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

Aida I. Kawana, Nasr H. El-hammamy*, Nabila M.El-Mallah and Heba M. Moharem

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

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 \(5-8 \times 10^{-8}\) \(\Omega^{-1}\) cm\(^{-1}\). The density of n-butanol was determined using 25ml pyknometer at 25 ± 0.02°C and was found to be 0.80572 g / cm\(^3\).

Its viscosity was measured at 25 ± 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 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 ± 0.1 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 \(\Lambda\) (estimated from the extrapolation of \(\Lambda\) vs \(C^{1/2}\) plot) introduced to Fuoss-Kraus-Shedlovsky (F.K.S.) equation, to obtain accurate values,

\[
\frac{1}{\Lambda S(z)} = \frac{1}{\Lambda_o} + \frac{(C\Lambda S(z)f^2)}{K_D \Lambda_o^2}
\]

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 \(z\) could be calculated from the following equation

\[
z = \alpha(C\Lambda)^2 / \Lambda_o^{3/2}
\]

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

\[
J = \sigma_1 \Lambda_o + \sigma_2
\]

where \(\sigma_1\) and \(\sigma_2\) are the function of \(J\). The derived constants are represented in Table II. \(\Lambda\) increases from acetylthiocholine bromide to perchlorate according to the ionic equivalent conductance of anions, The values of \(a^\circ\) 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: \(Br^- > I^- > ClO_4^-\), which is in accordance with the trend of \(a^\circ\) 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: \(ClO_4^- > I^- > Br^-\). And the trend \(K_A\) increases with increase the size of anion (except \(I^-\)).

In the earlier study (2-4) on the conductance of \(s\)-acetylthiocholine halides and perchlorate in methanol, ethanol and n-propanol at 25°C authors found that the order of salvation (\(a^\circ\) is \(Br^- > I^- > ClO_4^-\) while \(K_A\) (in methanol) increases from \(ClO_4^-\) to \(Br^-\) in the trend \(ClO_4^- > I^- > Br^-\), \(K_A\) (in ethanol) increases from \(ClO_4^-\) to \(Br^-\) in the trend: \(ClO_4^- > I^- > Br^-\), 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 salvation ($a^\circ$) 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)

$$\ln K_A = \ln \left(4\pi Na^3/3000\right) + \left(e^2/a^\circ DkT\right) + U$$  (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:

$$\begin{align*}
(s\text{-Acetylthiocholine})^- + X^- (\text{solvent})_n & \quad \overset{K_1}{\rightleftharpoons} \\
(s\text{-Acetylthiocholine})^+ (\text{solvent})_n X^- & \quad \text{Case (I)} \\
(s\text{-Acetylthiocholine}) X (\text{solvent})_{n-1} & \quad \text{Case (II)}
\end{align*}$$

The association constant is given by the following expression:

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

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

$$K_1 = \frac{4\pi Na^3}{3000} e^b$$  (6)

and $b = \frac{e^2}{a^\circ DkT}$
K2 was thus calculated. The results complied in TABLE III, indicate that K1 increases from Br⁻ to ClO₄⁻ 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,

\[ R^\pm = 0.8194 \times 10^{-8} / \lambda^\pm \eta. \]  \hspace{1cm} (7)

Where \( \lambda^\pm \) is obtained from the intercept of the straight line resulting from the plots of Walden product \( \Lambda \eta \) vs the reciprocal of the molecular weight as previously discussed (5), where \( \lambda^+ \) for s-acetylthiocholine+ represented by the average value of \( \lambda^+ \) of the bromide, iodide and perchlorate salts. From the data in TABLE IV, it can be seen that the values of a° 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**

<table>
<thead>
<tr>
<th>Acetylthiocholine bromide</th>
<th>Acetylthiocholine iodide</th>
<th>Acetylthiocholine perchlorate</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 10^4 ) C</td>
<td>( \Lambda )</td>
<td>( 10^4 ) C</td>
</tr>
<tr>
<td>8.4040</td>
<td>10.436</td>
<td>7.8702</td>
</tr>
<tr>
<td>7.6485</td>
<td>10.721</td>
<td>7.1797</td>
</tr>
<tr>
<td>6.4901</td>
<td>11.202</td>
<td>6.0756</td>
</tr>
<tr>
<td>6.0098</td>
<td>11.431</td>
<td>5.6683</td>
</tr>
<tr>
<td>5.6094</td>
<td>11.641</td>
<td>5.2638</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>salts</th>
<th>( \Lambda ) (ohm(^{-1})equiv(^{-1})cm(^2))</th>
<th>J</th>
<th>K(\Lambda)</th>
<th>a° (Å)</th>
<th>(\sigma\Lambda)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ac.Th.Br</td>
<td>19.702 (\pm 0.45797)</td>
<td>2513.7</td>
<td>2248.1</td>
<td>5.963</td>
<td>0.011</td>
</tr>
<tr>
<td>Ac.Th. I</td>
<td>20.657 (\pm 0.41641)</td>
<td>2256.0</td>
<td>2177.8</td>
<td>5.363</td>
<td>0.051</td>
</tr>
<tr>
<td>Ac.Th.ClO(4)</td>
<td>23.476 (\pm 0.42666)</td>
<td>2427.7</td>
<td>4175.7</td>
<td>4.613</td>
<td>0.07</td>
</tr>
</tbody>
</table>

**TABLE III: Calculated values of K₂ and U of Acetylthiocholine Haides and Perchlorate in n-butanol at 25°C**

<table>
<thead>
<tr>
<th>salts</th>
<th>K(\Lambda)</th>
<th>K₁</th>
<th>K₂</th>
<th>U</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ac.Th.Br</td>
<td>2248.1</td>
<td>114.599</td>
<td>18.617</td>
<td>2.98</td>
</tr>
<tr>
<td>Ac.Th.I</td>
<td>2177.8</td>
<td>151.463</td>
<td>13.378</td>
<td>2.67</td>
</tr>
<tr>
<td>Ac.Th.ClO(4)</td>
<td>4175.7</td>
<td>254.196</td>
<td>12.427</td>
<td>2.79</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>salts</th>
<th>(\lambda^+) (^{(1)})</th>
<th>(\lambda^-) (^{(1)})</th>
<th>(\lambda^+) (^{(1)})</th>
<th>(\lambda^-) (^{(1)})</th>
<th>(\lambda^+) (^{(1)})</th>
<th>(\lambda^-) (^{(1)})</th>
<th>R⁺ (Å)</th>
<th>R⁻ (Å)</th>
<th>R⁺+R</th>
<th>a° (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ac.Th.ClO(4)</td>
<td>23.437</td>
<td>0.29048</td>
<td>11.22</td>
<td>12.217</td>
<td>±0.365</td>
<td>2.8208</td>
<td>5.534</td>
<td>4.613</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fig. 1: Variation of J and $\alpha^0$ in n-butanol at 25°C

REFERENCES


