

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

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Abstract. Thermodynamic parameters (ΔH^0 , ΔG^0 , ΔS^0) and the activation energy (ΔE_s) were calculated to explain the limiting equivalent conductance (Λ_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 (Λ_0) increase regularly with increase in temperature. For all salts of *s*-acetylthiocholine, (Λ_0) indicates that higher mobility of the ions in all solvent systems studied. The free energy change ΔG^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 (ΔH^0) for three salts (Br^- , I^- and ClO_4^-) show that the association processes are endothermic in nature. Entropy change (ΔS^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

Resumen. Los parámetros termodinámicos (ΔH^0 , ΔG^0 , ΔS^0) y la energía de activación (ΔE_s) fueron calculados para explicar la conductancia equivalente límite (Λ_0) y la constante de asociación (K_A) a diferentes temperaturas, obtenidas con medidas de conductividad, de soluciones metanólicas de halogenuros y perclorato de *s*-acetiltio-colina. Estos parámetros fueron obtenidos utilizando la ecuación de Fuoss-Onsager. Los valores de (Λ_0) se incrementan directamente con el incremento de la temperatura. Los valores obtenidos de (Λ_0) para todas las sales de *s*-acetiltio-colina indican que existe una gran movilidad de los iones en todos los sistemas estudiados. Los valores para la variación de energía libre ΔG^0 son negativos para todas las sales (Br^- , I^- y ClO_4^-) en las soluciones estudiadas. El notable incremento de la asociación interiónica a altas temperaturas está directamente relacionado con la disminución de la permitividad de las soluciones. Los valores positivos del (ΔH^0) para tres sales (Br^- , I^- y ClO_4^-) indican que los procesos de asociación son de naturaleza endotérmica. Los valores del cambio de entropía (ΔS^0) son positivos debido a la disminución de la solvatación del par iónico en comparación con la del ion libre. Este comportamiento podría estar ocasionado por un incremento en los grados de libertad de la asociación, relacionado directamente por la liberación de moléculas del solvente.

Palabras clave: Sales de *s*-acetiltio-colina, asociación iónica, energía de activación, funciones termodinámicas.

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 (ΔH^0 , ΔG^0 , ΔS^0) and activation energy (ΔE_s) were calculated and compared according to interaction of solvent at different temperatures.

Fuoss and Onsager [4], used the sphere in continuum model and gave the following 3-parameter equation for the 1:1 associated electrolyte.

$$\Lambda = \Lambda_0 - S(C\gamma)^{1/2} + EC\gamma \log C\gamma + (J - B\Lambda_0)C\gamma - K_A C\gamma \Lambda f^2.$$

Where, Λ is the equivalent conductance $\text{ohm}^{-1} \text{equiv}^{-1} \text{cm}^2$, C is the concentration (equiv/l) and ion association constant (K_A) was determined using Fuoss and Onsager three parameter. γ is the degree of dissociation which can be calculated using the following equation:

$$\gamma = \Lambda/\Lambda_0 - S(C\Lambda/\Lambda_0)^{1/2}$$

S and E being the theoretically predicted constants, which depend on the dielectric constant D , the viscosity η , and the absolute temperature T of the medium. J is a term which includes the ion and ion-solvent interactions and is given by the equation

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

Where σ_1 and σ_2 are functions of the closest distance of approach a^0 in addition to η 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 Λ_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.

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

where A is the frequency factor, R is the ideal gas constant and ΔE_s is the Arrhenius activation energy of transport processes. The ΔE_s values have been computed from the slope ($-\Delta E_s/2.303RT$) 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 ΔE_s 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 Λ_0 values. The free energy change ΔG^0 for the association process is calculated from equation (2), [7]

$$\Delta G^0 = -RT \ln K_A. \quad (2)$$

Also it is evident from Tables 1, 2 and 3, that the free energy change (ΔG^0) values are negative for the three salts (Br^- , Γ 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, (ΔH^0), can be obtained from the slope ($-\Delta H^0/2.303R$) of the plot of $\log K_A$ against. $1/T$ by using the Van't Hoff's isochore equation

$$d \ln K_A/dT = \Delta H^0/RT^2 \quad (3)$$

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

T (K)	Λ_0 [7-10] (ohm ⁻¹ equiv ⁻¹ cm ²)	K_A [7-10]	ΔE_s^0 (kJ mol ⁻¹)	ΔH^0 (kJ mol ⁻¹)	ΔG^0 (kJ mol ⁻¹)	ΔS^0 (J mol ⁻¹ K ⁻¹)
298	125.73	36.38	11.61	115.76	-8.90	418.35
303	131.38	47.99			-9.75	414.24
308	140.80	—			—	—
313	157.80	311.03			-14.94	417.57

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

T (K)	Λ_0 [7-10] (ohm ⁻¹ equiv ⁻¹ cm ²)	K_A [7-10]	ΔE_s^0 (kJ mol ⁻¹)	ΔH^0 (kJ mol ⁻¹)	ΔG^0 (kJ mol ⁻¹)	ΔS^0 (J mol ⁻¹ K ⁻¹)
298	131.69	—	10.86	136.65	—	—
303	137.86	28.30			-8.42	478.79
308	146.46	41.99			-9.57	474.75
313	163.10	160.94			-13.22	478.84

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

T (K)	Λ_0 [7-10] (ohm ⁻¹ equiv ⁻¹ cm ²)	K_A [7-10]	ΔE_s^0 (kJ mol ⁻¹)	ΔH^0 (kJ mol ⁻¹)	ΔG^0 (kJ mol ⁻¹)	ΔS^0 (J mol ⁻¹ K ⁻¹)
298	140.49	60.92	10.64	66.36	-10.18	256.85
303	146.39	70.44			-10.72	254.38
308	156.08	—			—	—
313	172.98	207.90			-13.89	256.39

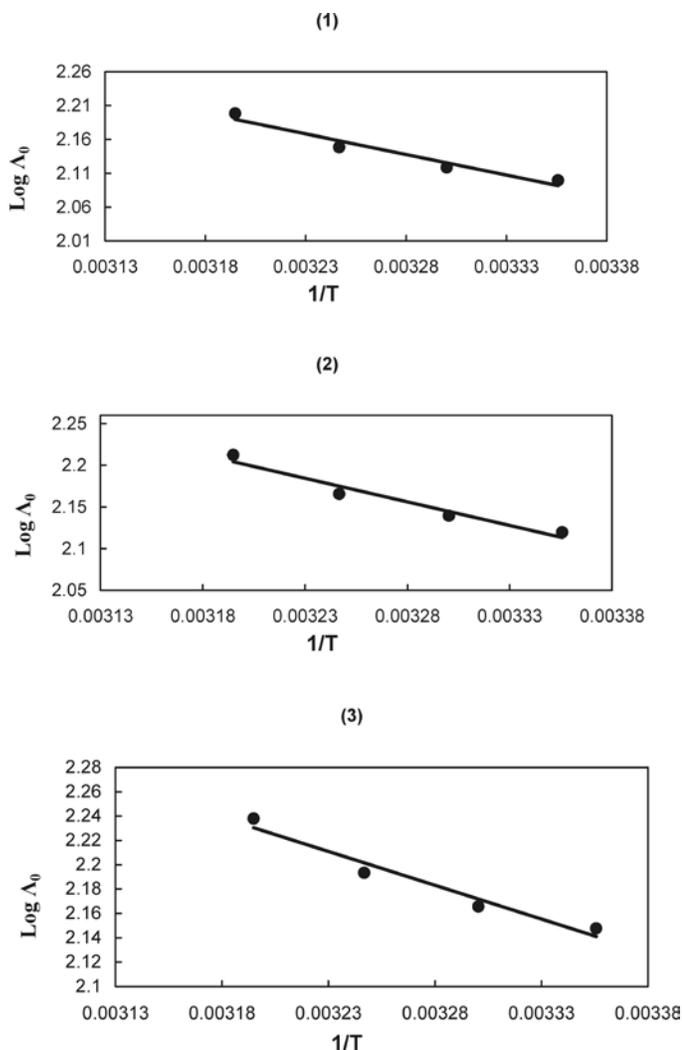


Fig. 1. The variation of $\log \Lambda_0$ vs. $1/T$ for *s*-acetylthiocholine (1) bromide, (2) iodide and (3) perchlorate in methanol at different temperatures.

Then,

$$2.303 \log K_A = -(\Delta H^0/R)(1/T) + \Delta S^0/R \quad (4)$$

or

$$2.303R \log K_A = \left(\Delta S^0 - \frac{\Delta H^0}{T} \right) \quad (5)$$

The positive values of (ΔH^0) for the three salts (Br^- , I^- and ClO_4^-) show that the association processes are endothermic in nature and the calculated entropy change (ΔS^0) , from Gibbs equation;

$$\Delta G^0 = \Delta H^0 - T\Delta S^0. \quad (6)$$

The positive values of (ΔS^0) for three salts (Br^- , I^- and ClO_4^-) indicates the randomness of ions in all solvent systems studied.

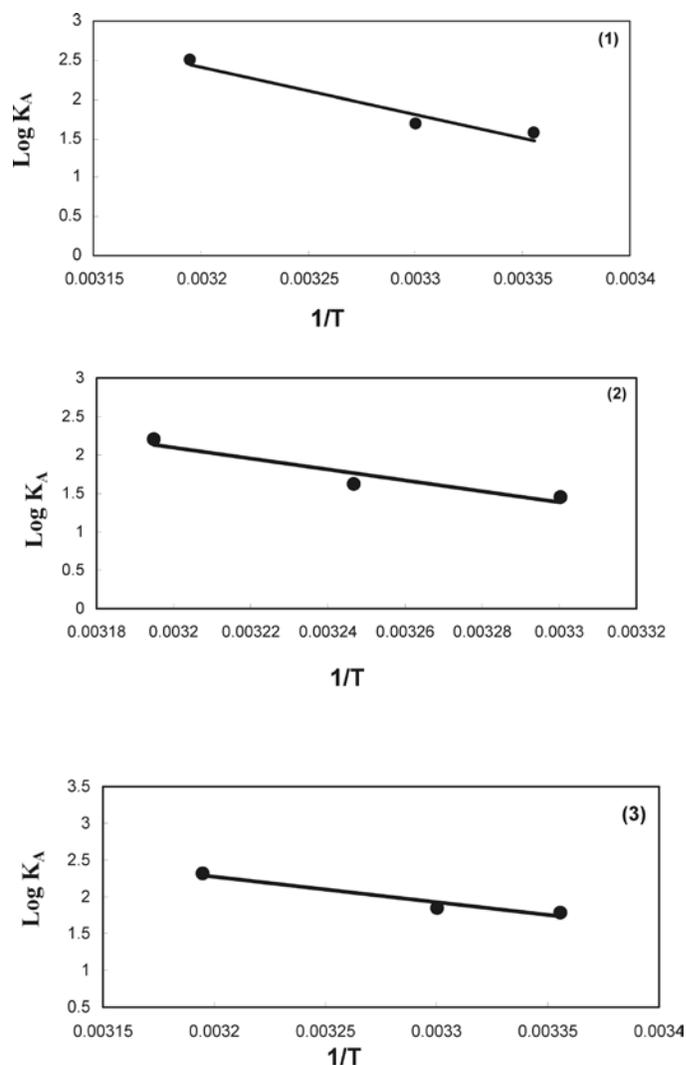


Fig. 2. The variation of $\log K_A$ vs. $1/T$ for *s*-acetylthiocholine (1) bromide, (2) iodide and (3) perchlorate in methanol at different temperatures.

The values of ΔH^0 , ΔG^0 , ΔS^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). (ΔG^0) values decrease with increase in temperature. The decrease in (ΔG^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 (ΔG^0) values. It was observed that (ΔH^0) values decrease in the order: $\text{I}^- > \text{Br}^- > \text{ClO}_4^-$. The (ΔH^0) values were found to be positive in all alcohols. Positive and high (ΔH^0) values can be attributed to the interaction between ions [8]. As presented in Tables (1-3) (ΔS^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 ΔG^0 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 disorderness [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 K_A values of Co (III) complexes of chloride and bromide increase with increase in temperature. It is evident that the activation energy E_s is positive for both K_A in all solvents, free energy change ΔG^0 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 ΔH^0 for both complexes show that the association processes are endothermic in nature. The positive value of ΔS^0 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 ΔG^0 values decrease with increase in temperature. The decrease in ΔG^0 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 ΔG^0 values. The experimental values of ΔG^0 for FeCl₃ varied in the order: MeOH > EtOH > 1-PrOH > 1-BuOH in the temperature range studied in this work. It was observed that ΔH^0 values of FeCl₃ in alcoholic organic solvents decrease in the order of MeOH > EtOH > *n*-PrOH > *n*-BuOH. ΔH^0 values were found to be positive in all alcohols. Positive and high ΔH^0 can be attributed to the interaction between ions. ΔS^0 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 ΔS^0 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 ΔS^0 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 ΔH^0 and ΔS^0 values for FeCl₃ can be attributed to the counter balance entropy change resulting from both short- and long- term desolvation of ions. Positive (ΔS^0) 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 Λ_0 and K_A for complex at different temperatures was reported. It was found that Λ_0 and K_A increase with increasing temperatures. Thus from the plot of log Λ_0 vs. 1/T for complex of in water at different temperatures, the $\Delta E_S(+ve)$ value has been evaluated, and also ΔH^0 , ΔG^0 and ΔS^0 for complex. It was found that ΔH^0 and ΔS^0 are positive at a particular temperatures but ΔG^0 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, ΔS^0 was constant but ΔG^0 decreases the negativity with increasing the temperature.

El-Hammamy *et al.* [16], measured the conductance of 1:1 *s*-acetylthiocholine salts (Cl⁻, Br⁻, I⁻ and ClO₄⁻) in water at different temperatures (25, 30, 35 °C) and the data were analyzed using Fuoss-Onsager equation. Values of Λ_0 , K_A and a^0 were obtained (solvation). It was found that Λ_0 and a^0 increase, while K_A decrease with increasing the temperatures for all salts of *s*-acetylthiocholine according to electrostatic attraction theory. Thus from the plot of log Λ_0 vs. 1/T for *s*-acetylthiocholine halides and perchlorate in water at different temperatures, ΔE_S values have been evaluated, also ΔH^0 , ΔG^0 and ΔS^0 for salts. It was found that negative values of ΔH^0 , ΔG^0 and ΔS^0 in water at different temperatures; negative value of ΔH^0 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 ΔH^0 , ΔG^0 and ΔS^0 , 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.* [18] 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 Λ_0 , K_A and a^0 (solvation) were obtained. It was found that Λ_0 and K_A increase with increasing the temperature. Thus from the plot of log Λ_0 vs. 1/T for each salt in acetonitrile solutions at different temperatures, $\Delta E_S(+ve)$ values have been evaluated, and also ΔH^0 , ΔG^0 and ΔS^0 all the salts. It was found that ΔH^0 and ΔS^0 are positive values at a particular temperatures but ΔG^0 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 $(1.6 - 7.3) \times 10^{-7} \Omega^{-1} \text{ cm}^{-1}$. 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 (η_{25°) = $0.5448 \times 10^{-2} \text{ P}$, (η_{30°) = $0.5030 \times 10^{-2} \text{ P}$ and (η_{35°) = $0.4620 \times 10^{-2} \text{ P}$, (η_{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.

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