



Electrical conductivity of s-acetylthiocholine halides and perchlorate in 2-propanol at 25 °C

Nasr H. El-Hammamy, Aida I. Kawana, Marwa N. El-Hammamy and Heba M. Moharem

*Department of Chemistry, Faculty of Science, University of Alexandria, Alexandria, Egypt,
P.O. 426 Ibrahimia, Alexandria 21321, Egypt*

ABSTRACT

The conductance of s-acetylthiocholine halides and perchlorate has been measured in 2-propanol at 25 °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.

Key words: Conductivity, s-acetylthiocholine halides and perchlorate, 2-propanol, ionic association.

INTRODUCTION

Studies on electrolytic conductance of s- acetylthiocholine halides and perchlorate solutions in water, methanol, ethanol, n-propanol and n-butanol at 25 °C, have been reported recently (1-5). The present communication reports a precise study of the conductance of s-acetylthiocholine halides and perchlorate in 2-propanol at 25 °C in order to throw light on the behaviour of these salts in branched simple solvents.

MATERIALS AND METHODS

The s-acetylthiocholine bromide, iodide and perchlorate were purified as reported in literature (1), 2-propanol (B.D.H) was purified previously reported (6). The specific conductance for purified 2-propanol was found to be $(5-8 \times 10^{-8}) \Omega^{-1} \text{cm}^{-1}$. The density of pure 2-propanol was determined at 25 °C was found to be 0.78097 g / cm^3 .

Its viscosity was measured at 25 °C, it was found to be 0.02079 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.

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 $1/\Lambda S_{(z)}$ versus $(C\Lambda S_{(z)} f^2)$ 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 (8) 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 (8)

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

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^- (except the salt of iodide) 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^-).

Matesich *et al* (7) measured the conductances of quaternary ammonium salts of Cl^- , Br^- , I^- and ClO_4^- in 2-propanol at 25°C . They found the order of solvation (a°) to be $\text{Cl}^- > \text{Br}^- > \text{I}^- > \text{ClO}_4^-$ and the order of association, $\text{ClO}_4^- > \text{I}^- > \text{Br}^- > \text{Cl}^-$, which is in agreement with the present results. El-Hammamy *et al* (6) measured the conductances of acetylcholine halides and perchlorate in 2-propanol at 25°C . They found the order of solvation (a°) to be $\text{Cl}^- > \text{Br}^- > \text{I}^- > \text{ClO}_4^-$ and the order of association $\text{ClO}_4^- > \text{I}^- > \text{Br}^- > \text{Cl}^-$, which is in agreement with the present

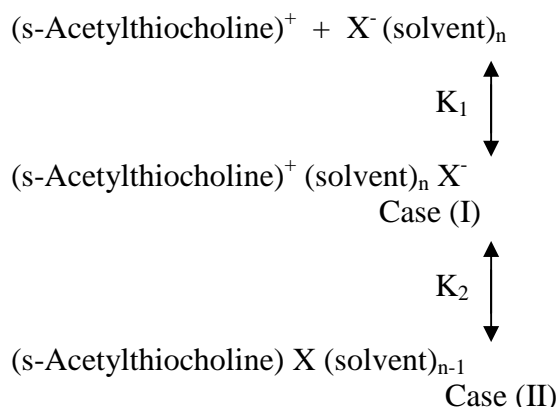
results El—Hammamy et al (2-5), measured the conductances of acetylthiocholine halides and perchlorate in methanol, ethanol, n-propanol and n-butanol solutions at 25°C. They found that the same trend of solvation (a°) and association for all organic solvents are in agreement with the present results. The gradual decrease of a° with K_A among the studied salts (s-acetylthiocholine halides and perchlorate in 2-propanol at 25°C) 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 Boltzmann 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 (9). 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 give by equation

$$R^\pm = 0.8194 \times 10^{-8} / \lambda_o^\pm \eta_o$$

In the present case λ_o^- values were obtained from the intercept of the straight lines resulting from the plots of Walden products $\Lambda_o \eta_o$ versus the reciprocal of the molecular weight as previously discussed (11). To calculate λ_o^+ for (s-acetylthiocholine)⁺, the average value obtained for λ_o^+ in case of the 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 smaller than the electrostatic radii ($R^+ + R^-$) which obtained from Stokes' equation. The surprisingly lower a° values are probably attributed to ion association.

TABLE.I: Conductance of Acetylthiocholine salts in 2-propanol at 25°C

Acetylthiocholine bromide		Acetylthiocholine iodide		Acetylthiocholine perchlorate	
$10^4 C^*$	Λ^{**}	$10^4 C$	Λ	$10^4 C$	Λ
9.8106	13.48	10.203	13.78	8.9568	15.95
8.5409	13.95	9.0469	14.15	8.0112	16.35
7.5630	14.52	8.0619	14.63	7.3185	16.65
6.8290	14.79	7.2996	14.97	6.6547	17.03
5.8793	15.36	6.3141	15.55	5.9620	17.45
5.1501	15.82	5.6869	19.91	5.3256	17.85
4.6602	16.23	5.1151	16.32	4.8464	18.21
4.2645	16.57	4.6253	16.73	4.5739	18.39

* equiv L⁻¹ ** ohm⁻¹ equiv⁻¹ cm²

TABLE:II. Characteristic parameters for Acetylthiocholine salts in 2-propanol at 25°C.

salts	Λ_o (ohm ⁻¹ equiv ⁻¹ cm ²)	J	K_A	a° (Å)	σ_Λ
Ac.Th.Br	24.276± 0.36667	2080.4	1595.3	5.45	0.063
Ac.Th. I	23.552± 0.37278	2007.8	1069.3	5.075	0.024
Ac.Th.ClO ₄	28.497± 0.39427	2067.2	1832.7	4.375	0.09

TABLE:III. Calculated values of K_2 and U of Acetylthiocholine Halides and Perchlorate in 2-propanol at 25°C.

salts	K_A	K_1	K_2	U
Ac.Th.Br	1595.3	81.347	18.611	2.946
Ac.Th.I	1069.3	97.127	10.009	2.399
Ac.Th.ClO ₄	1832.7	154.523	11.86	2.473

TABLE:IV. Calculation of the radii of the ions for Acetylthiocholine salts in 2-propanol at 25°C.

salts	Λ_o ⁽¹⁾	$\lambda_o^- \eta_o$ ⁽²⁾	λ_o^- ⁽¹⁾	λ_o^+ ⁽¹⁾	Av. λ_o^+ ⁽¹⁾	R^+ (Å)	R^- (Å)	$R^+ + R^-$	a° (Å)
Ac.Th.Br	24.269	0.23804	11.45	12.819	12.21		3.443	6.671	5.45
Ac.Th.I	23.554	0.26902	12.94	10.614	±1.06	3.228	3.046	6.274	5.075
Ac.Th.ClO ₄	28.427	0.31684	15.24	13.197			2.586	5.814	4.375

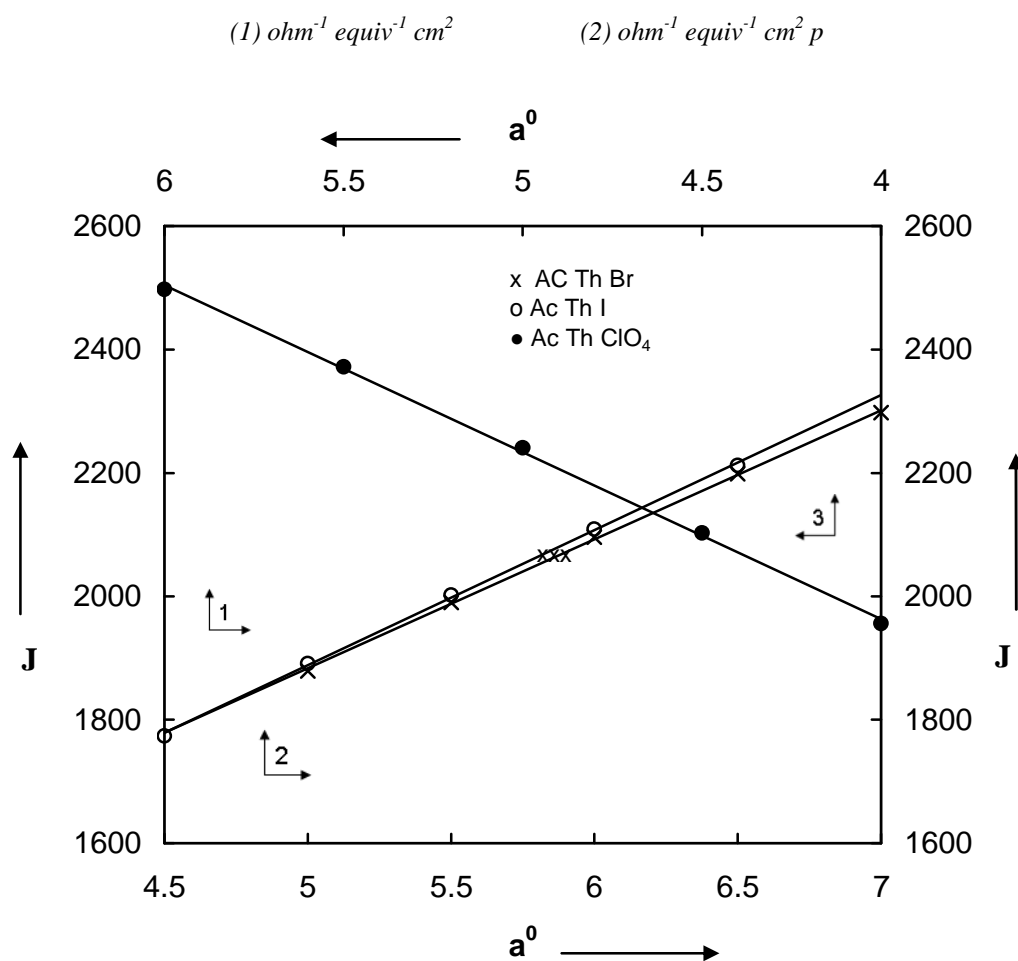


Fig 1. Variation of J with a° in 2-propanol at 25°C

REFERENCES

- [1] A.I. Kawana, *Bull. Electrochem.*, 16, 225 (2000).
- [2] Nasr H. El-Hammamy, Aida I. Kawana and Heba M. Moharem, *Alex. Pharm. Sci.*, submitted for publication (2010).
- [3] N.H. El-Hammamy, A.M. Ismaeil, M.F. Amira and N.S. El-Sisy, *J. Indian Chem. Soc.*, 86, 878 (2009).
- [4] A.I. Kawana, M.T. Mohamed and N.H. El-Hammamy, *J. Indian Chem. Soc.*, 84, 816 (2007).
- [5] Aida I. Kawana, Nasr H.El-Hammamy and Heba M. Moharem, (in communication) (2010).
- [6] N. H. El-Hammamy and A.I. Kawana, *J. Indian Chem. Soc.*, 71, 627-629 (1994)
- [7] M. A. Matesich, J. A. Nadas and D. F. Evans, *J. Phys. Chem.*, 74, 4568 (1970).
- [8] R.M. Fuoss and L.Onsager, *J. Phys. Chem.*, 61, 668 (1957); R.M. Fuoss, *J. Amer. Chem. Soc.*, 81, 2659 (1959).
- [9] D.F. Evans and P. Gardam, *J.Phys. Chem.*, 73, 158 (1969).
- [10] F. Accascina, A. D Aprano and R. Triolo, *J. Phys. Chem.*, 71, 3469(1967).
- [11] N. H. El-Hammamy , M. F. Amira, S. Abou El-Enein and F. M. Abd El- Halim, *J. Indian Chem. Soc.*, 23, 43 (1984).