CHAPTER IV

Viscosities of Some Symmetrical Tetraalkylammonium Salts in Acetonitrile at 288.15, 298.15, 308.15, and 318.15 K

Introduction

Viscometry has been widely used for the investigation of the behaviour of ions in nonaqueous solvents[1]. Earlier studies on the viscosities of tetraalkylammonium bromides in acetonitrile were limited only to one or two temperatures. Moreover, in some cases where comparisons of the literature[1-7] values are possible, the disagreement is as high as 25%. In order to remove the disparities among the existing literature viscosity *B*–coefficients of these electrolytes, and some contradicitions regarding temperature dependences of the *B*-values of tetrabutylammonium tetraphenylborate–an electrolyte often used as a "reference electrolyte" for the evalution of ionic *B*-values, it seemed necessary to perform an extensive experimental investigation of tetraalkylammonium bromides along with tetrabutylammonium tetraphenylborate in acetonitrile as a function of temperature and to make a critical examination of published results.

We have, therefore, redetermined the viscosities of tetraethylammonium bromide (Et_4NBr), tetrapropylammonium bromide (Pr_4NBr), tetrabutylammonium bromide (Bu_4NBr), tetrapentylammonium bromide (Pen_4NBr), tetrahexylammonium bromide (Hex_4NBr), tetraheptylammonium bromide (Hep_4NBr), and tetrabutylammonium tetraphenylborate (Bu_4NBPh_4) in acetonitrile at 298.15, and 308.15 K. The study has also been extended to two other temperatures, viz. 288.15, and 318.15 K in order to investigate the temperature dependence over a wide range of temperature. Ionic viscosity B-values have been derived on the basis of the reference electrolyte Bu_4NBPh_4.

Experimental

Acetonitrile is the same as that used in our earlier studies[8,9] and its purification has been described there.Properties of the purified solvent at 288.15, 298.15, 308.15, and 318.15 K together with the available literature values [3,10–13] are reported in Table 1. Our values agree well with the literature data.

Tetraalkylammonium bromides were of purum or puriss grade (Fluka) and were purified as described earlier by us[8].Tetrabutylammonium tetraphenylborate was prepared and purified as reported in the literature[14].

A stock solution for each salt was prepared by mass, and the working solutions were obtained by mass dilution. The conversion of the molality into molarity was done using the density values.

The densities. ρ, were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm^3 and an internal diameter of the capillary of about 0.1 cm. The pycnometer was calibrated at 288.15, 298.15, 308.15, and 318.15 K with triply distilled water and benzene. The temperature of the bath was controlled to ± 0.01 K. Details have been described earlier[15-17]. The reproducibility of the density measurements was ± (3 x 10^{-5}) $g.cm^{-3}$.

The kinematic viscosities, ν, were measured by means of a suspended Ubbelohde viscometer. The time of efflux was measured with a stopwatch to ± 0.1 s. The viscometer was kept in vertical position in a water thermostat controlled to ± 0.01 K. The absolute temperature was determined by a calibrated platinum resistence thermometer and Muller bridge. The efflux time for water at 298.15 K was about 540 s. The kinematic viscosity (ν) and the absolute viscosity (η) are given by the following equations :

$$\nu = Ct - K/t \qquad (1)$$

$$\eta = \nu\rho \qquad (2)$$

where t is the efflux time, ρ is the density, and C and K are the characteristic constants of the viscometer. The values of the constants C and K determined by using the density and viscosity

values of water and benzene[17] were found to be 1.648 x 10^{-5} $cm^2 .s^{-2}$ and –0.02331647 cm^2, respectively. The calibration constants were also checked with acetonitrile. The estimated error of the viscosity measurements was ± 0.1%.

In all cases the experiments were performed at least in five replicates for each composition and at each temperature, and the results were averaged.

Results

The relative viscosity (η_r) and the density (ρ) data for the electrolyte solutions as functions of molar concetration (c) in acetonitrile at 288.15, 298.15, 308.15, and 318.15 K are given in Table 2. The viscosity data of the electrolytes were analysed by the Jones-Dole equation as described in the literature[18].

$$\eta_r = 1 + Ac^{1/2} + Bc \qquad (3)$$

where A and B, the characteristic parameter for salt and solvent, depend on ion-ion and ion-solvent interaction respectively.

The plots of $(\eta_r - 1) / c^{1/2}$ versus $c^{1/2}$ were found to be linear in all cases over the whole concentration range of the electrolytes studied This indicates that ion pairing is not occuring to any great extent in this salt solution. This is in agreement with our earlier[8,9,19] investigation on the behaviour of these salts in acetonitrile.

The A values can be calculated theoretically from the physical parameters of the solvent and the limiting ionic equivalent conductances using the Falkenhagen and Vernon equation

$$A_{theo} = \frac{0.2577\Lambda^0}{\eta_0 (\varepsilon T)^{0.5} \lambda_+^0 \lambda_-^0} \left[1 - 0.6863 \left(\frac{\lambda_+^0 - \lambda_-^0}{\Lambda^0}\right)^2\right] \qquad (4)$$

as described earlier by us[20]. A_{theo} values at 298.15 K reported in Table 3 were calculated according to eqution (3) using ε = 35.95 and conductometric data from our ealier work[9,19].

The viscosity *B*-coefficients were obtained by the method of least squares from equation 3 using theoretical A values. In view of weak temperature dependence of the A-coefficients in many solvents[21,22] including acetonitrile[3] and non-availability of limiting ionic conductances at different temperatures, the A values at 298.15 K have been utlized at other temperatures. The viscosity B-coefficients obtained at various temperature are given in Table 4. The literature data[1-7] for *B*-coefficients are also included in this Table for comparison.

The viscosity data have also been analysed on the basis of the transition-state treatment of the relative viscosity of electrolyte solutions as suggested by Feakins *et. al.*,[23]

$$B = \frac{\bar{V}_1^0 - V_2^0}{1000} + \frac{\bar{V}_1^0}{1000}\left(\frac{\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq}}{RT}\right) \qquad (5)$$

In the above equation $\bar{V}_1^0$ and V_2^0 are the partial molar volumes of solvent and solute, respectively. $\Delta\mu_2^{0\neq}$ the contribution per mole of solute to the free energy of activation for viscous flow of the solution, has been determined from the above relationship and are reported in Table 5. $\Delta\mu_1^{0\neq}$ the free energy of activation per mole of pure solvent is given by the equation[24].

$$\Delta\mu_1^{0\neq} = \Delta G_1^{0\neq} = RT \ln (\eta_0 \bar{V}_1^0 / hN) \qquad (6)$$

where N is the Avogadro's number.

Discussion

The viscosity *B*-coefficients (Table 4) for all the electrolytes are large and positive, and increase in acetonitrile as we go from tetraethylammonium bromide through tetraheptylammoni- um bromide at all the temperatures investigated. As can be seen from Table 4 that our experimental B values, in general, show fair agreement with the available literature data. It needs to be pointed out that the salts Bu_4NBr and Bu_4NBPh_4, for which a number of *B* values are available from different sources, exhibit significant scatter among the literature *B* values.

The *B*-coefficients show moderate temperature dependence and the values decrease with increase of temperature as observed earlier in some dipolar aprotic solvents like sulfolane[21] dimethylsulfoxide[25], propylene carbonate[18], dimethylformamide[14] etc. Furthermore, from Table 4 we see that, although dB / dT is small, it is negative in sign for all the electrolytes, indicating that these behave as structure makers in this solvent medium. For Bu_4NBPh_4, while the data from Lawrence *et. al*[6]. show a weak positive temperature dependence of the B values, those from other sources[3,4] reveal clear negative dB / dT values–though differing from each other very much.

The ionic *B* values were calculated using Bu_4NBPh_4 as the "reference electrolyte" from the following equation[20] :

$$B\,(Bu_4NBPh_4) = B\,(Bu_4N^+) + B\,(Ph_4B^-) \qquad (7)$$

$$B\,(Bu_4N^+) \;/\; B\,(Ph_4B^-) = (5.00/5.35)^3 \qquad (8)$$

The ionic *B* values obtained from the above relationships are given in Table 6. This Table shows that the viscosity *B*-coefficients for cations and anions are positive and are also very high. The observed order of the ionic *B* values. $Hep_4N^+ > Hex_4N^+ > Pen_4N^+ > Bu_4N^+ > Pr_4N^+ > Et_4N^+$, shows that the obstruction of the solvent viscous flow increases with decrease of the ion charge density and with decrease of the size of the hydrodynamic entity by solvation.

There is so far no report on the temperature dependence of the ionic *B* values for the ions investigated here, with the exception of Bu_4N^+ and Ph_4B^- ions[1]. The dB_ε / dT values of the cations and anions in this study (*cf.* Table 6) are generally found to be negative (structure–making). The behavior of tetraalkylammonium ions in acetonitrile, arising mainly from the interaction of alkyl groups and solvent molecules, is similar to that observed in sulfolane[21], and in propylene carbonate[18].

The values of $\Delta\mu_2^{0\neq}$ for tetraalkylammonium ions in acetonitrile (Table 6) decrease in the order $Hep_4N^+ > Hex_4N^+ > Pen_4N^+ > Bu_4N^+ > Pr_4N^+ > Et_4N^+$, and for anions $Ph_4B^- > Br^-$. However, these values are found to be positive, and hence the formation of the transition-state is made less favourable in the presence of these ions.

Ionic *B*-coefficients have also been analysed on the basis of Einstein's equation as described earlier[20].

$$B_{\pm} = 2.5 \frac{4}{3} \pi \frac{R_{\pm}^{3} N}{1000} \qquad (9)$$

where $R_{\pm}$ is the radius of the ion assumed to be rigid sphere moving in a continuum and 2.5 is the shape factor for a sphere. The values of $R_{\pm}$ are shown in Table 7.

The $R_{\pm}$ values for tetraalkylammonium ions are found to be in reasonable agreement with the crystallographic radii of these ions (Table 7). The results indicate these ions are scarcely solvated in acetonitrile and behave as spherical entities. However, the R_{-} value of bromide ion is found to be much higher compared to its crystallographic radius, indicating that it is solvated in acetonitrile by ion-dipole interactions. Similar results have also been obtained from our earlier conductometric[9,19] and volumetric[8] measurements on these systems. Thus it appears that the large sizes of the tetraalkylammonium ions, their low surface charge density coupled with the medium relative permittivity of acetonitrile render these ions to be free, unassociated and, almost unsolvated in this medium within the investigated temperature range.

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Table 1. Properties of Acetonitrile at 288.15, 298.15, 308.15, and 318.15 K

T / K	ρ / g.cm^{-3}		η_0 / mPa.s	
	this work	lit.	this work	lit.
288.15	0.78735	0.7874[a]	0.3770	0.375[a]
298.15	0.77686	0.7766[b]	0.3446	0.341[a]
		0.77685[c]		0.341[b]
		0.7759[e]		0.344[c]
		0.77682[d]		
308.15	0.76564	0.7663[a]	0.3125	0.313[a]
		0.76581[b]		0.314[b]
		0.7662[c]		0.314[c]
		0.76560[e]		
318.15	0.75498	0.75271[b]	0.2893	0.293[b]
		0.7559[c]		0.289[c]

[a]ref. 3. [b]ref. 10. [c]ref. 12. [d]ref. 11. [e]ref. 13.

Table 2. Concentration (c), Density (ρ) and Relative Viscosity (η_r) of Tetraalkyl-ammonium Bromides and Tetraabutylammonium Tetraphenylborate in Acetonitrile at 288.15, 298.15, 308.15, 318.15 K

c / mol.dm^{-3}	ρ / g.cm^{-3}	η_r	c / mol.dm^{-3}	ρ / g.cm^{-3}	η_r	c / mol.dm^{-3}	ρ / g.cm^{-3}	η_r
				T = 288.15 K				
	Et_4NBr			Pr_4NBr			Bu_4NBr	
0.00990	0.78836	1.0088	0.01075	0.78843	1.0103	0.00906	0.78831	1.010
0.01912	0.78929	1.0159	0.02001	0.78935	1.0182	0.01982	0.78944	1.021
0.02201	0.78958	1.0181	0.02497	0.78984	1.0223	0.02537	0.79002	1.027
0.02981	0.79036	1.0241	0.02954	0.79029	1.0261	0.02988	0.79049	1.031
0.03473	0.79085	1.0281	0.03555	0.79088	1.0311	0.03594	0.79112	1.037
0.04036	0.79141	1.0322	0.03984	0.79130	1.0348	0.04046	0.79159	1.042
	Pen_4NBr			Hex_4NBr			Hep_4NBr	
0.00990	0.78844	1.0121	0.01057	0.78849	1.0140	0.00962	0.78838	1.015
0.01998	0.78954	1.0237	0.02021	0.78952	1.0261	0.01931	0.78941	1.029
0.02532	0.79012	1.0293	0.02445	0.78997	1.0308	0.02545	0.79006	1.038
0.03012	0.79064	1.0347	0.02953	0.79051	1.0372	0.02952	0.79049	1.044
0.03558	0.79123	1.0404	0.03520	0.79111	1.0438	0.03502	0.79107	1.052
0.04031	0.79174	1.0455	0.04098	0.79172	1.0510	0.03920	0.79151	1.058
	Bu_4NBPh_4							
0.00934	0.78854	1.0157						
0.01980	0.78986	1.0313						
0.02761	0.79084	1.0429						
0.03337	0.79156	1.0515						
0.04043	0.79244	1.0617						
0.04437	0.79293	1.0679						

T = 298.15 K

Et_4NBr			Pr_4NBr			Bu_4NBr		
0.00996	0.77785	1.0083	0.01015	0.77787	1.0090	0.01002	0.77789	1.0110
0.02005	0.77884	1.0157	0.01991	0.77883	1.0172	0.02004	0.77891	1.0212
0.02497	0.77932	1.0192	0.02503	0.77933	1.0213	0.02498	0.77941	1.0262
0.02991	0.77980	1.0228	0.03006	0.77982	1.0250	0.03014	0.77993	1.0309
0.03497	0.78029	1.0267	0.03500	0.78030	1.0290	0.03500	0.78042	1.0358
0.04006	0.78078	1.0303	0.04016	0.78080	1.0328	0.04009	0.78093	1.0409

Pen_4NBr			Hex_4NBr			Hep_4NBr		
0.00985	0.77789	1.0115	0.00988	0.77790	1.0130	0.01007	0.77794	1.0152
0.02019	0.77896	0.0226	0.02005	0.77896	1.0248	0.02003	0.77900	1.0292
0.02494	0.77945	1.0272	0.02506	0.77948	1.0310	0.02504	0.77953	1.0360
0.03001	0.77997	1.0329	0.03009	0.78000	1.0368	0.03006	0.78006	1.0431
0.03508	0.78047	1.0379	0.03503	0.78051	1.0424	0.03490	0.78047	1.0495
0.03998	0.78099	1.0432	0.03999	0.78102	1.0483	0.04014	0.78112	1.0569

Bu_4NBPh_4		
0.01090	0.77828	1.0167
0.01911	0.77934	1.0281
0.02588	0.78021	1.0378
0.02947	0.78067	1.0429
0.03667	0.78159	1.0531
0.04020	0.78204	1.0580

T = 308.15 K

Et_4NBr			Pr_4NBr			Bu_4NBr		
0.00985	0.76660	1.0078	0.00987	0.76662	1.0088	0.00983	0.76664	1.0108
0.01974	0.76755	1.0146	0.01965	0.76758	1.0167	0.01978	0.76764	1.0203
0.02476	0.76803	1.0183	0.02467	0.76807	1.0205	0.02467	0.76813	1.0251
0.02970	0.76850	1.0216	0.02962	0.76855	1.0242	0.02969	0.76863	1.0299
0.03456	0.76896	1.0252	0.03457	0.76903	1.0280	0.03451	0.76911	1.0346
0.03965	0.76944	1.0286	0.03965	0.76952	1.0319	0.03955	0.76961	1.0395

Pen_4NBr			Hex_4NBr			Hep_4NBr		
0.00965	0.76664	1.0113	0.00975	0.76667	1.0120	0.00983	0.76670	1.0146
0.01988	0.76769	1.0217	0.01979	0.76772	1.0237	0.01977	0.76776	1.0281
0.02458	0.76817	1.0267	0.02469	0.76823	1.0288	0.02475	0.76829	1.0347
0.02950	0.76867	1.0315	0.02970	0.76875	1.0346	0.02966	0.76881	1.0412
0.03453	0.76918	1.0369	0.03453	0.76925	1.0396	0.03448	0.76932	1.0476
0.03927	0.76966	1.0416	0.03938	0.76975	1.0453	0.03950	0.76985	1.0542

Bu_4NBPh_4		
0.00971	0.76693	1.0154
0.02020	0.76831	1.0304
0.02463	0.76889	1.0366
0.03191	0.76984	1.0468
0.03483	0.77022	1.0508
0.03991	0.77088	1.0579

T = 318.15 K

Et_4NBr			Pr_4NBr			Bu_4NBr		
0.00960	0.75591	1.0076	0.00957	0.75593	1.0084	0.00963	0.75596	1.0106
0.01945	0.75685	1.0145	0.01927	0.75688	1.0155	0.01957	0.75696	1.0200
0.02441	0.75732	1.0181	0.02419	0.75736	1.0193	0.02437	0.75744	1.0247
0.02928	0.75778	1.0213	0.02903	0.75783	1.0231	0.02928	0.75793	1.0294
0.03407	0.75823	1.0245	0.03400	0.75831	1.0269	0.03401	0.75840	1.0337
0.03907	0.75870	1.0279	0.03898	0.75879	1.0305	0.03895	0.75889	1.0386

Pen_4NBr			Hex_4NBr			Hep_4NBr		
0.00948	0.75597	1.0103	0.00963	0.75601	1.0116	0.00966	0.75604	1.0135
0.01964	0.75702	1.0205	0.01956	0.75706	1.0228	0.01951	0.75711	1.0265
0.02421	0.75749	1.0248	0.02430	0.75756	1.0278	0.02441	0.75764	1.0329
0.02910	0.75799	1.0295	0.02926	0.75808	1.0332	0.02924	0.75816	1.0391
0.03399	0.75849	1.0345	0.03403	0.75858	1.0381	0.03398	0.75867	1.0453
0.03861	0.75896	1.0390	0.03882	0.75908	1.0435	0.03891	0.75920	1.0517

Bu_4NBPh_4		
0.00925	0.75624	1.0142
0.02000	0.75769	1.0293
0.02462	0.75831	1.0357
0.03000	0.75903	1.0431
0.03825	0.76013	1.0544
0.04201	0.76063	1.0595

Table 3. Theoretical A Coefficients of Electrolytes in Acetonitrile at 298.15 K.

electrolyte	$A/dm^{3/2}\ mol^{-1/2}$
Et_4NBr	0.0155
Pr_4NBr	0.0170
Bu_4NBr	0.0181
Pen_4NBr	0.0189
Hex_4NBr	0.0197
Hep_4NBr	0.0203
Bu_4NBPh_4	0.0240

Table 4. Viscosity B/dm^{3}mol^{-1} Coefficients of Electrolytes in Acetonitrile at 288.15, 298.15, 308.15, and 318.15 K.

	T / K			
electrolyte	288.15	298.15	308.15	318.15
Et_4NBr	0.714	0.68 (0.650[a], 0.690[f])	0.653 (0.640[a])	0.638
Pr_4NBr	0.778	0.745 (0.706[a])	0.713 (0.704[a])	0.697
Bu_4NBr	0.979	0.935 (0.839[a], 0.74[b], 0.91[c], 0.93[f])	0.900 (0.829[a])	0.881
Pen_4NBr	1.033	0.990 (0.984[a])	0.953 (0.952[a])	0.931
Hex_4NBr	1.153	1.103 (1.100[a])	1.059 (1.091[a])	1.028
Hep_4NBr	1.375	1.321 (1.309[a])	1.257 (1.313[a])	1.222
Bu_4NBPh_4	1.398 (1.52[d],1.50[c])	1.336 (1.330[a], 1.32[c], 1.35[d], 1.43[c], 1.35[f])	1.319 (1.353[a], 1.25[d], 141[e])	1.307

[a]ref. 6. [b]ref. 5. [c]ref. 2. [d]ref. 3. [e]ref. 4. [f]ref. 7.

Table 5. $\Delta\mu^{0}{}_{2}^{*}$ / kJ mol^{-1} Values of Electrolytes in Acetonitrile at 288.15, 298.15, 308.15, and 318.15 K

	T / K			
electrolyte	288.15	298.15	308.15	318.15
Et_4NBr	45.98	45.67	45.15	45.30
Pr_4NBr	52.28	51.92	51.75	51.64
Bu_4NBr	64.50	64.03	63.71	64.06
Pen_4NBr	70.00	69.90	69.63	69.94
Hex_4NBr	78.92	78.55	78.07	78.11
Hep_4NBr	92.46	92.05	90.90	90.99
Bu_4NBPh_4	96.15	95.32	96.40	97.65

Table 6. Ionic Viscosity B -Coefficients and $\Delta\mu^{0\neq}_2$ Values in Acetonitrile at 288.15, 298.15, 308.15, and 318.15 K

ion	T = 288.15 K		T = 298.15 K		T = 308.15 K		T = 318.15 K	
	B	$\Delta\mu^{0\neq}_2$	B	$\Delta\mu^{0\neq}_2$	B	$\Delta\mu^{0\neq}_2$	B	$\Delta\mu^{0\neq}_2$
	dm^3mol^{-1}	kJ mol^{-1}	dm^3mol^{-1}	kJ mol^{-1}	dm^3mol^{-1}	kJ mol^{-1}	dm^3mol^{-1}	kJ mol^{-1}
Et_4N^+	0.363	24.69	0.349	24.48	0.346	24.77	0.344	25.13
Pr_4N^+	0.427	30.99	0.410	30.73	0.406	31.37	0.403	31.47
Bu_4N^+	0.628	43.21	0.600	42.84	0.593	43.33	0.587	43.89
Pen_4N^+	0.684	48.71	0.655	48.71	0.646	49.25	0.637	49.77
Hex_4N^+	0.799	57.63	0.768	57.36	0.752	57.69	0.734	57.94
Hep_4N^+	1.023	71.17	0.986	70.86	0.950	70.52	0.928	70.82
Br^-	0.351	21.29	0.335	21.19	0.307	20.38	0.294	20.17
Ph_4B^-	0.770	52.94	0.736	52.48	0.726	53.07	0.720	53.76

Table 7. Ionic Radii R_+ in Acetonitrile at 298.15 K

ion	r_c / nm[a]	R_+ / nm
Et_4N^+	0.400	0.331
Pr_4N^+	0.452	0.402
Bu_4N^+	0.500	0.456
Pen_4N^+	0.529	0.470
Hex_4N^+	0.560	0.496
Hep_4N^+	0.586	0.539
Ph_4B^-	0.535	0.489
Br^-	0.195	0.376

[a]Crystallographic radii.