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Electrical Conductivity of s-Acetylthiocholine Halides and Perchlorate in Methanol at 40°C

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ABSTRACT

The conductance of s-acetylthiocholine halides and perchlorate has been measured in methanol at 40°C.The data were analyzed using Fuoss-Onsager equation for 1:1 associated electrolytes and the characteristic functions, $\Lambda_{\circ}$ (equivalent conductance at infinite dilution), a° [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° confirming the above model.

Keywords: Conductivity, s-acetylthiocholine salts, methanol, ionic association.

INTRODUCTION

Studies on electrolytic conductance of s-acetylthiocholine halides and perchlorate solutions in water, methanol, ethanol, n-propanol, n-butanol and 2-propanol at 25°C, have been reported recently (1-6). The present communication reports a precise study of the conductance of s-acetylthiocholine halides and perchlorate in methanol at 40°C in order to throw light on the behaviour of these salts in simple solvents.

EXPERIMENTAL SECTION

S-acetylthiocholine bromide, iodide and perchlorate were purified as reported in the literature (1), methanol (B.D.H) was purified as previously reported (7). The specific conductance of thepurified methanol at 40°C was found to be (4.9-7.3 × 10^{-7}) $\Omega^{-1}cm^{-1}$. The density of methanol was determined at 40°C. It was found to be 0.7765 g / cm^3.

Its viscosity was measured at 40°C, it was found to be 0.4220× 10^{-2} p. The dielectric constant value was used as reported in literature (8).

All solutions were reported by reducing weight to vacuo. Salts were weighed on 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 meter (Conductivity Bridge) was model Crison Cl P31 and the cell with bright platinum electrodes was used. The cell constant was 0.1 $cm^{-1}$for dilute solutions.

RESULTS AND DISCUSSION

The measured equivalent conductance data are shown in *Table I.* An approximate value of $\Lambda_\circ$ (estimated from the extrapolation of Λ vs. $C^{1/2}$ plot) introduced into Fuoss-Kraus-Shedlovsky (F.K.S) equation to obtain accurate values:

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

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

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

where α is the limiting tangent. Plot of 1/Λ $S_{(z)}$ vs. ($C\Lambda S_{(z)}f^2$) gives 1/$\Lambda_\circ$ as the intercept and 1/ K_D $\Lambda_\circ^2$ as the slope. More accurate values of $\Lambda_\circ$, $\overset{\circ}{a}$ and K_A were obtained from Fuoss-Onsager equation (9), with the aid of special computer program on an IBM-PC, starting by the value $\Lambda_\circ$ which was obtained from (F.K.S.) equation. The accuracies required in these computation are ± 0.02 for $\Lambda_\circ$; ± 2 for J <200, ± 5 for J = (200→1000) and ± 10 for J > 1000.

Fig. 1 shows the variation of a° with J. by the aid of this calibration curve, the average value of a° determined from the corresponding average value of J. Knowing that J is being a function of a° and is represented by the following equation (9).

$$J = \sigma_1 \Lambda_\circ + \sigma_2 \qquad (3)$$

where σ_1 and σ_2 are the function of J. The derived constants are represented in *Table II.* In This Table, $\Lambda_\circ$ increases from acetylthiocholine Br^- to ClO_4^- according to the ionic equivalent conductance of the anions. The values of a° decrease with increasing the size of anions indicating that it controls the extent of ion pairing. The solvation of these anions increases in the order: Br^- > I^- > ClO_4^-, which is in accordance with the 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: ClO_4^- > I^- > Br^- and the trend of K_A increases with decreasing the size of the anions.

El-Hammamy et al (2-6), measured the conductances of acetylthiocholine halides and perchlorate in methanol, ethanol, n-propanol , n-butanol and 2-propanol solutions at 25°C. They found that the same trend of solvation (a°) for all organic solvents are in agreement with the present results.

The gradual decrease of a° with K_A among the studied salts (s-acetylthiocholine halides and perchlorate in methanol at 40°C) was attributed to the relative position of the anion with respect to the cation which may not be completely spherical. The decrease of K_A with increasing the size of the anions of s-acetylthiocholine halides and perchlorate can be explained in the light of the U term in the following equation (10).

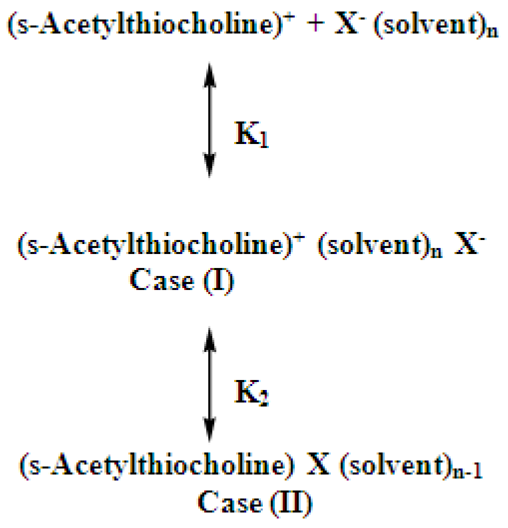
$$\ln K_A = \ln (4\pi N a^{\circ 3}/3000) + (e^2 / a^{\circ} DkT) + U \qquad (4)$$

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 which they can form.

The values of U term of s-acetylthiocholine halides and perchlorate are given in *Table III.* The results reveal that the value of U slightly decrease from Br^- to ClO_4^-, i.e. ion – dipole interaction term (E_s/kT) is more predominant than the entropy term.

Finally, the solvent separated ion-pair model is applied (11). In this model a multiple-step association is occurred, i.e. solvent separated-ion pair can be illustrated by the following scheme:



The association constant is given by the following expression:

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

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

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

and

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

K_2 was thus calculated. The results complied in *TABLE III*, indicated that K_1 increases from Br^- to ClO_4^- i.e., the ion-pair prefers the more solvated form (case I) than the desolvated form (case II).

Radii of ions

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

$$R^{\pm} = 0.8194 \times 10^{-8} / \lambda_{\circ}^{\pm} \eta_{\circ}$$

In the present case $\lambda^-_{\circ}$ values were obtained from the intercept of the straight lines resulting from plots of Walden products $\Lambda_{\circ} \eta_{\circ}$ versus the reciprocal of the molecular weight as previously discussed (12). To calculate $\lambda^+_{\circ}$ for (s-acetylthiocholine)$^+$, the average value obtained for $\lambda^+_{\circ}$ in case of Br^-, I^- and 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° are greater than the electrostatic radii (R^++R^-) which obtained from Stokes' equation. The surprisingly greater a° values are probably attributed to ion solvation.

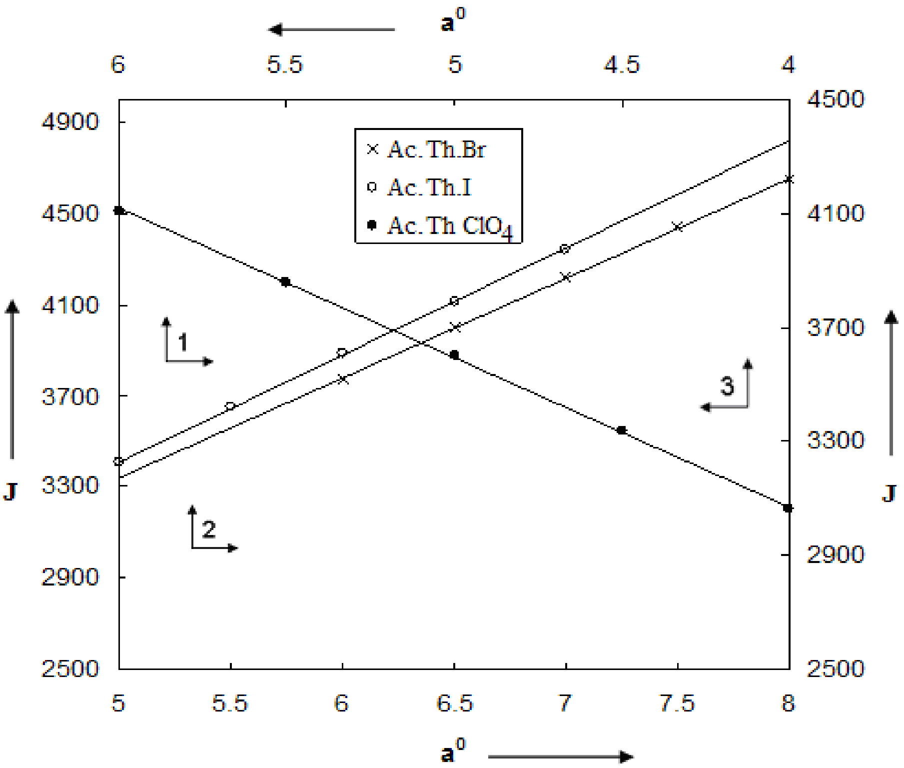


Fig .1: Variation of J and a° in methanol at 40 °C

TABLE I: Conductance of s-Acetylthiocholine salts in methanol at 40°C

Acetylthiochline bromide		Acetylthiocholine iodide		Acetylthiocholine perchlorate	
10^4 C*	Λ**	10^4 C	Λ	10^4 C	Λ
14.860	115.196	13.288	132.725	14.513	134.292
13.033	117.272	11.735	135.068	12.833	137.224
13.216	117.865	10.528	136.526	11.543	140.003
11.822	120.108	9.4909	137.954	10.259	141.638
10.751	122.280	8.6191	139.015	9.4051	142.955
9.8719	123.745	7.9261	140.649	8.6395	144.265
9.1540	124.929	7.3240	141.425	7.9960	145.459
8.4435	123.204	6.8356	142.876	7.4777	146.705
7.8631	127.252	6.3898	143.540	6.9981	147.910

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

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

salts	$\Lambda_\circ$ (ohm^{-1} $equiv^{-1}$ cm^2)	J	K_A	a° (Å)	σ_Λ
Ac.Th.Br	157.80± 0. 38	4109.2	311.00	6.775	0.38
Ac.Th. I	163.10± 0. 33	3892.1	160.94	6.025	0.33
Ac.Th.ClO_4	172.98± 0.44	3508.4	207.90	4.8125	0.44

TABLE III: Calculated values of K_2 and U of s-Acetylthiocholine Halides and Perchlorate in methanol at 40°C.

salts	K_A	K_1	K_2	U
Ac.Th.Br	311.03	11.81	25.35	3.27
Ac.Th.I	160.94	11.64	12.83	2.63
Ac.Th.ClO_4	207.90	12.78	15.27	2.79

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