Thermodynamic Studies of Ion Association of s-Acetylthiocholine Halides and Perchlorate in Methanol Solutions

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Abstract. Thermodynamic parameters ($\Delta H^0$, $\Delta G^0$, $\Delta S^0$) and the activation energy ($\Delta E_s$) were calculated to explain the limiting equivalent conductance ($\Lambda_0$) and ion association constant ($K_A$) of s-acetylthiocholine halides and perchlorate in methanol solutions at different temperatures by using conductance measurements. It has been evaluated by using Fuoss-Onsager equation. It is evident that the values of ($\Lambda_0$) increase regularly with increase in temperature. For all salts of s-acetylthiocholine, ($\Lambda_0$) indicates that higher mobility of the ions in all solvent systems studied. The free energy change ($\Delta G^0$) values are negative for all salts ($Br^-$, $I^-$ and $ClO_4^-$) in solvent systems studied. Clearly strengthening the interionic association at higher temperatures is largely caused by a decrease in the permittivity of the solvent. The positive values of ($\Delta H^0$) for three salts ($Br^-$, $I^-$ and $ClO_4^-$) show that the association processes are endothermic in nature. Entropy change ($\Delta S^0$) values were positive for all salts because of decrease in solvation of ion-pair compared to that of the free ion. This may be attributed to increase in the degree of freedom upon association, mainly due to the release of solvent molecules.

Key words: s-acetylthiocholine salts, ion association, activation energy and thermodynamic functions.

Introduction

In a wide temperature range, conductivity measurements for electrolyte solution can give a detailed information for ion-ion and ion-solvent interactions [1, 2]. Primary alcohols (MeOH, EtOH, 1-PrOH and 1-BuOH) are polar solvents, having a lower relative permittivity than that of water. Alcohols associate in liquid by hydrogen bond. In the primary alcohols, ionic association is interpreted in terms of a multiple-step association process involving hydrogen bonded solvated of anions in the homologous series methanol through 1-pentanol by Matesich et al. [3]. Thus in this study, it was attempted to obtain some information on the association of s-acetylthiocholine halides and perchlorate in methanol solutions at different temperatures (25, 30, 35 and 40 °C) by conductometric measurements.

The limiting equivalent conductance and association constants for these salts in methanol solutions at (25, 30, 35 and 40 °C) were determined by analyzing conductivity data terms of Fuoss-Onsager equation [4]. The Thermodynamic functions ($\Delta H^0$, $\Delta G^0$, $\Delta S^0$) and activation energy ($\Delta E_s$) were calculated and compared according to interaction of solvent at different temperatures.
Where $\sigma_1$ and $\sigma_2$ are functions of the closest distance of approach $d^0$ in addition to $\eta$ and $D$.

$s$-acetylthiocholine is one of the acetylcholine families. Acetylcholine is a universal neurotransmitter in center nervous system. One of its hazards effect is accumulation. Accumulation will cause increased firing of neurons which lead to general hyper activity i.e. toxic to the nerve system.

**Results and Discussion**

It is evident from Tables 1, 2 and 3, that the values of $\Lambda_0$ increase regularly with increase in temperature for salts of $s$-acetylthiocholine bromide, iodide and perchlorate, indicating less solvation or higher mobility of the ions in all solvent systems studied. This is due to the fact that the increased thermal energy results in greater bond breaking and also variation in vibrational, rotational and translational energy of molecules lead to higher frequency and higher mobility of ions [5]. Also, it is clear that the association constant ($K_A$) values increase with increase in temperature and with increase in alcohol content and also with the increase of the $-\text{CH}_2-$ group in alcohol [5].

Since the conductance measurements of an ion depend on its mobility, it is quite reasonable to treat the conductance data similar to the one that employed for the processes taking place with change of temperature [6], i.e.

$$\Lambda_0 = Ae^{-\Delta E_0^{eq}/RT} \quad \text{or} \quad \log \Lambda_0 = \log A - (\Delta E_0^{eq}/2.303RT), \quad (1)$$

where $A$ is the frequency factor, $R$ is the ideal gas constant and $\Delta E_0^{eq}$ is the Arrhenius activation energy of transport processes. The $\Delta E_0^{eq}$ values have been computed from the slope ($-\Delta E_0^{eq}/2.303RT$) of the plot of $\log \Lambda_0$ vs. $1/T$ and recorded in Tables 1, 2, 3 and Fig. 1.

From the tables, the activation energy $\Delta E_0^{eq}$ is positive value for the three salts in all solvents. Its values were decreased from Br$^-$ to ClO$_4^-$, indicating that higher mobility of the ions in solution and hence higher $\Lambda_0$ values. The free energy change $\Delta G_0^{eq}$ for the association process is calculated from equation (2), [7]

$$\Delta G_0^{eq} = -RT \ln K_A.$$  \hspace{1cm} (2)

Also it is evident from Tables 1, 2 and 3, that the free energy change ($\Delta G_0^{eq}$) values are negative for the three salts (Br$^-$, I$^-$ and ClO$_4^-$) in all solvent systems studied. This means that the association process is favored over the dissociation process in all solvent systems.

According to the results of the calculated thermodynamic parameters as shown by Tables 1, 2, 3 and Fig. 2, the standard enthalpy changes, ($\Delta H_0^{eq}$), can be obtained from the slope ($-\Delta H_0^{eq}/2.303R$) of the plot of log $K_A$ against $1/T$ by using the Van’t Hoff’s isochore equation

$$d \ln K_A/dT = \Delta H_0^{eq}/RT^2 \quad \hspace{1cm} (3)$$

**Table 1.** Thermodynamic Parameters of $s$-acetylthiocholine Bromide.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$\Lambda_0^{[7-10]}$ (ohm$^{-1}$ equiv$^{-1}$ cm$^2$)</th>
<th>$K_A^{[7-10]}$</th>
<th>$\Delta E_0^{eq}$ (kJ mol$^{-1}$)</th>
<th>$\Delta H_0^{eq}$ (kJ mol$^{-1}$)</th>
<th>$\Delta G_0^{eq}$ (kJ mol$^{-1}$)</th>
<th>$\Delta S_0^{eq}$ (J mol$^{-1}$ K$^{-1}$)</th>
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<tr>
<td>298</td>
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<td>-9.75</td>
<td>414.24</td>
</tr>
<tr>
<td>308</td>
<td>140.80</td>
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<tr>
<td>313</td>
<td>157.80</td>
<td>311.03</td>
<td></td>
<td></td>
<td>-14.94</td>
<td>417.57</td>
</tr>
</tbody>
</table>

**Table 2.** Thermodynamic Parameters of $s$-acetylthiocholine Iodide.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$\Lambda_0^{[7-10]}$ (ohm$^{-1}$ equiv$^{-1}$ cm$^2$)</th>
<th>$K_A^{[7-10]}$</th>
<th>$\Delta E_0^{eq}$ (kJ mol$^{-1}$)</th>
<th>$\Delta H_0^{eq}$ (kJ mol$^{-1}$)</th>
<th>$\Delta G_0^{eq}$ (kJ mol$^{-1}$)</th>
<th>$\Delta S_0^{eq}$ (J mol$^{-1}$ K$^{-1}$)</th>
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<td>160.94</td>
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<td>478.84</td>
</tr>
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</table>

**Table 3.** Thermodynamic Parameters of $s$-acetylthiocholine Perchlorate.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$\Lambda_0^{[7-10]}$ (ohm$^{-1}$ equiv$^{-1}$ cm$^2$)</th>
<th>$K_A^{[7-10]}$</th>
<th>$\Delta E_0^{eq}$ (kJ mol$^{-1}$)</th>
<th>$\Delta H_0^{eq}$ (kJ mol$^{-1}$)</th>
<th>$\Delta G_0^{eq}$ (kJ mol$^{-1}$)</th>
<th>$\Delta S_0^{eq}$ (J mol$^{-1}$ K$^{-1}$)</th>
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</table>
Thermodynamic Studies of Ion Association of s-Acetylthiocholine Halides and Perchlorate in Methanol Solutions

Then,

\[ 2.303 \log K_A = -(\Delta H^0/R)(1/T) + \Delta S^0/R \]  \hspace{1cm} (4)

or

\[ 2.303R \log K_A = \left( \Delta S^0 - \frac{\Delta H^0}{T} \right) \]  \hspace{1cm} (5)

The positive values of (\Delta H^0) for the three salts (Br\(^-\), I\(^-\) and ClO\(_4^-\)) show that the association processes are endothermic in nature and the calculated entropy change (\Delta S^0), from Gibbs equation;

\[ \Delta G^0 = \Delta H^0 - T\Delta S^0. \]  \hspace{1cm} (6)

The positive values of (\Delta S^0) for three salts (Br\(^-\), I\(^-\) and ClO\(_4^-\)) indicates the randomness of ions in all solvent systems studied.

![Graph 1](image1.png)  
**Fig. 1.** The variation of log \( \Lambda_0 \) vs. 1/T for s-acetylthiocholine (1) bromide, (2) iodide and (3) perchlorate in methanol at different temperatures.

![Graph 2](image2.png)  
**Fig. 2.** The variation of log \( K_A \) vs. 1/T for s-acetylthiocholine (1) bromide, (2) iodide and (3) perchlorate in methanol at different temperatures.

The values of \( \Delta H^0, \Delta G^0, \Delta S^0 \) are recorded in Tables 1, 2 and 3. For s-acetylthiocholine bromide, iodide and perchlorate in methanol at different temperatures (25, 30, 35 and 40 °C), \( \Delta G^0 \) values decrease with increase in temperature. The decrease in (\Delta G^0) values for the (three salts) to more negative values at increasing temperature favors the transfer of the released solvent molecules into bulk solvent and leads to a smaller (\Delta G^0) values. It was observed that (\Delta H^0) values decrease in the order: I\(^-\) > Br\(^-\) > ClO\(_4^-\). The (\Delta H^0) values were found to be positive in all alcohols. Positive and high (\Delta H^0) values can be attributed to the interaction between ions [8]. As presented in Tables (1-3) (\Delta S^0) values were positive because of decrease in the solvation of ion-pair compared to that of the free ion [2, 9, 10]. This may be attributed to increase in the degree of freedom upon association, mainly due to the release of solvent molecules.

The main factors which govern the standard entropy of ion association of electrolytes are (i) the size and shape of ions, (ii)
charge density on ions, (iii) electrostriction of the solvent molecules around the ions and (iv) the penetration of the solvent molecules inside the space of ions [11].

Bag et al. [12], measured the conductance of Co (III) complex monochloride in MeOH-H₂O mixtures at different temperatures (25, 30, 35, 40 °C). It was found that, at a particular temperature ΔG⁰ becomes more negative. This indicates that ion-pair association is favored with lowering of dielectric constant of medium. A positive entropy change is explained on the assumption that iceberg structure around the cation is broken when association takes place leading to an increase in the degree of disorderliness [13].

Dash et al. [5], measured the conductance of Co (III) complex of chloride and bromide in different composition of H₂O-MeOH, H₂O-EtOH and H₂O in n-PrOH at different temperatures. It was found that the association constant K₄ values of Co (III) complexes of chloride and bromide increase with increase in temperature. It is evident that the activation energy Eₛ is positive for both K₄ in all solvents, free energy change ΔG⁰ values are negative for both association constants in solvent with increasing the temperature. This indicates that the association process is favored over dissociation process in all solvent systems. The positive values of AH⁰ for both complexes show that the association processes are endothermic in nature. The positive value of ΔS⁰ indicates the randomness of ions in solvent system studied [5].

Pura [8], measured the conductance of ferric chloride (FeCl₃) in primary alcohols at different temperatures. It was found that, at particular temperature ΔG⁰ values decrease with increase in temperature. The decrease in ΔG⁰ values for FeCl₃ to more negative values with increasing temperature favor the transfer of the released solvent molecules into the bulk solvent and lead to a smaller ΔG⁰ values. The experimental values of ΔG⁰ for FeCl₃ varied in the order: MeOH > EtOH > 1-PrOH > 1-BuOH in the temperature range studied in this work. It was observed that ΔH⁰ values of FeCl₃ in alcoholic organic solvents decrease in the order of MeOH > EtOH > n-PrOH > n-BuOH. ΔH⁰ values were found to be positive in all alcohols. Positive and high ΔH⁰ can be attributed to the interaction between ions. ΔS⁰ values of FeCl₃ in primary alcohols are found to decrease in the order MeOH < EtOH < n-PrOH < n-BuOH, indicating a weakening in the ion solvation due to the formation of ion pairs. The values of ΔS⁰ for all alcohols used in the study were positive because of the decrease in solvation of the ion pairs compared to that of the free ions. The positive ΔS⁰ values for FeCl₃ in all alcohols may be attributed to the increase in the degree of freedom upon association mainly due to the release of solvent molecules. In other words, the solvation of ions weakens as soon as the ion pair formation occurs. The radii of solvent molecules and the degree of solvation decreases with of –CH₂– groups of primary alcohols. For that reason, higher increase in entropy is observed, and the changes of entropy become more positive values from MeOH to n-BuOH. Positive values of ΔH⁰ and ΔS⁰ values for FeCl₃ can be attributed to the counter balance entropy change resulting from both short- and long- term desolvation of ions. Positive (ΔS⁰) values attributed to desolvation of ions are also supported by the positive enthalpy values indicating a lack of the covalent bonds [8].

El-Hammamy et al. [14], measured the conductance of cobalt (III) the complex chloropentaammine chloride in water at different temperatures 40 → 60 °C and the data were analyzed using Fuoss-Edelson equation [15]. The obtained values of ΔG₀ and K₄ for complex at different temperatures was reported. It was found that ΔG₀ and K₄ increase with increasing temperatures. Thus from the plot of log Λ₀ vs. 1/T for complex of in water at different temperatures, the ΔEₛ(+/ve) value has been evaluated, and also ΔH₀, ΔG₀ and ΔS₀ for complex. It was found that ΔH₀ and ΔS₀ are positive at a particular temperatures but ΔG₀ is negative, this is due to the solvation processes is less but association of ion increase with thermodynamic parameters. Endothermic solvation needs energy to break the bonds around free ion and ion-pairs, ΔS₀ was constant but ΔG₀ decreases the negativity with increasing the temperature.

El-Hammamy et al. [16], measured the conductance of 1:1 s-acetylthiocholine salts (C1-, Br⁻, I⁻ and ClO₄⁻) in water at different temperatures (25, 30, 35 °C) and the data were analyzed using Fuoss-Edelson equation. Values of ΔG₀, ΔH₀, ΔG₄ and ΔS₄ were obtained (solvation). It was found that ΔG₀ and ΔS₄ increase, while K₄ decrease with increasing the temperatures for all salts of s-acetylthiocholine according to electrostatic attraction theory. Thus from the plot of log Λ₀ vs. 1/T for s-acetylthiocholine halides and perchlorate in water at different temperatures, ΔEₛ values have been evaluated, also ΔH₀, ΔG₀ and ΔS₀ for salts. It was found that negative values of ΔH₀, ΔG₀ and ΔS₀ in water at different temperatures; negative value of ΔH₀ indicated that ion association processes were exothermic. The solvated radii were also increased with temperature indicating a higher solvation process due to increase in the electronic clouds around the solvated molecules as a result of an increase in their vibration and rotational motion. The limiting equivalent conductance and dissociation degree were also increased as the temperature increased, indicating higher solvation process [16]. The negative values of different thermodynamic parameters ΔH₀, ΔG₀ and ΔS₀, for all salts under test in the used solvent, indicated exothermic association process with less energy-consuming and more stabilization [17]. While in [18], El-Hammamy et al. measured the conductance of s-acetylthiocholine salts (Br⁻, I⁻ and ClO₄⁻) in acetonitrile at different temperatures (25, 30, 35, 40 °C) the data were analyzed using Fuoss-Onsager equation. The values of ΔG₀, ΔH₀ and ΔS₀ (solvation) were obtained. It was found that ΔG₀ and K₄ increase with increasing the temperature. Thus from the plot of log Λ₀ vs. 1/T for each salt in acetonitrile solutions at different temperatures, ΔEₛ(+/ve) values have been evaluated, and also ΔH₀, ΔG₀ and ΔS₀ all the salts. It was found that ΔH⁰ and ΔS⁰ are positive values at a particular temperatures but ΔG⁰ is negative. This is due to the solvation processes is less but association of ion increase with thermodynamic parameters. Endothermic solvation needs energy to break the bond around free ion and ion-pairs, i.e., endothermic solvation process was less energy consuming and more stabilized.
Experimental

The s-acetylthiocholine bromide, iodide and perchlorate were purified as reported in the literature [19], methanol (B.D.H) was purified previously as reported in reference [20]. The specific conductance for purified methanol at different temperatures (25, 30, 35 and 40 °C) was found to be in the range \((1.6 − 7.3) \times 10^{-7} \text{Ω}^{-1} \text{cm}^{-1}\). 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 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. The solvent constants used in all calculations were taken as reported [21-24], i.e., densities \((d_{25°}) = 0.78657 \text{g} \cdot \text{cm}^{-3}\), \((d_{30°}) = 0.7862 \text{g} \cdot \text{cm}^{-3}\), \((d_{35°}) = 0.7815 \text{g} \cdot \text{cm}^{-3}\), \((d_{40°}) = 0.7765 \text{g} \cdot \text{cm}^{-3}\), respectively, the viscosities \((\eta_{25°}) = 0.5448 \times 10^{-2} \text{P}\), \((\eta_{30°}) = 0.5030 \times 10^{-2} \text{P}\) and \((\eta_{35°}) = 0.4620 \times 10^{-2} \text{P}\), \((\eta_{40°}) = 0.4220 \times 10^{-2} \text{P}\), respectively and the dielectric constants \((D_{25°}) = 32.63\), \((D_{30°}) = 30.68\), \((D_{35°}) = 29.90\), \((D_{40°}) = 29.03\), respectively.

References