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## **Electrical Conductivity of s-Acetylthiocholine Halides and Perchlorate in Acetonitrile at 40 °C**

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### **ABSTRACT**

The conductance of s-acetylthiocholine halides and perchlorate has been measured in acetonitrile at 40 °C. The data were analyzed using the Fuoss-Onsager equation for 1:1 associated electrolytes and the characteristic functions,  $\Lambda$  (equivalent conductance at infinite dilution),  $a^\circ$  [contact distance of approach (solvation)] and  $K_A$  (association constant) were computed.  $K_A$  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 above model.

**Keywords:** Conductivity, s-acetylthiocholine salts, acetonitrile, ionic association.

### **INTRODUCTION**

Studies on electrolytic conductance of s-acetylthiocholine halides and perchlorate solutions in acetonitrile at 25, 30, 35 °C has been reported recently (1-3). The present communication reports a precise study of the conductance of s-acetylthiocholine halides and perchlorate in acetonitrile at 40 °C, in order to throw light on the behaviour of these salts in simple solvents.

### **EXPERIMENTAL SECTION**

The s-acetylthiocholine bromide, iodide and perchlorate were purified as reported (4), acetonitrile (B.D.H) was purified previously reported (5). The specific conductance for purified acetonitrile at 40 °C was found to be  $(5-8 \times 10^{-8}) \Omega^{-1} \text{cm}^{-1}$ . The density of pure acetonitrile was determined at 40 °C. It was found to be 0.7492 g / cm<sup>3</sup>. Its viscosity was measured at 40 °C, it was found to be  $0.2995 \times 10^{-2}$  poise. The dielectric constant value was 34.74 (6). 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  $0.1 \text{ cm}^{-1}$  for dilute solutions.

## RESULTS AND DISCUSSION

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

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

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

$$z = \alpha (C\Lambda)^2 / \Lambda_0^{3/2} \quad (2)$$

in which  $\alpha$  is the limiting tangent. The plot of  $1/\Lambda S_{(z)}$  vs.  $(C\Lambda S_{(z)} f^2)$  gives  $1/\Lambda_0$  as the intercept and  $1/K_D \Lambda_0^2$  as the slope. More accurate values of  $\Lambda_0$ ,  $a^\circ$  and  $K_A$  were obtained from Fuoss-Onsager equation (7), with the aid of special computer program on an IBM-PC, starting by the value  $\Lambda_0$  which was obtained from (F.K.S) equation. The accuracies required in these computation are  $\pm 0.02$  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 reading , where  $J$  is being a function of  $a^\circ$  and has the following equation (7)

$$J = \sigma_1 \Lambda_0 + \sigma_2 \quad (3)$$

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 s-acetylthiocholine bromide to perchlorate according to the ionic equivalent conductance of anions. The values of  $a^\circ$  decrease with increasing the size of anions. This supports the opinion (8) that for salts with common cations, the size of the anion becomes the essential factor in controlling the extend of ion pairing.

**TABLE. I: Conductance of s-Acetylthiocholine salts in acetonitrile at 40°C**

Acetylthiocholine bromide		Acetylthiocholine iodide		Acetylthiocholine perchlorate	
$10^4 C^*$	$\Lambda^{**}$	$10^4 C$	$\Lambda$	$10^4 C$	$\Lambda$
12.250	181.40	5.8564	195.64	5.5696	187.43
10.498	184.60	5.1984	197.79	4.7961	190.41
9.1204	187.50	4.6656	199.12	4.2025	193.38
8.1769	190.11	4.2436	200.79	3.7636	195.47
6.9169	193.32	3.6481	202.97	3.2041	198.61
6.0516	195.56	3.2761	204.26	2.8224	200.81
5.3361	197.66	2.9584	205.58	2.4964	203.05
4.840	199.24	2.6896	206.67	2.2201	204.68

\* equiv  $L^{-1}$       \*\*  $ohm^{-1} equiv^{-1} cm^2$

The solvation of these anions of s-acetylthiocholine halides and perchlorate increases in the direction:  $Br^- > I^- > ClO_4^-$ , 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 increased in the order:  $\text{ClO}_4^- > \text{I}^- > \text{Br}^-$ . In our case the trend is that  $K_A$  increases with increasing the size of anions.

**TABLE:II. Characteristic parameters for s-Acetylthiocholine salts in acetonitrile at 40 °C.**

salts	$\Lambda_\infty$ ( $\text{ohm}^{-1} \text{equiv}^{-1} \text{cm}^2$ )	J	$K_A$	$a^\circ$ (Å)	$\sigma_\Lambda$
Ac.Th.Br	221.98	4200.3	182.10	8.037	0.21
Ac.Th.I	222.77	3999.7	197.89	7.51	0.12
Ac.Th. $\text{ClO}_4$	224.86	3657.4	365.9	6.64	0.23

**TABLE:III. Calculated values of  $K_2$  and U of s-Acetylthiocholine Halides and Perchlorate in acetonitrile 40 °C.**

salts	$K_A$	$K_1$	$K_2$	U
Ac.Th.Br	182.1	8.845	19.587	3.02
Ac.Th.I	197.89	8.254	22.975	3.17
Ac.Th. $\text{ClO}_4$	365.9	7.452	48.100	3.89

**TABLE:IV. Calculation of the radii of the ions for s-Acetylthiocholine salts in acetonitrile at 40 °C.**

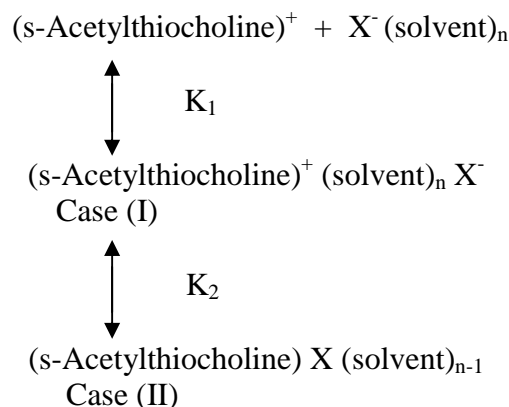
salts	$\Lambda_\infty$ <sup>(1)</sup>	$\lambda_\infty^- \eta_v$ <sup>(2)</sup>	$\lambda_\infty^-$ <sup>(1)</sup>	$\lambda_\infty^+$ <sup>(1)</sup>	Av. $\lambda_\infty^+$ <sup>(1)</sup>	$R^+$ (Å)	$R^-$ (Å)	$R^+ + R^-$	$a^\circ$ (Å)
Ac.Th.Br	221.98	0.34841	116.33	105.65			2.352	4.948	8.04
Ac.Th.I	222.77	0.35131	117.30	105.47	105.41±0.203	2.596	2.332	4.928	7.51
Ac.Th. $\text{ClO}_4$	224.86	0.35868	119.76	105.10			2.284	4.880	6.64

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

El-Hammamy *et al.* (1-3) found that, for s-acetylthiocholine halides and perchlorate, the order of solvation ( $a^\circ$ ) in acetonitrile at 25 °C, 30 °C and 35 °C was  $\text{Br}^- > \text{I}^- > \text{ClO}_4^-$ , i.e., solvation ( $a^\circ$ ) decreased with increasing the size of anions, a fact which agree with our results. Conductance measurements studies of s-acetylthiocholine halides and perchlorate in methanol (9), ethanol (10), n-propanol (11), n-butanol (12) and 2-propanol (13) at 25 °C, were reported to follow the order of solvation ( $a^\circ$ ) of  $\text{Br}^- > \text{I}^- > \text{ClO}_4^-$ , which agree with our results. The gradual decrease of  $a^\circ$  with increase of  $K_A$  among the studied 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 could be explained in the light of the U term in equation (14)

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

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.



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 increases from Br<sup>-</sup> to ClO<sub>4</sub><sup>-</sup>, i.e. entropy ΔS / k is more predominant than the ion – dipole interaction term. Finally, the solvent separated ion-pair model can be applied (8). In this model a multiple-step association was suggested as illustrated scheme 1:

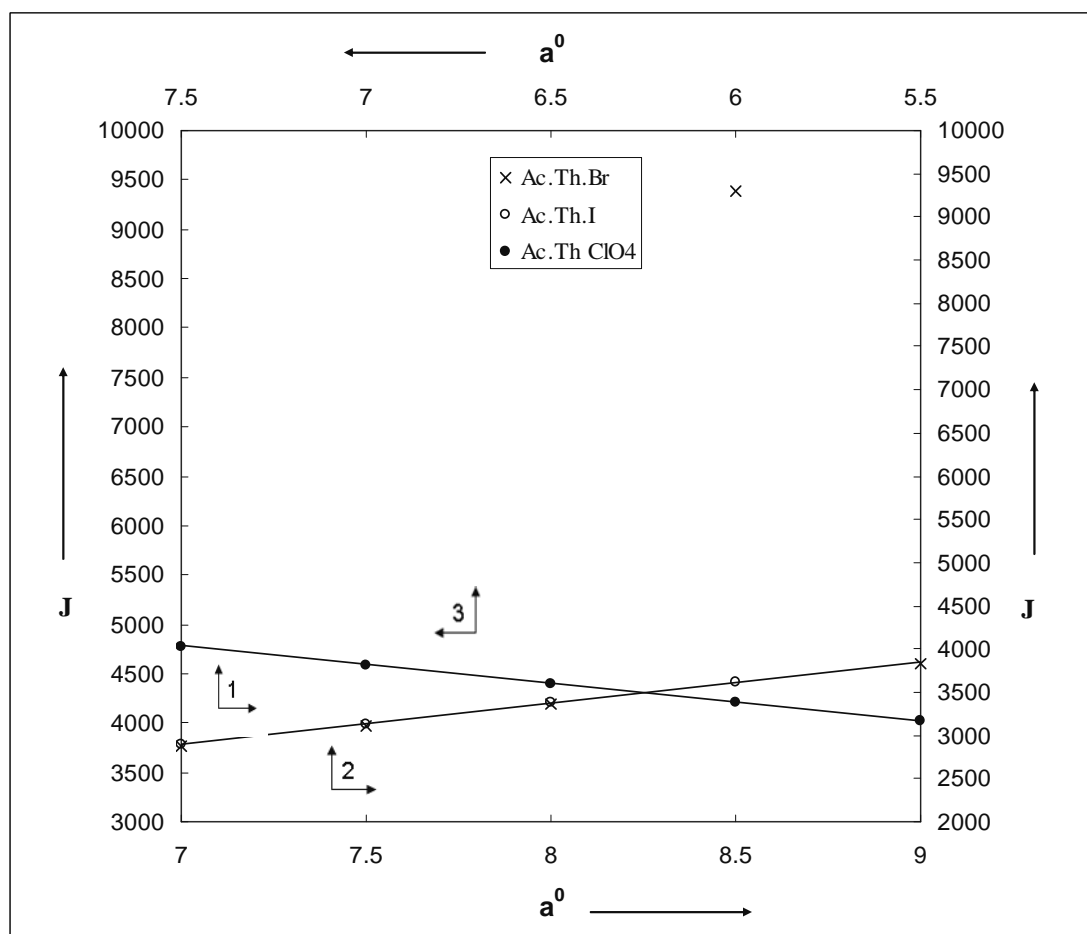
The association constant is given by the following expression :

$$K_A = K \Sigma = \frac{[C_{(\text{ion-pairs})}]}{[C_{(\text{s-acetylthiocholine})^+}] [C_{X^-(\text{solvent})_n}]} = K_1 (1+K_2), \quad (5)$$

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

$$K_1 = \frac{4\pi N a^{\circ 3}}{3000} e^b, \quad (6)$$

$K_2$  was thus calculated. The results compiled in **TABLE III**, indicated that  $K_2$  increased from Br<sup>-</sup> to ClO<sub>4</sub><sup>-</sup>, i.e., the ion-pair preferred the desolvated form (case II) than the solvated form (case I).



**Fig .1:** Variation of J and  $a^\circ$  in acetonitrile at 40 °C

**Radii of ions**

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

$$R^\pm = 0.8194 \times 10^{-8} / \lambda^\pm \eta_0 \quad (7)$$

In the present case  $\lambda^\pm$  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 (15). To calculate  $\lambda^+$  for (s-acetylthiocholine)<sup>+</sup>, the average value obtained for  $\lambda^+$  in case of the  $\text{Br}^-$ ,  $\text{I}^-$  and  $\text{ClO}_4^-$  was used in calculations. Applying Stokes' equation, one may obtain the values of both  $R^+$  and  $R^-$ . 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 ( $R^+ + R^-$ ) which obtained from Stokes' equation. The surprisingly greater  $a^\circ$  values are probably attributed to ion solvation.

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