

Conductance and viscosity measurements of some 1:1 electrolytes in dimethylformamide + methanol mixtures at 25, 30 and 40°C

S P Jauhar* & Seema Sandhu

Department of Chemistry, Panjab University, Chandigarh 160 014, India

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Molar conductances and viscosities of some 1:1 alkali metal and tetraalkyl ammonium salts have been measured in dimethylformamide (DMF) + methanol (MeOH) mixtures containing 100, 89.3, 69.1, 49.6, 29.9 and 10.7 mol% DMF and pure MeOH at 25°C. The conductance data have been analysed by Shedlovsky method setting ion – size parameter equal to Bjerrum critical distance suggested by Justice to calculate Λ_0 and K_A . Calculation of limiting ionic conductances and solvated radii shows preferential solvation of ions in these mixtures. The viscosity data have been analysed using the Jones – Dole equation. The ion – solvent interaction parameter, viscosity B – coefficients have been found to be positive for all the electrolytes in all the systems. The ionic B_± coefficients have been evaluated by taking Bu₄NBPh₄ as reference electrolyte. Conductances and viscosities of three salts, NaBr, NaBPh₄ and Bu₄NBr, have been measured at 30 and 40°C in different solvent mixtures. The limiting ionic conductances and ionic viscosity B – coefficients for the ions show decreased solvation with increase in temperature.

Dimethylformamide (DMF) + methanol (MeOH) mixtures are among the most promising solvent mixtures for studying ion – solvent interactions and particularly preferential solvation. Both the solvents have almost the same dielectric constant but DMF is a dipolar aprotic solvent which preferentially solvates the cations while MeOH being a dipolar protic solvent can solvate the cations and anions to an almost equal extent. Conductance and transference number studies^{1,2} have highlighted the preferential solvation of some uni – univalent electrolytes in these solvent mixtures. Though viscosity measurements like other transport properties of electrolyte solutions provide useful information about the kinetic entities from which ion – solvent interactions and preferential solvation can be inferred, such studies are lacking in these solvent mixtures. In the present paper, we report conductance and viscosity measurements of some 1:1 alkali metal and tetraalkylammonium salts in DMF + MeOH mixtures at different temperatures to elucidate the solvation behaviour of ions in these solvent mixtures.

Materials and Methods

DMF (BDH) was purified by storing it over sodium carbonate (25% v / w) for 24 hours with occasional shaking, refluxed under vacuum and then distilled. The fraction boiling at 73°C/60 mm Hg was collected over 4 Å molecular sieves. The purified solvent had

specific conductance : $(1 - 2) \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$; density : 0.9443 g cm^{-3} and viscosity : 0.796 mPa.s (all at 25°C)

MeOH (AnalaR BDH) was dried by storing over 4 Å molecular sieves for 24 hours. After decantation, the solvent was refluxed over 4 Å molecular sieves for 15-20 hours and distilled through a long vertical fractionating column. The fraction distilling at 64.5°C (specific conductance : $1-4 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$, density : 0.7866 g cm^{-3} and viscosity : 0.545 mPa.s , all at 25°C) was collected for use.

Tetrabutylammonium tetraphenylboride (Bu₄NBPh₄) was prepared and purified by the method given earlier³. All other electrolytes were purified by literature methods⁵. Conductances of the solutions were measured at 25, 30 and 40°C (± 0.01) with a calibrated digital conductivity meter (Model CC-601, Century Instruments, Chandigarh) at a frequency of 1000 Hz. The conductance measurements were made in the same manner as reported earlier⁶.

The reproducibility of molar conductance measurements was found to be within $\pm 0.02 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$. Viscosities to an accuracy of $\pm 0.002 \text{ mPa.s}$ were measured at different temperatures with a modified Ubbelohde capillary type viscometer as described earlier⁷. The densities to an accuracy of $\pm 0.0001 \text{ g cm}^{-3}$ were measured⁷ using bicapillary pycnometer.

Results and Discussion

Conductances of LiBr, NaBr, KBr, NaI, NaSCN, NaClO₄, NaBPh₄, KNO₃, AgNO₃, Me₄NBr, Et₄NBr, Pr₄NBr, Bu₄NBr and Bu₄NBPh₄ have been measured in DMF + MeOH mixtures containing 100, 89.3, 69.1, 49.7, 29.9, 10.7 mol% DMF and pure MeOH in the electrolyte concentration range of $4.3 - 50.0 \times 10^{-4}$ mol dm⁻³ at 25°C. The conductance data have been analysed by using Shedlovsky^{8,9} method using Bjerrum critical distance (*q*) suggested by Justice^{10,11} in place of *R* for the calculation of mean activity coefficients of the electrolytes. The details of the method used for the analysis of conductance data were same as described by Gill and co-workers¹. The values of η , ϵ and *q* are summarized in Table 1. The standard deviations of Λ_0 and K_A values obtained by applying statistical equations were always found to be less than $\pm 0.2\%$ and $\pm 10\%$ respectively. The root mean square deviations σ between calculated and experimental values in no case exceeded the experimental uncertainty of our conductance measurements. This shows good applicability of Shedlovsky's equation to the present conductance data.

There exists a large number of conductance equations¹² which require very high precision. As the precision of our conductance data is $\pm 0.2\%$, therefore, the use of any other conductance equation which requires a precision in conductance much better than $\pm 0.01\%$ was not thought appropriate to analyse the present conductance data. However, the limiting molar conductances, which are of interest to us, obtained by different conductance equations do not differ significantly. The Λ_0 and K_A values thus obtained are recorded in Table 2. Comparison of our data with the literature data (Table 2) shows a close agreement.

Inspection of Table 2 reveals that the limiting molar conductance Λ_0 values for all the electrolytes increase with decrease in DMF content in DMF + MeOH mixtures. Similar behaviour has also been reported by Gill and other workers for some electrolytes in DMF + MeOH and DMF + AN(acetonitrile) mixtures^{1,14} in which, with the addition of MeOH or AN to DMF, the Λ_0 values have been found to increase. The increase in limiting molar conductance with decrease in concentration of DMF in DMF + MeOH mixtures may be attributed to the smaller size of the solvent molecules and also to the weak association between DMF and MeOH mixtures through hydrogen bonding.

Limiting ionic molar conductances

We have reported² the limiting ionic conductances of Ag⁺ and NO₃⁻ ions at different compositions of DMF + MeOH mixtures, obtained from transference number data. Using the $\lambda_{\text{NO}_3^-}$, the limiting ionic conductances of all other ions are calculated from corresponding Λ_0 values, employing Kohlrausch law of independent migration of ions. All the results are recorded in Table 3.

To throw light on the solvation behaviour of ions in DMF + MeOH mixtures, the actual solvated radii (*r_i*) for different ions have been calculated by using Gill's modification of the Stokes law^{18,19}:

$$r_i = \frac{|Z|F^2}{6\pi\eta_0 N\lambda_{\pm}^0} + 0.0103 \epsilon + r_y \quad \dots(1)$$

where *r_i* is the actual solvated radius of the ion and *r_y* is a constant equal to 0.85 for dipolar non-associated solvents and 1.13 for hydrogen-bonded and other associated solvents. The *r_i* values obtained are also listed in Table 3.

A perusal of Table 3 shows that the *r_i* values for all the anions Br⁻, I⁻, SCN⁻, ClO₄⁻, BPh₄⁻ and NO₃⁻ in DMF + MeOH mixtures increase regularly with decrease in DMF content. These results show an increased solvation of anions with increasing amount of MeOH. This behaviour is in accordance with the fact that most of the anions are strongly solvated in dipolar protic solvent methanol due to hydrophobic solvation. For the cations, however, the *r_i* values do not vary significantly in a regular manner. For alkali metal cations and Ag⁺ ion, the *r_i* values decrease in the order: Li⁺ > Na⁺ > K⁺ > Ag⁺.

This is due to the fact that smaller the size, higher is the charge density and more is solvation. The *r_i* values for tetraalkylammonium ions decrease according to their size indicating their poor solvation in DMF + MeOH mixtures. The irregular trend in *r_i* values for cations suggests competition between two solvents to solvate the cations because both DMF and MeOH can solvate the cations.

Viscosity measurements

Densities and viscosities of solutions of LiBr, NaBr, NaI, NaClO₄, NaSCN, NaBPh₄, Et₄NBr, Pr₄NBr, Bu₄NBr, and Bu₄NBPh₄ in different DMF + MeOH mixtures have been measured in the concentration range $4.7 - 800 \times 10^{-4}$ mol dm⁻³ at 25°C. The viscosity data were analysed for A- and B-

Table 1—Dielectric constant (ϵ), viscosities (η) and bjerrum critical distances (q) of DMF + MeOH mixtures at 25°, 30° and 40°C

Mole% DMF	25°C			30°C			40°C		
	ϵ	η (cP)	q (Å)	ϵ	η (cP)	q (Å)	ϵ	η (cP)	q (Å)
100	37.6	0.796	7.46	35.3	0.777	7.82	33.2	0.738	8.05
89.3	37.9	0.769	7.40	35.6	0.730	7.76	33.5	0.665	7.98
69.1	38.3	0.719	7.32	36.0	0.670	7.67	33.9	0.624	7.88
49.6	38.1	0.669	7.36	35.8	0.630	7.71	33.7	0.584	7.93
29.9	37.3	0.610	7.52	35.0	0.585	7.89	32.9	0.542	8.12
10.7	35.4	0.569	7.92	33.1	0.540	8.34	31.0	0.497	8.62
0.00	32.6	0.545	8.60	30.3	0.510	9.11	28.2	0.470	9.48

Table 2—Limiting molar conductances, Λ_0 (ohm⁻¹ cm² mol⁻¹) and association constants, K_A (dm³ mol⁻¹) of some 1 : 1 electrolytes in different DMF + MeOH mixtures (mol% DMF) at 25°C

Electrolyte	100		89.3		69.1		49.6		29.9		10.7		0.00	
	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
LiBr	75.8 (76.7) ^a	28.1	76.7	11.2	79.2	11.4	83.1	—	86.8	20.3	92.1	14.9	97.6	30.2
NaBr	80.9 (83.1) ^a	26.2	83.3	30.6	85.8	—	89.5	20.0	91.6	—	97.5	18.2	100.4 (101.6) ^c	29.1
KBr	82.2 (84.7) ^a	—	84.5	—	87.9	—	94.1	—	99.5	—	105.3	—	110.4 (108.9) ^c	15.0
NaI	80.5 (81.1) ^a	—	83.0	—	84.4	—	88.2	—	91.2	—	100.3	—	107.9	12.6
NaSCN	89.2	—	92.0	—	94.3	—	99.1	—	101.3	—	107.6	—	112.2	—
NaClO ₄	82.3 (82.3) ^a	20.8	86.5	21.6	89.9	19.3	98.5	32.5	103.2	40.2	110.9	43.0	116.0 (116.2) ^d	30.6
NaBPh ₄	53.6 (54.6) ^b	—	55.8	—	60.2	—	65.4	—	67.4	—	78.6	—	82.2	—
KNO ₃	91.4	20.6	91.9	17.2	94.6	—	99.5	24.0	105.4	15.2	114.0	—	118.2	21.4
AgNO ₃	93.6 (92.6) ^a	24.7	92.6	13.3	93.5	6.3	99.9	50.0	105.0	35.9	114.0	7.0	119.2 (120.6) ^f	44.6
Me ₄ NBr	89.7	13.2	90.8	—	96.9	—	100.8	—	106.4	—	117.3	—	126.0 (125.2) ^e	—
Et ₄ NBr	87.3 (89.1) ^a	55.9	92.6	23.9	97.6	31.5	103.6	44.7	105.7	45.0	115.7	42.2	117.7 (117.0) ^e	34.3
Pr ₄ NBr	80.4 (82.9) ^a	16.2	81.4	—	84.2	—	87.5	—	93.9	15.5	98.0	—	103.3 (102.6) ^e	25.5
Bu ₄ NBr	76.4	—	77.5	—	82.2	28.9	84.1	—	87.0	—	93.9	—	96.2 (95.4) ^e	—
Bu ₄ NBPh ₄	49.1	—	50.0	—	56.6	—	60.0	—	62.8	—	74.7	—	76.0	—

a : Ref. 13 ; b : ref. 14 ; c : ref. 15 ; d : ref. 16 e ; ref. 17 ; f : ref. 1

Table 3—Limiting ionic molar conductances ($\lambda_{\pm}^{\circ}$) and actual solvated radii (r_i) of some ions in DMF + MeOH mixtures at 25°C

Ion	DMF + MeOH (mol% DMF)											
	100		89.3		69.1		49.6		29.9		10.7	
	$\lambda_{\pm}^{\circ}$	r_i	$\lambda_{\pm}^{\circ}$	r_i	$\lambda_{\pm}^{\circ}$	r_i	$\lambda_{\pm}^{\circ}$	r_i	$\lambda_{\pm}^{\circ}$	r_i	$\lambda_{\pm}^{\circ}$	r_i
Li ⁺	27.9	4.9	28.5	4.9	34.0	4.7	36.1	4.8	38.1	5.0	42.1	4.9
Na ⁺	33.0	4.3	35.1	4.3	40.6	4.2	42.5	4.3	42.9	4.6	47.5	4.5
K ⁺	34.3	4.2	36.3	4.2	42.7	4.0	47.1	4.0	50.8	4.1	55.3	4.0
Ag ⁺	36.5	4.0	37.0	4.2	41.6	4.1	47.4	4.0	50.4	4.1	55.2	4.1
Me ₄ N ⁺	41.8	3.7	42.6	3.8	51.7	3.6	53.8	3.7	57.7	3.8	67.3	3.6
Et ₄ N ⁺	39.4	3.8	44.4	3.7	52.4	3.5	56.6	3.4	57.0	3.8	65.7	3.6
Pr ₄ N ⁺	32.5	4.4	33.3	4.5	39.0	4.3	40.5	4.4	45.2	4.5	48.0	4.4
Bu ₄ N ⁺	28.5	4.8	29.3	4.9	37.0	4.4	37.1	4.7	38.3	5.0	43.9	4.7
Br ⁻	47.9	3.4	48.2	3.5	45.2	3.9	47.0	4.0	48.7	4.2	50.0	4.3
I ⁻	47.5	3.4	47.9	3.5	43.8	3.9	45.7	4.1	48.3	4.2	52.8	4.2
SCN ⁻	56.2	3.1	56.9	3.2	53.7	3.5	56.6	3.5	58.4	3.8	60.1	3.9
ClO ₄ ⁻	49.3	3.3	51.4	3.4	49.3	3.7	56.0	3.7	60.3	3.7	63.4	3.7
BPh ₄ ⁻	20.6	6.2	20.7	6.4	19.6	7.2	22.9	6.7	24.5	6.9	30.8	6.1
NO ₃ ⁻	57.1	3.0	55.6	3.0	51.9	3.5	52.4	3.7	54.6	3.9	58.7	3.9

coefficients using the Jones Dole equation²⁰ in the form:

$$\frac{\eta}{\eta_0} = 1 + AC^{1/2} + BC \quad \dots(2)$$

which may be rearranged as:

$$\left(\frac{\eta}{\eta_0} - 1 \right) / C^{1/2} = A + BC^{1/2} \quad \dots(3)$$

where η and η_0 are the viscosities of the solution and of the pure solvent respectively, C is the molar concentration and A and B are viscosity coefficients characteristic of the salt and the solvent. The viscosity A - and B - coefficients have been computed by the least squares method from the linear plots of $(\eta / \eta_0 - 1) / C^{1/2}$ and $C^{1/2}$ and are recorded in Table 4.

Inspection of Table 4 reveals that viscosity B - coefficients measured in all DMF + MeOH mixtures are positive for all the electrolytes studied. The experimental B - coefficients at 25°C in DMF and MeOH have been compared with viscosity coefficients of a few electrolytes already available^{14,21,22} in literature (Table 4) and there is a good agreement.

The B -coefficients for Pr₄NBr and Bu₄NBr increase from 100 mol% DMF to 29.9 mol% DMF

and decreases thereafter. However, for Et₄NBr, the B -coefficient value decreases or increases within 0.53 ± 0.05 between 100 mol% DMF and 0.00 mol% DMF. The viscosity B - coefficient for LiBr, NaBr, NaI, NaClO₄ and NaSCN also increase from 100 mol% DMF to 29.9 mol%DMF and decrease thereafter up to pure MeOH. However, for NaBPh₄ and Bu₄NBPh₄, except for 0.00 mol% DMF, the variation in viscosity B - coefficient is small (within ± 0.07 for NaBPh₄ and ± 0.04 for Bu₄ NBPh₄).

In DMF + MeOH mixtures, both the solvents have almost same dielectric constant but DMF has larger molecular volume and negligible tendency of hydrogen bonding as compared to MeOH, so viscosity B -coefficients for different electrolytes are likely to be larger in DMF as compared to MeOH. However, in DMF + MeOH mixtures, there may be competition between the two solvents to solvate the ions and therefore, irregular trends have been observed in some cases. This is also in accordance with conductance behaviour of ions.

Ionic viscosity B - coefficients

To throw light on ion - solvent interactions, the viscosity B - coefficients are not sufficient because the ions with opposite charges may have different pattern

Table 4—Viscosity A ($\text{dm}^{3/2} \text{mol}^{-1/2}$) and viscosity B ($\text{dm}^3 \text{mol}^{-1}$) coefficients of some 1:1 electrolytes in DMF + MeOH at 25°C

Electrolyte		DMF + MeOH Mixture (mol% DMF)						
		100	89.3	69.1	49.6	29.9	10.7	0.0
LiBr	B	0.72	0.72	0.73	0.78	0.83	0.78	0.78
	A	0.07	-0.01	0.09	0.12	0.10	0.02	0.02
NaBr	B	0.69	0.69	0.70	0.77	0.85	0.76	0.70
	A	0.05	0.04	0.01	0.04	0.06	0.00	0.01
NaI	B	0.65	0.67	0.74	0.74	0.81	0.71	0.64
	A	0.03	0.04	0.03	0.03	0.00	0.06	0.09
NaClO ₄	B	0.80(0.89) ^a	0.82	0.89	0.90	0.96	0.86	0.81(0.79) ^b
	A	0.02	0.06	0.00	0.00	-0.01	0.01	0.02
NaSCN	B	0.76	0.77	0.85	0.87	0.94	0.89	0.89
	A	0.04	0.04	0.06	0.07	-0.06	0.07	-0.01
NaBPh ₄	B	1.65(1.70) ^a	1.67	1.69	1.66	1.75	1.62	1.28(1.37) ^b
	A	-0.03	-0.02	-0.04	0.12	0.00	0.02	0.05
Et ₄ NBr	B	0.56	0.55	0.53	0.52	0.58	0.53	0.48(0.48) ^c
	A	0.08	0.07	0.06	0.03	0.05	0.06	0.04
Pr ₄ NBr	B	0.73	0.78	0.80	0.84	0.90	0.71	0.70(0.66) ^c
	A	0.03	0.01	0.02	0.02	0.00	-0.01	0.01
Bu ₄ NBr	B	0.96	0.98	0.99	1.02	1.08	1.07	0.86(0.85) ^c
	A	0.08	-0.01	-0.01	0.01	0.07	0.05	0.02
Bu ₄ NBPh ₄	B	1.92(1.92) ^a	1.94	1.90	1.93	1.98	1.93	1.44(1.44) ^b
	A	-0.02	-0.01	-0.05	-0.01	-0.01	-0.01	-0.03

(a) Ref. 9 : 9; (b) ref : 18; (c) ref : 19

of solvation. It is, therefore, essential to split the viscosity B – coefficient value into its ionic contributions. However, there is no experimental method to divide B – values of the electrolytes into B₊ and B₋ values and thus, indirect methods have been mostly used, based upon the choice of some reference electrolytes^{12,23}. Gill and co-workers^{24,25} have suggested a method for splitting B – values of electrolytes into ionic B₊ and B₋ values especially in non-aqueous solvents, taking Bu₄NBPh₄ as the reference electrolyte. The model is based on Eqs (4 and 5):

$$\frac{B_{\text{Bu}_4\text{N}^+}}{B_{\text{BPh}_4^-}} = \left(\frac{r_{\text{Bu}_4\text{N}^+}}{r_{\text{BPh}_4^-}} \right)^3 = \left(\frac{5.00}{5.35} \right)^3 \quad \dots(4)$$

$$B_{\text{Bu}_4\text{NBPh}_4} = B_{\text{Bu}_4\text{N}^+} + B_{\text{BPh}_4^-} \quad \dots(5)$$

Using Eqs (4) and (5), the B – coefficients of the electrolytes in DMF + MeOH mixtures from Table 4, have been divided into B₊ and B₋ values. These are reported in Table 5.

The inspection of Table 5 shows that viscosity B-coefficients for cations do not follow regular order while the viscosity B-coefficients for anions show regular increase with decrease in DMF content in DMF + MeOH mixtures. The irregularity in case of cations may be due to competition between the two solvents in different mixtures to solvate the cations. The trend in viscosity B-coefficients for anions show that the anions are preferentially solvated by MeOH. The viscosity B-coefficients for anions decrease in the order : BPh₄⁻ > ClO₄⁻ > SCN⁻ > Br⁻ > I⁻

Table 5—Ionic viscosity B – coefficients ($\text{dm}^3 \text{mol}^{-1}$) of some 1:1 electrolytes in DMF + MeOH (mol% DMF) mixtures at 25°C

Ion	DMF + MeOH mixture (mol% DMF)						
	100	89.29	69.08	49.60	29.90	10.69	0.00
Li^+	0.62	0.61	0.59	0.63	0.65	0.59	0.57
Na^+	0.59	0.58	0.56	0.62	0.67	0.57	0.49
Et_4N^+	0.46	0.44	0.39	0.37	0.40	0.34	0.27
Pr_4N^+	0.63	0.67	0.66	0.69	0.72	0.52	0.49
Bu_4N^+	0.86	0.87	0.85	0.87	0.90	0.88	0.65
Br^-	0.10	0.11	0.14	0.15	0.18	0.19	0.21
I^-	0.06	0.07	0.10	0.12	0.14	0.14	0.15
ClO_4^-	0.21	0.22	0.25	0.28	0.29	0.29	0.29
SCN^-	0.17	0.17	0.21	0.25	0.27	0.32	0.32
BPh_4^-	1.06	1.07	1.05	1.06	1.08	1.05	0.79

Table 6—Limiting molar conductances (Λ_0 , $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$) and association constant K_A ($\text{dm}^3 \text{mol}^{-1}$) of some 1 : 1 electrolytes in DMF + MeOH mixtures at 30° and 40°C

Electrolyte	DMF + MeOH mixture (mol% DMF)													
	100		89.3		69.1		49.6		29.9		10.7		0.00	
	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
30°C														
NaBr	87.9	18.9	90.5	12.8	93.9	—	98.0	—	100.3	—	106.5	16.4	112.1	—
NaBPh ₄	58.8	—	61.1	—	65.9	—	71.5	—	73.7	12.4	85.7	—	90.0	—
Bu ₄ NBr	83.2	16.0	84.2	12.7	90.0	—	92.1	—	95.3	16.1	112.8	—	105.3	—
40°C														
NaBr	103.6	16.3	106.2	—	110.0	—	115.5	—	117.7	17.1	125.0	—	131.6	16.6
NaBPh ₄	69.1	—	71.1	—	77.3	—	84.0	—	86.6	—	100.6	—	105.5	—
Bu ₄ NBr	98.0	25.4	98.8	17.7	105.6	30.1	108.1	—	111.8	—	120.7	18.9	123.6	—

Table 7—Limiting ionic conductances ($\lambda_{\pm}$) and solvated radii of some ions in DMF + MeOH mixtures (mol% DMF) at different temperatures*

Ion	Temp.	100		89.3		69.1		49.6		29.9		10.7		0.00	
		$\lambda_{\pm}^{\circ}$	r_i	$\lambda_{\pm}^{\circ}$	r_i	$\lambda_{\pm}^{\circ}$	r_i	$\lambda_{\pm}^{\circ}$	r_i	$\lambda_{\pm}^{\circ}$	r_i	$\lambda_{\pm}^{\circ}$	r_i	$\lambda_{\pm}^{\circ}$	r_i
Na^+	25	30.1	4.6	31.9	4.6	32.9	4.8	36.8	4.7	37.4	5.0	42.7	4.8	46.0	4.7
	30	33.0	4.40	34.9	4.5	36.2	4.7	40.1	4.6	40.8	4.9	46.5	4.7	50.2	4.6
	40	38.7	4.1	40.9	4.3	42.4	4.4	47.4	4.3	48.0	4.6	54.5	4.5	58.9	4.4
Bu_4N^+	25	25.6	5.3	26.1	5.4	29.3	5.2	31.4	5.3	32.8	5.5	39.1	5.1	39.8	5.2
	30	28.3	5.0	28.6	5.2	32.3	5.1	34.2	5.2	35.8	5.3	42.8	5.0	43.4	5.1
	40	33.1	4.6	33.5	4.9	38.0	4.8	40.0	4.9	42.1	5.0	50.2	4.7	50.9	4.8
Br^-	25	50.8	3.3	51.4	3.4	52.8	3.5	52.7	3.7	54.2	3.9	54.8	4.1	56.4	4.1
	30	54.9	3.1	55.6	3.3	57.7	3.4	57.9	3.6	59.5	3.7	60.0	3.9	61.9	4.0
	40	64.9	2.9	65.3	3.1	67.6	3.2	68.1	3.4	69.7	3.5	70.5	3.7	72.7	3.8
BPh_4^-	25	23.5	5.6	23.9	5.7	27.3	5.5	28.6	5.7	29.9	5.9	35.6	5.5	36.2	5.6
	30	25.8	5.2	26.2	5.5	29.7	5.4	31.4	5.5	32.9	5.6	39.2	5.3	39.8	5.5
	40	30.4	4.8	30.8	5.2	34.9	5.0	36.6	5.1	38.6	5.3	46.1	5.0	46.6	5.2

* The values at 25°C are also obtained by Bu₄NBPh₄ assumption

Table 8—Viscosity A (dm^{3/2} mol^{-1/2}) and viscosity B (dm³ mol⁻¹) coefficients of some 1:1 electrolytes in DMF + MeOH at 30° and 40°C

Electrolyte		DMF + MeOH mixture (mol% DMF)						
		100	89.3	69.1	49.6	29.9	10.7	0.00
30°C								
NaBr	B	0.62	0.66	0.69	0.70	0.72	0.70	0.69
	A	0.07	0.07	-0.01	0.02	0.03	-0.01	0.05
NaBPh ₄	B	1.57	1.60	1.59	1.57	1.61	1.57	1.29
	A	-0.02	0.02	-0.05	-0.02	-0.02	0.01	0.09
Bu ₄ NBr	B	0.93	0.96	0.97	0.90	1.06	1.05	0.84
	A	-0.06	0.08	-0.01	0.05	0.08	0.01	0.02
Bu ₄ NBPh ₄	B	1.88	1.90	1.87	1.89	1.95	1.91	1.44
40°C								
NaBr	B	0.60	0.63	0.67	0.67	0.69	0.68	0.67
	A	0.09	0.06	-0.02	0.01	0.01	0.01	-0.02
NaBPh ₄	B	1.54	1.56	1.59	1.57	1.60	1.56	1.28
	A	-0.02	-0.06	-0.07	-0.06	-0.08	-0.05	0.02
Bu ₄ NBr	B	0.93	0.94	0.94	0.97	1.00	1.02	0.82
	A	-0.01	0.01	0.01	0.01	0.01	0.07	0.04
Bu ₄ NBPh ₄	B	1.85	1.87	1.86	1.87	1.91	1.88	1.43

Table 9 – Ionic viscosity B – coefficients (dm³ mol⁻¹) of some 1:1 ions in DMF + MeOH mixtures at different temperatures.

Ion	DMF + MeOH mixture (mol% DMF)																				
Temp.	100			89.29			69.08			49.60			29.90			10.69			0.00		
	25	30	40	25	30	40	25	30	40	25	30	40	25	30	40	25	30	40	25	30	40
Na ⁺	0.59	0.54	0.52	0.58	0.55	0.53	0.56	0.56	0.55	0.62	0.55	0.54	0.67	0.56	0.55	0.57	0.52	0.51	0.49	0.50	0.49
Bu ₄ N ⁺	0.86	0.85	0.83	0.87	0.85	0.84	0.85	0.84	0.83	0.87	0.85	0.84	0.90	0.90	0.86	0.88	0.86	0.85	0.65	0.65	0.64
Br ⁻	0.10	0.08	0.08	0.11	0.11	0.10	0.14	0.13	0.11	0.15	0.15	0.13	0.18	0.16	0.14	0.19	0.18	0.17	0.21	0.19	0.18
BPh ₄ ⁻	1.06	1.03	1.02	1.07	1.05	1.03	1.05	1.03	1.03	1.06	1.04	1.03	1.08	1.05	1.05	1.05	1.05	1.03	0.79	0.79	0.79

Conductance and viscosity studies at higher temperatures

To study the effect of temperature, conductance and viscosity measurements of three salts Bu₄NBr, NaBPh₄ and NaBr have been carried out in different DMF + MeOH mixtures at 30 and 40°C. The conductance data have been analysed by using Shedlovsky's method. The dielectric constant and Bjerrum critical distances used for calculating Λ_0 and K_A are given in Table 1. The Λ_0 and K_A values are recorded in Table 6.

To calculate limiting ionic conductances at these temperatures, Bu₄NBPh₄ assumption has been used due to the lack of transference number data at these temperatures. The molar conductances of Bu₄NBPh₄ at all compositions were calculated by applying Kohlrausch law. The limiting ionic conductances of

Bu₄N⁺ and BPh₄⁻ ions at 30 and 40°C have been calculated using following Eqs (6) and (7) :

$$\frac{\lambda_{\text{Bu}_4\text{N}^+}^0}{\lambda_{\text{BPh}_4^-}^0} = \frac{5.35 - (0.0103 \epsilon + r_y)}{5.00 - (0.013 \epsilon + r_y)} \quad \dots(6)$$

$$\Lambda_{\text{Bu}_4\text{NBPh}_4}^0 = \lambda_{\text{Bu}_4\text{N}^+}^0 + \lambda_{\text{BPh}_4^-}^0 \quad \dots(7)$$

The limiting ionic conductances and effective solvated radii calculated using Eqs (6) and (7) are reported in Table 7. The $\lambda_{\pm}^0$ values increase with increase in temperature due to increase in kinetic energy with rise temperature. The r_i values of Br⁻ ion increase continuously from 100 mol% DMF to pure MeOH showing that Br⁻ is preferentially solvated by MeOH even at higher temperatures.

The viscosity data at 30 and 40°C have been analysed by Jones – Dole equation as already

discussed and viscosity A- and B-coefficients thus obtained are recorded in Table 8. The viscosity B-coefficients for Bu_4NBPh_4 in DMF + MeOH mixtures at 30 and 40°C have been calculated on the basis of additive contributions of individual ions from the B-values of Bu_4NBr , NaBPh_4 and NaBr as :

$$B_{\text{Bu}_4\text{NBPh}_4} = B_{\text{Bu}_4\text{NBr}} + B_{\text{NaBPh}_4} - B_{\text{NaBr}} \quad \dots(8)$$

These values were further used to calculate ionic viscosity B – coefficients for Bu_4N^+ and BPh_4^- using Eqs (4) and (5). The values are recorded in Table 9. The values of ionic viscosity B-coefficients for these ions at 25°C are also recorded for the sake of comparison.

The viscosity B – coefficients for all the ions decrease with rise in temperature. This decrease in viscosity ionic B – coefficient with increase in temperature has also been observed by other workers in aqueous as well as in non-aqueous solvent mixtures. The decrease in B – coefficient with temperature may be due to disruption in structure at higher temperatures as a result of increase in kinetic energy.

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