CHAPTER IV

Viscosities of some tetraalkylammonium bromides in 2-ethoxyethanol at 308.15, 313.15, 318.15 and 323.15 K

Introduction

Recently, we have initiated a comprehensive program to study the solvation and association behaviour of several 1:1 electrolytes in different nonaqueous solvents from the measurements of various transports, thermodynamic and spectroscopic properties[1-5]. As a part of this series of investigations, we have, very recently, reported[6,7] the results of conductance measurements on a number of tetraalkylammonium salts *e.g.*, tetraethylammonium bromide (Et_4NBr), tetrapropylammonium bromide (Pr_4NBr), tetrabutylammonium bromide (Bu_4NBr), tetrapentylammonium bromide (Pen_4NBr), and tetraheptylammonium bromide (Hep_4NBr) in 2-ethoxyethanol at 308.15, 313.15, 318.15 and 323.15 K. We have now extended this work to study the viscometric behavior of these electrolyte solutions since viscometry is well-suited to provide information concerning the solvation of the ions and their effects on the structure of the solvent in the near environment of the solute particles[8-10].

Experimental

2-Ethoxyethanol (G. R. E. Merck) was dried with potassium carbonate and distilled twice in an all glass distillation set immediately before use and the middle fraction was collected. The densities, and viscosities of 2-ethoxyethanol at 308.15, 313.15, 318.15 and 323.15 K are reported in Table 1. The physical properties of the purified solvent are found to be in good agreement with the literature values[11-15]. Also included in this table are the relative permittivities (ε) of 2-ethoxyethanol at different temperatures obtained from the literature[7,11].

Tetraalkylammonium bromides were of purum or puriss grade (Fluka) and were purified as described in the literature[16]. These salts were purified by recrystallization and the higher homologues (tetrapentylammonium bromide and tetraheptylammonium bromide) were recrystallized twice to ensure maximum purity. The recrystallized salts were dried *in vacuo* at elevated temperatures for 12h immediately prior to use.

The kinematic viscosities (ν) were measured by means of a suspended level Ubbelohde viscometer. The viscometer was kept in a vertical position in a water thermostat controlled to ± 0.01 K. The kinematic viscosity (ν) and the absolute viscosity (η) are given by the following equations:

$$\nu = Ct - K/t \tag{1}$$

$$\eta = \nu\rho \tag{2}$$

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 the viscosity values of water and 2-methoxyethanol[17], were found to be 1.646×10^{-5} $\text{cm}^2 \cdot \text{s}^{-2}$ and -0.02331647 cm^2, respectively. The calibration constants were also checked with methanol[18]. The estimated error of the viscosity measurements was ± 0.05 %. The required densities (ρ) were measured with an Ostwald-Sprengel type pycknometer having a bulb volume of 25 cm^3 and an internal diameter of the capillary of about 0.1 cm. The relative viscosity (η_r) was obtained as the ratio of the absolute viscosity of the solution (η) to that of the pure solvent (η_0).

The solutions were prepared by mass for the viscosity runs, the molalities being converted to molarities by the use of densities. In order to avoid moisture pick-up, all solutions were prepared in a dehumidified room with utmost care. In all cases the experiments were performed at least in five replicates for each solution and the results were averaged. Several independent solutions were prepared and the runs were performed to ensure the reproducibility of the results.

Results and discussion

The measured relative viscosities (η_r) and densities (ρ) of electrolyte solutions as functions of molar concentrations (c) at 308.15, 313.15, 318.15 and 323.15 K are given in Table 2.

The relative viscosities of the electrolytes in solution are generally analyzed by the Jones-Dole equation[19]:

$$\eta_r = 1 + Ac^{1/2} + Bc \tag{3}$$

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

As the electrolytes investigated here are found to be somewhat associated from our earlier conductivity measurements[6,7], the viscosity data have been analyzed by the following equation [19]:

$$\eta_r = 1 + A(\alpha c)^{1/2} + B\alpha c + B'(1-\alpha)c \tag{4}$$

Here A, B, and B' are the characteristic constants and α is the degree of dissociation of the ion pair.

Eq. (4) can be rearranged to give

$$[\eta_r - 1 - A(\alpha c)^{1/2}]/\alpha c = B + B'\left(\frac{1-\alpha}{\alpha}\right) \tag{5}$$

For the evaluation of B-coefficients from Eq. (5), plots of $[\eta_r - 1 - A(\alpha c)^{1/2}]/\alpha c$ against $(1-\alpha)/\alpha$ were constructed. These were found to be linear in all cases. A representative plot displays the variation of $[\eta_r - 1 - A(\alpha c)^{1/2}]/\alpha c$ against $(1-\alpha)/\alpha$ at 308.15 K (Fig.1). The values of α were calculated from the conductance data[6,7] using the equations described in the literature[9]. The A values were calculated theoretically from the physical parameters of the solvent and the limiting ionic equivalent conductances using the Falkenhagen and Vernon equation [20]:

$$A = \frac{0.2577\Lambda^0}{\eta_0(\varepsilon T)^{1/2}\lambda_+^0\lambda_-^0}\left[1 - 0.6863\left(\frac{\lambda_+^0 - \lambda_-^0}{\Lambda^0}\right)^2\right] \tag{6}$$

where η_0 is the coefficient of viscosity of the solvent, ε is its relative permittivity, T is the temperature in absolute scale, and Λ^0, λ_+^0, and λ_-^0 are the limiting equivalent conductivities of the electrolyte, cation, and anion respectively. The values of the A coefficients thus obtained are recorded in Table 3. These have been used for the analysis of the viscosity data. The viscosity B-coefficients have also been included in Table 3. The viscosity data have also been analyzed on the basis of the transition-state treatment of the relative viscosity of electrolyte solutions, as suggested by Feakins *et. al.*[21]:

$$B = \frac{\bar{V}_1^0 - \bar{V}_2^0}{1000} + \frac{\bar{V}_1^0}{1000}\left(\frac{\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq}}{RT}\right) \tag{7}$$

In the above equation, $\bar{V}_1^0$ and $\bar{V}_2^0$ are the partial molar volumes of the solvent and solute, respectively. The contribution per mole of solute to the free energy of activation for viscous flow of the solution, $\Delta\mu_2^{0\neq}$, has been determined from the above relationship and is reported in Table 3. The free energy of activation per mole of the pure solvent, $\Delta\mu_1^{0\neq}$ is given by the equation:

$$\Delta\mu_1^{0\neq} = \Delta G_1^{0\neq} = RT\ln\left(\frac{\eta_0\bar{V}_1^0}{hN}\right) \tag{8}$$

where N is the Avogadro's number and the other symbols have their usual significance.

The action parameters for viscous flow for the electrolytes obtained from Eq. (7) are given in Table 3.

The viscosity *B*-coefficients shown in Table 3 are large and positive for all the electrolytes studied. The *B* values for the tetraalkylammonium bromides increase regularly as we go from tetraethylammonium bromide through tetraheptylammonium bromide. From this table we see that $\Delta\mu_2^{0\neq}$ values for all the electrolytes are also large and positive, and they follow the same pattern as the *B* values.

In order to investigate the specific behavior of the individual ions comprising these electrolytes, it is necessary to split the viscosity *B*-coefficients into their ionic components.

Krumgalz[22] proposed a method, to be applied for nonaqueous solvents, based on his contention that the larger tetraalkylammonium ions are essentially unsolvated in such solvents. Plots of the *B*-coefficients of iodides of these cations in several organic solvents against the cubes of the radii of the ions are indeed found to be linear for Bu_4N^+ and larger cations, values being known upto Hep_4N^+ [22]. The intercepts of the straight lines then give the *B*-coefficient of the counterion, iodide.

$$B(R_4N^+) = B(I^-) + br^3_{R_4N^+} \tag{9}$$

The slope depends on the solvent and the temperature. The *B*-coefficient of Pr_4NI may conform to the straight line obtained using the larger cations in some solvents and not in others, whereas the values for Et_4NI and Me_4NI generally fall below the line. Possibly the position of these tetraalkylammonium ions are caused by the shape of these ions during the viscous flow process in 2-ethoxyethanol making a relatively smaller contribution to *B*-values. This would result from a more compact arrangement of the alkyl groups around the central nitrogen.

Since, the tetraalkylammonium ions investigated in this work are found to be unsolvated in 2-ethoxyethanol from our earlier conductivity study[6,7], the method of Krumgalz[22] described above should, in principle, be applicable to the present viscosity data. In fact, we obtained very good straight lines (*cf.* Fig. 2) for tetraalkylammonium bromides with tetrapropylammonium and larger cations when B (R_4NBr) values are plotted against the cubes of the radii of the cations (r) obtained from the literature[23-25] at all temperatures investigated (Et_4NBr being an exception, B-coefficients of which always fall below the lines). The ionic viscosity B-coefficients obtained following the Krumgalz method[22] are given in Table 4.

The observed order of the viscosity B-values for the tetraalkylammonium ions (Table 3), $Hep_4N^+ > Pen_4N^+ > Bu_4N^+ > Pr_4N^+ > Et_4N^+$ (anion being common), shows that the obstruction of the solvent viscous flow increases with an increase in the size of these species in solution. This clearly indicates lack of solvation of these ions in 2-ethoxyethanol solutions. Had these ions been solvated in 2-ethoxyethanol, the smaller ions with greater charge density would have been more solvated and the order of the ionic viscosity B-coefficients would have been in the reverse order which is, obviously, not the case here.

Fig. 3 shows the temperature dependence of the viscosity B-coefficients of the bromide and tetraalkylammonium ions in 2-ethoxyethanol. For all the ions studied, the B-values are positive and their temperature coefficients are small; although positive coefficients are exhibited by the tetraalkylammonium ions, they are negligibly small. Bromide ion, however, shows a comparatively larger negative temperature coefficient. The temperature dependence of the B-coefficients for the tetraalkylammonium ions in methanol, *N*-methylformamide, *N*-methylpropionamide, and *N*-methylacetamide are also small[10,26,27], and we find the same behavior in the present solvent medium. This finding is in sharp contrast to the abnormally large temperature dependence of the B-coefficients in water[10], and the remarkable difference can be ascribed to the extensive-hydrogen-bonded structure of water. The negligibly small dB/dT values of the tetraalkylammonium ions indicate that they behave neither as structure breaker nor as structure maker in 2-ethoxyethanol whereas the negative dB/dT value for bromide ion in this medium demonstrates its structure-making behavior.

The ionic free energies of activation for viscous flow, $\Delta\mu_2^{0\neq}$ (ion), based on a method similar to that used for the separation of the viscosity *B*-coefficients have been presented in Table 4. The $\Delta\mu_2^{0\neq}$ values of the tetraalkylammonium ions are always found to be positive thus indicating that the formation of the transition state is made less favorable in the presence of these ions. The ionic $\Delta\mu_2^{0\neq}$ values in the present series of tetraalkylammonium ions increase steadily with the formula weight of the cations (*cf.* Table 4); this behavior is reasonable when solvation effects are not over-riding.

References

1 C. Guha, J. M. Chakraborty, S. Karanjai and B. Das. *J. Phys. Chem.*, 107, 12814 (2003).

2 D. Das, B. Das and D. K. Hazra. *J. Solution Chem.*, **32**, 77 (2003).

3 D. Das, B. Das and D. K. Hazra. *J. Solution Chem.*, **32**, 85 (2003).

4 J. M. Chakraborty and B. Das. *Z. Phys. Chem.*, **218**, 219 (2004).

5 D. Das, B. Das and D. K. Hazra. *J. Mol. Liq.*, **111**, 15 (2004).

6 P. Haldar and B. Das. *Z. Phys. Chem.*, **218**, 599 (2004).

7 P. Haldar and B. Das. *Z. Phys. Chem.*, **218**, 1129 (2004).

8 R.W. Gurney, In *Ionic processes in solution*, Dover Publications, New York, 1962.

9 J. Crudden, G. M. Delaney, D. Feakins, P. J. O'Reilley, W. E. Waghorne and K. G. Lawrence. *J. Chem. Soc., Faraday Trans.* 1, **82**, 2195 (1986).

10 H. D. B. Jenkins and Y. Marcus. *Chem. Rev.* **95**, 2695 (1995).

11 G. Douheret and A. Pal. *J. Chem. Eng. Data.*, **32**, 40 (1998).

12 Y. Marcus, *In Ion solvation*, John Wiley & Sons, New York, 1985.

13 M. I. Aralaguppi, C. V. Jadar and T. M. Aminabhavi. *J. Chem. Eng. Data.*, **42**, 301 (1997).

14 A. Pal and S. Kumar, *Phys. Chem. Liq.* **41**, 423 (2003).

15 G. Chandrasekhar, P. Ventatesu and M. V. Prabhakara Rao. *J. Chem. Eng. Data.*, **45**, 590 (2004).

16 D. F. Evans, C. Zawoyski and R. L. Kay. *J. Phys. Chem.*, **69**, 387, (1965).

17 B. Das and D. K. Hazra. J. Chem. Eng. Data. **38**, 361 (1993).

18 N. Saha, B. Das and D. K. Hazra, *J. Chem. Eng. Data.*, **40**, 1264, (1995).

19 G. Jones and M. Dole, *J. Am. Chem. Soc.*, **51**, 2950, (1929).

20 H. Falkenhagen and E. L. Vernon. *Phys. Z.* **33**, 140, (1932).

21 D. Feakins, D. J. Freemantle and K. G. Lawrence. *J. Chem. Soc., Faraday Trans.* 1, 70, 795 (1974).

22 S. Krumgalz. *J. Chem. Soc., Faraday Trans.* 1, **76**, 1275 (1980).

23 P. K. Muhuri and D. K. Hazra, *Z. Naturforsch.* **48a**, 523 (1993).

24 D. S. Gill and M. B. Sekhri, *J. Chem. Soc., Faraday Trans.*, 1, **78**, 119 (1982).

25 J. F. Coetzee and G. P. Cunningham, *J. Am Chem. Soc.,* **87**, 2529 (1965).

26 R. L. Kay, T. Vituccio, C. Zawoyski and D. F. Evans, *J. Phys. Chem.*, **70**, 2336 (1966).

27 R. L. Kay, C. Zawoyski and D. F. Evans, *J. Phys. Chem.*, **69**, 4208 (1965).

Table 1. Physicochemical properties of 2-ethoxyethanol at different temperatures.

T / K	ρ_0 / g cm^{-3}		η_0 / mPa. s		ε
	exptl.	lit.	exptl.	lit.	
298.15	0.92497	0.92502 (11) 0.9252 (12) 0.9258 (13)	1.8277	1.85 (12)	13.38
308.15	0.91735	0.91674 (14) 0.91671 (15) 0.9163 (13)	1.5179		12.81
313.15	0.91370		1.3594		12.52
318.15	0.90994		1.1893		12.25
323.15	0.90602		1.0871		11.99

Table 2. Molar concentrations, densities and relative viscosities of some tetraalkylammoniumbromides in 2-ethoxyethanol at 308.15, 313.15, 318.15 and 323.15 K

c /mol dm^{-3}	ρ /g cm^{-3}	η_r	c /mol dm^{-3}	ρ /g cm^{-3}	η_r
308.15 K					
Et$_4$NBr			Pr$_4$NBr		
0.01015	0.91836	1.0080	0.01008	0.91838	1.0091
0.02031	0.91933	1.0160	0.02016	0.91935	1.0181
0.03046	0.92029	1.0237	0.03024	0.92032	1.0271
0.04062	0.92127	1.0314	0.04032	0.92130	1.0362
0.05077	0.92222	1.0397	0.05040	0.92226	1.0453
0.06092	0.92318	1.0477	0.06048	0.92323	1.0541
Bu$_4$NBr			Pen$_4$NBr		
0.00999	0.91842	1.0106	0.00996	0.91844	1.0111
0.0199	0.91939	1.0211	0.01992	0.91941	1.0214
0.02997	0.92037	1.0312	0.02988	0.92039	1.0317
0.03996	0.92136	1.0411	0.03984	0.92138	1.0418
0.04995	0.92233	1.0511	0.04980	0.92234	1.0518
0.05994	0.92331	1.0611	0.05976	0.92333	1.0621
Hep$_4$NBr					
0.01012	0.91847	1.0128			
0.02024	0.91944	1.0246			
0.03036	0.92043	1.0346			
0.04048	0.92142	1.0458			
0.05060	0.92238	1.0561			
0.06072	0.92336	1.0689			
313.15 K					
Et$_4$NBr			Pr$_4$NBr		
0.01011	0.91471	1.0081	0.01004	0.91473	1.0092
0.02023	0.91572	1.0162	0.02008	0.91575	1.0183
0.03034	0.91674	1.0239	0.03012	0.91675	1.0274

Table 2. Continued

Table 2. (Contd.)

c /mol dm^{-3}	ρ /g cm^{-3}	η_r	c /mol dm^{-3}	ρ /g cm^{-3}	η_r
0.04046	0.91774	1.0319	0.04016	0.91775	1.0365
0.05058	0.91876	1.0401	0.05021	0.91876	1.0457
0.06070	0.91975	1.0480	0.06025	0.91975	1.0545
Bu$_4$NBr			Pen$_4$NBr		
0.00995	0.91475	1.0107	0.00992	0.91476	1.0112
0.01990	0.91577	1.0212	0.01984	0.91576	1.0216
0.02985	0.91676	1.0314	0.02976	0.91677	1.0319
0.03980	0.91778	1.0412	0.03968	0.91779	1.0421
0.04976	0.91878	1.0512	0.04961	0.91879	1.0521
0.05971	0.91979	1.0612	0.05935	0.91982	1.0621
Hep$_4$NBr					
0.01008	0.91481	1.0129			
0.02016	0.91581	1.0249			
0.03024	0.91682	1.0368			
0.04032	0.91785	1.0462			
0.05038	0.91885	1.0566			
0.06049	0.91987	1.0695			
318.15 K					
Et$_4$NBr			Pr$_4$NBr		
0.01007	0.91095	1.0083	0.01000	0.91099	1.0094
0.02014	0.91196	1.0163	0.02000	0.91198	1.0185
0.03022	0.91297	1.0239	0.03000	0.91298	1.0277
0.04029	0.91396	1.0321	0.04000	0.91399	1.0368
0.05037	0.91498	1.0401	0.0500	0.91501	1.0461
0.06045	0.91601	1.0482	0.06000	0.91604	1.0549
Bu$_4$NBr			Pen$_4$NBr		
0.00991	0.91101	1.0109	0.00988	0.91103	1.0115
0.01982	0.91201	1.0213	0.01976	0.91202	1.0220
0.02973	0.91299	1.0315	0.02964	0.91300	1.0323

Table 2 (Contd.)

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c /mol dm^{-3}	ρ /g cm^{-3}	η_r	c /mol dm^{-3}	ρ /g cm^{-3}	η_r
0.03964	0.91401	1.0413	0.03952	0.91403	1.0425
0.04956	0.91504	1.0515	0.04941	0.91505	1.0527
0.05947	0.91607	1.0613	0.05929	0.91608	1.0630
Hep$_4$NBr					
0.01004	0.91107	1.0133			
0.02008	0.91207	1.0253			
0.03012	0.91305	1.0373			
0.04016	0.91409	1.0468			
0.05020	0.91509	1.0571			
0.06024	0.91612	1.0699			
323.15 K					
Et$_4$NBr			Pr$_4$NBr		
0.01003	0.90703	1.0084	0.00996	0.90705	1.0095
0.02006	0.90802	1.0165	0.01991	0.90805	1.0187
0.03009	0.90905	1.0240	0.02987	0.90907	1.0280
0.04012	0.91004	1.0324	0.03983	0.91009	1.0371
0.05016	0.91107	1.0407	0.04980	0.91112	1.0465
0.06019	0.91208	1.0485	0.05975	0.91213	1.0554
Bu$_4$NBr			Pen$_4$NBr		
0.00987	0.90708	1.0110	0.00984	0.90709	1.0116
0.01978	0.90806	1.0215	0.01967	0.90807	1.0222
0.02960	0.90909	1.0316	0.02951	0.90911	1.0325
0.03947	0.91012	1.0413	0.03935	0.91014	1.0427
0.04934	0.91115	1.0515	0.04920	0.91116	1.0530
0.05921	0.91215	1.0614	0.05904	0.91216	1.0631
Hep$_4$NBr					
0.00999	0.90704	1.0135			
0.01999	0.90812	1.0257			
0.02999	0.90916	1.0378			
0.03999	0.91019	1.0474			
0.04999	0.91118	1.0577			
0.05999	0.91221	1.0706			

Table 3. Theoretical *A*-coefficients, the viscosity *B*-coefficients and the free energies of activation for viscous flow of electrolytes in 2-ethoxyethanol at 308.15, 313.15, 318.15, and 323.15 K.

Electrolyte	A /dm$^{\frac{3}{2}}$ mol$^{-\frac{1}{2}}$	B /dm^3 mol^{-1}	$\Delta\mu_2^{\theta\neq}$ /kJ mol^{-1}
308.15 K			
Et_4NBr	0.0290	0.216 ± 0.001	21.52
Pr_4NBr	0.0309	0.444 ± 0.001	29.02
Bu_4NBr	0.0328	0.554 ± 0.005	33.44
Pen_4NBr	0.0356	0.649 ± 0.001	37.51
Hep_4NBr	0.0417	0.833 ± 0.002	45.55
313.15 K			
Et_4NBr	0.0316	0.196 ± 0.001	20.91
Pr_4NBr	0.0339	0.428 ± 0.001	28.65
Bu_4NBr	0.0361	0.534 ± 0.006	33.02
Pen_4NBr	0.0391	0.629 ± 0.001	37.13
Hep_4NBr	0.0460	0.820 ± 0.004	45.46
318.15 K			
Et_4NBr	0.0354	0.179 ± 0.001	20.41
Pr_4NBr	0.0378	0.411 ± 0.001	28.23
Bu_4NBr	0.0406	0.512 ± 0.004	32.54
Pen_4NBr	0.0444	0.603 ± 0.001	36.62
Hep_4NBr	0.0514	0.814 ± 0.004	45.57
323.15 K			
Et_4NBr	0.0377	0.168 ± 0.002	20.16
Pr_4NBr	0.0404	0.396 ± 0.001	27.95
Bu_4NBr	0.0444	0.493 ± 0.005	32.32
Pen_4NBr	0.0476	0.587 ± 0.001	36.40
Hep_4NBr	0.0551	0.800 ± 0.004	45.52

Table 4. Ionic viscositiy *B*-coefficients, and ionic free energies of activation for viscous flow in 2-ethoxyethanol at 308.15, 313.15, 318.15, and 323.15 K.

ion	308.15 K	313.15 K	318.15 K	323.15 K
$B_{\pm}$/dm^3 mol^{-1}				
Et_4N^+	0.099	0.102	0.117	0.125
Pr_4N^+	0.327	0.333	0.349	0.353
Bu_4N^+	0.437	0.439	0.450	0.450
Pen_4N^+	0.532	0.534	0.541	0.544
Hep_4N^+	0.716	0.725	0.752	0.757
Br^-	0.117	0.095	0.062	0.044
$\Delta\mu_2^{\theta\neq}$ /kJ mol^{-1}				
Et_4N^+	6.56	6.65	7.19	7.43
Pr_4N^+	14.06	14.39	15.01	15.22
Bu_4N^+	18.48	18.76	19.32	19.59
Pen_4N^+	22.55	22.87	23.40	23.67
Hep_4N^+	30.59	31.20	32.35	32.79
Br^-	14.96	14.2	13.2	12.73

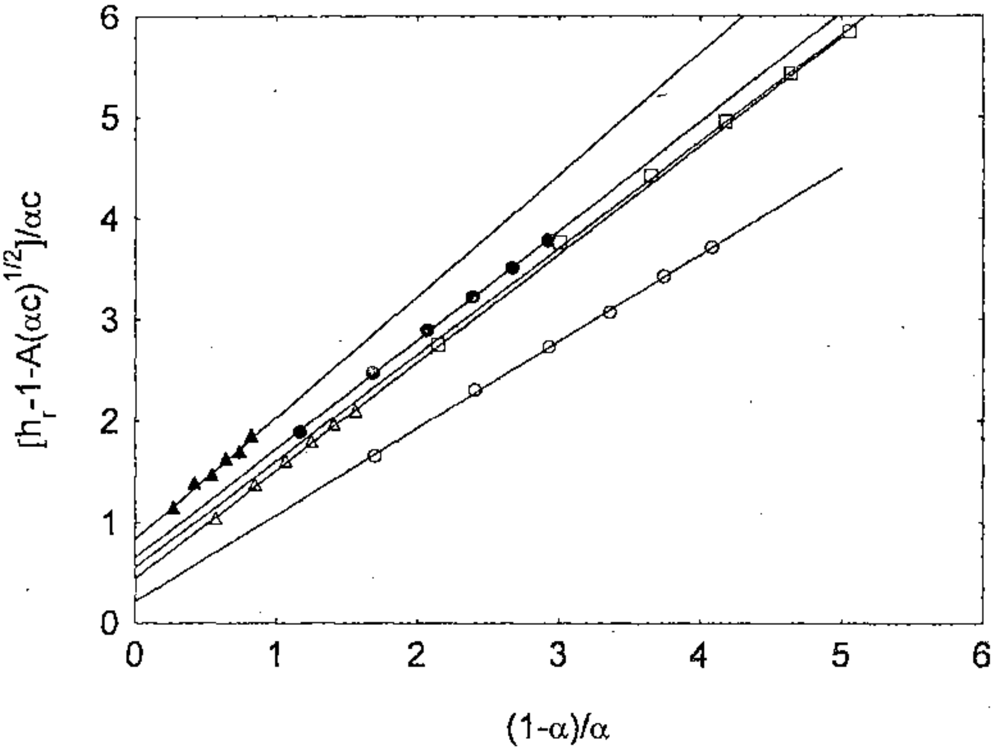

Fig. 1. Variation of $[\eta_r - 1 - A(\alpha c)^{1/2}]/\alpha c$ against $(1-\alpha)/\alpha$ at 308.15 K in 2-ethoxyethanol for Et_4NBr (○), Pr_4NBr (△), Bu_4NBr (□), Pen_4NBr (●) and Hep_4NBr (▲).

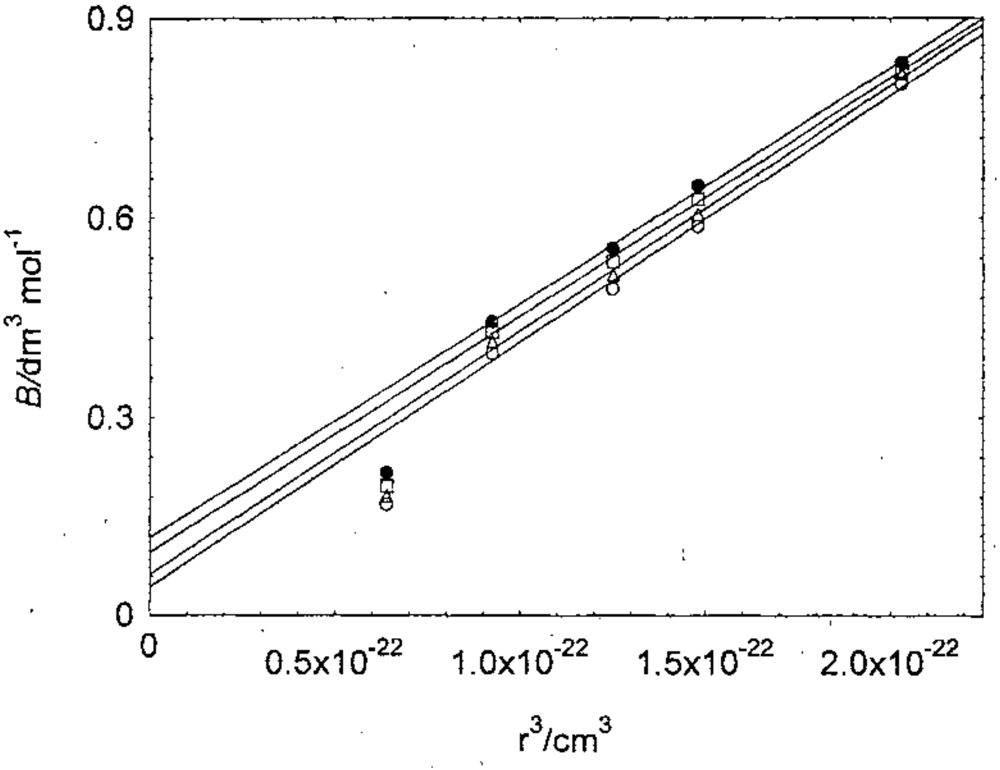

Fig. 2. Representative plot for the variation of the viscosity *B*-coefficient of the tetraalkylammonium bromides against the cube of cationic radius in 2-ethoxyethanol at 308.15 K (○), 313.15 K (△), 318.15 K (□) and 323.15 K (●).

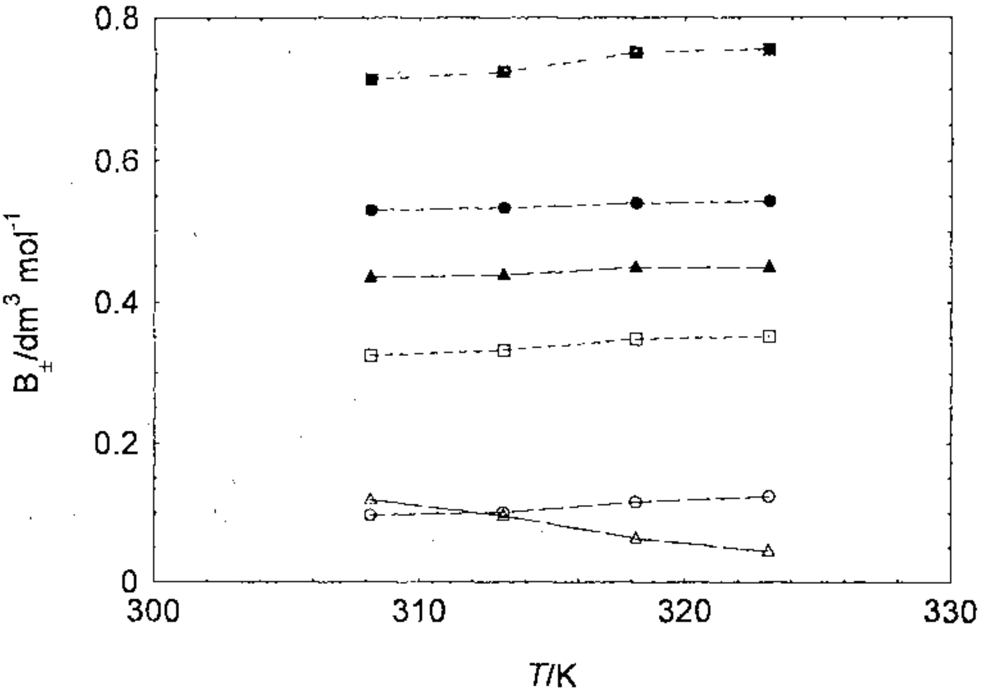

Fig. 3. Temperature dependence of the ionic viscosity *B*-coefficients in 2-ethoxyethanol for Br^-(△), Et_4N^+(○), Pr_4N^+(□), Bu_4N^+(▲), Pen_4N^+(●), Hep_4N^+(■).