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, Λ_0 (equivalent conductance at infinite dilution), a° (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° 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^{1,2} have clearly supported our findings concerning the influence of solvent on the association of ions. Hafez *et al.*³, have found that the decrease in Λ_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^{4,5} have measured the conductance of alkali metal iodides in methanol, ethanol and *n*-propanol at 25 °C. They found that Λ_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^{4,6} 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 relation⁶

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

Accasina *et al.*⁷, studied the conductance of LiClO_4 in dioxane-water mixtures at 25 °C and found a slight curvature

for applying ionic association equation⁶. Hafez *et al.*³ 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 equation⁶. In other cases a slight curvature was due to the interference of ion-solvent interaction⁸. El-Hammamy *et al.*⁹ measured the conductance of *N*- $\bar{N}$ -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.*¹⁰⁻¹² and Ahmed¹⁰ 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 equation⁶. 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 bonding¹³, 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 Λ_0 , a° 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 literature¹⁴. Methanol (B.D.H), ethanol (B.D.H), *n*-propanol (B.D.H) and *n*-butanol (B.D.H) were purified as previously reported¹⁵⁻¹⁸. The specific conductances for purified alcohols are listed in Table-5. The densities, viscosities and dielectric constant values were depicted¹⁵⁻¹⁸ in Table-5. All solutions were reported by reducing weight to *vacuo*. Salts were weighed using microbalance which reads to ± 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 cm^{-1} for dilute solutions.

RESULTS AND DISCUSSION

The measured equivalent conductance data are shown in Table-1. An approximate value of Λ_0 was estimated from of Λ versus $C^{1/2}$ plot. More accurate values of Λ_0 were estimated from the Fuoss-Kraus-Shedlovsky (F.K.S) equation,

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

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 α is the limiting tangent. The plot of $1/\Lambda S_{(z)}$ versus $(C A S_{(z)} f^2)$ gives $1/\Lambda_0$ as the intercept and $1/K_D \Lambda_0^2$ as the slope. The true values of Λ_0 , a° and K_A were derived using Fuoss-Onsager equation¹⁹ and starting by the value Λ_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 ± 0.02 for Λ_0 ; ± 2 for $J < 200$, ± 5 for $J = (200 \rightarrow 1000)$ and ± 10 for $J > 1000$. Fig. 1 shows the variation of a° with J , from which the average value of a° 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° and has the following equation¹⁹

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

where σ_1 and σ_2 are the functions of J . The derived constants are represented in Table-2. It reveals that Λ_0 decreases from methanol to *n*-butanol according to the ionic equivalent conduc-

Fig. 1. Variation of J and a° 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	Λ_0 (ohm ⁻¹ equiv ⁻¹ cm ²)	J	K_A	a° (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° 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° . 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: $K_A \text{Cl}^-$ (*n*-BuOH) > *n*-PrOH > EtOH > MeOH. In our case the trend is that K_A increases with increase the $-\text{CH}_2-$ group of alcohol increase, i.e., K_A increases from *n*-BuOH > *n*-PrOH > EtOH > MeOH.

El-Hammamy *et al.*^{11,12}, 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 ⁴ C (equiv L ⁻¹)	Λ (ohm ⁻¹ equiv ⁻¹ cm ²)	10 ⁴ C (equiv L ⁻¹)	Λ (ohm ⁻¹ equiv ⁻¹ cm ²)	10 ⁴ C (equiv L ⁻¹)	Λ (ohm ⁻¹ equiv ⁻¹ cm ²)	10 ⁴ C (equiv L ⁻¹)	Λ (ohm ⁻¹ equiv ⁻¹ cm ²)
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° and K_A for all organic solvents are in agreement with the present results. The gradual decrease of a° 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 $-\text{CH}_2-$ 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 equation⁷

$$\ln K_A = \ln \left(\frac{4\pi N a^{\circ 3}}{3000} \right) + \left(\frac{e^2}{a^\circ D k T} \right) + U$$

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 applied²⁰. 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:

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

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

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

$$b = \frac{e^2}{a^\circ D k T}$$

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 λ_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 discussed²¹. To calculate λ_0^+ for (*s*-acetylthiocholine)⁺, the average values obtained for λ_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° (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° values are probably attributed to ion solvation. In case of (*n*-BuOH) a° was smaller than the electrostatic radii ($R^+ + R^-$) which obtained from Stokes' equation. The surprisingly smaller a° 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 Λ_0 and K_A was obtained for tetrabutyl ammonium halides and perchlorate in different alcohol^{1,2} at 25 °C (Table-6).

From the above picture of the variation of both Λ_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^{1,2} 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 theory⁶. 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^{4,5}, that the association constant

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

Solvent	Λ (ohm ⁻¹ equiv ⁻¹ cm ²)	$\lambda_0^- \eta_0$ (ohm ⁻¹ equiv ⁻¹ cm ² p)	λ_0^- (ohm ⁻¹ equiv ⁻¹ cm ²)	λ_0^+ (ohm ⁻¹ equiv ⁻¹ cm ²)	R^+ (Å)	R^- (Å)	$R^+ + R^-$	a° (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

TABLE-5
SOLVENT PROPERTIES AT 25 °C¹⁵⁻¹⁸

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

TABLE-6
Λ₀ AND K_A VALUES IN DIFFERENT ALCOHOLS AT 25°C FOR
TETRABUTYL AMMONIUM HALIDES AND PERCHLORATE^{1,2}

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

TABLE-7
CONDUCTANCE DATA FOR SOME
ALKALI METAL SALTS AT 25 °C^{4,5}

Salt	Methanol		Ethanol		<i>n</i> -Propanol	
	Λ ₀	K _A	Λ ₀	K _A	Λ ₀	K _A
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^{4,5} assumption namely, the formation of solvent-separated ion pairs. Lee and Wheaton^{4,5} obtained a similar behaviour for alkali iodides in different alcohols.

Fig. 2 shows the plot of log K_A versus 1/D, which is linear as expected from the relation⁶:

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

Fig. 2. Variation of log K_A versus 1/D for *s*-acetylthiocholine-chloride at 25 °C

Accasina *et al.*⁷, studied the conductance of LiClO₄ in dioxane-water mixtures at 25 °C. They found a slight

curvature. Hafez *et al.*³ 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 equation⁶. In other cases a slight curvature was due to the interference of ion solvent interaction⁸.

Application of Zwanzig theory: Fuoss²² has given a relationship between the ionic conductivity of an ion in different solvents with solvent properties. Boyd²³ and Zwanzig²⁴ have improved it and expressed λ_i⁰ 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 Mori²⁵, 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_i 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 ⁰ - Chloride ⁻	52.31	21.87	10.39	7.76

TABLE-9
PURE SOLVENT PARAMETERS AT 25 °C^{25,26}

Solvent	ε ₀	ε _∞	10 ¹¹ τ (s)	10 ² η ₀ (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

ε₀: Static (low frequency) dielectric constant of pure solvent at 25 °C.
ε_∞: Optical (infinite frequency) dielectric constant of pure solvent at 25 °C. τ: Dielectric relaxation time of pure solvent at 25 °C. η₀: Bulk viscosity of pure solvent at 25 °C.

Table-11 gives values of radii (r_i) 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_i) obtained from the slope and intercept of the straight line for Cl⁻ ion

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

Solvent	$\lambda_0\text{Cl}^-$	$10^2\eta_0$	$\lambda^0\text{Cl}^- \times \eta_0$	$[15.5/\lambda^0\text{Cl}^- \times \eta_0] = L^*$	$10^{11}\tau$	$10^{10}\tau/\eta_0$	ϵ_0	ϵ_∞	$\epsilon_0 - \epsilon_\infty$	$10^{-2}\epsilon_0^2$	$R^* = [10^{10}\tau/\eta_0 (\epsilon_0 - \epsilon_\infty)/\epsilon_0^2]$	$10^{11}R^*$
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)
Cl^-	2.37	7.32	1.81
Br^-	1.45	6.47 ²⁷	1.95
I^-	1.42 ²⁷	6.86 ²⁷	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 Cl^- to I^- slightly decreases with increasing ionic size. This may be attributed to decreased solvation as previously reported in a similar work^{25,27,28}, Nightingale²⁷ and kay *et al.*²⁸, 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 Gardam²⁰ 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.*²⁷, calculated the hydrated radii and hydrodynamic radii for acetylcholine ion and Cl^- , Br^- , I^- and ClO_4^- and *s*-alkylisothiuronium ions (*s*-*n*-Meis⁺, *s*-*n*-Buis⁺, *s*-*n*-Amis⁺ and *s*-*n*-Heptis⁺) in H_2O , MeOH, *n*-PrOH and CH_3CN 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 Cl^- , Br^- and I^- . Slightly decrease with increasing ion size. This may be attributed to decreased solvation as previously reported in a similar work¹. The increase in the value of hydrodynamic radii (r_i intercept) for *s*-*n*-Meis⁺, *s*-*n*-Buis⁺, *s*-*n*-Amis⁺ and *s*-*n*-Heptis⁺ 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. Mohareem, *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. Mohareem, *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. Mohareem, *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).