

CHAPTER VI

Viscosities of some tetraalkylammonium and alkali metal salts in 2-ethoxyethanol + water mixed solvent media 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 transport, thermodynamic and spectroscopic properties¹⁻⁵. 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 (Et₄NBr), tetrapropylammonium bromide (Pr₄NBr), tetrabutylammonium bromide (Bu₄NBr), tetrapentylammonium bromide (Pen₄NBr), and tetraheptylammonium bromide (Hep₄NBr) 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 particles⁸⁻¹⁰.

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 purified solvent had a density (ρ_0) of 0.92497 g·cm⁻³ and a viscosity (η_0) of 1.8277 mPa·s at 298.15 K; these values are found to be in good agreement with the literature values^{11,12}. Triply distilled water with a specific conductance of less than 10⁻⁶ S·cm⁻¹ at 308.15 K was used for the preparation of the mixed solvents by mass. The physical properties of 2-ethoxyethanol-water mixed solvents used in this study at 308.15, 313.15, 318.15, and 323.15 K are reported in Table 1. The relative permittivities of 2-ethoxyethanol-water mixtures

at the experimental temperatures were obtained with the equations as described in the literature¹³ using the literature density and relative permittivity data of the pure solvents^{7,14} and the densities of the mixed solvents given in Table 1.

Tetraalkylammonium bromides were of purum or puriss grade (Fluka) and were purified as described in the literature¹⁵. These salts were purified by recrystallization. The recrystallized salts were dried *in vacuo* at elevated temperatures for 12 h immediately prior to use.

Sodium tetraphenylborate (Fluka, purissimum) was recrystallized from acetone and dried *in vacuo* at 353.15 K for 72 h. Sodium bromide (Fluka, purum) was dried *in vacuo* for 72 h and was used without further purification.

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:

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

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

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-methoxyethanol¹⁶, were found to be $1.646 \times 10^{-5} \text{ cm}^2 \text{ s}^{-2}$ and -0.02331647 cm^2 , respectively. The calibration constants were also checked with methanol¹⁷. The estimated error of the viscosity measurements was ± 0.05 %. The required 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 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 several 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 equation¹⁸:

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

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 (Chapter V), the viscosity data have been analyzed by the following equation⁹:

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

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

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

For the evaluation of B -coefficients from Eq. (5), plots of $[\eta, -1 - A(\alpha\alpha)^{1/2}]/\alpha\alpha$ against $(1-\alpha)/\alpha$ were constructed. These were found to be linear in all cases. The values of α were calculated from the conductance data (Chapter V) using the equations described in the literature⁹. The A values were calculated theoretically from the physical parameters of the solvent and the limiting ionic equivalent conductances using the Falkenhagen and Vernon equation¹⁹:

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

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.*²⁰:

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

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, $\Delta\mu_2^{0*}$, has been determined from the above relationship and is reported in Table 3. The free energy of activation per mole of the pure solvent, $\Delta\mu_1^{0*}$ is given by the equation:

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

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

The activation 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 found to be large and positive in 2-ethoxyethanol-water mixtures for the electrolytes studied. The B values for the tetraalkylammonium bromides increase regularly as we go from tetraethylammonium bromide to tetrabutylammonium bromide. From this table we see that $\Delta\mu_2^{0\#}$ 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 of the electrolytes into their ionic components. The ionic B -values were calculated using tetrabutylammonium tetraphenylborate (Bu_4NBPh_4) as the "reference electrolyte" from the following equations^{21,22}:

$$B(\text{Bu}_4\text{NBPh}_4) = B(\text{Bu}_4\text{N}^+) + B(\text{Ph}_4\text{B}^-) \quad (9)$$

$$\frac{B_{\text{Ph}_4\text{B}^-}}{B_{\text{Bu}_4\text{N}^+}} = \frac{r_{\text{Ph}_4\text{B}^-}^3}{r_{\text{Bu}_4\text{N}^+}^3} = \left(\frac{5.35}{5.00} \right)^3 \quad (10)$$

The r -values for the Bu_4N^+ and Ph_4B^- ions were taken from the literature^{23,24}.

The ionic B -coefficients obtained from the above relationships are given in Table 4. This table shows that in 2-ethoxyethanol-water mixed solvent media the viscosity B -coefficients for all cations and anions are positive and are also very high with the exception of sodium ion. The observed order of the ionic B values for the molecular ions, $\text{Ph}_4\text{B}^- > \text{Bu}_4\text{N}^+ > \text{Pr}_4\text{N}^+ > \text{Et}_4\text{N}^+$, shows that the obstruction

of the solvent viscous flow increases with an increase of size of these species in solution. This clearly indicates lack of solvation of these ions in 2-ethoxyethanol-water mixed solvent media within the temperature range investigated. Had these ions been solvated in aqueous 2-ethoxyethanol solutions, 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. In case of Na^+ ion, it might be that the viscosity of the solvent is very little modified by its presence in solution resulting in a very low viscosity B coefficient for this ion.

Figs. 1-3 shows the temperature dependence of the ionic viscosity B -coefficients in 2-ethoxyethanol-water mixtures. For all the ions studied, the B -values are positive (except sodium ion for which B -values are found to slightly negative at least for two temperatures investigated in 2-ethoxyethanol-water mixture containing 75 per cent of 2-ethoxyethanol) and their temperature coefficients (which are always positive) are negligibly small. The temperature dependence of the B -coefficients for the tetraalkylammonium ions in methanol, N -methylformamide, N -methylpropionamide, and N -methylacetamide are also small^{10,25,26}, and we find the same behavior in the present mixed solvent media. This finding is in sharp contrast to the abnormally large temperature dependence of the B -coefficients in water¹⁰, and the remarkable difference can be ascribed to the extensive hydrogen-bonded structure of water. The negligibly small dB/dT values of the investigated ions indicate that they behave neither as structure breaker nor as structure maker in 2-ethoxyethanol-water mixtures.

The ionic free energies of activation for viscous flow, $\Delta\mu_2^{0\ddagger}$ (ion), based on a method similar to that used for the separation of the viscosity B -coefficients have been presented in Table 4. The $\Delta\mu_2^{0\ddagger}$ values of the ions investigated 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 in 2-ethoxyethanol-water mixed solvent media. The ionic $\Delta\mu_2^{0\ddagger}$ values for the tetraalkylammonium and tetraphenylborate ions increase monotonically with the formula weight of these

ions (*cf.* Table 4) thus supporting their scarce solvation in the present mixed solvent media.

The composition dependence of the ionic viscosity B -coefficients in 2-ethoxyethanol-water mixtures are depicted in Figs. 4-7. The reason for the observed change in the viscosity B -coefficients of the ions (except the sodium ion) in the region of 70-80 weight per cent of 2-ethoxyethanol may be attributed to the structural changes and changed ion-solvent interactions in this region. Intermolecular hydrogen bonding gives water a distinct geometrical structure in the form of three dimensional arrays. Due to lack of non-chemical forces, water has an open and flexible structure²⁷. The addition of 2-ethoxyethanol to water first strengthens the three dimensional structure of water. Further addition of 2-ethoxyethanol causes depolymerisation of water structure but interactions between 2-ethoxyethanol and water lead to the formation of 2-ethoxyethanol-water complexes, with a bigger solvodynamic entity. Viscosity thus increases upto approximately 40-50 weight per cent of 2-ethoxyethanol after which 2-ethoxyethanol-water structure breaks down leading to a decrease in the viscosity B -coefficients of the ions.

It may thus be concluded that the tetraalkylammonium, tetraphenylborate and bromide ions greatly modify the viscosity of the 2-ethoxyethanol-water mixed solvent media. In case of Na^+ ion, however, the viscosity of the solvent is very little modified by its presence in solution resulting in a very low viscosity B -coefficient for this ion. The tetraalkylammonium and tetraphenylborate ions are found to remain unsolvated in 2-ethoxyethanol-water mixed solvent media within the temperature range investigated. Moreover, the investigated ions behave neither as structure breaker nor as structure maker and the formation of the transition state is made less favorable in the presence of these ions in 2-ethoxyethanol-water mixed solvent media.

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Table 1. Properties of 2-ethoxyethanol + water mixtures with 0.25, 0.50, and 0.75 mass fractions (w_1) of 2-ethoxyethanol at 308.15, 313.15, 318.15 and 323.15 K

T/K	$\rho_0/\text{g cm}^{-3}$	$\eta_0/\text{mPa s}$	ϵ
$w_1 = 0.25$			
308.15	1.00354	1.8430	60.13
313.15	1.00021	1.5293	58.70
318.15	0.99781	1.2738	57.37
323.15	0.99582	1.0923	56.11
$w_1 = 0.50$			
308.15	0.99361	1.9234	44.30
313.15	0.98514	1.7195	43.03
318.15	0.98004	1.4552	41.95
323.15	0.97610	1.2762	40.96
$w_1 = 0.75$			
308.15	0.95451	1.7002	27.93
313.15	0.95147	1.5293	27.29
318.15	0.94873	1.3498	26.68
323.15	0.94625	1.1901	26.10

Table 2. Molar concentrations, densities and relative viscosities of some tetraalkylammonium and alkali metal salts in 2-ethoxyethanol + water mixtures with 0.25, 0.50 and 0.75 mass fractions (w_1) of 2-ethoxyethanol at 308.15, 313.15, 318.15 and 323.15 K

$c/\text{mol.dm}^{-3}$	$\rho/\text{g.cm}^{-3}$	η_r	$c/\text{mol.dm}^{-3}$	$\rho/\text{g.cm}^{-3}$	η_r
Et₄NBr					
$T = 308.15 \text{ K}$			$T = 313.15 \text{ K}$		
0.00998	1.00479	1.0036	0.00995	1.00144	1.0038
0.01996	1.00606	1.0069	0.01989	1.00266	1.0074
0.02994	1.00725	1.0103	0.02984	1.00389	1.0109
0.03992	1.00854	1.0133	0.03979	1.00513	1.0146
0.04990	1.00982	1.0172	0.04973	1.00636	1.0182
0.05988	1.01104	1.0205	0.05968	1.00761	1.0219
$T = 308.15 \text{ K}$			$T = 313.15 \text{ K}$		
0.00992	0.99902	1.0039	0.00990	0.99702	1.0041
0.01984	1.00023	1.0076	0.01980	0.99823	1.0078
0.02977	1.00144	1.0113	0.02971	0.99944	1.0110
0.03969	1.00266	1.0151	0.03961	1.00065	1.0147
0.04961	1.00388	1.0186	0.04951	1.00186	1.0181
0.05953	1.00510	1.0221	0.05941	1.00308	1.0216
Pr₄NBr					
$T = 308.15 \text{ K}$			$T = 313.15 \text{ K}$		
0.01016	1.00481	1.0039	0.01013	1.00148	1.0041
0.02032	1.00602	1.0075	0.02025	1.00275	1.0081
0.03048	1.00736	1.0111	0.03038	1.00403	1.0120
0.04064	1.00865	1.0147	0.04051	1.00531	1.0159
0.05080	1.00993	1.0183	0.05063	1.00660	1.0198
0.06096	1.01118	1.0219	0.06076	1.00789	1.0237

Table 2 (contd.)

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$c/\text{mol.dm}^{-3}$	$\rho/\text{g.cm}^{-3}$	η_r	$c/\text{mol.dm}^{-3}$	$\rho/\text{g.cm}^{-3}$	η_r
$T = 318.15 \text{ K}$			$T = 323.15 \text{ K}$		
0.01010	0.99904	1.0042	0.01008	0.99705	1.0044
0.02020	1.00028	1.0082	0.02016	0.99828	1.0085
0.03030	1.00152	1.0123	0.03024	0.99951	1.0127
0.04040	1.00276	1.0159	0.04032	1.00075	1.0167
0.05050	1.00400	1.0199	0.05040	1.00199	1.0209
0.06060	1.00525	1.0239	0.06048	1.00324	1.0250
Bu ₄ NBr					
$T = 308.15 \text{ K}$			$T = 313.15 \text{ K}$		
0.01023	1.00482	1.0052	0.01020	1.00147	1.0053
0.02046	1.00615	1.0101	0.02039	1.00273	1.0103
0.03069	1.00739	1.0149	0.03059	1.00400	1.0151
0.04092	1.00867	1.0194	0.04078	1.00528	1.0196
0.05115	1.00995	1.0243	0.05098	1.00665	1.0246
0.06138	1.01123	1.0289	0.06117	1.00784	1.0294
$T = 318.15 \text{ K}$			$T = 323.15 \text{ K}$		
0.01017	0.99905	1.0054	0.01015	0.99706	1.0055
0.02034	1.00030	1.0105	0.02030	0.99830	1.0106
0.03051	1.00155	1.0153	0.03045	0.99955	1.0155
0.04068	1.00281	1.0198	0.04060	1.00080	1.0202
0.05085	1.00407	1.0248	0.05075	1.00206	1.0254
0.06102	1.00534	1.0297	0.06090	1.00332	1.0302
NaBr					
$T = 308.15 \text{ K}$			$T = 313.15 \text{ K}$		
0.01023	1.00421	1.0025	0.01020	1.00086	1.0026
0.02046	1.00488	1.0049	0.02039	1.00151	1.0050
0.03069	1.00554	1.0072	0.03059	1.00216	1.0074
0.04092	1.00621	1.0096	0.04078	1.00281	1.0099
0.05115	1.00688	1.0118	0.05098	1.00347	1.0122
0.06138	1.00755	1.0141	0.06117	1.00412	1.0146

Table 2 (contd.)

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$c/\text{mol.dm}^{-3}$	$\rho/\text{g.cm}^{-3}$	η_r	$c/\text{mol.dm}^{-3}$	$\rho/\text{g.cm}^{-3}$	η_r
$T = 318.15 \text{ K}$			$T = 323.15 \text{ K}$		
0.01017	0.99844	1.0027	0.01015	0.99643	1.0028
0.02034	0.99908	1.0051	0.02030	0.99704	1.0053
0.03051	0.99971	1.0075	0.03045	0.99766	1.0077
0.04068	1.00034	1.0102	0.04060	0.99829	1.0105
0.05085	1.00098	1.0126	0.05074	0.99889	1.0131
0.06102	1.00161	1.0151	0.06089	0.99950	1.0156
NaBPh ₄					
$T = 308.15 \text{ K}$			$T = 313.15 \text{ K}$		
0.01012	1.00488	1.0058	0.01009	1.00152	1.0060
0.02024	1.00622	1.0113	0.02017	1.00284	1.0116
0.03036	1.00755	1.0169	0.03026	1.00417	1.0175
0.04048	1.00889	1.0223	0.04034	1.00550	1.0232
0.05060	1.01023	1.0278	0.05043	1.00684	1.0289
0.06072	1.01157	1.0332	0.06052	1.00818	1.0345
$T = 318.15 \text{ K}$			$T = 323.15 \text{ K}$		
0.01006	0.99912	1.0062	0.01004	0.99711	1.0064
0.02012	1.00043	1.0121	0.02008	0.99841	1.0124
0.03018	1.00175	1.0178	0.03012	0.99972	1.0179
0.04025	1.00307	1.0235	0.04016	1.00103	1.0244
0.05031	1.00440	1.0295	0.05021	1.00235	1.0304
0.06037	1.00573	1.0352	0.06025	1.00367	1.0364
$w_1 = 0.50$					
Et ₄ NBr					
$T = 308.15 \text{ K}$			$T = 313.15 \text{ K}$		
0.01003	0.99505	1.0055	0.00994	0.98657	1.0057
0.02006	0.99648	1.0108	0.01989	0.98800	1.0111
0.03009	0.99792	1.0161	0.02983	0.98943	1.0167
0.04012	0.99935	1.0213	0.03978	0.99086	1.0221
0.05015	1.00079	1.0264	0.04972	0.99229	1.0278
0.06018	1.00222	1.0321	0.05967	0.99373	1.0331

Table 2 (contd.)

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$c/\text{mol.dm}^{-3}$	$\rho/\text{g.cm}^{-3}$	η_r	$c/\text{mol.dm}^{-3}$	$\rho/\text{g.cm}^{-3}$	η_r
$T = 318.15 \text{ K}$			$T = 323.15 \text{ K}$		
0.00989	0.98146	1.0058	0.00985	0.97751	1.0060
0.01979	0.98289	1.0114	0.01971	0.97893	1.0119
0.02968	0.98432	1.0171	0.02956	0.98035	1.0177
0.03957	0.98575	1.0236	0.03941	0.98177	1.0232
0.04947	0.98727	1.0282	0.04927	0.98319	1.0295
0.05936	0.98862	1.0337	0.05912	0.98462	1.0349
Pr₄NBr					
$T = 308.15 \text{ K}$			$T = 313.15 \text{ K}$		
0.00982	0.99502	1.0059	0.00974	0.98654	1.0061
0.01964	0.99638	1.0115	0.01947	0.98794	1.0121
0.02946	0.99783	1.0171	0.02921	0.98935	1.0179
0.03928	0.99926	1.0227	0.03895	0.99075	1.0238
0.04910	1.00064	1.0283	0.04868	0.99217	1.0297
0.05892	1.00208	1.0339	0.05842	0.99358	1.0357
$T = 318.15 \text{ K}$			$T = 323.15 \text{ K}$		
0.00969	0.98144	1.0062	0.00964	0.97729	1.0064
0.01937	0.98284	1.0122	0.01929	0.97848	1.0123
0.02906	0.98424	1.0181	0.02892	0.97967	1.0182
0.03874	0.98564	1.0239	0.03856	0.98087	1.0244
0.04843	0.98705	1.0299	0.04819	0.98207	1.0303
0.05812	0.98847	1.0356	0.05781	0.98327	1.0363
Bu₄NBr					
$T = 308.15 \text{ K}$			$T = 313.15 \text{ K}$		
0.01009	0.99506	1.0071	0.01000	0.98658	1.0072
0.02018	0.99650	1.0138	0.02001	0.98802	1.0141
0.03027	0.99795	1.0205	0.03001	0.98947	1.0210
0.04036	0.99939	1.0271	0.04002	0.99092	1.0276
0.05045	1.00084	1.0338	0.05002	0.99238	1.0343
0.06054	1.00228	1.0404	0.06003	0.99385	1.0411

Table 2 (contd.)

Table 2 (contd.)

$c/\text{mol.dm}^{-3}$	$\rho/\text{g.cm}^{-3}$	η_r	$c/\text{mol.dm}^{-3}$	$\rho/\text{g.cm}^{-3}$	η_r
$T = 318.15 \text{ K}$			$T = 323.15 \text{ K}$		
0.00995	0.98148	1.0074	0.00991	0.97732	1.0075
0.01990	0.98292	1.0143	0.01982	0.97855	1.0146
0.02986	0.98436	1.0210	0.02972	0.97978	1.0213
0.03981	0.98581	1.0278	0.03962	0.98102	1.0282
0.04977	0.98727	1.0346	0.04951	0.98226	1.0351
0.05972	0.98873	1.0414	0.05941	0.98350	1.0420
NaBr					
$T = 308.15 \text{ K}$			$T = 313.15 \text{ K}$		
0.01036	0.99442	1.0031	0.01027	0.98594	1.0033
0.02072	0.99523	1.0061	0.02054	0.98674	1.0064
0.03108	0.99604	1.0090	0.03081	0.98754	1.0096
0.04144	0.99685	1.0119	0.04109	0.98834	1.0124
0.05180	0.99766	1.0147	0.05136	0.98914	1.0157
0.06216	0.99847	1.0176	0.06163	0.98995	1.0188
$T = 318.15 \text{ K}$			$T = 323.15 \text{ K}$		
0.01022	0.98082	1.0034	0.01018	0.97686	1.0036
0.02044	0.98161	1.0065	0.02035	0.97762	1.0068
0.03065	0.98239	1.0099	0.03053	0.97839	1.0102
0.04087	0.98317	1.0125	0.04070	0.97915	1.0128
0.05109	0.98396	1.0162	0.05088	0.97991	1.0166
0.06130	0.98474	1.0194	0.06105	0.98068	1.0199
NaBPh ₄					
$T = 308.15 \text{ K}$			$T = 313.15 \text{ K}$		
0.01037	0.99523	1.0075	0.01028	0.98675	1.0077
0.02074	0.99685	1.0148	0.02056	0.98837	1.0151
0.03111	0.99847	1.0219	0.03085	0.99000	1.0226
0.04148	1.00009	1.0289	0.04113	0.99163	1.0299
0.05185	1.00171	1.0363	0.05141	0.99326	1.0373
0.06222	1.00333	1.0435	0.06170	0.99491	1.0447

Table 2 (contd.)

Table 2 (contd.)

$c/\text{mol.dm}^{-3}$	$\rho/\text{g.cm}^{-3}$	η_r	$c/\text{mol.dm}^{-3}$	$\rho/\text{g.cm}^{-3}$	η_r
$T = 318.15 \text{ K}$			$T = 323.15 \text{ K}$		
0.01023	0.98164	1.0078	0.01018	0.97769	1.0080
0.02046	0.98325	1.0153	0.02037	0.97928	1.0153
0.03069	0.98486	1.0225	0.03056	0.98087	1.0228
0.04091	0.98648	1.0301	0.04075	0.98248	1.0304
0.05115	0.98810	1.0374	0.05094	0.98409	1.0379
0.06138	0.98973	1.0449	0.06113	0.98571	1.0453
$w_1 = 0.75$					
Et_4NBr					
$T = 308.15 \text{ K}$			$T = 313.15 \text{ K}$		
0.01007	0.95571	1.0068	0.01004	0.95271	1.0071
0.02014	0.95682	1.0134	0.02008	0.95394	1.0139
0.03021	0.95821	1.0201	0.03012	0.95519	1.0208
0.04028	0.95931	1.0269	0.04016	0.95643	1.0272
0.05035	0.96053	1.0334	0.05020	0.95767	1.0347
0.06042	0.96172	1.0397	0.06024	0.95892	1.0415
$T = 318.15 \text{ K}$			$T = 323.15 \text{ K}$		
0.01001	0.94995	1.0073	0.00998	0.94745	1.00735
0.02002	0.95117	1.0142	0.01997	0.94865	1.0147
0.03003	0.95239	1.0215	0.02995	0.94986	1.0220
0.04004	0.95361	1.0285	0.03993	0.95107	1.0292
0.05005	0.95484	1.0356	0.04992	0.95228	1.0365
0.06006	0.95607	1.0425	0.05990	0.95349	1.0438
Pr_4NBr					
$T = 308.15 \text{ K}$			$T = 313.15 \text{ K}$		
0.00993	0.95569	1.0076	0.00990	0.95269	1.0078
0.01986	0.95686	1.0149	0.01980	0.95391	1.0152
0.02979	0.95806	1.0222	0.02970	0.95514	1.0227
0.03972	0.95925	1.0295	0.03960	0.95637	1.0302
0.04965	0.96043	1.0368	0.04950	0.95761	1.0377
0.05958	0.96159	1.0441	0.05941	0.95885	1.0453

Table 2 (contd.)

Table 2 (contd.)

$c/\text{mol.dm}^{-3}$	$\rho/\text{g.cm}^{-3}$	η_r	$c/\text{mol.dm}^{-3}$	$\rho/\text{g.cm}^{-3}$	η_r
$T = 318.15 \text{ K}$			$T = 323.15 \text{ K}$		
0.00987	0.94993	1.0079	0.00984	0.94744	1.0080
0.01974	0.95114	1.0154	0.01969	0.94862	1.0158
0.02961	0.95235	1.0231	0.02953	0.94982	1.0235
0.03948	0.95356	1.0307	0.03938	0.95101	1.0312
0.04936	0.95478	1.0383	0.04923	0.95221	1.0389
0.05923	0.95600	1.0460	0.05907	0.95342	1.0465
Bu_4NBr					
$T = 308.15 \text{ K}$			$T = 313.15 \text{ K}$		
0.00978	0.95568	1.0089	0.00975	0.95267	1.0091
0.01956	0.95684	1.0174	0.01950	0.95388	1.0179
0.02934	0.95801	1.0259	0.02925	0.95509	1.0264
0.03912	0.95917	1.0344	0.03900	0.95631	1.0346
0.04890	0.96034	1.0428	0.04876	0.95754	1.0433
0.05868	0.96150	1.0511	0.05851	0.95876	1.0520
$T = 318.15 \text{ K}$			$T = 323.15 \text{ K}$		
0.00972	0.94991	1.0092	0.00970	0.94742	1.0094
0.01944	0.95110	1.0180	0.01939	0.94859	1.0181
0.02916	0.95230	1.0262	0.02909	0.94977	1.0268
0.03889	0.95350	1.0349	0.03878	0.95095	1.0354
0.04861	0.95470	1.0435	0.04848	0.95214	1.0442
0.05840	0.95591	1.0524	0.05818	0.95334	1.0531
NaBr					
$T = 308.15 \text{ K}$			$T = 313.15 \text{ K}$		
0.01047	0.95513	1.0037	0.01044	0.95210	1.0038
0.02094	0.95574	1.0073	0.02087	0.95273	1.0075
0.03141	0.95636	1.0108	0.03131	0.95336	1.0111
0.04188	0.95697	1.0143	0.04175	0.95399	1.0146
0.05235	0.95759	1.0179	0.05219	0.95462	1.0183
0.06282	0.95820	1.0214	0.06263	0.95525	1.0219

Table 2 (contd.)

Table 2 (contd.)

$c/\text{mol.dm}^{-3}$	$\rho/\text{g.cm}^{-3}$	η_r	$c/\text{mol.dm}^{-3}$	$\rho/\text{g.cm}^{-3}$	η_r
$T = 318.15 \text{ K}$			$T = 323.15 \text{ K}$		
0.01041	0.94934	1.0040	0.01041	0.94932	1.0042
0.02081	0.94995	1.0076	0.02081	0.94991	1.0078
0.03122	0.95056	1.0112	0.03122	0.95050	1.0115
0.04163	0.95117	1.0147	0.04163	0.95109	1.0151
0.05203	0.95178	1.0185	0.05203	0.95168	1.0187
0.06244	0.95240	1.0223	0.06243	0.95227	1.0228
NaBPh ₄					
$T = 308.15 \text{ K}$			$T = 313.15 \text{ K}$		
0.01061	0.95582	1.0092	0.01058	0.95282	1.0093
0.02122	0.95713	1.0180	0.02116	0.95418	1.0183
0.03183	0.95844	1.0269	0.03173	0.95554	1.0272
0.04244	0.95975	1.0360	0.04231	0.95691	1.0362
0.05305	0.96106	1.0449	0.05290	0.95829	1.0453
0.06366	0.96236	1.0537	0.06348	0.95968	1.0542
$T = 318.15 \text{ K}$			$T = 323.15 \text{ K}$		
0.01055	0.95007	1.0095	0.01052	0.94759	1.0096
0.02109	0.95141	1.0185	0.02104	0.94893	1.0188
0.03164	0.95277	1.0277	0.03156	0.95028	1.0279
0.04219	0.95412	1.0367	0.04208	0.95164	1.0372
0.05274	0.95549	1.0459	0.05260	0.95300	1.0463
0.06330	0.95686	1.0551	0.06313	0.95437	1.0556

Table 3. Theoretical A -coefficients, the viscosity B -coefficients and the free energies of activation for viscous flow of electrolytes in 2-ethoxyethanol + water mixtures with 0.25, 0.50, and 0.75 mass fractions (w_1) of 2-ethoxyethanol at 308.15, 313.15, 318.15 and 323.15 K

Electrolyte	$A / \text{dm}^{3/2} \text{mol}^{-1/2}$	$B / \text{dm}^3 \text{mol}^{-1}$	$\Delta\mu_2^{\beta\ddagger} / \text{kJ mol}^{-1}$
$w_1 = 0.25$			
$T = 308.15 \text{ K}$			
Et ₄ NBr	0.0059	0.294	52.55
Pr ₄ NBr	0.0063	0.318	61.62
Bu ₄ NBr	0.0067	0.447	82.78
NaBr	0.0049	0.190	35.30
NaBPh ₄	0.0116	0.447	84.26
$T = 313.15 \text{ K}$			
Et ₄ NBr	0.0067	0.307	54.51
Pr ₄ NBr	0.0071	0.330	63.39
Bu ₄ NBr	0.0075	0.450	83.93
NaBr	0.0056	0.193	35.85
NaBPh ₄	0.0124	0.455	86.02
$T = 318.15 \text{ K}$			
Et ₄ NBr	0.0076	0.313	55.68
Pr ₄ NBr	0.0080	0.334	64.69
Bu ₄ NBr	0.0084	0.454	85.30
NaBr	0.0064	0.194	36.19
NaBPh ₄	0.0133	0.474	89.06
$T = 323.15 \text{ K}$			
Et ₄ NBr	0.0083	0.334	58.60
Pr ₄ NBr	0.0088	0.342	66.20
Bu ₄ NBr	0.0092	0.455	86.28
NaBr	0.0071	0.196	36.76
NaBPh ₄	0.0140	0.480	90.77

Table 3 (contd.)

Table 3 (contd.)

Electrolyte	$A / \text{dm}^{3/2} \text{mol}^{-1/2}$	$B / \text{dm}^3 \text{mol}^{-1}$	$\Delta\mu_2^{\theta*} / \text{kJ mol}^{-1}$
$w_1 = 0.50$			
$T = 308.15 \text{ K}$			
Et ₄ NBr	0.0076	0.465	55.34
Pr ₄ NBr	0.0081	0.512	64.04
Bu ₄ NBr	0.0085	0.616	77.70
NaBr	0.0074	0.224	31.29
NaBPh ₄	0.0108	0.608	77.61
$T = 313.15 \text{ K}$			
Et ₄ NBr	0.0080	0.481	56.93
Pr ₄ NBr	0.0084	0.535	66.39
Bu ₄ NBr	0.0088	0.632	79.50
NaBr	0.0078	0.238	32.59
NaBPh ₄	0.0112	0.624	79.41
$T = 318.15 \text{ K}$			
Et ₄ NBr	0.0089	0.489	57.85
Pr ₄ NBr	0.0093	0.542	67.34
Bu ₄ NBr	0.0097	0.646	81.22
NaBr	0.0085	0.244	33.21
NaBPh ₄	0.0120	0.634	80.84
$T = 323.15 \text{ K}$			
Et ₄ NBr	0.0095	0.506	59.76
Pr ₄ NBr	0.0100	0.551	70.52
Bu ₄ NBr	0.0103	0.654	84.49
NaBr	0.0090	0.257	34.58
NaBPh ₄	0.0126	0.645	82.58

Table 3 (contd.)

Table 3 (contd.)

Electrolyte	$A / \text{dm}^{3/2} \text{mol}^{-1/2}$	$B / \text{dm}^3 \text{mol}^{-1}$	$\Delta\mu_2^{\theta\pm} / \text{kJ mol}^{-1}$
$w_1 = 0.25$			
$T = 308.15 \text{ K}$			
Et ₄ NBr	0.0130	0.530	44.97
Pr ₄ NBr	0.0140	0.598	51.84
Bu ₄ NBr	0.0147	0.747	63.13
NaBr	0.0147	0.193	24.02
NaBPh ₄	0.0188	0.634	57.88
$T = 313.15 \text{ K}$			
Et ₄ NBr	0.0134	0.553	46.35
Pr ₄ NBr	0.0144	0.610	52.72
Bu ₄ NBr	0.0148	0.778	65.18
NaBr	0.0146	0.206	24.72
NaBPh ₄	0.0184	0.663	59.74
$T = 318.15 \text{ K}$			
Et ₄ NBr	0.0136	0.568	47.61
Pr ₄ NBr	0.0145	0.620	53.77
Bu ₄ NBr	0.0149	0.787	66.35
NaBr	0.0144	0.227	26.03
NaBPh ₄	0.0182	0.693	61.98
$T = 323.15 \text{ K}$			
Et ₄ NBr	0.0145	0.578	48.58
Pr ₄ NBr	0.0151	0.634	55.08
Bu ₄ NBr	0.0158	0.796	67.45
NaBr	0.0149	0.242	23.49
NaBPh ₄	0.0189	0.706	63.24

Table 4. Ionic viscosity B -coefficients in 2-ethoxyethanol-water mixtures at 308.15, 313.15, 318.15 and 323.15 K

Ion	$B_{\pm}/\text{dm}^3 \text{ mol}^{-1}$			
	T = 308.15 K	T = 313.15 K	T = 318.15 K	T = 323.15 K
	$w_1 = 0.25$			
Et ₄ N ⁺	0.163	0.177	0.189	0.212
Pr ₄ N ⁺	0.187	0.200	0.210	0.220
Bu ₄ N ⁺	0.316	0.320	0.330	0.332
Na ⁺	0.059	0.063	0.070	0.073
Br ⁻	0.131	0.130	0.124	0.123
Ph ₄ B ⁻	0.388	0.392	0.404	0.407
	$w_1 = 0.50$			
Et ₄ N ⁺	0.298	0.307	0.308	0.320
Pr ₄ N ⁺	0.345	0.361	0.361	0.365
Bu ₄ N ⁺	0.449	0.458	0.466	0.468
Na ⁺	0.057	0.064	0.064	0.071
Br ⁻	0.167	0.174	0.181	0.186
Ph ₄ B ⁻	0.551	0.560	0.570	0.574
	$w_1 = 0.75$			
Et ₄ N ⁺	0.317	0.330	0.344	0.348
Pr ₄ N ⁺	0.385	0.387	0.396	0.404
Bu ₄ N ⁺	0.534	0.555	0.563	0.566
Na ⁺	-0.020	-0.017	0.003	0.012
Br ⁻	0.213	0.223	0.224	0.230
Ph ₄ B ⁻	0.654	0.380	0.690	0.694

Table 5. Ionic free energies of activation for viscous flow in 2-ethoxyethanol-water mixtures at 308.15, 313.15, 318.15 and 323.15 K

Ion	$\Delta\mu_{\pm}^{\theta\ddagger}/\text{kJ mol}^{-1}$			
	T = 308.15 K	T = 313.15 K	T = 318.15 K	T = 323.15 K
	$w_1 = 0.25$			
Et ₄ N ⁺	28.98	30.85	32.48	35.37
Pr ₄ N ⁺	38.05	39.73	41.49	42.97
Bu ₄ N ⁺	59.21	60.27	62.10	63.05
Na ⁺	11.73	12.19	12.99	13.53
Br ⁻	23.57	23.66	23.20	23.23
Ph ₄ B ⁻	72.53	73.83	76.07	77.24
	$w_1 = 0.50$			
Et ₄ N ⁺	33.38	34.20	34.50	34.82
Pr ₄ N ⁺	42.08	43.66	44.03	45.58
Bu ₄ N ⁺	55.74	56.77	59.91	59.55
Na ⁺	9.33	9.86	9.90	9.64
Br ⁻	21.96	22.73	23.31	29.94
Ph ₄ B ⁻	68.28	69.55	70.94	72.94
	$w_1 = 0.75$			
Et ₄ N ⁺	25.43	26.20	27.24	29.31
Pr ₄ N ⁺	32.30	32.57	33.40	35.81
Bu ₄ N ⁺	43.59	45.03	45.98	48.18
Na ⁺	4.48	4.57	5.66	4.22
Br ⁻	19.54	20.15	20.37	19.27
Ph ₄ B ⁻	53.40	55.17	56.32	59.02

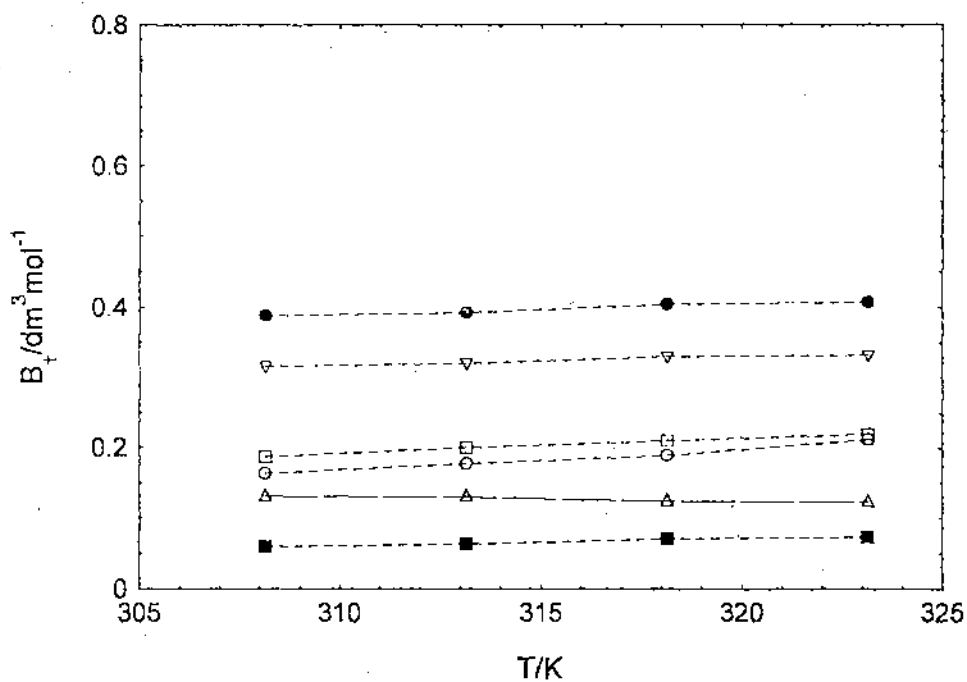


Fig. 1. Temperature dependence of the ionic viscosity B coefficients in 2-ethoxyethanol-water mixtures ($w_1 = 0.25$) for Na^+ (■), Br^- (△), Et_4N^+ (○), Pr_4N^+ (□), Bu_4N^+ (▽), Ph_4B^- (●).

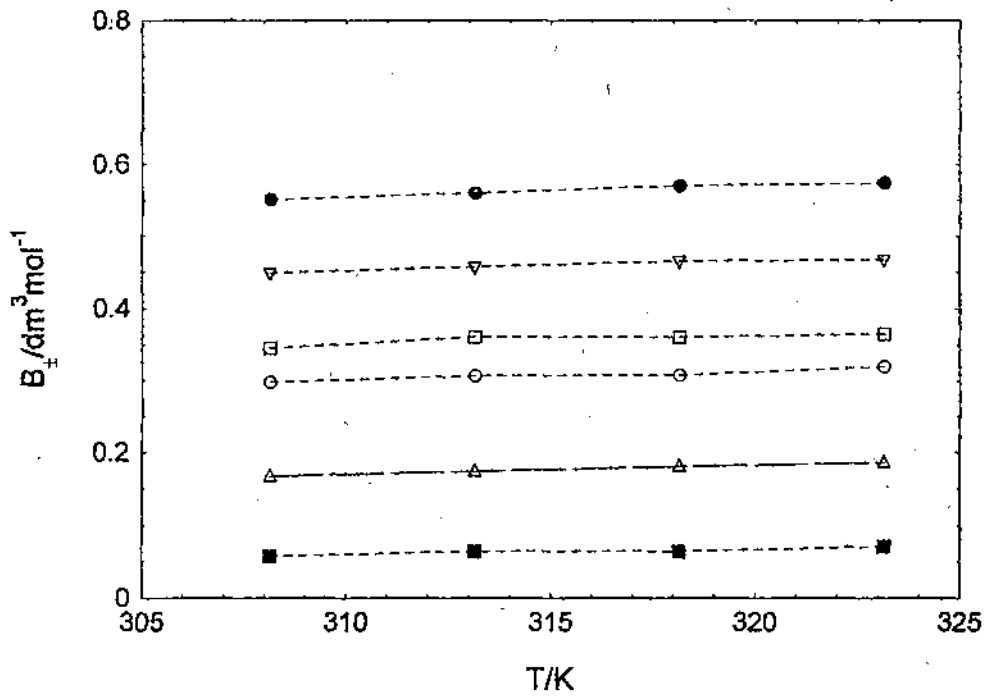


Fig. 2. Temperature dependence of the ionic viscosity B coefficients in 2-ethoxyethanol-water mixtures ($w_1 = 0.50$) for Na^+ (■), Br^- (Δ), Et_4N^+ (○), Pr_4N^+ (◻), Bu_4N^+ (▽), Ph_4B^- (●).

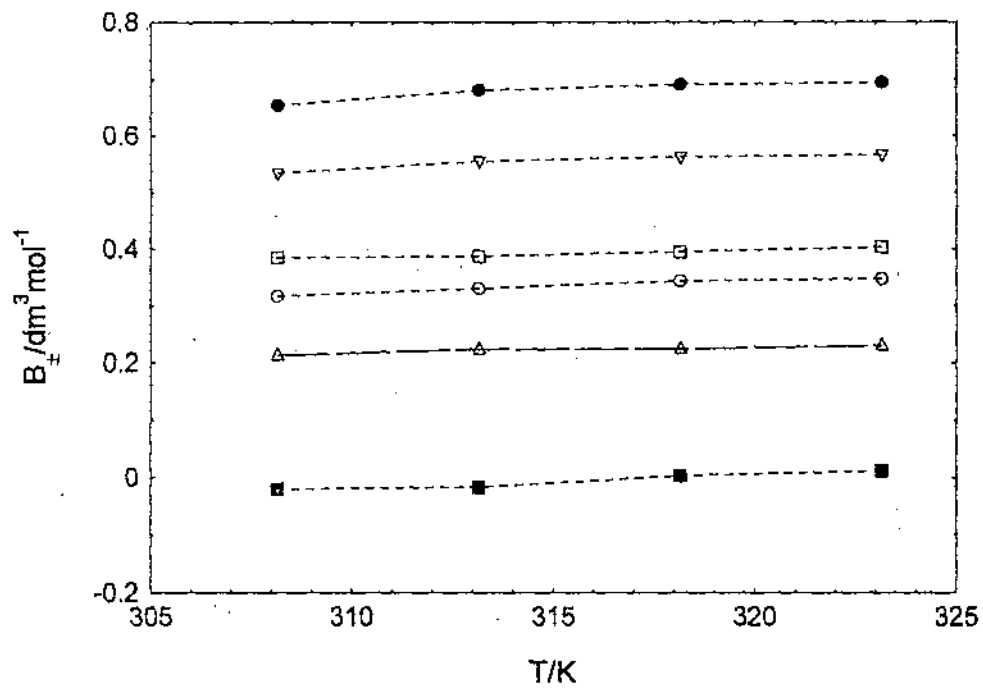


Fig. 3. Temperature dependence of the ionic viscosity B coefficients in 2-ethoxyethanol-water mixtures ($w_1 = 0.75$) for Na^+ (■), Br^- (△), Et_4N^+ (○), Pr_4N^+ (◻), Bu_4N^+ (▽), Ph_4B^- (●).

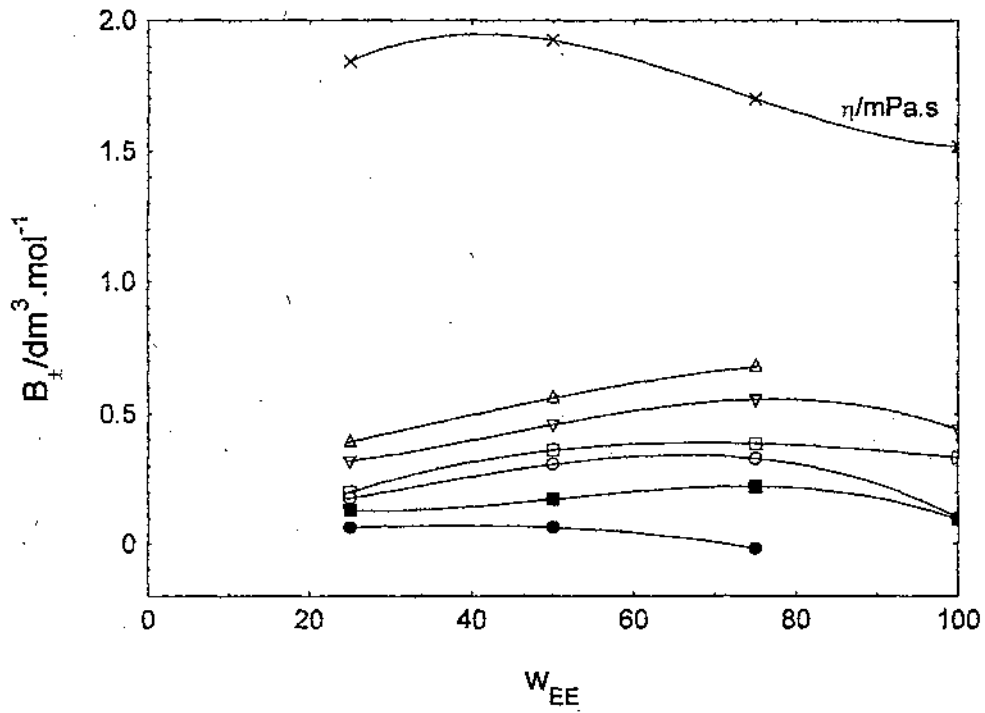


Fig. 4. Solvent composition dependence of the ionic viscosity B coefficients in 2-ethoxyethanol-water mixtures at 308.15 K: Na^+ (\bullet), Br^- (\blacksquare), Et_4N^+ (\circ), Pr_4N^+ (\square), Bu_4N^+ (∇), Ph_4B^- (Δ).

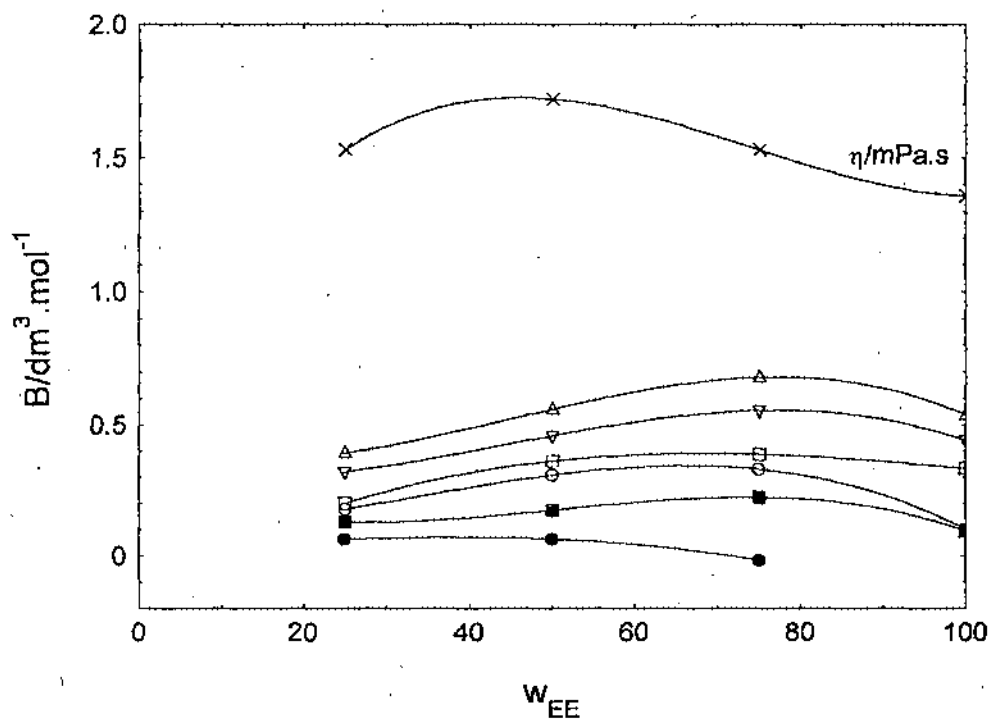


Fig. 5. Solvent composition dependence of the ionic viscosity B coefficients in 2-ethoxyethanol-water mixtures at 313.15 K: Na^+ (\bullet), Br^- (\blacksquare), Et_4N^+ (\circ), Pr_4N^+ (\square), Bu_4N^+ (∇), Ph_4B^- (Δ).

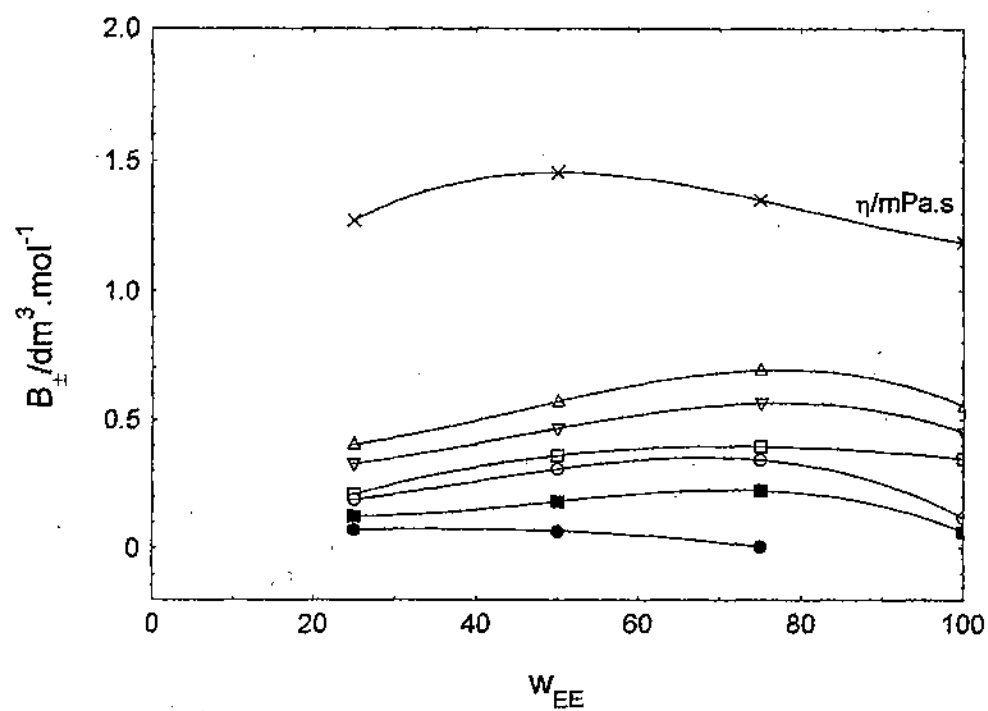


Fig. 6. Solvent composition dependence of the ionic viscosity B coefficients in 2-ethoxyethanol-water mixtures at 318.15 K: Na^+ (\bullet), Br^- (\blacksquare), Et_4N^+ (\circ), Pr_4N^+ (\square), Bu_4N^+ (∇), Ph_4B^- (Δ).

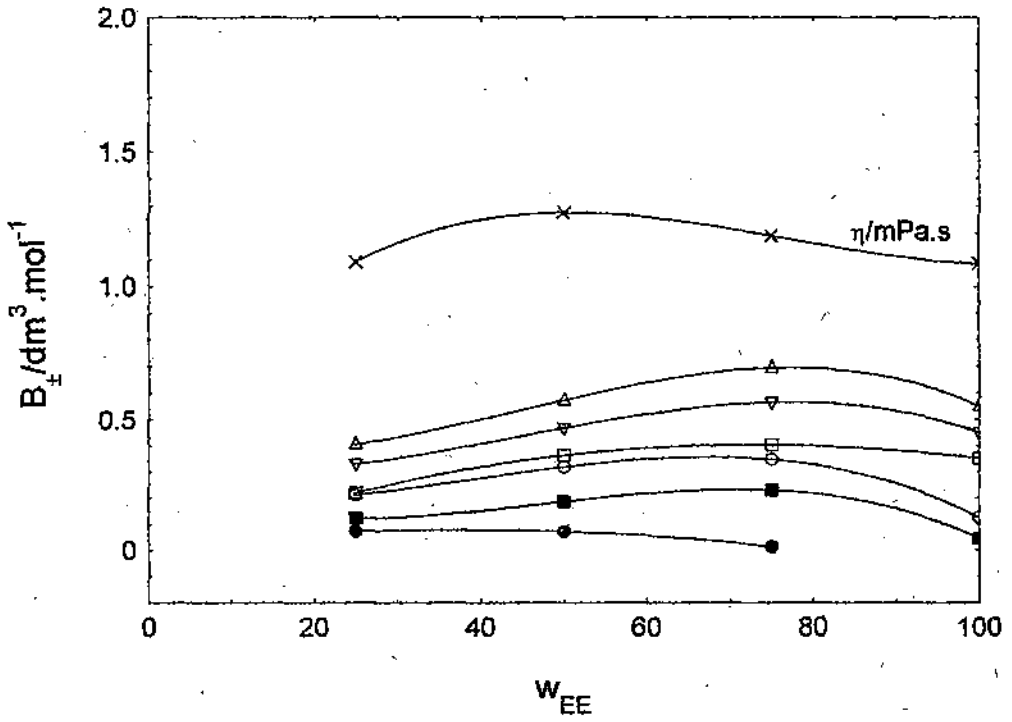


Fig. 7. Solvent composition dependence of the ionic viscosity B coefficients in 2-ethoxyethanol-water mixtures at 323.15 K: Na^+ (\bullet), Br^- (\blacksquare), Et_4N^+ (\circ), Pr_4N^+ (\square), Bu_4N^+ (∇), Ph_4B^- (Δ).