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## **Electrical conductivity of s-Acetylthiocholine halides and perchlorate in n-butanol**

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### **ABSTRACT**

*The conductance of s-acetylthiocholine halides and perchlorate has been measured in n-butanol at 25°C. The data were analyzed using the Fuoss=Onsager equation for 1:1 associated electrolytes and the characteristic function,  $\Lambda$  (equivalent conductance at infinite dilution),  $a$  (contact distance of approach) and  $K_A$  (association constant) has been derived. The association constant  $K_A$  was analyzed on the basis of the solvent separated-ion pair model.*

### **INTRODUCTION**

Studies on electrolytic conductance of acetylthiocholine halides and perchlorate solutions in water, methanol, ethanol and n-propanol at 25°C, have been reported recently (1-4). The paper represents a precise study of the conductance of acetylthiocholine halides and perchlorate in n-butanol at 25°C in order to throw light on the behaviour of the behaviour of these salts in simple solvents.

### **EXPERIMENTAL SECTION**

n-butanol, s-acetylthiocholine bromide, iodide and perchlorate were purified as reported elsewhere (5, 6). The specific conductance for conductivity n-butanol (after purification) was found to be  $(5-8 \times 10^{-8}) \Omega^{-1}\text{cm}^{-1}$ . The density of n-butanol was determined using 25ml pycnometer at  $25 \pm 0.02$  °C and was found to be  $0.80572 \text{ g / cm}^3$ .

Its viscosity was measured at  $25 \pm 0.02$  °C using the viscometer with a flow-time at 250 s for water. It was found to be 0.02589 p. The dielectric constant value used was that reported by Evans and Gardam (7).

**Conductance Measurements**

Cell with bright platinum electrodes and a cell constant of  $0.1 \text{ cm}^{-1}$ . Conductance meter (model Crison Cl P31), was used for measuring the specific conductance of dilute solutions

**Preparation of Solutions**

All solution were prepared by weight reduced to vacuo. Salts were weighed by difference on a microbalance which reads to  $\pm 0.1 \text{ mg}$ . Dilution were carried out successively into the cell by siphoning the solvent by means of weighing pipette.

**RESULTS AND DISCUSSION**

The measured equivalent conductance are shown in **Table I**. An approximate value of  $\Lambda_{\infty}$  (estimated from the extrapolation of  $\Lambda$  vs  $C^{1/2}$  plot) introduced to Fuoss-Kraus-Shedlovsky (F.K.S.) equation, to obtain accurate values,

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

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  $z$  could be calculated from the following equation

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

$\Lambda_{\infty}$  in the equation is the limiting tangent. The plot of  $1/\Lambda S_{(z)}$  vs  $(C\Lambda C_{(z)} f^2)$  gives  $1/\Lambda_{\infty}$  as the intercept and  $1/K_D \Lambda_{\infty}^2$  as the slope. More accurate values of  $\Lambda_{\infty}$ ,  $\alpha$  and  $K_A$  are obtained from Fuoss-Onsager equation (8), with the aid of special computer program (IBM – PC) starting with the value  $\Lambda_{\infty}$  which was obtained previously from (F.K.S.) equation. The accuracies required in these computation are  $\pm 0.02$  for  $\Lambda_{\infty}$ ;  $\pm 2$  for  $J < 200$ ,  $\pm 5$  for  $J = (200-1000)$  and  $\pm 10$  for  $J > 1000$ . **Fig. 1** shows the variation of  $\alpha$  with  $J$ . By the aid of this calibration curve, the average value of  $\alpha$  determined from the corresponding average value of  $J$  (which is previously obtained from the computer readings) Knowing that  $J$  is a function of  $\alpha$  and is represented by the following equation (8)

$$J = \sigma_1 \Lambda_{\infty} + \sigma_2 \quad (3)$$

where  $\sigma_1$  and  $\sigma_2$  are the function of  $J$ . The derived constants are represented in **Table II**.  $\Lambda_{\infty}$  increases from acetylthiocholine bromide to perchlorate according to the ionic equivalent conductance of anions, The values of  $\alpha$  decrease with increasing the size of anions indicating that it controls the extent of ion pairing. The salvation of these anions increases in the order:  $\text{Br}^- > \text{I}^- > \text{ClO}_4^-$ , which is in accordance with the trend of  $\alpha$  values. From the electrostatic point of view, since the distance between the cation and the anion increases in the same order, the force of attraction increase in the order:  $\text{ClO}_4^- > \text{I}^- > \text{Br}^-$ . And the trend  $K_A$  increases with increase the size of anion (except  $\text{I}^-$ ).

In the earlier study (2-4) on the conductance of s-acetylthiocholine halides and perchlorate in methanol, ethanol and n-propanol at  $25^\circ \text{C}$  authors found that the order of salvation ( $\alpha$ ) is  $\text{Br}^- > \text{I}^- > \text{ClO}_4^-$  while  $K_A$  (in methanol) increases from  $\text{ClO}_4^-$  to  $\text{Br}^-$  in the trend:  $\text{ClO}_4^- > \text{I}^- > \text{Br}^-$ ,  $K_A$  (in ethanol) increases from  $\text{ClO}_4^-$  to  $\text{Br}^-$  in the trend :  $\text{ClO}_4^- > \text{I}^- > \text{Br}^-$ , while  $K_A$  (in n-propanol) is

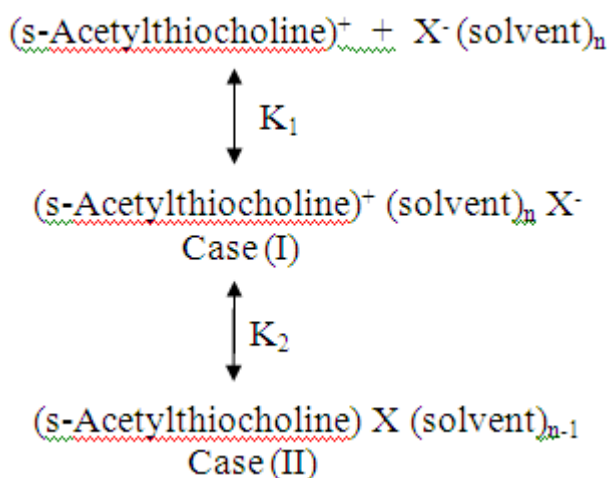
irregularly varied with the size of anion. The gradual decrease of  $a^\circ$  with the  $K_A$  among the studied salts was attributed to the relative position of the anion with respect to the cation which may not be completely spherical. Conductance measurement of acetylcholine halides and perchlorate in n-butanol at 25°C (5) gives the order of solvation ( $a^\circ$ ) as  $\text{Cl}^- > \text{Br}^- > \text{I}^- > \text{ClO}_4^-$  and the trend of  $K_A$  regularly increase with increase of the size of anion (except iodide) which is also similar to present work. The increase of  $K_A$  with increasing the size of anion of s-acetylthiocholine halides and perchlorate can be explained in the light of the U term included in the following equation (9)

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

where,  $U = \Delta S / k - E_s / KT$

$\Delta S / k$  is the entropy Boltzman constant ratio which illustrates the probability of the orientation of solvent molecules around the free ions, and  $E_s / KT$  is an energy relationship which includes the energy of solvent molecules with respect to both free ion and ion-pair. The values of U term of s-acetylthiocholine halides and perchlorate are given in *Table III*.

The result reveal that the value of U slightly decrease from  $\text{Br}^-$  to  $\text{ClO}_4^-$ . The ion – dipole term becomes more predominant than the entropy term. Therefore the solvent separated ion-pair model can be now applied (10). In this model a multiple step association is suggested and can be illustrated by the following scheme:



The association constant is given by the following expression:

$$K_A = K \Sigma = \frac{[\text{ionpairs}]}{[(\text{Acetylthiocholine})^+] [\text{X}^- (\text{solvent})_n]} = K_1 (1+K_2) \quad (5)$$

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

$$K_1 = \frac{4\pi N a^{\circ 3}}{3000} e^b \quad (6)$$

and  $b = \frac{e^2}{a^\circ DkT}$

$K_2$  was thus calculated. The results compiled in **TABLE III**, indicate that  $K_1$  increases from Br<sup>-</sup> to ClO<sub>4</sub><sup>-</sup> i.e., the ion-pair prefers the more solvated form (case I) than the desolvated form (case II).

The electrostatic radius ( $R^+$  or  $R^-$ ) is given by Stokes' equation,

$$R^\pm = 0.8194 \times 10^{-8} / \lambda_\infty^\pm \eta. \quad (7)$$

Where  $\lambda_\infty^\pm$  is obtained from the intercept of the straight line resulting from the plots of Walden product  $\Lambda_\infty \eta$  vs the reciprocal of the molecular weight as previously discussed (5), where  $\lambda_\infty^+$  for s-acetylthiocholine<sup>+</sup> represented by the average value of  $\lambda_\infty^\pm$  of the bromide, iodide and perchlorate salts. From the data in **TABLE IV**, it can be seen that the values of  $a^\circ$  are smaller than the electrostatic radii ( $R^+ + R^-$ ) which obtained from Stokes' equation. This is due to the association of ions (5).

**TABLE I: Conductance of Acetylthiocholine salts in n-butanol at 25°C**

Acetylthiocholine bromide		Acetylthiocholine iodide		Acetylthiocholine perchlorate	
$10^4 C^*$	$\Lambda^{**}$	$10^4 C$	$\Lambda$	$10^4 C$	$\Lambda$
11.876	9.423	11.133	10.164	10.089	9.713
10.467	9.795	9.7831	10.578	8.9277	10.101
9.3179	10.142	8.6835	10.905	7.9090	10.507
8.4040	10.436	7.8702	11.245	7.1753	10.856
7.6485	10.721	7.1797	11.532	6.6313	11.054
6.9912	10.985	6.5848	11.785	6.1905	11.344
6.4901	11.202	6.0756	12.120	5.8374	11.584
6.0098	11.431	5.6683	12.241	5.4480	11.895
5.6094	11.641	5.2638	12.589		

\* equiv L<sup>-1</sup>      \*\* ohm<sup>-1</sup> equiv<sup>-1</sup> cm<sup>2</sup>

**TABLE II: Characteristic parameters for Acetylthiocholine salts in n-butanol at 25°C**

salts	$\Lambda_\infty$ (ohm <sup>-1</sup> equiv <sup>-1</sup> cm <sup>2</sup> )	J	$K_A$	$a^\circ$ (Å)	$\sigma_\Lambda$
Ac.Th.Br	19.702 ± 0.45797	2513.7	2248.1	5.963	0.011
Ac.Th. I	20.657 ± 0.41641	2256.0	2177.8	5.363	0.051
Ac.Th.ClO <sub>4</sub>	23.476 ± 0.42666	2427.7	4175.7	4.613	0.07

**TABLE III: Calculated values of  $K_2$  and U of Acetylthiocholine Halides and Perchlorate in n-butanol at 25°C**

salts	$K_A$	$K_1$	$K_2$	U
Ac.Th.Br	2248.1	114.599	18.617	2.98
Ac.Th.I	2177.8	151.463	13.378	2.67
Ac.Th.ClO <sub>4</sub>	4175.7	254.196	12.427	2.79

**TABLE IV: Calculation of the radii of the ions for Acetylthiocholine salts in n-butanol at 25°C**

salts	$\Lambda_\infty$ (1)	$\lambda_\infty^- \eta$ (2)	$\lambda_\infty^-$ (1)	$\lambda_\infty^+$ (1)	Av. $\lambda_\infty^+$ (1)	$R^+$ (Å)	$R^-$ (Å)	$R^+ + R^-$	$a^\circ$ (Å)
Ac.Th.Br	19.694	0.21307	8.23	11.464			3.8456	6.559	5.963
Ac.Th.I	20.637	0.24129	9.32	11.317	11.666	2.713	3.396	6.109	5.363
Ac.Th.ClO <sub>4</sub>	23.437	0.29048	11.22	12.217	±0.365		2.8208	5.534	4.613

(1) ohm<sup>-1</sup> equiv<sup>-1</sup> cm<sup>2</sup>      (2) ohm<sup>-1</sup> equiv<sup>-1</sup> cm<sup>2</sup> p

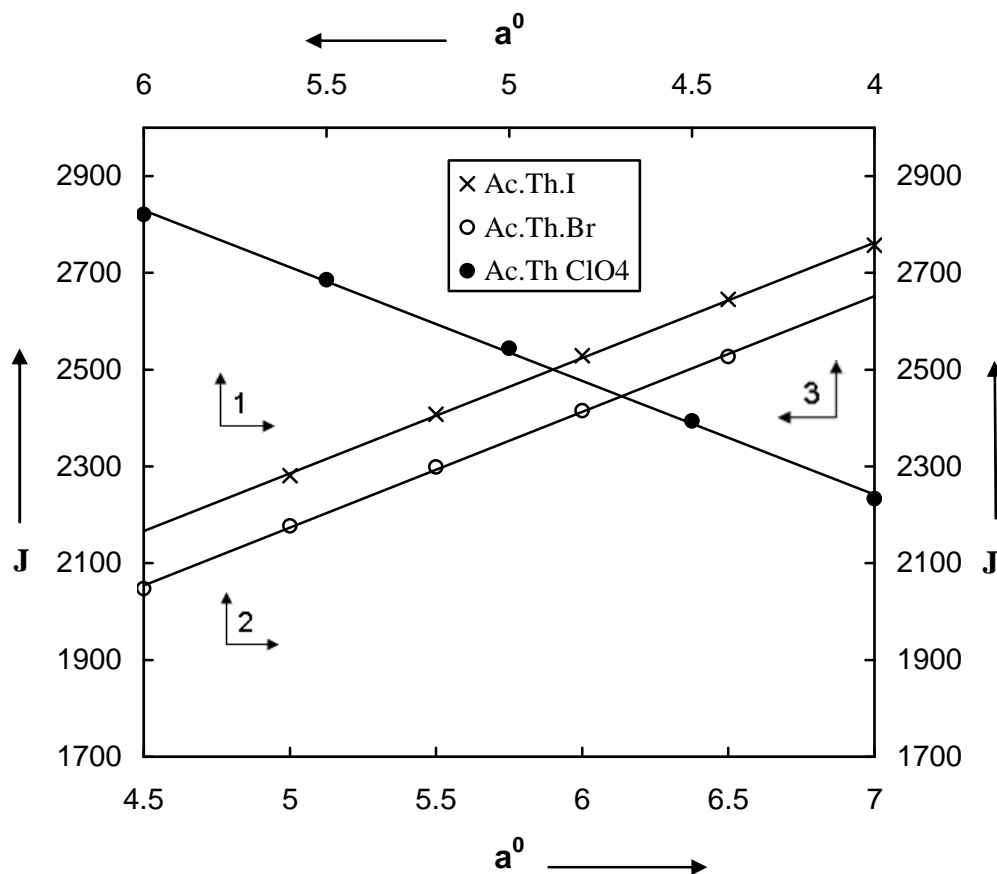


Fig .1: Variation of J and  $a^\circ$  in n-butanol at 25°C

## REFERENCES

- [1] Nasr.H. El-Hammamy, Aida I. Kawana, Moustafa M. El-Kholy, Mohamed F. Amira and Ghada A. Ibrahim, *Alex. J. Pharm. Sci.*, 23 (2), 79-81(2009).
- [2] Nasr.H. El-Hammamy, Aida I. Kawana, Shawky El-Shazly and Heba M. Moharem, *Alex. J. Pharm. Sci.*, submitted for publication (2010).
- [3] N.H. El-Hammamy, A.M. Ismaeil and M.F. Amira and N.S. El-Sisy, *J. Indian Chem. Soc.*, 86, 878-881 (2009).
- [4] A.I. Kawana, M.T. Mohamed and N.H. El-Hammamy, *J. Indian Chem. Soc.*, 84, 816-819 (2007).
- [5] N.H. El-Hammamy, A.I.Kawana, Sh.A. El-shazly and F.F. El-bardisy, *Bull. Electrochem.*, 10. 307 (1994).
- [6] A.I. Kawana, *Bull. Electrochem.*, 16, 225 (2000).
- [7] D.F. Evans and P. Gardam, *J. Phys. Chem.*, 72, 3281 (1968).
- [8] R.M. Fuoss and L.Onsager, *J. Phys. Chem.*, 61, 668 (1957); *J. Amer. Chem. Soc.*, 81, 2659 (1959).
- [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).