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Conductance and ion association studies of unsymmetrical complex chloropentamine cobalt (III) chloride in water at different temperatures

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ABSTRACT

Conductance of complex chloropentammine cobalt (III) chloride has been measured in water at different temperatures (30, 35, 40, 50 and 60 °C). The limiting equivalent conductance (Λ_0) and ion association constant (K_A) for complex in water have been evaluated using Fuoss-Edelson equation. The influence of solvent on the solvation of ions has been discussed. Temperature variation of the association constant has been studied to evaluate the thermodynamic parameters.

Keywords: Ion association, activation energy and thermodynamic parameters.

INTRODUCTION

The measurement of electrical conductivities of dilute solutions of salts or complexes are considered to be one of the important methods for studying the ion-pair or multiple-ion association not only in aqueous solutions but also in non-aqueous, or mixed ones (1-4). Also, conductivity measurements were used to evaluate the hydration free energy of some electrolytic solutions and to study the nature of the solute-solvent interaction (5). The present work aims to determine the conductance values of complex of chloropentammine cobalt (III) chloride has been measured in water at (30, 35, 40, 50 and 60 °C) to examine the validity of Fuoss-Edelson equation . The limiting equivalent conductance (Λ_0), the ion association constant (K_A) and the solvation for complex have been evaluated. These values have been used to discuss qualitatively the nature of the ion-ion, ion-solvent and solvent-solvent interaction of complex.

Temperature variation of (K_A) has been studied to get the thermodynamic parameters as a function of the solvent structure.

MATERIALS AND METHODS

Chloropentammine cobalt (III) chloride reported and purified by published method (6-7). Conductivity water was obtained as reported in the literature (8). Its specific conductunace amounts to $(2-5)\times 10^{-6}$ $\Omega^{-1}cm^{-1}$.The solvent constants used in all calculations were taken as reported in the literature [(9)]. A "Pye" 11700 conductance bridge was used for measuring the resistance of solutions at 5 K c/s.

RESULTS AND DISCUSSION

The experimental data of conductance measurement of 2:1 complex of chloropentammine cobalt (III) chloride in water at different temperatures were analyzed using Fuoss-Edelson equation [(10)]. Since the conductance of an ion depends on its mobility, it is reasonable to treat the conductance data similar to the one that employs for rate processes taking place with change of temperature [(11)], i.e.,

$$\Lambda_0 = Ae^{-\Delta Es/RT} \qquad \text{or} \qquad \ln \Lambda_0 = \ln A - \Delta Es/RT$$

Where A is the frequency factor, R is the ideal gas constant and ΔEs is the Arrhenius activation energy of transport processes. Thus from the plot of log Λ_0 vs. 1/T for complex of chloropentammine cobalt (III) chloride in water at different temperatures, the ΔEs value has been computed from the slope [(12)] and recorded in Tables (1) and Fig (1).

Table (1) : Thermodynamic Parameters of Chloropentammine Co(III) Complex Chloride [Co (III)$(NH_3)_5$ Cl]Cl_2 in water at different temperatures

T (K)	a° (A°)	$\Lambda_\circ$ (ohm^{-1} equiv^{-1} cm^2)	K_A	ΔE_s° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔG° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})
303	3.53	200.90	542.43	26.779	-251.134	-15.861	-776.48
308	3.83	221.23	114.49			-12.139	-775.96
313	4.02	225.35	22.45			-8.095	-776.98
323	3.27	300.74	351.57		210.331	-15.793	699.92
333	1.73	544.03	2861.10			-22.035	697.79

A perusal of Table (1) shows that the value of $\Delta E_S(+ve)$. This indicates higher mobilites of ions in solutions and hence Λ_0 increases with increasing temperatures.

The free energy change (ΔG^0) for association is calculated from the relation[(13)] $(\Delta G^0 = -RT \ln K_A)$. The heat of association (ΔH^0) is obtained from the slope of the plot of log K_A vs. $1/T$ (Fig.2,3). The entropy change (ΔS^0) is calculated from Gibbs-Helmholtz equation; $(\Delta G^0 = \Delta H^0 - T\Delta S^0)$ from second law of thermodynamics.

The values of these thermodynamic functions are given in Table (1). The negative value of (ΔH^0) indicates that ion association processes are exothermic in nature in water at (30, 35 and 40^0C) temperatures. The positive value of (ΔH^0) at 50 and 60 °C indicates that ion association processes are endothermic.

At (30, 35 and 40) temperatures K_A decreases and a^0 (solvation) increases with increasing the temperatures from $30 \rightarrow 40^0 C$. Also $\Delta H^0, \Delta G^0, \Delta S^0$ are negative values but the negativity of ΔG^0 decrease with increasing temperature from $30 \rightarrow 40^0 C$, but in case of ΔS contains constant negative values from $30 \rightarrow 40^0 C$.

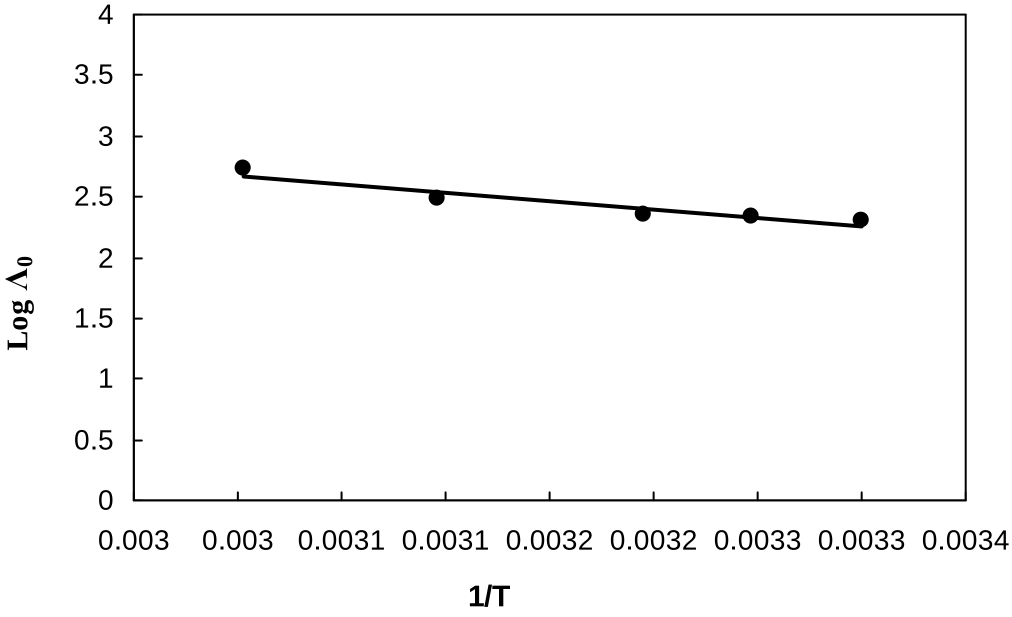

Fig (1): The variation of log Λ_0 vs. 1/T for [Co $(NH_3)_5$ Cl] Cl_2 in water at different temperatures

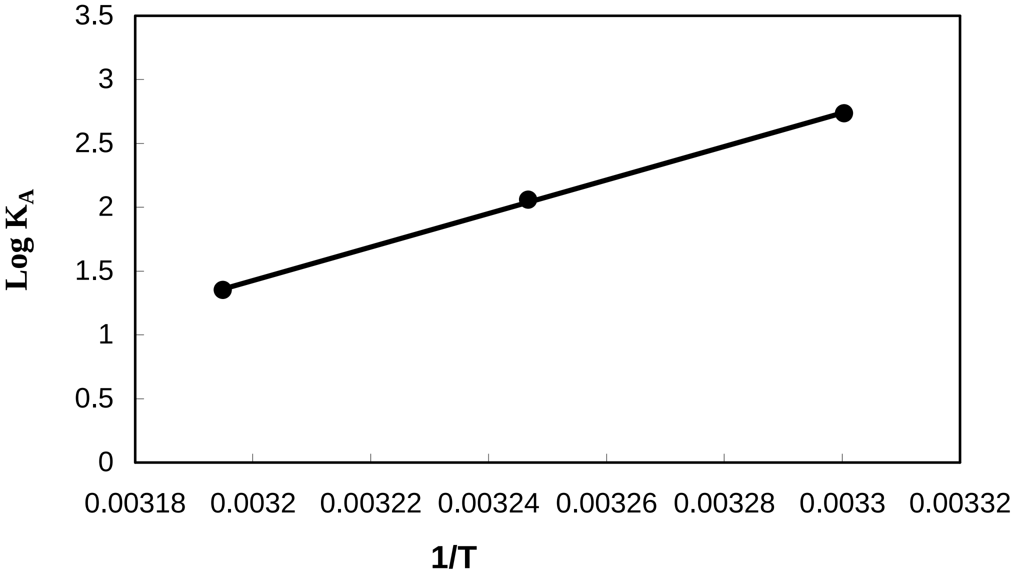

Fig (2): The variation of log K_A vs. 1/T for [Co $(NH_3)_5$ Cl] Cl_2 in water at different temperatures
$(30 \rightarrow 40^0 C)$

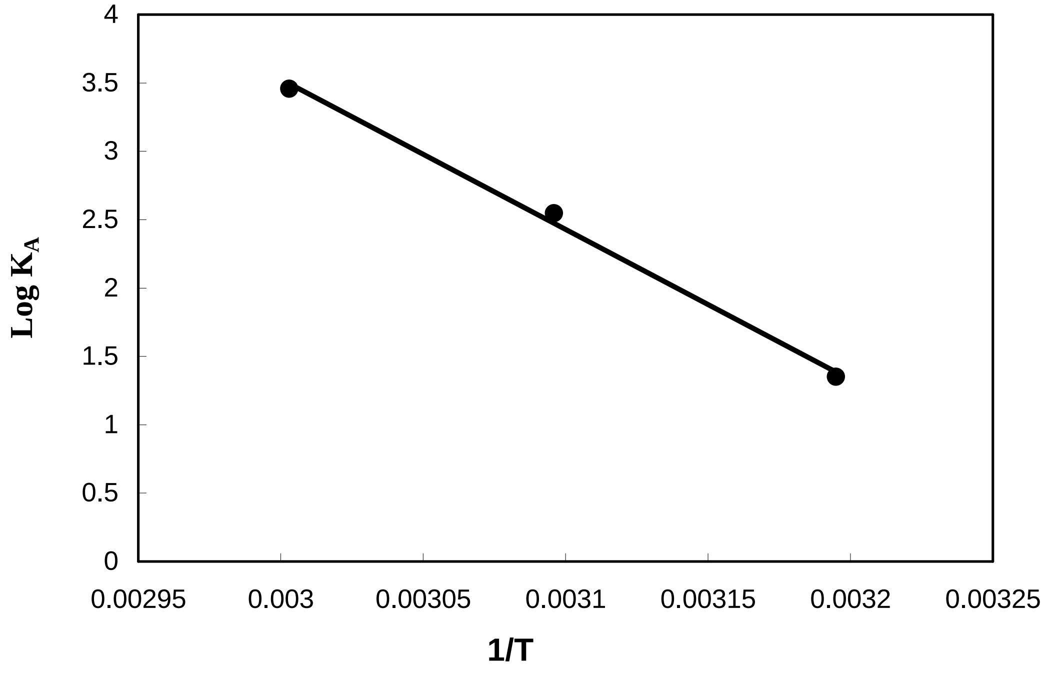

Fig (3): The variation of log K_A vs. 1/T for [Co $(NH_3)_5$ Cl] Cl_2 in water at different temperatures $(40 \rightarrow 60^0C)$

The effect of temperature (table 1), can be noticed from decreasing in the negative values of the associating free energy as the temperature raise from $30 \rightarrow 40^0C$.

Also the solvated radii are increased with the temperature range $30 \rightarrow 40^0C$ indicating a higher solvation process due to increase in the electronic clouds around the solvated molecules as a result of increase in their vibration and rotation motion.

The limiting equivalent conductance $30 \rightarrow 60^0C$ and dissociation degree $30 \rightarrow 40^0C$ were also increase as the temperature increased $30 \rightarrow 40^0C$ indicating higher solvation process (14). The negative value of different thermodynamic parameters $\Delta H^0, \Delta G^0, \Delta S^0$ for a complex under consideration in the used solvents, indicate exothermic association process, i.e., the association process is less energy consuming and more stabilized (11).

But in case of cobalt (III) complex values of temperature $50 \rightarrow 60^0C$, the ΔH^0 and ΔS^0 are positive but ΔG^0 is negative, this is due to in two temperatures (50,60^{0}C) 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, i.e., endothermic solvated process and ΔS^0 as constant but ΔG^0 decreases the negativity with increasing the temperature.

Bag et al.(15), measured the conductance of cobalt (III) complex monochloride in MeOH-H_2O mixtures at different temperatures. It was found that, at a particular temperature ΔG^0 becomes more negative with increase in temperatures. 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 (16).

Dash et al.(17), measured the conductance of cobalt (III) complex of chloride and bromide in different composition of H_2O-MeOH, H_2O-EtOH and H_2O in n-PrOH at different temperatures. It was found that the association constant K_A values of cobalt (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 increase 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.
The ΔG^0 values as seen in table (1) decrease with the increase in temperature. The decrease in ΔG^0 values of chloropentammine cobalt (III) complex chloride to more negative values at increasing temperature favors the transfer of the released solvent molecules into the bulk solvent and leads to a smaller ΔG^0 values.

The ΔH^0 values in table (1) were found to be positive in all alcohols (18). Positive and high ΔH^0 values can be attributed interactions between ions.

As presented in table (1), ΔS^0 values of cobalt (III) complex are found to decrease with increase temperature, indicating a weakening in the solvation due to the formation of ion pairs.

The main factors which govern the standard entropy of ion association of electrolytes are (i) the size and shape of ions, (ii) charge density of ions, (iii) electrostriction of the solvent molecules around the ions and (iv) The penetration of the solvent molecules inside the space of the ions (19).

The values of ΔS^0 for chloropentammine cobalt (III) complex chloride used in the study were positive because of the decrease in solvation of the ion pairs compared to that of the free ions (20-22). The positive ΔS^0 values given in table (1) 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.

Positive values of ΔH^0 and ΔS^0 for chloropentammine chloride can be attributed to counterbalance of the enthalpy term by a favorable entropy change resulting from the short- and long-range desolvation of both ions. Positive ΔS^0 values attributed to desolvation of both ions are also supported by the positive enthalpy values indicating a lack of covalent bonds.
El-Hammamy et al.(23), measured the conductance of 1:1 acetylthiocholine salts (Cl^-, Br^-, I^- and ClO_4^-) in water at different (25,30,35^{0}C) were analyzes using Fuoss-Onsager equation (24), it obtained the values of Λ_0, K_A and a^0 (solvation). It was found that Λ_0 and a^0 increase with increase the temperature 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 acetylthiocholine halides and perchlorate in water at different temperatures, ΔE_S values have been evaluated ,also $\Delta H^0, \Delta G^0$ *and* ΔS^0 for salts. It was found that negative values of $\Delta H^0, \Delta G^0 \, and \, \Delta S^0$ in water at different temperatures; negative value of ΔH^0 indicated that ion association processes were exothermic in nature in all solvents at all temperatures. 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 (14).The negative values of different thermodynamic parameters $\Delta H^0, \Delta G^0 \, and \, \Delta S^0$, for all salts under test in the used solvent, indicated exothermic association process was less energy-consuming and more stabilized (11).

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