Study of Ion-Solvent Interactions of Lithium Bromide in, DMSO, H₂O and DMSO- H₂O Mixtures at 25°C

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Summary: The relative viscosities were measured for LiBr and reference salt Bu₄BBPh₄, KCl in a wide range composition of mixture of DMSO and water at 25 °C to obtain Jones-Dole B-coefficients. The B-coefficients of these electrolytes in DMSO were positive which behave as structure makers while in H₂O and DMSO-H₂O) mixtures, the B-coefficients values are less positive showing weak structure-making effects. The values of ionic B-coefficients are suggesting that the Li⁺ ion is structure-maker while Br⁻ is structure- breaking in H₂O) and Mix III i.e. 20 % DMSO + 80 % water.

Introduction

The knowledge of ion-solvent interactions in aqueous and non-aqueous media is of considerable fundamental and technological importance. The potentialities of non-aqueous solvents in thermodynamic, kinetic and analytical techniques in organic and inorganic synthesis as well as in industrial applications have been well recognised [1,2].

In non- aqueous batteries, two important factors are the choice of electrolyte solution and the optimisation of its salt concentration. An electrolyte solution having high specific conductivity and with negligible ion –ion solvent interactions is required to maintain low internal resistance in the cell. Knowledge of the state of association of the electrolytes and the interactions between the solvent molecules is essential for the optimal choice of the solvent and electrolyte. To this end, various classical techniques such as electrical conductivity, viscosity and ultrasonic velocity measurements have been employed to study the status of association of the electrolytes [3, 4].

Dimethylsulfoxide (DMSO) is an aprotic solvent and has useful properties in organic synthesis [5,6] and important applications in electrochemistry [7]. The physical and the dipolar properties of DMSO make the solvent promising for high-energy-density battery application. The transport behaviour of ions in DMSO, and the role of DMSO as a solvent in organic reactions, both require the understanding of the nature of ion-solvent interactions. Transport parameters of electrolyte solutions such as ionic conductance and viscosity can provide informations concerning the nature of the kinetic entities from

which the ion-solvent interaction can be inferred [8, 9].

The main theme of this study is to investigate the behaviour of the kinetic entities called mobile ions in the proposed solvents such as water and DMSO. In this study, the reason for the selection of water and DMSO is to observe the physical changes in the behaviour of a protic to an aprotic binary solvent system.

Considering the structure and dielectric constant of DMSO, studies of salt in mixtures of DMSO with water, acetonitrile and nitrobenzene could be an ideal approach towards the ion-solvent interactions in mixed solvents. These considerations led us to study the solvation properties of 1:1 electrolytes in H₂O, DMSO and H₂O-DMSO mixtures. Water is characterised by protic structure whereas DMSO is aprotic in character [10]. The results from the present study together with solvation values in water and DMSO may reveal characteristic changes (i.e. differences of interaction of electrolytes with solvent molecules) associated with the transfer of electrolytes from the protic (water) to an aprotic solvents (DMSO).

Results and Discussion

The measured physical parameters like densities (ρ_o) and viscosities (η_o) for Dimethyl sulfoxide (DMSO), water (H₂O) and DMSO–H₂O mixtures containing 100, 60, 40 20 and 0 % mole DMSO are reported in Table-1 for temperatures of 25 °C. The data obtained in this study for densities (ρ_o)

Table-1: Densities (ρ_o) and viscosities (η_o) for DMSO, H_2O and DMSO –H_2O mixtures at 25°C.

Wt % DMSO	Mole fraction	Density g/cm³	Viscosity cP
100 % pure DMSO	1.00	1.09541	1.966
60 % DMSO + 40 % water	0.2570	1.08231	3.421
40 % DMSO + 60 % water	0.1333	1.05347	2.221
20 % DMSO + 80 % water	0.0545	1.02420	1.340
100 % Pure H_2O	0.0000	0.99715	0.890

and viscosities (η_o) of the pure solvents H_2O and DMSO at 25°C coincided with the values obtained by other authors [14].

The plots of densities (ρ_o) and viscosities (η_o) versus weight percentage of DMSO are presented in Fig. 1 & 2. The plot of densities (ρ_o) showed small deviations from linearity in mixture 1 (60 % DMSO). The trend in the physical properties of these binary solvent mixtures can be explained by starting from the lowest concentration of DMSO (i.e. 0, 20, 40, 60), where the addition of DMSO causes a slight increase in densities of the solvent mixtures, which indicates small structural effects in DMSO – H_2O mixtures. The above structural effects of aqueous solvent mixtures may be due to high dielectric constant of water, which alters the densities of the solvent mixtures.
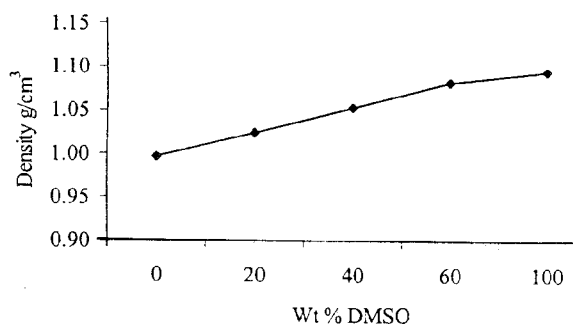
Fig 1 .   Density versus wt % DMSO in DMSO-H_2O mixture at 25 °C.

The same trend is observed in the plot of viscosities. Similar changes in viscosity were also found by other researchers. The viscosity of water-dioxane [15], water- dialkylated amide [16, 17], and water- alcohol [18], showed a sharp maximum or minimum in the plots of viscosity versus solvent compositions. It is observed that at 60% composition of DMSO, the viscosity of the DMSO –H_2O mixture was at its maximum indicating the highest molecule
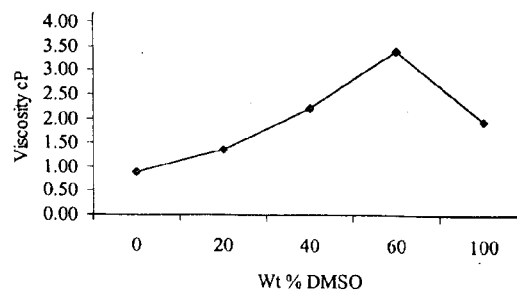
Fig 2.   Viscosity versus wt % DMSO in DMSO-H_2O mixture at 25 °C.

packing in this region, which caused the hindrance in the flow of solvent mixture which resulted in the increase in viscosities of binary solvent mixture.

Relative viscosities, viscosities and the densities of LiBr have been measured in the concentration range (15-1000) $\times 10^{-4}$ mol dm^{-3} in DMSO, H_2O and DMSO-H_2O mixtures over the entire composition range and reported in Table 2 at 25 °C.

The results of the measurements of the relative viscosities η_r for non-aqueous electrolyte solutions are found to fit the Jones-Dole equation [13].

$$\eta r = \eta/\eta_0 = 1 + AC^{\frac{1}{2}} + BC$$

In this equation, η and η_0 are the viscosities of the solution and the pure solvent or solvent mixtures respectively, C is the molar concentration and A and B are the constants at a given temperature and are characteristic of the solvent and the salt. The A coefficient accounts for ion-ion interactions and the B parameter is a measure of the ion solvent interactions. For the evaluation of A and B coefficients, the plots of $(\eta-\eta_0)/\eta_0 \times C^{\frac{1}{2}}$ versus $C^{\frac{1}{2}}$ have been constructed and found to be linear over the whole concentration range studied. The A and B coefficients in each case were obtained from intercepts and slopes of these plots by the method of least squares.

The values of the A- coefficients obtained at 25°C are listed in Table 3 and variation is observed in A- coefficient in various compositions of solvent mixtures. Smaller values of A –coefficient at higher composition of water in binary solvent mixtures imply that ion hydration is greater than ion-ion interaction.

Table-2: The density (g cm^{-3}), viscosity (cP) and relative viscosity (η_r) of LiBr in dimethyl sulphoxide (DMSO), water (H_2O) and different mixtures of DMSO and water at 25 °C.

C mol dm^{-3}	Density (ρ) g cm^{-3}	Viscosity (η) cP	Relative Viscosity (η_r)	C mol dm^{-3}	Density (ρ) g cm^{-3}	Viscosity (η) cP	Relative viscosity (η_r)
LiBr in 100.00 %DMSO				LiBr in 20 % DMSO + 80 % Water			
0.019	1.0969	2.0086	0.1573	0.13	1.02633	1.36391	0.1518
0.025	1.0973	2.0182	0.1664	0.19	1.02698	1.36875	0.1540
0.033	1.0978	2.0385	0.2047	0.26	1.02756	1.37391	0.1568
0.040	1.0985	2.0536	0.2228	0.36	1.02866	1.38093	0.1603
0.049	1.0990	2.0655	0.2277	0.44	1.02959	1.38593	0.1630
LiBr in 60 % DMSO + 40 %Water				LiBr in 100.00 %Water			
0.016	1.09230	3.54164	0.2765	0.014	0.99823	0.90605	0.1518
0.021	1.09482	3.55945	0.2322	0.019	0.99940	0.90899	0.1539
0.026	1.09689	3.57962	0.2887	0.025	0.99960	0.91309	0.1547
0.032	1.09999	3.59789	0.2911	0.035	0.99980	0.91712	0.1599
0.046	1.10992	3.64706	0.2972	0.045	1.00067	0.92118	0.1627
LiBr in 40 % DMSO + 60% Water							
0.016	1.07230	2.29664	0.2670				
0.021	1.07482	2.30723	0.2709				
0.026	1.07689	2.31910	0.2733				
0.032	1.08000	2.33058	0.2774				
0.046	1.08007	2.35451	0.2814				

Table-3: Viscosity A x 10^2(dm^{-3} mol^{-1}) coefficients and viscosity B (dm^3 mol^{-1}) coefficients of the Jones-Dole equation for LiBr in DMSO and DMSO mixtures at 25 °C

	A coefficient	B coefficient
25 °C 100 % pure DMSO	0.0287	0.2944
60 % Mix 1	0.2116	0.2167
40 % Mix 2	0.2465	0.1606
20 % Mix 3	0.1507	0.12651
0 % Pure H$_2$O	0.1379	0.1482

The B coefficient values obtained at 25° for LiBr in the different solvent mixtures are listed in Table 3. It was found that the viscosity B- coefficient of the electrolyte in pure DMSO is large and positive. It was also noted that the viscosities of the solutions are increased with an increase in the concentration of electrolytes, which is a common feature in most non-aqueous solvents like sulpholane (TMS) [19], hexamethylphosphotriamide (HMPT) [20], acetonitrile (AN) [21]; propylene carbonate (PC) [22,23]; tetramethylurea (TMU) [21,24], Methanol [25]; N-methylformamide [26]; and ethylenecarbonate (EC) [27] and also in the mixtures of non-aqueous solvents [28,29,30]. The large and positive values of viscosity B-coefficients indicate the structure making effect of ions on the DMSO solvent. It is clear from the literature that in dipolar aprotic solvents [31], the structure breaking contribution is negligible due to the positive and large values of the B-coefficients that come from the tendency of the ions to attract the solvent molecules around themselves centrosymmetrically. When an ion is

introduced in to a liquid, it interacts with the solvent dipole to form the solvent sheath, and cause the alteration in the liquid structure and the orientation of the molecules surrounding the ion. The degree to which the ion alters the neighbouring solvent structure depends on the ionic charge, size, and shape.

According to literature [32] the interaction energy between a small alkali metal ion and the solvent dipole in DMSO is at least six times greater than the solvent- solvent (DMSO-DMSO) inter-action. The same effect is observed in the present study which shows that the interaction of small alkali metal ions especially Li$^+$ with DMSO is much stronger than the DMSO-DMSO interaction. These strong interactions immobilize neighbouring DMSO molecules and produce large obstructions to their flow, which results in an increase in solution viscosity and causes large B-coefficients values which measure the structure making contribution. The experimentally observed values of the viscosity B- coefficients 0.929 dm^3 mol^{-1} for the salt LiBr in pure DMSO are in good agreement with the available literature values 0.907 dm^3 mol^{-1} at 25°C .

The studies of B- coefficients in binary solvent (DMSO-H$_2$O) mixtures were tabulated in Table 3. A gradual and regular decrease in the values of the B-coefficients were observed as the DMSO content was decreased. Decrease in B-coefficient values show, that the ions cause weaker orientation effects in the solvation layer. In the water rich region the values of

B-coefficients were changed gradually with the solvent composition and smaller B-values were then found in DMSO- H₂O system. The same trend was observed in the study of KCl and KBr dissolved in H₂O-HMPT (hexamethyl phosphoric triamide) binary mixtures [33] and in another study of the salts NaCl, NaBr, NaI and KCl in H₂O-DMSO mixtures [34].

It was observed in Table 3 that in water the B-coefficients for LiBr have small and positive values, which increase with the increase in the concentration of the electrolyte. In LiBr the B values are positive, and due to cation Li⁻ is small and therefore have high surface charge densities. Consequently, such ions will strongly orient adjacent water molecules. So the B-coefficient values of these salts were found to be positive and this trend was also observed during the literature survey [35]. The present measurement of B-coefficients $(0.1148 \pm 0.001 \; dm^3 \; mol^{-1})$ for lithium bromide in pure water was in good agreement with $(0.113 \; dm^3 \; mol^{-1})$ by [36,37].

The values of the B-coefficients of the reference salts are presented in Table 4. These values are large and positive in pure DMSO. Relative viscosity data has shown an increase which follows the increase in the concentration of the reference salts in DMSO. The B-coefficients found in the present study are consistent with the literature values for similar substances. B-coefficients values are comparable with the literature values [38].

Table 4. Viscosity B coefficients (dm³ mol⁻¹) for reference salts at 25°C

Ref Salts	Mix 1	Mix 2	Mix 3	Mix 4	H₂O
Bu₄BBPh₄	1.270	-	-	-	-
Bu₄NBr	0.901	-	-	-	-
KCl	-	0.326	0.322	0.146	-0.018

The B-coefficients of lithium bromide in different compositions of DMSO in the present work are positive and much higher than water. DMSO is generally considered bulkier and less structured than water. A solute with positive B-coefficients in a given solvent is considered to have a structure making effect. On the other hand in the case of B-coefficients of lithium bromide in different compositions of binary solvent mixtures (DMSO) and in pure water, less positive values were observed respectively. A solute with less positive and negative B-coefficient in a given solvent is considered to be a structure breaking solute. The present results indicate that in DMSO all salts having positive B-coefficient

values behave as structure makers, while in H₂O and DMSO-H₂O mixtures, the B-coefficient values are less positive showing the weak structure- making effect.

4.3. Ionic B-coefficients

To achieve a better understanding of ion-solvent interactions, it is necessary to split the B-coefficients into the individual ionic B-coefficients, B_+ and B_-. However, there is no experimental method related to viscosity which separately determines the ionic B-coefficients. A number of methods have been suggested by various workers [29, 33, 37-39] to split B-coefficients of electrolytes into the contributions of the individual ions.

Most of these methods depend upon the choice of the reference salt for which cation-solvent and anion-solvent interactions may be considered equal. This criterion is realized for large polyatomic ions that are minimally solvated, so we chose the tetra butyl ammonium tetra phenyl borate and tetrabutylammoniumbromide. In the present work Gill and Sharma's approach [39], was used to resolve viscosity B-coefficients into the contributions of individual ions. This method like the method of Krumgalz [37] is based on the assumption that BU₄N⁺ and Ph₄B⁻ ions with large alkyl groups are not solvated in non-aqueous solvents and their dimensions in such solvents are constants. Studies by Gill et al., [40,41] confirm that the ionic radii of BU₄N⁻ and Ph₄B⁻ in non-aqueous solvents and in non-aqueous mixed solvents remain constant and equal to 5.00 and 5.35Å respectively, with an average uncertainty of ± 2%.

The splitting of B into ionic B ± have been resolved by the equation

$$\frac{B \; Ph_4B^-}{B \; BU_4N^+} = \frac{r^3 Ph4B^-}{r^3 BU_4N^-} = \frac{(5.35)^3}{(5.00)^3} \qquad 3$$

$$B \, (exp) \, Bu_4NBPh_4 = B \, Ph_4B^- + BBU_4N^+ \qquad 4$$

Using the equation 3 and 4, the B-coefficients have been divided in to ionic B_+ and B_-. The values are shown in Table 5 which shows that the B_+ and B-values for BU₄N⁺, Ph₄B⁻ and Br⁻ ions increased gradually with an increase in electrolyte concentration.

This above method of splitting of electrolyte B-coefficients in to ionic contributions is not

Table 5. Ionic B coefficients of ions in DMSO, Mix 1, Mix II, Mix III and water at 25°C

Ref Salts	DMSO	Mix 1	Mix II	Mix III	H₂O
Bu₄N	0.5708	-	-	-	-
K⁺	0.5080	0.163	0.161	0.0730	-0.009
Li⁺	0.5994	0.1745	0.1557	0.1490	0.1491
BPh₄	0.6992	-	-	-	-
Cl⁻	-	0.163	0.1610	0.0730	-0.009
Br⁻	0.3330	0.037	0.0109	-0.0225	-0.0343

applicable in aqueous solutions. Gurney's method [42] for aqueous solution was thus used. This method simply assumes that the positive and negative ion contributions are simply equal and thus:

$$B\,(K^+) = B\,(Cl^-) = \tfrac{1}{2}\,B\,(KCl)$$

This sub division cannot be applied in the case of organic solvents because the behaviour of the ions in the non-aqueous solvents is entirely different [43, 44]. The Gurney approach is used in the present study whenever water-rich solutions are involved. Many other researchers have adopted the same practice in their studies for water rich solvent mixtures [34]. Using the Gurney approach, the values of the ionic B-coefficients for the ions (Li⁺,K⁺ and Br⁻) in pure water and in DMSO-H₂O mixtures at 25°C were obtained and are reported in Table 5.

In DMSO-H₂O mixtures where the mole percentage of DMSO is 60%, 40% and 20%, the electrolyte has small positive ionic B-coefficient values indicating that all these electrolytes have a structure breaking component. This character is due to the Br⁻ ion because it has a smaller ionic B-coefficient value and also has negative values in 40% and 20%. DMSO-H₂O mixtures.

In DMSO-H₂O mixtures, the B-coefficient increases with an increase in DMSO content. The addition of dimethylsulphoxide to water causes the breaking of water structure by formation of DMSO-H₂O bonds which leads to a less structured solvent. There is thus a decrease in the structure breaking ability of the ions compared with that of pure water.

A complete comparison of the present study with the literature is not possible because of meagre published ionic B-coefficient values for alkali bromides in DMSO-H₂O mixtures. The measured ionic B-coefficient values of the ions in water are in good agreement with the values already reported in the literature. In this study it was observed that all the

values of ionic B-coefficient of (Li⁺) were positive and small showing the weak structure making effects associated with the increase in ionic radius in DMSO-H₂O mixtures [45]. It was also observed that Br⁻ ions maintain negative B-coefficient values in all DMSO-H₂O mixtures, except in 60% DMSO mole fraction. From this it can be concluded that Br⁻ ion behaved as a structure breaker in water and in all DMSO-H₂O mixtures except in 60% DMSO mole fraction mixtures.

The low $B_\pm$ values of alkali metal ions and Br⁻ ions in water (Table 5) are due to the breakdown of the tetrahedral structural of water and the formation of strongly structured solvated ion. It is observed that this behaviour is more dominant in ions with larger ionic radius [46].

Experimental

Dimethylsulfoxide (DMSO) has proved to be a particularly versatile and useful solvent since it became commercially available. The purification of DMSO for electrochemical studies has been surveyed by Reddy [11] on the behalf of the IUPAC Commission. Water is the principal impurity in DMSO and the recommended procedure is to remove water with molecular sieve type 5A, followed by distillation.

Dimethylsulfoxide 99% (Fluka) was stored over well-dried 5 Å molecular sieves for several days and then filtered. The solvent was distilled in the presence of P₂O₅, and was used for various measurements. Dimethylsulfoxide + water mixtures of compositions 0, 10, 30, 50, 70, 90 and 100 mass % DMSO (corresponding to mole fractions of 0, 0.466, 0.1586, 0.3054, 0.5064, 0.7983, and 1 of DMSO) were prepared by mixing a known mass of water and dimethylsulfoxide in glass-stoppered flasks

The salt LiBr was purified by re-crystallization. Then these re-crystallized electrolytes were dried at 130-150°C for several hours prior to use. Owing to the hygroscopic nature of the bromides, these salts were stored in vacuum desiccators over P₂O₅ [12] for viscometer measure-ments. BU₄NBPh₄ (Andrich) was precipitated with water from acetone solution and dried at 70°C. This salt was also recovered after a set of measurements by precipitation from the DMSO solution using water. Bu₄NBr was purified by conventional methods [11]. Tetrabutyl-ammonium-bromide (Aldrich) m.p: 103°C

was r e-crystallized from benzene and n-hexane. The re-crystallized salt was dried at 117 to 120°C for several hours prior to use.

Densities of the pure solvents (DMSO and H_2O) and of solvent mixtures (DMSO- H_2O mixture) and of salt solutions were determined by using a specific density bottle of volume 15 cm^3. The specific density bottle was calibrated using double distilled water and benzene at 25°C. The specific density bottle filled with air or bubble free experimental liquid was kept in a transparent- walled water bath for 10 to 15 min. minimum to attain thermal equilibrium. When the level of the meniscus remained unchanged for 15 min the system was considered to be at equilibrium. The specific density bottle was removed from thermostatic water bath, dried and weighed. The density of the solution was calculated by dividing the weight in grams of the liquid by the volume in milliliters of the density bottle. The estimated accuracy of density measurements of solutions was ± 0.00001 gm cm^{-3}.

For viscosity measurements, an ubbelhode type glass capillary tube suspended level viscometer was used for all viscosity measurements. A flow time of 450 seconds was detained for distilled water at 25 °C. Capillary flow measurement involves the liquid or solution draining through a fine bore tube. The viscosity is determined from measured flow rate. The viscometer had a capillary length of 12.2 cm and a c apillary d iameter o f 0 .45 m m a nd w as c alibrated by using distilled water, n-hexane, methanol and acetone. Cleaning of the viscometer with clean mixture (sulfuric-chromic acid) was done at frequent intervals to ensure proper drainage of the solution.

The viscometer was suspended in a water thermostat maintained at 25°C with an uncertainty of ± 0.01 °C. At first 20 cm^3 of the reference liquid of accurately known viscosity η_1 was added from a pipette to the viscometer and its flow time t_1 was obtained. Same procedure was repeated for the liquid of interest to obtain the viscosity η_2 by its rate of flow t_2. At least tree replicate of each data set reproducible to 0.05 Sec. was obtained, results were averaged and standard deviation and errors were determined. The overall accuracy of viscosity measurements was estimated to be ± 0.01.

Viscosity values η_2 were determined from measurements of flow times t_1 and t_2 of liquids of the

respective densities ρ_1 and ρ_2 using the following relation

$$\frac{\eta_1}{\eta_2} = \frac{t_1 \rho_1}{t_2 \rho_2}$$

The absolute viscosities of DMSO, H_2O, DMSO-H_2O mixtures and their solutions with lithium bromide were determined at 25°C. Viscosities were measured at series of concentration for lithium bromide; the lowest concentration being 0.01mole per liter and the highest concentration was about 0.4 moles per liter, which was found empirically to be the practical limit of the linear relationship that is the Jones-Dole equation [13]. Experimental values of viscosities of the solution $\eta_1 = \eta$ and of solvents (H_2O, DMSO, H_2O-DMSO mixtures) as η_0 are used to determine the relative viscosities η_r or ψ of the solution which was used in Jones-Dole equation.

$$(\psi/\eta_r = \eta/\eta_o = 1 + AC^{1/2} + BC)$$

Experimental values of densities and viscosities were used to calculate the A and B coefficients in the Jones- Dole equation.

Conclusions

The present study indicated that in DMSO Li Br having positive B – coefficient values behaved as structure maker, while in water and DMSO–H_2O mixtures B–coefficient values were less positive showing weak structure making effect.

From this study it was also concluded that Li^+ behaved as structure- maker in DMSO and all DMSO– H_2O mixtures and in water, the structure making effect is decreased with the increase in the composition of water. It is also observed that the Br^- ions maintain negative B-coefficients values in all DMSO– H_2O mixtures except in 60% DMSO mole fraction. From this it can be concluded that the Br^- ion behaves as a structure breaker in H_2O and in all DMSO– H_2O mixtures except in 60% DMSO mole fraction mixtures.

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