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**JOURNAL OF ULTRA CHEMISTRY**

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website:- [www.journalofchemistry.org](http://www.journalofchemistry.org)**Conductance Studies of Alkali Metal Halides in 10%(W/W)  
2-(Ethoxy) Ethanol-Water Mixture**

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**Abstract**

Conductance behavior of Sodium, Potassium and Rubidium chlorides and Potassium bromide and iodide in 10% (W/W) 2-(ethoxy) ethanol – water mixture has been studied at 30°, 35° and 40°C. The equivalent conductance data have been analysed by making use of Fuoss-Kraus, Shedlovsky and Fuoss(1980) conductance equations to evaluate  $\Lambda_0$  and  $K_A$ . There is a reasonable agreement between  $\Lambda_0$  and  $K_A$  values obtained by Fuoss-Kraus and Shedlovsky extrapolation techniques. But the values obtained by Fuoss (1980) equation are greater. An attempt is made to split  $\Lambda_0$  values of different electrolytes into ionic contribution. Different theories of ion-pair formation have been applied in order to evaluate the distance of closest approach. It is observed that all the theories exhibit their inability to predict the exact ion-association process. Walden products  $(\lambda_0^\pm \eta_0)$  are calculated to understand the solvation behavior.

**Key words:** Electrical conductance, liquid mixtures, solute – solvent interactions, alkali metal salts, 2-(Ethoxy) ethanol Walden product, Fuoss equation.

**I. Introduction**

The study of solute-solvent interactions in n-(Alkoxy) Alkanols and its aqueous mixtures is not only important because of their wide use as industrial solvent but also from the more theoretical point of

investigating the effect of simultaneous presence of the etheric and hydroxyl group on the interaction of such molecule<sup>1</sup>. A survey of literature indicated that 2-(Butoxy) ethanol<sup>2,3</sup> is the only solvent widely studied among the n-(Alkoxy) Alkanols and 2- (Methoxy) ethanol to some extent<sup>4</sup>. 2- (Ethoxy) ethanol is

amphiprotic, dipolar solvent, behaves unique due to “Quasi-aprotic” character. It is found that no work is reported on solute-solvent interactions in 2- (Ethoxy) ethanol-water mixture and hence is adopted as a solvent in the present investigation to study the behaviour of various electrolytes.

## II. Experimental

2-(Ethoxy) ethanol (E.merk sample) is first refluxed with TinII chloride as per the described earlier<sup>5</sup>. The refluxed solvent is then purified by drying over anhydrous potassium carbonate and then fractionally distilled. The middle fraction distilling between 133° – 134° C is collected.

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 desiccator. 10% 2-(Ethoxy) ethanol-water mixture is

prepared weight by weight. Salt solutions of desired concentrations are prepared each time by weight.

The instrumental details of the conductance bridge is as described earlier<sup>6</sup>.

All the measurements are made in a thermostat maintained at 30°, 35° and 40° with an accuracy of  $\pm 0.01^\circ\text{C}$ .

## III. Results and Discussion

The equivalent conductances of solutions of various electrolytes in 10%(W/W) 2-(ethoxy) ethanol-water mixture are determined at 30°, 35° and 40° C and are presented in Table 1.

The conductance data of these salts is analysed by making use of the Fuoss(1980) conductance equation<sup>7</sup>. The calculations were performed using IBM 360 computer. For applying the programme, the ion – size parameter R is replaced by ‘q’ where ‘q’ is the Bjerrum critical distance given by

$$q = \frac{e^2}{DkT}$$

Table 1

Equivalent conductances of NaCl, KCl, RbCl, KBr & KI in 10%(W/W) 2(OEt) EtOH – water mixture			
$C \times 10^4$	30°	35°	40°
NaCl			
326.00	105.89	116.59	129.05
378.00	101.22	111.95	123.94
543.00	95.35	111.06	120.41
638.00	96.32	107.77	119.69
709.00	99.23	106.83	118.69
839.00	90.36	106.36	118.69
947.00	93.98	103.20	108.84
1049.00	92.92	93.17	100.77
Initial value of $\wedge_0$	117.862	138.597	157.24
KCl			
283.00	116.03	127.23	140.08
412.00	112.84	123.52	136.98
506.00	109.25	119.20	133.46
601.00	110.94	120.67	132.94
694.00	108.04	118.77	133.19

879.00	109.33	115.59	117.26
975.00	100.91	105.22	114.26
1077.00	95.03	107.34	113.93
Initial value of $\wedge_0$ 135.07 153.33 174.27			
RbCl			
211.00	121.57	133.25	147.35
296.00	119.23	127.69	142.13
406.00	114.59	123.30	137.23
510.00	114.68	123.07	134.73
605.00	111.66	121.16	133.62
705.00	108.34	-	132.91
800.00	104.44	119.33	125.38
908.00	-	110.26	119.49
1004.00	100.44	-	-
Initial value of $\wedge_0$ 140.40 149.31 169.92			
KBr			
108.00	127.21	139.43	153.93
206.00	120.45	131.09	145.03
305.00	113.75	124.61	137.93
398.60	110.44	121.15	132.60
497.50	107.71	121.37	131.54
614.00	109.31	119.38	130.63
704.80	105.61	118.86	129.99
808.00	104.69	115.46	122.66
905.00	99.64	107.46	116.21
1008.70	96.63	-	114.81
Initial value of $\wedge_0$ 138.31 150.30 179.35			
KI			
109.40	129.94	136.94	150.14
209.00	119.44	132.70	142.94
318.20	111.88	121.70	134.96
400.80	108.76	120.02	131.88
511.60	108.14	119.75	129.98
603.00	107.77	118.18	128.03
725.60	105.26	117.85	126.26
805.70	99.63	115.79	124.20
898.50	97.78	109.77	123.57
1022.70	95.31	108.48	121.65
Initial value of $\wedge_0$ 141.11 147.82 160.157			

(A similar replacement of ion – size parameter by ‘q’ was also applied by earlier investigators<sup>8,9</sup> in Fuoss – Hsia equation). The conductance data is also analysed on the basis of Fuoss-Kraus and Shedlovsky extrapolation techniques. The Fuoss (1980) conductance equation<sup>7</sup> can be symbolically represented as

$$\Lambda = \gamma \left[ \Lambda_0 (1 + \Delta X_E / X) + \Delta_{V^+} + \Delta \Lambda_H + \Delta \Lambda_C \right] \quad (1)$$

Where all the symbols have their usual meaning. The details of Fuoss-Kraus and Shedlovsky extrapolation techniques are as given earlier<sup>9</sup>. The  $\Lambda_0$  and  $K_A$  values obtained by the three methods namely (Fuoss-1980, Fuoss-Kraus and Shedlovsky) are presented in Tables 2.

A comparison of the  $\Lambda_0$  values obtained by these methods show that  $\Lambda_0$  values obtained by Fuoss-Kraus and Shedlovsky methods are almost equal and are less than the  $\Lambda_0$  values obtained by Fuoss (1980) equation. Since the Fuoss (1980) method

is well developed conductance equation, the further discussion of the conductance data is made only from the values obtained by Fuoss (1980) conductance equation. From the tables it is clear that the  $\Lambda_0$  values follow the order  $Na^+ < K^+ < Rb^+$  for common anion and  $Cl^- < Br^- < I^-$  for common cation at all temperatures studied. The observation with respect to cations is in accordance with results reported by A.A Ansari [10] in 2-propanol – water mixture. Since  $\Lambda_0$  values increase with increase in ionic size in a dielectric medium due to hydrophobic hydration of cations<sup>11</sup>.

The  $\Lambda_0$  increases with temperatures for all the salts studied. The positive temperature coefficient of conductance was explained<sup>12</sup> on the basis that increase in temperature causes.

- (i) the rupture of hydrogen bonding
- (ii) will facilitate the rotation of solvent molecules by increasing the force causing the rotation.

Table - 2

$\Lambda_0$  &  $K_A$  values from various conductance equations in 10% (W/W) 2-(Ethoxy) ethanol-water mixture at 30°C, & 35°C & 40°C

Salt	Fuoss-Kraus		Shedlovsky		Fuoss (1980)	
	$\Lambda_0$	$K_A$	$\Lambda_0$	$K_A$	$\Lambda_0$	$K_A$
NaCl	109.25	0.54	109.31	0.57	112.50	4.11
KCl	126.97	1.00	126.07	0.96	131.35	4.92
RbCl	131.38	1.30	131.42	1.35	136.60	5.97
KBr	128.70	2.10	128.71	1.44	135.06	6.75
KI	129.90	2.54	129.93	1.80	138.40	8.47
35°C						
NaCl	127.93	1.07	127.93	1.12	135.15	6.26
KCl	138.09	0.80	137.50	0.93	158.40	10.27
RbCl	139.91	0.89	139.88	0.92	145.50	5.05
KBr	140.53	1.11	140.45	1.16	146.63	6.01
KI	137.87	0.91	138.10	0.97	144.44	5.54
40°C						
NaCl	138.57	0.49	138.42	0.42	153.78	7.82
KCl	159.86	1.56	159.91	1.61	171.24	8.99
RbCl	157.91	1.16	157.91	1.21	165.39	6.55
KBr	156.99	1.48	157.17	1.52	165.59	7.85
KI	149.18	0.69	149.19	0.73	156.83	5.24

### Single ion Conductance :

The limiting equivalent conductance is the only property which can be split into ionic contributions by a direct method until now. This method makes use of the transference number data. However in the present solvent system which is under investigation, the transference numbers are not available. Hence an indirect method is resorted for separating the limiting equivalent conductances into ionic contributions.

By studying a series of tetraalkyl ammonium bromides<sup>13</sup> and making use of the methods suggested by

(i) Walden<sup>14</sup> and (ii) Pickering and Kraus<sup>15</sup> the  $\Lambda_0$  values of  $Br^-$  ion is obtained. The single ion conductance's of other ions are obtained on the additivity basis. These values are presented in Table 3. An observation of the table shows that the values obtained by the two methods are in reasonable agreement within the experimental limits at 35°C. However there is a small difference in the  $\lambda_{0\pm}$  values at 30° & 40° C. For further calculations and discussions the  $\lambda_0^\pm$  values obtained by the method of Walden<sup>14</sup> ((i) of table 3) are used.

In general the results show that the ionic conductance increases with an increase in crystallographic radius of alkali and halide ions at 30°C following the order  $Na^+ < Rb^+ < K^+$  and  $Cl^- < Br^- < I^-$ . A similar trend was noticed Nandi *et.al.*<sup>16</sup>. However at higher temperatures *i.e.*, at 35° and 40° the order is altered as  $Na^+ < Rb^+ < K^+$  and  $I^- < Br^- < Cl^-$

A comparison of the  $\lambda_0$  values of various ions of the present investigation with the values reported in pure water<sup>15</sup> indicate that the  $\lambda_0$  values of various alkali and halide ions are less than the  $\lambda_0$

values in pure water. This can be attributed to the addition of 10%(W/W) 2-(Ethoxy) ethanol to water which is causing a strong structural influence. A study of other properties in the same solvent system shows that the strong structural influence is anticipated through breaking of hydrogen bond<sup>5,17</sup>.

### $K_A$ VALUES :

Examination of Table 2 shows that the  $K_A$  values obtained by Fuoss (1980) equation are larger than the  $K_A$  values obtained from Fuoss-Kraus and Shedlovsky extrapolation techniques. A similar trend was also reported by Ananta Swamy *et.al.*<sup>18</sup> and Islam *et.al.*,<sup>19</sup>, when  $K_A$  values obtained by advanced equations are compared with the values obtained by earlier equations.

The table shows that the order of Fuoss (1980)  $K_A$  values is  $NaCl < KCl < RbCl$  at 30°C and  $RbCl < NaCl < KCl$  at 35° and 40°C. The anion size dependence of  $K_A$  for Potassium halides in the present solvent system is interesting. If it is assumed that the electrostatic interaction is the main mechanism for forming ion-pairs, then in general it can be assumed that for solutions in the same solvent, the weaker the ionic solvation the less the stability of free ions and the shorter the distance between oppositely charged ions in the ion-pairs. Consequently strong ion-pairs are formed. Therefore, an increase of the  $K_A$  values from chlorides to iodides should be expected from this solution effect; This is true in the present case at 30°*i.e.*,  $K_A$  of  $KCl < KBr < KI$ . However at 35° and 40°C, an inversion in order of association constant was observed. The same effect was also reported for Potassium halides in Ethanol<sup>20</sup> and 2,2,2-Trifluoro ethanol<sup>21</sup>. They attributed this effect to the phenomenon of "localized hydrolysis". Hence in the present case the solvent molecules in the cation solvation shell are considerably polarised. Owing to this polarization, some anions can interact with the hydrogen atoms of polarized solvent molecules. Which leads to the formation of solvent separated ion-pairs.

Table - 3  
Limiting Ionic conductances obtained by the two methods

	30°		35°		40°	
Iron	(i)	(ii)	(i)	(ii)	(i)	(ii)
Na <sup>+</sup>	46.87	47.99	49.61	49.67	66.59	67.61
K <sup>+</sup>	65.72	67.51	72.86	72.92	84.05	85.07
Rb <sup>+</sup>	70.97	69.09	59.96	60.02	78.20	79.22
Cl <sup>-</sup>	65.63	63.84	85.54	85.48	87.19	86.17
Br <sup>-</sup>	69.34	67.55	73.77	73.71	81.54	80.52
I <sup>-</sup>	72.68	70.89	71.58	71.52	72.78	71.76

Table - 4  
Theoretical values of Association constants according to different theories at  
30°, 35° and 40° C in 10% (W/W) 2-(Ethoxy) ethanol – water mixture

	30°				35°				40°			
Salt	K <sub>B</sub>	K <sub>F</sub>	K <sub>DR</sub>	K <sub>EKYY</sub>	K <sub>B</sub>	K <sub>F</sub>	K <sub>DR</sub>	K <sub>EKYY</sub>	K <sub>B</sub>	K <sub>F</sub>	K <sub>DR</sub>	K <sub>EKYY</sub>
NaCl	0.96	1.18	16.92	0.93	1.10	0.94	17.65	0.99	1.21	0.96	18.12	1.03
KCl	0.65	1.87	11.99	0.80	0.61	0.97	12.47	0.85	0.78	1.00	12.77	0.88
RbCl	0.39	1.92	10.70	0.75	0.60	1.00	11.11	0.81	0.64	1.02	11.37	0.84
KBr	0.40	1.92	10.78	0.76	0.61	0.99	11.19	0.81	0.65	1.02	11.45	0.84
KI	0.39	2.00	9.34	0.71	0.41	1.04	9.68	0.75	0.45	1.06	9.88	0.78

Table - 5  
'a' values predicted by Bjerrum, Fuoss, DR and EKYY Theories at different temperatures

	30°				35°				40°			
Salt	a <sub>B</sub>	a <sub>F</sub>	a <sub>DR</sub>	a <sub>EKYY</sub>	a <sub>B</sub>	a <sub>F</sub>	a <sub>DR</sub>	a <sub>EKYY</sub>	a <sub>B</sub>	a <sub>F</sub>	a <sub>DR</sub>	a <sub>EKYY</sub>
NaCl	1.23	4.58	5.52	4.52	1.06	5.20	4.32	5.36	1.00	5.55	3.89	5.42
KCl	1.13	5.46	4.89	5.77	0.90	6.88	3.40	7.20	0.96	6.53	3.64	6.80
RbCl	1.01	6.05	4.36	6.55	1.16	5.65	4.88	6.06	1.07	6.11	4.25	6.53
KBr	1.00	6.28	4.08	6.79	1.08	5.97	4.42	6.40	0.99	6.48	3.88	6.90
KI	1.00	7.11	3.65	7.99	1.11	6.10	4.63	6.78	1.17	5.95	4.83	6.57

#### *Ion-Association*

Various theories of ion-association namely Bjerrum<sup>22</sup> Fuoss<sup>23</sup>, Danison and Ramsey<sup>24</sup>, and Ebeling, Kraeft, Yokoyama and Yamatera<sup>25,26</sup> are used to compare with the experimentally obtained association constants in two ways<sup>6</sup>.

- (i) The ion-size parameter 'a' required by each of the theory to predict the experimentally determined association constant values in 10% (W/W) 2-(Ethoxy)

ethanol-water mixture is calculated and are presented in Tables 4,5. These are compared with the known inter-ionic distances taken from the crystallographic data. The agreement between these two values of 'a' for a given solute-solvent system can be considered as a measure of the success of the theory.

- (ii) The ion-size parameter 'a' of a solute is taken from the known crystallographic data and then

substituted in the association constant expression for calculating the theoretical  $K_A$  values *i.e.*,  $K_B$ ,  $K_F$ ,  $K_{DR}$  and  $K_{EKYY}$  and then these are compared with the experimental  $K_A$  values.

From the results in the table 5 it is evident that the Bjerrum theory predicts very low values for 'a' for all the salts in the present solvent system. In the case of alkali metal salts, Fuoss and EKYY theories predict the 'a' values of almost same magnitude. However, DR theory agrees well with Fuoss and EKYY theories initially but predicts lower values as the size of the electrolyte increases.

Tables 4 shows that Fuoss, Bjerrum, EKYY theories give very low association constant values while DR theory gives high values. From the above discussion it may be said that in the present solvent system and for the studied 1:1 electrolytes, all the theories of ion-pair formation exhibit their inability to predict the extent of ion association.

#### Stokes' Radius :

The Stokes radius for various alkali and halide

ions is calculated using the formula  $r_s = \frac{0.820 |Z|}{\lambda_{0\pm} \eta_0}$ .

Usually if the stokes' radius is greater than the crystallographic radius, salvation in postulated.

The Stokes radius for various ions is given in Table 6. The results show that the Stokes radius decreases with increasing crystallographic radius in the case of alkalimetal and halide ions. (Figure 1) indicates that stokes radius of alkali metal and halide ions is a linear function of crystallographic radius of these ions. Since the stokes radius of  $Na^+$  is larger

than the crystallographic radius it can be said that this ion is solvated in the present solvent system and it is also evident that all the anions remain unsolvated.

#### Walden Product :

The Walden Products ( $\lambda_{0\pm} \eta_0$ ) of various ions are calculated and are presented in Table 7. Various investigators felt that the temperature dependence of Walden product of various ions gives valuable information regarding the nature of the ion in the medium.

Generally the larger alkalimetal and halide ions possess an excess mobility in aqueous solutions owing to their ability to break hydrogen bonds in their immediate vicinity and thereby reducing the local viscosity. An increase in temperature reduces the amount of hydrogen bonding and thereby reduces the effectiveness of these ions are structure breakers. Hence a decrease in Walden product with temperature for structure breaking ions is due to the fact that there is less structure to break at higher temperatures. For the strong structure breaking ions such as  $K^+$ ,  $Rb^+$ ,  $Br^-$  &  $I^-$  ions the Walden product decreases with temperature as expected in the present solvent system also. But  $Cl^-$  ion does not exhibit any order. In case of  $Na^+$  ion, it is less effective as a structure breaker and its conductance is mainly controlled by electrostatic solvation that varies relatively little with increasing temperature and it also does not exhibit any order. The ( $\lambda_{0\pm} \eta_0$ ) tend to increase with an increase in crystal radius of the

Table - 6  
Stokes' radius of various ions in 10%(W/W) 2-(Ethoxy) ethanol-water mixture

Ion	Stokes radius $r_s$ in $\text{\AA}^0$			Crystallographic Radius $\text{\AA}^0$
	30 <sup>0</sup>	35 <sup>0</sup>	40 <sup>0</sup>	
$Na^+$	1.49	1.69	1.42	0.95
$K^+$	1.13	1.15	1.12	1.33
$Rb^+$	1.05	1.40	1.20	1.48
$Cl^-$	1.13	0.98	1.08	1.81
$Br^-$	1.07	1.14	1.16	1.95
$I^-$	1.02	1.18	1.29	2.16

cations in the present solvent system under investigation. The role of high electrostatic charge density on the alkalimetal ions thus favours strong ion-solvent interactions. This is also clear from the solvo dynamic radius of the ions in the order

$Na^+ > K^+ > Rb^+$ , in spite of the reverse order of their crystallographic radius.

Table - 7  
Walden products of various ions

Ion	30 <sup>0</sup>	35 <sup>0</sup>	40 <sup>0</sup>
Na <sup>+</sup>	0.517	0.483	0.578
K <sup>+</sup>	0.725	0.710	0.730
Rb <sup>+</sup>	0.783	0.584	0.679
Cl <sup>-</sup>	0.724	0.833	0.757
Br <sup>-</sup>	0.765	0.719	0.708
I <sup>-</sup>	0.802	0.697	0.632

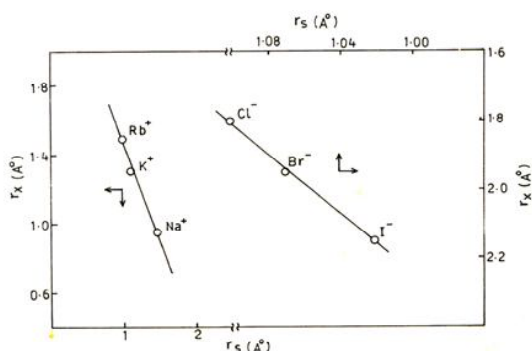


Fig - 1 : Plot of Crystallographic radius ( $r_x$ ) Vs Stokes radius ( $r_s$ ) at 30<sup>0</sup>C

#### IV. Conclusion

1. Addition of 2-(Ethoxy)Ethanol to water show strong structural influence on water by breaking hydrogen bonds.

2. In 10%(W/W) 2-(Ethoxy) ethanol-water mixture and for the studied electrolytes(NaCl, KCl, RbCl, KBr, KI) all theories of ion association show their inability to predict the extent of ion association.

3. K<sup>+</sup>, Rb<sup>+</sup>, Br<sup>-</sup> and I<sup>-</sup> are structure breakers while Na<sup>+</sup> is less effective in breaking the structure of the solvent.

#### VI. Scope of Future Work :

Electrical conductivity of electrolyte

solutions (in water rich region of aqueous –organic liquid mixtures) is one of the transport properties more frequently request by chemists, biologists and engineers due to its greater interest in various fields of research and industry<sup>16,27-29</sup>. This research work planned to extend the study of other properties like partial molar volumes , viscosity both using alkali metal salts and tetra alkyl ammonium salts to understand solute-solvent interactions.

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