

CONDUCTANCE AND VISCOMETRIC STUDIES OF SOME TETRAALKYLAMMONIUM AND SODIUM SALTS IN ACETONITRILE-DIMETHYL SULFOXIDE MIXTURES AT 35 °C

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Molar conductances and viscosities of Bu_4NBPh_4 , NaBPh_4 and R_4NBr (R ethyl, propyl and butyl) at 35 °C in acetonitrile (AN), dimethyl sulfoxide (DMSO) and their binary mixtures have been reported. The conductivity data has been analysed by the Shedlovsky conductance equation and viscosity data by the Jones-Dole equation. Resolution of limiting molar conductivity (Λ_0) and viscosity B coefficient of electrolytes into their ionic components have been achieved by the reference salt method. Viscosity A coefficients have been compared with theoretical A_n coefficients. Derived conductance and viscosity parameters have been discussed in terms of the ion-solvent interaction.

In previous studies^{1–3}, we reported conductance and viscosity parameters for some of the tetraalkylammonium, alkali metal and Cu(I) and Ag(I) salts in acetonitrile (AN), dimethyl sulfoxide (DMSO) and in their binary mixtures at 25 °C. Of the two solvents, DMSO is known to possess small chain like structure through dipole-dipole type of interactions, while AN shows strong tendency to form dimers by association⁴. Therefore, in order to estimate the influence of temperature on the solvent structure and hence on the ionic solvation, the conductance and viscosity studies of Bu_4NBPh_4 , Bu_4NBr , Pr_4NBr , Et_4NBr and NaBPh_4 in AN, DMSO and AN-DMSO mixtures at higher temperature, i.e. 35 °C have been reported in this paper.

EXPERIMENTAL

The purification procedures for AN (Merck) and DMSO (a.r. grade) and electrolytes were the same as reported earlier^{1–3}. Binary mixtures of AN and DMSO were prepared by weight. The physical properties such as viscosity η_0 ($\text{kg m}^{-1} \text{s}^{-1}$), density d (kg m^{-3}) and dielectric constant D of binary mixtures were measured as reported elsewhere^{1–3} (Table I). The experimental procedures for the measurements of conductance, viscosity and density of electrolyte solutions were the same as discussed in our previous studies^{1–3}. The reproducibility of conductivity, viscosity and density measurements were $\pm 0.2\%$, $\pm 0.1\%$ and $\pm 0.1 \text{ kg m}^{-3}$, respectively.

RESULTS AND DISCUSSION

Conductance Measurements

Molar conductances of Bu_4NBP_4 , Bu_4NBr , Pr_4NBr , Et_4NBr and NaBP_4 in AN, DMSO and AN-DMSO mixtures containing 12.0, 33.2, 58.2, 73.4 and 93.2 mole% AN have been measured at 35 °C in the concentration range of $(3 - 60) \cdot 10^{-4} \text{ mol dm}^{-3}$. Since the accuracy of the present conductance measurements is not better than $\pm 0.2\%$, and the complete conductance equations demand an accuracy much better than $\pm 0.1\%$, therefore, the entire conductance data was analysed in the light of the Shedlovsky conductance equation^{5,6} to evaluate the limiting molar conductivity Λ_0 ($\text{S cm}^2 \text{ mol}^{-1}$) and the ion-association constant K_A ($\text{dm}^3 \text{ mol}^{-1}$) of the electrolytes. The Λ_0 and K_A values thus obtained have been reported in Table II.

A reasonably good agreement between the present Λ_0 values for Bu_4NBP_4 (125.2 $\text{S cm}^2 \text{ mol}^{-1}$) and for Pr_4NBr (188.0 $\text{S cm}^2 \text{ mol}^{-1}$) in AN and for NaBP_4 (30.5 $\text{S cm}^2 \text{ mol}^{-1}$) in DMSO with the corresponding literature values 124.8 $\text{S cm}^2 \text{ mol}^{-1}$ (reported by Gill and co-workers⁷) 187.9 $\text{S cm}^2 \text{ mol}^{-1}$ (reported by Papadopoulos and co-workers⁸) and 30.8 $\text{S cm}^2 \text{ mol}^{-1}$ (reported by Yao and Bennion⁹) respectively, reveals the precision of the present conductance measurements in AN-DMSO mixtures at 35 °C.

Limiting Ionic Conductances and Solvated Radii

Due to lack of the transport number data in AN-DMSO mixtures at 35 °C, the Λ_0 values reported in Table II were resolved into the ionic contributions λ_i^0 values on the basis of the reference salt method. Because, the experimental evidence to date for the reference-salt method of Λ_0 value division has proved very convincing^{4,9 - 11}. The fundamental assumption in such devices is that the large constituent ions of reference

TABLE I
Dielectric constant (D), viscosity (η_0) and density (d) of AN, DMSO and AN-DMSO mixtures at 35 °C

mole % AN	D	$\eta_0 \cdot 10^3$ $\text{kg m}^{-1} \text{ s}^{-1}$	$d \cdot 10^{-3}$ kg m^{-3}
0.0	44.7	1.652	1.0861
12.0	43.2	1.339	1.0541
33.2	41.0	0.933	0.9956
58.2	38.1	0.630	0.9223
73.4	36.9	0.459	0.8753
93.2	34.6	0.334	0.7944
100.0	34.1	0.314	0.7663

salts remain unsolvated in dipolar aprotic solvents due to their small charge density effect. On the basis of this assumption Gill and co-workers¹² suggested a model consisting of following Eqs (1) and (2) using Bu_4NBPh_4 as a reference salt

$$\lambda_+^0 / \lambda_-^0 = [0.535 + (0.0103 D + r_y)] / [0.50 + (0.0103 D + r_y)] \quad (1)$$

and

$$\lambda_{\text{Bu}_4\text{N}^+}^0 + \lambda_{\text{Ph}_4\text{B}^-}^0 = \Lambda_0 (\text{Bu}_4\text{NBPh}_4) \quad (2)$$

where 0.535 and 0.500 are the crystallographic radii of Ph_4B^- and Bu_4N^+ respectively in nm, D is the dielectric constant of the solvent medium and r_y is an adjustable parameter equal to 0.085 nm for structureless solvent and 0.113 nm for structured solvent.

The good applicability of this model has been demonstrated in ref.¹⁰ for some organic solvents, in which precise values for Bu_4NBPh_4 are available.

In case of DMSO it is widely accepted that due to dipole-dipole interactions DMSO is more likely a structured solvent while AN is structureless. Therefore, in the present case r_y is taken equal to 0.113 nm for DMSO and 0.085 nm for AN. In AN-DMSO mixtures, however, r_y value has been obtained by the interpolation between 0.085 and 0.113 nm as suggested by Gill and Nording¹³.

Using Eqs (1) and (2) the Λ_0 values for Bu_4NBPh_4 in Table II have been split into λ_+^0 and λ_-^0 values. Using these λ_i^0 values, the Λ_0 values for all other electrolytes in Table II were resolved into λ_i^0 values using Kohlraush's law. The λ_i^0 values thus obtained have been reported in Table III.

The present λ_i^0 ($17.3 \text{ S cm}^2 \text{ mol}^{-1}$) value for Na^+ in DMSO has been found in good agreement with the corresponding λ_i^0 ($17.43 \text{ S cm}^2 \text{ mol}^{-1}$) value obtained by Yao and Bennion⁹, however Yao and Bennion have used (i-amyl)₃ BuNBPh_4 as a reference salt.

Stoke's radii for Bu_4N^+ , Pr_4N^+ , Et_4N^+ , Na^+ , Br^- and Ph_4B^- ions have been calculated using the λ_i^0 values for these ions in Table III and Eq. (3).

$$r_i = 0.82 / \lambda_i^0 \eta_0 + 0.0103 D + r_y, \quad (3)$$

where η_0 is the viscosity of the medium taken from Table I and all other symbols have their usual significances. Equation (3) is one of the modified forms of the Stoke's law proposed by Gill¹⁴ for the evaluation of solvated ionic radii by addition of a term proportional to the solvent dielectric constant. The r_i values thus obtained have also been summarized in Table III.

The r_i values for Bu_4N^+ , Pr_4N^+ , Et_4N^+ and Ph_4B^- ions are found to remain practically constant equal to their crystallographic radii¹⁴ i.e. 0.50, 0.45, 0.40 and 0.54 nm respectively over the entire solvent composition range of AN-DMSO mixtures. These values have also been found in close agreement with the corresponding r_i values reported at 25 °C (refs¹⁻³). These observations, therefore, suggest the absence of solvation of these ions.

TABLE II
 Λ_0 ($\text{S cm}^2 \text{ mol}^{-1}$) and K_A ($\text{dm}^3 \text{ mol}^{-1}$)^a values in AN, DMSO and AN-DMSO mixtures at 35 °C

Electrolytes	Solvent (mole % AN)									
	0.0	12.0	33.2	58.2	73.4	93.2	100.0	Λ_0	K_A	
	Λ_0	K_A	Λ_0	K_A	Λ_0	K_A	Λ_0	K_A	Λ_0	K_A
Bu_4NBP_4	27.7	—	33.8	—	47.5	—	68.4	—	92.4	15
Bu_4NBr	44.7	—	54.0	—	73.8	—	102.8	12	132.7	18
Pr_4NBr	47.3	—	56.1	—	77.0	—	108.1	15	138.0	19
Et_4NBr	50.9	—	60.6	—	82.4	—	116.1	—	148.0	18
NaBP_4	30.5	—	37.2	—	52.1	—	77.5	—	104.9	—
									142.7	—
									180.4	—

^a $K_A < 10$ have no physical significance⁶ and are, therefore, not reported in this table.

TABLE III
 λ_0^0 ($\text{S cm}^2 \text{ mol}^{-1}$) and corresponding r_i (nm) values in AN, DMSO and AN-DMSO mixtures at 35 °C

Ion	Solvent (mole % AN)									
	0.0	12.0	33.2	58.2	73.4	93.2	100.0	λ_0^0	r_i	
	λ_0^0	r_i	λ_0^0	r_i	λ_0^0	r_i	λ_0^0	r_i	λ_0^0	r_i
Bu_4N^+	14.5	0.50	17.7	0.50	24.9	0.50	35.8	0.50	48.3	0.50
Ph_4B^-	13.2	0.54	16.1	0.53	22.6	0.53	33.0	0.53	44.1	0.54
Pr_4N^+	17.1	0.45	19.8	0.46	28.1	0.46	41.1	0.45	53.6	0.45
Et_4N^+	20.7	0.40	24.3	0.41	33.5	0.41	49.1	0.40	63.6	0.41
Na^+	17.3	0.44	21.1	0.44	29.5	0.44	44.5	0.43	60.8	0.42
Br^-	30.2	0.32	36.3	0.32	48.9	0.33	67.0	0.33	84.4	0.34
									110.8	0.34
									114.1	0.35

Krumgalz and co-workers¹⁵ have also demonstrated from the infrared spectra of solvent molecules for Bu_4NBr and Bu_4NI solutions in AN and N,N-dimethylformamide (DMF) that Bu_4N^+ cation does not effect the valence bonds of $-\text{C}\equiv\text{N}$ and $(\text{CH}_3)_2\text{N}-\text{C}=\text{O}$ groups of the solvents.

The r_i values for Na^+ , on the other hand, remain practically constant equal to 0.44 nm upto ≈ 33.2 mole% AN and then decreases continuously with further addition of AN to 0.40 nm in pure AN. At 25 °C, however, the r_i values for Na^+ were found to remain practically constant equal to 0.46 ± 0.01 nm upto ≈ 73.4 mole% AN. It is, therefore, evident from the comparison of r_i values for Na^+ in AN-DMSO mixtures at 25 and 35 °C, that solvation effect of Na^+ has reduced with rise in temperature. Nevertheless, the trends are consistent and seem to indicate that DMSO is quite strongly preferred over AN in DMSO-rich region of AN-DMSO mixtures. Solvation of Na^+ in AN-DMSO mixtures thus makes an interesting comparison with the solvation mechanism of large tetraalkylammonium and tetraphenylboride ions.

The r_i values for Br^- do not show such significant nonlinear variation with the solvent composition and, therefore, no preferential solvation can be depicted. But, it is noted that r_i values for Br^- in DMSO are relatively smaller than in AN and AN-rich region of AN-DMSO mixtures. Although, the molecular volume of DMSO (0.119 nm³) is larger than the molecular volume of AN (0.089 nm³). Therefore, weak Br^- -AN interactions cannot be denied. The possible interaction sites appears to be the protons and nitrile carbon atom, as suggested by Pople and Gordon¹⁶ from the approximate molecular orbital calculations for charge distribution for AN.

Viscosity Measurements

Viscosity of Bu_4NBPh_4 , Bu_4NBr , Pr_4NBr , Et_4NBr and NaBPh_4 has been measured in AN, DMSO and AN-DMSO mixtures over the entire solvent composition range as in the conductance measurements in the concentration range $(15 - 426) \cdot 10^{-4}$ mol dm⁻³ at 35 °C. Since the ion-association constants for the electrolytes from the conductance data were found not significantly large, therefore, the entire viscosity data has been analysed in the light of the Jones-Dole equation¹⁷, Eq. (4)

$$\eta_r = \eta/\eta_0 = 1 + A C^{1/2} + B C, \quad (4)$$

where η_0 is the viscosity of pure solvent or solvent mixtures and η is the viscosity of electrolyte solution and C is the concentration of electrolyte. Plots of Eq. (4) in the form $(\eta_r - 1)/(C)^{1/2}$ vs $C^{1/2}$ were found linear in all the cases over the entire concentration range of the electrolyte which therefore confirms the validity of Eq. (4). Viscosity coefficients A and B of Eq. (4) were evaluated using least-squares treatment and have been summerized in Table IV and V, respectively. A coefficients in AN, DMSO and

TABLE IV
Viscosity A ($\text{dm}^{3/2} \text{ mol}^{-1/2}$) coefficients^a in AM, DMSO and AN-DMSO mixtures at 35 °C

Electrolytes	Solvent (mole % AN)					
	0.0	12.0	33.2	58.2	73.4	93.4
	$A \cdot 10^2$	$A \cdot 10^2$	$A \cdot 10^2$	$A \cdot 10^2$	$A \cdot 10^2$	$A \cdot 10^2$
Bu_4NBP_4	2.2	1.92	2.4	1.96	2.1	2.05
Bu_4NBr	1.8	1.24	2.0	1.29	2.0	1.33
Pr_4NBr	1.4	1.15	1.5	1.23	2.0	1.31
Et_4NBr	1.6	1.06	1.10	1.12	1.7	1.21
NaBP_4	2.0	1.75	2.0	1.80	1.8	1.90

	$A \cdot 10^2$					
Bu_4NBP_4	2.1	2.2	2.2	2.1	2.16	2.4
Bu_4NBr	2.5	1.63	2.5	1.47	2.1	2.09
Pr_4NBr	2.0	1.55	2.0	1.42	2.5	2.4
Et_4NBr	1.5	1.55	1.5	1.31	2.0	2.0
NaBP_4	1.3	1.43	1.3	1.21	1.7	1.72
	1.8	1.52	1.5	1.12	1.96	1.9
	1.56	1.52	1.5	1.10	2.2	2.0
	1.56	1.52	1.5	1.12	2.02	1.9
	2.35	2.6	2.6	2.11	2.6	2.4
						1.76

^a The maximum uncertainty in A value is $\pm 10\%$

AN-DMSO mixtures were also calculated theoretically using Falkenhagen-Vernon equation¹⁸, Eq. (5)

$$A_{\eta} = \frac{0.2577 \Lambda_0}{\eta_0 (D T)^{1/2} \lambda_+^0 \lambda_-^0} [1 - 0.6863 (\lambda_+^0 - \lambda_-^0) / \Lambda_0]^2 \quad (5)$$

and reported in Table IV. The relevant solvent properties used in Eq. (5) have been taken from Table I, the Λ_0 and λ_i^0 values from Table II and III, respectively.

A comparison of A and A_{η} values summarized in Table IV, reveals that in most of the cases the agreement is good. In some cases, however, agreement between A and A_{η} values is poor. A similar difficulty was encountered by Kay and co-workers¹⁹ for some tetraalkylammonium salts in aqueous solutions, who attributed the discrepancies to a surface tension effect resulting from surface active impurities.

Viscosity B coefficients for all electrolytes were found to be positive and large. This is a common feature of many electrolytes in pure and mixed non-aqueous solvents^{9,12,20-24}. Solvent systems in which the agreement between A and A_{η} values is good, the B coefficients for the electrolytes were also obtained from the average value of the (practically constant) apparent B coefficients calculated at each concentration by Eq. (6).

$$B = \eta_r - 1 - A_{\eta} C^{1/2} / C \quad (6)$$

B values in DMSO for Bu_4NBr (0.85 ± 0.01), Pr_4NBr (0.70 ± 0.01) and NaBPh_4 (1.19 ± 0.02) $\text{dm}^3 \text{ mol}^{-1}$ in Table V are found to be in good agreement with the corresponding literature values: 0.842, 0.695 and 1.178 $\text{dm}^3 \text{ mol}^{-1}$, respectively, as reported by Lawrence and co-workers²⁵. However, B value for NaBPh_4 is found to be about 10% higher than the value reported by Yao and Bennion⁹ (Yao and Bennion have reported B value for NaBPh_4 in DMSO at 35 °C equal to 1.07 $\text{dm}^3 \text{ mol}^{-1}$). Similarly, in AN, our B values for Bu_4NBPh_4 (1.27 ± 0.01), Bu_4NBr (0.84 ± 0.03), Pr_4NBr (0.68 ± 0.01), and for Et_4NBr

TABLE V
Viscosity B ($\text{dm}^3 \text{ mol}^{-1}$) coefficients^a in AN, DMSO and AN-DMSO mixtures at 35 °C

Electrolytes	Solvent (mole % AN)						
	0.0	12.0	33.2	58.2	73.4	93.2	100.0
Bu_4NBPh_4	1.30	1.30	1.30	1.28	1.29	1.27	1.27
Bu_4NBr	0.85	0.85	0.86	0.86	0.85	0.85	0.84
Pr_4NBr	0.70	0.71	0.73	0.72	0.71	0.70	0.68
Et_4NBr	0.67	0.68	0.69	0.69	0.67	0.67	0.64
NaBPh_4	1.19	1.18	1.17	1.16	1.14	1.13	1.13

^a Maximum uncertainty in B value is $\pm 0.03 \text{ dm}^3 \text{ mol}^{-1}$.

$(0.64 \pm 0.01) \text{ dm}^3 \text{ mol}^{-1}$ are in good agreement with the values $1.25 \text{ dm}^3 \text{ mol}^{-1}$ for Bu_4NBPh_4 as reported by Gill and co-workers⁷, and 0.829 , 0.704 and $0.640 \text{ dm}^3 \text{ mol}^{-1}$ for Bu_4NBr , Pr_4NBr and Et_4NBr , respectively, as reported by Lawrence and co-workers²⁶. But, our B value for NaBPh_4 in AN, $1.13 \pm 0.01 \text{ dm}^3 \text{ mol}^{-1}$ is about 9% lower than the value reported by Lawrence and co-workers²⁶ (Lawrence and co-workers have reported B value for NaDPh_4 in AN at 35°C equal to $1.237 \text{ dm}^3 \text{ mol}^{-1}$).

Viscosity B coefficients of R_4NI and alkali metal iodides in propylene carbonate²⁷ (PC) (a less structured solvent than DMSO) were found to be almost temperature independent. In DMSO, B coefficients for some electrolytes, however, show a decrease with rise in temperature⁹. Recently, Gill and co-workers⁷ have also reported a decrease in B values for some electrolytes in AN-pyridine mixtures with rise in temperature. Present results also show a net decrease in the B values for all electrolytes in AN-DMSO mixtures (Table V) from their corresponding B values at 25°C reported earlier¹⁻³.

Trends in the B values for electrolytes summarized in Table V show no steady change except for NaBPh_4 with change in solvent composition at 35°C . At 25°C , on the other hand, the B values for all the electrolytes decreased steadily as AN is added in AN-DMSO mixtures¹⁻³. These results, therefore, tentatively indicate stronger solvent structural effects like mutual solvation of solvent molecules with the addition of co-solvent at 35°C involving partial disruption of molecular association of DMSO solvent.

Viscosity B_+ and B_- Values

Increasing interest has been developed in recent years to resolve the total B value of an electrolyte into ionic contribution, in mixed solvents, in order to analyse the ion-solvent interactions in conjunction with the solvent composition. However, there exists no direct method for this purpose and, therefore, indirect methods have been suggested. Gill and Sharma²¹, based on the Bu_4NBPh_4 assumption have suggested a method, by which the observed B values of the electrolytes in pure as well as in mixed dipolar aprotic solvents can be split into the contribution of individual ions. This model is based on the following equations :

$$B_+ / B_- = (5.00 / 5.35)^3 \quad (7)$$

for Bu_4NBPh_4 , and

$$B_+ + B_- = B. \quad (8)$$

Using Eqs (6) and (7) and the principle of additive properties, Eq. (8), the B values of Table V have been resolved into B_+ and B_- values. These ionic B values have been reported in Table VI.

TABLE VI
Ionic B (dm³ mol⁻¹)^a and corresponding r_i (nm) values in AN, DMSO and AN-DMSO mixtures at 35 °C

Ion	Solvent (mole % AN)											
	0.0			12.0			33.2			58.2		
	B_i	r_i	B_i	r_i	B_i	r_i	B_i	r_i	B_i	r_i	B_i	r_i
Bu ₄ N ⁺	0.58	0.45	0.58	0.45	0.58	0.45	0.58	0.45	0.58	0.45	0.57	0.45
Ph ₄ B ⁻	0.72	0.49	0.72	0.49	0.72	0.48	0.70	0.48	0.71	0.48	0.70	0.48
Pr ₄ N ⁺	0.45	0.42	0.46	0.42	0.46	0.42	0.44	0.41	0.43	0.41	0.43	0.40
Et ₄ N ⁺	0.42	0.41	0.43	0.41	0.42	0.41	0.41	0.40	0.39	0.40	0.39	0.39
Na ⁺	0.47	0.42	0.46	0.42	0.46	0.42	0.46	0.42	0.45	0.42	0.44	0.41
Br ⁻	0.25	0.35	0.25	0.35	0.27	0.35	0.28	0.36	0.28	0.36	0.28	0.36

^a Maximum uncertainty in B_+ is ± 0.03 dm³ mol⁻¹.

The viscosity B_{\pm} values can be analysed on the basis of Einstein's²⁸ equation (9)

$$B_{\pm} = 2.5 \frac{4}{3} \pi \frac{r_{\pm}^3 N}{1000}, \quad (9)$$

where r_{\pm} is the effective radius of the ion assumed as rigid sphere moving in a continuum, 2.5 is the shape factor for a sphere. Using Eq. (9) the r_i values in nm for Bu_4N^+ , Pr_4N^+ , Et_4N^+ , Ph_4B^- , Na^+ and Br^- ions corresponding to their B_{\pm} values have been calculated and reported in Table VI. The r_{\pm} values are found to be in reasonably good agreement with the corresponding r_i values obtained from conductance studies (Table IV). Yao and Bennion⁹ have also found that for effective spherical ionic entity like Na^+ , Ph_4B^- and $(\text{i}-\text{amyl})_3\text{BuN}^+$ the agreement between the r_i values obtained from conductance and viscosity data in DMSO is good, but the discrepancy for SCN^- , CF_3SO_3^- and ClO_4^- ions was assumed due to other shapes for these ions in viscous flow process.

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