



## COMPARATIVE STUDY ON CONDUCTANCE MEASUREMENTS AT 25°C OF IONIC ASSOCIATION OF ACETYLCHOLINE AND S-ACETYLTHIOCHOLINE BROMIDES IN AQUEOUS AND NON-AQUEOUS SOLVENTS

\*NASR H. EL-HAMMAMY <sup>A</sup>, AIDA I. KAWANA<sup>B</sup> AND MOUSTAFA M. EL-KHOLY<sup>B</sup>

Department of Chemistry, Faculty of Science <sup>a</sup>, Faculty of Education <sup>b</sup>,  
Alexandria University, Ibrahimia, P.O Box 426, Alexandria 21321, Egypt.

\*Corresponding author

elhammamy@yahoo.com

### ABSTRACT

Conductance measurements of ion-pair association of acetylcholine and s- acetylthiocholine bromides in aqueous and non-aqueous solvents at 25°C were found to depend on the association of the cation and increased with increasing cation crystallographic radius. Solvation of cation increased with increasing cationic size in aqueous and non-aqueous solvents. The association constant  $K_A$  was analyzed on the basis of solvent separated- ion pair model

### KEYWORDS

Acetylcholine, S-Acetylthiocholine bromides, cation solvation in aqueous and non-aqueous solvents.

### INTRODUCTION

The effect of anionic size on the conductance of some salts in aqueous and non-aqueous solvents at 25°C has been discussed (1), using Fuoss-Onsager equation. Interaction between solvent molecules and salts of big ions represented a good example for studying conductance measurements of solute-solvent interaction. In present paper, the effect of cationic size on the conductance of acetylcholine and s-acetylthiocholine bromides in aqueous and non-aqueous solvents has been studied using Fuoss-Onsager equation (1). The results have been discussed in the light of variation of both the association constant  $K_A$  and the closest distance of approach  $a^\circ$  (solvation). The solvent separated-ion pair model has been applied to analyze the values obtained for  $K_A$ .

### MATERIALS AND METHODS

Acetylcholine bromide, s-acetylthiocholine bromide and aqueous and non-aqueous solvents (water, ethanol (BDH) and n-propanol(BDH) were purified as reported(2-7). Density, viscosity and dielectric constant were determined in previous work (2-7), in Table 1. An Erlenmeyer cell was used with platinum electrodes. Its cell constant was  $0.05443 \pm 0.43$  % as calculated using the Lind, Zwolenik and Fuoss equation. A "pye" conductance bridge model 11700, was used for measuring the resistances of solutions.

### RESULTS AND DISCUSSION

## COMPARATIVE STUDY ON CONDUCTANCE MEASUREMENTS AT 25°C OF IONIC ASSOCIATION OF ACETYLCHOLINE AND S-ACETYLTHIOCHOLINE BROMIDES IN AQUEOUS AND NON-AQUEOUS SOLVENTS

Table I records the properties of aqueous and non-aqueous solvents at 25°C. Table II records the increase of the values of  $a^\circ$  (solvation of cation) with increase of ionic size of cation. The corresponding values of  $K_A$  also increased with increasing the cationic size except in case of n-propanol, it decreases with increasing crystallographic radius of cation. The increasing values of  $a^\circ$  with increasing the cationic size, may be indicate the solvation of these salts (cations) in aqueous and non-aqueous followed the order: s-acetylthiocholine > acetylcholine. Considering the electrostatic point of view,  $K_A$  should increase with increasing the size of cations. This correlation can be attributed to the position of the anion relative to the cation. So it may not attain complete spherical shape (8). In addition contrary to prediction of electrostatic theory,  $\Lambda^\circ$ ,  $J$ ,  $a^\circ$  and  $K_A$  increased according to cationic size, as evidenced by electrolytes have the same anion and different cations (Table II). D' Aprano (9) calculated the parameters  $\Lambda^\circ$ ,  $a^\circ$  and  $K_A$  for some alkali perchlorates in methanol at 25°C and found that  $K_A$  increased with increasing the size of cation.

**Table I**

| Solvent          | Dielectric constant (D) | Density (d) (g cm <sup>-3</sup> ) | Viscosity (η) (poise)   | Specific conductance (κ) ohm <sup>-1</sup> cm <sup>-1</sup> |
|------------------|-------------------------|-----------------------------------|-------------------------|---|
| H <sub>2</sub> O | 78.54                   | 0.99704                           | 0.8903×10 <sup>-2</sup> | 5.7 × 10 <sup>-7</sup>                                      |
| Et-OH            | 24.33                   | 0.78744                           | 1.0840×10 <sup>-2</sup> | (5.2-9)× 10 <sup>-8</sup>                                   |
| n-PrOH           | 20.33                   | 0.79966                           | 1.9520×10 <sup>-2</sup> | (2.3-4) × 10 <sup>-8</sup>                                  |

**Table II**

**Characteristic Parameters for Acetylcholine and s-acetylthiocholine Bromides in water, ethanol and n-propanol at 25°C.**

| Solvent          | salt                    | $\Lambda_n^{(a)}$ | J    | $K_A$  | $a^{(b)}$ | $\sigma_A$ |
|------------------|-------------------------|-------------------|------|--------|-----------|------------|
| H <sub>2</sub> O | Acetylcholine Br(2)     | 110.49            | 278  | 20.86  | 5.55      | 0.085      |
|                  | Acetylthiocholine Br(3) | 101.63            | 309  | 59.29  | 6.66      | 0.060      |
| EtOH             | Acetylcholine Br(4)     | 44.60             | 1042 | 65.46  | 2.49      | 0.082      |
|                  | Acetylthiocholine Br(5) | 43.42             | 2053 | 142.42 | 6.51      | 0.004      |
| n-PrOH           | Acetylcholine Br(6)     | 22.36             | 1288 | 194.68 | 4.03      | 0.054      |
|                  | Acetylthiocholine Br(7) | 45.78             | 3433 | 132.26 | 6.49      | 0.095      |

Derived from Fuoss-Onsager Equation (2-7)  
 $a - \text{cm}^2 \text{equiv}^{-1} \text{ohm}^{-1}$        $b - \text{Å}$

**COMPARATIVE STUDY ON CONDUCTANCE MEASUREMENTS AT 25°C OF IONIC ASSOCIATION OF ACETYLCHOLINE AND S-ACETYLTHIOCHOLINE BROMIDES IN AQUEOUS AND NON-AQUEOUS SOLVENTS**

**Table III**

**Calculated values of  $K_2$  and  $U$  for salts of Acetylcholine and S-acetylthiocholine Bromides in water Ethanol and n-Propanol at 25°C. (2-7)**

| Solvent    | Salt                    | $K_A$  | $K_1$  | $K_2$ | $U$   |
|------------|-------------------------|--------|--------|-------|-------|
| water      | Acetylcholine Br(2)     | 20.86  | 1.56   | 12.38 | 2.59  |
|            | Acetylthiocholine Br(3) | 59.29  | 2.137  | 26.74 | 3.32  |
|            | Acetylcholine Br(4)     | 65.46  | 65.45  | -0.84 | -0.82 |
| ethanol    | Acetylthiocholine Br(5) | 142.42 | 24.00  | 4.933 | 1.78  |
|            | Acetylcholine Br(6)     | 194.68 | 147.17 | -0.86 | -0.28 |
| n-Propanol | Acetylthiocholine Br(7) | 132.26 | 46.93  | 1.818 | 1.04  |

A similar behaviour was also found for these salts in water, acetonitrile and sulfolane. These led to conclude that the association behaviour of alkali perchlorate in different solvents was governed by the degree of solvation of cations, on one hand and, on the other, by the protic properties of solvent used. Lee and Wheaton (11-12) reported similar behaviour for alkali iodides in ethanol at 25°C, and association constants were found to increase with increasing the size of cation in order of: CsI > RbI > KI > NaI. This had been explained by assuming the formation of solvent separated-ion pairs.

El-Hammamy (8) et al. studied the conductance of three acetylcholine halides and one perchlorate salt in methanol and n-propanol at 25°C. They found that  $\Lambda^\circ$ ,  $a^\circ$  and  $K_A$  values increased with increasing the size of anion. The value of  $a^\circ$  indicated solvation of anions of these salts in methanol and n-propanol in the order  $\text{ClO}_4^- > \text{I}^- > \text{Br}^- > \text{Cl}^-$ .

The value of  $K_A$  also increased with increasing the size of anions. The gradual increase of  $a^\circ$  with increase of  $K_A$  has been attributed to the position of anions relative to the cation. Therefore, cations and anions will may not be completely spherical. Similar results were obtained when the conductance of acetylcholine halides and perchlorate was studied in ethanol at 25°C (12). Also the same results were obtained in case of studying conductance of acetylcholine and S-acetylthiocholine chlorides in n-propanol at 25°C (13). In the present investigation, the increase of  $K_A$  for acetylcholine and S-acetylthiocholine bromides in aqueous and non-aqueous solvents can be explained in the light of  $U$  term included in the association constant equation (14).

and where

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

where

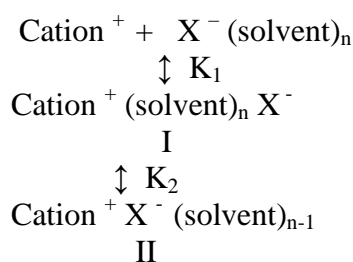
$$U = \Delta S / k - E_s / kT$$

## COMPARATIVE STUDY ON CONDUCTANCE MEASUREMENTS AT 25°C OF IONIC ASSOCIATION OF ACETYLCHOLINE AND S-ACETYLTHIOCHOLINE BROMIDES IN AQUEOUS AND NON-AQUEOUS SOLVENTS

$\Delta S / k$  is entropy / Boltzmann constant ratio which illustrates the probability of orientation of solvent molecules around free ions.  $E_s/KT$  is an energy relationship, i.e. energy of solvent molecules with respect to the two free ions and the pairs formed

The values of U term for acetylcholine and s-acetylcholine bromides in different solvents are given in Table III, which shows that U term increases as the cationic size increases (in aqueous and non-aqueous solvents) and the entropy term ( $\Delta S/kT$ ) is more predominant than the ion-dipole interaction term ( $E_s/KT$ ). Application of the solvent separated-ion pair model (15) on the compounds under investigation, indicated that a multiple-steps association occurred, i.e. the solvent separated and contact ion pairs occurred are illustrated in scheme 1

Scheme 1:



$$\begin{aligned}
 K_A = \sum K &= \frac{[C_{(ion-pairs)}]}{[(C_{(Cation^+)})][C_{X^- (solvent)_n}]} \\
 &= K_1 (1 + K_2)
 \end{aligned}$$

$\sum K = K_A$  is obtained from conductance measurements, and

$$K_1 = 4\pi N a^{\circ 3} / 3000 e^b$$

where

$b = \frac{e^2}{D a^{\circ} k T}$  The results (Table III) indicated that  $K_1$  decreased (in case of ethanol and n-propanol at 25°C) but in case of water,  $K_1$  increased and  $K_2$  increased as the cationic size increased. This means that, as the cationic size increased, the ion-pair preferred more desolvated form (case II) than the solvated form (case I). In conclusion, the disturbance due to orientation of solvent molecules around the ions increased by increasing the cationic size, i.e. the step of desolvation for s-acetylthiocholine bromide occurred more rapidly than in acetylcholine bromide, a property that is consistent with the results of both U and  $K_A$



## COMPARATIVE STUDY ON CONDUCTANCE MEASUREMENTS AT 25°C OF IONIC ASSOCIATION OF ACETYLCHOLINE AND S-ACETYLTHIOCHOLINE BROMIDES IN AQUEOUS AND NON-AQUEOUS SOLVENTS

### REFERENCES

- 1 – R. M. Fuoss and L. Onsager, *J. Phys. Chem.*, 61,668(1957);  
*J. Amer. Chem. Soc.*, 81, 2659(1959).
- 2– N. H. El-Hammamy, M. F. Amira, S.A. Abou El-Enein and F. M. Abd El-Halim, *Indian J. Chem.*, 23A, 43(1984).
- 3 – *M. Sc. Thesis*, Nader S. El-Sisy(2008).
- 4 – N. H. El-Hammamy, M. Abou Sakkina, S. A. Abou El-Enein and A. A. Zaghloul, *Egypt. J. Chem.*, 35, 475(1992).
- 5 – N. H. El-Hammamy, A. M. Ismaeil, M. F. Amira and N. S. El-Sisy, *J. Indian Chem. Soc.*, 86, 878(2009).
- 6 – N. H. El-Hammamy, A. A. Hasanein, M. F. Amira and F. M. El-Halim, *J. Electrochem. Soc.(India)*, 33, 43(1984).
- 7 – A. I. Kawana, M. T. Mohamed and N. H. El-Hammamy, *J. Indian Chem. Soc.*, 84, 816(2007).
- 8 – H. Sadek and A. M. Hafez, *Proc. Pakistan. Sci.*, 11, 1(1974).
- 9 – A. D'Aprano, *J. Phys. Chem.*, 76, 2920(1972).
- 10 – W. H. Lee and R. J. Wheaton, *J. Chem. Soc. Faraday Trans.*, 75, 1128(1979).
- 11 – B. A. AKrawi, W. H. Lee and R. J. Wheaton, *Acta Chem. Scand*, A34, 307(1980).
- 12 – N. H. El-Hammamy, A. A. Hasanein, M. F. Amira and F. El-Halim, *J. Indian Chem. Soc.*, 31, 512(1984).
- 13 – N. H. El-Hammamy, M. M. El-Kholy and Aida I. Kawana, *Alex. J. Pharm. Sci.*, 23(1) 31(2009).
- 14 – F. Accascina, A. D'Aprano and R.Triolo, *J. Phys. Chem.*,71,3469(1967).
- 15 – D. F. Evans and P. Gardam, *J. Phys. Chem*, 73,158(1969).