



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

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ABSTRACT

The conductance of *s*-acetylthiocholine halides and perchlorate has been measured in acetonitrile 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 salts, acetonitrile, ionic association.

INTRODUCTION

Acetonitrile is an archetype for dipolar aprotic solvents with simple molecular structure and high solvation power for many salts (1,2). Consequently, the interplay between ion solvation and association of electrolyte solutions in acetonitrile has attracted considerable interest, see for instance ref.(3-6). Conductance measurements were made on a series of typical 1:1 electrolyte: *s*-acetylthiocholine halides and perchlorate salts. The principal objective was to establish the extend of association of ions (ion pair formation) in acetonitrile and to elucidate the nature of the solute *s*-acetylcholine halides and perchlorate salts. In the present work, conductance measurements are reported for *s*-acetylcholine halides and perchlorate in acetonitrile at 30 °C. The possibility of application of Fuoss-Onsager equation (7) to these electrolytic solutions has been studied by derivation of the characteristic constants Λ_{∞} , a° and K_A . The effect of anionic size on the conductance of studied salts has also been discussed from point of view of the variation of both K_A and a° . The solvent separated-ion pair model has been used to analyze the association constant K_A .

MATERIALS AND METHODS

The s-acetylthiocholine bromide, iodide and perchlorate were purified as reported (8), acetonitrile (B.D.H) was purified previously reported (9). The specific conductance for purified acetonitrile at 30°C was found to be $(4.7 \times 10^{-8}) \Omega^{-1}\text{cm}^{-1}$. The density of acetonitrile was determined at 30°C. It was found to be 0.7712 g/cm^3 . Its viscosity was measured at 30°C, it was found to be 0.3270×10^{-2} poise and the dielectric constant was 35.97(10). 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 (estimated from the extrapolation of Λ vs. $C^{1/2}$ plot) introduced to Fuoss-Kraus-Shedlovsky (F.K.S) equation to obtain accurate values of Λ_0 ,

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

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 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. More accurate values of Λ_0 , a° 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 Λ_0 which was obtained from (F.K.S) equation. 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 by the aid of this calibration curve, the average value of a° determined from the corresponding average value of J (which is previously obtained from the computer readings). J is being a function of a° and is represented by the following equation (7)

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

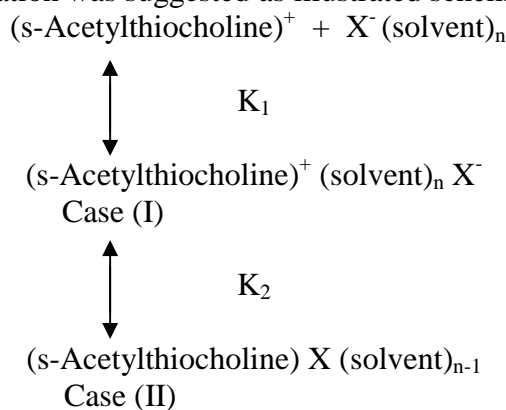
where σ_1 and σ_2 are the function of J . The derived constants are represented in **Table II**. Λ_0 increased from s-acetylthiocholine bromide to perchlorate according to the ionic equivalent conductance of anions. The values of a° decreased with increasing the size of anions indicating that it has controlled the extend of ion pairing. The solvation of these anions increased in the order: $\text{Br}^- > \text{I}^- > \text{ClO}_4^-$, which agreed with the trend of a° . From the electrostatic point of view, since the distance between the cation and the anion increased in the same order, the force of attraction increased in the order: $\text{ClO}_4^- > \text{I}^- > \text{Br}^-$. In our case the trend indicated that K_A increased with decreasing the size of anions.

El-Hammamy *et al.* (11) found that, for s-acetylthiocholine halides and perchlorate, the order of solvation (a°) 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 (12), ethanol (13), n-propanol (14), n-butanol (15) and 2-propanol (16) at 25°C. They were reported to follow the order of solvation (a°) of $\text{Br}^- > \text{I}^- > \text{ClO}_4^-$, which agree with our 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 decreasing the size of anions of s-acetylthiocholine halides and perchlorate could be explained in the light of the U term in equation 4 (17)

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

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 results revealed that the value of U slightly decreased from Br^- to ClO_4^- as the trend was $\text{Br}^- > \text{I}^- > \text{ClO}_4^-$. The ion – dipole interaction term $E_s/k T$ becomes predominant than the entropy term. Therefore, the solvent separated ion-pair model can be applied (18). In this model a multiple-step association was suggested as illustrated scheme 1:



The association constant is given by the following expression (equation 5):

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

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 complied in **TABLE III**, indicated that K_2 decreased from Br^- to ClO_4^- , i.e., the ion-pair preferred the more solvated form (case I) than the desolvated form (case II).

Radii of ions

The electrostatic radii R^+ and R^- are given by equation (7):

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

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 (19). 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. The surprisingly greater a° values are probably attributed to ion solvation.

The derived constants are represented in **Table V**. Λ_0 increases regularly with increase in temperature for salts of Br⁻, I⁻ and ClO₄⁻ in acetonitrile, indicating less solvation or higher mobility of ions in acetonitrile 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 (20).

TABLE.I: Conductance of Acetylthiocholine salts in acetonitrile at 30°C

Acetylthiocholine bromide		Acetylthiocholine iodide		Acetylthiocholine perchlorate	
10 ⁴ C*	Λ **	10 ⁴ C	Λ	10 ⁴ C	Λ
13.542	136.50	8.0089	186.11	8.0656	196.03
12.110	140.40	6.9696	188.80	6.8121	198.71
10.824	144.40	6.2500	191.11	5.9049	200.31
9.7969	147.62	5.5696	192.77	5.1984	202.23
7.8961	154.31	5.0176	194.97	4.3681	204.32
6.7600	159.26	4.4100	196.87	3.7636	205.98
5.9536	162.80	3.8416	199.21	3.3124	207.11
5.4756	166.41	3.3856	200.85	2.9241	208.23

* equiv L⁻¹ ** ohm⁻¹ equiv⁻¹ cm²

TABLE:II. Characteristic parameters for Acetylthiocholine salts in acetonitrile at 30°C.

salts	Λ_0 (ohm ⁻¹ equiv ⁻¹ cm ²)	J	K _A	a° (Å)	σ_Λ
Ac.Th.Br	216.0	3751.8	679.62	7.11	0.30
Ac.Th. I	220.17	3535.0	216.06	6.54	0.27
Ac.Th.ClO ₄	221.28	3098.3	118.83	5.50	0.18

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

salts	K _A	K ₁	K ₂	U
Ac.Th.Br	679.62	7.880	85.248	4.46
Ac.Th.I	216.06	7.337	28.449	3.38
Ac.Th.ClO ₄	118.83	6.796	16.486	2.86

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

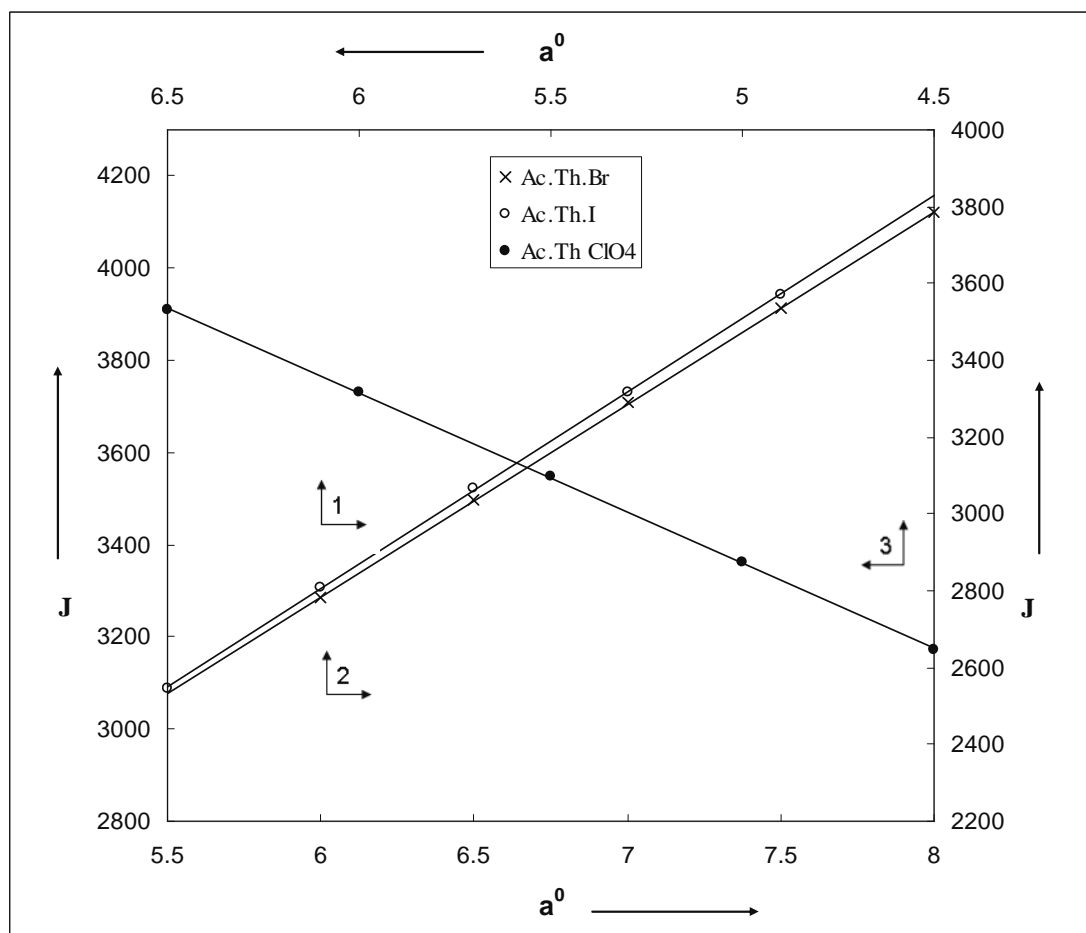
salts	Λ_0 (1)	$\lambda_0^- \eta_0$ (2)	λ_0^- (1)	λ_0^+ (1)	Av. λ_0^+ (1)	R ⁺ (Å)	R ⁻ (Å)	R ⁺ +R ⁻	a° (Å)
Ac.Th.Br	216.08	0.34904	106.74	109.34			2.348	4.60	7.11
Ac.Th.I	220.17	0.35375	108.18	111.99	111.16±1.21	2.254	2.316	4.57	6.54
Ac.Th.ClO ₄	221.28	0.35689	109.14	112.14			2.296	4.55	5.50

(1) ohm⁻¹ equiv⁻¹ cm²

(2) ohm⁻¹ equiv⁻¹ cm² p

TABLE V: conductance Parameters of s-acetylthiocholine halides and perchlorate at 25°C (11) and 30 °C in acetonitrile by using Fuoss-Onsager equation.

Salt	T (°C)	ϵ	Λ_{∞} ($\text{ohm}^{-1} \text{equiv}^{-1} \text{cm}^2$)	K_A
Ac.Th.Br	25(11)	36.61	214.01	454.92
	30	35.97	216.08	679.62
Ac.Th.I	25(11)	36.61	216.44	83.30
	30	35.97	220.17	216.06
Ac.Th.ClO ₄	25(11)	36.61	216.83	19.16
	30	35.97	221.28	118.83

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

Λ_{∞} values increased with increase in temperature for $\text{Mg}(\text{ClO}_4)_2$ and $\text{Ni}(\text{ClO}_4)_2$ in acetonitrile (21). These results are in agreement with present results. The association constant K_A values increase with increase in temperature for salts Br^- , I^- and ClO_4^- . This may be attributed to decrease in the relative permittivity of the solvent (21,22). The results are in agreement with the finding of the literature published (21,22). The association constant K_A are generally increased as the temperature increased for all investigated system (21,22). 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 (21,23).

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