



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

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ABSTRACT

The conductance of s-acetylthiocholine halides and perchlorate has been measured in methanol at 30 °C. The data were analyzed using the Fuoss-Onsager equation for 1:1 associated electrolytes and the characteristic functions, Λ_∞ (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 halides and perchlorate, 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 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), methanol (B.D.H) was purified previously reported (7). The specific conductance for purified methanol at 30 °C was found to be $(2.6-3.7 \times 10^{-7}) \Omega^{-1} \text{cm}^{-1}$. The density of methanol was determined at 30 °C was found to be 0.7862 g / cm^3 .

Its viscosity was measured at 30°C, it was found to be 0.5030×10^{-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 Λ_0 was estimated from of Λ vs. $C^{1/2}$ plot. More accurate values of Λ_0 were estimated from the Fuoss-Kraus-Shedlovsky equation,

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

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

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

in which α is the limiting tangent. The plot of $1/\Lambda S_{(z)}$ vs. $(C\Lambda S_{(z)} f^2)$ gives $1/\Lambda_0$ as the intercept and $1/K_D \Lambda_0^2$ as the slope. The true values of Λ_0 , a° and K_A were derived using Fuoss-Onsager equation (9) and starting by the value Λ_0 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 Λ_0 ; ± 2 for $J < 200$, ± 5 for $J = (200 \rightarrow 1000)$ 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 (9)

$$J = \sigma_1 \Lambda_0 + \sigma_2$$

where σ_1 and σ_2 are the function of J . The derived constants are represented in **Table II**. **Table II** reveals that Λ_0 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 (9) 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° . 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 I^-).

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°) 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

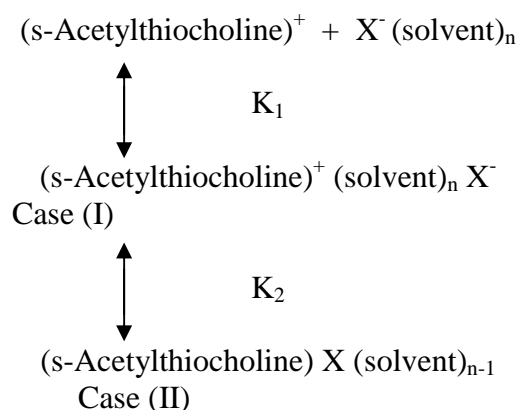
completely spherical. The increase of K_A with increasing the size of anions of *s*-acetylthiocholine halides and perchlorate can be explained in the light of the U term in equation (10)

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

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 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 (11). 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:

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

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 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

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

In the present case λ^- 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 (12). To calculate λ^+ for (s-acetylthiocholine)⁺, the average value obtained for λ^+ in case of the Br⁻, I⁻ and ClO₄⁻ 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. This is due to the solvation of ions (2).

The derived constants are represented in **Table V**. Λ_0 increases regularly with increase in temperature for salts of Br⁻, I⁻ and ClO₄⁻ indicating less solvation or higher mobility of ions in methanol system studied. 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 (13).

TABLE I: Conductance of s-Acetylthiocholine salts in methanol at 30°C

Acetylthiocholine bromide		Acetylthiocholine iodide		Acetylthiocholine perchlorate	
10 ⁴ C*	Λ **	10 ⁴ C	Λ	10 ⁴ C	Λ
15.586	115.155	11.733	125.230	10.001	132.650
13.94	116.089	10.441	125.870	8.977	133.316
12.537	116.899	9.448	126.500	8.160	134.020
11.347	117.690	8.616	127.070	7.491	134.673
10.390	118.315	7.971	127.470	6.902	135.159
9.5047	118.920	7.4361	127.830	6.4515	135.550
8.8100	119.447	6.9613	128.252	6.0360	135.990
8.2171	120.015	6.5522	128.520	5.6610	136.412
7.6826	120.311	6.1654	128.830	5.2695	136.800

* equiv L⁻¹, ** ohm⁻¹ equiv⁻¹ cm²

TABLE II: Characteristic parameters for s-Acetylthiocholine salts in methanol at 30°C

salts	Λ_0 (ohm ⁻¹ equiv ⁻¹ cm ²)	J	K _A	a ^o (Å)	σ_Λ
Ac.Th.Br	131.38± 0.06	3168.9	47.989	6.5	0.06
Ac.Th. I	137.86± 0.05	3121.1	28.304	6.03	0.05
Ac.Th.ClO ₄	146.39± 0.07	2894.2	70.445	5.0	0.07

TABLE III: Calculated values of K₂ and U of s-Acetylthiocholine Halides and Perchlorate in methanol at 30°C.

Salts	K _A	K ₁	K ₂	U
Ac.Th.Br	47.99	10.97	3.37	1.48
Ac.Th.I	28.30	10.86	1.61	0.96
Ac.Th.ClO ₄	70.45	11.44	2.73	1.32

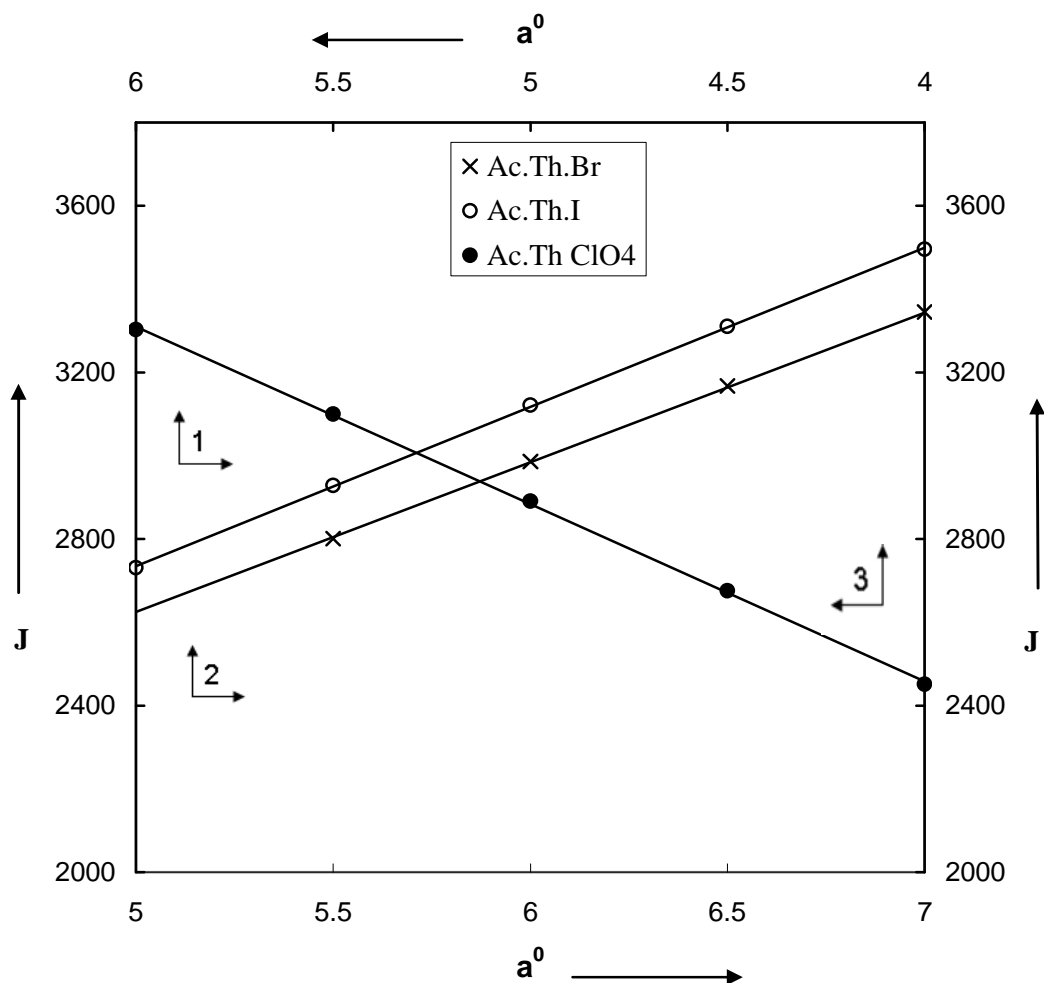
TABLE IV: Calculation of the radii of the ions for s-Acetylthiocholine salts in methanol at 30°C.

salts	Λ_0 (1)	$\lambda_0^- \eta_0$ (2)	λ_0^- (1)	λ_0^+ (1)	Av. λ_0^+ (1)	R ⁺ (Å)	R ⁻ (Å)	R ⁺ +R ⁻	a ^o (Å)
Ac.Th.Br	131.38	0.30029	59.7	71.68	71.81 ±0.37	2.269	2.729	4.997	6.50
Ac.Th.I	137.86	0.32947	65.5	72.36					
Ac.Th.ClO ₄	146.39	0.37725	75.0	71.39					

(1) ohm⁻¹ equiv⁻¹ cm², (2) ohm⁻¹ equiv⁻¹ cm² p

TABLE V: Conductance parameters s-Acetylthiocholine halides and perchlorate at 25°C (2) and 30°C in methanol by using Fuoss-Onsager equation

Salts	T °C	ϵ_0	Λ_0^*	K_A	a^{***}	λ^-	λ^+
Ac.Th.Br	25	32.63	125.72	36.38	5.98	56.26	69.22±0.61
	30	30.63	131.38	47.99	6.50	59.70	71.81±0.37
Ac.Th.I	25	32.63	131.09	44.31	5.50	62.30	69.22±0.61
	30	30.63	137.86	28.30	6.03	65.50	71.81±0.37
Ac.Th.ClO ₄	25	32.63	140.49	60.92	5.00	70.35	69.22±0.61
	30	30.63	146.49	70.45	5.00	75.00	71.81±0.37

**Fig .1: Variation of J and a^0 in methanol at 30 °C**

Λ_0 values increased with increase in temperature for FeCl₃ in methanol, ethanol, n-propanol and n-butanol (14). These results are in agreement with present results. The association constant K_A values increase with increase in temperature for salts Br⁻, I⁻ and ClO₄⁻. This may be attributed to decrease in the relative permittivity of the solvent (14). The results are in agreement with the finding of the literature published (14). The association constant K_A values increase with increase in temperature and with increase in alcohol content and also with increase the -CH₂-group in alcohol (13). The association constants, K_A , are generally increased as the temperature increased for all investigated system (13). The thermal motion probably destroys the solvent structure and hence the mobility of ions should increase, this may account to the fact that the values of K_A increase as the temperature increased (15).

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