Viscosity Study of Ion Solvation in DMSO-DMF and DMSO-MeOH Solvent Systems at 25°C

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Viscocity of Ph_4PBPh_4, Bu_4NBPh_4, Bu_4NNO_3, $LiNO_3$, $NaNO_3$, KNO_3 and $AgNO_3$ have been measured in DMSO, DMF, MeOH, DMSO-DMF and DMSO-MeOH solvent systems at 25°C and the data analysed to arrive at Jones-Dole A and B coefficients. The B coefficients have been separated to ionic components using the data of symmetrical reference electrolyte Ph_4PBPh_4. The results are interpreted in terms of different behaviour of ions in the two solvent mixtures.

Investigation of viscosity of electrolyte solutions and arriving at the ionic contributiond to Jones-Dole coefficients in mixed solvent systems is useful for evaluating ion-solvent interactions, since these coefficients reflect the contribution of cosphere of the ions. The B coefficients can be derived by fitting viscosity data to Jones-Dole equation [1]. The separation of B coefficients to ionic contributions can be achieved by using symmetrical model electrolytes like Bu_4NBBu_4 and Ph_4PBPh_4 in pure solvents like N,N-dimethylformamide (DMF) [2], dimethylsulphoxide (DMSO) [3], acetonitrile (AN) [4] and hexamethyl-phosphoramide (HMPA) [5].

In our previous paper [6], we have determined the ionic B values in DMSO-methanol solvent mixtures using Ph_4PBPh_4 as the reference electrolyte. In the present case, we have used the same procedure to resolve the experimentally determined B values for Ph_4PBPh_4, Bu_4NBPh_4, Bu_4NNO_3, $LiNO_3$, $NaNO_3$, KNO_3 and $AgNO_3$ in DMSO-DMF and DMSO-MeOH solvent systems into ionic components.

EXPERIMENTAL

Preparation and purification of Ph_4PBPh_4, Bu_4NBPh_4 and Bu_4NNO_3 are described earlier [7]. $LiNO_3$ (AR grade from SRL Pvt. Ltd. Bombay) $NaNO_3$, KNO_3 (both AR grade from Glaxo Laboratories Pvt. Ltd. Bombay) and $AgNO_3$ (AR grade from Merck) were dried in vacuum for 24 to 48 hrs without further purification. DMSO and DMF (both AR grade from SRL Pvt. Ltd. Bombay) and MeOH (AR from Ranbaxy laboratories, India) were purified as described earlier [6,7].

Viscosity measurements were carried out with a precision of ±0.1% using Ubbelhode

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suspended level viscometer whose flow time for distilled water was 676.7±0.2 sec at 25°C. The density measurements were carried out with a precision of ±0.01% using two different sealable pycnometers of 20 and 30 ml capacity. All measurements were carried out in water bath precise to ±0.01°C. Experimental procedure for both measurements was the same as described earlier [7].

RESULTS AND DISCUSSION

B Coefficients

Viscosity of (65 - 770)x10^{-4} mol.dm^{-3} solutions of Bu_4NBPh_4, Bu_4NNO_3, $LiNO_3$, $NaNO_3$ and $AgNO_3$ have been measured in DMF, DMSO and different mixtures of these containing 10 to 90 % DMF at 25°. In case of solutions of Bu_4NNO_3, $LiNO_3$, $NaNO_3$ and $AgNO_3$ in MeOH and DMSO-MeOH mixtures, measurements were carried out in the concentration range 60 - 750 x 10^{-4} mol.dm^{-3} because of limitation in solubility. Measurements could not be carried out for KNO_3 in pure DMF and MeOH due to poor solubility. Study of KNO_3 in DMF-MeOH was restricted to 70.07 mole % MeOH in the concentration range 60 - 750 x 10^{-4} mol.dm^{-3}, but in the rest of the solvent mixtures, measurement was restricted to 45 - 600 x 10^{-4} mol.dm^{-3}.

Table 1

Jones-Dole Viscosity B (dm^3.$mole^{-1}$) and A (dm^3.$mole^{-1})^{1/2}$ in Different Solvent Media

Temperature 25°C

mol% Solvent	0		10		30		50		70		90		100	
Salt	B	10^2A	B	10^2A	B	10^2A	B	10^2A	B	10^2A	B	10^2A	B	10^2A
Increasing mol % of DMF in DMSO - DMF Mixtures														
Ph_4PBPh_4	1.76	2.2	1.76	2.1	1.77	2.2	1.78	2.4	1.78	2.7	1.80	2.4	1.84	2.2
Bu_4NBPh_4	1.35	2.0	1.35	2.0	1.35	2.3	1.36	2.3	1.39	2.2	1.42	2.2	1.43	2.3
Bu_4NNO_3	0.77	1.2	0.76	1.5	0.79	1.8	0.82	1.8	0.85	2.0	0.91	1.6	0.95	1.4
KNO_3	0.69	1.1	0.69	1.4	0.71	1.2	0.71	1.6	0.71	1.9	-	-	-	-
$NaNO_3$	0.69	1.1	0.68	1.0	0.71	1.2	0.71	1.3	0.72	1.9	0.75	1.8	0.81	1.8
$AgNO_3$	0.83	1.0	0.83	1.5	0.83	1.0	0.80	1.2	0.79	1.2	0.84	1.3	0.89	1.4
$LiNO_3$	0.75	1.2	0.74	1.2	0.76	1.3	0.78	1.4	0.76	1.8	0.75	1.8	0.77	2.0
Increasing mol % of MeOH in DMSO - MeOH Mixtures														
Bu_4NNO_3	0.75	1.4	0.84	1.2	0.90	1.5	0.94	1.2	0.94	1.6	0.93	1.7	0.93	1.8
KNO_3	0.70	1.0	0.76	1.0	0.83	1.2	0.85	1.3	0.84	1.4	-	-	-	-
$NaNO_3$	0.71	0.9	0.77	0.9	0.79	1.1	0.82	1.1	0.83	1.3	0.81	1.3	0.80	1.6
$AgNO_3$	0.87	1.1	0.92	1.0	0.95	1.0	0.94	1.2	0.93	1.4	0.80	1.6	0.70	1.5
$LiNO_3$	0.75	1.4	0.83	1.3	0.88	1.4	0.91	1.4	0.91	1.4	0.87	1.7	0.83	2.0

The entire viscosity data were fitted to Jones-Dole equation in the form:

$$(\eta/\eta_o - 1) / C^{1/2} = A + BC^{1/2} \quad \ldots (2)$$

using a least squares computer programme. The A and B coefficient data are presented in Table 1. The B values for Ph_4PBPh_4 and Bu_4NBPh_4 in DMSO-MeOH have been reported earlier [6].

A perusal of Table 1 shows that B value for Ph_4PBPh_4 and Bu_4NBPh_4 in DMSO-DMF increase only slightly with addition of DMF . The B values for $AgNO_3$, KNO_3 and $LiNO_3$ remain practically constant over the entire solvent composition range but it increases for $NaNO_3$ and Bu_4NNO_3 with increase of DMF in the mixture.

On the other hand the B values for these electrolytes in DMSO-MeOH show a slight maximum at about 50-70 mole % MeOH.

There are several factors that contribute to the variation of B coefficients in different solvent systems: (i) Structure breaking is much more important in three dimentionally structured solvents than in less structured solvents. This gives a negative contribution to B value. (ii) For solvents of comparable solvating abilities, the larger B coefficients is normally associated with the solvents having the larger molar volume.

In the present solvent systems, no solvent component is structured. It is also evident from their large and positive B values for all the electrolytes in both DMSO-DMF and DMSO-MeOH solvent systems.

Ionic $B_\pm$ Coefficient and Ionic Solvation

In our earlier report, we resolved the experimentally determined B coefficients into ionic contributions ($B_\pm$) in pure DMF, DMSO [8] and in DMSO-MeOH solvent systems [6] on the assumption of equal contribution of Ph_4P^+ and BPh_4^-. On the same assumption, the ionic B values for Li^+, Na^+, K^+, Ag^+, NO_3^-, Bu_4N^+ and Ph_4B^- in DMSO-DMF solvent systems have been obtained. In DMSO-MeOH system, the ionic B values for Ph_4P^+ and Ph_4B^-

Table 2

Ionic Viscosity $B_\pm$ Coefficients ($dm^3.mole^{-1}$) for Some Ions

Temperature 25°C

Mol %	0	10	30	50	70	90	100
Mol % DMF in DMSO-DMF system							
Ph_4P^+	0.88	0.88	0.89	0.89	0.89	0.90	0.92
Ph_4B^-	0.88	0.88	0.88	0.89	0.89	0.90	0.92
Bu_4N^+	0.45	0.45	0.45	0.47	0.50	0.52	0.51
NO_3^-	0.32	0.31	0.34	0.35	0.35	0.39	0.44
Li^+	0.43	0.43	0.42	0.43	0.41	0.36	0.35
Na^+	0.37	0.37	0.37	0.36	0.37	0.36	0.37
K^+	0.37	0.38	0.37	0.36	0.36	-	-
Ag^+	0.51	0.50	0.49	0.45	0.44	0.45	0.45
Mol % MeOH in DMSO-MeOH system							
NO_3^-	0.32	0.37	0.38	0.37	0.39	0.39	0.42
Li^+	0.43	0.46	0.50	0.52	0.52	0.48	0.41
$+Na^+$	0.39	0.40	0.41	0.45	0.44	0.42	0.38
K^+	0.38	0.39	0.45	0.48	0.45	-	-
Ag^+	0.55	0.55	0.57	0.57	0.54	0.41	0 28

have been reported earlier and used here to get the ionic B values of the other ions. All the values are reported in Table 2.

DMSO-DMF Solvent System

Interesting results emerge from the variation of $B_\pm$ values. It may be noted that B_+ values for Ph_4P^+, Na^+ and K^+ and B_- value for Ph_4B^- remain nearly constant over the entire range of solvent composition. Ph_4P^+ and Ph_4B^- are large ions and remain mostly unsolvated and hence the $B_\pm$ values are independent of the solvent composition. Na^+ and K^+ appear to be solvated by DMSO and DMF in the same way. This is consistant on the basis of free energy considerations [7-9]. The B_+ value of Ag^+ below 50 mol % DMF remains constant and equal to that in pure DMSO (0.50 $dm^3.mol^{-1}$) whereas above 50 mol % DMF, it becomes equal to that in pure DMF (0.45 $dm^3.mol^{-1}$). Although the solvation of Ag^+ follows much the same pattern as Na^+ and K^+, Ag^+ being a transition metal ion of d^{10} electronic structure, it undergoes specific interactions with electron donor solvents like DMSO and DMF [7,10]. The variation of B_+ can be interpreted to mean the existence of preferential solvation of Ag^+ by DMSO in DMF-rich region and by DMF in DMSO-rich region in DMSO-DMF mixxture.

B_+ value of Li^+ remains independent of solvent composition up to 70 mol % DMF and then it decreases to the value in pure DMF. This suggests that Li^+ is preferentially solvated by DMSO in DMSO-DMF mixtures. Li^+, being the smallest cation, has the highest charge density and is expected to undergo relatively strong ion-solvent interactions. In DMSO, the interaction is through the oxygen of the S=O group.

Irrespective of its charge, large Bu_4N^+ acts as unsolvated species in dipolar aprotic solvents [8]; but unlike the case of Ph_4P^+, the B_+ for Bu_4N^+ increases with the addition of DMF in DMSO-DMF mixtures. This may be due to the contribution of the molar volume of the solvent components (DMF = 0.077 $dm^3.mol^{-1}$ and DMSO = 0.071 $dm^3.mol^{-1}$) [6]. The B_- of NO_3^- ions also increases linearly with DMF content. Similar argument is presumed to hold good in this case also since anions are known to be unsolvated in dipolar aprotic solvents [10].

DMSO-MeOH Solvent System

In DMSO-MeOH solvent system, however, the variation of B_+ values for Li^+, Na^+ and K^+ show a slight maximum at about 50-70 mol % MeOH. But the value for Ag^+ remain practically constant upto 70 mol % MeOH and, it starts decreasing thereafter towards the value in pure MeOH. These observations are found to be consistant with our earlier work [6]. In case of NO_3^-, the B_- value increases from 0.32 $dm^3.mol^{-1}$ in pure DMSO to 0.37 $dm^3.mol^{-1}$ with the addition of 10 mol % MeOH. Further addition of MeOH, however, does not bring any observable change in the B_- value. The dependence of B_- value for NO_3^- on solvent composition are thus found to be similar to that of ClO_4^- reported earlier [6], which indicates that both NO_3^- and ClO_4^- behave similarly in DMSO-MeOH solvent system.

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