CONDUCTANCE AND VISCOSITY STUDIES OF ION SOLVATION IN MIXED DMSO–MeOH SOLVENT

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Solvation behavior of Li^+, Na^+, K^+, Ag^+, Cl^-, Br^-, I^- and ClO_4^- ions is reported at 25 °C from conductance and viscosity measurements of $LiClO_4$, $NaClO_4$, $KClO_4$, $AgClO_4$, LiCl, Bu_4NClO_4, Bu_4NBr, Bu_4NI, Ph_4PBPh_4, Bu_4NBPh_4, $NaBPh_4$, Ph_4PBr and NaBr in mixed DMSO–MeOH solvent. Anomalous behavior of Ag^+ is interpreted as resulting from specific ion–solvent interactions. However, Li^+, Na^+ and K^+ interact preferentially with DMSO electrostatically through oxygen atom of SO group. Initial decrease in solvation of alkali metal ions on addition of MeOH to pure DMSO is interpreted as an indication of strong intermolecular interactions between solvent components preferably through the hydrogen bond formation. The region of relatively strong intermolecular interactions is found between 10 and 40 mole % MeOH. The viscosity studies imply the existence of interactions between Br^- or I^- and DMSO. The studies however, indicate poor solvation of anions in this solvent system.
Keywords: Cations; Solvation; Dimethyl sulfoxide; Methanol; Ion–solvent interaction; Solvent mixtures; Viscosity; Conductance.

Mixtures of protic and dipolar aprotic solvents have been a favorite solvent systems to affect the rate of reactions involving ionic species[1–3]. Several reasons for this situation may be suggested. In the first place, the variation in reactivity of ions can be attributed to ion–solvent interactions. Secondly, the role of intermolecular interactions cannot be overestimated. The investigation of the latter effect is of particular interest because intermolecular interactions through hydrogen bond formation are evidently important[4] in such solvent systems, which can significantly change both the rate and the pattern of reaction process. In other words, a thorough characterization of ionic species in such solvent systems is required. The present paper, therefore, is a contribution to our understanding of ion solvation in binary mixtures of dimethyl sulfoxide (DMSO), a protophilic dipolar aprotic solvent and methanol (MeOH), an amphiprotic hydroxy solvent. In this study the

conductance and viscosity measurements of solutions of various electrolytes are reported.

EXPERIMENTAL

Materials

Solvents. The DMSO used was AR grade supplied by Sisco Research Laboratories Pvt., Ltd., Bombay. For some of the initial measurements it was dried over calcium hydride with vigorous stirring for about 5–6 h. The solvent was left standing undisturbed overnight and distilled under reduced pressure. Additional treatment however, had no significant effect on results. Therefore, for subsequent measurements, DMSO was used as received. The MeOH was also AR grade, supplied by Ranbaxy Laboratory, Ltd. It was, however, dried over vacuum-dried 4Å molecular sieves with occasional shaking for about 4–6 h, left standing undisturbed overnight and distilled gently using a Vigreux column.

Electrolytes. Anhydrous lithium perchlorate ($LiClO_4$, min. content 99%) was obtained from Fluka. Tetrabutylammonium bromide and iodide (Bu_4NBr, and Bu_4NI) were puriss. electrochemical grade supplied by Fluka. Tetraphenylphosphonium bromide (Ph_4PBr), sodium tetraphenylborate ($NaBPh_4$), sodium bromide ($NaBr$), sodium perchlorate ($NaClO_4$) and potassium pechlorate ($KClO_4$) (all GR grade) were obtained from Merck. Anhydrous lithium chloride (LiCl, min. content 99%) was obtained from Fluka. All these electrolytes were dried under vacuum before use without any additional treatment. The electrolytes tetraphenylphosphonium tetraphenylborate (Ph_4PBPh_4), tetrabutylammonium tetraphenylborate (Bu_4NBPh_4), tetrabutylammonium perchlorate (Bu_4NClO_4) and silver perchlorate ($AgClO_4$) were synthesized as described earlier[5].

Methods

Conductance measurements were made at frequency of 1 kHz using a calibrated digital conductivity meter. A conductance cell of a cell constant 0.568 ± 0.003 cm^{-1} was employed. The cell constant was determined at 25 °C with a KCl solution according to the method of Fuoss *et al.*[6] The conductance measurement was made in the concentration range of $3–60 \cdot 10^{-4}$ mol dm^{-3}; the maximum error limit of measurement was ±0.2%. A calibrated Ubbelohde-type suspended-level viscosimeter with a flow time of 676.6 s for distilled water at 25 °C was employed for viscosity measurement. Viscosity measurements of electrolyte solutions were performed in a concentration range of $75–550 \cdot 10^{-4}$ mol dm^{-3}. An accuracy of ±0.1% was attained. Densities were measured pycnometrically with an accuracy of ±0.01% and permittivity with a universal dielectrometer[7] type OH-301 (Radelkis, Hungary). Determination of the known permittivities for some pure solvents checked the reliability of the method. The results were obtained with an accuracy within ±1%.

All measurements were taken in a thermostatic water bath with an accuracy of ±0.05 °C. The solvent mixtures were prepared by a weight with an accuracy of ±0.03%. The specific conductance of solvent mixtures ranged from 1 to $5 \cdot 10^{-7}$ S cm^{-1} at 25 °C. The calibration of the equipment and glass apparatus was periodically checked.

RESULTS

Conductance Measurements

The densities, viscosities, permittivities and Bjerrum's critical distances for DMSO, MeOH and their binary mixtures are summarized in Table I. They were used for analysis of conductance data of the electrolyte solutions. The analysis of the conductance data was performed in terms of limiting molar conductance, Λ_0 (S cm^2 mol^{-1}) and ion-association constant, K_A (mol^{-1} dm^3) using a Shedlovsky conductivity model[8]. The Λ_0 and K_A values of the electrolytes are reported in Table II.

A good agreement (within one conductance unit) between the observed Λ_0 values for Ph$_4$PBPh$_4$, Bu$_4$NBPh$_4$ and NaBPh$_4$ and those obtained from the following additivity relations, suggests the internal consistency of the present conductance data.

$$\Lambda_0(Ph_4PBPh_4) = \Lambda_0(Ph_4PBr) - \Lambda_0(NaBr) + \Lambda_0(NaBPh_4) \tag{1a}$$

$$\Lambda_0(Bu_4NBPh_4) = \Lambda_0(Bu_4NBr) - \Lambda_0(NaBr) + \Lambda_0(NaBPh_4) \tag{1b}$$

TABLE I
Permittivities (D), viscosities (η_0), densities (ρ) and Bjerrum's critical distances (q) of DMSO, MeOH and DMSO–MeOH solvent system at 25 °C

MeOH, mole %	D	η_0, cP	ρ, g cm^{-3}	q, Å
0	46.7	2.0010	1.0949	6.00
10.01	46.3	1.7599	1.0787	6.05
20.03	46.0	1.5479	1.0605	6.09
30.01	45.8	1.3614	1.0401	6.12
39.98	45.3	1.1974	1.0178	6.19
50.02	44.8	1.0532	0.9920	6.26
60.10	43.5	0.9263	0.9631	6.44
70.07	41.3	0.8147	0.9299	6.79
80.10	38.8	0.7166	0.8907	7.22
90.04	35.3	0.6302	0.8429	7.94
100.00	32.6	0.5543	0.7865	8.60

TABLE II
Λ_0 (S cm² mol⁻¹) and K_A (dm³ mol⁻¹) values for some electrolytes in DMSO, MeOH and DMSO–MeOH solvent systems at 25 °C

Salt	MeOH, mole %																					
	0		10.01		20.03		30.01		39.98		50.02		60.10		70.07		80.01		90.04		100	
	Λ_0	K_A	Λ_0	K_A	Λ_0	K_A	Λ_0	K_A	Λ_0	K_A	Λ_0	K_A	Λ_0	K_A	Λ_0	K_A	Λ_0	K_A	Λ_0	K_A	Λ_0	K_A
Ph₄PBPh₄	21.7	–	25.6	–	28.8	10	32.9	14	37.0	15	42.0	16	46.5	16	51.2*	–	58.5*	–	64.4*	–	73.0*	–
Bu₄NBPh₄	23.2 (23.3)ᵃ	–	27.4	10	30.2	12	34.0	10	38.6	10	44.2	–	49.3	–	54.8	–	61.9	–	68.5	–	76.2 (76.0)ᵍ	–
Bu₄NClO₄	35.9 (36.12)ᵇ	–	38.9	–	42.5	–	48.3	11	53.0	14	59.6	14	67.4	20	75.3	20	87.3	14	95.8	–	110.3 (110.1)ʰ	–
Bu₄NI	35.5 (36.0)ᶜ	–	40.0	–	42.8	–	48.0	–	53.5	–	58.1	–	65.0	–	72.0	–	81.7	–	93.2	–	102.0 (101.7)ʰ	–
Bu₄NBr	36.4 (35.8)ᵈ	–	39.0	–	41.6	–	46.7	–	51.7	–	56.9	–	63.8	–	71.5	–	80.9	–	87.5	–	95.5 (95.5)ʰ	–
Ph₄PBr	34.3	–	37.9	–	40.9	10	44.9	11	50.9	12	55.1	–	61.1	–	68.7	–	77.8	–	84.3	–	92.3	–
NaBPh₄	25.0 (25.39)ᵉ	–	30.2	–	34.1	–	40.2	–	44.2	–	47.9	–	53.4	–	59.2	–	65.0	–	72.3	–	82.4 (81.8)ᵍ	–
NaClO₄	38.3 (38.4)ᶜ	–	41.9	14	47.1	10	54.2	17	58.9	11	63.4	11	71.3	10	79.4	–	90.0	–	99.3	–	116.6 (115.8)ʰ	–
KClO₄	39.6 (39.0)ᶜ	–	43.7	13	48.3	12	54.9	15	58.8	–	64.7	–	73.9	–	81.9	–	94.3	–	104.1	–	123.1ʰ	–
LiClO₄	35.8 (35.45)ᶠ	–	39.5	–	44.3	–	50.0	19	54.7	20	61.0	20	69.1	23	75.2	20	85.7	17	93.9	10	110.8 (110.6)ⁱ	–
AgClO₄	40.0 (40.6)ᵇ	–	42.8	–	47.5	–	53.8	–	57.6	–	64.5	–	72.7	–	81.4	–	95.2	–	105.1	–	122.1 (121.2)ⁱ	–
NaBr	38.2 (38.1)ᶜ	–	41.7	–	45.7	–	51.9	–	57.5	–	60.9	–	68.1	–	76.7	–	84.3	–	92.0	–	101.7 (101.7)ⁱ	–
LiCl	36.4	–	40.1	–	43.2	12	46.8	–	51.8	–	58.2	–	63.5	–	69.2	–	76.9	–	84.8	–	92.2 (92.0)ʲ	–

ᵃ Ref.[5], ᵇ ref.[23], ᶜ ref.[24], ᵈ ref.[25], ᵉ ref.[26], ᶠ by addition from refs[23,24], ᵍ ref.[15], ʰ ref.[27], ⁱ ref.[28], ʲ ref.[29] * Value obtained using additivity relation (1a).

$$\Lambda_0(NaBPh_4) = \Lambda_0(NaClO_4) - \Lambda_0(Bu_4NClO_4) + \Lambda_0(Bu_4NBPh_4) \qquad (1c)$$

Limiting molar ionic conductance, λ_i^0 values reported in Table III have been obtained by resolving Λ_0 ones reported in Table II into ionic contribution using assumption[9] $\lambda^0(Ph_4P^+) \approx \lambda^0(Ph_4B^-)$. The corresponding effective ionic radii, r_i (nm), calculated using a Stokes' law modification[10] have also been reported in Table III. In the following equation

$$r_i = 0.82/\lambda_i^0 \eta_0 + 0.0103D + r_y, \qquad (2)$$

η_0 values were taken from Table I and r_y, an adjustable solvent parameter, was set to 0.113 nm as suggested by Gill and Nording[11].

Viscosity Measurement

The viscosity data were analyzed in terms of the Jones–Dole[12] equation using a least-squares treatment

$$\eta/\eta_0 = 1 + AC^{1/2} + BC, \qquad (3)$$

where η/η_0 is the viscosity of the electrolyte solution relative to that of the solvent system, C is the molar concentration and A and B are constants characteristic for the electrolyte. A and B coefficients for electrolytes are summarized in Tables IV and V, respectively. However, coefficient A, which represents the contribution from interionic electrostatic forces, was compared with those calculated from the Falkenhagen–Vernon[13] equation

$$A_\eta = 0.2577\Lambda_0/(DT)^{1/2}\lambda_i^0\eta_0[1 - 0.6863\{(\lambda_+^0 - \lambda_-^0)/\Lambda_0\}^2]. \qquad (4)$$

A reasonably close agreement can be observed between A and A_η values. This coincides with the negligible K_A values of electrolytes[14] reported in Table II.

Coefficient B which represents the ion–solvent interaction, is a specific and approximately additive property of ions of a strong electrolyte at a given temperature. Therefore, following the additivity relations for B values, the internal consistency of present viscosity data was checked by comparing the experimental B values of $NaBPh_4$, Ph_4PBPh_4 and Bu_4NBPh_4 with those obtained as follows.

TABLE III
λ_i^0 (S cm^2 mol^{-1}) and corresponding r_i (nm) values in DMSO, MeOH and DMSO–MeOH solvent system at 25 °C (the values reported in parentheses are based on the Bu$_4$NBPh$_4$ assumption[15])

Ion	0		10.01		20.03		30.01		39.98		50.02		60.10		70.07		80.01		90.04		100	
	λ_i^0	r_i	λ_i^0	r_i	λ_i^0	r_i	λ_i^0	r_i	λ_i^0	r_i	λ_i^0	r_i	λ_i^0	r_i	λ_i^0	r_i	λ_i^0	r_i	λ_i^0	r_i	λ_i^0	r_i
Ph$_4$B$^-$	10.9 (11.0)	0.54	12.8 (13.0)	0.53	14.4 (14.4)	0.53	16.5 (16.2)	0.53	18.4 (18.4)	0.53	21.0 (21.0)	0.53	23.3 (23.4)	0.54	25.6 (26.1)	0.55	29.3 (29.3)	0.54	32.3 (32.6)	0.55	36.5 (36.3)	0.55
Bu$_4$N$^+$	12.3 (12.2)	0.49	14.6 (14.4)	0.48	15.8 (15.8)	0.50	17.5 (17.8)	0.50	20.1 (20.2)	0.50	23.2 (23.2)	0.50	26.0 (25.9)	0.50	29.2 (28.7)	0.50	32.6 (32.6)	0.50	36.2 (35.9)	0.51	39.7 (39.9)	0.52
Li$^+$	12.2	0.50	15.2	0.47	17.6	0.46	19.2	0.47	21.8	0.47	24.6	0.48	26.7	0.49	29.1	0.50	31.0	0.52	34.3	0.53	40.2	0.52
Na$^+$	14.7	0.45	17.6	0.43	20.4	0.42	23.4	0.42	26.0	0.42	27.0	0.45	29.9	0.45	33.3	0.46	35.3	0.48	39.7	0.48	46.0	0.47
K$^+$	16.0	0.42	19.4	0.40	21.6	0.41	24.1	0.41	25.9	0.42	28.3	0.43	32.5	0.43	35.8	0.44	39.6	0.44	44.5	0.44	52.5	0.43
Ag$^+$	16.4	0.41	18.5	0.41	20.8	0.42	23.0	0.42	24.7	0.44	28.1	0.44	31.3	0.44	35.3	0.44	40.5	0.44	45.5	0.44	51.5	0.43
Cl$^-$	24.2	0.33	24.9	0.35	25.6	0.37	27.6	0.38	30.0	0.39	33.6	0.39	36.8	0.40	40.1	0.41	45.9	0.40	50.5	0.41	52.0	0.43
Br$^-$	24.1	0.33	24.4	0.35	25.8	0.37	29.2	0.37	31.6	0.38	33.7	0.39	37.8	0.39	42.3	0.39	48.3	0.39	51.3	0.40	55.8	0.41
I$^-$	23.2	0.34	25.4	0.34	27.0	0.36	30.5	0.36	33.4	0.37	24.9	0.39	39.0	0.39	42.8	0.39	49.1	0.39	57.0	0.38	62.5	0.38
ClO$_4^-$	23.6	0.33	24.3	0.35	26.7	0.36	30.8	0.36	32.9	0.37	36.4	0.37	41.0	0.37	46.1	0.37	54.7	0.36	59.6	0.36	70.6	0.36

MeOH, mole %

$$B(Ph_4PBPh_4) = B(Ph_4PBr) - B(NaBr) + B(NaBPh_4) \qquad (5a)$$

$$B(Bu_4NBPh_4) = B(Bu_4NBr) - B(NaBr) + B(NaBPh_4) \qquad (5b)$$

$$B(NaBPh_4) = B(NaClO_4) - B(Bu_4NClO_4) + B(NaBPh_4) \qquad (5c)$$

An agreement (within ± 0.02 dm^3 mol^{-1}) between the two sets of B values was obtained. However, due to poor solubility of Ph$_4$PBPh$_4$ in pure MeOH, the B(Ph$_4$PBPh$_4$) values reported in Table IV were obtained from Eq. (*5a*).

TABLE IV
Visscosity coefficients A ($\cdot\ 10^2$) and A_η ($\cdot\ 10^2$) (dm$^{-3/2}$ mol$^{-1/2}$) of electrolytes in DMSO, MeOH and DMSO–MeOH solvent system at 25 °C (maximum uncertainty in A values is ± 0.1 dm$^{-3/2}$ mol$^{-1/2}$)

Salt	MeOH, mole %													
	0		10.01		30.01		50.02		70.07		90.04		100	
	A	A_η	A	A_η	A	A_η	A	A_η	A	A_η	A	A_η	A	A_η
Bu$_4$NBPh$_4$	1.9	1.9	1.8	1.8	2.0	1.9	2.0	1.9	2.0	2.1	2.2	2.3	–	–
Bu$_4$NClO$_4$	1.2	1.3	1.3	1.3	1.4	1.4	1.3	1.4	1.3	1.5	1.7	1.7	1.9	1.8
Bu$_4$NI	1.2	1.3	1.4	1.3	1.4	1.4	1.5	1.5	1.6	1.6	1.5	1.7	1.7	1.9
Bu$_4$NBr	1.1	1.2	1.3	1.3	1.4	1.4	1.5	1.5	1.4	1.6	1.6	1.8	1.8	2.0
Ph$_4$PBr	1.1	1.3	1.2	1.4	1.6	1.4	1.5	1.6	1.8	1.7	1.8	2.0	2.0	2.0
NaBPh$_4$	1.5	1.7	1.6	1.6	1.6	1.7	1.6	1.8	1.8	2.0	2.1	2.2	2.0	2.3
NaClO$_4$	1.3	1.2	1.4	1.2	1.2	1.2	1.4	1.4	1.3	1.4	1.7	1.6	1.8	1.6
KClO$_4$	1.1	1.1	1.2	1.2	1.3	1.2	1.4	1.3	1.5	1.4	–	–	–	–
LiClO$_4$	1.2	1.3	1.2	1.3	1.2	1.3	1.4	1.4	1.4	1.4	1.6	1.7	1.6	1.8
AgClO$_4$	1.2	1.1	1.1	1.2	1.3	1.2	1.2	1.3	1.5	1.4	1.5	1.5	1.6	1.6
NaBr	1.1	1.1	1.1	1.2	1.1	1.2	1.3	1.4	1.6	1.5	1.7	1.8	2.0	1.9
LiCl	1.4	1.3	1.2	1.3	1.5	1.4	1.4	1.5	1.6	1.7	2.0	1.9	2.2	2.1

The $B_{\pm}$ values for various ions reported in Table VI were obtained using the $B(Ph_4P^+) \approx B(Ph_4B^-)$ assumption[5]. Interestingly, it can be seen in Table VI that $B(Bu_4N^+)$ and $B(Ph_4B^-)$ calculated from the Bu_4NBPh_4 assumption[15], are in poor agreement with those obtained from the $B(Ph_4P^+) \approx B(Ph_4B^-)$ assumption. However, no such disagreement is observed in conductance measurements (Table III). This, as suggested by Lawrence *et al.*[9], can be attributed to different viscous flow patterns of the solvent around these large ions of different shapes. The use of unsymmetrical reference electrolyte, such as Bu_4NBPh_4 for the division of the B coefficient of the electrolyte into ionic contribution has to be, therefore, regarded with caution. However, the B values of NaCl, LiBr, KBr, LiI, NaI and KI equal to 0.81, 0.90, 0.85, 0.89, 0.84 and 0.84 $dm^3 mol^{-1}$, respectively, obtained by addition of $B_{\pm}$ values from Table VI, were found in excellent agreement with those reported by Lawrence *et al.*[16].

TABLE V
Viscosity coefficients B ($dm^{-3} mol^{-1}$) in DMSO, MeOH and DMSO–MeOH solvent system at 25 °C (maximum uncertainty in B value is ± 0.02 $dm^3 mol^{-1}$)

Salt	MeOH, mole %						
	0	10.01	30.01	50.02	70.07	90.04	100
Ph_4PBPh_4	1.75	1.82	1.92	1.97	2.00	1.94	1.83
Bu_4NBPh_4	1.31	1.38	1.48	1.55	1.55	1.51	1.43
Bu_4NClO_4	0.74	0.86	0.90	0.96	0.96	0.92	0.91
Bu_4NI	0.89	0.92	0.95	0.98	0.96	0.85	0.81
Bu_4NBr	0.90	0.93	0.96	0.97	0.95	0.85	0.80
Ph_4PBr	1.35	1.37	1.40	1.40	1.40	1.28	1.24
$NaBPh_4$	1.25	1.31	1.38	1.43	1.45	1.40	1.30
$NaClO_4$	0.69	0.80	0.80	0.85	0.86	0.82	0.79
$KClO_4$	0.69	0.78	0.81	0.87	0.86	–	–
$LiClO_4$	0.74	0.84	0.86	0.92	0.93	0.87	0.83
$AgClO_4$	0.85	0.94	0.94	0.95	0.94	0.80	0.70
$NaBr$	0.85	0.86	0.86	0.86	0.85	0.74	0.67
$LiCl$	0.86	0.89	0.92	0.97	0.98	0.96	0.90

DISCUSSION

Cation Solvation

It can be seen in Table III that within the limit of experimental uncertainty (± 0.01 nm), the r_i, values of Li$^+$, Na$^+$, K$^+$ and Ag$^+$ decrease in the order Li$^+$ > Na$^+$ > Ag$^+$ ≅ K$^+$ over the entire solvent composition range. This is consistent with the increasing order of their respective crystallographic radii[1] (0.06, 0.095, 0.126 and 0.133 mn). However, after the initial decrease in the r_i values of Li$^+$, Na$^+$ and K$^+$ from 0.50, 0.45 and 0.42 ± 0.01 nm in pure DMSO to 0.47, 0.43 and 0.40 ± 0.01 nm, respectively by the addition up to ≈10 mole % MeOH, they do not change (beyond the experimental error) with the MeOH concentration rising up to ≈40 mole %. Above 40 mole % MeOH, the r_i values show a steady rise up to 0.53 (for Li$^+$) and 0.48 nm (for Na$^+$) at ≈90 mole % MeOH, which are equivalent to the values in pure MeOH. The

TABLE VI
Ionic coefficients $B_\pm$ (mol^{-1} dm^3) in DMSO, MeOH and DMSO–MeOH solvent system at 25 °C obtained using the $B(Ph_4P^+) \approx B(Ph_4B^-)$ assumption. (The values reported in parentheses are based on the Bu_4NBPh_4 assumption[15])

Ion	MeOH, mole %						
	0	10.01	30.01	50.02	70.07	90.04	100
Ph$_4$B$^-$	0.88	0.96	0.96	0.99	1.00	0.97	0.92
	(0.72)	(0.76)	(0.81)	(0.85)	(0.85)	(0.83)	(0.79)
Bu$_4$N$^+$	0.43	0.47	0.52	0.56	0.55	0.54	0.51
	(0.59)	(0.62)	(0.67)	(0.70)	(0.70)	(0.68)	(0.64)
Li$^+$	0.43	0.45	0.48	0.52	0.52	0.49	0.43
Na$^+$	0.38	0.41	0.42	0.45	0.45	0.44	0.39
K$^+$	0.38	0.39	0.43	0.46	0.45	–	–
Ag$^+$	0.54	0.55	0.56	0.55	0.53	0.42	0.30
Cl$^-$	0.43	0.44	0.44	0.45	0.46	0.47	0.47
Br$^-$	0.47	0.46	0.44	0.40	0.40	0.31	0.29
I$^-$	0.46	0.45	0.43	0.41	0.41	0.31	0.31
ClO$_4^-$	0.31	0.39	0.38	0.40	0.41	0.40	0.38

r_i value of K$^+$, on the other hand, increases from 0.42 nm at ≈40 mole % MeOH to 0.44 nm at ≈70 mole % MeOH, which is equivalent already to the r_i value yielded in pure MeOH. This behavior of Li$^+$, Na$^+$ and K$^+$ contrasts strongly with that of Ag$^+$ especially in DMSO-rich regions. For the corresponding solvent composition, practically no effect of MeOH on the r_i value of Ag$^+$ is indicated. It reaches a value of 0.41 ± 0.01 nm in pure DMSO, increases to 0.44 nm at ≈40 mole % MeOH and then becomes constant. The different behavior of Ag$^+$ can be assigned to different types of ion–solvent interactions. As Ag$^+$ represents a transition metal ion of d^{10} electronic configuration, it is likely to prefer specific type of interactions with DMSO in addition to direct electrostatic binding.

The ability of Ag$^+$ to undergo specific interaction with DMSO may be attributed to Lewis acid–base interaction *via* the sulfur atom. This is not possible in the case of Li$^+$, Na$^+$ and K$^+$ interacting with DMSO preferably electrostatically *via* oxygen atom of SO group. The existence of these interactions, supported by thermodynamic[17] and infrared spectroscopic[18] studies, is also apparent from initial decrease in r_i value of Li$^+$, Na$^+$ and K$^+$. In other words, these results manifest the existence of relatively strong interactions between DMSO and MeOH molecules not broken by interactions with alkali metal ions. A similar conclusion has been reached by Baltzer *et al.*[19] from the NMR studies of Na$^+$ solvation in DMSO–MeOH mixtures.

It seems however, that solvent mixtures containing 10–40 mole % MeOH correspond to the region of maximum intermolecular interactions where r_i becomes almost independent on solvent composition. This behavior of Li$^+$, Na$^+$, K$^+$ and Ag$^+$ actually shows their preferential solvation by DMSO, since these cations have a favorable free-energy change from water to DMSO ($\Delta G_{tr} < 0$) and unfavorable free-energy change from water to MeOH ($\Delta G_{tr} > 0$) (ref.[20]). An increase of r_i values in the region above 40 mole % MeOH can, therefore, be interpreted as a molecular rearrangement, where the long-range intermolecular interactions extend outside the short-range ion–solvent interactions. In solvent mixtures where components have different dielectric constants, solvent sorting extends outside the first solvation sphere due to the long-range intermolecular interactions[21].

The ionic B_+ values for Li$^+$, Na$^+$, K$^+$ and Ag$^+$ reported in Table VI also confirm our previous conclusions. The fact that B_+ remains constant for Li$^+$, Na$^+$ and K$^+$ in the region of 0–30 mole % MeOH (within the experimental error ±0.02 dm^3 mol^{-1}) suggests that these alkali metal ions are preferentially solvated by DMSO in DMSO–MeOH mixtures. Also, the fact that Ag$^+$ undergoes specific interaction with DMSO appears to result in a constant B_+ value of 0.55 ± 0.02 dm^3 mol^{-1} up to ≈70 mole % MeOH. Above 70 mole %

MeOH, the solvent sorting effect may be assigned to a decrease in B_+ values for Li$^+$, Na$^+$ and Ag$^+$. The observed increase in the B_+ values with the addition of DMSO to pure MeOH suggests higher DMSO content than in the bulk mixture, which is in good agreement with the conductance studies. Furthermore, Feakins and Lawrence[16] have suggested that there is a tendency for B coefficients to increase with rising molar volume of the solvent. DMSO has a molar volume of 0.071 and MeOH 0.041 dm^3 mol^{-1}. Hence if DMSO is incorporated in the cation solvation sphere, an increase in the B_+ value can be expected. Relatively strong bonding between DMSO molecules and Ag$^+$ increases substantially B_+ value of Ag$^+$ from 0.30 dm^3 mol^{-1} in pure MeOH to 0.42 dm^3 mol^{-1} just by the addition of about 10 mole % DMSO.

Anion Solvation

Let us now consider the r_i and B_- values of Cl$^-$, Br$^-$, I$^-$ and ClO$_4^-$ in order to take an account of their behavior in DMSO–MeOH mixtures. Table III reveals that in pure MeOH r_i values of Cl$^-$, Br$^-$ and I$^-$ decrease in the order Cl$^-$ > Br$^-$ > I$^-$. This is in accord with the Parker's scheme[1] of anion solvation in protic solvents as a result of hydrogen bonding. Thus, the observed pattern is consistent with the inverse order of the ion size[1], Cl$^-$ < Br$^-$ < I$^-$ (Cl$^-$, 0.181 nm; Br$^-$, 0.195 nm; I$^-$, 0.216 nm). The ClO$_4^-$, whose ion size[1] (0.200 nm) is smaller than that of I$^-$, may feature dispersion of the negative charge on the tetrahedrally arranged oxygen atoms. On the other hand, in pure DMSO, $r_i \approx 0.33$ nm for all of these anions and remains almost constant despite their differences in size. Also, a smooth increase of r_i with rising MeOH concentration contrasts with independence of ion size on these values in the mixtures. It is believed that the effect of intermolecular interactions on anion solvation is practically identical supporting thus the fact that anions are poorly solvated in dipolar aprotic solvents[1].

The B_- values of Cl$^-$ and ClO$_4^-$ (Table VI) show a similar relation between solvent composition and r_i values. In the case of Br$^-$ and I$^-$, the B_- decreases with MeOH concentration in contrast with corresponding r_i values (Table III). Since this behavior suggests the preferential solvation of Br$^-$ and I$^-$ by DMSO arising from higher DMSO polarizability[1]. However, it is of particular interest that such an anomalous behavior is observed in viscosity data rather than in conductance.

Finally, the r_i values of Bu$_4$N$^+$ and Ph$_4$B$^-$ ions are very close to their ionic sizes[10] (0.500 and 0.535 nm, respectively) and remain practically independent of solvent composition except for acetonitrile (AN)–MeOH (ref.[15]) and in *N,N*-dimethylformamide (DMF)–MeOH mixtures[22]. In these mixtures the

r_i values of Bu_4N^+ and Ph_4B^- increase with increasing concentration of MeOH, which is indicative of solvophobic interactions of these ions with the alcohol. A similar conclusion can be drawn from the solvent composition dependence of $B_\pm$ values for these large ions reported in Table VI. Therefore, on the basis of present observations we can suggest an existence of relatively strong intermolecular interactions in DMSO–MeOH mixtures.

Conclusions

The overall change in r_i and B_+ values of Li^+, Na^+, K^+ and Ag^+ on the DMSO–MeOH mixture composition is small, but nonlinear. Effect of intermolecular interactions on ion–solvent interactions, which corresponds to the preferential solvation of Li^+, Na^+, K^+ and Ag^+ by DMSO can be suggested. The existence of specific interactions in addition to common electrostatic binding can be expected for Ag^+ ions. A smooth increase in r_i value for anions with rising MeOH concentration can reflect the contribution of hydrogen bonding. An identical argument could be presented for B_- values of Cl^- and ClO_4^-. From viscosity data, there are indications of binding Br^- and I^- to DMSO. To explain this fact we may consider the polarizability interactions. Also, it can be stated that anion–solvent interactions are not sensitive to ion size in pure DMSO as well as in DMSO–MeOH mixtures. All these indications support the Parker's scheme of ion solvation in protic and dipolar aprotic solvents identifying MeOH to be noncomparable to DMSO as cation solvating medium[19].

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