Electrical Conductivity of s-Acetylthiocholine Halides and Perchlorate in ethanol at 30°C

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ABSTRACT

The conductance of s-acetylthiocholine halides and perchlorate has been measured in ethanol at 30°C.The data were analyzed using the Fuoss-Onsager equation for 1:1 associated electrolytes and the characteristic functions, $\Lambda_\circ$ (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.

Keywords: Conductivity, s-acetylthiocholine salts, ethanol, ionic association, solvation.
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INTRODUCTION

When the higher alcohols are chosen as the solvent system, the pattern of ionic association of hydroxyl solvents may be investigated without such complications as three dimensional structural effects or small association constants. This homologous series also allows investigation over wide variation of dielectric constant, viscosity and temperature. This paper, reports a precise study of the conductance of s-acetylthiocholine halides and perchlorate in ethanol at 30°C, in order to throw light on the behaviour of these salts in simple solvents.

MATERIALS AND METHODS

The s-acetylthiocholine bromide, iodide and perchlorate were purified as reported in literature (1), ethanol (B.D.H) was purified previously reported (2). The specific conductance for purified ethanol at 30°C was found to be (1.2-1.26 $\times$ 10^{-8}) Ω^{-1}cm^{-1}. The density of ethanol was determined at 30°C was found to be 0.7808 g / cm^3.

Its viscosity was measured at 30°C, it was found to be 0.992$\times$ 10^{-2} p. The dielectric constant value was used as reported in literature (3). 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.

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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 $\Lambda_\circ$ was estimated from of Λ vs. $C^{1/2}$ plot. More accurate values of $\Lambda_\circ$ were estimated from the Fuoss-Kraus-Shedlovsky equation,

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

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

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

in which α is the limiting tangent. The plot of $1/\Lambda\, S_{(z)}$ vs. $(C\Lambda S_{(z)} f^2)$ gives $1/\Lambda_\circ$ as the intercept and $1/K_D \Lambda_\circ^2$ as the slope. The true values of $\Lambda_\circ$, a° and K_A were derived using Fuoss-Onsager equation (4) and starting by the value $\Lambda_\circ$ 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 ± 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, 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 equation (4)

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

where σ_1 and σ_2 are the function of J. The derived constants are represented in *Table II*. *Table II* reveals that $\Lambda_\circ$ increases from acetylthiocholine Br$^-$ to ClO$_4^-$ according to the ionic equivalent conductance of anions. The values of a° decrease with increasing the size of anions. This supports the opinion (4) 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: 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$^-$. In our case the trend is that K_A increases with increase the size of anions.

Table I: Conductance of S-acetylthiocholine Salts in Ethanol at 30°C.

Acetylthiocholine bromide		Acetylthiocholine iodide		Acetylthiocholine perchlorate	
10^4 C	Λ	10^4 C	Λ	10^4 C	Λ
9.6314	51.045	5.0071	55.561	5.6917	57.359
8.4002	51.400	4.3018	55.977	4.8261	58.252
7.4271	51.711	3.7633	56.345	4.2306	58.881
6.6553	51.959	3.3481	56.648	3.7428	59.408
5.8090	52.259	2.8845	56.991	3.3458	59.781
5.0916	52.541	2.5226	57.304	3.0326	60.210
4.5453	52.757	2.29312	57.490	2.7661	60.511
4.1314	52.940	2.0455	57.706	2.5475	60.804
				2.3632	61.104

10^4 C is in equiv. L^{-1}   *Λ is in ohm^{-1} equiv^{-1} cm^2*

**TABLE:II. Characteristic parameters for Acetylthiocholine salts in Ethanol at 30˙C.**

salts	$\Lambda_\circ$ (ohm^{-1} equiv^{-1} cm^2)	J	K_A	a° (Å)	σ_Λ
Ac.Th.Br	56.872	3169.7	27.914	8.0	0.011
Ac.Th. I	61.095	3265.7	78.846	7.5	0.010
Ac.Th.ClO$_4$	66.302	3372.0	201.23	6.99	0.048

TABLE:III. Calculated values of K₂ and U of Acetylthiocholine Halides and Perchlorate in Ethanol 30˙C.

salts	K_A	K_1	K_2	U
Ac.Th.Br	27.914	24.011	0.163	3.329
Ac.Th.I	78.846	24.040	2.280	1.188
Ac.Th.ClO$_4$	201.23	24.434	7.236	2.108

TABLE IV: Conductance parameters s-Acetylthiocholine halides and perchlorate at 25°C and 30°C in ethanol by using Fuoss-Onsager equation

Salts	T °C	$\epsilon_\circ$	$\Lambda_\circ{}^*$	a°
Ac.Th.Br	25	24.33	43.42	6.5
	30	23.56	56.87	8.0
Ac.Th.I	25	24.33	46.00	6.0
	30	23.56	61.10	7.5
Ac.Th.ClO$_4$	25	24.33	51.96	5.5
	30	23.56	66.30	6.9
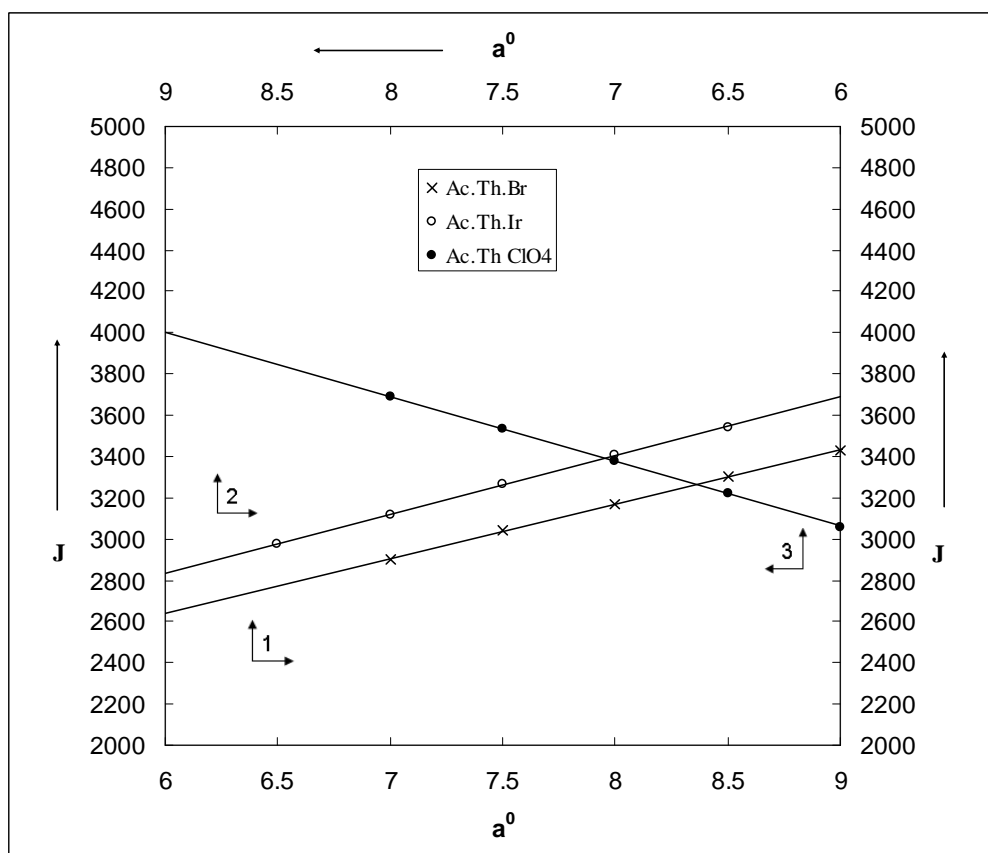
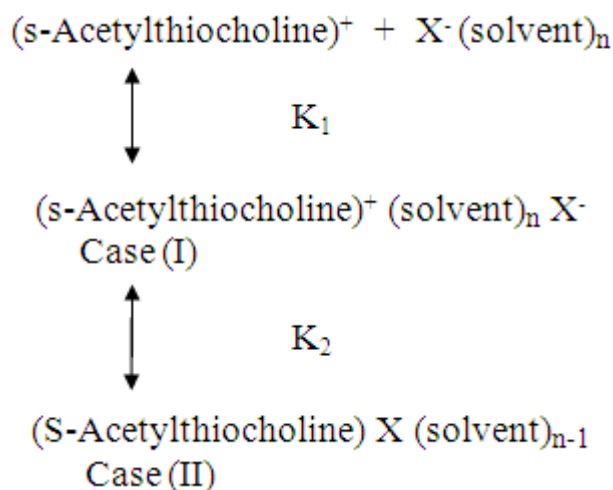**Fig .1: Variation of J and aᵒ in ethanol at 30 ᵒC**

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El-Hammamy et al (5,2,6-8), measured the conductances of acetylthiocholine halides and perchlorate in methanol (5), ethanol (2), n-propanol (6), n-butanol (7) and 2-propanol(8) solutions at $25°C$.They found that the same trend of salvation ($a°$) and association for all organic solvents are in agreement with the present results. The gradual decrease of $a°$ 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 (9)

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

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 decrease from Br^- to ClO_4^-, i.e. ion – dipole interaction term $E_s/k\,T$ is more predominant than the entropy term. 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:

$$(s\text{-Acetylthiocholine})^+ \ + \ X^- (solvent)_n$$

$$\updownarrow \quad K_1$$

$$(s\text{-Acetylthiocholine})^+ (solvent)_n \, X^-$$
$$\text{Case (I)}$$

$$\updownarrow \quad K_2$$

$$(S\text{-Acetylthiocholine}) \, X \, (solvent)_{n-1}$$
$$\text{Case (II)}$$

The association constant is given by the following expression:

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

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

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

K_2 was thus calculated. The results complied in ***TABLE III***, indicate that K_2 increases from Br^- to ClO_4^- i.e., the ion-pair prefers the more solvated form (case II) than the solvated form (case I). The derived constants are represented in ***TABLE IV,*** $\Lambda_\circ$ increases regularly with increase in the temperature for salts Br^-, I^- and ClO_4^-, indicating higher mobility of ionsin ethanol at $30^\circ C$. This is due to the fact that the increased thermal energy results in greater bond breaking and variation in vibrational, rotational and translational energy of the molecules that lead to higher frequency and higher mobility of the ions (11). $\Lambda_\circ$ values increased with increase in temperature for $FeCl_3$ in methanol, ethanol, n-propanol and n-butanol (12). These results are in agreement with present results. The salvation in ***TABLE IV,*** increases with increased the temperature from 25-30°C for salts of s-acetylthiocholine Br^- to ClO_4^- . The same results were obtained for these salts in methanol (13) at different temperatures (25-30°C) and acetonitrile fom 25-30°C (14).

REFERENCES

[1] A.I. Kawana, *Bull. Electrochem*., 16, 225 (**2000**).

[2] N.H. El-Hammamy, A.M. Ismaeil, M.F. Amira and N.S. El-Sisy, *J. Indian Chem. Soc*., 86, 878 (**2009**).

[3] Dortmund Data Bank, Software and separation Technology (**2009**).

[4] R.M. Fuoss and L.Onsager, J. Phys. Chem.,61, 668 (1957); R.M. Fuoss, *J. Amer. Chem. Soc*., 81, 2659 (**1959**).

[5] N.H. El-Hammamy, A. I. Kawana, S.A.El-Shazly and H. M. Moharem, *J. Alex. Pharm. Sci*., 24(2), 97-100(**2010**).

[6] A.I. Kawana, M.T. Mohamed and N.H. El-Hammamy, *J. Indian Chem. Soc*., 84, 816 (**2007**).

[7] A. I. Kawana, N. H.El-Hammamy, N.M.El-Mallah and H. M. Moharem, *J. Chem. Phara. Res.,* 2(6), 301-305 (**2010**).

[8] N. H. El-Hammamy , A.I. Kawana, M. N. El-Hammamy and H. M. Moharem, J. *Advances in Applied Science Research*, 2(1), 90-94(**2011**).

[9] F. Accascina, A. D´Aprano and R. Triolo, *J. Phys. Chem*., 71, 3469 (**1967**).

[10] D.F. Evans and P. Gardam, *J. Phys. Chem*., 73, 158 (**1969**).

[11] U-N.Dash, J.R.Mahapatra and B.Lal, *J. Molecular Liquids*, 124, 13-18 (**2006**).

[12] S.Pura, J. *Molecular Liquids*, 136, 64-70 (**2007**).

[13] N. H. El-Hammamy , A.I. Kawana, M. N. El-Hammamy and H. M. Moharem, *J. Chem.Sci,* 2(3), 51(**2011**).

[14] N. H. El-Hammamy , A.I. Kawana, M. N. El-Hammamy and H. M. Moharem, *J. Chem.Sci*, 2(4), 292(**2011**).