

Viscosity Coefficients of KCl, NaCl, NaI, KNO₃, LiNO₃, NaBPh₄ and Bu₄NI in Water - Dimethyl Sulfoxide Binary Mixtures With a Low Organic Solvent Content

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Abstract: In this work the viscosities of KCl, NaCl, NaI, KNO₃, LiNO₃, NaBPh₄ and Bu₄NI solutions (from ~0.01 mol dm⁻³ to ~0.05 mol dm⁻³) in water (1) + dimethyl sulfoxide (DMSO) (2) binary mixtures with mole fractions of DMSO, $x_2 = 0.01, 0.02, 0.05, 0.075, 0.10$ and 0.15 , were determined at 298.15 K. The viscosities measured were used to evaluate the viscosity B -coefficients by means of Jones-Dole's equation. The results obtained allowed us to determine the values of B_{\pm} coefficients for individual ions using the assumption about the equality $B(\text{Bu}_4\text{N}^+) = B(\text{BPh}_4^-)$. All the results have been discussed in terms of ion-solvent interactions.

Keywords: viscosity of solutions, water + dimethyl sulfoxide (DMSO) mixtures, Jones-Dole equation, viscosity B -coefficients.

INTRODUCTION

VISCOSITY, one of the most important transport properties is used in this work to characterize ion-solvent interactions. A survey of the subject literature and our previous papers show the studies of the transport properties of electrolyte solutions give a very useful information about the ion-ion and ion-solvent interactions occurring in electrolyte solutions. The investigation of the viscosity of solutions have been used for such studies.^[1–11] In these studies, it is of particular importance to determine the values of viscosity B -coefficients of Jones-Dole's equation, which are associated with the ion-solvent interactions.^[1] Our earlier research concerned the viscometric properties of various types of electrolyte solutions (mainly the solutions of strongly associating electrolyte) in water^[2–5], and mixed solvent.^[6–10]

In the present study, precise viscosity data for KCl, NaCl, NaI, KNO₃, LiNO₃, NaBPh₄ and Bu₄NI in water (1) + dimethyl sulfoxide (DMSO) (2) binary mixtures (with mole fraction of DMSO, $x_2 = 0.01, 0.02, 0.05, 0.075, 0.10$, and

0.15) in the concentration range of ~0.01 mol dm⁻³ to ~0.05 mol dm⁻³ at 298.15 K are reported.

The results obtained were used to determine the values of the viscosity B -coefficients of Jones-Dole's equation and the values of B_{\pm} coefficients for individual ions using, as in our previous work,^[12] the assumption of the equality $B(\text{Bu}_4\text{N}^+) = B(\text{BPh}_4^-)$ in all the binary mixtures studied. All the results have been discussed in terms of ion-solvent interactions. Only a few B values for NaCl, KCl, NaI, Bu₄NI and NaBPh₄ solutions in water – DMSO mixtures ($x_{\text{DMSO}} \leq 0.15$) can be found in literature. Moreover, the values reported differ significantly.

EXPERIMENTAL

Dimethyl sulfoxide (DMSO) (99.5 % Fluka) was stored over 4A type molecular sieves for several days and then distilled under atmospheric pressure. Water content, determined by Karl-Fischer method, was lower than 0.01 %. To prepare aqueous solutions, triple-distilled and degassed water with a specific conductance lower than 0.5×10^{-6} S cm⁻¹ was used. All the salts used in this work:

KCl (99.99 % Merck), NaCl (≥ 99.5 % Aldrich), NaI (≥ 99.5 % Aldrich), KNO₃ (99.99 % Aldrich), LiNO₃ (99.99 % Aldrich), NaBPh₄ (≥ 99.5 % Aldrich) and Bu₄NI (≥ 99 % Aldrich) were dried and purified by the method reported in our previous works and literature.^[1-4,8]

All the solutions were prepared by gravimetric method using a precision Sartorius RC 210D analytical balance with the uncertainty of ± 0.00001 g. The values of molar concentrations were calculated on the basis of the density data with the uncertainty $0.00001 \text{ mol dm}^{-3}$. The apparatus and the experimental technique used for viscometric and densimetric measurements have been described elsewhere.^[19]

The viscosities of the solutions were determined with a Ubbelohde viscometer (SI Analytics) and an automatic flow time measuring system AVS 350 (SI Analytics). The viscometer with a measurement stand was immersed in a thermostat bath filled with water. An effective mixing was obtained using additionally two R14 IKA stirrers. A Haake DC-30 (Thermo HAAKE, Germany) heating circulator was used to control the temperature with an accuracy of ± 0.01 K. The densities of solutions were measured using an Anton Paar model DMA 5000 densimeter with a precision of $\pm 1 \times 10^{-6} \text{ g cm}^{-3}$, and accuracy $\pm 5 \times 10^{-6} \text{ g cm}^{-3}$. The estimated uncertainty of the measured viscosity data was in all cases lower than 0.05 %.

RESULTS AND DISCUSSION

The values of absolute dynamic viscosity, η_0 of the binary mixtures (H₂O + DMSO) studied and the relative viscosity ($\eta_r = \eta / \eta_0$) of KCl, NaCl, NaI, KNO₃, LiNO₃, NaBPh₄, and Bu₄NI solutions in these mixtures as a function of concentration (in the concentration range $\sim 0.01 \text{ mol dm}^{-3} < c < \sim 0.05 \text{ mol dm}^{-3}$) were measured at $T = 298.15$ K. All these data are presented in Table 1 and Tables 2a–2g.

Table 1. Dynamic viscosity (η_0) and relative permittivity (ϵ_r) of water (1) + dimethyl sulfoxide (DMSO) (2) mixtures at 298.15 K.

x_2	ϵ_r	$\eta_0 \cdot 10^{-2} / \text{mPa s}$
0.000	78.40	0.0089
0.010	78.39	0.0097
0.020	78.28	0.0105
0.050	77.94	0.0133
0.075	77.49	0.0158
0.100	77.02	0.0185
0.150	76.01	0.0242

Table 2a. Experimental values of the relative viscosity of KCl in water (1) + dimethyl sulfoxide (DMSO) (2) binary mixtures, at 298.15 K.

x_2	$c / \text{mol dm}^{-3}$	η_r	x_2	$c / \text{mol dm}^{-3}$	η_r
0.01	0.010706	1.0004	0.075	0.012069	0.9993
	0.021295	1.0004		0.021757	0.9990
	0.028966	1.0004		0.033170	0.9988
	0.041377	1.0005		0.042322	0.9985
	0.050982	1.0006		0.053225	0.9991
0.02	0.011211	1.0005	0.10	0.011210	1.0006
	0.020771	1.0005		0.021921	1.0016
	0.031225	1.0006		0.036700	1.0022
	0.040621	1.0008		0.042140	1.0031
	0.050895	1.0009		0.053212	1.0039
0.05	0.011392	1.0005	0.15	0.012594	1.0080
	0.021308	1.0008		0.022888	1.0069
	0.030955	1.0010		0.033094	1.0060
	0.041301	1.0012		0.043285	1.0044
	0.051394	1.0015		0.054084	1.0026

Table 2b. Experimental values of the relative viscosity of NaCl in water (1) + dimethyl sulfoxide (DMSO) (2) binary mixtures, at 298.15 K.

x_2	$c / \text{mol dm}^{-3}$	η_r	x_2	$c / \text{mol dm}^{-3}$	η_r
0.01	0.010903	1.0016	0.075	0.011301	1.0020
	0.020933	1.0027		0.022335	1.0039
	0.030353	1.0037		0.032003	1.0053
	0.040525	1.0047		0.041697	1.0068
	0.050752	1.0056		0.052807	1.0086
0.02	0.009154	1.0013	0.10	0.012309	1.0024
	0.020215	1.0027		0.022094	1.0040
	0.031126	1.0039		0.032624	1.0058
	0.040866	1.0051		0.042703	1.0074
	0.05076	1.0061		0.053012	1.0090
0.05	0.009889	1.0018	0.15	0.010145	1.0021
	0.021137	1.0035		0.022042	1.0041
	0.031571	1.0045		0.030766	1.0058
	0.041474	1.0058		0.042702	1.0083
	0.051668	1.0067		0.054016	1.0104

Table 2c. Experimental values of the relative viscosity of NaI in water (1) + dimethyl sulfoxide (DMSO) (2) binary mixtures, at 298.15 K.

x_2	$c / \text{mol dm}^{-3}$	η_r	x_2	$c / \text{mol dm}^{-3}$	η_r
0.01	0.011239	1.0008	0.075	0.011092	1.0010
	0.020353	1.0012		0.021777	1.0016
	0.030743	1.0015		0.032025	1.0021
	0.040752	1.0018		0.042186	1.0027
	0.050917	1.0021		0.052378	1.0030
0.02	0.011222	1.0008	0.10	0.011959	1.0011
	0.020716	1.0013		0.022826	1.0017
	0.030579	1.0017		0.03229	1.0023
	0.041046	1.0020		0.04236	1.0028
	0.051251	1.0023		0.053378	1.0035
0.05	0.011217	1.0010	0.15	0.012638	1.0012
	0.021198	1.0015		0.022589	1.0019
	0.041561	1.0023		0.033085	1.0026
	0.051952	1.0026		0.043284	1.0033
				0.054209	1.0039

Table 2d. Experimental values of the relative viscosity of KNO₃ in water (1) + dimethyl sulfoxide (DMSO) (2) binary mixtures, at 298.15 K.

x_2	$c / \text{mol dm}^{-3}$	η_r	x_2	$c / \text{mol dm}^{-3}$	η_r
0.01	0.011579	0.9998	0.075	0.012290	0.9996
	0.021528	0.9995		0.021782	0.9991
	0.031194	0.9992		0.031896	0.9985
	0.040473	0.9988		0.042550	0.9980
	0.050757	0.9983		0.052435	0.9974
0.02	0.010910	0.9999	0.10	0.011367	0.9996
	0.020735	0.9993		0.020690	0.9992
	0.031020	0.9988		0.032522	0.9986
	0.041322	0.9985		0.043013	0.9981
	0.051675	0.9981		0.053645	0.9977
0.05	0.011033	0.9996	0.15	0.012011	0.9999
	0.021721	0.9991		0.022311	0.9994
	0.031111	0.9988		0.033358	0.9987
	0.041390	0.9984		0.043836	0.9980
	0.051631	0.9980		0.054409	0.9975

Table 2e. Experimental values of the relative viscosity of LiNO₃ in water (1) + dimethyl sulfoxide (DMSO) (2) binary mixtures, at 298.15 K.

x_2	$c / \text{mol dm}^{-3}$	η_r	x_2	$c / \text{mol dm}^{-3}$	η_r
0.01	0.012287	1.0021	0.075	0.010256	1.0021
	0.022436	1.0033		0.022004	1.0039
	0.031302	1.0044		0.031595	1.0054
	0.041299	1.0056		0.041928	1.0070
	0.050820	1.0066		0.052077	1.0085
0.02	0.010970	1.0018	0.10	0.011225	1.0024
	0.021524	1.0031		0.021633	1.0041
	0.030935	1.0043		0.032051	1.0058
	0.041185	1.0055		0.042623	1.0074
	0.051065	1.0067		0.052724	1.0090
0.05	0.011166	1.0020	0.15	0.011516	1.0025
	0.021393	1.0034		0.022341	1.0045
	0.031477	1.0048		0.032626	1.0062
	0.041448	1.0061		0.043175	1.0081
	0.051596	1.0075		0.053592	1.0095

Table 2f. Experimental values of the relative viscosity of NaBPh₄ in water (1) + dimethyl sulfoxide (DMSO) (2) binary mixtures, at 298.15 K.

x_2	$c / \text{mol dm}^{-3}$	η_r	x_2	$c / \text{mol dm}^{-3}$	η_r
0.01	0.010316	1.0130	0.075	0.011112	1.0109
	0.020491	1.0255		0.022020	1.0214
	0.030661	1.0380		0.032087	1.0342
	0.040322	1.0498		0.042335	1.0468
	0.050479	1.0623		0.052199	1.0599
0.02	0.010442	1.0123	0.10	0.011147	1.0104
	0.020435	1.0238		0.021100	1.0206
	0.031139	1.0362		0.031800	1.0329
	0.040844	1.0480		0.042245	1.0454
	0.050194	1.0598		0.052248	1.0578
0.05	0.011849	1.0120	0.15	0.012237	1.0116
	0.021177	1.0224		0.021848	1.0210
	0.031404	1.0345		0.032932	1.0326
	0.041289	1.0474		0.043203	1.0439
	0.051095	1.0600		0.052753	1.0546

Table 2g. Experimental values of the relative viscosity of Bu₄NI in water (1) + dimethyl sulfoxide (DMSO) (2) binary mixtures, at 298.15 K.

x_2	$c / \text{mol dm}^{-3}$	η_r	x_2	$c / \text{mol dm}^{-3}$	η_r
0.01	0.012467	1.0156	0.075	0.010789	1.0106
	0.020373	1.0251		0.021550	1.0213
	0.030322	1.0370		0.031341	1.0322
	0.039646	1.0481		0.041867	1.0445
	0.050026	1.0605		0.052215	1.0573
0.02	0.010777	1.0133	0.10	0.011260	1.0109
	0.021020	1.0248		0.021313	1.0211
	0.030962	1.0359		0.032032	1.0325
	0.040698	1.0474		0.042220	1.0437
0.05	0.049187	1.0574	0.15	0.051938	1.0545
	0.010038	1.0112		0.013645	1.0123
	0.019373	1.0205		0.023332	1.0251
	0.024310	1.0256		0.033044	1.0324
	0.038969	1.0407		0.043027	1.0400
	0.049082	1.0511		0.053586	1.0498

The results of viscosity of the electrolytes studied were analyzed on the basis of Jones–Dole’s equation:^[20,21]

$$\eta_r = \frac{\eta}{\eta_0} = 1 + A \cdot c^{1/2} + B \cdot c \quad (1)$$

Falkenhagen’s A coefficient is a theoretical measure of ion-ion interactions. On the other hand, viscosity B -coefficient, Jones-Dole’s coefficient, is an empirical function of the ion-solvent interaction.

In this paper the values of A coefficient were calculated by the method proposed by Falkenhagen and Vernon:^[22–24]

$$A = \frac{0.2577\Lambda_0}{\eta_0(\varepsilon_r T)^{0.5}\lambda_+^0\lambda_-^0} \left[1 - 0.6863 \left(\frac{\lambda_+^0 - \lambda_-^0}{\Lambda_0} \right)^2 \right] \quad (2)$$

where ε_r and η_0 are relative permittivity and dynamic viscosity of the solvent and Λ_0 , λ_+^0 , λ_-^0 are limiting molar conductivities of the electrolyte, cation, and anion respectively, at temperature T .

From equation (1) it follows that using the values of A calculated with the use of equation (2), the values of coefficient B can be calculated according to equation (3):

$$(\eta_r - 1 - A \cdot c^{1/2}) / c = B \quad (3)$$

Thus, the values of the viscosity B -coefficients determined with the use of equation (3), should be independent of the concentration and may be considered as the arithmetic mean of the values obtained for different concentrations. Such a procedure was used by us many times in our previous papers.^[2–10,12] The values of limiting molar conductances of the electrolytes (Λ_0), and ions (λ_+^0 , λ_-^0), necessary to calculate the coefficient A [Eq. 2], were taken from literature.^[25–28]

The enlisted viscosities (η_0) and relative permittivities (ε_r) of water - DMSO mixtures (Table 1) were taken from literature (ref.28). The values of coefficients A and B of Jones-Dole’s equation and the values of limiting molar conductances of the electrolytes tested in a mixed solvent having high water content are collected in Table 3.

The dependencies of B -coefficient as a function of the composition of a mixed solvent are presented in Figure 1 showing a significant difference between the values of the coefficient B of the electrolytes containing large organic ions (Bu₄N⁺, BPh₄⁻) and B values of the other electrolytes containing only inorganic ions. As is known, the values of coefficients B depend on many factors related to both ions and solvent. Among other things, this coefficient is affected by both the size and charge of the ions. The ratio of charge to the square of the crystallographic radius of ions (*i.e.* surface charge density) considerably influence the interaction of ion with solvent.^[29,30] The relationship between the viscosity of solution and the size of the ion follows from Einstein’s equation.^[1] In the case of large ions such as Bu₄N⁺ and BPh₄⁻, the surface charge density is very low. For this reason the interactions with the solvent molecules (water) are weak. Consequently it leads to the solvation of these ions in a different way, *i.e.* hydrophobic solvation. The high values of B of the electrolytes containing ions Bu₄N⁺ and BPh₄⁻ are mainly the consequence of the large size of these ions. Figure 1 also shows, that the absolute change in B in the case of a salt containing the ions Bu₄N⁺ and BPh₄⁻ are much larger than in the case of other inorganic salts.

However, a more detailed analysis of the data contained in Table 3 and dependencies shown in Figure 1 leads to the conclusion that the ratio $\Delta B_{\max} / B_{\max}$ (ΔB_{\max} a maximal change in the value B , B_{\max} - the maximum value of B) is comparable for both types of salt in the composition range of the mixtures tested. In the case of electrolytes containing inorganic ions, we can assume that the surface charge density of ions has a dominant influence on the ion-dipole interactions. These interactions are responsible for the effective size of ions in the solution. They also affect the

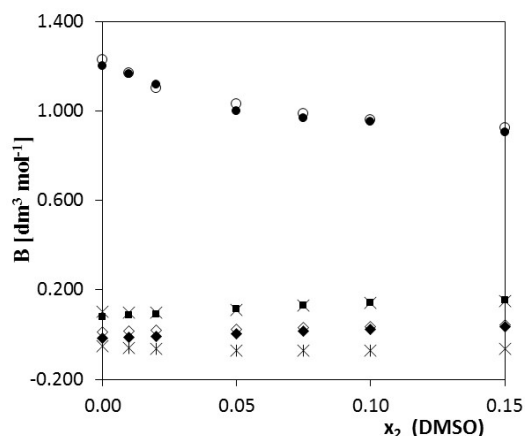


Figure 1. Variation in viscosity B -coefficient with mole fraction of DMSO, x_2 in (water + DMSO) binary mixtures of electrolytes: (◆) KCl, (■) NaCl, (◇) NaI, (×) LiNO₃, (∗) KNO₃, (○) NaBPh₄, and (●) Bu₄NI at 298.15 K.

structure of the solvent. This explains, for example, the increase in the value of B -coefficient with decreasing crystallographic radius of the cation. Finally, the interactions of ion-dipole type are associated with selective solvation, a very important phenomenon in the case of binary solvents. The values of B -coefficients are the sum of the analogous values of cation and anion. The analysis of changes in the B -coefficient as a function of the organic component content in water should rather be related to the changes in B -coefficients of ions. The issue related to the anion and cation contribution to B values have been the subject of research in many research centers. The B coefficients of individual ions can not be determined experimentally. Accordingly, the methods applied are based on more or less rational assumptions, using the known values B for electrolyte or in the case of extrapolative methods based on the knowledge of coefficient B for several electrolytes. A detailed literature

Table 3. Values of viscosity A -coefficients^(a), B -coefficients^(b) and limiting molar conductances Λ_0 of Jones-Dole's equation of all the electrolytes studied in water (1) + dimethyl sulfoxide (DMSO) (2) mixtures, at 298.15 K.

	x_2	0.000 ^(c)	0.010	0.020	0.050	0.075	0.100	0.150
KCl	A	–	0.00709	0.00696	0.00675	0.00665	0.00665	0.00659
	B	–0.014	–0.011	–0.006	0.005	0.018	0.026	0.034
	Λ_0	149.95	139.03	128.54	102.48	86.15	73.35	55.24
NaCl	A	–	0.00597	0.00590	0.00580	0.00577	0.00578	0.00581
	B	0.0790	0.086	0.089	0.115	0.132	0.144	0.156
	Λ_0	126.59	117.85	109.54	88.4	74.88	63.93	48.81
NaI	A	–	0.00598	0.00595	0.00596	0.00601	0.00602	0.00603
	B	0.0120	0.016	0.0200	0.026	0.031	0.036	0.046
	Λ_0	126.92	117.54	108.6	85.78	71.6	61.23	46.96
KNO ₃	A	–	0.00507	0.00497	0.00484	0.00480	0.00480	0.00490
	B	–0.0520	–0.058	–0.062	–0.069	–0.073	–0.071	–0.063
	Λ_0	145.00	137.07	128.82	105.12	89.51	76.65	57.72
LiNO ₃	A	–	0.00702	0.00696	0.00713	0.00718	0.00720	0.00733
	B	0.103	0.1010	0.098	0.111	0.131	0.141	0.150
	Λ_0	110.07	102.69	95.97	75.87	64.06	54.81	41.30
NaBPh ₄	A	–	0.01152	0.01145	0.01086	0.01069	0.01059	0.01047
	B	1.229	1.169	1.101	1.030	0.988	0.959	0.925
	Λ_0	69.98	65.47	61.08	51.08	43.88	37.87	29.49
Bu ₄ NI	A	–	0.00934	0.00947	0.00946	0.00961	0.00957	0.00965
	B	1.202	1.167	1.120	0.999	0.970	0.951	0.905
	Λ_0	96.26	87.33	79.38	61.62	50.66	43.34	32.91

^(a) Unit: A , $\text{dm}^{3/2} \text{mol}^{-1/2}$.

^(b) Unit: B , $\text{dm}^3 \text{mol}^{-1}$.

^(c) From Ref. [1].

^(d) Unit: Λ_0 , $\text{S cm}^2 \text{mol}^{-1}$.

review of these methods was made in 1995 in the monograph by Marcus and Jenkins.^[1] Most of the experimental data relate to the viscosimetric properties of electrolyte solutions in water. Based on these data, Kaminsky has proposed the equality of $B(K^+) = B(Cl^-)$.^[31] The above assumption is based on the similarity of the conductivity properties of K^+ and Cl^- ions. Marcus^[1] after a detailed analysis of experimental data came to the conclusion that a slightly better assumption would be the equality of $B(Rb^+) = B(Br^-)$ suggested by Krumgalz.^[32] Based on this assumption, Marcus^[1] has determined the values of viscosity B -coefficients for a very large number of different types of ions in water. It should be noted that the differences between the values of B_{\pm} calculated according to the assumptions proposed by Kaminsky and Krumgalz, respectively, are very slight (± 0.002). Such differences are comparable with the errors of determining coefficient B . The most plausible assumption in the case of organic solvents and their mixtures with water seems to be the equality of the B -coefficients for large ions, *e.g.* $B(Bu_4N^+) = B(BPh_4^-)$.^[33]

This is supported by quite similar values of various physico-chemical properties of those ions. A very similar mobility (often identical) of these ions in different solvents constitutes a particularly strong argument. Of course, this remark also applies to the limiting molar conductance of these ions. The molar conductivity of electrolyte is one of the few parameters that can be separated into the contributions of ions, using direct methods to measure the transfer numbers.^[34] Therefore, the conclusion about the similarity of the mobility of ions Bu_4N^+ and BPh_4^- is confirmed experimentally. The partial molar volume of the electrolyte is also a physical quantity whose value can be divided into the contributions of ions. Using the method of Zana and Yeager^[35–37] one can determine the so-called absolute partial molar volumes of ions, which for Bu_4N^+ and BPh_4^- ions are very similar in various organic and aqueous-organic solvents.

Therefore, in the present study the method of Tuan-Fuoss^[33] ($B(Bu_4N^+) = B(BPh_4^-)$) is used to calculate the B_{\pm} values for all ions in the mixtures (H₂O + DMSO). The results obtained are summarized in Tables 4 and 5. In Figures 2 and 3, the plot of B_+ and B_- versus the mole fraction of DMSO, x_2 are presented. As shown in Figures 2 and 3, the viscosity B -coefficients for a large organic ions such as Bu_4N^+ , $B(BPh_4^-)$, systematically decrease with increasing the content of DMSO in the binary mixtures under investigation. In the case of such large ions, the changes in viscosity B -coefficients are attributable to the hydrophobic solvation of ions. These changes may also result from changes in the structure of (water + DMSO) mixtures. It is also worth noticing, that in the case of pure DMSO, the values of B of ions Bu_4N^+ , $B(BPh_4^-)$ are smaller than the

same values in water.^[1] The values B of ions BPh_4^- and Bu_4N^+ in DMSO are in the range 0.714–0.861 and 0.422–0.650, respectively.^[1] Thus, in the case of water (Table 4 and 5), B values for these ions are considerably higher than in DMSO. It is not surprising that the addition of DMSO to water, causes the values B to decrease for these large organic ions. The decrease in these values is more pronounced in the composition range of 0.00–0.05 mole fraction of DMSO. This may result from the destruction of the three-dimensional structure of water and the disappearance of hydrophobic hydration. In the case of inorganic ions, the values B in water (Table 4 and 5) are much smaller than in the DMSO.^[1] In DMSO, the values of B for inorganic ions cited in [1] are as follows: Li^+ (0.426–0.590), Na^+ (0.350–0.540), K^+ (0.362–0.590), Cl^- (0.258–0.440), I^- (0.272–0.454) and NO_3^- (0.27). A wide range of the B values of the specified ion mainly results from different methods of the division of coefficient B into ionic B_{\pm} contributions.^[1] Therefore, it is very important to choose the most rational division method coefficient B of electrolyte into B_{\pm} . In any case the values of B_{\pm} of inorganic ions in DMSO are much larger than those in water. It is possible that the values of B_{\pm} in DMSO are higher due to a higher dipole moment and the larger size of DMSO molecules compared to water.^[38,39]

In the case of inorganic cations, the addition of DMSO to water does not cause major changes in the values of B_{\pm} . Thus, these values seem to be stabilized. This may suggest a lack of significant changes in the hydration shell of ions, while adding a small amount of dimethyl sulfoxide to water. Thus, the cations are preferentially hydrated.

It is worth mentioning that the changes in the value of B_+ accompanying the addition of propane-1-ol to water, observed by us earlier^[12], were considerably higher.

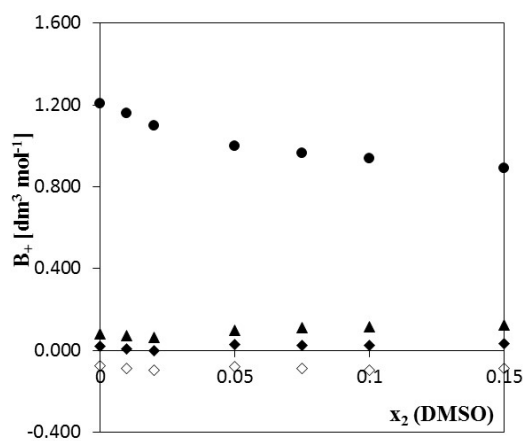


Figure 2. Changes in the dependences of B_+ against mole fraction of DMSO, x_2 in (water + DMSO) binary mixtures for the following cations: (●) Bu_4N^+ , (◆) Na^+ , (◇) K^+ , and (▲) Li^+ at 298.15 K.

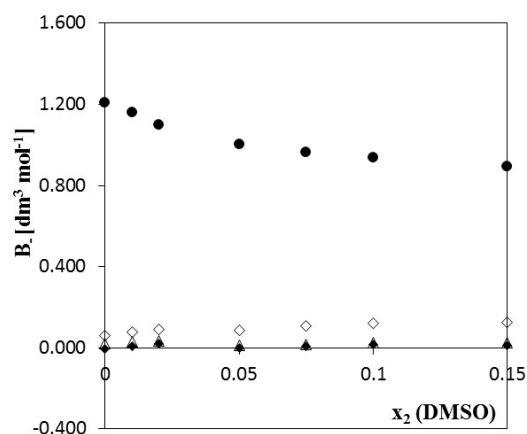


Figure 3. Changes in the dependences of B_- against mole fraction of DMSO, x_2 in (water + DMSO) binary mixtures for the following anions: (●) BPh₄⁻, (◆) I⁻, (◇) Cl⁻, and (Δ) NO₃⁻ at 298.15 K.

As shown in Figure 2, the value of B_+ in a mixture (water + DMSO) decreases with the inorganic ion size, *i.e.*, with the decrease in the surface charge density.

The reduction in surface charge density favors weakening the electrostatic interactions of the cation with the dipoles of the solvent and thus reducing the effective size of ions and reducing the value of B_+ . The values of the viscosity B_+ coefficients practically do not change with increasing the content of DMSO in the mixtures. As in the case of cations, a change in the content of DMSO in the mixtures with water does not significantly influence the values of coefficient B_- of anions. It appears that small changes in the value of B_- also result from the selective hydration of anions in the mixtures with a high water content. It is worth noting that the values of B_- of the ions of nitrate and iodide are very similar despite the clear differences between the sizes of these ions.^[38] The B_-

values for iodide are quite similar to those of much smaller nitrate anion. The most frequently observed trend, is that increasing the size of ions lowers their surface charge density and thus the values of viscosity B_- coefficients (particularly in the case of cations). As can be seen in the case of ions NO₃⁻ and I⁻, this trend does not occur. It seems that a large polarizability of iodide ion may increase the interaction of this ion with the solvent dipoles. This in turn does not facilitate the reduction in the value of B_- . As we can see in Figure 3, the values of B_- of nitrate ion are much lower than those of chloride ion. This is surprising taking into account the similar values of crystallographic radii of chloride and nitrate ions.^[38] However, similar effects could be observed for mixtures of water and propan-1-ol.^[12] It could be that the differences between the viscosity B_- coefficients of chloride and nitrate ions are mainly connected with the structure of these ions rather than with their size. The addition of water to dimethylsulfoxide (this paper) or propan-1-ol^[12] causes changes in the water structure. The molecules of propan-1-ol added to water behave in a manner characteristic of aqueous solutions of amphiphilic molecules.^[40] At low concentrations of alcohol a structure with a low entropy is formed. The studies of the mixtures of water and alcohol with its low content make it possible to observe the formation of "cages" of stable hydrogen bonds situated around the hydrophobic groups.^[41]

One can speak about the creation of cages of water molecules around the alcohol molecules.^[42] At higher alcohol contents, there may occur a self-association between the alcohol molecules.^[42] Some authors assume that the self-aggregation of propane-1-ol molecules can occur already when its content amounts to 0.03 mole fraction.^[43] In the case of water-rich mixtures, water molecules are orientated to form hydrogen bonds surrounding two hydrophobic methyl groups of the

Table 4. Values of viscosity B_+ -coefficients^(a) of cations calculated on the assumption $B(\text{Bu}_4\text{N}^+) = B(\text{BPh}_4^-)$ in water (1) + dimethyl sulfoxide (DMSO) (2) mixtures, at 298.15 K.

x_2	B_+			
	Li ⁺	K ⁺	Na ⁺	Bu ₄ N ⁺
0.000	0.081	-0.074	0.019	1.210
0.010	0.070	-0.088	0.009	1.160
0.020	0.065	-0.096	0.000	1.101
0.050	0.099	-0.081	0.029	1.001
0.075	0.113	-0.090	0.024	0.963
0.100	0.117	-0.095	0.022	0.937
0.150	0.123	-0.089	0.033	0.892

^(a) Unit: B_+ , dm³ mol⁻¹.

Table 5. Values of viscosity B_- coefficients^(a) for anions calculated on the assumption $B(\text{Bu}_4\text{N}^+) = B(\text{BPh}_4^-)$ in water (1) + dimethyl sulfoxide (DMSO) (2) mixtures, at 298.15 K

x_2	B_-			
	Cl ⁻	I ⁻	NO ₃ ⁻	BPh ₄ ⁻
0.000	0.060	-0.007	0.022	1.210
0.010	0.077	0.007	0.030	1.160
0.020	0.089	0.019	0.034	1.101
0.050	0.086	-0.002	0.012	1.001
0.075	0.108	0.007	0.017	0.963
0.100	0.121	0.014	0.024	0.937
0.150	0.123	0.013	0.027	0.892

^(a) Unit: B_- , dm³ mol⁻¹.

dimethylsulfoxide molecule.^[44] A slightly higher DMSO content in water causes the destruction of its structure.^[44,45] In the area of high concentration of DMSO, intermolecular associates of different types are created. On the basis of the enthalpy of mixing^[46] and density^[47] measurements, the existence of DMSO · 2H₂O associates was suggested. It seems, however, that the correlation of changes in the structure of a mixed solvent with changes in the value of the coefficient *B* Jones-Dole equation is an extremely difficult task which demands more systematic studies.

CONCLUSION

In this paper the viscosities of KCl, NaCl, NaI, KNO₃, LiNO₃, NaBPh₄ and Bu₄NI electrolytes were determined in H₂O + dimethyl sulfoxide (DMSO) mixtures (up to 0.15 mole fraction of DMSO) as a function of concentration (~0.01 mol dm⁻³ to ~0.05 mol dm⁻³) to obtain the viscosity *B*-coefficient at *T* = 298.15 K. Using the assumption of the equality *B*(Bu₄N⁺) = *B*(BPh₄⁻), the values of *B*_± coefficients for individual ions have been calculated. It has been found that for large organic ions Bu₄N⁺ and BPh₄⁻ the values of the coefficients *B* are much higher than those of inorganic ions (Na⁺, K⁺, Cl⁻, I⁻ and NO₃⁻). In the case of inorganic ions, the additions of dimethyl sulfoxide to water does not cause significant changes in the viscosity *B*_± values. The values of viscosity *B*_±-coefficients were analyzed mainly in terms of the possible ion-solvent interactions.

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