



## Conductance of *s*-Acetylthiocholine Chlorides in Non-Aqueous Solvents at 25 °C

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The conductance of *s*-acetylthiocholine chlorides has been measured in methanol, ethanol, *n*-propanol and *n*-butanol at 25 °C. The data were analyzed using the Fuoss-Onsager equation for 1:1 associated electrolytes and the characteristic functions,  $\Lambda_0$  (equivalent conductance at infinite dilution),  $a^\circ$  (contact distance of approach) *i.e.*, solvation and  $K_A$  (association constant) were calculated. The association constant values were analyzed on the basis of the solvent separated-ion pair model. The electrostatic Stokes' radii ( $R^+ + R^-$ ) were calculated and their sum was compared with the value of  $a^\circ$  confirming the ion pair model. The plot of  $\log K_A$  versus  $1/D$  gave a straight line according to ionic association equation. Zwanzig theory of dielectric friction has been applied to chloride ion in different solvents at 25 °C. The values of the radius from the slope (hydrated radius) and the intercept (hydrodynamic radius) were examined and the reason for such difference discussed on the basis of the assumptions of Zwanzig theory.

**Key Words:** Conductance, *s*-Acetylthiocholine chlorides, Non-aqueous solvents, Solvation, Ionic association, Zwanzig theory.

### INTRODUCTION

Recent studies of kay and co-workers on the conductance of several alkyl ammonium halides in methanol and ethanol<sup>1,2</sup> have clearly supported our findings concerning the influence of solvent on the association of ions. Hafez *et al.*<sup>3</sup>, have found that the decrease in  $\Lambda_0$  for *s-n*-alkyl isothiouranium bromides in methanol, ethanol and *n*-propanol, is attributed to the decrease in ion mobility as the dielectric constant of the solvent decreases, while the increase of  $K_A$  (ion-association) may be due to the increase of the number of non conducting ion-pairs under such condition of the decrease in mobility. Lee and Wheaton<sup>4,5</sup> have measured the conductance of alkali metal iodides in methanol, ethanol and *n*-propanol at 25 °C. They found that  $\Lambda_0$  decreases while  $K_A$  increases with the decrease of the dielectric constant of the medium and they have suggested an assumption namely, the formation of solvent-separated ion pairs. Lee and wheaton<sup>4,6</sup> have obtained a simple behaviour for alkali iodides in different alcohols, they found that the plot of  $\log K_A$  versus  $1/D$ , which is linear as expected from the relation<sup>6</sup>

$$\log K_A = \log K_A^0 + \left( \frac{e^2}{a^\circ DkT} \right)$$

Accasina *et al.*<sup>7</sup>, studied the conductance of  $\text{LiClO}_4$  in dioxane-water mixtures at 25 °C and found a slight curvature

for applying ionic association equation<sup>6</sup>. Hafez *et al.*<sup>3</sup> measured the conductance of *s-n*-alkyl isothiouranium bromides, iodides and picrate in ethanol, *n*-propanol and *n*-butanol. They found that in more cases straight lines were obtained according to ionic association equation<sup>6</sup>. In other cases a slight curvature was due to the interference of ion-solvent interaction<sup>8</sup>. El-Hammamy *et al.*<sup>9</sup> measured the conductance of  $\text{N-N}$ -diphenyl-*s-n*-alkyl-isothiouranium bromides in methanol, ethanol, *n*-propanol and *n*-butanol at 25 °C. They found that a curvature in the same plot. This behaviour was explained as being due to the solute-solvent interaction. El-Hammamy *et al.*<sup>10-12</sup> and Ahmed<sup>10</sup> measured the conductance of acetylcholine halides and perchlorate in methanol, ethanol and *n*-propanol at 25 °C and found straight lines according to ionic association equation<sup>6</sup>. The effect of solvent is two fold: (a) it can stabilize the ion-pairs due to the hydrogen bond chains in alcohols, (b) it can solvate anions by hydrogen bonding<sup>13</sup>, so that  $K_A$  value increases.

In the present work, *s*-acetylthiocholine chloride is selected as electrolyte with large cation size and small anion size. The effect of anion size on the conductance of salt can be discussed on the light of the variation of  $\Lambda_0$ ,  $a^\circ$  and  $K_A$  values in methanol, ethanol, *n*-propanol and *n*-butanol at 25 °C. The conductance measurements in *n*-alcohols at 25 °C can be analyzed using the Fuoss-Onsager equation and derived constants may be illustrating the electrolyte-solvent interaction.

## EXPERIMENTAL

The *s*-acetylthiocholine chloride was purified as reported in literature<sup>14</sup>. Methanol (B.D.H), ethanol (B.D.H), *n*-propanol (B.D.H) and *n*-butanol (B.D.H) were purified as previously reported<sup>15-18</sup>. The specific conductances for purified alcohols are listed in Table-5. The densities, viscosities and dielectric constant values were depicted<sup>15-18</sup> in Table-5. All solutions were reported by reducing weight to *vacuo*. Salts were weighed using microbalance which reads to  $\pm 0.1$  mg. Dilution was carried out successively into the cell by siphoning the solvent by means of weighing pipette. Conductivity Bridge of model Crison Cl P31 and the cell with bright platinum electrodes were used. The cell constant was  $0.1 \text{ cm}^{-1}$  for dilute solutions.

## RESULTS AND DISCUSSION

The measured equivalent conductance data are shown in Table-1. An approximate value of  $\Lambda_0$  was estimated from of  $\Lambda$  versus  $C^{1/2}$  plot. More accurate values of  $\Lambda_0$  were estimated from the Fuoss-Kraus-Shedlovsky (F.K.S) equation,

$$\frac{1}{\Lambda S_{(z)}} = \frac{1}{\Lambda_0} + \frac{(K_A S_{(z)} f^2)}{K_D \Lambda_0^2}$$

where  $K_D$  is the dissociation constant and  $S_{(z)}$  is the Shedlovsky's function which was tabulated by Daggett for different values of  $z$ . The value of  $z$  were calculated from the following equation

$$z = \frac{\alpha(CA)^2}{\Lambda_0^{3/2}}$$

where  $\alpha$  is the limiting tangent. The plot of  $1/\Lambda S_{(z)}$  versus  $(CA S_{(z)} f^2)$  gives  $1/\Lambda_0$  as the intercept and  $1/K_D \Lambda_0^2$  as the slope. The true values of  $\Lambda_0$ ,  $a^\circ$  and  $K_A$  were derived using Fuoss-Onsager equation<sup>19</sup> and starting by the value  $\Lambda_0$  which was obtained from (F.K.S.) equation. In our calculations a computer program on an IBM-PC machine was used. The accuracy required in these computation were  $\pm 0.02$  for  $\Lambda_0$ ;  $\pm 2$  for  $J < 200$ ,  $\pm 5$  for  $J = (200 \rightarrow 1000)$  and  $\pm 10$  for  $J > 1000$ . Fig. 1 shows the variation of  $a^\circ$  with  $J$ , from which the average value of  $a^\circ$  could be obtained by interpolation through the knowledge of the average value of  $J$ .

This value was obtained from the computer readings where  $J$  is being a function of  $a^\circ$  and has the following equation<sup>19</sup>

$$J = \sigma_1 \Lambda_0 + \sigma_2$$

where  $\sigma_1$  and  $\sigma_2$  are the functions of  $J$ . The derived constants are represented in Table-2. It reveals that  $\Lambda_0$  decreases from methanol to *n*-butanol according to the ionic equivalent conduc-

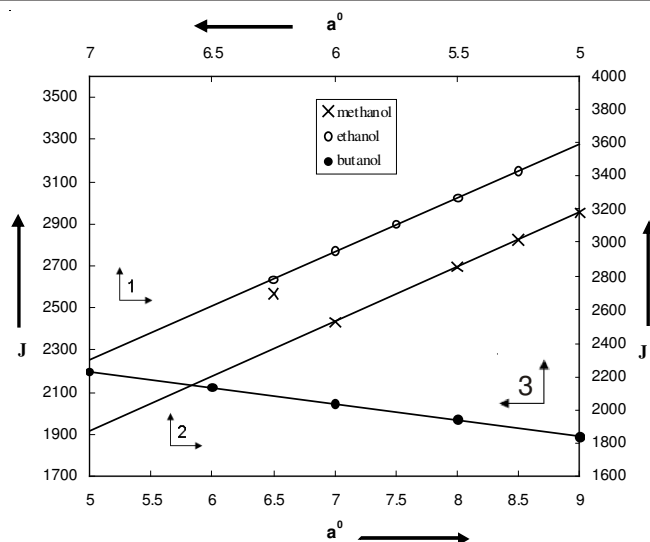


Fig. 1. Variation of  $J$  and  $a^\circ$  for *s*-acetylthiocholine chlorides in non-aqueous solvents at 25 °C

TABLE-2  
CHARACTERISTIC PARAMETERS FOR  
ACETYLTHIOCHOLINE CHLORIDE IN NON  
AQUEOUS SOLVENTS AT 25 °C

Solvent	$\Lambda_0$ (ohm <sup>-1</sup> equiv <sup>-1</sup> cm <sup>2</sup> )	$J$	$K_A$	$a^\circ$ (Å)
Methanol	104.42	2694.7	21.296	7.99
Ethanol	55.986	2.898.0	302.78	7.60
<i>n</i> -Propanol	46.959	3428.7	721.33	6.91
Butanol	17.444	2030.0	2941.3	5.94

tance of anions. This decrease is attributed to the decrease in the ionic mobility as the dielectric constant decreases, while the increase of  $K_A$  from methanol to *n*-butanol may be due to the increase of the number of non conducting ion pairs under such condition of the decrease in ionic mobility. The values of  $a^\circ$  decrease with decreasing the dielectric constant of medium. The solvation of the anions of *s*-acetylthiocholine chloride increases in the direction: *s*-acetylthiocholine chloride (MeOH) > EtOH > *n*-PrOH > *n*-BuOH, which is in accordance with trend of  $a^\circ$ . From the electrostatic point of view, since the distance between the cation and the anion increases in the same order, the force of attraction increases in the order:  $K_A Cl^-$  (*n*-BuOH) > *n*-PrOH > EtOH > MeOH. In our case the trend is that  $K_A$  increases with increase the  $-CH_2-$  group of alcohol increase, *i.e.*,  $K_A$  increases from *n*-BuOH > *n*-PrOH > EtOH > MeOH.

El-Hammamy *et al.*<sup>11,12</sup>, measured the conductances of acetylthiocholine and *s*-acetylthiocholine halides (bromide and

TABLE-1  
CONDUCTANCE OF ACETYLTHIOCHOLINE CHLORIDE IN NON-AQUEOUS SOLVENT AT 25 °C

Methanol		Ethanol		<i>n</i> -Propanol		Butanol	
10 <sup>4</sup> C (equiv L <sup>-1</sup> )	$\Lambda$ (ohm <sup>-1</sup> equiv <sup>-1</sup> cm <sup>2</sup> )	10 <sup>4</sup> C (equiv L <sup>-1</sup> )	$\Lambda$ (ohm <sup>-1</sup> equiv <sup>-1</sup> cm <sup>2</sup> )	10 <sup>4</sup> C (equiv L <sup>-1</sup> )	$\Lambda$ (ohm <sup>-1</sup> equiv <sup>-1</sup> cm <sup>2</sup> )	10 <sup>4</sup> C (equiv L <sup>-1</sup> )	$\Lambda$ (ohm <sup>-1</sup> equiv <sup>-1</sup> cm <sup>2</sup> )
9.2649	96.386	12.217	42.365	20.879	26.475	8.5155	8.4356
8.1880	96.849	11.020	43.000	16.133	28.534	7.5776	8.7492
7.2954	97.284	9.9876	43.632	13.067	30.114	6.8130	8.9932
6.6154	97.621	9.1576	44.229	11.358	31.037	6.1766	9.2819
5.2357	98.364	8.4082	44.730	9.8367	31.854	5.7043	9.5068
4.4241	98.848	7.7626	45.180	8.7791	32.509	5.2820	9.7178
3.7561	99.278	7.1892	45.650	7.8705	33.067	4.8995	9.9055
—	—	—	—	7.2425	33.558	—	—

iodide) and perchlorate in normal and branched alcohols at 25 °C. They found that the same trend of  $a^\circ$  and  $K_A$  for all organic solvents are in agreement with the present results. The gradual decrease of  $a^\circ$  with increase of  $K_A$  among the studies salts was attributed to the relative position of the anion with respect to the cation which may not be completely spherical. The increase of  $K_A$  with increasing  $-CH_2-$  chain in alcohols which was decreasing the size of anions of *s*-acetylthiocholine chlorides can be explained in the light of the U term in equation<sup>7</sup>

$$\ln K_A = \ln \left( \frac{4\pi Na^{\circ 3}}{3000} \right) + \left( \frac{e^2}{a^\circ DkT} \right) + U$$

where,  $U = \frac{\Delta S}{k} - \frac{E_s}{kT}$

$\Delta S/k$  is the entropy Boltzman constant ratio which illustrates the probability of the orientation of solvent molecules around the free ions and  $E_s/kT$  is an energy relationship which includes the energy of the solvent molecules with respect to both free ions and ion-pair which they can form. The values of U term of *s*-acetylthiocholine chlorides in non aqueous solvents are given in Table-3. The result reveals that the value of U slightly increase from MeOH to *n*-BuOH, *i.e.*, the entropy term  $\Delta S/kT$  is more predominant than ion-dipole interaction term  $E_s/kT$ . Finally, the solvent separated ion-pair model is applied<sup>20</sup>. In this model a multiple-step association is occurs, *i.e.*, solvent separated-ion pair can be illustrated by the following scheme:

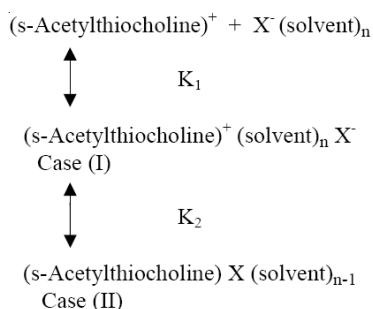


TABLE-3  
CALCULATED VALUES OF  $K_2$  AND U FOR ACETYLTHIOCHOLINE CHLORIDE IN NON-AQUEOUS SOLVENTS AT 25 °C

Solvent	$K_A$	$K_1$	$K_2$	U
Methanol	21.296	11.030	0.931	0.65
Ethanol	302.78	22.984	12.139	2.782
<i>n</i> -Propanol	721.33	43.795	15.47	2.802
Butanol	2941.3	115.278	24.515	3.239

The association constant is given by the following expression:

$$K_A = K\Sigma = \frac{[C_{(\text{ion-pairs})}]}{[C_{(s\text{-acetylthiocholine})^+}][C_{X^-(\text{solvent})_n}]} = K_1(1 + K_2)$$

TABLE-4  
CALCULATION OF THE RADII OF THE IONS FOR ACETYLTHIOCHOLINE CHLORIDE IN NON-AQUEOUS SOLVENT AT 25 °C

Solvent	$\Lambda$ (ohm <sup>-1</sup> equiv <sup>-1</sup> cm <sup>2</sup> )	$\lambda_0^- \eta_0$ (ohm <sup>-1</sup> equiv <sup>-1</sup> cm <sup>2</sup> p)	$\lambda_0^-$ (ohm <sup>-1</sup> equiv <sup>-1</sup> cm <sup>2</sup> )	$\lambda_0^+$ (ohm <sup>-1</sup> equiv <sup>-1</sup> cm <sup>2</sup> )	$R^+$ (Å)	$R^-$ (Å)	$R^+ + R^-$	$a^\circ$ (Å)
Methanol	104.42	0.8498	52.31	52.11	2.886	2.875	5.762	7.99
Ethanol	55.986	0.24096	21.87	34.116	2.180	3.401	5.580	7.60
<i>n</i> -Propanol	46.959	0.20281	10.39	36.566	1.207	4.040	5.247	6.91
<i>n</i> -Butanol	17.444	0.20061	7.76	9.684	3.268	4.079	7.347	5.94

$$K_1 = \frac{4\pi Na^{\circ 3}}{3000} e^b$$

where,  $K_A = K\Sigma$  is obtained from the conductance measurements and

$$b = \frac{e^2}{a^\circ DkT}$$

$K_2$  was thus calculated. The results compiled in Table-3, indicate that  $K_2$  increases from  $Cl^-$  in MeOH to  $Cl^-$  in *n*-BuOH *i.e.*, the ion-pair prefers the desolvated form (case II) than the solvated form (case I).

**Radii of ions:** The electrostatic radii  $R^+$  and  $R^-$  are given by equation:

$$R^\pm = \frac{0.8194 \times 10^{-8}}{\lambda_0^\pm \eta_0}$$

In the present case  $\lambda_0^-$  values were obtained from the intercept of the straight lines resulting from the plots of Walden products  $\Lambda_0 \eta_0$  versus the reciprocal of the molecular weight as previously discussed<sup>21</sup>. To calculate  $\lambda_0^+$  for (*s*-acetylthiocholine)<sup>+</sup>, the average values obtained for  $\lambda_0^+$  in case of MeOH to *n*-BuOH were used in calculations. Applying Stokes' equation, one may obtain the values of both  $R^+$  and  $R^-$  (Table-4). It can be seen from Table-4 that the values of  $a^\circ$  (in case of MeOH, EtOH and *n*-PrOH) are greater than the electrostatic radii ( $R^+ + R^-$ ) which obtained from Stokes' equation. The surprisingly greater  $a^\circ$  values are probably attributed to ion solvation. In case of (*n*-BuOH)  $a^\circ$  was smaller than the electrostatic radii ( $R^+ + R^-$ ) which obtained from Stokes' equation. The surprisingly smaller  $a^\circ$  value is probably attributed to ion association.

**Application of ion association equation in non aqueous solvent:** The association constant should be only a function of the dielectric constant. Their values increase with decreasing dielectric constant of the medium. This is found to be true in studying the behaviour of *s*-acetylthiocholine chlorides in MeOH, EtOH, *n*-PrOH and *n*-BuOH at 25 °C. The association constant was also generally found to increase with increasing anionic size in each alcohol (Table-2). The same behaviour of  $\Lambda_0$  and  $K_A$  was obtained for tetrabutyl ammonium halides and perchlorate in different alcohol<sup>1,2</sup> at 25 °C (Table-6).

From the above picture of the variation of both  $\Lambda_0$  and  $K_A$  with dielectric constant of alcohols, one may conclude that the sphere in continuum model cannot apply to these systems. Kay and his workers<sup>1,2</sup> studied some salts of the tetra-alkyl-ammonium in methyl alcohol. They obtained values of  $K_A$  higher than those expected by using the Bjerrum-Fuoss theory<sup>6</sup>. They explained their results on the hypothesis that the ion pair association is affected by the particular structure of alcohol. It can be readily seen from Table-7<sup>4,5</sup>, that the association constant

TABLE-5  
SOLVENT PROPERTIES AT 25 °C<sup>15-18</sup>

Solvent	Density (d) (g/cm <sup>3</sup> )	Viscosity (η) (poise)	Dielectric constant	Specific conductance (Ω <sup>-1</sup> cm <sup>-1</sup> )
MeOH	0.78657	0.5448 × 10 <sup>-2</sup>	32.63	1.6-3.9 × 10 <sup>-7</sup>
EtOH	0.78511	1.0840 × 10 <sup>-2</sup>	24.33	1.2-1.6 × 10 <sup>-8</sup>
<i>n</i> -PrOH	0.79960	1.9520 × 10 <sup>-2</sup>	20.33	2.3-4.8 × 10 <sup>-8</sup>
<i>n</i> -BuOH	0.80572	2.5890 × 10 <sup>-2</sup>	17.51	1.0-3.8 × 10 <sup>-8</sup>

TABLE-6  
Λ<sub>0</sub> AND K<sub>A</sub> VALUES IN DIFFERENT ALCOHOLS AT 25°C FOR TETRABUTYL AMMONIUM HALIDES AND PERCHLORATE<sup>1,2</sup>

Salt	Methanol		Ethanol		<i>n</i> -Propanol	
	Λ <sub>0</sub>	K <sub>A</sub>	Λ <sub>0</sub>	K <sub>A</sub>	Λ <sub>0</sub>	K <sub>A</sub>
Bu <sub>4</sub> NCl	91.38	0	41.54	39	12.16	149
Bu <sub>4</sub> NBr	95.37	2.6	43.31	75	22.92	266
Bu <sub>4</sub> NI	101.72	15.6	46.56	123	24.60	415
Bu <sub>4</sub> NClO <sub>4</sub>	—	—	—	—	27.13	769

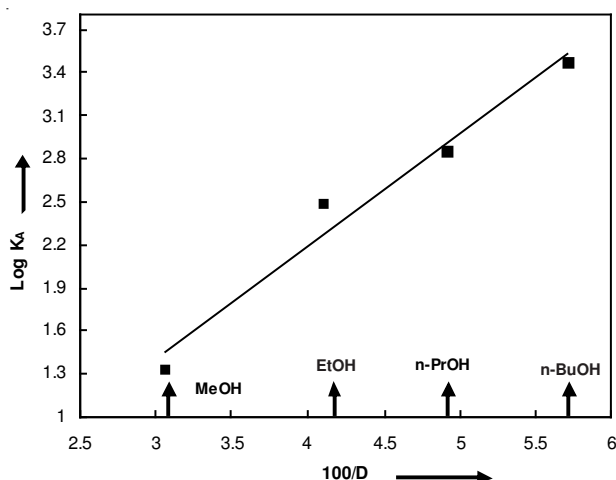
TABLE-7  
CONDUCTANCE DATA FOR SOME ALKALI METAL SALTS AT 25 °C<sup>4,5</sup>

Salt	Methanol		Ethanol		<i>n</i> -Propanol	
	Λ <sub>0</sub>	K <sub>A</sub>	Λ <sub>0</sub>	K <sub>A</sub>	Λ <sub>0</sub>	K <sub>A</sub>
NaI	108.5	12.8	47.57	55.8	24.38	199.9
KI	115.51	13.2	50.70	81.9	26.31	350.2
RbI	119.68	18.6	52.18	105.4	26.99	472.0
CSI	124.22	23.1	53.63	140.5	27.72	646.4

increases with increasing cation size, in order of CsI > RbI > KI > NaI. This can be explained by adopting the Lee and Wheaton<sup>4,5</sup> assumption namely, the formation of solvent-separated ion pairs. Lee and Wheaton<sup>4,5</sup> obtained a similar behaviour for alkali iodides in different alcohols.

Fig. 2 shows the plot of log K<sub>A</sub> versus 1/D, which is linear as expected from the relation<sup>6</sup>:

$$\log K_A = \log K_A^\circ + \left( \frac{e^2}{a^\circ DkT} \right)$$

Fig. 2. Variation of log K<sub>A</sub> versus 1/D for *s*-acetylthiocholine-chloride at 25 °C

Accasina *et al.*<sup>7</sup>, studied the conductance of LiClO<sub>4</sub> in dioxane-water mixtures at 25 °C. They found a slight

curvature. Hafez *et al.*<sup>3</sup> measured the conductance of *s*-*n*-alkyl isothiuronium bromides, iodides and picrate in EtOH, *n*-PrOH and *n*-BuOH and found that in most cases straight lines were obtained according to ionic association equation<sup>6</sup>. In other cases a slight curvature was due to the interference of ion solvent interaction<sup>8</sup>.

**Application of Zwanzig theory:** Fuoss<sup>22</sup> has given a relationship between the ionic conductivity of an ion in different solvents with solvent properties. Boyd<sup>23</sup> and Zwanzig<sup>24</sup> have improved it and expressed λ<sub>i</sub><sup>0</sup> as

$$\lambda_i^0 = \frac{F^2}{N[6\pi\eta_0\gamma_i + (2e^2\tau/er_i^3)/(\epsilon_0 - \epsilon_\infty)/\epsilon_0^2]} \quad (1)$$

It was considered interesting to examine the applicability of Fuoss-Royd-Zwanzig theory to present data. Eqn. 1 can be used most conveniently in the linear form suggested by Alkinson and Mori<sup>25</sup>, where results in a number of solvents are to be compared. When eqn. 1 is inverted and rearranged with insertion of the numerical constant and radii in Å, we obtain

$$\left( \frac{F^2}{\eta_0\lambda_i^0} \right) = 6\pi r_i + \left( \frac{2e^2}{3r_i^3} \right) \left[ \frac{\tau}{\eta_0} (\epsilon_0 - \epsilon_\infty) / \epsilon_0^2 \right]$$

or

$$\left( \frac{15.5}{\eta_0\lambda_i^0} \right) = 18.8r_i + \left( \frac{15.3 \times 10^{12}}{r_i^3} \right) \left[ \frac{\tau}{\eta_0} (\epsilon_0 - \epsilon_\infty) / \epsilon_0^2 \right] \quad (2)$$

$$L^* = 18.8r_i + \left( \frac{15.3 \times 10^{12}}{r_i^3} \right) R^* \quad (3)$$

For convenience in plotting, this can be written as

$$L^* = \frac{15.5}{\eta_0\lambda_i^0} \text{ and } R^* = \left[ \frac{\tau}{\eta_0} (\epsilon_0 - \epsilon_\infty) / \epsilon_0^2 \right]$$

So that a plot of L\* versus R\* should be linear and r<sub>i</sub> can be obtained from both intercept and slope. Table-8 summarizes the ionic conductance of the chloride ion in pure solvents. Table-9 gives the solvent parameters needed for the F.B.Z calculations.

TABLE-8  
IONIC EQUIVALENT CONDUCTANCE OF THE CHLORIDE ION IN PURE SOLVENTS AT 25 °C

Solvent	Methanol	Ethanol	<i>n</i> -Propanol	<i>n</i> -Butanol
λ <sup>0</sup> Chloride <sup>-</sup>	52.31	21.87	10.39	7.76

TABLE-9  
PURE SOLVENT PARAMETERS AT 25 °C<sup>25,26</sup>

Solvent	ε <sub>0</sub>	ε <sub>∞</sub>	10 <sup>11</sup> τ (s)	10 <sup>2</sup> η <sub>0</sub> (poise)
MeOH	32.63	5.3	6.9	0.544
EtOH	24.33	4.5	14.4	1.084
<i>n</i> -PrOH	20.33	3.24	37.12	1.952
<i>n</i> -BuOH	17.45	2.95	47.73	2.589

ε<sub>0</sub>: Static (low frequency) dielectric constant of pure solvent at 25 °C.  
ε<sub>∞</sub>: Optical (infinite frequency) dielectric constant of pure solvent at 25 °C. τ: Dielectric relaxation time of pure solvent at 25 °C. η<sub>0</sub>: Bulk viscosity of pure solvent at 25 °C.

Table-11 gives values of radii (r<sub>i</sub>) calculated from the intercept and slope of the straight line graph in Fig. 3. A quantitative test for eqn. 3 is to compare the values of (r<sub>i</sub>) obtained from the slope and intercept of the straight line for Cl<sup>-</sup> ion

TABLE-10  
 APPLICATION OF ZWANZIG EQUATION FOR CHLORIDE IN DIFFERENT SOLVENTS AT 25 °C

Solvent	$\lambda_0\text{Cl}^-$	$10^2\eta_0$	$\lambda^0\text{Cl}^- \times \eta_0$	$[15.5/\lambda^0\text{Cl}^- \times \eta_0] = L^*$	$10^{11}\tau$	$10^{10}\tau/\eta_0$	$\epsilon_0$	$\epsilon_\infty$	$\epsilon_0 - \epsilon_\infty$	$10^{-2}\epsilon_0^2$	$R^* = [10^{10}\tau/\eta_0 (\epsilon_0 - \epsilon_\infty)/\epsilon_0^2]$	$10^{11}R^*$
MeOH	52.31	0.5442	0.285	54.454	6.9	126.803	32.63	5.3	27.33	10.647	3.255	32.549
EtOH	21.87	1.084	0.237	65.381	14.4	132.841	24.33	4.5	19.83	5.919	4.450	44.501
<i>n</i> -PrOH	10.39	1.952	0.203	76.425	37.12	190.164	20.33	3.24	17.09	4.133	7.863	78.631
<i>n</i> -BuOH	7.76	2.589	0.201	77.150	47.73	184.357	17.45	2.95	14.5	3.045	8.779	87.788

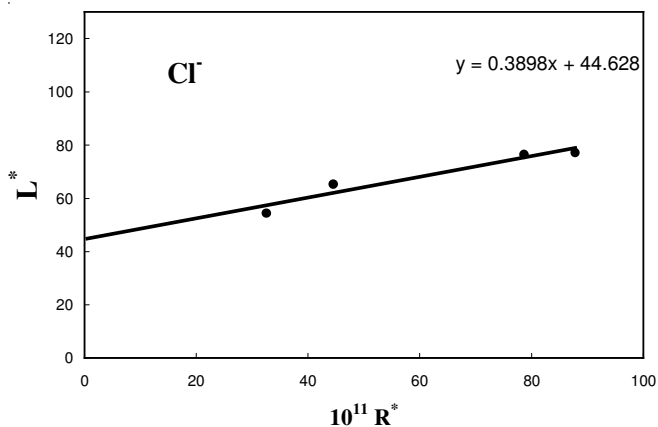

 Fig. 3. A plot of eqn. 3 for chloride ion in MeOH, EtOH, *n*-PrOH and *n*-BuOH at 25 °C

TABLE-11

HYDRODYNAMIC RADII FROM INTERCEPT AND ALSO HYDRATION RADII FROM SLOPE OF F.B.Z EQUATION

Ion	$r_i$ (Å) (Intercept)	$r_i$ (Å) (Slope)	$r_i$ (Å) (Pauling)
$\text{Cl}^-$	2.37	7.32	1.81
$\text{Br}^-$	1.45	6.47 <sup>27</sup>	1.95
$\text{I}^-$	1.42 <sup>27</sup>	6.86 <sup>27</sup>	2.16

(Fig. 3). It is noted that the two are different. It can be seen that the radii from the slope increases with increase in size of anions. However the radius from the intercept for  $\text{Cl}^-$  to  $\text{I}^-$  slightly decreases with increasing ionic size. This may be attributed to decreased solvation as previously reported in a similar work<sup>25,27,28</sup>. Nightingale<sup>27</sup> and Kay *et al.*<sup>28</sup>, calculated the hydrated radii and hydrodynamic radii for tetra-alkyl ammonium ions. They found that the hydrated radius increases with increasing ion size. The intercept value reflects factor closely related to the ion solvent interaction for a particular ion. Evan and Gardam<sup>20</sup> applied F.B.Z equation for tetra-alkylammonium salts in MeOH, EtOH, *n*-PrOH and *n*-BuOH at 25 °C. They attributed the scattering of the points and difference between the (intercept) and (slope) values to certain specific factors such as solvation which are ignored in the continuum model and these play an important role in determining ionic mobility. El-Hammamy *et al.*<sup>27</sup>, calculated the hydrated radii and hydrodynamic radii for acetylcholine ion and  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$  and  $\text{ClO}_4^-$  and *s*-alkylisothiuronium ions (*s*-*n*-Meis<sup>+</sup>, *s*-*n*-Buis<sup>+</sup>, *s*-*n*-Amis<sup>+</sup> and *s*-*n*-Heptis<sup>+</sup>) in  $\text{H}_2\text{O}$ , MeOH, *n*-PrOH and  $\text{CH}_3\text{CN}$  at 25 °C. They found that the

radii from the slope increase with increase in size for both cation and anions. However the radius from intercept for  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$ . Slightly decrease with increasing ion size. This may be attributed to decreased solvation as previously reported in a similar work<sup>1</sup>. The increase in the value of hydrodynamic radii ( $r_i$  intercept) for *s*-*n*-Meis<sup>+</sup>, *s*-*n*-Buis<sup>+</sup>, *s*-*n*-Amis<sup>+</sup> and *s*-*n*-Heptis<sup>+</sup> with increase in ion size may also attributed to ion solvation interaction.

## REFERENCES

- D.F. Evans and P. Gardam, *J. Phys. Chem.*, **72**, 3281 (1968).
- R.L. Kay, C. Zowowski and D.F. Evans, *J. Phys. Chem.*, **69**, 4208 (1965).
- A.M. Hafez, H. Sadek and M.Sh. Ramadan, *Electrochim. Acta*, **24**, 957 (1979).
- W.H. Lee and R.J. Wheaton, *J. Chem. Soc. Faraday Trans.*, **75**, 1128 (1979).
- B.A. Akrawi, W.H. Lee and R.J. Wheaton, *Acta Chem. Scand.*, **34A**, 2307 (1980).
- R.M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958).
- F. Accascina, A.D' Aprano and R. Triolo, *J. Phys. Chem.*, **71**, 3160 (1967).
- H. Sadek and R.M. Fuoss, *J. Am. Chem. Soc.*, **81**, 4507 (1959).
- N.H. El-Hammamy, S.T. El-Deeb and M.M.A. Gouda, *Pak. J. Sci. Ind. Res.*, **26**, 35 (1983).
- N.H. El-Hammamy and A.M. Ahmed, *Pak. J. Sci. Ind. Res.*, **31**, 697 (1988).
- N.H. El-Hammamy, M.M. El-Kholy and M.F. Amira, *J. Indian Chem. Soc.*, **85**, 1112 (2008).
- N.H. El-Hammamy, A.I. Kawana, S.A. El-Shazly and H.M. Moharem, *J. Alex. Pharm. Sci.*, **24**, 100 (2010).
- G. Pistoia and G. Pecci, *J. Phys. Chem.*, **74**, 1450 (1970).
- A.I. Kawana, *Bull. Electrochem.*, **16**, 225 (2000).
- N.H. El-Hammamy, A.I. Kawana, S.A. El-Shazly and H.M. Moharem, *J. Alex. Pharm. Sci.*, **24**, 97 (2010).
- N.H. El-Hammamy, A.M. Ismaeil, M.F. Amira and N.S. El-Sisy, *J. Indian Chem. Soc.*, **86**, 878 (2009).
- A.I. Kawana, M.T. Mohamed and N.H. El-Hammamy, *J. Indian Chem. Soc.*, **84**, 816 (2007).
- A.I. Kawana, N.H. El-Hammamy, N.M. El-Mallah and H.M. Moharem, *J. Chem. Pharm. Res.*, **2**, 301 (2010).
- R.M. Fuoss and L. Onsager, *J. Phys. Chem.*, **61**, 668 (1957); R.M. Fuoss, *J. Am. Chem. Soc.*, **81**, 2659 (1959).
- D.F. Evans and P. Gardam, *J. Phys. Chem.*, **73**, 158 (1969).
- N.H. El-Hammamy, M.F. Amira, S. Abou El-Enein and F.M. Abd El-Halim, *J. Indian Chem. Soc.*, **23**, 43 (1984).
- R.M. Fuoss, *Proc. Nat. Acad. Sci. USA*, **45**, 807 (1959).
- R.H. Boyd, *J. Chem. Phys.*, **35**, 1281 (1961).
- R. Zwanzig, *J. Chem. Phys.*, **38**, 1603, 1605 (1963).
- G. Atkinson and Y. Mori, *J. Phys. Chem.*, **71**, 3523 (1967).
- F. Buckley and A.A. Maryott, *Nat. Bur. Sids. Circular*, 589 (1958).
- N.H. El-Hammamy, A.I. Kawana and F.M. Abd El-Halim, *J. Electrochem. Soc. India*, **36**, 255 (1987).