

# VISCOSITY & RELATED PARAMETERS OF 1- 1 ELECTROLYTES IN 10% (W/W) 2- (ETHOXY) ETHANOL - WATER MIXTURE

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**Abstract :** Relative viscosities of  $\text{Me}_4\text{NBr}$ ,  $\text{Et}_4\text{NBr}$ ,  $\text{Pr}_4\text{NBr}$  and  $\text{Bu}_4\text{NBr}$  in 10% (W/W) 2-(Ethoxy) ethanol - water mixture are measured at 30°, 35° and 40°C. The data has been analyzed on the basis of Jones-Dole equation. The viscosity B-coefficients, and their temperature coefficients show that  $\text{Et}_4\text{NBr}$ ,  $\text{Pr}_4\text{NBr}$  and  $\text{Bu}_4\text{NBr}$  are structure makers in the present solvent system contrast to  $\text{Me}_4\text{NBr}$  a structure breaker. The B-Coefficients are divided into their ionic components. B-values of  $\text{R}_4\text{N}^+$  ions are divided into  $B_{\text{Einst}}$  and  $B_{\text{Reinf}}$  values. Solute - solvent interaction parameters ( $\Delta$ ) are calculated to understand the structural effect of solute. Applying transition state theory quasi-thermodynamic parameters are also calculated. Positive solvation numbers for  $\text{Et}_4\text{NBr}$ ,  $\text{Pr}_4\text{NBr}$  and  $\text{Bu}_4\text{NBr}$  indicate structure making property of these ions. The dimensions of the  $\text{R}_4\text{N}^+$  ions are also calculated.

**Index Terms** - Viscosity, Solute - Solvent interactions, Electrolyte solutions, Tetra alkyl ammonium bromides, 2-(Ethoxy) ethanol, Mixed solvents.

## I. INTRODUCTION

Viscosity measurements are very useful in providing information regarding ion-solvent interactions and the modifications induced by the ions in the solvent structure<sup>1</sup>. n-(Alkoxy) alkanols known as cellosolves are good industrial solvents. In recent years these solvents have drawn the attention of various investigators. The study of n-(Alkoxy) alkanols is of interest not only because of their wide use as industrial solvents but also from the more theoretical point of investigating the effect of presence of both etheric and hydroxyl groups on the interaction of such molecules<sup>2,3</sup>. In spite of the potential applications of these solvents there are relatively a few solute - solvent interaction studies<sup>4,5</sup> in this class of substances and their water mixtures. A survey of literature indicated that 2-(Butoxy) ethanol and 2-(Methoxy) ethanol are the solvents studied to some extent<sup>7-10</sup> and little work has been reported on the viscosities in 2-(Ethoxy) ethanol - water mixtures.

Hence 10% (W/W) 2-(Ethoxy) ethanol - water mixture is adopted as solvent where some modifications are expected (water rich region) in the structure of water. In the present investigation the viscosity and related parameters are studied in 10% (W/W) 2-(Ethoxy) ethanol - water mixture at three different temperatures 30°C, 35°C, 40°C.

## II. EXPERIMENTAL

### 2.a Material and Methods

2-(Ethoxy) ethanol (E.Merk sample) is first refluxed for an hour with Tin II chloride to remove traces of peroxide as per the procedure discussed in our earlier communications<sup>11</sup>. The refluxed solvent is then dried over anhydrous potassium carbonate and then fractionally distilled. The middle fraction distilling between 133°-134°C is collected.

Tetra methyl ammonium Bromide, Tetra ethyl ammonium bromide, Tetra propyl ammonium bromide and Tetra butyl ammonium bromide (Aldrich chemicals) are dried at 110° C in a hot air oven and stored in a desiccator. Preparation of solutions is as described earlier<sup>11</sup>.

In the present study viscosity measurements are made with an Ostwald type viscometer with a flow time of 130.7 sec for water at 30°C. The precision of the measured relative viscosities is  $\pm 0.0007$ .

## III. RESULTS AND DISCUSSION

The relative viscosities of Tetra alkyl ammonium bromides ( $\text{Me}_4\text{NBr}$ ,  $\text{Et}_4\text{NBr}$ ,  $\text{Pr}_4\text{NBr}$  and  $\text{Bu}_4\text{NBr}$ ) in 10% (W/W) 2-(Ethoxy) ethanol water mixture are determined at 30°, 35° and 40°C and are presented in Table 1.

The results are analyzed on the basis of Jones - Dole equation

$$\eta_r = \frac{\eta}{\eta_0} = 1 + A\sqrt{C} + BC \text{ -----[1]}$$

Since the measurements of the viscosities are being conducted with solutions, whose molar concentrations are less than 0.12, the additional DC<sup>2</sup> term is not added. The A and B coefficients are obtained by fitting the experimental data into the equation 1, by the method of least squares.

A-coefficients are calculated theoretically by using equation 2 proposed by Falkenhagen and Vernon<sup>12</sup>.

$$A_{(Theor)} = \frac{0.2577 \wedge_0}{\eta_0 (\epsilon T)^{1/2} \lambda_0^+ \lambda_0^-} \left[ 1 - 0.6863 \frac{(\lambda_0^+ - \lambda_0^-)}{\wedge_0} \right] \text{-----[2]}$$

Where  $\lambda_0, \eta_0$  &  $\epsilon$  have their usual significance<sup>12</sup>

Ionic conductance and the dielectric constants of the 10% (W/W) 2-(Ethoxy) ethanol - water mixture are taken from the conductance measurements of our investigation<sup>13,14</sup>. The calculated theoretical  $A_\eta$  values are presented in table 2

### 3.a B-Coefficients:

The B-coefficients obtained from equation 1 are presented in Table 3 but before entering into the analysis it is time to note here that, according to Desnoyers and Perron<sup>15</sup>, the measurement of viscosity over a narrow concentration range may lead to some uncertainties in the determination of B-coefficients which may be true in the present investigation. It is seen from the table that Pr<sub>4</sub>NBr exhibits some abnormalities in the viscosity behavior.

TABLE : 1

Molar concentration (c), Relative viscosity of tetra alkyl ammonium bromides in 10% (W/W) 2-(Ethoxy) ethanol water mixture at 30°, 35° and 40°C

$C \times 10^3 \text{ g.mole litre}^{-1}$ 30°	$\frac{\eta}{\eta_0}$	$C \times 10^3 \text{ g.mole litre}^{-1}$ 35°	$\frac{\eta}{\eta_0}$	$C \times 10^3 \text{ g.mole litre}^{-1}$ 40°	$\frac{\eta}{\eta_0}$
<b>Tetra methyl ammonium bromide</b>					
25.72	1.00173	25.72	1.00204	25.72	1.00244
45.26	1.00262	45.26	1.00307	45.26	1.00347
49.70	1.00305	49.70	1.00337	49.70	1.00383
60.40	1.00342	60.40	1.00406	60.40	1.00475
71.63	1.00460	71.63	1.00461	71.63	1.00571
83.35	1.00510	83.35	1.00534	83.35	1.00654
91.69	1.00554	91.69	1.00583	91.69	1.00722
102.97	1.00590	102.97	1.00666	102.97	1.00786
111.04	1.00639	111.04	1.00765	111.04	1.00866
121.05	1.00674	121.05	1.00832	121.05	1.00942
<b>Tetra ethyl ammonium bromide</b>					
20.55	1.00808	20.55	1.01029	20.55	1.01184
30.48	1.01390	30.48	1.01468	30.48	1.01562
40.06	1.01851	40.06	1.01896	40.06	1.01959
50.48	1.02236	50.48	1.02227	50.48	1.02273
56.93	1.02455	56.93	1.02532	56.93	1.02593
71.02	1.02794	71.02	1.02811	71.02	1.02901
80.19	1.036155	80.19	1.03182	80.9	1.03187
95.51	1.03754	95.51	1.03725	95.51	1.03600
111.30	1.04189	111.30	1.04125	111.30	1.04131
<b>Tetra propyl ammonium bromide</b>					
30.78	1.02237	30.78	1.02041	30.78	1.02165
40.60	1.02933	40.60	1.02636	40.60	1.02705
50.46	1.03629	50.46	1.03504	50.46	1.03522
60.53	1.04741	60.53	1.04476	60.53	1.04382
71.23	1.05747	71.23	1.05460	71.23	1.05424
79.66	1.06465	79.66	1.06085	79.66	1.06022

89.92	1.07123	89.92	1.06750	89.92	1.06567
100.39	1.07872	100.39	1.07344	100.39	1.07277
120.00	1.09208	120.00	1.08718	120.00	1.08424
<b>Tetra butyl ammonium bromide</b>					
29.82	1.03819	29.82	1.03632	29.82	1.03714
40.91	1.04800	40.91	1.04584	40.91	1.04428
50.80	1.05961	50.80	1.05608	50.80	1.05283
63.51	1.07268	63.51	1.06825	63.51	1.06698
79.58	1.08547	79.58	1.08104	79.58	1.07628
91.04	1.09895	91.04	1.09359	91.04	1.09059
101.51	1.11192	101.51	1.10479	101.51	1.10102
111.11	1.12096	111.11	1.11446	111.11	1.10898
119.99	1.13376	119.99	1.12618	119.99	1.12113

**TABLE : 2**  
**Theoretical ( $A_{\eta}$ ) Coefficients of ( $R_4NBr$ ) salts in 10%(W/W) 2(Ethoxy) ethanol-water at 30°, 35° and 40°C**

Salt	$(A_{\eta} \times 10^3)$		
	30°	35°	40°
$Me_4NBr$	7.16	6.80	6.84
$Et_4NBr$	7.14	7.45	7.55
$Pr_4NBr$	7.33	7.86	8.69
$Bu_4NBr$	8.53	8.68	8.97

**TABLE : 3**  
**A,B Viscosity coefficients of ( $R_4NBr$ ) salts in 10% (W/W) 2-(Ethoxy) ethanol-water mixture**

Salt	30°		35°		40°	
	A ( $dm^3 mole^{-1}$ ) <sup>-1/2</sup>	B ( $dm^3 mole^{-1}$ )	A ( $dm^3 mole^{-1}$ ) <sup>-1/2</sup>	B ( $dm^3 mole^{-1}$ )	A ( $dm^3 mole^{-1}$ ) <sup>-1/2</sup>	B ( $dm^3 mole^{-1}$ )
$Me_4NBr$	0.0026	0.0505	0.0022	0.0591	0.0028	0.0685
$Et_4NBr$	0.0200	0.3285	0.0387	0.2620	0.0547	0.2065
$Pr_4NBr$	0.0238	0.8635	0.0292	0.8376	0.0105	0.7605
$Bu_4NBr$	0.0529	0.9307	0.0532	0.8675	0.0648	0.7865

These are (i) an unexpected negative A-coefficient disobeying linear increase along the tetra alkyl series.

(ii) When the B-coefficients for  $R_4NBr$  salts in the present solvent system are compared with that of the values in pure water, all the values decrease. But the decrease is very much less in case of  $Pr_4NBr$  than the other  $R_4NBr$  salts. This type of abnormalities in viscosity properties for larger tetra alkyl ammonium salts is suggested to be due to the presence of small quantities of surface active reagents<sup>12</sup>. Hence in the further analysis of the results and in the discussion, the magnitude of the B-coefficients and its derived parameters are not taken into consideration. But the sign of the values are only used to explain the behavior.

An observation of the B-coefficients of the electrolytes studied (table 3) shows that the B-values are positive of,  $Et_4NBr$ ,  $Pr_4NBr$  and  $Bu_4NBr$ . This indicates that the alignment of solvent molecules with the ions, undoubtedly promotes the structure of the solvent molecules in its immediate vicinity. Generally it can be said that a decrease in the structure of the solvent due to the solute, results in a lower B-value and an enhancement of the structure of the solvent results in a higher B-value. In case of inorganic salts, the structure breaking salts will have negative B-values showing that the hydrodynamic contribution (influence

of the size of the ion) though positive is dominated by the negative contribution of the charge of the ion. For  $Me_4NBr$  at all temperatures B-values are relatively very low compared to others.

In case of solutions of large organic solutes such as tetra alkyl ammonium salts, the contribution of hydrodynamic effect is sufficiently high. Hence the B-values of large tetra alkyl ammonium ions starting from  $Et_4NBr$  are positive. From the above discussion it can be said that  $Et_4NBr$ ,  $Pr_4NBr$  and  $Bu_4NBr$  are structure makers in the present solvent system.

The positive B-value observed for  $Me_4NBr$  is in contradiction to the structure breaking tendency of this salt in aqueous solutions. This contradiction supports the emphasis that the sign and magnitude of  $\frac{dB}{dT}$  rather than the sign of B, provides a better index of the solute - solvent interactions. It is shown that for

net structure makers  $\frac{dB}{dT}$  is always negative, while it is positive for net structure breakers. The temperature

coefficients of the B-values of the salts under investigation are presented in Table (4). From the sign of  $\frac{dB}{dT}$

values it can be concluded that  $Et_4NBr$ ,  $Pr_4NBr$  and  $Bu_4NBr$  are overall structure makers (negative  $\frac{dB}{dT}$ )

while  $Me_4NBr$  is a nett structure breaker (Positive  $\frac{dB}{dT}$ ) in the 10% (W/W) 2-(Ethoxy) ethanol - water mixture.

**TABLE : 4**  
 **$\frac{dB}{dT}$  coefficients in 10%(W/W) 2-(Ethoxy) ethanol - water mixture**

Temp/Salt	30° – 35° C	35° – 40° C
$Me_4NBr$	0.002	0.002
$Et_4NBr$	-0.013	-0.011
$Pr_4NBr$	-0.005	-0.015
$Bu_4NBr$	-0.013	-0.016

### 3.b Ionic B-coefficients:

B-coefficients of the salts are divided into ionic contributions to understand the nature of ion - solvent interactions of the individual ionic components. Any method of splitting B-coefficient into ionic components for binary solvent systems, is not likely to be free of criticism since these methods are proposed for pure water<sup>16</sup> as solvent. Therefore, assuming that the method applicable for pure water will also apply to the water rich binary systems, the method suggested by Kaminsky<sup>16,17</sup> is used in the present study to separate the B-coefficients into ionic contributions. The method of Kaminsky<sup>16,17</sup> assumes that at every temperature  $B_{K^+} = B_{Cl^-}$ . To apply this method a series of alkali metal halides are studied in the present solvent system<sup>13</sup> and the ionic B-coefficients for the reference ion are obtained as -0.0576, -0.0532, -0.0599 at 30°, 35° and 40°C respectively. The B-coefficients of the other ions are calculated on the basis of the additivity of B-coefficients. The ionic B -coefficients along with  $\frac{dB_{ion}}{dT}$  values are presented in table 5.

Based on the sign of the  $\frac{dB_{ion}}{dT}$  it can be concluded that  $Et_4N^+$ ,  $Pr_4N^+$  and  $Bu_4N^+$  are structure makers while  $Me_4N^+$  and  $Br^-$  are structure breakers in the 10% (W/W) 2-(Ethoxy) ethanol - water mixture

Table : 5

Ionic B-Coefficients and  $\frac{dB_{\pm}}{dT}$  values in 10%(W/W) 2-(Ethoxy) ethanol - water mixture

Ion	$B_{\pm}$ 30°	$B_{\pm}$ 35°	$B_{\pm}$ 40°	$\frac{dB_{\pm}}{dT}$ (30° – 35°)C
$Me_4N^+$	0.1081	0.1123	0.1284	0.0008
$Et_4N^+$	0.3861	0.3152	0.2664	-0.0142
$Pr_4N^+$	0.9211	0.8908	0.8207	-0.0060
$Bu_4N^+$	0.9883	0.9207	0.8464	-0.0135
$Br^-$	-0.0576	-0.0532	-0.0599	0.0009

### 3.c COMPONENTS OF B-COEFFICIENTS :

The ionic B-coefficients are assumed to be due to four major contributions<sup>17</sup>

$B^{ion} = B_{Einst}^{ion} + B_{Orient}^{ion} + B_{stru}^{ion} + B_{reinf}^{ion}$ . Where all the terms have their usual significance. For aqueous solutions containing large tetra alkyl ammonium ions, the values of  $B_{orient}^{ion}$  &  $B_{stru}^{ion}$  are negligible, the former due to the small surface charge of the ions and the latter due to the fact that the hydrophobic hydration of these ions, as opposed to inorganic ions, is realized without destruction of the intrinsic water structure<sup>17,18</sup>. Hence for aqueous solutions

$$B^{R_4N^+} = B_{Einst}^{R_4N^+} + B_{reinf}^{R_4N^+} \dots\dots\dots (3)$$

Making use of the Einstein's equation<sup>19,20</sup> and taking into consideration the suggestion of Robinson and Stokes<sup>21</sup>, Krumgalz<sup>22</sup> gave an equation to calculate

$$B_{Einst}^{R_4N^+} = 6.037 \times 10^{21} r_{R_4N^+}^3 \text{ l.mol}^{-1} \dots\dots (4)$$

Krumgalz felt that, it will be suitable to use hydration radius of the  $R_4N^+$  ions needed for the calculation of  $B_{reinf}^{R_4N^+}$  value. It is argued that when temperature increases, the hydrophobic hydration of large tetra alkyl ammonium ions decreases, because of the destruction of the ice-like water structure and the disappearance of the intermolecular cages for placing the organic chains of these ions. Hence the  $B_{reinf}^{R_4N^+}$  value must decrease and approach zero when hydrophobic hydration disappears. It is evident from table 6 that in the present case also the  $B_{reinf}^{R_4N^+}$  value decreases with increase in temperature for larger tetra alkyl ammonium ions (starting from  $Et_4NBr$ ) thus confirming the observations of Krumgalz. However the value for  $Me_4NBr$  increases with temperature indicating the dominance of electrostriction associated with the ion.

TABLE : 6  $B_{Einst}$  &  $B_{Reinf}$  values for  $R_4NBr$  ions

	$B_{Einst}^{R_4N^+}$			$B_{reinf}^{R_4N^+}$		
	30°	35°	40°	30°	35°	40°
$Me_4N^+$	0.1370	0.0718	0.0681	-0.0289	0.0405	0.0603
$Et_4N^+$	0.1340	0.1340	0.1340	0.2521	0.1812	0.1324
$Pr_4N^+$	0.1603	0.1916	0.3516	0.7608	0.6992	0.4691
$Bu_4N^+$	0.5120	0.3828	0.4347	0.4763	0.5379	0.4117

### 3.d APPLICATION OF TRANSITION STATE THEORY

The relative viscosities of tetra alkyl ammonium halides in 10% (W/W) 2-(Ethoxy) ethanol - water mixture are analyzed by applying transition state theory<sup>23</sup>. According to Feakins et al...<sup>23</sup>

$$B = \frac{\bar{V}_1^0 - \bar{V}_2^0}{1000} + \frac{\bar{V}_1^0}{1000} \left( \frac{\Delta\mu_2^{0\#} - \Delta\mu_1^{0\#}}{RT} \right) \dots\dots (5)$$

Where  $\bar{V}_1^0$  and  $\bar{V}_2^0$  are the partial molar volumes of solvent and solute respectively.  $\Delta\mu_2^{0\#}$  is the contribution per mole of the solute to the free energy of activation for the viscous flow of the solution,  $\Delta\mu_1^{0\#}$  is the free energy of activation per mole of the pure solvent given by the equation

$$\Delta\mu_1^{0\#} = RT \ln \frac{\eta_0 \bar{V}_1^0}{hN} \dots\dots\dots(6)$$

In a series  $\Delta\mu_2^{0\#}$ , like B-coefficients, decreases with increase in the size and mass of the cation and for nett structure makers  $\Delta\mu_2^{0\#} > \Delta\mu_1^{0\#}$  while for nett structure breakers  $\Delta\mu_2^{0\#} < \Delta\mu_1^{0\#}$ . If these parameters are known at different temperature it is also possible to know the activation enthalpy  $\Delta\bar{H}_2^{0\#}$  and activation entropy  $\Delta\bar{S}_2^{0\#}$  by the equations

$$\frac{d(\Delta\mu_2^{0\#})}{dT} = -\Delta\bar{S}_2^{0\#} \dots\dots\dots 7$$

$$\Delta\bar{H}_2^{0\#} = \Delta\mu_2^{0\#} + T\Delta\bar{S}_2^{0\#} \dots\dots\dots 8$$

Making use of the equation 5-7,  $\Delta\mu_2^{0\#}$ ,  $\Delta\bar{H}_2^{0\#}$  &  $T\Delta\bar{S}_2^{0\#}$  are calculated and presented in Table 7

From the table it is evident that for nett structure makers such as  $Et_4NBr$ ,  $Pr_4NBr$  &  $Bu_4NBr$  these observations are in keeping with the conclusions given by Feakins et al... However  $Me_4NBr$  though structure breaker in the present solvent system do not follow the general principle  $\Delta\mu_2^{0\#} < \Delta\mu_1^{0\#}$ . Based on the above in acceptability of the general rule by some salts, it can be argued that it will be better to consider the magnitude and sign of  $T\Delta\bar{S}_2^{0\#}$  which involves the  $\frac{d(\Delta\mu_2^{0\#})}{dT}$  term, as a criterion to classify the electrolytes as structure makers or structure breakers in the present investigation. Thus depending on the sign of the enthalpy and entropy values it can be concluded that the negative entropy and enthalpies are associated with the structure breaking electrolytes while positive values are associated with the structure making electrolytes. The negative  $\Delta\bar{H}_2^{0\#}$  and  $T\Delta\bar{S}_2^{0\#}$  for  $Me_4NBr$  indicate that this electrolyte is a nett structure breaker and on the other hand the positive  $\Delta\bar{H}_2^{0\#}$  and  $T\Delta\bar{S}_2^{0\#}$  indicate the structure making ability of  $Et_4NBr$ ,  $Pr_4NBr$  and  $Bu_4NBr$

**Table : 7**

**Thermodynamic parameters of activation energy of viscous flow of  $R_4NBr$  salts in 10%(W/W) 2-(Ethoxy) ethanol-water mixture at 30°,35°, and 40°C**

Electrolyte	30°			35°			40°		
	$\Delta\mu_2^{0\#}$	$T\Delta\bar{S}_2^{0\#}$	$\Delta\bar{H}_2^{0\#}$	$\Delta\mu_2^{0\#}$	$T\Delta\bar{S}_2^{0\#}$	$\Delta\bar{H}_2^{0\#}$	$\Delta\mu_2^{0\#}$	$T\Delta\bar{S}_2^{0\#}$	$\Delta\bar{H}_2^{0\#}$
$Me_4NBr$	7.03	-16.67	-9.64	7.21	-16.95	-9.74	7.58	-17.22	-9.64
$Et_4NBr$	16.96	110.04	127.00	14.95	118.86	133.81	13.33	113.67	147.00
$Pr_4NBr$	35.89	79.12	115.01	35.24	80.43	155.67	33.28	81.73	115.01
$Bu_4NBr$	39.95	116.71	156.66	118.64	118.64	156.72	36.10	120.56	156.66

These results are in accordance with the conclusions drawn from the sign of  $\frac{dB}{dT}$  values of the respective electrolytes

An attempt to separate  $\Delta\bar{H}_2^{0\#}$  and  $T\Delta\bar{S}_2^{0\#}$  into ionic contribution is made based on the usual assumption of equality of effects for the potassium and chloride ions, following the method used by Feakins<sup>23</sup>. The single ion enthalpies and entropies of Tetra alkyl ammonium ions along with the reference bromide ion are presented in Table 8. From the tables (7) and (8) it is clear that both  $\Delta\bar{H}_2^{0\#}$  and  $T\Delta\bar{S}_2^{0\#}$  are positive for structure making ions such as  $Et_4NBr$ ,  $Pr_4NBr$  and  $Bu_4NBr$ . According to Feakins this indicates that; the formation of a transition state is associated with bond breaking and a decrease in order. This suggests that the slip plane is somewhere in the region of centro-symmetric order.

On the other hand, the negative  $\Delta\bar{H}_2^{0\#}$  and  $T\Delta\bar{S}_2^{0\#}$  values for structure breaking ions such as  $Me_4N^+$  show that the transition state is associated with bond making and an increase in order. It suggests that the slip plane is in the disordered region. It is interesting to note here that the single ion enthalpies and entropies of  $R_4N^+$  ions are much greater than those of alkali metal ions<sup>13</sup> where ion - solvent interactions are strong. This is exactly opposite to that observed by Das et al.<sup>24</sup> in pure DMSO an aprotic polar solvent.

**TABLE : 8**  
**Thermodynamic parameters of the ions in 10%(W/W) 2-(Ethoxy) ethanol - water mixture**

Ion	30 <sup>o</sup> $T\Delta\bar{S}_2^{0\#}$	35 <sup>o</sup> $T\Delta\bar{S}_2^{0\#}$	40 <sup>o</sup> $T\Delta\bar{S}_2^{0\#}$	$\Delta\bar{H}_2^{0\#}$
$Me_4N^+$	19.55	19.87	20.19	-12.45
$Et_4N^+$	107.16	115.94	110.70	124.19
$Pr_4N^+$	76.24	77.51	78.76	112.20
$Bu_4N^+$	113.83	115.72	117.59	153.85
$Br^-$	2.88	2.92	2.97	2.81

This tendency can be attributed to the entirely different solvation mechanism in aqueous and mixed-aqueous solutions compared to the solvation mechanism in non-aqueous solvents such as DMSO. In a series of tetra alkyl ammonium ions, ionic enthalpies increase with the increasing radius of the cation as observed in the present case (Table 8). It is interesting to note that out of all the tetra alkyl ammonium ions studied, only exhibits a negative ionic enthalpy, indicating it's similarity with the structure breaking inorganic ions, and tell that the electrostriction involved with the ion is no more negligible.

### 3.e SOLUTE - SOLVENT INTERACTION PARAMETER ( $\Delta$ )

Desnoyers et al.<sup>25</sup> stated that the sign and magnitude of  $\Delta$  can probably be used as a criterion for determining the nett structural effect of the solute. According to them a positive  $\Delta$  value would correspond to an overall structure maker and negative  $\Delta$  value would indicate structure breaker.

The solute - solvent interaction parameters ( $\Delta$ ) are calculated from B-coefficients making use of the relation  $\Delta = B^A + B^S = B - 0.0025\bar{V}_2^{0\#}$

Where the terms have their usual significance<sup>25</sup>. The needed  $\bar{V}_2^{0\#}$  values of the salts are taken from the molar volume data of our investigation<sup>13</sup>

In Table 9 the sign of the  $\Delta$  values indicate that  $Pr_4NBr$ ,  $Bu_4NBr$  are structure makers and  $Me_4NBr$  is a structure breaker. In case of tetra alkyl ammonium ions it increases with increase in the size of the cation. The order is  $Bu_4NBr > Et_4NBr > Me_4NBr$  (The exception is  $Pr_4NBr$ ). From an observation of the values it can be seen that the solute-solvent interaction parameter ( $\Delta$ ) is positive and large for structure makers, decreases along the series and become large negative for strong structure breaker. This observation is common irrespective of the nature of electrolyte i.e., whether alkali metal halide<sup>13</sup> or tetra alkyl ammonium halide.

**TABLE - 9**  
**Solute - solvent interaction parameter( $\Delta$ ) for salts**

Salt	$Me_4NBr$	$Et_4NBr$	$Pr_4NBr$	$Bu_4NBr$
	-0.245	0.074	0.269	0.176
$\Delta$ values in (lit/mole) at 30°C				

### 3.f SOLVATION NUMBERS

Solvation numbers of the ions can be calculated making use of the equation

$$\bar{V}_{\pm} = V_{ion}^0 + n_s \cdot \bar{V}_s^0 \dots\dots\dots (10)$$

Where  $V_{ion}^0$  is the free ionic volume calculated from the relation  $V_{ion}^0 = 2.32 r_0^3$  where  $r_0$  is Pauling's ionic radius in Å,  $\bar{V}_s^0$  is the volume of the solvent,  $\bar{V}_{\pm}$  is the ionic molar volume obtained from the relation  $B_{\pm} = 2.5 \bar{V}_{\pm}$ . ( $\bar{V}_s^0$  is taken equal to the volume of water assuming that there is no considerable change in the solvent volume with the addition of 10%(W/W) co-solvent). The results thus obtained are presented in Table 10. The positive solvation number of  $Et_4N^+$ ,  $Pr_4N^+$  &  $Bu_4N^+$  agrees with the general observation that the positive solvation numbers are associated with structure making properties. However the solvation number of  $Me_4N^+$  do not agree with this general rule.

**TABLE - 10**

**Free ionic volume ( $V_{ion}^0$ ). Ionic molar volumes (from B-coefficients =  $\bar{V}_{\pm}$  and solvation numbers ( $n_s$ ) of various ions in 10%(W/W) 2-(Ethoxy) ethanol - water mixture at 30°, 35° & 40° C**

Ion	$V_{ion}^0$	30°			35°			40°		
		$B_{\pm}$	$\bar{V}_{\pm}$	$n_s$	$B_{\pm}$	$\bar{V}_{\pm}$	$n_s$	$B_{\pm}$	$\bar{V}_{\pm}$	$n_s$
$Me_4N^+$	10.08	0.1081	43.24	5.01	0.1123	44.92	5.26	0.1284	51.36	6.23
$Et_4N^+$	21.95	0.3861	154.44	20.01	0.3152	126.08	15.73	0.2664	106.56	12.78
$Pr_4N^+$	37.59	0.9211	368.44	49.98	0.8908	356.32	48.15	0.82007	328.38	43.92
$Bu_4N^+$	56.62	0.9883	395.32	51.16	0.9207	368.28	47.08	0.8464	338.56	42.59
$Br^-$	18.68	-0.0576	-23.04	-6.30	-0.0532	-21.28	-6.03	0.0599	-23.96	-6.44

It is interesting to note in the present investigation, that the solvation numbers of structure making ions decrease with increasing temperature and that for structure breaking ions increase with temperature and it finds a similarity to the observation of Palepu<sup>27</sup>. Plot of  $B_{\pm}$  against ionic radius expected to be linear<sup>27</sup> also found true (Figure 1) with  $R_4N^+$  ions also. The correlation of solvation numbers with ionic B-coefficients shows that solvation numbers of positive and negative ions have different linear relationships<sup>22</sup> with  $B_{\pm}$  coefficient. In the present study also different linear relationships observed when solvation number plotted against  $B_{\pm}$  ion (Figure2) and solvation number plotted against Pauling's crystal radius (figure 3). This is supporting the idea<sup>28</sup> that structure making ions have positive ionic molar volume, solvation number and entropy change while structure breaking ions have negative values of these.

### 3.g Dimensions of the ions

On the hypothesis that ion behave like a rigid spheres with ( $r_{\pm}$  radius) moving in continuum the following relation is proposed on the basis of Jones Dole and Einstein's equation<sup>20</sup>

$$B_{\pm} = 2.5 \left( \frac{4\pi}{3} \right) \frac{R_{\pm}^3 N}{1000} \dots\dots\dots (11)$$

Where the terms of their usual significance and 2.5 is shape factor for a sphere. From the  $R_{\pm}$  values obtained it is possible to say whether the ions are solvated or not comparing with crystallographic radius (table 11). In case of structure making ions  $Et_4N^+$ ,  $Pr_4N^+$  and  $Bu_4N^+$ ,  $R_{\pm}$  calculated in much larger than crystallographic radius showing heavy solvation in the present solvent system. Though  $Me_4N^+$  is a structure breaker has  $R_{\pm}$  greater than crystallographic radius. These  $R_{\pm}$  values measured from viscosity B-coefficients are much greater than  $R_{\pm}$  values obtained from molar volume data<sup>13</sup>. This difference is due to the fact that the viscosity property takes into consideration all the solvent molecules that move with the ion as one hence it counts the solvent molecules that are in secondary solvation shell. To study the effect of temperature on solvation numbers and ionic volumes, the temperature coefficients of these two parameters are calculated and presented in Table 12. For structure making ions such as  $Et_4N^+$ ,  $Pr_4N^+$  &  $Bu_4N^+$  the



$\frac{d(n_s)}{dT}$  &  $\frac{d\bar{V}_{\pm}}{dT}$  are negative and for structure breaking ions such as  $Me_4N^+$  &  $Br^-$   $\frac{d(n_s)}{dT}$  &  $\frac{d\bar{V}_{\pm}}{dT}$  are positive.

These results further support the conclusions drawn from the temperature coefficients of the B-values.

The structure breaking ions in solutions disrupt the solvent structure by pushing solvent molecules apart in both primary and secondary solvation spheres around them. The magnitude of solvation numbers suggests that the structure breaking ability in 10%(W/W) 2-(Ethoxy) ethanol-water mixture follows the order

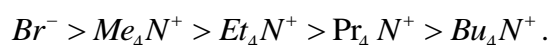


TABLE 11

$R \pm$  calculated for various ions (in Å) in 10% W/W 2-(Ethoxy) ethanol water mixture at 30°, 35° and 40°C

Ion	30°	35°	40°	Pauling's radius
$Me_4N^+$	2.58	2.61	2.73	2.16*
$Et_4N^+$	3.94	3.8	3.48	2.80*
$Pr_4N^+$	5.26	5.21	5.07	3.35*
$Bu_4N^+$	5.39	5.26	5.12	3.84*
$Br^-$	-2.09	-2.03	-2.12	1.95

\*Real dimensions of ions <sup>29</sup>

TABLE 12

Temperature coefficients of ionic volume ( $\bar{V}_{\pm}$ ) and Solvation number ( $n_s$ ) at 30° – 35° C range

Ion	$d\bar{V}_{\pm} / dT$	$d(n_s) / dT$
$Me_4N^+$	0.33	0.05
$Et_4N^+$	-5.67	-0.85
$Pr_4N^+$	-2.42	-0.36
$Bu_4N^+$	-5.41	-0.82
$Br^-$	0.35	0.05

### 3.h CONCLUSION

- From the sign of  $\frac{dB}{dT}$  values it can be concluded that  $Et_4NBr$ ,  $Pr_4NBr$  and  $Bu_4NBr$  are overall structure makers while  $Me_4NBr$  is a nett structure breaker in 10% (W/W) 2 - (Ethoxy) ethanol - water mixture.
- Depending on the sign of the enthalpy and entropy values it can be concluded that the negative entropy and enthalpies are associated with the structure breaking electrolytes while positive values are associated with the structure making electrolytes. The negative  $\Delta\bar{H}_2^{0\#}$  and  $T\Delta\bar{S}_2^{0\#}$  for  $Me_4NBr$  indicate that this electrolyte is a nett structure breaker and on the other hand the positive  $\Delta\bar{H}_2^{0\#}$  and  $T\Delta\bar{S}_2^{0\#}$  indicate the structure making ability of  $Et_4NBr$ ,  $Pr_4NBr$  and  $Bu_4NBr$ .
- Magnitude of solvation numbers suggests that the structure breaking ability of in 10%(W/W) 2-(Ethoxy) ethanol-water mixture follows the order  $Br^- > Me_4N^+ > Et_4N^+ > Pr_4N^+ > Bu_4N^+$ .

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