

CHAPTER - III

Viscosity B-Coefficients of Tetraalkylammonium bromides
in 2-Methoxy ethanol at 25 °C and 30 °C.

The potentiality of 2-methoxy ethanol (ME) as solvent for use in non-aqueous batteries and its application in organic synthesis^{1,2} and electrochemical³ studies have been widely stressed. These necessitate the study of the transport properties of various ions in the 'quasi aprotic' solvent ME conductometrically and viscometrically. The viscometric method is known to give valuable information regarding ion-solvent interactions. Although a number of extensive viscometric studies⁴⁻⁵ have been made in various solvents with different electrolytes, but literature provides no information regarding the viscometric studies of tetraalkylammonium halides in ME. This led us to study the viscometric properties of tetraalkylammonium bromides R_4NBr ($R = C_2H_5$ to C_7H_{15}) in ME at 25 °C and 30 °C.

Experimental

The purification of the electrolytes and other experimental details have been described in Chapter - II. The concentration range in which the viscosity measurements have been made was $(90-500) \times 10^{-4} \text{ mol dm}^{-3}$. The solvent properties are given in Table 1.

Results and Calculations

The relative viscosities of the electrolytes in non-aqueous solvents may be represented by Jones-Dole equation²¹ (1)

where η and η_0 are the viscosities of the solution and the solvent respectively, C is the molar concentration.

$$(\eta/\eta_0 - 1)/\sqrt{C} = A + B\sqrt{C} \quad \dots(1)$$

A and B are characteristic constants specific to the ion and the solvent. The A-co-efficient depends on the ion-ion interactions and can be calculated from the physical properties of the solvent and the solution.

The B-co-efficient represents the ion-solvent interactions conditioned by ion-size and cannot be calculated a priori.

Since we have seen strong association of the electrolytes in this solvent by conductance measurements, so the viscosity data were analysed by equation (2) as suggested by Fekins et al²² instead of eqn. (1)

$$\eta_r = 1 + A\sqrt{\alpha c} + B_i \alpha c + B_p (1-\alpha)c \quad \dots(2)$$

where A, B_i and B_p are the characteristic constants, α is the degree of association of the ion pair. For analysis of viscosity data by eqn. (2), first the equivalent conductances Λ of the electrolytes at various concentrations were used in an iterative procedure to find both Λ° and the association constant K_a of the ion pair. The degree of association (α) has been evaluated in the following way using equations (3) to (5):

$$K_A = \frac{1-\infty}{\infty^2 c \gamma_{\pm}^2} \quad \dots (3)$$

$$\log_{10} \gamma_{\pm} = \frac{-A_{\gamma} (\infty c)^{1/2}}{1 + B_{\gamma} (\infty c)^{1/2}} \quad \dots (4)$$

$$\text{and } \Lambda = \Lambda^{\circ} - \left(\frac{A_{\Lambda} + B_{\Lambda} \Lambda^{\circ}}{1 + B_{\gamma} (\infty c)^{1/2}} \right) (\infty c)^{1/2} \quad \dots (5)$$

The Bjerrum distance 'q' is written for the distance of closest approach of free ions in the equation for the activity co-efficient γ_{\pm} , in equation (4) and in the empirical modification by Robinson and Stokes²³ of the Onsager equation, i.e. the eqn. (5). Λ is the conductivity of the ionised fraction of the electrolyte, and A_{γ} , B_{γ} , A_{Λ} and B_{Λ} are the appropriate Debye-Huckel co-efficients.

A short series of conductivity measurements of high precision was made for each system at molarities of electrolyte in the range 0.002-0.05 mol dm⁻³. Though the lower concentration shows a good result for the measurement of conductance but is too much difficult for the measurement of η_{∞} . From the conductivity measurements we obtained values of Λ° , the limiting equivalent conductance of the electrolyte. The limiting equivalent

conductances of the ions were calculated from the 'reference electrolyte' Bu_4NBBu_4 . Table 3 summarizes the information obtained from the conductivity measurements.

Equation (2) was rearranged to give

$$(\kappa_p - 1 - A\sqrt{cc})/cc = B_i + B_p \left(\frac{1-\alpha}{\alpha} \right) \quad \dots (6)$$

The $(\kappa_p - 1 - A\sqrt{cc})/cc$, concentration C and density ρ values of the solutions of different electrolytes at different temperature are reported in Table 2.

The A -values were theoretically calculated from the physical properties of the solvent and the limiting ionic equivalent conductances using the relation

$$A_{theo} = \frac{0.2577 \Lambda^{\circ}}{\eta_0 (\epsilon T)^{1/2} \lambda_+^{\circ} \lambda_-^{\circ}} \left[1 - 0.6863 \left(\frac{\lambda_+^{\circ} - \lambda_-^{\circ}}{\Lambda^{\circ}} \right)^2 \right] \quad \dots (7)$$

The values of the A co-efficients, calculated from the dielectric constant of ME and conductometric data for tetraalkyl ammonium salts in ME at 25°C have been recorded in Table 4.

The A -values in eqn. (5) for analysis of the data were substituted to make them equal to the limiting theoretical values calculated using the Falkenhagen Vernon equation²⁴ i.e.

eqn. (7). The plots of $(\eta_p - 1 - A\sqrt{cc})/cc$ against $1 - \alpha/c$ were linear in all cases. The intercept at $1 - \alpha/c = 0$ were taken as the required value of B_1 . The B-coefficients reported in Table 5 for the electrolytes were obtained from these plots using the least square method. Such plots for the electrolytes in ME are shown in figures 1 and 2.

In view of weak temperature dependence of the A-coefficients and non-availability of dielectric constant values at higher temperatures, the A-values at 25°C have been utilized at other temperature namely 30°C.

Viscosity data have also been analysed on the basis of a transition state treatment of the relative viscosity of electrolytic solutions as suggested by Feakins et al.²⁵ The B-coefficient is expressed by the equation

$$B = \frac{\bar{V}_1^{\circ} - \bar{V}_2^{\circ}}{1000} + \frac{\bar{V}_1^{\circ}}{1000} \left(\frac{\Delta u_2^{\neq} - \Delta u_1^{\neq}}{RT} \right) \quad \dots (8)$$

where \bar{V}_1° and \bar{V}_2° are the partial molar volumes of the solvent and solute respectively. Δu_2^{\neq} is the contribution per mole of solute to the free energy of activation for viscous flow of the solution. Δu_1^{\neq} , the free energy of activation per mole of the pure solvent is given by²⁶

$$\Delta u_1^{\neq} = \Delta \epsilon_1^{\neq} = RT \ln \left(\frac{n_1 \bar{V}_1^{\circ}}{hN} \right) \quad \dots (9)$$

The activation parameters for viscous flow for the electrolytes are presented in Table 6. Enthalpies of activation of electrolytes have been calculated with the help of Gibb-Helmholz equation since B-coefficient have been determined at two different temperatures. The results are also recorded in Table 6.

Discussion

Since all the salts have the same anion (Br^-), Table 4 indicates that the ionic A-values for the tetraalkyl ammonium ions increase in the order:



The results are in agreement with the limiting equivalent conductances of ions²⁷. The conductance of R_4N^+ decreases as the size of R increases. It is apparent that cation-solvent interactions should decrease with increasing radius, the interactions between large R_4N^+ ions and the solvent would be small.

That A is not sensitive to temperature can be explained from equation (7). Though λ_+^0 or λ_-^0 increase with temperature ϵ and η_0 decrease with temperature, the net result being an almost independence of A-values with temperature.

The viscosity B-coefficients (Table 5) for the tetraalkyl-ammonium bromides are large and positive, and increase as we go from tetraethyl ammonium bromide to tetraheptylammonium bromide.

This is a common feature in most non-aqueous solvents like DMSO⁴⁻⁹, TMS¹⁰, HMPT¹¹, AM¹², PC^{13,14}, TMU^{12,15}, MeOH¹⁶, NMP¹⁷, NMP¹⁸, F¹⁹ and EC²⁰. The B coefficients in almost all the dipolar aprotic solvents show a weak temperature dependence as compared with stronger temperature dependence in aqueous solutions^{16,28,29}. In the present study the tetraalkylammonium bromides show a strong temperature dependence in ME as observed in water. This may be due to the 'quasi-protic' nature of ME.

The changes in the Δu_2^{\neq} follow the same pattern as the B-values. ΔH_2^{\neq} and $T \Delta S_2^{\neq}$ values also decrease from Et₄NBr to Hept₄NBr. In order to distinguish the effect each single has in 2-methoxy ethanol, the ionic B-values were calculated using Bu₄NBBu₄³⁰⁻³³ and Bu₄NBPh₄³⁴⁻³⁷ as the reference electrolytes by equations (10) and (11).

$$B_{\text{Bu}_4\text{N}^+} = B_{\text{Bu}_4\text{B}^-} = \frac{1}{2} B_{\text{Bu}_4\text{NBBu}_4} \quad \dots (10)$$

$$\frac{B_{\text{Ph}_4\text{B}^-}}{B_{\text{Bu}_4\text{N}^+}} = \frac{r_{\text{Ph}_4\text{B}^-}^3}{r_{\text{Bu}_4\text{N}^+}^3} = \left(\frac{5.35}{5.00} \right)^3 \quad \dots (11)$$

The average B_{ion} values of tetraalkylammonium ions are recorded in Tables 7(a) and 7(b). The ionic free energies of activation of viscous flow based on the division of Bu₄NBBu₄ have been recorded in Table 8.

The ionic B-coefficients for the tetraalkylammonium ions have been found to increase continuously from Et_4N^+ to Hept_4N^+ in ME. The B_{ion} values increase with increasing temperature. Some interesting conclusions may be derived from the analysis of $\frac{dB}{dT}$ of salts. The $\frac{dB}{dT}$ values (Table 9) of tetraalkylammonium bromide are positive indicating the structure breaking properties of these salts in ME. The $\frac{dB}{dT}$ value of Me_4NBr in water is positive and characteristic of structure breaker^{39,39}. The bromide ion generally causes the structure breaking. Me_4N^+ is known to be a structure breaker in water⁴⁰. Thus the temperature has a little effect on the structure breaking effect of ME containing these salts. The $\frac{dB_+}{dT}$ values (Table 10) of Et_4N^+ to Hept_4N^+ are positive (structure breaking). An analysis of B_{\pm} coefficients can be made on the basis of Einstein's equation⁴¹

$$B_{\pm} = 2.5 \frac{4\pi}{3} \frac{R_{\pm}^3 N}{1000} \dots (12)$$

where R_{\pm} is the radius of the ion assumed as a rigid sphere moving in a continuum and 2.5 is the shape factor for a sphere. The number of n_B of solvent molecules bound to the ion in the primary sphere of solvation can be calculated by combining the the Jones-Dole equation with Einstein's¹⁷

$$B_{\pm} = \frac{2.5}{1000} (V_1 + n_B V_B) \dots (13)$$

where V_1 represents the bare ion molar volume and is related to the crystallographic radius r_c of the ion. V_s is the solvent molar volume. The values of R_g and n_g are shown in Tables 11 and 12 respectively. The values may be compared with the corrected Stokes radii obtained from conductance studies⁴². For cations R_g values are much less than r_c values showing that these ions are scarcely solvated in this medium.

On the other hand it is difficult to explain the high n_g as well as R values for Br^- ions because they are generally believed to be unsolvated in this class of solvents¹¹.

Viscometric results are also analysed using equation (9) which derives from the transition state theory. Table 6 shows that Δu_1^{\neq} are very low and ΔH_2^{\neq} and $T\Delta S_2^{\neq}$ are highly negative for all the tetraalkylammonium salts, the corresponding ionic values are given in Table 8. ΔS_2^{\neq} measures the degree to which the ground state solvent must be broken up to form the transition state solvent. The greater this disruption, the easier it is for the ions to increase their co-ordination in the transition state and the lower is Δu_2^{\neq} . This suggests that ion solvent bond making in the transition state becomes more important. From Table 8 we note that as the size of the tetraalkylammonium ion increases, Δu_2^{\neq} increases and ΔS_2^{\neq} decreases. This can only be explained in terms of increased ion-solvent bond making in the transition state. However, we see that the change in ionic Δu_2^{\neq} value (Table 8) is much more in case of larger ions than the

smaller ones. If the solvent offers no appreciable structure resistance to the co-ordination of the solvent molecules in the ground state, steric inhibition will now limit the co-ordination of ions, and this will affect the smaller ion more than the larger. With a bond breaking mechanism the effects on Δu_2^{\neq} will be complex, but the relief of steric hindrance in the transition state would be one factor tending to decrease Δu_2^{\neq} for the smaller relative to the larger ions. This suggests that the attainment of the transition state for viscous flow is accompanied by increased ion-solvent bond making in the transition state. It may be noted from Table B that Δu_2^{\neq} for all the ions is positive, thus the formation of the transition state is less favourable by the presence of these ions. Δu_2^{\neq} for the Br^- ion is lower than the cations and this suggests that cations interact with ME more strongly than the anion.

It is to be noted that the single ion B value of Δu_2^{\neq} etc given here are based on the equal division of B-values of large molecules Bu_4NBEu_4 or Bu_4NBPh_4 . The method however has strongly been criticized by Krungalz⁴³. According to him, equality of the dimensions of Bu_4N^+ or Ph_4B^- does not necessarily imply equality of B co-efficients of these ions as they are likely to be both solvent and ion structure dependent. Krungalz supposed that the large R_4N^+ are not solvated in organic solvents in the normal sense involving significant electrostatic interactions. Thus our results are in good agreement with the view point of Krungalz.

Table 1 : solvent properties of 2-Methoxy Ethanol (ME) at different temperatures.

Temperature in °C	25 °C	30 °C
density (ρ)/gcm ⁻³	0.96002	0.95772
Viscosity/10 ⁻³ kg ⁻¹ s ⁻¹	1.5414	1.3933
$\Delta u_1^{\neq 0}$ KJ/mol ⁻¹	14.18	14.16
$\Delta \ddagger_1^{\neq 0}$ KJ/mol ⁻¹	15.37	
$T\Delta s_1^{\neq 0}$ KJ/mol ⁻¹	1.19	

Dielectric constant of ME have been taken from literature value³

³ H. Sadek, Th.F. Tadros and A.A.El-Harakany, Electrochim. Acta., 16, 329, 1971.

Table 2 : density (ρ), Concentration (mol l⁻¹), relative viscosity (η_r), $L-\alpha/\alpha$ and $(\eta_r - 1 - A\sqrt{c})/c$ of tetraalkylammonium bromides and the two reference electrolytes viz Bu_4NBBu_4 & Bu_4NBF_4 in 2-methoxy ethanol at 25 °C

salt	$\gamma \frac{(\eta_r - 1 - A\sqrt{c})}{c}$	η_r	Conc	$L-\alpha/\alpha$	Density (ρ)
Tetraethylammonium bromide	0.700	1.00503	0.00963	0.9702	0.96064
	1.299	1.01203	0.02417	2.2091	0.96158
	1.478	1.01436	0.02904	2.5607	0.96198
	1.667	1.01867	0.03883	2.9706	0.96250
	1.816	1.02357	0.04857	3.2809	0.96312
	0.801	1.00721	0.00963	0.4994	0.96057
Tetrapropyl- ammonium bromide	1.010	1.01436	0.01233	0.7215	0.96112
	1.100	1.01806	0.02419	0.8112	0.96139
	1.180	1.02178	0.02908	0.8914	0.96167
	1.301	1.02906	0.03890	1.0280	0.96221
	1.421	1.03675	0.04878	1.1496	0.96275

Contd..

Table 2 (Contd..)

salt	$Y \left(\frac{n_p - 1 - \frac{A \cdot V \cdot K \cdot C}{R \cdot C}}{R \cdot C} \right)$	n_p	Conc	$1 - \alpha / \alpha$	Density (ρ)
Tetrabutyl- ammonium bromide	1.350	1.00955	0.00964	0.7759	0.96042
	1.651	1.01884	0.01934	1.0290	0.96082
	1.990	1.02400	0.02422	1.2346	0.96102
	2.350	1.02975	0.02912	1.6140	0.96121
	2.475	1.04905	0.04889	1.7201	0.96208
	1.347	1.00981	0.00964	0.7499	0.96038
Tetrapentyl- ammonium bromide	1.660	1.01880	0.01936	1.0710	0.96075
	1.781	1.02325	0.02425	1.1968	0.96093
	1.880	1.02764	0.02916	1.3081	0.96111
	2.082	1.03682	0.03905	1.5000	0.96146
	2.281	1.04650	0.04902	1.6720	0.96182

Contd..

Table 2 (Contd..)

	1.600	1.01278	0.00964	0.5514	0.96026
Tetrahexyl-	2.001	1.02544	0.01937	0.8024	0.96049
ammonium bromide	2.175	1.03214	0.02428	0.9000	0.96061
	2.325	1.03879	0.02920	0.9918	0.96073
	2.575	1.05224	0.039118	1.1519	0.96095
	2.850	1.06592	0.04913	1.3207	0.96118
	2.001	1.00502	0.00965	0.6237	0.96023
Tetraheptyl-	2.505	1.02783	0.01939	1.0500	0.96043
ammonium bromide	2.550	1.04041	0.02925	1.1071	0.96064
	2.775	1.05331	0.03920	1.2784	0.96084
	2.950	1.06575	0.04926	1.4260	0.96104

Contd..

Table 2 (Contd..)

	1.350	1.01265	0.00964	0.3579	0.95939
Tetrabutylammonium tetrabutyl borate	1.700	1.02574	0.01936	0.5429	0.95878
	1.851	1.03267	0.02425	0.6162	0.95847
	1.950	1.03920	0.02917	0.6787	0.95816
	2.200	1.06579	0.03906	0.7929	0.95757
	2.400	1.06879	0.04903	0.8899	0.95696
	1.661	1.02257	0.00964	0.9927	0.96024
Tetrabutylammonium tetraphenyl borate	2.027	1.03379	0.01979	1.5400	0.96045
	2.441	1.04139	0.02416	1.7422	0.96075
	2.628	1.04733	0.02951	1.9230	0.96087
	2.803	1.07078	0.04922	2.0962	0.96095

Contd..

Table 2 (Contd..)

Salt	Temperature 30 °C				
	$\gamma \left(\frac{n_x - 1 - A\sqrt{c}}{c} \right)$	n_x	Conc	$L \cdot c / d$	Density (ρ)
$(C_2H_5)_4NBr$	1.000	1.00660	0.00950	0.9700	0.95820
	1.775	1.01570	0.02409	2.2091	0.95892
	2.025	1.01890	0.02896	2.5816	0.95916
	2.250	1.02482	0.03871	3.9714	0.95964
	2.651	1.03093	0.04852	3.2826	0.96012
$(C_3H_7)_4NBr$	1.275	1.01050	0.00961	0.4984	0.95809
	1.625	1.02151	0.01927	0.7214	0.95849
	1.750	1.02702	0.02413	0.8114	0.95867
	1.875	1.03291	0.02842	0.8914	0.95886
	2.075	1.04434	0.03878	1.0280	0.95923
	2.250	1.05606	0.04863	1.1486	0.95961
$(C_4H_9)_4NBr$	1.700	1.01152	0.00961	0.7750	0.95802
	2.051	1.02278	0.01929	1.0290	0.95834
	2.325	1.02876	0.02416	1.2346	0.95848
	2.824	1.03919	0.02904	1.6021	0.95863
	2.975	1.05825	0.04875	1.7130	0.95923

Contd..

Table 2 (Contd..)

$(C_5H_{11})_4NBr$	1.675	1.01169	0.00962	0.7499	0.95794
	2.001	1.02207	0.01931	1.0702	0.95815
	2.125	1.02718	0.02418	1.1960	0.95826
	2.225	1.03212	0.02908	1.3060	0.95837
	2.425	1.04233	0.03893	1.5012	0.95858
	2.575	1.05202	0.04885	1.6720	0.95879
$(C_6H_{13})_4NBr$	1.975	1.01524	0.00962	0.5513	0.95787
	2.325	1.02904	0.01933	0.8024	0.95801
	2.475	1.03609	0.02422	0.9004	0.95808
	2.600	1.04294	0.02912	0.9920	0.95816
	2.800	1.05643	0.03901	1.1445	0.95830
	3.072	1.07071	0.04898	1.3200	0.95845

Contd..

Table 2 (Contd..)

$(C_7H_{15})_4NBr$	2.450	1.01787	0.009525	0.86236	0.95782
	2.735	1.03788	0.02425	1.0080	0.95798
	2.825	1.04432	0.02917	1.1079	0.95803
	3.011	1.05745	0.03903	1.2780	0.95814
	3.111	1.05905	0.04912	1.4261	0.95824
$(C_4H_9)_4NB(C_4H_9)_4$	1.575	1.01431	0.00962	0.3679	0.95719
	1.950	1.02898	0.01932	0.5429	0.95669
	2.100	1.03653	0.02420	0.6162	0.95643
	2.200	1.04367	0.02911	0.6787	0.95618
	2.425	1.07313	0.03898	0.7927	0.95567
	2.651	1.07542	0.04894	0.8899	0.95517
$(C_4H_9)_4NB(C_6H_{13})_4$	2.551	1.0142	0.00963	0.9927	0.95601
	3.010	1.0255	0.01969	1.5400	0.95711
	3.250	1.1251	0.02416	1.7421	0.95823
	3.501	1.1372	0.02949	1.9230	0.95910
	3.702	1.1858	0.04912	2.0962	0.96015

Table 3 : Conductances of tetraalkylammonium bromides and the two reference electrolytes in 2-Methoxy Ethanol at 25°C

$10^4 C$ (mol l ⁻¹)	Et_4NBr (ohm ⁻¹ cm ² mol ⁻¹)	$10^4 C$ (mol l ⁻¹)	Pr_4NBr (ohm ⁻¹ cm ² mol ⁻¹)	$10^4 C$ (mol l ⁻¹)	Bu_4NBr (ohm ⁻¹ cm ² mol ⁻¹)
486.671	15.36	487.798	14.02	488.998	12.78
398.264	16.38	389.010	14.70	291.199	14.23
299.036	18.83	290.079	15.50	242.192	14.76
246.673	20.08	241.997	16.20	193.400	15.40
		193.264	17.10	96.378	17.34
96.266	21.52	96.267	19.48		
	<u>Pent₄NBr</u>		<u>Hex₄NBr</u>		<u>Hept₄NBr</u>
490.199	11.54	491.301	10.88	492.611	10.52
391.499	12.28	391.118	11.60	391.978	11.15
291.600	13.03	292.001	12.30	292.495	11.96
242.511	13.56	242.798	13.04	193.897	13.20
193.601	14.20	193.702	13.65	96.501	13.31
96.397	16.47	96.397	15.81		

Table 3 (Contd..)

<u>Bu₄NBBU₄</u>		<u>Bu₄NBPh₄</u>	
10 ⁴ C (mol l ⁻¹)	\wedge (ohm ⁻¹ cm ² mol ⁻¹)	10 ⁴ C (mol l ⁻¹)	\wedge (ohm ⁻¹ cm ² mol ⁻¹)
490.311	11.52	492.211	12.30
391.600	12.00	295.116	13.73
291.697	12.87	241.796	14.44
242.502	13.24	197.965	15.60
198.596	14.10	95.602	16.54
96.399	15.63		

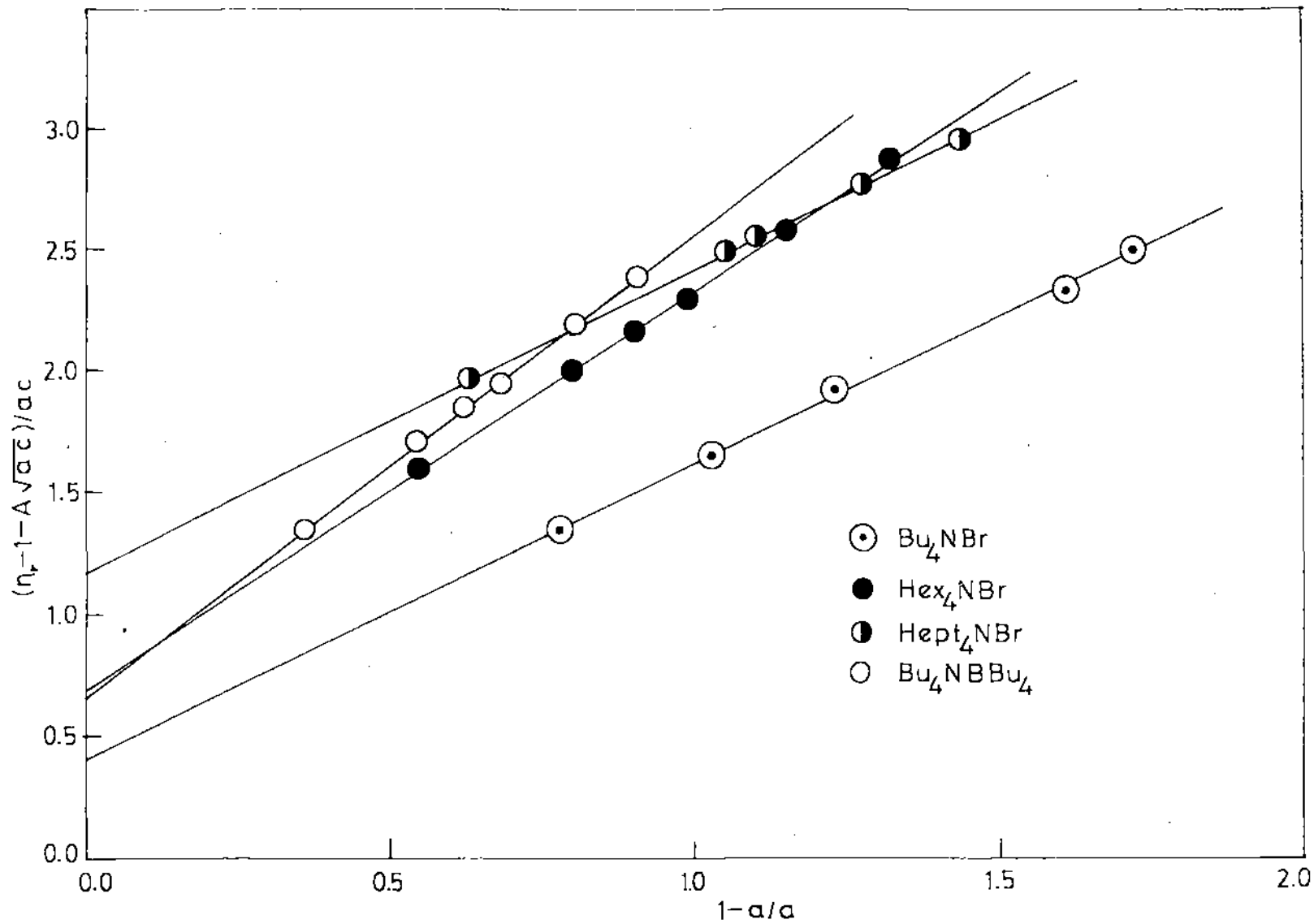


Fig.1 Plot of $(n_p - 1 - A\sqrt{ac})/ac$ vs $(1-a)/a$ of R_4NBr & Bu_4NBBu_4 salts in ME at 25°C

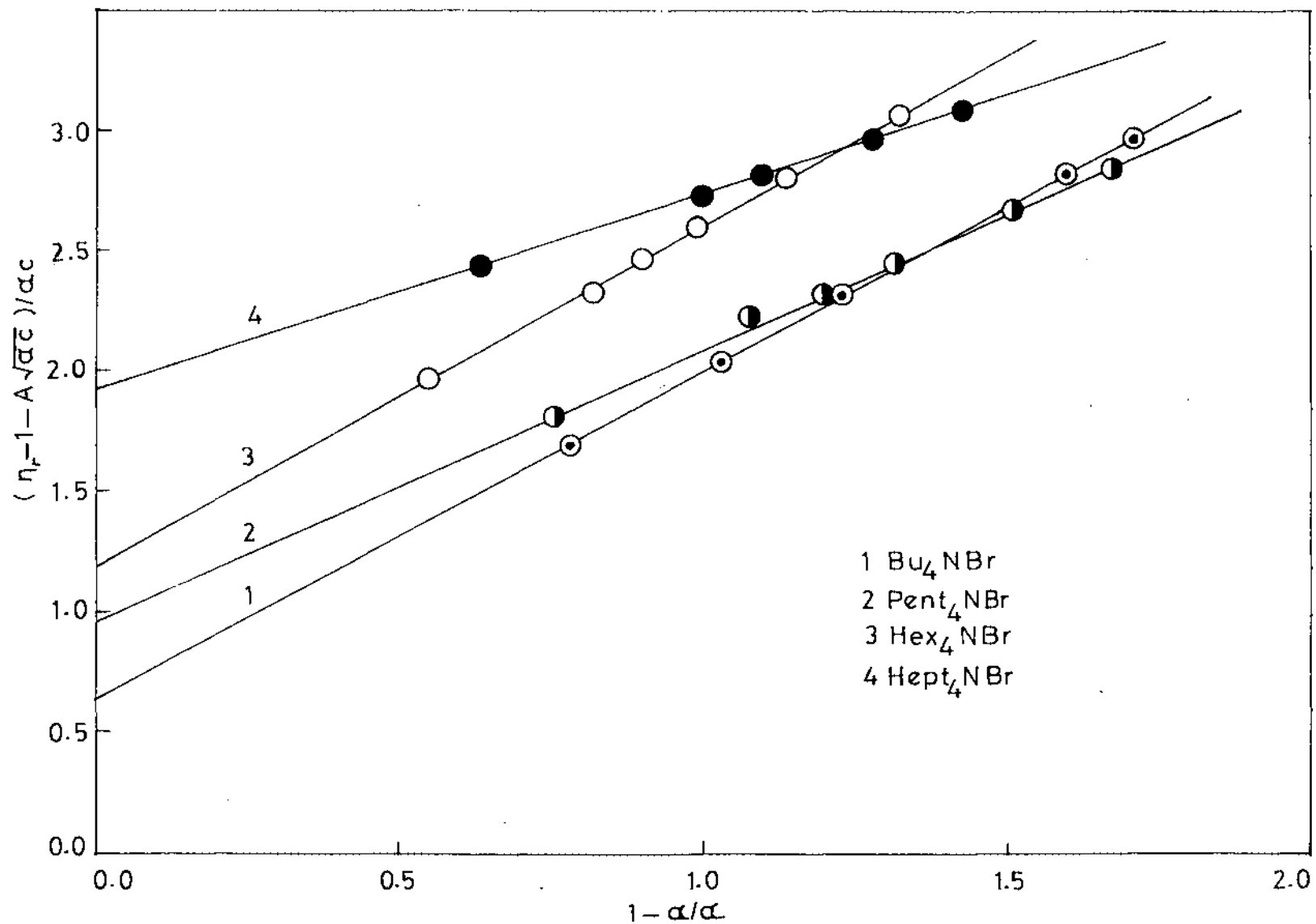


Fig. 2 Plot of $(n_r - 1 - A\sqrt{\alpha c})/\alpha c$ vs $1 - \alpha/a$ of $R_4\text{NBr}$ salts in ME at 30°C

Table 4 : Theoretical A-values of tetraalkylammonium bromides and the two reference electrolytes at 25°C

Salt	$\frac{A}{\text{dm}^{3/2} \text{mol}^{-1/2}}$	Salt	$\frac{A}{\text{dm}^{3/2} \text{mol}^{-1/2}}$
Et ₄ NBr	0.0215	Hept ₄ NBr	0.0345
Pr ₄ NBr	0.0244	Bu ₄ NBBu ₄	0.0326
Bu ₄ NBr	0.0260	Bu ₄ NBPh ₄	0.0201
Pent ₄ NBr	0.0281		
Hex ₄ NBr	0.0308		

Table 5 : B-co-efficients of the Tetraalkylammonium bromides and two reference electrolytes at different temperatures in 2-Methoxy Ethanol

Salt	25 ^o C	30 ^o C
Et ₄ NBr	0.231	0.394
Pr ₄ NBr	0.327	0.517
Bu ₄ NBr	0.425	0.654
Pent ₄ NBr	0.607	0.948
Hex ₄ NBr	0.703	1.191
Hept ₄ NBr	1.258	1.911
Bu ₄ NBBu ₄	0.609	0.838
Bu ₄ NBPh ₄	0.678	0.932

The maximum uncertainty of the B coefficient is \pm 0.005

Table 6 : Activation parameters for viscous flow

Salt	Temperature	$\Delta U_2^{\ddagger 0a}$ (KJ mol ⁻¹)	$\Delta H_2^{\ddagger 0b}$ (KJ mol ⁻¹)	$T\Delta S_2^{\ddagger 0c}$ (KJ mol ⁻¹)
Et ₄ NBr	25°C	9.53	-335.45	-345.04
	30°C	15.38		
Pr ₄ NBr	25°C	14.63	-393.27	-407.90
	30°C	21.46		
Bu ₄ NBr	25°C	19.99	-454.43	-474.42
	30°C	27.92		
Pent ₄ NBr	25°C	27.63	-669.39	-697.02
	30°C	39.34		
Hex ₄ NBr	25°C	32.84	-937.45	-970.29
	30°C	49.12		
HOct ₄ NBr	25°C	52.08	-1228.72	-1280.80
	30°C	73.56		
Bu ₄ N ₂ EBU ₄	25°C	34.11	-492.16	-526.27
	30°C	42.94		
Bu ₄ N ₂ Ph ₄	25°C	35.34	-496.89	-532.23
	30°C	44.27		

Errors : generally ^a ± 0.1 or better; ^b ± 5 or better

Table 7a : Ionic B (in $\text{dm}^3\text{mol}^{-1}$) co-efficients at different temperatures in ME using Bu_4NBBu_4 as 'reference salt'

	25 °C	30 °C
Et_4N^+	0.112	0.159
Pr_4N^+	0.207	0.282
Bu_4N^+	0.305	0.419
Pent_4N^+	0.488	0.712
Hex_4N^+	0.583	0.956
Hept_4N^+	1.138	1.675
Br^-	0.119	0.236

Table 7b : Ionic B ($\text{dm}^3\text{mol}^{-1}$) coefficients in ME using Bu_4NBPh_4 as 'reference salt'.

	25 °C	30 °C
Et_4N^+	0.111	0.158
Pr_4N^+	0.206	0.281
Bu_4N^+	0.304	0.419
Pent_4N^+	0.487	0.712
Hex_4N^+	0.583	0.955
Hept_4N^+	1.138	1.675
Ph_4B^-	0.373	0.513
Br^-	0.119	0.235

Table 8 : Ionic enthalpy and entropy of activation for viscous flow at 25°C

ION	$\Delta H_2^{\ddagger 0} / \text{KJ mol}^{-1}$	$\Delta H_2^{\ddagger e} / \text{KJ mol}^{-1}$	$T \Delta S_2^{\ddagger e} / \text{KJ mol}^{-1}$
Et_4N^+	5.85	-117.04	-122.89
Pr_4N^+	10.89	-173.87	-184.76
Bu_4N^+	16.25	-234.07	-250.32
Pent_4N^+	23.89	-451.12	-475.01
Hex_4N^+	29.10	-718.88	-747.98
Hept_4N^+	48.34	-1009.56	-1057.90
Br^-	3.74	-218.57	-222.31
Ph_4B^-	19.09	-262.82	-281.91

Table 9 : $\frac{dB}{dT}$ of Tetraalkylammonium bromides in Me.

Salt	$\frac{dB}{dT}$
Et ₄ NBr	0.033
Pr ₄ NBr	0.038
Bu ₄ NBr	0.046
Pent ₄ NBr	0.058
Hex ₄ NBr	0.097
Hept ₄ NBr	0.131
Bu ₄ NBBU ₄	0.045
Bu ₄ NBPh ₄	0.051

Table 10 • $\alpha D_{\frac{1}{2}} / \alpha T$ of Ions^a in ME

Salt

Et_4N^+	0.009
Pr_4N^+	0.014
Bu_4N^+	0.023
$Pent_4N^+$	0.045
Hex_4N^+	0.074
$Hept_4N^+$	0.107
Br^-	0.023
Ph_3B^-	0.028

^a Calculation based on $Bu_4N^+BPh_3^-$

Table 11: Ionic radii R_{\pm} (\AA) calculated by Einstein's equations in 1M at different temperatures.

Ions	R_{\pm} (a)		R_{\pm} (b)	
	25°C	30°C	25°C	30°C
Et_4N^+	2.61	2.93	2.61	2.93
Pr_4N^+	3.20	3.55	3.20	3.55
Bu_4N^+	3.64	4.05	3.64	4.03
Pent_4N^+	4.26	4.83	4.26	4.83
Hex_4N^+	4.52	5.33	4.52	5.33
Hept_4N^+	5.65	6.43	5.65	6.43
Br^-	2.67	3.34	2.67	3.34
Ph_4B^-	-	-	3.69	4.33

^a Calculations based on Bu_3NBu_4

^b Calculations based on Bu_4NBPh_4

Table 12 : Solvation number (n_s) of Ions in 2-Methoxy ethanol

Ion	r_c	n_s
Et_4N^+	4.00	-1.47
Pr_4N^+	4.52	-1.89
Bu_4N^+	4.94	-2.29
Pent_4N^+	5.29	-2.24
Hex_4N^+	5.60	-2.64
Hept_4N^+	5.83	-0.725
Br^-	1.95	0.369
Ph_4B^-	4.20	-0.473

R E F E R E N C E S

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