

CHAPTER - VI

Conductance measurements of Tetraalkylammonium
bromides in 2-methoxy ethanol (ME) + Water
mixtures at 25 °C

Studies on the transport properties of electrolytes in different solvents are of great importance to obtain information on the behaviour of ions in solutions. Recently, the much interest has been shown in the study of electrolytes in different alkoxy-ethanols, commercially known as cellosolves, having extensive use as solvents and solubilizing agents in many industry with interests ranging from pharmaceutical to plastic products¹. Still, these practical applications have not stimulated much interest for the study of their mixtures with water.

Conductance studies of quaternary ammonium halides in water have been made by Evans and Kay² to study the effects of interactions of water with the hydrophobic side chains of these electrolytes. We have studied the conductances of tetraalkylammonium bromides in 2-methoxy ethanol (ME) (Chapter-V of the present thesis) to understand the behaviour in these non-aqueous solvent. The conductometric studies of tetraalkylammonium salts in ME + H₂O mixtures would enable us to understand the ion-solvent interactions and other structural changes that may occur due to the addition of ME to water. Moreover, the variation of the Walden product with solvent composition can also be properly ascertained from such studies.

These considerations led us to undertake the present conductometric studies of tetraalkylammonium bromides, R_4NBr ($R = C_2H_5$ to C_5H_{11}), $NaBr$ and $NaBF_4$ in $ME + H_2O$ mixed solvents which we describe in this chapter. Salts of higher homologues i.e. Hex_4NBr and $Hept_4NBr$ have not been studied as they are insoluble and also coagulates in this solvent mixtures.

Experimental

2-methoxy ethanol (ME) and tetraalkylammonium bromides and other salts were purified in the way described earlier (Chapter II). Triply distilled water (specific conductance $< 1 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$) from all glass distilling set was used. Freshly distilled solvents were always utilised for solution preparation.

The solvent mixtures were prepared by weight. A stock solution for each salt ($\sim 0.1M$) in the appropriate solvent mixture was prepared by weight and the working solutions were obtained by weight dilution. The molar concentration of the solutions were calculated from molality and density values. The concentration varied between 10^{-2} - 10^{-4} M. The viscosity of solvent mixtures were taken from our works and density determinations were made using an Ostwald-Sprengel type pycnometer. Dielectric constants of the solvent mixtures were taken from the literature³.

A Pye-Unicom conductometric bridge (BN 9509) was used for measuring the conductances of the solutions at the frequency of 2kHz with a dip type cell of cell constant 0.731cm^{-1} and having an accuracy of $\pm 0.1\%$. The measurements were carried out in a thermostatic bath maintained at $25 \pm 0.005^\circ\text{C}$.

Results

The measured equivalent conductances and the corresponding molarities at different percentages of $\text{HS} + \text{H}_2\text{O}$ mixtures at different temperatures are given in Table 1. The density (ρ), viscosity (η_0) and dielectric constants (ϵ) have been reported in Chapter II.

The electrolytes under study may be assumed to be associated in $\text{HS} + \text{H}_2\text{O}$ mixtures. We have first analysed our data using Shedlovsky's⁴⁻⁵ method using the set of equations as given below:

$$\frac{1}{S\Lambda} = \frac{1}{\Lambda^0} + \frac{c\Lambda s f_{\pm}^2 K_A}{\Lambda_0^2} \quad \dots (1)$$

$$S = \left[\frac{B\sqrt{c\Lambda}}{2\Lambda_0^{3/2}} + \sqrt{\left(1 + \frac{\beta c\Lambda}{4\Lambda_0^3}\right)} \right]^2 \quad \dots (2)$$

$$\beta = \frac{8.204 \times 10^5 \Lambda^0}{(\epsilon T)^{3/2}} + \frac{82.5}{\eta (\epsilon T)^{1/2}} \quad \dots (3)$$

$$\log f_{\pm} = - \frac{1.8246 \times 10^6 (c_{\infty})^{1/2} / (\epsilon T)^{3/2}}{1 + 50.29 \times 10^8 R (c_{\infty})^{1/2} / (\epsilon T)^{1/2}} \quad \dots (4)$$

$$\alpha = \frac{S \Lambda}{\Lambda^{\circ}} \quad \dots (5)$$

The terms in the equations have their usual significance.

The Bjerrum critical distance $\eta = \frac{e^2}{2\epsilon kT}$ has been put equal to R in equation (4) to calculate the mean ionic activity coefficients. The association constants, K_A , and the limiting equivalent conductance (Λ°) have been iteratively calculated. A Nipro Z-650 Computer was used for the purpose.

The Λ° and K_A values thus obtained are recorded in Tables 2 and 3 respectively. The standard deviations in Λ° values were found to be less than $\pm 0.1\%$. The low values of the association constants ($K_A < 10$) below 50 wt% of BE suggest that the electrolytes are present as free ions in these solvent mixtures.

In order to improve our results, we have applied the recent method of computation suggested by Fuoss⁷. For a set of conductance data ($c_j, \Lambda_j, j=1 \dots m$), the three adjustable parameters Λ° , K_A and R can be obtained by solving the following set of equations (eqns. 6-11):

$$\Lambda = P \left[\Lambda^{\circ} (1 + R X) + E L \right] \quad \dots (6)$$

$$P = [1 - \alpha (1 - \gamma)] \quad \dots (7)$$

$$\gamma = 1 - K_A c \gamma^2 f^2 \quad \dots (8)$$

$$-\ln f = \beta k / 2 (1 + KR) \quad \dots (9)$$

$$\beta = e^2 / \epsilon RT \quad \dots (10)$$

$$K_A = K_R / (1 - \alpha) = K_R (1 + K_B) \quad \dots (11)$$

where RX and EL are relaxation and hydrodynamic terms respectively as derived by Fuoss and other terms have their usual significance. The parameters Λ^0 , K_A and R are obtained by solving the above equations. The calculations were performed from a Nipre B-650 Computer using the programme furnished by Prof. R.M. Fuoss. Initial Λ^0 value for the iteration procedure were obtained from Shedlovsky extrapolations of the data. The calculations were made by finding the values which minimize

$$\sigma^2 = \sum_j [\Lambda_j(\text{cal}) - \Lambda_j(\text{obs})]^2 / (n-2) \quad \dots (12)$$

for a sequence of R-values and from the plotting of $\sigma\% = 100\sigma/\Lambda^0$ against R, the best fit R corresponds to the maximum in the $\sigma\% - R$ curve.

The Λ° , K_{Λ} , R_{Λ} and $\delta\%$ are given in Table 4.

Discussion

The Λ° values obtained using Shedlovsky's method and the Fuoss method are reasonably in good agreement with each other with marginal variations.

From Fig. 1 observed that the viscosity (η_0) of solvent mixtures (ME + H₂O) increases rapidly to reach a maximum at about 32 mole % or 62 wt% of ME, where η_0 is nearly 3.2 times the viscosity of water and η_0 decreases afterwards. This indicates the three dimensional structure of water is increased with the addition of ME due to hydrophobic interactions of two methoxy groups in ME with water. The addition of ME first induces the breakdown of 3D structure of water. The breakdown of the structure of water with further addition of ME is however associated with the formation of ME - H₂O complex. The maximum structureness appears to occur at 32 mole% of ME, where structure formations between ME and water molecules takes place through hydrogen bonding and the maximum in η_0 can be attributed to ME - H₂O complexation. The sharply downward trends are of course the reflection of the usual structural breaking effect due to packing imbalance at higher compositions of the co-solvent.

The variations of Λ° value of R₄NBr salts with solvent composition are shown in Fig. 2. It can be found that Λ° -values of tetraalkylammonium bromides decrease as the alkyl chain length

increases (Table 4). This is an agreement with earlier findings in several pure and mixed solvents⁸ and can be attributed with the size and structure forming effect of the cations⁹ (anions being the same). Size and structure forming effect decrease as the alkyl chain length increases and so the mobility is in the reverse order. For any particular electrolyte, the Λ° values continuously decrease with the addition of ME, pass through a minimum around 60-80 wt% of ME and then increases with further addition of ME. For Et_4NBr the Λ° value at 60 wt% of ME is slightly greater than 40 wt% of ME. Similar observations have been made in case of NaBr and NaBPh_4 . The Λ° -values decrease with the increase in viscosity (η_0) of the solvent mixtures but the Walden product have been found to be different. However, the maximum η_0 almost coincides with the region of observed minima in Λ° . The results indicate that the hydrodynamic entity is of importance in both cases but the difference in solvation of ions is responsible for the change in mobility of the ions and hence Λ° .

The assumption that the dielectric constant is not involved in affecting the Λ° -values since the ionization would be complex at infinite dilution, is untenable as the change in Λ° values are not due to the change in number of ions. The difference in the mobility of the ions is actually responsible for the change in λ_+° or λ_-° of ions. The cations and anions are moving in the opposite directions and the attractive forces of the opposite ions

will decrease with increase in dielectric constant of the solvent medium and the mobility of the ions would depend inversely on the dielectric constant of the medium.

Among other factors, the equivalent conductance Λ° of an electrolyte at infinite dilution are likely to depend on:

- i) solvation of ions
- ii) flow of ions through the holes under the influence of electric field. The flow is likely to be determined by the energy required to occupy the volume of the hole into which the ion jumps plus that required by the ion to break bonds with other molecules.
- iii) the dielectric constant of the solvent which determines the ionizing capability of the solvent.

It is to be expected that the hydrodynamic entity around the tetraalkylammonium ions is likely to be greater in water than in ME but the increased values of Λ° in water may be due to greater freedom of ions to move through the polar hydrogen bonded solvent system having high dielectric constant. The three dimensional water structure have 'holes' through which the transference of ions can occur rather easily and making or breaking of solvated chains are quick enough to have a rapid transfer of ions through water. The transfer process is obviously difficult in ME + H₂O mixtures as the 'holes' may be blocked by ME or ME - H₂O complex and the structure making or breaking would be a slow process.

From Table 4 we find that association constants, K_a , are very low for all the electrolytes at 20 and 40 wt% of ME + H₂O mixtures. This indicates that salts are not associated in this solvent mixtures having high dielectric constants (69.7) ϵ \gg 57.6). However, at higher wt% of ME K_a is very high (42.1) ϵ \gg 26.5) and increases continuously for all the electrolytes.

The variation of Walden product, with the solvent composition has been shown in Figs 3 and 4. The $\overset{\circ}{\Lambda}\eta_0$ values of all the salts (Table 5) passed through a maximum at 60 wt% of ME.

The division of $\overset{\circ}{\Lambda}$ into $\overset{\circ}{\lambda}_+$ and $\overset{\circ}{\lambda}_-$ values in mixed solvents is of particular interest to get an idea about the ion-solvent interactions and preferential solvation of ions in solution.

In absence of the accurate transference data in these mixed solvents, we have to use the 'reference electrolyte' method for the division of $\overset{\circ}{\Lambda}$ into single ion values. The Bu_4NBF_4 ¹⁰ has been used as the 'reference electrolyte'. The $\overset{\circ}{\Lambda}_{\text{Bu}_4\text{NBF}_4}$ has been obtained from the relation:

$$\overset{\circ}{\Lambda}_{\text{Bu}_4\text{NBF}_4} = \overset{\circ}{\Lambda}_{\text{Bu}_4\text{NBr}} + \overset{\circ}{\Lambda}_{\text{NaBF}_4} - \overset{\circ}{\Lambda}_{\text{NaBr}} \quad \dots(13)$$

Bu_4NBF_4 was utilised by Fuoss and Hirsch¹¹ and later by Coetzee et al¹² to calculate the limiting ion conductances in several organic solvents assuming

$$\lambda_0^{25} \text{Bu}_4\text{N}^+ = \lambda_0^{25} \text{Ph}_4\text{B}^- \quad \dots (14)$$

though the validity is questioned in several solvents.

We have also used 'Bu₄NBPh₄' as reference electrolyte but instead of equal division we have divided Λ^0 value using the method similar to that proposed by Krungjalz¹³ for division of B-values.

$$\frac{B(\text{Bu}_4\text{N}^+)}{B(\text{Ph}_4\text{B}^-)} = \frac{r^3(\text{Bu}_4\text{N}^+)}{r^3(\text{Ph}_4\text{B}^-)} = \left[\frac{\lambda_0(\text{Ph}_4\text{B}^-)}{\lambda_0(\text{Bu}_4\text{N}^+)} \right]^3 \quad \dots (15)$$

$$\text{or } \frac{\lambda_0(\text{Bu}_4\text{N}^+)}{\lambda_0(\text{Ph}_4\text{B}^-)} = \frac{r(\text{Ph}_4\text{B}^-)}{r(\text{Bu}_4\text{N}^+)} = \frac{5.35}{5.00} = 1.07 \quad \dots (16)$$

The r-values have been taken from the works of Gill et al^{14,15}. The virtual organic solvent independence of the solvation radii of large Bu₄N⁺ and Ph₄B⁻ ions made by Krungjalz¹³ (and Gill)^{14,15} to suggest that these ions are unsolvated in organic solvents and therefore, their radii were calculated by equation

$$r_{\pm} = \frac{|z|F^2}{6\pi\eta_0 N \lambda_{\pm}^0} \quad \dots (17)$$

correspond to their true dimensions in solutions. The limiting conductance values of the ions using the method (equation 16) are given in Table 6. The ionic Walden products and the Stoke's radii of the ions have been reported in Tables 7 and 8 respectively.

Though nothing can be said definitely regarding the accuracy of the method but some indirect evidence regarding the reliability of the values may be provided. The value of the ratio $\lambda_0(\text{BPh}_4^-)/\lambda_0(\text{Bu}_4\text{N}^+)$ becomes 1.05 if we choose $r_{\text{Bu}_4\text{N}^+} = 3.85\text{\AA}$ ^{13,15} and $r_{\text{BPh}_4^-} = 4.08$ as suggested by Krungalz¹⁷⁻²⁰. Fuoss et al¹⁷⁻²⁰ from an extensive measurements of Λ° of R_4NBPh_4 salts in various mixed organic solvents assumed that the limiting transference number of Bu_4N^+ in Bu_4NBPh_4 is 0.519 and is independent of the solvent (this is claimed to be valid within $\pm 1\%$). This means a value of 1.079 for $\frac{\lambda_0\text{Bu}_4\text{N}^+}{\lambda_0\text{Ph}_4\text{B}^-}$ which is close to 1.07.

D'Aprano and Fuoss¹⁹ used ' Bu_4NBPh_4 ' to calculate single ion conductances in mixed organic solvents applying the relation $\lambda_0\text{Bu}_4\text{N}^+ = \frac{0.213}{\eta_0}$ and $\lambda_0\text{BPh}_4^- = \frac{0.201}{\eta_0}$... (18) which means $\lambda_0\text{Bu}_4\text{N}^+/\lambda_0\text{BPh}_4^- = 1.06$.

Moreover, since the charge and the number of ions are equal, the equivalent conductances of these ions are dependent on the mobilities of the solvated ions, the divisions may be in terms of the reciprocal of their vander Waals' volume of these ions i.e.

$$\frac{\lambda_0\text{Bu}_4\text{N}^+}{\lambda_0\text{Ph}_4\text{B}^-} = \frac{166.8}{179.1} = 1.04 \quad \dots (19)$$

The vander Waals' volumes have been taken from the works of Lawrence and Sacco²¹. However, the ratio comes out to be slightly lower than usual 1.06-1.08.

In absence of accurate transference data in non-aqueous binary mixtures of organic solvents, it is difficult to compare the single ion values and test the validity of the equation (16). But the values calculated by this method appear to be in order in different organic or mixed organic solvents. However, in aqueous binary mixtures the solvation pattern may be different and the validity of this method may be questioned but in absence of a suitable method, nothing can be said conclusively.

The limiting ion conductances in organic or binary organic mixtures can also be calculated using the empirical equation suggested by Gill²².

$$\lambda_i^{\circ} = \frac{|z|F^2}{6\pi\eta N[r_i - (0.0103\epsilon_0 + r_y)]} \quad \dots (20)$$

where r_i (in Å) is the crystallographic radius or true solvated radius of the ion and r_y (in Å) is an adjustable term equal to 0.85Å for the dipolar non-associated organic solvents and equal to 1.13Å for the hydrogen bonded alcohols or other highly associated solvents having dipolar associations. The method has been critically examined by Krungalz and Fleisher²³ who showed that comparatively good results are obtained only in butan-1-ol, acetonitrile and nitromethane. However, the $\lambda_{\circ}Bu_4N^+ / \lambda_{\circ}BPh_4^-$ values obtained from precise transference measurements are 1.073 in

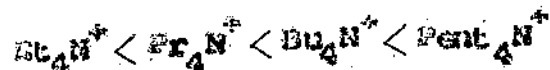
methanol, 1.055 in acetonitrile and 1.028 in nitromethane.

Recently, Gill et al²⁴ proposed the modified equation (21)

$$\frac{\lambda_0 \text{Bu}_4\text{N}^+}{\lambda_0 \text{Br}^-} = \frac{5.35 - (0.0103 \epsilon_0 + \epsilon_Y)}{5.00 - (0.0103 \epsilon_0 + \epsilon_Y)} \quad \dots(21)$$

and the ratio is close to 1.07 as used by us.

The variation of ionic conductances with solvent composition (Table 6) shows that the λ_+^0 values decrease as we go from Et_4N^+ to Pent_4N^+ in ME + H_2O mixtures and ME similar to those observed in water. The change in λ_+^0 is only marginal initially and the minimum is obtained at about 80 wt% of ME. The size and hydrophobic solvations in water and binary mixtures increase in the sequence



so that the λ_+^0 should be in the reverse order. The λ_+^0 of Na^+ , which is highly solvated by water, decreases and passes through a minimum at 80 wt% of ME. The Br^- ion is a structure breaker in water and λ_-^0 decreases continuously in ME + H_2O mixtures.

The ionic Walden products, $\lambda_+^0 \eta_0$, for the tetraalkyl ammonium ions (Fig. 5) show maxima only at 60 wt% of ME. For Na^+ ion (Fig. 6) the maximum $\lambda_+^0 \eta_0$ occurs at 60 wt% of ME. The Walden product of Br^- (Fig. 6) show a maximum at 60 wt% of ME

and then decreases. As the Walden product of an ion is inversely proportional to the effective radius of the ion in a solvent, the initial variation in the Walden products of R_4N^+ ions in ME + H_2O mixtures can be explained in terms of selective solvation of R_4N^+ ions by ME and H_2O molecules respectively. The decrease in the Walden product of R_4N^+ ions after 60 wt% of ME indicate the preferential solvation of R_4N^+ ions by ME in ME + H_2O mixtures.

The quantitative explanation for the variation of the Walden product with solvent composition is yet unknown though attempts have been made to derive a single satisfactory expression taking into account all types of ion-solvent interactions. In spite of some qualitative agreements, the complicated expression derived by Zwanzig²⁵ involving the solvent dielectric relaxation time, the solvent viscosity, static and infinite frequency dielectric constants fails to predict quantitatively the variations of the Walden product with solvent composition. This is quite natural as no single mathematical expression can cover all the ions and their interactions with various solvents as the ion-solvent interaction is quite specific for an ion and a particular solvent respectively. However, it is reasonable to believe like Hemmes²⁶ that the variations of the Walden product with solvent compositions are due to the variation of the electrochemical equilibrium between tetraalkylammonium ions and the solvent molecules on one hand, and selective solvation of ions and different types of complex formation between solvent molecules (e.g. ME- H_2O).

On the other hand as the composition of the mixed solvent change. They may be the reasons for the maximum and or minimum in the Walden product.

It is thus apparent that the selective solvation of ions, the viscosity of the medium, the nature of the exchange of ions with neighbouring solvent molecules and the movement of ions through the holes in hydrogen bonded solvent system are of importance to determine the variation of the Walden product with solvent composition.

We have also calculated the effective radii of ions in the solvent mixtures using the Stoke's model (Table 8). The values (Table 8) show that the effective radii are less than the crystallographic radii. But the values imply hydrophobic dehydration of cations in mixed solvents and solvation of cations by ME. The assumption that the large tetraalkylammonium ions are not solvated by organic solvents appears to be untenable as these ions may form an effective solvation sheath in ME and the effective solvation decreases with increase in radius of ion.

More extensive studied, however, are required to arrive at any reasonable conclusion about the conductance behaviour in different aquo-organic mixtures and the nature of ion-solvent interactions.

Table 1: Equivalent conductances of Tetraalkylammonium halides in ME + H₂O mixtures at 25°C
 $\bar{\Lambda}^{\circ}$ in mol lit⁻¹ and Λ in ohm⁻¹ cm² mol⁻¹

10 ⁴ c	$\bar{\Lambda}^{\circ}$	10 ⁴ c	$\bar{\Lambda}^{\circ}$	10 ⁴ c	$\bar{\Lambda}^{\circ}$
20% W/W (ME + H ₂ O) mixtures					
	Et ₄ NBr		Pr ₄ NBr		Bu ₄ NBr
601.011	48.01	801.001	45.38	801.001	42.37
699.999	63.72	600.002	47.67		
499.987	64.11	500.001	48.54	700.021	43.14
50.001	65.03	69.999	57.01	499.997	45.60
39.997	66.01	49.989	58.00	99.999	54.51
		40.002	58.51	60.033	55.67
30.002	67.04	29.997	59.17	39.997	57.00
19.995	67.51	19.998	59.65	29.989	57.51

Contd..

Table 1 (Contd..)

20% (w/w) OF ME

Pent ₄ NBr		N ₂ Br		NaBH ₄	
802.002	39.25	800.001	66.87	800.002	36.25
701.001	40.85	701.022	67.65	689.985	36.86
500.011	43.61	499.998	70.20	499.999	41.00
99.998	52.50	99.995	78.01	220.002	41.50
59.985	54.00	61.011	79.20	99.999	42.51
39.999	55.02	39.897	79.80	59.898	43.54
30.003	56.01	29.959	81.01	40.002	43.62
				29.989	44.50

Contd..

Table 1 (Contd..)

Et ₄ NBr		40% (w/w) of ME Et ₄ NBr		Bu ₄ NBr	
799.997	31.25	800.002	28.75	799.987	24.07
601.001	35.50	601.011	31.00	599.879	29.02
502.003	37.25	402.023	27.01	401.002	31.60
199.987	41.51	200.117	39.04	200.011	36.50
98.998	44.52	100.101	42.50	99.997	40.51
50.001	46.00	50.111	44.51	79.898	41.25
29.997	47.51	30.077	46.01	50.007	43.00
				29.999	45.01
Pent ₄ NBr		40% (ME + H ₂ O) NaBr		NaBrH ₄	
800.002	31.01	799.999	41.02	801.001	24.26
602.001	33.00	599.982	42.00	599.992	24.37
399.999	36.02	399.901	44.50	399.995	25.98
201.011	39.50	202.757	47.54	201.002	27.25
99.897	42.21	99.998	49.01	99.999	28.40
59.999	43.50	59.986	50.52	59.985	28.85
50.002	44.01	50.012	51.00	49.899	29.01
29.997	45.03	29.997	51.52	29.997	29.50

Contd..

Table I (Contd..)

Et ₄ NBr		60% (w/w) of ME Pr ₄ NBr		Bu ₄ NBr	
399.993	32.00	400.114	28.00	399.998	22.50
249.897	36.51	249.992	32.02	249.905	27.51
79.998	44.52	79.996	39.04	150.001	32.07
60.211	46.00	59.875	40.50	80.011	36.52
39.998	47.51	39.989	42.07	59.999	38.50
20.112	50.04	19.987	44.00	40.011	39.49
				20.012	42.55
Pent ₄ NBr		NaBr		NaBF ₄	
400.001	17.00	399.997	46.00	400.001	27.00
249.997	23.02	250.011	48.03	249.997	28.54
79.959	32.50	79.997	51.51	79.996	31.00
60.001	34.02	60.011	52.00	60.001	31.55
39.998	36.17	39.999	55.07	39.997	32.00
19.979	39.52	20.045	56.24	20.003	32.57

Contd..

Table 1 (Contd..)

Et ₄ NBr		80% (w/w) of MS Et ₄ NBr		Su ₄ NBr	
49.995	27.14	50.001	24.31	49.999	23.54
40.001	28.28	40.011	25.18	40.011	24.53
19.997	31.00	19.997	27.50	19.999	27.00
9.995	22.51	9.998	29.43	9.997	28.82
7.987	33.25	8.001	29.63	7.999	29.25
4.999	33.92	4.005	31.00	4.967	30.01
3.112	35.01	2.998	32.11	2.998	30.75
Pent ₄ NBr		NaBr		NaBPh ₄	
49.999	23.91	49.999	33.04	50.001	18.72
39.993	24.12	40.001	34.00	39.999	19.60
20.002	26.25	19.998	37.50	19.977	21.25
9.996	27.60	9.999	39.52	9.985	22.40
7.995	28.25	7.996	40.57	8.007	22.91
4.989	28.75	4.998	41.50	4.999	23.44
2.999	30.00	3.001	42.55	3.002	24.01

Table 2 : Limiting conductances (Λ°) of Tetraalkylammonium bromides, sodium bromide and sodium tetraphenyl borate in ME + H₂O mixtures (w/w) at 25°C (using Shedlovsky's method)

Salts	Wt% of ME				
	20%	40%	60%	80%	100%
Rt ₄ NBr	72.13	51.24	53.09	36.82	44.27
Cr ₄ NBr	62.15	49.39	46.55	33.35	38.35
Bu ₄ NBr	60.96	48.44	45.87	32.64	36.31
Pent ₄ NBr	59.46	48.25	44.11	31.05	34.17
NaBr	84.15	54.32	55.87	44.75	-
NaBPh ₄	47.11	31.49	34.22	25.40	-

Table 3 : association constants (K_a) of Tetraalkylammonium bromides, NaBr and NaBF_4 in $\text{ME} + \text{H}_2\text{O}$ (w/w) mixtures at 25 °C

Salts	20%	40%	60%	80%	100%
Et_4NBr	0.88	9.40	32.21	78.14	1124.14
Pr_4NBr	2.57	4.53	33.42	33.35	146.67
Bu_4NBr	4.31	8.55	59.76	93.77	261.49
Pent_4NBr	5.69	7.09	68.25	79.83	263.21
NaBr	1.14	3.55	4.24	86.93	-
NaBF_4	0.662	2.13	6.03	62.75	-

Table 4 : Conductance parameters from Kuoss (1978) equation for Tetraalkylammonium bromides, sodium bromide and sodium tetraphenyl borate in 2-Methoxy Ethanol (ME) + Water mixtures (w/w) at 25°C

Solvent	Salt	Λ°	K_2	R	Walden product ($\Lambda^{\circ}\eta_0$)	σ	σ°
20 wt% of ME	Tetraethyl ammonium bromide	72.45 (± 0.05)	3.19 (± 0.05)	15.0	0.988	0.08	0.117
	Tetrapropyl ammonium bromide	62.22 (± 0.07)	5.14 (± 0.09)	8.4	0.944	0.13	0.210
	Tetrapentyl ammonium bromide	61.13 (± 0.13)	6.98 (± 0.16)	7.1	0.927	0.19	0.312
	Tetrapentyl ammonium bromide	59.49 (± 0.14)	7.32 (± 0.14)	7.5	0.912	0.26	0.437
	Sodium bromide	84.54 (± 0.15)	3.40 (± 0.11)	8.0	1.282	0.25	0.292
	sodium tetraphenyl borate	47.65 (± 0.48)	1.45 (± 0.05)	7.5	0.722	0.28	0.587

Contd..

Table 4 (Contd..)

Solvent	Salt	Λ°	K_A	R	Walden product ($\Lambda^{\circ}\eta_0$)	σ	σ°
	Tetraethylammonium bromide	51.75 (± 0.11)	9.88 (± 0.65)	11.4	1.187	0.37	0.715
	Tetrapropyl ammonium bromide	50.35 (± 0.22)	9.98 (± 0.75)	7.0	1.191	0.32	0.675
40% (w/s) of BE	Tetrabutylammonium bromide	49.67 (± 0.26)	9.81 (± 0.81)	8.5	1.177	0.29	0.600
	Tetrapentyl ammonium bromide	48.32 (± 0.28)	9.02 (± 0.66)	3.5	1.153	0.25	0.517
	Sodium bromide	54.51 (± 0.18)	5.25 (± 0.26)	7.0	1.289	0.28	0.526
	Sodium tetraphenyl borate	31.50 (± 0.15)	2.95 (± 0.33)	7.5	0.745	0.24	0.789

Contd..

Table 4 (Contd..)

Solvent	Salt	Δ°	K_A	R	Walden product ($\Delta^{\circ} \eta_0$)	δ	δ'
60% (w/w) of ME	Tetraethylammonium bromide	54.07 (± 0.18)	32.40 (± 0.51)	19.5	1.559	0.13	0.231
	Tetrapropylammonium bromide	47.77 (± 0.07)	32.86 (± 0.38)	16.4	1.378	0.05	0.139
	Tetrapentylammonium bromide	46.75 (± 0.35)	61.73 (± 4.1)	17.1	1.347	0.19	0.411
	Tetrapentylammonium bromide	45.60 (± 0.05)	70.54 (± 5.55)	14.5	1.316	0.14	0.314
	Sodium bromide	56.94 (± 0.25)	5.576 (± 0.27)	18.5	1.643	0.31	0.544
	Sodium tetraphenyl borate	34.46 (± 0.08)	7.035 (± 0.34)	13.0	0.994	0.11	0.332

Contd..

Table 4 (Contd..)

Solvent	Salt	Δ°	K_{Δ}	R	Walden product ($\Delta^{\circ}\eta_0$)	σ	σ'
	Tetraethylammonium bromide	37.08 (± 0.16)	98.24 (± 5.29)	8.00	0.954	0.19	0.533
	Tetrapropylammonium bromide	33.49 (± 0.22)	117.71 (± 8.08)	18.3	0.853	0.16	0.478
80% (w/w) of Me	Tetrabutylammonium bromide	32.88 (± 0.18)	106.98 (± 3.85)	6.5	0.846	0.12	0.365
	Tetrapentylammonium bromide	31.36 (± 0.23)	82.34 (± 4.35)	9.5	0.808	0.15	0.478
	Sodium bromide	44.82 (± 0.15)	113.23 (± 3.88)	12.5	1.154	0.18	0.410
	Sodium tetraphenyl borate	28.43 (± 0.07)	95.96 (± 3.28)	13.4	0.655	0.09	0.372

Table 5 : Walden product of tetraalkylammonium bromides, NaBr & NaBPh₄ in ME + Water mixtures at 25°C (Δ° value from table - 4)

Wt% of ME	η in C. poise	ϵ	$\Delta^\circ \eta_0$					
			Et ₄ NBr	Pr ₄ NBr	Bu ₄ NBr	Pent ₄ NBr	NaBr	NaBPh ₄
0	0.8903	78.3	0.983	0.903	0.858	-	-	-
20	1.5164	69.7	0.988	0.944	0.927	0.912	1.282	0.722
40	2.3655	57.4	1.187	1.191	1.177	1.153	1.289	0.745
60	2.8049	42.1	1.559	1.378	1.347	1.316	1.643	0.994
80	2.5751	26.5	0.954	0.863	0.846	0.808	1.154	0.655
100	1.5414	16.9	0.674	0.598	0.566	0.532	-	-

Table 5: Limiting ionic conductances (λ_+^0, λ_-^0) at 25°C in ME + Water mixtures (w/w)
 (λ_-^0 -values are taken from Table 2)

Ion	0%	20%	40%	60%	80%	100%
Et_4N^+	32.32	23.85	15.85	19.89	11.17	21.42
Pr_4N^+	23.22	13.62	14.45	13.59	7.58	16.48
Bu_4N^+	19.31	12.53	13.78	12.52	6.97	14.42
pent_4N^+	-	10.89	12.43	11.42	5.45	12.22
Na^+	50.15	35.94	18.62	22.76	18.92	-
Br^-	79.25	48.60	35.89	34.18	25.91	32.32
BPh_4^-	-	11.71	12.88	11.70	6.51	-

Division based on $\text{Bu}_4\text{N}^+\text{BPh}_4^-$.

Table 7: Ionic Walden product in (ME + H₂O) mixtures at 25° C

wt% of ME	η_0 in c. poise	ϵ	$\Lambda_{\pm}^{\circ} \eta_0 / \text{cm}^2 \Omega^{-1} \text{mol}^{-1}$ poise						
			Na ⁺	Bt ₄ N ⁺	Pr ₄ N ⁺	Bu ₄ N ⁺	Pent ₄ N ⁺	BPh ₄ ⁻	Br ⁻
0	0.8903	78.3	0.446	0.297	0.208	0.172	-	-	0.697
20	1.5154	69.7	0.545	0.362	0.206	0.190	0.165	0.177	0.737
40	2.3655	57.4	0.460	0.375	0.342	0.325	0.293	0.305	0.848
60	2.8849	42.1	0.656	0.573	0.392	0.361	0.329	0.337	0.926
80	2.5751	26.5	0.487	0.287	0.195	0.179	0.140	0.167	0.657
100	1.5414	16.9	-	0.331	0.254	0.222	0.188	-	0.344

Table 8: Stoke's radii (R_S) in \AA of the ions in ME + H_2O mixtures (w/w) at 25 $^\circ\text{C}$ (Fuoss 1978)

IONS	0%	20%	40%	60%	80%	100%
Et_4N^+	27.6	1.33	2.17	1.43	2.73	2.48
Pr_4N^+	3.94	3.97	2.40	2.09	4.20	3.22
Bu_4N^+	4.77	4.31	2.51	2.27	4.57	3.69
Pent_4N^+	-	4.97	2.79	2.52	5.84	4.35
Br^-	1.18	1.11	0.966	0.832	1.23	2.38
Na^+	1.83	1.50	1.66	1.25	1.68	-
BF_4^-	-	4.63	2.69	2.43	4.91	-

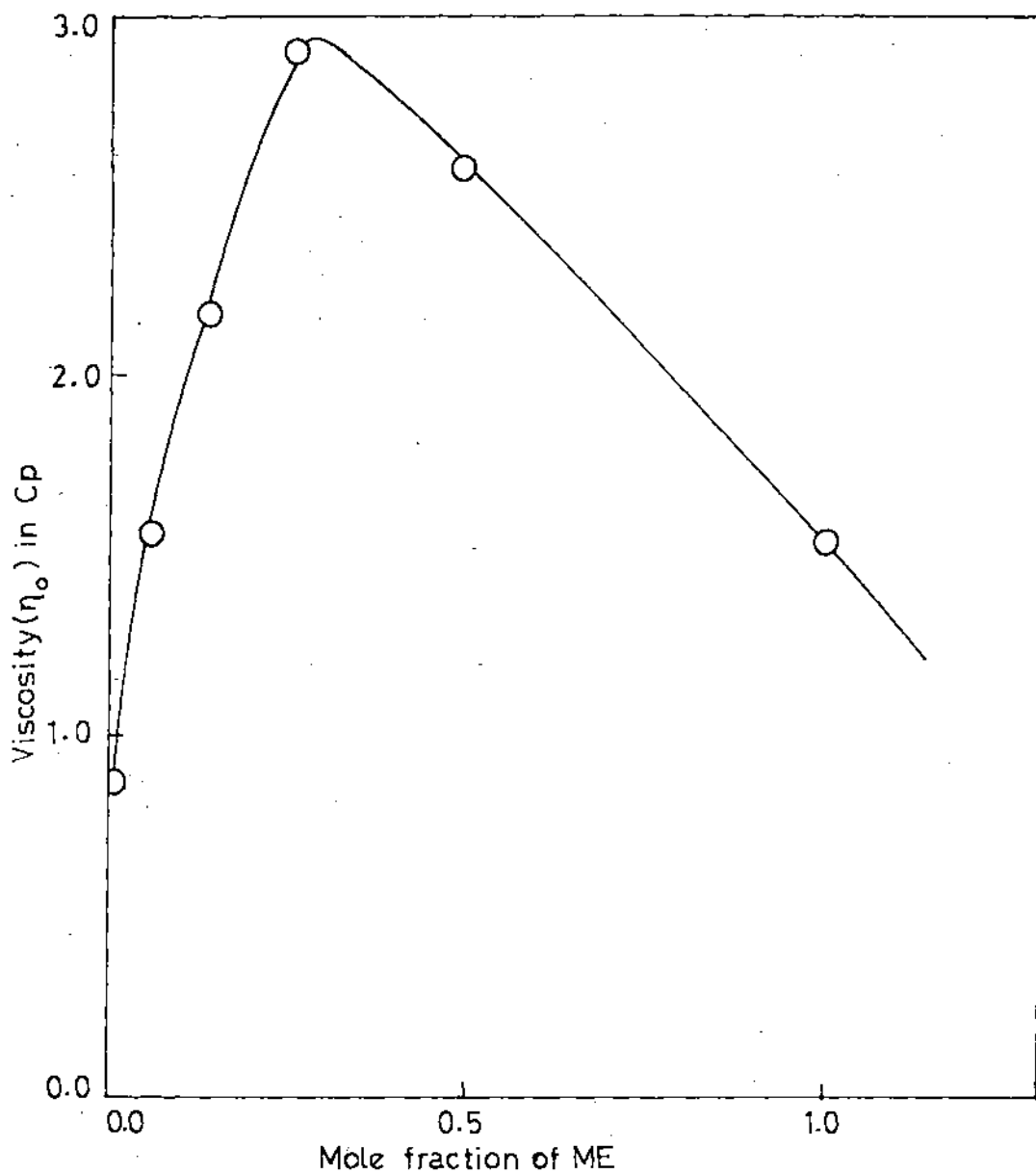


Fig.1 Variation of viscosity (η_0) with mole fraction of the solvent mixtures at 25°C

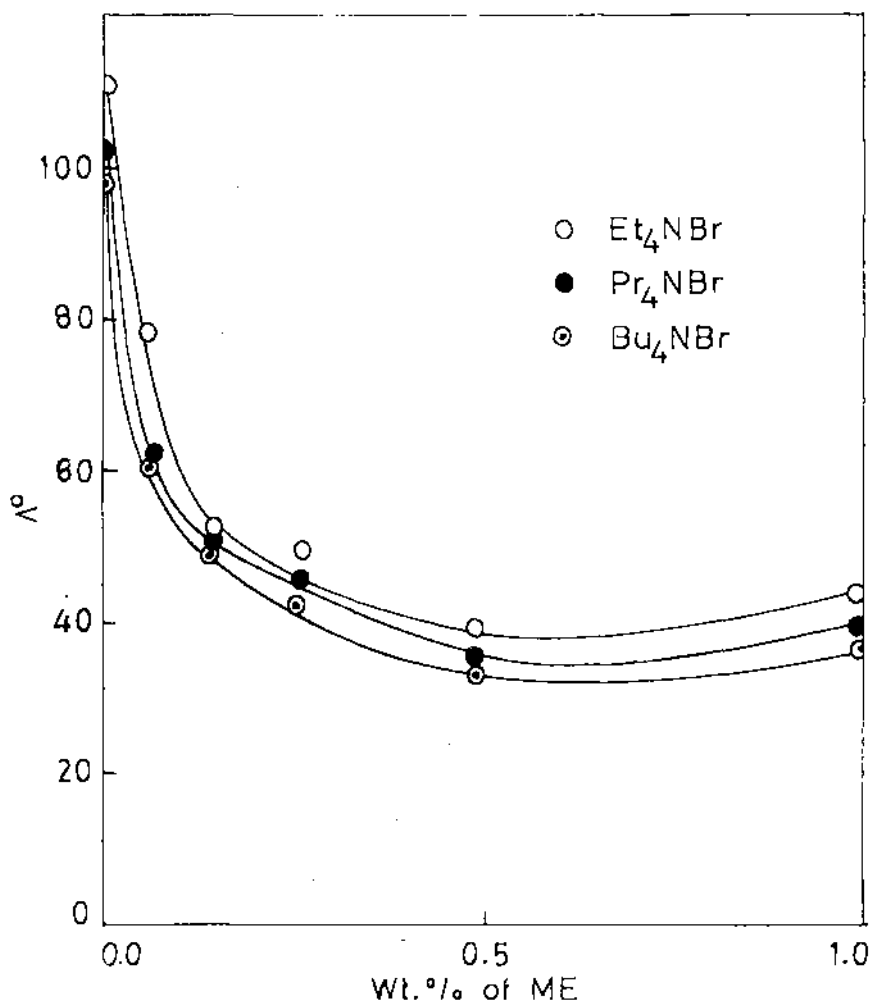


Fig 2 Variation of limiting equivalent conductance (Λ°) with composition of the solvent mixtures

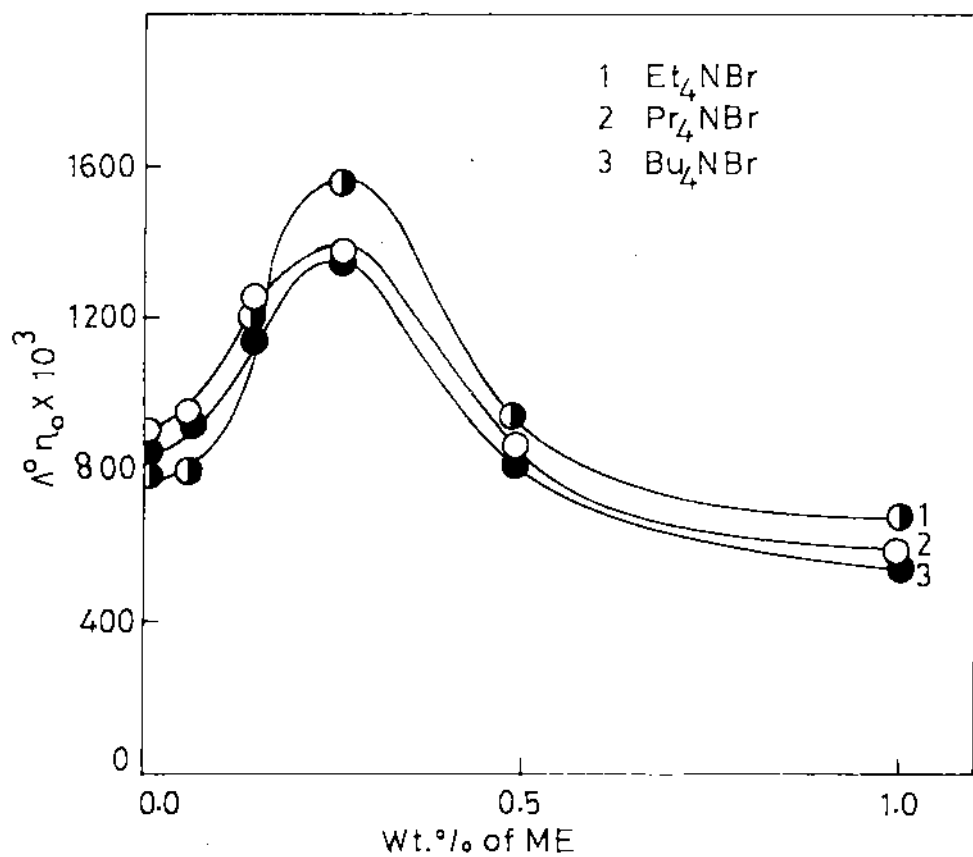


Fig. 3 Variation of Walden product ($\Lambda^\circ \eta_0$) of R_4NBr salts with composition of the solvent mixtures

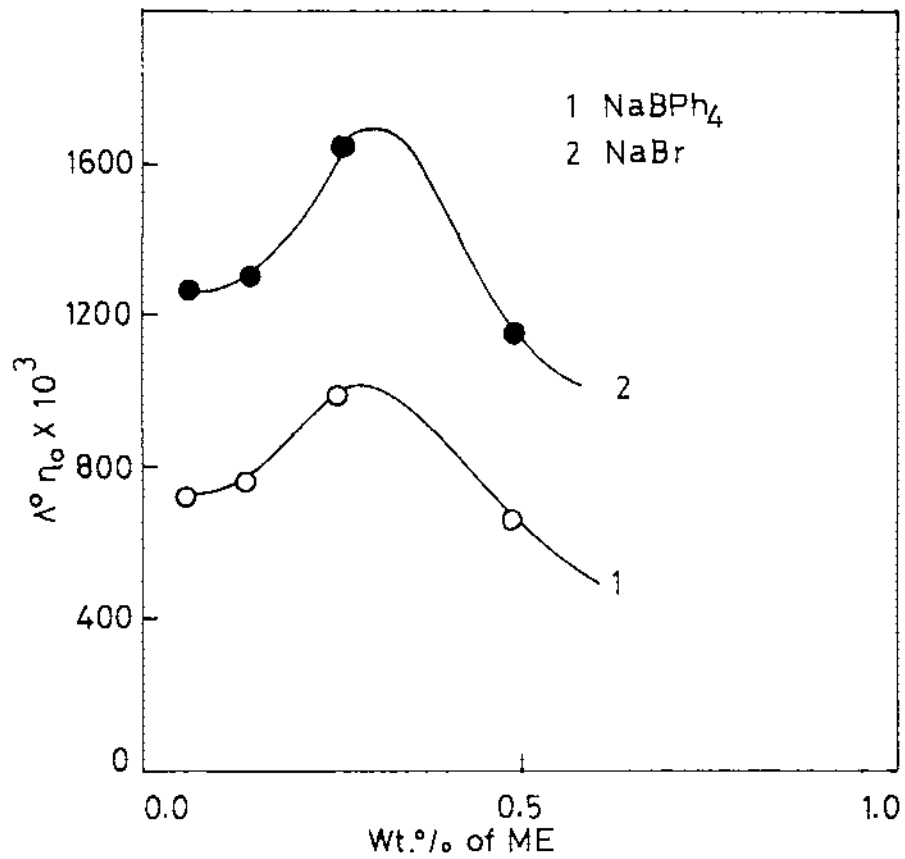


Fig. 4 Variation of Walden product ($\Lambda^\circ \eta_0$) of NaBPh₄ & NaBr salts with composition of the solvent mixtures

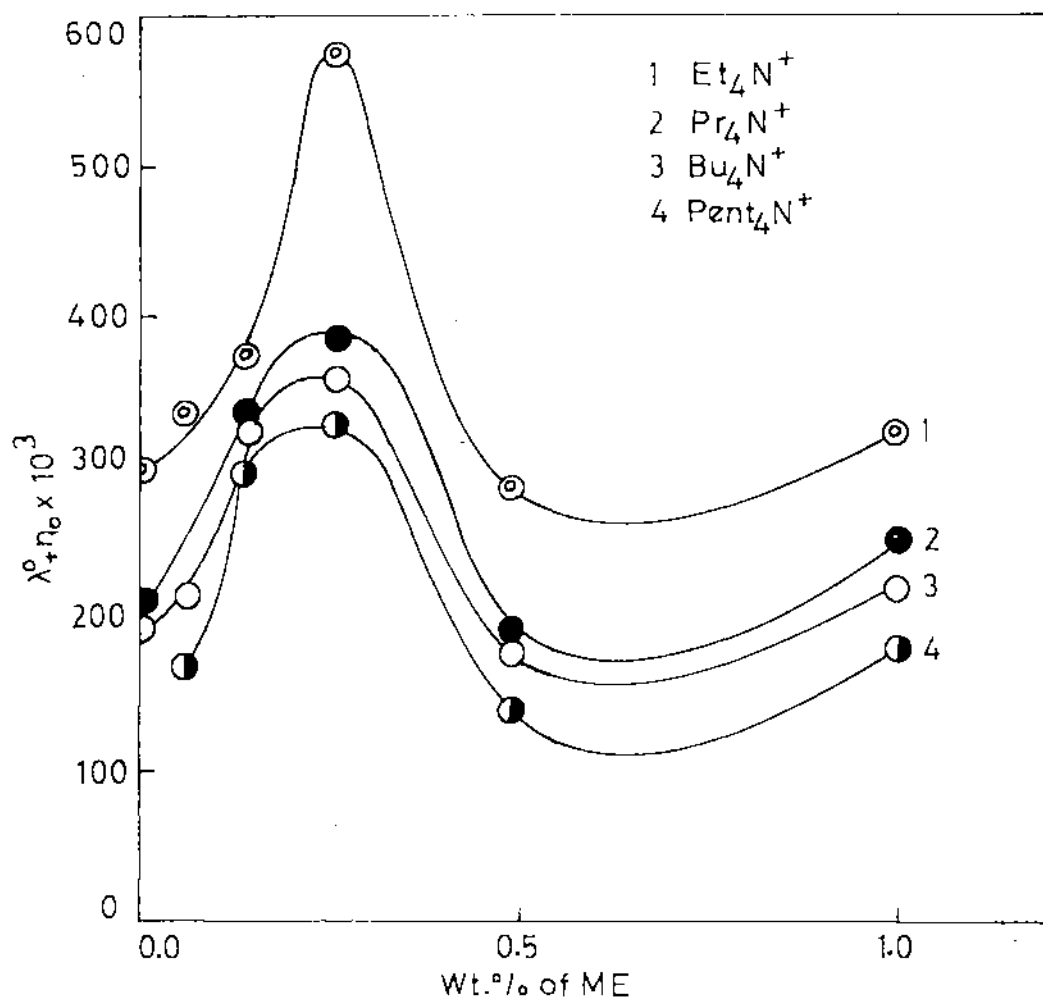


Fig.5 Variation of Walden product ($\lambda^{\circ} \eta_o$) of R_4N^+ ions with composition of the solvent mixtures

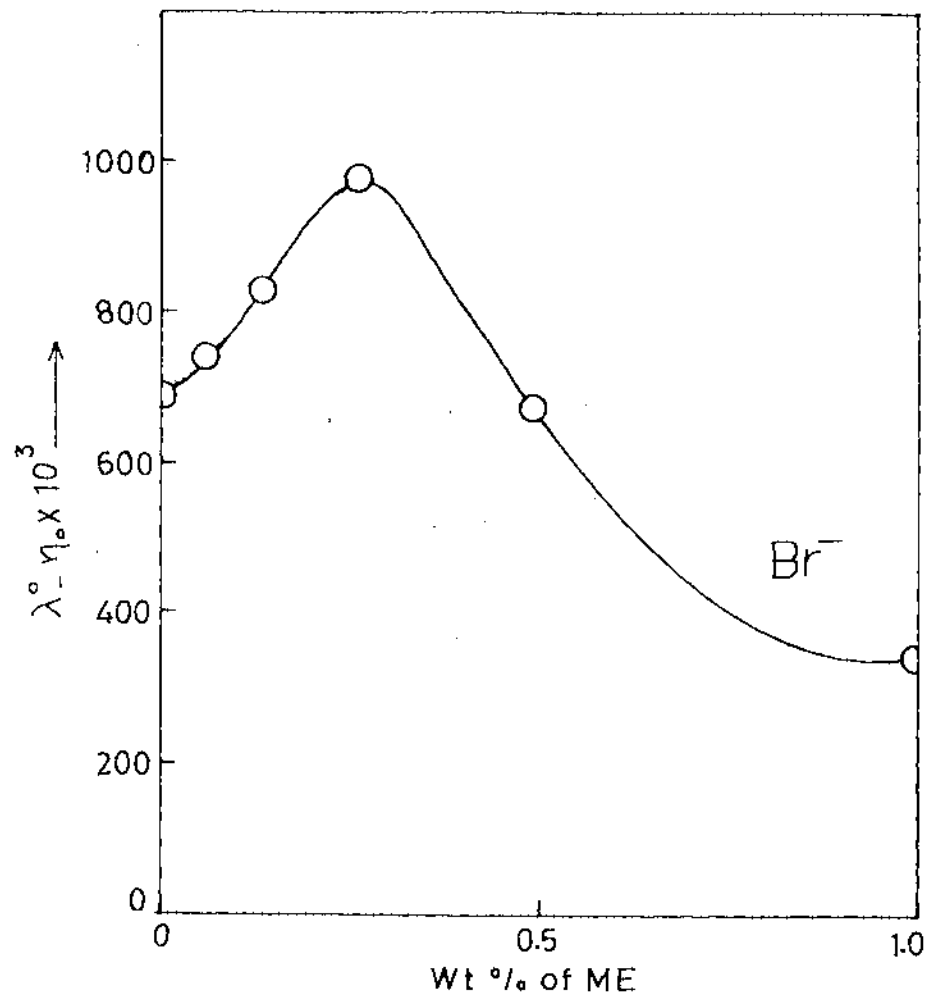
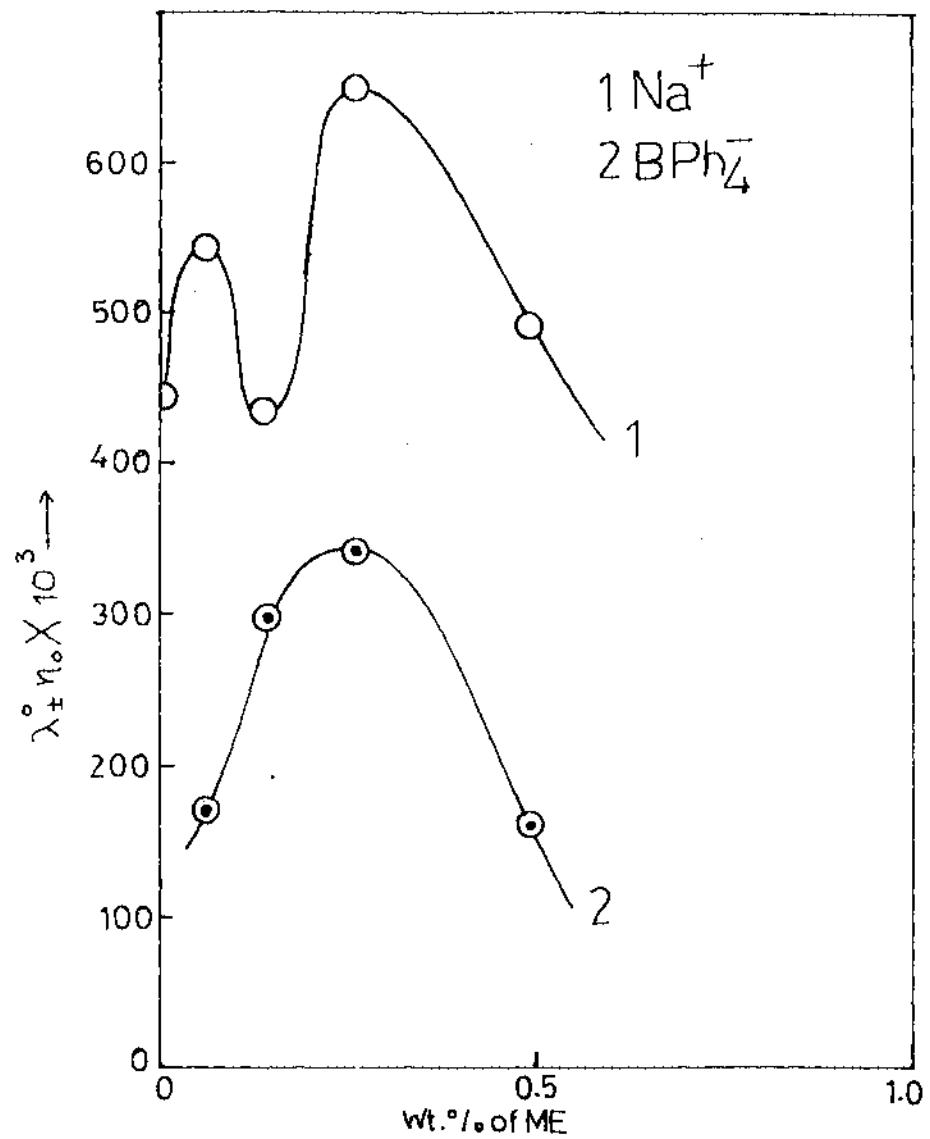


Fig.6 Variation of Walden product ($\lambda_{\pm}^{\circ}\eta_0$) of Na⁺, BPh₄⁻ & Br⁻ ions with composition of the solvent mixtures

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