Ionic Viscosity B-Coefficients of Some Tetraalkylammonium Ions in DMSO + Dioxane Mixtures at 35° and 45° C.

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Viscosity data of Bu_4NBr, Pr_4NBr, Et_4NBr, Bu_4NI, Bu_4NBPh_4, $NaBPh_4$ and NaI solutions in dimethylsulphoxide (DMSO) + dioxane mixtures were analysed by Jones-Dole equation. The experimental A-coefficients were compared with the theoretical values (A_{cal}) (using Falkenhagen-Vernon equation). The total B-coefficients of the electrolytes at 35° and 45° C were resolved into their ionic components. The variation of B_i values were examined as a function of solvent composition and temperature. The results indicated no preferential solvation of the ions in DMSO + dioxane mixtures.

Viscosity measurements of electrolytic solutions provide meaningful information about (i) the structural changes in solvent resulting from the addition of co-solvent and (ii) ion-solvent interactions in electrolyte solution. Viscometric measurements in pure aqueous, non-aqueous or aquo-organic mixed solvents have extensively been reported in the literature. But the real picture of ion-solvent interaction can not be presented in aqueous, non-aqueous binary mixtures because of the strong solvent structural effects [1,2]. In mixture of two dipolar, aprotic solvents, the solvent strucutral changes are very low. Therefore a real picture of ion-solvent interaction can be presented. Viscosity studies in dipolar aprotic mixtures [3-7] have generally been reported at 25° C though a limited number of such studies are available at higher temperatures. In the present investigation, solutions of some tetra alkylammonium salts were examined in DMSO + dioxane mixutres at 35° and 45° C using viscosity method.

EXPERIMENTAL

The solvents - DMSO (AR, SRL Pvt. Ltd. Bombay) and dioxane (AR, BDH) - were purified by the methods given earlier [8]. Binary mixtures of these solvents were prepared by weight. The physical properties like viscosity and density of solvent mixtures were measured at 35° and 45° C and reported in Table 1. Dielectric constant of the mixed solvents were calculated at the required temperatures and the results included in Table 1.

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Table 1

Dielectric constant* (D), viscosity (η_0 in cP) and density (d in g ml^{-1}) of solvent mixtures at 35° and 45° C

mol % DMSO	< D* > 35°C	45°C	< Viscosity > 35°C	45°C	< density > 35°C	45°C
100	44.7	43.3	1.652	1.392	1.0854	1.0755
90	40.5	39.2	1.527	1.294	1.0756	1.0656
75	34.1	33.0	1.381	1.181	1.0655	1.0557
60	27.7	26.8	1.271	1.090	1.0564	1.0452
45	2.3	20.7	1.181	1.021	1.0452	1.0353
30	14.9	14.5	1.118	0.963	1.0357	1.0257

* D values for mixed solvents were calculated using the equation

$D_{mix} = X_{DMSO} \times D_{DMSO} + X_{dioxan} \times D_{dioxan}$

where X_{DMSO} and X_{dioxan} are mol fractions in the mixtured solvent

and D_{DMSO} and D_{dioxan} are the dielectric constant of pure solvents at the specified temperature

The electrolytes used were prepared/ purified as per methods given elsewhere [6,9,10]. Solutions of different concentrations in the range 5 - 300 x 10^{-4} mole dm^{-3} were prepared in different solvent mixtures. Viscosities of solvent mixtures as well as that of the electrolytic solutions were measured at 35° and 45°C with an Ubbelohde suspended level viscometer calibrated with triply distilled water and other organic solvents. A sealable type pycnometer [11] of 20 ml capacity was also calibrated with distilled water and other organic solvents. The overall accuracy of the viscosity and density measurements are 0.2% and 1 X 10^{-4} g cm^{-3}.

RESULTS AND DISCUSSION

The viscosity data at 35° and 45° C were analysed by the Jones-Dole equation [12] in the form as used for un-associated electrolytes.

$$\eta_r = \eta/\eta_0 = 1 + A\sqrt{C} + BC \quad \ldots(1)$$

equations 1 and 2

$$\psi = \frac{\eta-\eta_0}{\eta_0\sqrt{C}} = A + B\sqrt{C} \quad \ldots(2)$$

where η_0 and η are the viscosities of pure solvent or solvent mixture and electrolytic solution. The plots of ψ vs $\sqrt{C}$ were found to be linear over the entire composition range of the electrolytes studied. A and B-coefficients of equation (2) were evaluated from the intercept and slope of these linear plots by least squares treatment. In all the cases viscosity A and B-coefficients were found to be positive and these values for the electrolytes are compiled in Tables 2 and 3 respectively.

A coefficients are calculated using Falkenhagen-Vernon equation [13] below

$$A_{cal} = \frac{0.2577\Lambda_0}{\eta_0(DT)^{1/2}\lambda_1\lambda_2}\left[1-0.6863\left(\frac{\lambda_1\lambda_2}{\Lambda_0}\right)^2\right] \quad \ldots(3$$

where Λ_0 is the limiting molar conductance of the salt, λ_1^0 and λ_2^0 are the limiting ionic conductances of the two ions of the electrolyte, T is the absolute temperature and all other symbols have thier usual significance. D values for the calculation were taken from Table 1. Λ_0, λ_1 and λ_2 values at the specified solvent mixtures were taken from our

conductance measurements at the specified temperature [14]. The calculated A values (A_{cal}) for the electrolytes are also included in Table 2. At both the tempeatures there is a good agreement (within experimental error) between the experimental and the theoretically calculated values.

The B-coefficient values are presented in Table 3. These values for some of the electrolytes in pure DMSO have been reported earlier. These with the relevent reference are included in the Table (given in brackets) for comparison. It can be seen that the two sets of B values are in close agreement with an uncertainty of ± 0.003 dm^3 mol^{-1}.

Table 2

Experimental and calculated values of A coefficient of different electrolytes in different DMSO + Dioxane mixtures (DMSO mol % specified)

Calculated values are in paranthesis

t /°C	A (A_{cal})X 10^2 values (in dm^3 $mol^{-1})^{1/2}$ in solvent mixtures					
	100	90	75	60	45	30 •
Bu_4NBPh_4						
35	1.8(1.91)	2.0(2.06)	2.4(2.33)	2.6(2.65)	3.2(3.10)	4.0 (-)
45	2.0(1.93)	2.2(2.09)	2.4(2.32)	2.8(2.65)	3.4(3.16)	4.10(-)
Bu_4NI						
35	1.5(1.27)	1.4(1.34)	1.6(1.57)	2.0(1.84)	2.3(2.19)	2.9(-)
45	1.4(1.28)	1.5(1.40)	1.5(1.61)	2.0(1.90)	2.2(2.27)	3.0(-)
Bu_4NBr						
35	1.3(1.25)	1.5(1.37)	1.8(1.58)	1.7(1.83)	2.4(2.18)	2.8(-)
45	1.4(1.27)	1.3(1.40)	1.7(1.60)	2.0(1.88)	2.4(2.26)	2.9(-)
Pr_4NBr						
35	1.2(1.19)	1.3(1.31)	1.7(1.51)	1.9(1.76)	2.2(2.10)	2.7(-)
45	1.2(1.20)	1.4(1.33)	1.5(1.54)	1.6(1.80)	2.2(2.14)	2.8(-)
Et_4NBr						
35	1.1(1.08)	1.3(1.17)	1.6(1.36)	1.6(1.59)	2.2(1.91)	2.6(-)
45	1.1(1.12)	1.3(1.25)	1.4(1.46)	1.8(1.72)	2.1(2.05)	2.7(-)
$NaBPh_4$						
35.	1.9(1.80)	2.2(1.96)	2.4(2.21)	2.6(2.46)	3.2(2.97)	3.8(-)
45	1.9(1.81)	1.9(1.95)	2.3(2.19)	2.6(2.50)	3.2(2.97)	3.6(-)
NaI						
35	1.3(1.19)	1.4(1.30)	1.7(1.51)	1.9(1.76)	1.9(2.10)	2.7(-)
45	1.2(1.20)	1.4(1.32)	1.6(1.52)	1.7(1.78)	2.2(2.14)	2.8(-)

•Since conductance at 30 mol % DMSO has not been measured, A_{cal} has not been computed

Table 3

Jones Dole B coefficients (dm^3 mol^{-1}) for some Electrolytes in DMSO-dioxan mixtures

(Literature values are included in brackets wherever available)

t /°C	B Coeff. in DMSO-dioxane Mixture contg DMSO mol % 100	90	75	60	45	30
Bu_4NBPh_4						
35	1.31	1.35	1.38	1.40	1.42	1.44
45	1.25	1.28	1.30	1.33	1.35	1.37
Bu_4NI						
35	0.84	0.85	0.87	0.89	0.91	0.93
45	0.79	0.81	0.83	0.85	0.87	0.89
Bu_4NBr						
35	0.85(0.84[18])	0.87	0.89	0.91	0.93	0.95
45	0.81	0.82	0.85	0.87	0.89	0.91
Pr_4NBr						
35	0.72(0.69[18])	0.75	0.77	0.79	0.82	0.84
45	0.69	0.70	0.73	0.75	0.77	0.79
Et_4NBr						
35	0.69(0.67[18])	0.71	0.73	0.75	0.77	0.80
45	0.65	0.66	0.68	0.70	0.72	0.73
$NaBPh_4$						
35	1.21	1.25	1.27	1.29	1.31	1.33
45	1.17(1.18[18])	1.20	1.22	1.24	1.26	1.28
NaI						
35	0.75(0.76[15])	0.76	0.77	0.78	0.81	0.82
45	0.72(0.72[15])	0.74	0.76	0.77	0.78	0.80

Maximum uncertainty of B values in this table is ±0.03 dm^3 mol^{-1}

In the present studies, the viscosity B-coefficients of each solute increased with the decrease in dielectric constant of the mixed solvent medium and these values decrease with the increase of temperature from 35° to 45° C. Some literature studies [15,16] also show a decrease in B-coefficients values for some solutes with the increase of temperature. The variation of B values of the tetraalkylammonium salts in DMSO and DMSO + dioxane mixtures at 35° and 45° C is in the order:

$Bu_4NBr > Pr_4NBr > Et_4NBr$

Ionic B± values

Viscosity B-coefficient of the electrolyte is a measure of solute-solvent interaction. Since the solute species in electrolyte solution are the ions, for understanding the ion-solvent interaction, it becomes important to resolve the total B-coefficient of an electrolyte into its ionic B± values.

In the present investigation, the B-coefficients of Bu_4NBPh_4 at 35 and 45° C were split up into its ionic B± values using a model proposed by Gill and coworkers [3] as follows:

$$\frac{B_{Ph_4B^-}}{B_{Bu_4N^+}} = \left(\frac{5.35}{5.00}\right)^3 \quad \ldots\ldots(4)$$

$$B_{Bu_4NBPh_4} = B_{Bu_4N^+} + B_{BPh_4^-} \quad \ldots\ldots(5)$$

where $B_{Bu4NBPh4}$ is the experimental B-coefficient value for Bu_4NBPh_4. Ionic B for Bu_4N^+ and PhB were determined from the experimental B coefficients of the salt both at 35° and 45° C using equations 4 and 5. The B-coefficients of the other electrolytes were resolved into their ionic contributions with the help of additivity relationship. The values thus obtained for different ions are presented in Table 4.

Table 4

Ionic B± coefficients (dm^3 mol^{-1}) for some ions in DMSO - dioxane mixtures

t /°C	< - B± in solvent mixtures containing DMSO mol % — >					
	100	90	75	60	45	30
Bu_4N^+						
35	0.59	0.60	0.62	0.63	0.64	0.65
45	0.56	0.57	0.58	0.60	0.61	0.62
Pr_4N^+						
35	0.46	0.48	0.50	0.51	0.53	0.54
45	0.44	0.45	0.46	0.48	0.49	0.50
Et_4N^+						
35	0.43	0.44	0.46	0.47	0.48	0.50
45	0.40	0.41	0.42	0.43	0.44	0.44
Na^+						
35	0.50(0.51)	0.51	0.52	0.52	0.53	0.54
45	0.49(0.48)	0.50	0.51	0.52	0.53	0.53
Ph_4B^-						
35	0.72	0.75	0.76	0.77	0.78	0.79
45	0.69	0.71	0.72	0.73	0.74	0.75
Br^-						
35	0.26(0.27)	0.27	0.27	0.28	0.29	0.30
45	0.25(0.26)	0.25	0.27	0.27	0.28	0.29
I^-						
35	0.25(0.25)	0.25	0.25	0.26	0.27	0.28
45	0.23(0.24)	0.24	0.25	0.25	0.26	0.27

Literature values from ref 15 are shown in brackets

The B± values of some ions in DMSO are found to be in good agreement with literature values (given in parenthesis in Table 4). It was observed that the B± coefficients of the ions at a given temperature increase with the increase of dioxan content in the mixtures. This trend was the same as observed for B coefficients of electrolyte.

The solvation behaviour of an ion can be explained on the basis of variation of its B_1 value as a function of solvent composition. The non-linear variation of B_1 coefficient with solvent composition is said to indicate preferential solvation. However it is found that B_1 coefficients of Bu_4N^+, Pr_4N^+, Et_4N^+, Na^+, Ph_4B^-, Br^- and I^- ions were found to vary linearly with the solvent composition at each temperature. Therefore these ions do not show preferential solvation in DMSO + dioxane mixtures. In the present solvent system Na^+ ion also does not show any change in solvation behaviour from pure DMSO to 30 mol % DMSO. This is in contrast with some literature studies in DMF + Ac [3], DMSO + AN [5] and DMF + AN [17] mixtures, but is in agreement with some similar literature studies [5,6].

ACKNOWLEDGEMENT

P. Bisht thanks the Council of Scientific and Industrial Research, New Delhi for the award of Senior Research Fellowship.

REFERENCES

1. F. Franks and D.J.G. Ives, *Q.Rev.*, **20** (1966) 1.

2. P. Assarsson and F.R. Eirich, *J.Phys.Chem.*, **72** (1968) 2710.

3. D.S. Gill and A.N. Sharma, *J.Chem.Soc. Faraday Trans.I*, **78** (1982) 475.

4. D.S. Gill and M.S. Chauhan, *Z.Phys.Chem.(N.F.)*, **140** (1984) 149.

5. V.K. Syal, S.Chauhan and M.S. Chauhan, *Z.Phys.Chem.(N.F.)*, **159** (1988) 49.

6. V.K. Syal, S.Chauhan and ,M.S. Chauhan, *Indian J. Chem.*, **29A** (1990) 693.

7. V.K. Syal, J.M. Bajaj, S.Chauhan and M.S. Chauhan, *J. Indian Chem. Soc.*, **69** (1992) 801.

8. V.K. Syal and P.C. Ranowt, *Indian J.Chem.*, **24A** (1985) 16.

9. D.S. Gill and R. Nording, *Z.Phys.Chem. (N.F.)*, **136** (1983) 117.

10. D.S. Gill and J.S. Cheema, *Electrochimica Acta*, **27** (1982) 755, 1267.

11. A. Weissberger and B.W. Rossiter, *Physical Methods in Chemistry part IV*, **Wiley, New York** (1972).

12. G.Jones and M.Dole, *J.Am.Chem.Soc.*, **51** (1929) 2950.

13. H.Falkenhagen and E.L. Vernon, *Z.Phys.chem.*, **33** (1932) 140.

14. V.K. Syal and P.Bisht, *Indian J. Chem Techno.* **1** (1994) 233.

15. R.T.M. Bicknell, K.G. Lawrence, M.A. Seeley, D.Feakins and L.Werblan, *J.Chem.Soc. Faraday Trans.I*, **76** (1980) 637.

16. D.S. Gill and B.Singh, *J.Chem.Soc. Faraday Trans. I*, **84** (1988) 4417.

17. D.S. Gill and J.S. Cheema, *Z.Phys.Chem. (N.F.)* **134** (1983) 205.

18. K.G. Lawrence, R.T.M. Bicknell, A. Sacco and A.D. Atti, *J.Chem.Soc. Faraday Trans.I*, **81** (1985) 1133.

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