Electrical Conductivity of S-Acetylthiocholine Halides and Perchlorate in Ethanol at 40 ºC

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The conductance of S-acetylthiocholine halides and perchlorate has been measured in ethanol at 40 ºC. The data were analyzed using the Fuoss-Onsager equation for 1:1 associated electrolytes and the characteristic functions, $\Lambda_\circ$ (conductance at infinite dilution), a^0 (contact distance) and K_A (association constant) were computed. K_A values were analyzed on the basis of the solvent separated-ion pair model.

Key Words: Conductivity, S-Acetylthiocholine salts, Ionic association.

INTRODUCTION

In continuation of our conductometric studies on S-acetylthiocholine salts in simple solvents[1-5], the present work aims at determing the conductance values of the solution of S-acetylthiocholine halides and perchlorate in pure ethanol at 40 ºC to throw light on the behaviour of these salts in simple solvents and to examine the validity of Fuoss-Onsager equation for 1:1 associated electrolytes[6].

The association constant (K_A) and the closest distance of approach (aº) for the studied salts have been evaluated. These values have been used to discuss qualitatively the nature of the ion-ion and ion-solvent interaction of the S-acetyl-thiocholine salts in pure ethanol at 40 ºC.

EXPERIMENTAL

Ethanol, S-acetylthiocholine bromide, iodide and per-chlorate were purified as reported elsewhere[2]. The specific conductance for purified ethanol was found to be (1.2-1.26 × 10⁻⁸) Ω^{-1} cm⁻¹. The density of ethanol was determined at 40 ºC was found to be 0.7722 g/cm³. Its viscosity was measured at 40 ºC, it was found to be 0.7775×10^{-2} p. The dielectric constant value was used as reported in literature[7]. 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. Conductance Bridge was model Crison C lp 31 and 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-1. An approximate value of $\Lambda_\circ$ was estimated from Λ *versis* $C^{1/2}$ plot. More accurate values of $\Lambda_\circ$ were estimated from the Fuoss- Kraus-Shedlovsky equation,

TABLE-1
CONDUCTANCE OF S-ACETYLTHIOCHOLINE
SALTS IN ETHANOL AT 40 ºC

Acetylthiochline bromide		Acetylthiocholine iodide		Acetylthiocholine perchlorate	
10^4 C*	Λ**	10^4 C*	Λ**	10^4 C*	Λ**
9.8091	57.990	15.767	60.567	7.5746	65.604
8.6014	58.595	13.458	61.259	6.6246	66.355
7.6142	59.231	11.833	61.790	5.8518	67.151
6.8824	59.840	10.494	62.264	5.2496	67.757
5.8415	60.520	8.8403	62.927	4.5792	68.440
5.1031	61.139	7.6689	63.426	4.0552	69.027
4.5532	61.560	6.6189	63.897	3.6492	69.514
4.0805	62.002	5.7422	64.330	3.2813	70.031

*equiv L⁻¹, **ohm⁻¹ equiv⁻¹ cm².

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

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

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

In which α is the limiting tagent. 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 eqn. 6 and starting by the value $\Lambda_\circ$ which was obtained from (FKS) equation.

In present 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 $J = (200 \to 1000)$ 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[6]
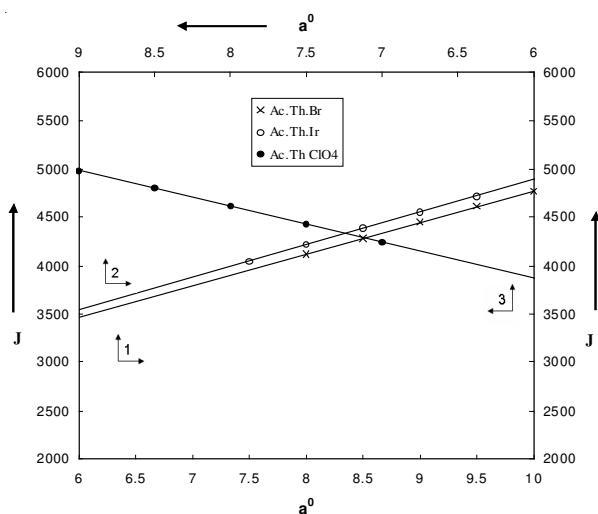

Fig. 1. Variation of J and a° in ethanol at 40 ºC

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

where σ_1 and σ_2 are the function of J. The derived constants are represented in Table-2. Table-2 reveals that $\Lambda_\circ$ increases from S-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[6] 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 S-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 order: $ClO_4^- > I^- > Br^-$. In our case the trend is that K_A increases with increase the size of anions (except I^-).

El-Hammamy et al.[2-6,8], measured the conductances of S-acetylthiocholine halides and perchlorate in methanol, ethanol, n-prpanol, n-butanol, 2-propanol and acetonitrile solutions at 25 ºC. They found that the same trends of solvation (a°) 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].

TABLE-2
CHARACTERISTIC PARAMETERS FOR ACETYLTHIOCHOLINE SALTS IN ETHANOL AT 40 ºC

Salts	$\Lambda_\circ$ (ohm^{-1} equiv^{-1} cm^2)	J	K_A	a° (Å)	σ_A
Ac.Th.Br	68.802	4448.7	136.89	9.0	0.055
Ac.Th. I	70.846	4385.9	52.402	8.5	0.037
Ac.Th.ClO$_4$	77.273	4616.0	177.37	8.0	0.035

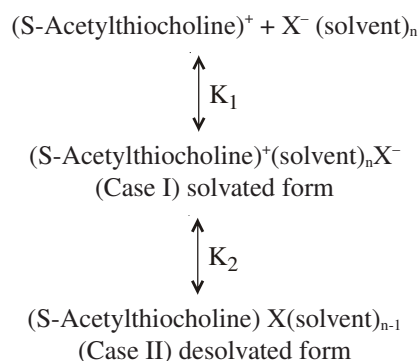$$\ln K_A = \ln\left(\frac{4\pi Na^{03}}{3000}\right) + \frac{e^2}{a^\circ DkT} + U$$

where
$$U = \frac{\Delta S}{k} - \frac{Es}{kT}$$

$\Delta S/k$ is the entropy Boltzman constant ratio which illustrates the probability of the orientation of solvent molecules around the free ions and Es/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 halides and perchlorate are given in Table-3. The result reveals that the value of U slightly increase from Br^- to ClO_4^- (except I^-), i.e., the entropy term more predominant than the ion-dipole 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:

TABLE-3
CALCULATED VALUES OF K_2 AND U OF ACETYLTHIOCHOLINE HALIDES AND PERCHLORATE IN ETHANOL 40 ºC

Salts	K_A	K_1	K_2	U
Ac.Th.Br	136.89	26.722	4.123	1.634
Ac.Th.I	52.402	26.348	0.989	0.688
Ac.Th.ClO$_4$	177.37	26.222	5.764	1.912

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

$$\updownarrow K_1$$

$$(\text{S-Acetylthiocholine})^+(\text{solvent})_n X^-$$
$$(\text{Case I}) \text{ solvated form}$$

$$\updownarrow K_2$$

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

The association constant is given by expression:

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

$$= K_1(1 + K_2)$$

where $K\Sigma = K_A$ is obtained from conductance measurements $K_1 = (4\pi Na^{03}/3000)e^b$ then K_2 can be calculated $b = e^2/a^\circ DkT$ K_2 was thus calculated. The results complied in Table-3, indicate that K_2 increases from Br^- to ClO_4^- i.e., the ion-pair prefers the desolvated form (case II) than the solvated form (case I).

The derived constants are represented in Table-4, $\Lambda_\circ$ increases regularly with increase in the temperatures for salts Br^-, I^- and ClO_4^-, indicating higher mobility of ions in ethanol at 40 °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 solvation (a°) in Table-4 increases with increased the temperature from (35-40 °C) for salts of S-acetylthiocholine Br^- to ClO_4^-. The same results were obtained for these salts in ethanol[13] and acetonitrile at different temperatures from (30-35 °C)[14].

TABLE-4
CONDUCTANCE PARAMETERS OF *s*-ACETYLTHIOCHOLINE SALTS AT 35 AND 40 °C IN ETHANOL BY USING FUOSS-ONSAGER EQUATION

Salt	Temp (°C)	ε_0	$\Lambda_\circ$	a°
Ac.Th.Br	35	22.85	63.66	8.5
	40	22.14	68.80	9.0
Ac.Th.I	35	22.85	66.59	8.0
	40	22.14	70.85	8.5
Ac.Th.ClO_4^-	35	22.85	75.53	7.5
	40	22.14	77.27	8.0

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