.3194
0.0259	0.93606	0.7831	0.77399	0.3222
0.0357	0.93654	0.7892	0.77512	0.3253
0.0453	0.93700	0.7950	0.77626	0.3283
0.0551	0.93746	0.8009	0.77732	0.3311
	$w_A = 50\%$			
0.0028	0.88663	0.6864		
0.0057	0.88682	0.6880		
0.0108	0.88715	0.6906		
0.0152	0.88743	0.6929		
0.0251	0.88807	0.6978		
0.0354	0.88873	0.7030		
0.0454	0.88938	0.7079		
0.0553	0.89002	0.7127		
		$[C_5H_{11}]_4NBr$		
	$w_A = 0\%$		$w_A = 70\%$	
0.0021	0.99569	0.8002	0.83910	0.5414
0.0054	0.99574	0.8043	0.83933	0.5430
0.0103	0.99583	0.8102	0.83980	0.5461
0.0156	0.99592	0.8166	0.84022	0.5487
0.0230	0.99605	0.8253	0.84099	0.5536
0.0350	0.99625	0.8395	0.84186	0.5589
0.0459	0.99644	0.8523	0.84266	0.5638
0.0560	0.99662	0.8642	0.84355	0.5692
	$w_A = 10\%$		$w_A = 90\%$	
0.0023	0.97868	0.7994	0.79279	0.3604

Table 2. (Continued)

c	d	η	d	η	c	d	η	d	η
mol dm^{-3}	g cm^{-3}	mPa s	g cm^{-3}	mPa s	mol dm^{-3}	g cm^{-3}	mPa s	g cm^{-3}	mPa s
0.0052	0.97876	0.8029	0.79312	0.3617	0.0353	0.93642	0.7989	0.77530	0.3265
0.0101	0.97889	0.8085	0.79365	0.3636	0.0458	0.93688	0.8082	0.77647	0.3298
0.0156	0.97903	0.8148	0.79410	0.3653	0.0561	0.93734	0.8173	0.77755	0.3328
0.0252	0.97928	0.8256	0.79516	0.3690		$w_A = 50\%$			
0.0352	0.97955	0.8367	0.79615	0.3724	0.0026	0.88661	0.6866		
0.0455	0.97982	0.8482	0.79718	0.3760	0.0053	0.88679	0.6885		
0.0563	0.98010	0.8602	0.79818	0.3795	0.0107	0.88713	0.6920		
	$w_A = 30\%$		$w_A = 100\%$		0.0157	0.88744	0.6953		
0.0025	0.93496	0.7693	0.77147	0.3152	0.0256	0.88807	0.7016		
0.0054	0.93509	0.7720	0.77184	0.3164	0.0352	0.88868	0.7076		
0.0104	0.93531	0.7767	0.77240	0.3181	0.0453	0.88932	0.7139		
0.0158	0.93555	0.7816	0.77295	0.3197	0.0558	0.88998	0.7204		
0.0258	0.93599	0.7905	0.77414	0.3232					

set reproducible to 0.05 s were obtained, and results were averaged. The K and L were obtained by measuring the flow times of pure water at three temperatures (298.15, 303.15, and 308.15)K at which dynamic viscosities are known. Linear regression analysis of a plot of $\eta t/d$ against t^2 for pure water at three temperatures provides estimates of K=3.063395×10^{-5} cm^2 s^{-2} and L=−0.91974 cm^2, as slope and intercept of the plot; with a correlation coefficient of 0.999. Knowledge of K and L allows determination of viscosities from the flow times and densities for ACN+water and solutions of salts using Eq. 1. The estimated accuracy of experimental viscosities was ±0.1%.

The solvent properties are recorded in Table 1.

Results and Discussion

The experimental density and viscosity values for KCl, KBr, and R_4NBr in the ACN+water mixtures at 303.15 K are listed in Table 2. Viscosity B-coefficients of the Jones–Dole equation[12] have been determined according to equation

$$\eta_r = \eta/\eta_0 = 1 + Ac^{1/2} + Bc, \tag{2}$$

where η and η_0 are the viscosities of the solution and pure solvent (ACN, water, or ACN+water mixture) respectively, c is the molar concentration and A and B are viscosity coefficients.

The plots of $(\eta_r - 1)/c^{1/2}$ versus $c^{1/2}$ were found to be linear for all salts in ACN+water mixtures. The A and B coefficients of these salts in ACN+water mixtures, obtained as intercepts and slopes of the straight lines, have been recorded in Table 3. Experimentally determined viscosity A and B-coefficients for salts in ACN+water mixtures are compared with those reported by Kumar et al.[13] The agreement is reasonably good.

Ionic viscosity B-coefficients were obtained on the assumption that $(1/2)B(\mathrm{KCl})=B(\mathrm{K}^+)=B(\mathrm{Cl}^-)$. Using the ionic B-coefficient for the K^+ ion, the B-coefficients for all other ions have been calculated for the entire ACN+water range. All these values are collected in Table 3. Since there are no established methods to split the viscosity B-coefficients into ionic contributions, the ionic viscosity B-coefficients we report here may contain large uncertainties arising from the assumption made in the splitting. Our values of ionic B-coefficients and the interpolated values of the ionic B-coefficients available in the literature[13—19] agreed to within 2%.

The B-coefficient is a measure of effective solvodynamic volume of solvated ions, the size and shape effect of solute as well as structural effects induced by the solute–solvent interaction[2] and makes the major contribution to relative viscosity (η_r) in Eq. 2.

When a solute dissolves in a solvent, a hole is made in the liquid with rupture of intermolecular bonds, and the solute is inserted. Some of the solvent molecules are attached to the ions because of ion–solvent interactions and this causes an increase in the viscosity of the solutions (which is positive contribution to the viscosity B-coefficient). On the other hand, these solvent molecules must be wrenched out of the bulk solvent and this breaking of the solvent structure causes a decrease in viscosity of solution. (a negative contribution to viscosity B-coefficient). Thus, the B-coefficient is the resultant of these two opposite factors.

It is well known that water molecules tend to form cage-like structures around R_4N^+ ions and the alkyl chains of these ions are partially hidden in these cages. The clathrate-like structure formed about the hydrocarbon portion of the R_4N^+ ions increases as the length of the alkyl chain increases. Consequently, alkyl chain appears to cause a greater degree of disorder in the solvent. This is called hydrophobic hydration of these ions in aqueous solutions.[20]

According to Krumgalz,[21] the B-coefficient of ion can be split into several terms:

$$B(\mathrm{ion}) = B_{\mathrm{Einst}}(\mathrm{ion}) + B_{\mathrm{orient}}(\mathrm{ion}) + B_{\mathrm{str}}(\mathrm{ion}) + B_{\mathrm{reinf}}(\mathrm{ion}), \tag{3}$$

where B_{Einst} and B_{orient} for viscosity increase are attributed to the shape and size of the ion and orientation of polar solvent molecules in the region of centrosymmetrical order around the ion, respectively. B_{str}, viscosity decrease and B_{reinf}, a viscosity increase, are attributed to destruction or enhancement of solvent structure outside the ordered region. For less structured ACN, the terms B_{str} and B_{reinf} are almost absent; for larger R_4N^+ ions, B_{orient} will be inoperative due to shielding of the charge, thus leaving only the first term of Eq. 3.

The $B_\pm$ values for K^+, Cl^-, Br^-, and $[CH_3]_4N^+$ ions in-

Table 3. Viscosity A ($dm^{3/2}\ mol^{-1}$), B ($dm^3\ mol^{-1}$), and Ionic B ($dm^3\ mol^{-1}$) Coefficients in Different Mass% ACN

Mass% ACN	Our data			Literature data[a]			
	303.15 K			298.15 K		308.15 K	
	A	B	B_+	A	B	A	B
			KCl				
0	0.005	−0.002	−0.001	0.005	−0.014	0.006	0.0098
10	0.012	0.001	0.0005				
20				0.018	0.015	0.020	0.030
30	0.019	0.098	0.049				
40				0.016	0.181	0.022	0.196
50	0.020	0.272	0.136				
60				0.020	0.344	0.020	0.387
70	0.028	0.458	0.229				
80				0.029	0.508	0.041	0.552
90	0.023	0.711	0.357				
100	0.021	0.803	0.401				
			KBr				
0	0.005	−0.043	−0.001	0.005	−0.049	0.005	−0.026
10	0.010	−0.028	0.0005				
20				0.017	−0.003	0.014	0.016
30	0.015	0.078	0.049				
40				0.011	0.143	0.021	0.163
50	0.016	0.226	0.136				
60				0.016	0.290	0.013	0.315
70	0.016	0.374	0.229				
80				0.014	0.417	0.024	0.468
90	0.018	0.633	0.357				
100	0.019	0.789	0.401				
			$[CH_3]_4NBr$				
0	0.003	0.094	0.136	0.007	0.101		0.100
10	0.007	0.099	0.128				
20				0.008	0.100	0.009	0.120
30	0.008	0.176	0.147				
40				0.006	0.219	0.010	0.247
50	0.009	0.285	0.195				
60				0.010	0.322	0.008	0.337
70	0.014	0.463	0.318				
80				0.023	0.403	0.016	0.434
			$[C_2H_5]_4NBr$				
0	0.005	0.330	0.372	0.008	0.343		0.320
10	0.006	0.323	0.352				
20				0.007	0.318	0.006	0.322
30	0.009	0.320	0.291				
40				0.012	0.322	0.008	0.320
50	0.016	0.346	0.256				
60				0.019	0.368	0.027	0.344
70	0.020	0.430	0.285				
80				0.010	0.530	0.027	0.473
90	0.021	0.539	0.263				
100	0.022	0.648	0.261				
			$[C_3H_7]_4NBr$				
0	0.001	0.780	0.821		0.82		0.73
10	0.012	0.618	0.647				
20				0.009	0.548	0.013	0.485
30	0.013	0.474	0.445				
40				0.012	0.474	0.017	0.393
50	0.013	0.455	0.364				

a) From Ref. 13.

Table 3. (Continued)

Mass%	Our data			Literature data[a)]			
ACN	303.15 K			298.15 K		308.15 K	
	A	*B*	B_+	*A*	*B*	*A*	*B*
60				0.005	0.498	0.018	0.467
70	0.013	0.531	0.387				
80				0.010	0.602	0.012	0.587
90	0.016	0.634	0.358				
100	0.017	0.751	0.364				
			$[C_4H_9]_4NBr$				
0	0.004	1.133	1.174	0.008	1.148		1.12
10	0.012	0.940	0.969				
20				0.016	0.844	0.012	0.736
30	0.015	0.752	0.723				
40				0.013	0.750	0.020	0.626
50	0.016	0.678	0.588				
60				0.009	0.719	0.021	0.647
70	0.016	0.690	0.545				
80				0.017	0.748	0.020	0.719
90	0.019	0.746	0.470				
100	0.022	0.888	0.500				
			$[C_5H_{11}]_4NBr$				
0	0.014	1.440	1.482				
10	0.014	1.363	1.391				
30	0.017	1.111	1.082				
50	0.016	0.872	0.782				
70	0.018	0.896	0.751				
90	0.020	0.931	0.655				
100	0.023	0.980	0.592				

crease slowly with increase in ACN upto 30 mass% ACN. A steep increase with further increase of ACN content in water was observed for these ions. Ibuki and Nakahara[22)] pointed out that the dielectric friction plays an important role in determining the solvent composition dependence of the ionic *B*-coefficients of the small Li^+ ion in methanol+water mixtures. Therefore, there may be a similar effect on the K^+, Cl^-, and Br^- ions in ACN+water mixtures, since the dielectric constant[23)] of the solvent decreases with an increase in the ACN content. The $[CH_3]_4N^+$ ion is also a structure breaker because of its small size, as compared to that of the other R_4N^+ ions, and the solvent structure around this ion is still under the influence of its charge. The B_+ values for $[C_2H_5]_4N^+$ and $[C_3H_7]_4N^+$ ions decrease with increase in mass% ACN, reach a minimum around 50 mass% ACN and then increase upto 70 mass% ACN. Further addition of ACN doesn't show any significant increase. This is supposed to arise from an increase in structure-breaking ability of ions with an increase of solvent order and a decrease in surface ionic field. In other words, the minimum points out two opposing interactions (ion-dipole and hydrophobic) experienced by these R_4N^+ ions in these mixed solvents. The small subsequent increase of the B_+ values may be attributed to some interactions of these ions with the excess ACN molecules (water structure breaking by ACN). For $[C_4H_9]_4N^+$ and $[C_5H_{11}]_4N^+$ ions, the B_+ values steeply decrease with increase in mass% of ACN. This indicates that R_4N^+ ions are embedded in the cavities (formed by the enforced water molecules) and stabilized by weak hydrogen bonding on the sites of cages by Br^- ion–water molecules.[20)]

It may, therefore, be concluded that the solvation behavior of R_4N^+ ions in pure and mixed non-aqueous solvents differs qualitatively from the solvation behavior of smaller ions.

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