

## Electrical Conductivity of s-Acetylthiocholine Halides and Perchlorate in Methanol at 35 °C

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### ABSTRACT

The conductance data of s-acetylthiocholine halides and perchlorate in methanol solution at 35 °C are presented. The data were analyzed using the Fuoss-Onsager equation to obtain the characteristic parameters: equivalent conductance at infinite dilution  $\Lambda_{\infty}$ , the closest distance of approach (solvation)  $a^{\circ}$  and association constant  $K_A$ . The trend of  $K_A$  is discussed in the light of the solvent separated-ion pair model. The electrostatic Stokes' radii  $R^+$  and  $R^-$  are calculated and their sum is compared with the value of  $a^{\circ}$ .

**Keywords:** Conductivity, s-acetylthiocholine halides and perchlorate, methanol, ionic association.

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### INTRODUCTION

It has been found recently that the dielectric constant of the medium plays a very important role concerning of the behaviour of electrolytes in solution. Various factors may influence the dielectric constant of the medium in the immediate neighbourhood of an ion (1). It was found that in very dilute solutions the dielectric constant of the pure solvent is the proper value to use for the so-called "limiting law". Furthermore, it has been shown that changes of the dielectric constant of the medium are closely connected with the corresponding changes of the velocity of homogeneous reaction in solutions. An approach to a theoretical interpretation correlating the changes in medium and the simultaneous changes in the velocity of certain catalyzed reaction was reported (2). The effect of solvent may be considered as being two fold (a) stabilize the pairs due to the hydrogen bond chains in the alcohol and (b) solvate anions by hydrogen bonding (3), so that the expected  $K_A$  values may increase with the anionic radius of salts with the same cation. The participation of alcohols in the ion-pair formation equilibrium, therefore, should involve both steric and coulombic effects. On the basis of this approach, the structure modifications of the alcoholic polymers generated by added solvents should result in a variable influence of the alcohol molecules on the ion-pair association of electrolytes. Several 3-parameter equations (4-5)

and 4-parameter equations (6-9) were suggested to illustrate the relation between  $\Lambda_\infty$ ,  $a^\circ$  and  $K_A$ . All of which are based on model of charged hard spheres in a dielectric medium.

This paper reports measurements of the conductance of s-acetylthiocholine halides and perchlorate in methanol at 35°C. The possibility of applying Fuoss-Onsager 3-parameter equation 1:1 associated electrolytes is studied. The solvent separated-ionpairs model (10) is used to analyze  $K_A$ . Finally,  $a^\circ$  comparison is made between the summation of stokes' electrostatic radii and  $a^\circ$ .

## MATERIALS AND METHODS

The s-acetylthiocholine bromide, iodide and perchlorate were purified as reported in literature (11), methanol (B.D.H) was purified previously reported (12). The specific conductance for purified methanol at 35°C was found to be  $[(4.7-7.6) \times 10^{-7}] \Omega^{-1}\text{cm}^{-1}$ . The density of methanol was determined at 35°C was found to be 0.7815 g / cm<sup>3</sup>.

Its viscosity was measured at 35°C, it was found to be  $0.4620 \times 10^{-2}$  p. The dielectric constant value was used as reported in literature (12). All solutions were reported by reducing weight to vacuo. Salts were weighed on 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 meter (Conductivity Bridge) was model Crison Cl P31 and the cell with bright platinum electrodes was used. The cell constant was 0.1 cm<sup>-1</sup> for dilute solutions.

## RESULTS AND DISCUSSION

The measured equivalent conductance data are shown in **Table I**. An approximate value of  $\Lambda_\infty$  was estimated from of  $\Lambda$  vs.  $C^{1/2}$  plot. More accurate values of  $\Lambda_\infty$  were estimated from the Fuoss-Kraus-Shedlovsky equation,

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

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 can be calculated from the following equation

$$z = \alpha (C\Lambda)^2 / \Lambda_\infty^{3/2}$$

in which  $\alpha$  is the limiting tangent. The plot of  $1/\Lambda S_{(z)}$  vs.  $(C\Lambda S_{(z)} f^2)$  gives  $1/\Lambda_\infty$  as the intercept and  $1/K_D \Lambda_\infty^2$  as the slope. The true values of  $\Lambda_\infty$ ,  $a^\circ$  and  $K_A$  were derived using Fuoss-Onsager equation (4) and starting by the value  $\Lambda_\infty$  which was obtained from (F.K.S.) equation. In our calculations a computer program on an IBM-PC machine was used. The accuracies required in these computation are  $\pm 0.02$  for  $\Lambda_\infty$ ;  $\pm 2$  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 (4)

$$J = \sigma_1 \Lambda_\infty + \sigma_2$$

where  $\sigma_1$  and  $\sigma_2$  are the function of  $J$ . The derived constants are represented in **Table II**. **Table II** reveals that  $\Lambda_0$  increases from acetylthiocholine  $\text{Br}^-$  to  $\text{ClO}_4^-$  according to the ionic equivalent conductance of anions. The values of  $a^\circ$  decrease with increasing the size of anions. This supports the opinion (10) that for salts with common cation, the size of the anion becomes the essential factor in controlling the extent of ion – pairing. The solvation of these anions of acetylthiocholine halides and perchlorate increases in the direction:  $\text{Br}^- > \text{I}^- > \text{ClO}_4^-$ , which is in accordance with the 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:  $\text{ClO}_4^- > \text{I}^- > \text{Br}^-$ . In our case the trend is that  $K_A$  increases with increase the size of anions (except  $\text{ClO}_4^-$ ).

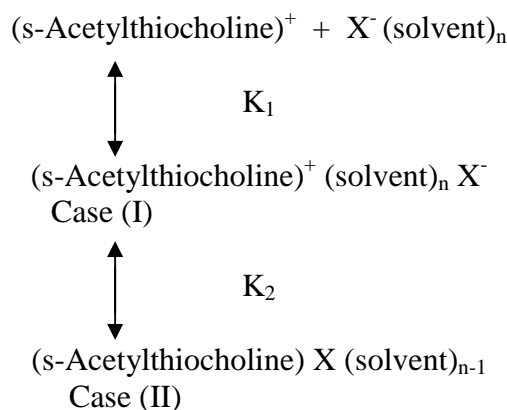
El-Hammamy *et al* (13-18), measured the conductances of acetylthiocholine halides and perchlorate in methanol, ethanol, n-propanol, n-butanol and 2-propanol solutions at  $25^\circ\text{C}$  and methanol at  $30^\circ\text{C}$ . They found that the same trend of solvation ( $a^\circ$ ) and association for all organic solvents are in agreement with the present results. The gradual decrease of  $a^\circ$  with  $K_A$  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 the size of anions of s-acetylthiocholine halides and perchlorate can be explained in the light of the  $U$  term in equation (19)

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

where,

$$U = \Delta S / k - E_s / k T$$

$\Delta S / k$  is the entropy/Boltzman constant ratio which illustrates the probability of the orientation of solvent molecules around the free ions, and  $E_s / k T$  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 halides and perchlorate are given in **Table III**. The result reveals that the value of  $U$  slightly increase from  $\text{Br}^-$  to  $\text{I}^-$ , entropy/boltzman ratio term  $\Delta S / k$  is the probability of orientation of solvent molecules around the free ions is more predominant than the ion-dipole interaction term (except  $\text{ClO}_4^-$ ). Finally, the solvent separated ion-pair model is applied (10). In this model a multiple-step association is occurs, i.e. solvent separated-ion pair can be illustrated by the following scheme:



The association constant is given by the following expression:

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

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

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

$K_2$  was thus calculated. The results compiled in **TABLE III**, indicate that  $K_1$  increases from  $\text{Br}^-$  to  $\text{ClO}_4^-$  i.e., the ion-pair prefers the more solvated form (case I) than the desolvated form (case II).

**TABLE.I: Conductance of s-Acetylthiocholine salts in methanol at 35°C**

Acetylthiocholine bromide		Acetylthiocholine iodide		Acetylthiocholine perchlorate	
$10^4 C^*$	$\Lambda^{**}$	$10^4 C$	$\Lambda$	$10^4 C$	$\Lambda$
16.977	124.200	15.485	128.705	7.0467	145.82
15.361	125.100	13.728	129.788	6.3642	146.350
14.141	125.690	12.585	130.634	5.7878	146.840
12.981	126.336	11.577	131.246	5.2832	147.270
11.972	126.908	10.676	131.916	4.8851	147.624
11.076	127.428	9.8194	132.460	4.5350	147.940
10.328	127.944	9.0959	133.209	4.2502	148.200
9.6931	128.379	8.4573	133.573	3.9801	148.490
9.1015	128.815	7.8934	134.058	3.7505	148.710
				3.5232	148.940

\* equiv L<sup>-1</sup>      \*\* ohm<sup>-1</sup> equiv<sup>-1</sup> cm<sup>2</sup>

**TABLE:II. Characteristic parameters for s-Acetylthiocholine salts in methanol at 35°C.**

salts	$\Lambda_0$ (ohm <sup>-1</sup> equiv <sup>-1</sup> cm <sup>2</sup> )	J	$K_A$	$a^{\circ}$ (Å)	$\sigma_A$
Ac.Th.Br	140.80± 0.05	3458.0	34.32	6.50	0.05
Ac.Th. I	146.46± 0.06	3172.9	41.99	5.25	0.06
Ac.Th.ClO <sub>4</sub>	156.08± 0.03	3150.2	15.83	5.00	0.03

**TABLE:III. Calculated values of  $K_2$  and U of s-Acetylthiocholine Halides and Perchlorate in methanol at 35°C**

salts	$K_A$	$K_1$	$K_2$	U
Ac.Th.Br	34.318	11.260	2.048	1.12250
Ac.Th.I	41.997	11.524	2.644	1.29321
Ac.Th.ClO <sub>4</sub>	15.833	12.900	0.185	0.20489

### Radii of ions

The electrostatic radii  $R^+$  and  $R^-$  are given Stokes' by equation

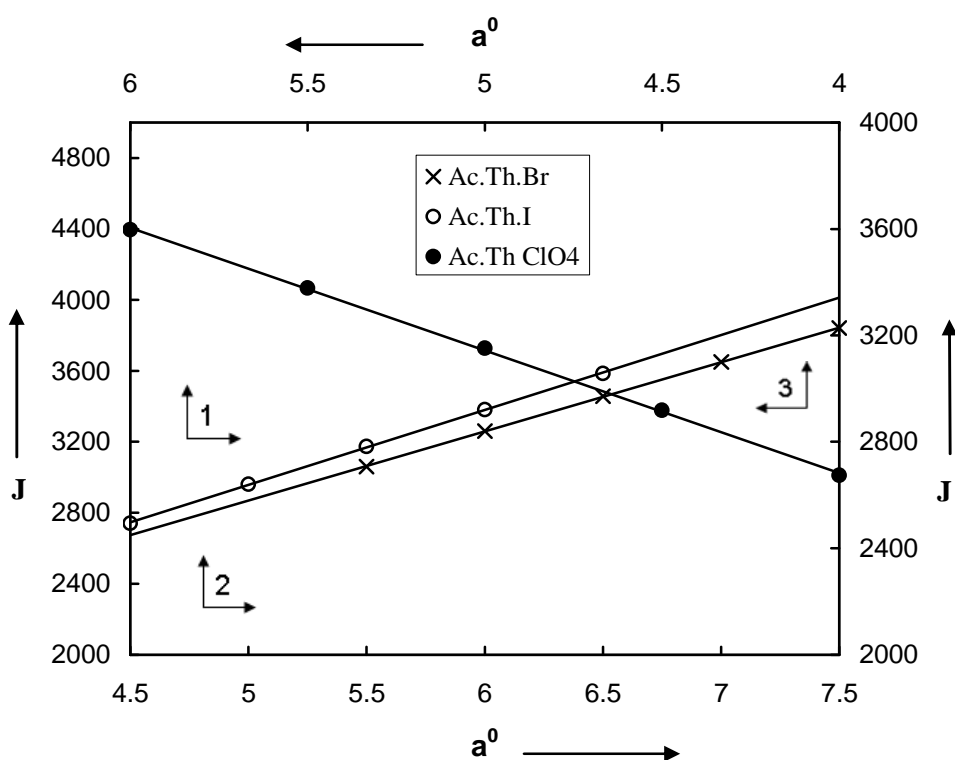
$$R^{\pm} = 0.8194 \times 10^{-8} / \lambda_0^{\pm} \eta_0$$

In the present case  $\lambda_{\infty}^{-}$  values were obtained from the intercept of the straight lines resulting from the plots of Walden products  $\Lambda_{\infty} \eta_{\infty}$  versus the reciprocal of the molecular weight as previously discussed (20). To calculate  $\lambda_{\infty}^{+}$  for (s-acetylthiocholine)<sup>+</sup>, the average value obtained for  $\lambda_{\infty}^{+}$  in case of the Br<sup>-</sup>, I<sup>-</sup> and ClO<sub>4</sub><sup>-</sup> was used in calculations. Applying Stokes' equation, one may obtain the values of both R<sup>+</sup> and R<sup>-</sup>. These data are recorded in **Table IV**. It can be seen from **TABLE IV** that the values of  $a^{\circ}$  are greater than the electrostatic radii (R<sup>+</sup>+R<sup>-</sup>) which obtained from Stokes' equation. This is due to the solvation of ions (13).

**TABLE:IV. Calculation of the radii of the ions for s-Acetylthiocholine salts in methanol at 35°C**

salts	<sup>(1)</sup> $\Lambda_{\infty}$	$\lambda_{\infty}^{-} \eta_{\infty}$ <sup>(2)</sup>	$\lambda_{\infty}^{-}$ <sup>(1)</sup>	$\lambda_{\infty}^{+}$ <sup>(1)</sup>	Av. $\lambda_{\infty}^{+}$ <sup>(1)</sup>	R <sup>+</sup> (Å)	R <sup>-</sup> (Å)	R <sup>+</sup> +R <sup>-</sup>	$a^{\circ}$ (Å)
Ac.Th.Br	140.80	0.29198	63.2	77.63	77.04±0.38	2.302	2.806	5.108	6.5
Ac.Th.I	146.46	0.32248	69.8	76.66					5.25
Ac.Th.ClO <sub>4</sub>	156.08	0.36590	79.2	76.86					5.0

(1)  $\text{ohm}^{-1} \text{equiv}^{-1} \text{cm}^2$                       (2)  $\text{ohm}^{-1} \text{equiv}^{-1} \text{cm}^2 \text{p}$



**Fig .1: Variation of J and  $a^{\circ}$  in methanol at 35°C**

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