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Viscosity and Related Quasi Thermodynamic Properties of Alkali Metal Salts In 10%(W/W) 2-(Ethoxy) Ethanol - Water Mixture

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Abstract

Relative viscosities of NaCl, KCl, KBr, RbCl, KI in 10% (W/W) 2-(Ethoxy) ethanol - water mixture are measured at 30^o, 35^o and 40^oC. Joules-Dole equation is used to analyze the data to calculate B-coefficients. Transition state theory is applied to calculate Enthalpy activation of viscous flow ($\Delta\bar{H}_2^{0\#}$) and entropy of activation of viscous flow ($\Delta\bar{S}_2^{0\#}$). The temperature coefficients of ($\Delta\bar{H}_2^{0\#}$), ($\Delta\bar{S}_2^{0\#}$) and B-coefficients show that in the present solvent system Na^+ is a structure making ion while $K^+, Rb^+, Cl^-, Br^-, I^-$ are structure breaking ions. An attempt is made to split the enthalpy and entropy values of the electrolytes into their ionic contributions. Solute-solvent interaction parameter (Δ), solvation numbers and ionic volumes are also calculated. These values support the conclusions drawn from $\Delta\bar{H}_2^{0\#}$ and $\Delta\bar{S}_2^{0\#}$. Dimensions of the ions are calculated from the viscosity B-coefficients and are compared with Pauling's crystal radius of the ions.

Key word : Viscosity, solute – solvent interaction, electrolyte solutions, 2-(Ethoxy)-ethanol, Solvation of ions.

I. Introduction

n-(Alkoxy) ethanols known as cello solves are good industrial solvents and find a large number of applications as it dissolve oils, resins, grease, waxes, nitrocellulose, and lacquers. They are also used as additives to gasoline as a result enriching of octane and reducing pollution[1,2]. In spite of the potential applications of these solvents there are relatively a few[3,4] solute-solvent interaction studies in this class of substances and their water mixtures. 2-(Butoxy)-ethanol, and 2-(Methoxy)-ethanol are the solvents studied to some extent[5-7] and in particular no work has been reported in 2-(Ethoxy)-ethanol water mixtures where some modifications are expected (water – rich region) in the structure of water. Among various interactions that occur in solutions ion-solvent and ion-ion interactions are prominent. These are associated with the physical and chemical properties of the mixtures. Studies on thermo-chemical properties (also transport properties) namely viscosity, density, conductivity, ultrasonic velocities and adiabatic compressibility's of ionic solutions assist in characterizing structures and properties of solutions[8,9].

This investigation is intended to study the viscosity and related parameters in $10\%(W/W)\,2-(EtO)EtOH-H_2O$ mixture. (i) To probe into the effect of temperature on solvation process. (ii) To study both the effect of cation size increase and anion size increase. (iii) To compare this data with viscosity and thermodynamic parameters of our previous work related to tetra alkyl ammonium bromides[4].

II. Experimental

Materials And Methods

Sodium chloride, Potassium chloride and Potassium Iodide (Sarabhai Chemicals G.R. grade), Rubidium chloride (E. Merk analar grade) and Potassium Bromide (LOBA chemie., G.R. grade) are dried at 110°C in a hot air oven and stored in a desiccators. Salt solutions of desired concentrations are prepared each time by weight[5,7].

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 my earlier communication[10]. The refluxed solvent is then dried over anhydrous Potassium carbonate and then fractionally distilled. The middle fraction distilling between 133° -134°C is collected. 10% 2-(Ethoxy) ethanol-water mixture is prepared weight by weight.

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

Results & Discussion

The relative viscosities of alkali metal salts in $10\%(W/W)\,2-(EtO)EtOH-H_2O$ mixture are determined at 30°C, 35°C and 40°C and are presented in Table 1.

Table-1 Molarity (C), Relative viscosity (η/η_0) of Alkali metal salts in $10\%(W/W)\,2-(EtO)EtOH-H_2O$ mixture at $30^o, 35^o \& 40^o C$.

C x 10^3 g.mole litre^{-1}	η/η_o	C x 10^3 g.mole litre^{-1}	η/η_o	C x 10^3 g.mole litre^{-1}	η/η_o
30°		35°		40°	
NaCl					
30.31	1.00157	30.31	1.00256	30.31	1.00344
37.77	1.00212	38.39	1.00319	38.39	1.00422
41.39	1.00255	41.39	1.00358	41.39	1.00457
54.35	1.00394	54.35	1.00469	54.35	1.00544
61.66	1.00468	63.79	1.00542	63.79	1.00613
70.89	1.00555	70.89	1.00630	70.89	1.00714
83.92	1.00830	83.92	1.00721	83.92	1.00874
94.68	1.00837	94.68	1.00902	94.68	1.00957

104.91	1.00947	104.91	1.01001	104.91	1.01054
112.03	1.01032	112.03	1.01074	112.03	1.01113
KCl					
28.30	0.99712	28.30	0.99703	20.30	0.99699
41.23	0.99678	41.23	0.99687	41.23	0.99664
51.98	0.99632	51.98	0.99643	51.98	0.99633
61.70	0.99949	61.70	0.99876	61.70	0.99819
71.20	0.99981	71.20	0.99921	71.20	0.99886
82.20	1.00001	82.20	0.99976	82.20	0.99902
91.04	1.00012	91.04	0.99991	91.04	0.99913
100.09	1.00020	100.09	1.00012	100.09	0.99968
110.60	1.00029	110.60	1.00018	110.60	1.00010
119.60	1.00041	119.60	1.00027	119.60	1.00019
RbCl					
21.11	0.99942	21.11	1.00072	21.11	1.00198
29.59	0.99935	29.59	1.00052	29.59	1.00169
40.60	0.99926	40.60	1.00021	40.60	1.00116
61.10	0.99911	50.98	0.99988	50.98	1.00063
70.50	0.99903	61.10	0.99958	61.10	1.00014
80.02	0.99856	70.50	0.99894	70.50	1.00009
90.80	0.99835	90.80	0.99852	90.80	0.99952
100.42	0.99760	100.42	0.99800	100.42	0.99938
108.90	0.99651	108.90	0.99715	108.90	0.99859
120.40	0.99409	120.40	0.99454	120.40	0.99596
KBr					
10.79	0.99683	10.79	0.99700	10.79	0.99663
20.60	0.99512	20.60	0.99629	20.60	0.99737
30.50	0.99737	30.50	0.99806	30.50	0.99872
39.86	0.99730	39.86	0.99745	39.86	0.99742
49.75	0.99755	49.75	0.99788	49.75	0.99807
61.40	0.99727	61.40	0.99760	61.40	0.99776
70.48	0.99703	70.48	0.99734	70.48	0.99735
80.80	0.99639	80.80	0.99706	80.80	0.99717
90.50	0.99583	90.50	0.99683	90.50	0.99691
100.87	0.99549	100.87	0.99638	100.87	0.99676
109.90	0.99503	109.90	0.99614	109.90	0.99634
116.21	0.99474	116.21	0.99568	116.21	0.99620
KI					
20.90	0.99946	20.90	0.99987	20.90	1.00034
31.82	0.99877	31.82	0.99949	31.82	1.00022
40.08	0.99801	40.08	0.99910	40.08	1.00019
51.16	0.99748	51.16	0.99878	51.16	1.00009
60.30	0.99663	60.30	0.99833	60.30	1.00002
72.56	0.99580	72.56	0.99782	72.56	0.99984
80.57	0.99493	80.57	0.99729	80.57	0.99966
89.85	0.99383	89.85	0.99671	89.85	0.99959
102.27	0.99276	102.27	0.99611	102.27	0.99946

It was observed that the relative viscosities (η_r) do not exhibit any order at very low concentrations (KCl, RbCl and KBr). Hence such η_r values are discarded and the remaining η_r values are used for the purpose of analysis. Fig. 1 show relative viscosity (η / η_o) as a function of Molarity and Fig. 2 (η / η_o) as a function of temperature for the salts studied.

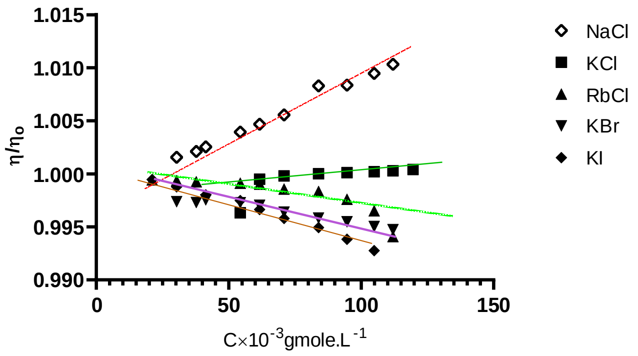

Fig.1: Variation of Relative viscosity with Molar concentration (C) of Alkali metal halides in 10%(W/W) 2-(Ethoxy) ethanol-water mixture at 30°C.

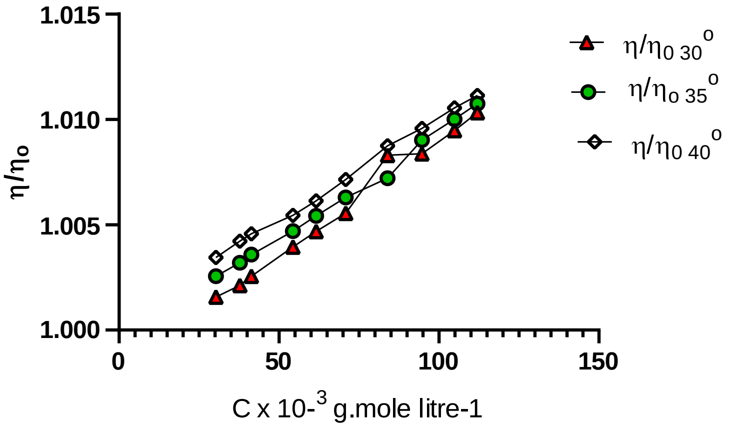

Fig: 2 Variation of Relative viscosity of NaCl with Molar concentration (C) in 10%(W/W) 2-(Ethoxy) ethanol-water mixture.

The results are analyzed on the basis of the Jones – Dole equation.

$$\eta_r = \eta / \eta_o = 1 + A\sqrt{C} + BC \qquad (1)$$

As the measurements of viscosities are conducted with solutions of low molar concentrations (less than 0.12) the additional DC^2 term is not added. By fitting the experimental data into the Jones- Dole equation (adopting the method of least squares) A and B coefficients are obtained. A-coefficients are calculated theoretically by using equation 2 proposed by Falkenhagen and Vernon[11]

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

Where $\lambda_o, \eta_0 \,\&\in$ have their usual significance[11].

Ionic conductance and the dielectric constants of the $10\%(W/W)\,2-(EtO)EtOH-H_2O$ mixture are taken from our conductance measurements[7]. The calculated theoretical A values are presented in Table 2. The A values experimentally determined are negative for KCl and KBr at all temperatures studied. A is not expected to have a negative value theoretically and it cannot be interpreted on the basis of Falkenhagen theory, in most of the cases involving mixed solvents[12,13].

Table 2. Theoretical (A_η) coefficients of salts in $10\%(W/W)\,2-(EtO)EtOH-H_2O$ at 30°, 35°&40°C.

Salt	$(Ax10^3)30^oC$	$(Ax10^3)35^oC$	$(Ax10^3)40^oC$
NaCl	5.56	5.52	5.37
KCl	4.86	4.61	4.79
RbCl	4.67	5.06	4.96
KBr	4.72	4.97	4.96
KI	4.61	5.04	5.24

B-Coefficients :

According to Desnoyers and Perron[14], the measurement of viscosity over a narrow range of concentration may lead to some uncertainties in the calculation of B-coefficients, also observed in the present investigation.

Table 3 shows that except for NaCl, for alkali metal salts B-values increase with increase in temperature. The B-values of all the alkali metal salts in 10%(W/W) 2-(Ethoxy) ethanol-water mixture are greater than in pure water (except for RbCl). This is the same effect found for structure breaking ions in pure water and is attributed to the reduction in the solvent structure at higher temperatures[15]. Thus the effect of the addition of 2-(Ethoxy) - ethanol to water is probably reducing the structuredness of water in water rich region. The observation that when 2-(Ethoxy) ethanol and water are mixed large amounts of heat are generated strengthen this inference. This exothermic mixing is an evidence for the existence of strong interactions which some extent may involve in the breaking the polymeric structure of water

Table 3. Viscosity Coefficients of Electrolytes in $10\%(W/W)\,2-(EtO)EtOH-H_2O$ mixture

Salt	30°C		35°C		40°C	
	A $(dm^3\, mole^{-1})^{-1/2}$	B $(dm^3\, mole^{-1})$	A $(dm^3\, mole^{-1})^{-1/2}$	B $(dm^3\, mole^{-1})$	A $(dm^3\, mole^{-1})^{-1/2}$	B $(dm^3\, mole^{-1})$
NaCl	-0.0173	0.1466	-0.0050	0.1091	0.0041	0.0866
KCl	-0.0009	0.0303	-0.0183	0.0576	-0.0263	0.0791
RbCl	0.0291	-0.1223	0.0235	-0.1014	0.0242	-0.0912
KBr	-0.0007	-0.0425	-0.0040	-0.0244	-0.0041	-0.0204
KI	0.0120	-0.1063	-0.0086	-0.0638	0.0048	-0.0200

B-values are positive for NaCl (similar to Et_4NBr, $\Pr_4 NBr \,\&\, Bu_4NBr$ salts in the same solvent[4]) stipulate the alignment of solvent molecules with the ions, indisputably enhances the structure of the solvent molecules in its immediate vicinity. Enhancement of the structure of the solvent results in a higher B-value while a decrease in the structure of the solvent due to the solute, results in a lower B-value. In the case of inorganic (RbCl, KBr and KI) 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 on the ion. (This author also reported that $Et_4NBr, \Pr_4 NBr \,\&\, Bu_4NBr$ [4] are structure makers in the same solvent system, as B-values are positive. Since for large organic solutes such as tetraalkylammonium salts, the contribution of the hydrodynamic effect is sufficiently high.)

The negative B-values observed for KBr, KI, RbCl show that these salts act as net structure breakers. Table 3 shows that the B-coefficients decrease along with the series of alkali metal ions as NaCl > KCl > RbCl and halide ions as KCl > KBr > KI. This confer the observations of Jones and Dole “B-coefficients decrease with increasing radius along with the alkali metal or halide series, in line with the expected decrease in the strength of the ion-solvent interactions”. It is arguable for water solutions that along the series the decrease in B is not only due to the decrease in structure making (with increasing ionic radius) but also due to an increase in structure breaking with a decrease in the surface ionic field. The Viscosity B-coefficients as a function of temperature are plotted in Fig 3.

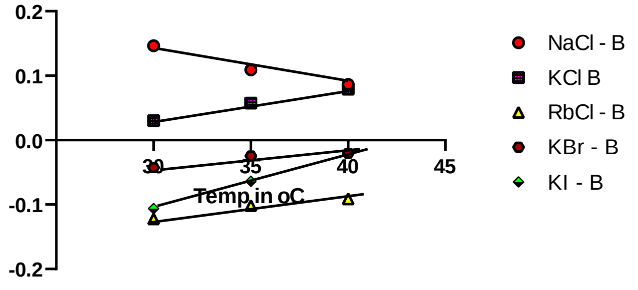

Fig .3 B-coefficient as a function of temperature

Positive B-value observed for KCl (also Me_4NBr [4]) is contradicting the structure breaking tendency of the ion in aqueous solutions supporting an emphasis that the sign and magnitude of $\frac{dB}{dT}$ is a better index of solute-solvent interactions rather than the sign of B, 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 are presented in Table 4.

Table 4. $\frac{dB}{dT}$ coefficients in $10\%(W/W)2-(EtO)EtOH-H_2O$ mixture

Temp./Salt	30°–35°C	35°–40°C
NaCl	-0.007	-0.0045
KCl	0.005	0.0040
RbCl	0.004	0.0020
KBr	0.003	0.0010
KI	0.008	0.0090

From the negative sign of $\frac{dB}{dT}$ it can be concluded that NaCl (also $Et_4NBr, \mathrm{Pr}_4 NBr$ & Bu_4NBr) is an overall structure maker. While positive $\frac{dB}{dT}$ of KCl, KBr, RbCl, KI (also Me_4NBr) are net structure breakers in the $10\%(W/W)2-(EtO)EtOH-H_2O$ mixture.

Ionic – B-coefficients:

B-coefficients of these electrolytes are divided into ionic contributions. No general method of separations of B-coefficients is available to apply both for the aqueous and aqueous-organic mixed solvent system. It is assumed that the methods applicable for pure water will also apply to the water-rich binary systems, the methods suggested by (i) Kaminsky[15] and (ii) Desnoyers *et al.*,[14] are used in the present study. The ionic B-coefficients at 30°C obtained by the two methods are presented in Table 5. for a purpose of comparison.

Table 5. Ionic B-coefficients

Ion/method	Na^+	K^+	Rb^+	Cl^-	Br^-	I^-
(i)Kaminsky	0.1315	0.0151	-0.1375	0.0151	-0.0576	-0.1214
(ii)Desnoyers	0.0778	-0.0385	-0.1911	0.0688	-0.0040	-0.0680

From our earlier study it is felt that the B_{ion} values obtained by method (ii) may not be reliable[4]. Therefore, for further calculation and discussion the B_{ion} values obtained by the method suggested by Kaminsky are used. For a hydrated ion a positive B coefficient estimates the effective radius of Frank's[16] region **A** where water is highly ordered about the ion. The existence of a finite but small B zone can be still expected about the hydrated ion, however small compared to **A** region. On the other hand negative B coefficient indicate that the region **B** intrude on **A** zone to the extent that for the larger ions effectively (because of weak electric field about such ions) no **A** region exists [17]. The ionic B-coefficients at $30^o, 35^o \& 40^o$ along with the $\frac{dB_{ion}}{dT}$ values for the range 30°-35° C are presented in **Table 6**.

Table 6. Ionic B-coefficients and $\frac{dB_\pm}{dT}$ values in $10\%(W/W)\,2-(EtO)EtOH-H_2O$ mixture.

Ion	$B_\pm$ 30°	$B_\pm$ 35°	$B_\pm$ 40°	$\frac{dB_\pm}{dT}(30^o-35^o)C$
Na^+	0.1315	0.0803	0.0470	-0.0102
K^+	0.0151	0.0288	0.0395	0.0027
Rb^+	-0.1375	-0.1302	-0.1307	0.0014
Cl^-	0.0151	0.0288	0.0395	0.0027
Br^-	-0.0576	-0.0532	-0.0599	0.0009
I^-	-0.1214	-0.0926	-0.0595	0.0058

On the basis of sign of $\frac{dB_{ion}}{dT}$ conclusions drawn are Na^+ (also $Et_4N^+, \Pr N_4^+ \& Bu_4N^+$) are structure makers while K^+, Rb^+, Cl^-, Br^- *and* I^- are structure breakers in the present solvent system.. These observations support the discussions of Rastogi[18] as per which highly hydrated ions like $Li^+, Na^+, Mg^{2+}, Ce^{3+}$ etc., in aqueous solutions can polarize water molecules in the region beyond the first solvation layer and so they act as structure promoters while the larger ions like $K^+, Rb^+, Cs^+, Cl^-, Br^- \& I^-$ with low surface charge are net structure breakers.

However considering both B-coefficient and $\frac{dB_{ion}}{dT}$ values and applying the classification of Nightingale[17]

(i) Na^+ (also $Et_4N^+, \Pr N_4^+ \& Bu_4N^+$) is **typical structure making** ions in the present solvent system since B > 0 (positive) and $\frac{dB_{ion}}{dT}$ < 0 (negative).

(ii) Rb^+, Br^- *and* I^- are **typical structure breaking** ions since B < 0 (negative) and $\frac{dB_{ion}}{dT}$ > 0 (positive)

(iii) K^+ *and* Cl^- are **anomalous structure makers** since B > 0 (positive) and $\frac{dB_{ion}}{dT}$ >0 (positive).

(While Me_4N^+ is structure breaker) in the $10\%(W/W)\,2-(EtO)EtOH-H_2O$ mixture.

Application of Transition state theory :

In a stationary or ground state solvent, the process of dissolving a solute at high dilutions is accompanied by two effects (i) Introduced ion can bring structural changes in the solvent; *i.e.*, changes the solvent-solvent interactions (ii) In this re-structured condition ion - solvent interaction. This naturally leads to enthalpy change ($\Delta\bar{H}_2^{0\#}$), entropy change ($\Delta\bar{S}_2^{0\#}$) and free energy change ($\Delta\mu_2^{0\#}$) .

The relative viscosities of NaCl, KCl, RbCl, KBr, KI are analyzed by applying transition state theory[19] to calculate the free energy of activation of viscous flow

$$B = \frac{\bar{V}_1^0 - \bar{V}_2^0}{1000} + \frac{\bar{V}_1^0}{1000}\left(\frac{\Delta\mu_2^{0\#} - \Delta\mu_1^{0\#}}{RT}\right) \qquad (3)$$

$$\Delta\mu_1^{0\#} = RT\ln\frac{\eta_0\bar{V}_1^0}{hN} \qquad (4)$$

Where all the terms have their usual meaning[4].

These values at different temperatures are used to calculate quasi thermodynamic parameters activation enthalpy ($\Delta\bar{H}_2^{0\#}$) and activation entropy ($\Delta\bar{S}_2^{0\#}$) using the equations 5,6 and presented in **Table 7**.

$$\frac{d(\Delta\mu_2^{0\#})}{dT} = -\Delta\bar{S}_2^{0\#} \qquad (5)$$

$$\Delta\bar{H}_2^{0\#} = \Delta\mu_2^{0\#} + T\Delta\bar{S}_2^{0\#} \qquad (6)$$

Like B-coefficient $\Delta\mu_2^{0\#}$ in a series decreases with an increase in the size of cation and mass of the cation. For structure makers $\Delta\mu_2^{0\#} > \Delta\mu_1^{0\#}$ while for structure breakers $\Delta\mu_2^{0\#} < \Delta\mu_1^{0\#}$

Table 7. Thermodynamic properties of activation energy of the viscous flow of alkali metal salts in $10\%(W/W)\,2-(EtO)EtOH-H_2O$ mixture at $30^0, 35^o$ & 40^oC

Electrolyte	30°C			35°C			40°C		
	$\Delta\mu_2^{0\#}$	$T\Delta\bar{S}_2^{0\#}$	$\Delta\bar{H}_2^{0\#}$	$\Delta\mu_2^{0\#}$	$T\Delta\bar{S}_2^{0\#}$	$\Delta\bar{H}_2^{0\#}$	$\Delta\mu_2^{0\#}$	$T\Delta\bar{S}_2^{0\#}$	$\Delta\bar{H}_2^{0\#}$
NaCl	6.63	53.35	59.98	5.45	54.23	59.68	4.87	55.11	59.98
KCl	3.43	-46.38	-42.95	4.28	-47.15	-42.87	4.96	-47.91	-42.95
RbCl	-1.18	-29.40	-30.58	-0.61	-29.89	-30.50	-0.21	-30.37	-30.58
KBr	1.65	-20.31	-18.66	2.19	-20.65	-18.46	2.32	-20.98	-18.66
KI	0.18	-76.09	-75.91	1.34	-77.34	-76.00	2.69	-78.60	-75.91

For structure makers such as NaCl [also $Et_4NBr, \Pr_4 NBr \& Bu_4NBr] \Delta\mu_1^{0\#} > \Delta\mu_1^{0\#}$ and for structure breakers such as RbCl, KBr and KI $\Delta\mu_2^{0\#} < \Delta\mu_1^{0\#}$ following Feakins[19] observations. However KCl [also Me_4NBr] though structure breaker in the present solvent system disobeys this general principle. The unacceptability of the general rule by some salts lead to consider that the magnitude and sign of $T\Delta\bar{S}_2^{0\#}$ (since it involves $\frac{d\left(\Delta\mu_2^{0\#}\right)}{dT}$ term) is a better criterion to classify the electrolytes as structure makers or structure breakers. The negative entropy and enthalpies are associated with the structure breaking while positive values are associated with the structure making electrolytes. The negative $\Delta\bar{H}_2^{0\#} \& T\Delta\bar{S}_2^{0\#}$ for KCl, RbCl, KBr, KI [also Me_4NBr] confirm their structure breaking nature while positive the structure making ability of NaCl, [also $Et_4NBr, \Pr_4 NBr$ and Bu_4NBr]

If the B-coefficients and the quantity of $\Delta\mu_2^{0\#}$ of NaCl and KCl in the present solvent system are compared with the values reported in pure water at 35^o, it is clear that the B and $\Delta\mu_2^{0\#}$ values are greater than in pure water (Table 8).

This increase in B and $\Delta\mu_2^{0\#}$ values can be reasoned as: The addition of 2-(Ethoxy) ethanol to water somewhat destroys the three-dimensional structure of water, hence the solvent offers little resistance to the co-ordination of the ions and solute-solvent bonds are largely broken to form a transition state. So that $\Delta\mu_2^{0\#}$ is large and is also the result of unequal $\Delta\bar{H}_2^{0\#} \& T\Delta\bar{S}_2^{0\#}$. It can be observed from **Table 7**, that $\Delta\bar{H}_2^{0\#} > T\Delta\bar{S}_2^{0\#}$ in the case of NaCl, KCl, KBr and KI. A similar observation was made by Feakins et al., for alkali metal halides in higher alcohol percentages of propanol – water mixtures where the three-dimensional structure of water is broken[19,20].

According to Eyring's theory of viscous flow "the movement of the lamina of liquid under the shearing force takes place by a sequence of events in which individual molecules move from one equilibrium position to another. The movement of the lamina is affected by the presence of ions in two ways. Ions move and also affect the movement of solvent molecules". So $\Delta\mu_2^{0\#}, \Delta\bar{H}_2^{0\#} \& T\Delta\bar{S}_2^{0\#}$ like quasi-thermodynamic parameters will contain the contributions arising from both these effects. (i) Formation of a cavity near an ion in the direction of laminar flow (involves breaking of ion – solvent bonds). (ii) Movement of a solvent molecule from a position next to an ion (also involves ion-solvent bond breaking). These ion-solvent bond-breaking effects make an important contribution to $\Delta\mu_2^{0\#}$. In a series of alkali metal ions it should decrease from $Li^+ to\, Cs^+$ [21]. The $\Delta\mu_2^{0\#}$ values order of the present investigation NaCl > KCl > RbCl and KCl > KBr > KI is also consistent with this. The negative and very low $\Delta\mu_2^{0\#}$ values for RbCl and KI in the present solvent system can be explained only in terms of increased ion-solvent bond making in the transition state.

A comparison of the $\Delta\mu_2^{0\#}$ values in the present solvent system and in pure water designates that $\Delta\mu_2^{0\#}$ values in $10\%(W/W)\, 2-(EtO)EtOH - H_2O$ mixture is less than in pure water (Table 8) revealing a fact that though with the addition of co-solvent the structure of water is broken, the breakdown of the water structure is not complete and hence still some order exists in the solvent structure.

Table 8. A comparison of the $\Delta\bar{H}_2^{0\#}$ and $T\Delta\bar{S}_2^{0\#}$ of NaCl , RbCl and KCl in water

	$10\%(W/W)\,2-(EtO)EtOH-H_2O$ mixture				Pure water [20,21]			
	B	$\Delta\mu_2^{0\#}$	$\Delta\bar{H}_2^{0\#}$	$T\Delta\bar{S}_2^{0\#}$	B	$\Delta\mu_2^{0\#}$	$\Delta\bar{H}_2^{0\#}$	$T\Delta\bar{S}_2^{0\#}$
NaCl	0.1091	5.45	54.23	59.68	0.089	5.11	-7	-12
RbCl	-0.0244	-0.61	-29.89	-30.50	-0.012	1.40	-22	-23
KCl	0.0576	4.28	-47.15	-42.87	0.010	2.79	-21	-23

Effect of ion on the solvent structure

An attempt to separate $\Delta\bar{H}_2^{0\#}\,\&\,T\Delta\bar{S}_2^{0\#}$ into ionic contribution is made based on the method adopted by Feakins (the equality of effects for K^+ *and* Cl^- ions,[19]) and are presented in Table 9

Table 9. Thermodynamic parameters of ions

Ion	30°C	35°C	40°C	$\Delta\bar{H}_2^{0\#}$
	$T\Delta\bar{S}_2^{0\#}$	$T\Delta\bar{S}_2^{0\#}$	$T\Delta\bar{S}_2^{0\#}$	
Na^+	76.54	77.80	79.06	81.45
K^+	-23.19	-23.57	-23.95	-21.47
Rb^+	-6.21	-6.31	-6.41	-9.10
Cl^-	-23.19	-23.57	-23.95	-27.47
Br^-	2.88	2.92	2.97	2.81
I^-	-52.90	-53.76	-54.64	-54.43

Solvent-solvent bonds are weaker in the transition state, compared to the ground-state. So in the transition state the solvent offers little resistance to the coordination of the solvent molecules by the ion. Hence the number of solvent molecules coordinated to the ion will tend to increase, resulted a negative contribution to $\Delta\mu_2^{0\#}$. This is in contradiction to the ion-solvent bond-breaking effect (described earlier) in which the total coordination number of the ion falls.

Based on the above discussion it can be perceived that an ion can increase the fluidity of the solution not by breaking the solvent-solvent bonds but by making ion-solvent bonds in the transition state. Ion-solvent bond making effect will be particularly important for a weakly coordinating ion such as Cs^+ and in a highly structured solvent. The changes in solvent-solvent bonding and solute-solvent bonding associated with the formation of the transition state decide $\Delta\bar{H}_2^{0\#}$. In the present investigation $\Delta\bar{H}_2^{0\#}$ values are negative for the structure breaking ions following the results reported by Feakins[19-21] for aqueous and mixed – aqueous solutions of alkali metal salts.

$\Delta\bar{H}_2^{0\#}$ and $T\Delta\bar{S}_2^{0\#}$ of NaCl in water when compared to the values of the present solvent system (Table 8) show that in the ground-state Na^+ is less completely coordinated making the ion-solvent bond formation more significant which results negative values of $\Delta\bar{H}_2^{0\#}$ & $T\Delta\bar{S}_2^{0\#}$. But in $10\%(W/W)$ $2-(EtO)EtOH-H_2O$ mixture the tetrahedral water structure is broken with the addition of co-solvent (of course breaking may not be complete) and hence Na^+ is completely coordinated leading to large positive $\Delta\bar{H}_2^{0\#}$ & $T\Delta\bar{S}_2^{0\#}$ values. Low values of $\Delta\mu_2^{0\#}$ intimate that in the ground state Rb^+ is less coordinated and in a more broken up transition state solvent the coordination increases. From table 9 it is clear that both $\Delta\bar{H}_2^{0\#}$ & $T\Delta\bar{S}_2^{0\#}$ are positive for structure making ions such as Na^+, [also $Et_4N^+, \Pr_4 N^+$ & Bu_4N^+]. Because the formation of the transition state is associated with bond breaking and a decrease in order and suggesting the slip plane is anywhere in the region of Centro symmetric order[19,20]. On the other hand, the negative $\Delta\bar{H}_2^{0\#}$ & $T\Delta\bar{S}_2^{0\#}$ values for structure breaking ions such as K^+, Rb^+, Cl^- & I^- the transition state is affiliated with bond making resulting an increase in order and the slip-plane is in the region of disorder.

It is interesting to note here that the ionic enthalpies and entropies of R_4N^+ ions[4] are much greater than those of alkali metal ions where ion-solvent interactions are strong. This is exactly opposite to that observed by Das *et al*.,[22] in DMSO as a solvent. This tendency can be attributed to the entirely different solvation mechanism in aqueous and mixed aqueous solutions compared to DMSO a non – aqueous solvent.

Solute – Solvent interaction Parameter (Δ)

The B-coefficients of NaCl, KCl, RbCl, KBr, KI are also used to calculate the solute-solvent interaction parameter (Δ). The procedure to calculate Δ values is as adopted earlier[4]. Table 9.

Table 9. Δ values of alkali metal halides in (lit/mole) at 30°C

NaCl	KCl	RbCl	KBr	KI
0.123	-0.025	-0.187	-0.137	-0.241

To determine the net structural effect of a solute the sign and magnitude of Δ can be adopted as a criterion[14]. A positive Δ value would probably refer an overall structure maker, while a negative Δ value a structure breaker. The required $\bar{V}_2^0$ values of the salts are taken from our molar volume data[10]. Based on the sign of Δ values NaCl (also $\Pr_4 NBr, Bu_4NBr$) is a structure maker and KCl, RbCl, KI (and Me_4NBr) are structure breakers, supporting the earlier conclusions drawn from the sign of $\frac{dB}{dT}$ of the corresponding salts. Table 9 also suggests that the values just like B-coefficient decrease along with the series of alkali metal halides. NaCl > KCl > RbCl; KCl > KBr > KI.

Solvation Numbers

Solvation numbers of ions are calculated using the relation $\bar{V}_{\pm} = V_{ion}^0 + n_S\bar{V}_S^0$

The procedure adopted is as described earlier[10] and the results are presented in Table 10.

In general it is accepted that a positive solvation number is correlated with structure making property while a negative a solvation numbers with structure breaking property. It can be noticed from Table 10 that positive solvation number of Na^+ [and $Et_4N^+, \Pr_4 N^+, Bu_4N^+$ also] are different in sign from the solvation numbers of Rb^+, Cl^-, Br^- & I^-.

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 $10\%(W/W)\,2-(EtO)EtOH-H_2O$ mixture at 30°, 35° and 40°C

Ion	V_{ion}^{0}	30°C			35°C			40°C		
		$B_{\pm}$	$\bar{V}_{\pm}$	n_S	$B_{\pm}$	$\bar{V}_{\pm}$	n_S	$B_{\pm}$	$\bar{V}_{\pm}$	n_S
Na^+	2.16	0.1315	52.60	7.62	0.0803	32.12	4.52	0.0470	18.80	2.51
K^+	5.93	0.0151	6.40	0.07	0.0288	11.52	0.84	0.0395	15.80	1.49
Rb^+	8.17	-0.1374	-54.96	-9.53	-0.1302	-52.08	-9.10	-0.1307	-52.28	-9.13
Cl^-	14.94	0.0151	6.40	-1.29	0.0288	11.52	-0.51	0.0395	15.80	-0.12
Br^-	18.68	-0.0576	-23.04	-6.30	-0.0532	-21.28	-6.03	0.0599	-23.96	-6.44
I^-	25.39	-0.1214	-48.56	-11.17	-0.0926	-37.04	-9.43	0.0595	-23.76	-7.42

However the solvation number of K^+ do not agree with this general rule. Krestov[23] assumed that solvation numbers of alkali metal ions when plotted against ionic radius will fall on one straight line. In ionic aqueous solutions, the change in entropy of water is also correlated with ionic radii and found a linear relationship for alkali metal and halide ions. Palepu[24] noticed the same when $B_{\pm}$ is plotted against ionic radii where cations and anions have different linear relationships with their $B_{\pm}$ coefficients. In the present investigation Fig. 4 show such a linear relation between $B_{\pm}$ and ionic radii of alkali metal and halide ions. Figures 4 and 5 show that in the present study also, different straight lines are obtained for cations and anions (i) when solvation numbers are plotted against corresponding $B_{\pm}$ ion values and (ii) when solvation numbers are plotted against Pauling's crystal radii.

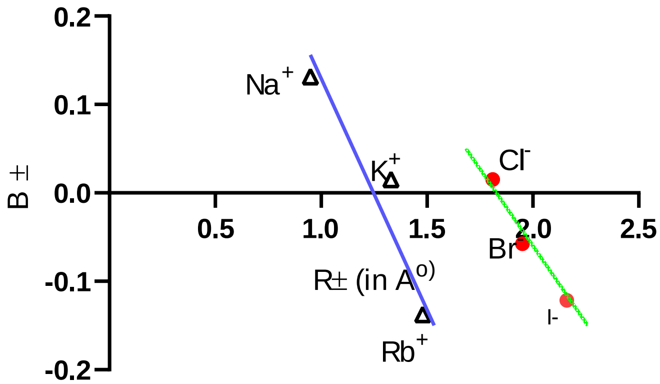

Fig 4. Plots of Ionic B Coefficient at 30 °C Vs Paulings Radius(in A°) for Alkali metal and halide ions in 2-ethoxy ethanol water mixture

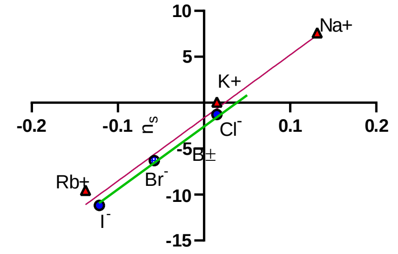

Fig 5. Plots of Solvation number(n_S) Vs Ionic B Coefficient ($B_{\pm}$) at 30^o C

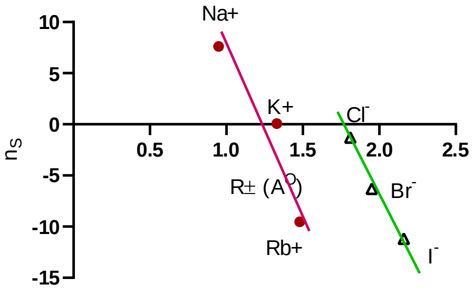

Fig 6. Plots of Solvation Number (n_S) Vs Paulings Radius(in A^o)
for Alkali metal and halide ions in 2-ethoxy ethanol water mixture at 30^o C

This supports the idea[11] that ionic molar volume, solvation number and entropy change are positive for structure making ions and negative for structure breaking ions[24,25]

In our study with a positive solvation number Na^+ is an electrostrictive structure making ion and with negative solvation numbers Rb^+, Cl^-, Br^- & I^- are structure breaking. An exception is the case of K^+ due to its very low solvation number (Me_4N^+ also [10]). In the present investigation the solvation numbers of structure making ions decrease with increasing temperature and for structure making ions increase with temperature, identical to the observations of Palepu[24]. The temperature coefficients of solvation numbers and ionic volumes are calculated to study the temperature dependency and presented in **Table 11**.

Table 11. Temperature coefficients of ionic volume $\frac{d\bar{V}_{\pm}}{dT}$ and solvation number (n_s) at $30^o - 35^oC$ range

Ion	$\frac{d\bar{V}_{\pm}}{dT}$	$\frac{d(n_S)}{dT}$
Na^+	-4.09	-0.62
K^+	1.02	0.15
Rb^+	0.57	0.08
Cl^-	1.02	0.15
Br^-	0.35	0.05
I^-	2.30	0.35

For structure making ions such as Na^+, the $\frac{d(n_S)}{dT}$ and $\frac{d\bar{V}_\pm}{dT}$ are negative and for structure breaking ions such as $K^+, Rb^+, Cl^-, Br^- \& I^-$. $\frac{d(n_S)}{dT} \& \frac{d\bar{V}_\pm}{dT}$ are positive, further supporting the inferences drawn from the temperature coefficient of the B-values. The structure breaking ions in solutions interrupt 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 $10\%(W/W)\,2-(EtO)EtOH-H_2O$ mixture follows the order.

(* values from reference 10)

$$I^- > Rb^+ > Br^- > Cl^- > K^+ > M^*e_4N^+ > Na^+$$
$$> Et^*{}_4N^+ > \Pr^*{}_4N^+ > Bu^*{}_4N^+$$

Dimensions of Ions :

As the ion behaves like a rigid sphere (with $R_\pm$ radius) moving in a continuum equation 9 is proposed based on Jones – Dole and Einstein's equations[26].

$$B_\pm = 2.5\left(\frac{4\pi}{3}\right)\frac{R_\pm^3 N}{1000} \qquad 9$$

Where N is the Avogadro's number, 2.5 is the shape factor for a sphere. By comparing $R_\pm$ values obtained with the crystallographic radius of the corresponding ions , it is possible to tell whether the ions are solvated or not.

The $R_\pm$ values calculated are much larger than the Pauling's crystallographic radius (**Table 12)** for structure making ions such as Na^+ [$Et_4N^+, \Pr_4N^+ \& Bu_4N^+$ also] because these ions are solvated in $10\%(W/W)\,2-(EtO)EtOH-H_2O$ mixture. The $R_\pm$ values for $Rb^+, Cl^-, Br^- \& I^-$ are much less (and even negative) than the crystallographic radius for structure breaking ions. In the case of K^+ (also Me_4N^+) though structure maker, the $R_\pm$ values are greater than the crystallographic radius. Moreover $R_\pm$ values obtained from viscosity B-coefficients are much greater than the $R_\pm$ values obtained from molar volume data[20]. The principal reason is that, the viscosity property takes into consideration all the solvent molecules that move with the ion as one entity. Hence it takes into account the solvent molecules of the secondary solvation shell also.

Table 12. $R_\pm$ calculated for ions (in A^0) in $10\%(W/W)\,2-(EtO)EtOH-H_2O$ mixture at $30^o, 35^o \& 40^o C$

	30^0	35^0	40^0	Pauling's radius
Na^+	2.75	2.33	1.95	0.95
K^+	1.34	1.66	1.84	1.33
Rb^+	-2.79	-2.74	-2.74	1.48
Cl^-	1.33	1.66	1.84	1.81
Br^-	-2.09	-2.03	-2.12	1.95
I^-	-2.68	-2.45	-2.11	2.16

Conclusions

i) The addition of 2-(Ethoxy) ethanol to water somewhat destroys the three-dimensional structure of water, hence the solvent offers little resistance to the co-ordination of the ions and solute-solvent bonds are largely broken to form a transition state

ii) From the B values and sign of the $\frac{dB}{dT}$ values it can be concluded that NaCl is an overall structure maker while KCl, KBr, RbCl, KI are net structure breakers in the 10% (W/W) 2-(Ethoxy) ethanol-water mixture.

(iii) On comparison of Δ values of alkali metal salts with R_4NBr salts in the same solvent system it is noticed that solute-solvent interaction parameter (Δ) is positive and large for structure makers, decrease along the series become large negative for strong structure breakers. This observation is true irrespective of the nature of electrolyte whether alkali metals salt or tetra alkyl ammonium salt

iv) The overall structure breaking ability of ions in $10\%(W/W)\,2-(EtO)EtOH-H_2O$ mixture follows the order.

$$I^- > Rb^+ > Br^- > Cl^- > K^+ > Me_4N^+ > Na^+ >$$
$$Et_4N^+ > \Pr_4N^+ > Bu_4N^+$$

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List of symbols and abbreviations used.

C: Molarity

η / η_0 :Relative viscosity

A and B: Coefficients of Jones- Dole viscosity equation

$\frac{dB}{dT}$: Temperature coefficient of Jones-Dole constant B

$\Delta \bar{H}_2^{0\#}$: Enthalpy activation of viscous flow

$\Delta \bar{S}_2^{0\#}$:Entropy of activation of viscous flow

$(\bar{V}_{\pm})$:Ionic volmue

V_{ion}^{0} : Free ionic volume,

$\bar{V}_{\pm}$: Ionic molar volumes

n_S : Solvation numbers

$R_{\pm}$: Ionic radius in solution

(Δ) : Solute – Solvent interaction Parameter

$\Delta \mu^{0\#}$: Free energy change

DMSO: Dimethylsulphoxide