

Ion Pair Formation of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ in Aqueous Medium at Different Temperatures-A Conductance Method

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(Received: 6 April 2010;

Accepted: 4 November 2010)

AJC-9249

Conductances of cobalt(II) chloride hexahydrate and pentaamminechlorocobalt(III) chloride has been measured in aqueous medium at 298.15 to 323.15 K. The conductance data in all cases have been analyzed by Shedlovsky equation to obtain limiting equivalent conductance (Λ_0) and association constant (K_A) values for the electrolyte. The limiting equivalent conductance and the ion association constants values for cobalt(II) chloride hexahydrate were found to be higher than those in pentaamminechlorocobalt(III) chloride. Based on the K_A values and temperature dependence of Λ_0 , the thermodynamic parameters viz., free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) have been determined. Both the associations are exothermic in nature which is determined by negative values of ΔH° . The chosen metal complexes show ion-pair association within experimental different temperature ranges; which is supported by negative values of ΔG° .

Key Words: Conductance, Ion-pair formation, Cobalt(II) chloride, Pentaamminechlorocobalt(III) chloride.

INTRODUCTION

The concept of ion pairs to the evaluation of the inter-ionic forces in electrolytic solution was first introduced by Bjerrum¹. The tendency of ions to associate into ion pairs depends on the balanced between the electrostatic force and thermal energy.

The first inter-ionic theory of electrolytic solution was that of Debye-Huckel^{2,3} and this theory has been used remarkably in interpreting the behaviour of ions in dilute solutions. The theoretical calculation for the decreased of ionic mobility with increasing concentration considered two effects. In the first place, when an ion moves through under the influence of an applied electric field, it tends to disturb the surrounding ionic atmosphere which exerts an opposing electric force and, secondly, the ion comprising the ionic atmosphere produced a counter-current of solvent which also retards the motion of the central ion⁴.

In solvents of low dielectric constant, where the electrostatic potential energy of an anion and a cation at contact is large compared to mean thermal energy kT , it is expected the association of ions as non conducting pairs. As the dielectric constant is increased the extents of association should decrease, but it should never become a non-zero chance that anion-cation contact will occur.

Conductance of 1:1 electrolytes has been extensively studied⁵⁻⁹ by using Shedlovsky equation¹⁰. For higher valent

unsymmetrical electrolytes limited work has been done. In the present work we have studied the conductance and ion association of 2:1 electrolyte salts copper(II) chloride hexahydrate and hexaamminechlorocobalt(III) chloride in aqueous medium at 298.15 to 323.15 K using Shedlovsky equation. The equivalent conductance at infinite dilution (Λ_0) and the association constant (K_A) for the complex salt have been evaluated. The thermodynamic parameters ΔG° , ΔH° and ΔS° have also been calculated from the temperature variations of the association constants.

EXPERIMENTAL

Among the various methods, the conductance method is one of the most sensitive and widely used methods for investigation of physico-chemical nature of ion-pair formation of simple and mixed solvents¹¹⁻¹³. The limiting molar conductance and the association constants of the complex ion with anions were calculated by using Shedlovsky method.

The electrical conductivities were measured by Eutech Instrument-pc 510 digital conductivity bridges with a dip type immersion conductivity cell were used. The solutions of different concentrations ($8.6 - 3.4 \times 10^{-3}$) were carefully prepared by dissolving requisite amount of the sample in conductivity water of low specific conductance ($< 3 \times 10^{-6} \text{ S cm}^{-1}$). Conductivity measurements were carried out over the temperature range 25-50 °C. All the dielectric constants and viscosities were obtained from literature. The temperature control in the

ranges of 25-50 °C were made by using water bath and thermometer. The measurement of weights were done by using a Metler Balance, model TB- 214. All calculations were done on IBM-PC-AT/386 using a basic programmed.

RESULTS AND DISCUSSION

Experimental data of conductance measurements of 2:1 $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ in aqueous medium by using Shedlovsky extrapolation Technique¹⁴. Shedlovsky method involves the linear extrapolation using eqn. 1,

$$\frac{1}{\Lambda S(z)} = \frac{1}{\Lambda_0} - \left(\frac{K_A}{\Lambda_0^2} \right) (C \Lambda f_{\pm}^2 S(z)) \quad (1)$$

where Λ is molar conductance at a concentration c (gmol dm^{-3}), the limiting molar conductance and K_A the observed association constant. The other symbols are given by

$$S(z) = \left(\frac{z}{2} \sqrt{1 + \left(\frac{z}{2} \right)^2} \right)^2$$

$$z = \left[\frac{\alpha \Lambda_0 + \beta}{\Lambda_0^{3/2}} \right] (C \Lambda)^{1/2}$$

$$\alpha = \frac{17.147 \times 10.5w}{(DT)^{3/2}}$$

$$w = z_+ z_- \frac{2q}{1+q^{1/2}}$$

$$q = \frac{z_+ z_-}{z_+ + z_-} \times \frac{\lambda_+ + \lambda_-}{z_+ \lambda_- + z_- \lambda_+}$$

$$\beta = \frac{151.47}{\eta(DT)q^{1/2}}$$

Z and λ are the valence and conductance of the ions, respectively, excluding their sign, D is the dielectric constant of the medium, η the viscosity (c.p.). The degree of dissociation (τ) is related to $S(z)$ by the equation,

$$\beta = \frac{\Lambda S(z)}{\Lambda_0}$$

f_{\pm} is the activity coefficient of the free ions and was calculated using eqn. 2,

$$-\log f_{\pm} = \frac{Az_+ z_+ \mu^{1/2}}{1 + BR\mu^{1/2}} \quad (2)$$

where

$$A = \frac{1.8247 \times 10^6}{(DT)^{1/2}}$$

$$B = \frac{0.5029 \times 10^{10}}{(DT)^{3/2}}$$

$$\mu = \frac{1}{2} \sum_i (c_i \tau_i) z_i^2$$

R is the maximum centre to centre distance between the ions in the ion-pair. At present there is no method of determining the value of R precisely^{15,16}. In order to treat the data in present system the R value is assumed to be $R = a + d$, where a , the sum of crystallographic radii of the ions, is approximately equal to 5 Å and d (Å) is given by¹⁷

$$d = 1.183 \left(\frac{M}{\rho} \right)^{1/3} \quad (3)$$

where M is the molecular weight of the solvent and ρ the density of the solution.

An initial value of Λ_0 was obtained by least square method (Λ) and concentration, C was introduced as input in computer programme. The mean activity coefficient f was determined by eqn. 2 for the above chosen complex salts¹⁸. From the linear plot of $1/\Lambda S(z)$ versus $C \Lambda f_{\pm}^2 S(z)$; Λ_0 and K_A was evaluated from the intercept $1/\Lambda_0$ and the slope K_A/Λ_0^2 , respectively¹⁵. The procedure was repeated using these new values of Λ_0 and K_A . All calculations were carried out by IBM-PC AT/386 using a basic program.

The change of free energy for the association process (ΔG°) was calculated from the equation:

$$\Delta G = -2.303RT \log_{10} K_A \quad (4)$$

The enthalpy change of association (ΔH°) was obtained from the slope of $\log K_A$ versus $1/T$. The change of association entropy (ΔS°) was calculated from the Gibbs-Helmholtz equation:

$$\Delta G^\circ = \left(\frac{\Delta H^\circ - \Delta G^\circ}{T} \right) \quad (5)$$

From Tables 1 and 2, the values of Λ_0 for the electrolytes increase invariably with increase in temperature in aqueous medium, indicating less solvation or higher mobility of ions⁵. This is due to the fact that the increase thermal energy results in bond breaking and leads to higher frequency and higher mobility of the ions. Values of Λ_0 for $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ are always greater than those values of complex $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ is most prone to the variation in vibrational, rotational and translational energy levels with temperature.

TABLE-1
VALUE OF LIMITING MOLAR CONDUCTANCE Λ_0 (Scm^3) AND ASSOCIATION CONSTANTS K_A ($\text{dm}^3 \text{mol}^{-1}$) OBTAINED BY SHEDLOVSKY TECHNIQUE FOR $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ IN AQUEOUS SOLUTION AT DIFFERENT TEMPERATURES

| | 298 K | 303 K | 308 K | 313 K | 318 K | 323 K |
|-------------|--------|--------|--------|--------|--------|--------|
| K_A | 28.96 | 29.54 | 30.40 | 31.89 | 32.46 | 33.16 |
| Λ_0 | 155.83 | 160.62 | 163.21 | 167.03 | 169.64 | 173.10 |

TABLE-2
VALUE OF LIMITING MOLAR CONDUCTANCE Λ_0 (Scm^3) AND ASSOCIATION CONSTANTS K_A ($\text{dm}^3 \text{mol}^{-1}$) OBTAINED BY SHEDLOVSKY TECHNIQUE FOR PENTAAMINECHLORO COBALT(III) CHLORIDE IN AQUEOUS SOLUTION AT DIFFERENT TEMPERATURES

| | 298 K | 303 K | 308 K | 313 K | 318 K | 323 K |
|-------------|--------|--------|--------|--------|--------|--------|
| K_A | 26.66 | 27.90 | 28.93 | 29.32 | 30.76 | 31.51 |
| Λ_0 | 128.83 | 132.38 | 138.77 | 142.38 | 148.70 | 155.78 |

The values of the K_A for these two complexes increase with rise in temperature (Fig. 1, Tables 1 and 2). The higher K_A values in the case of simple salt compared to complexes salt may be ascribed to the more coulombic type of interaction (specific short-range interaction) between the cobalt ion and chloride ion. This is so because the charge density of Co^{2+} ion is greater than that of the charge density of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ ion.

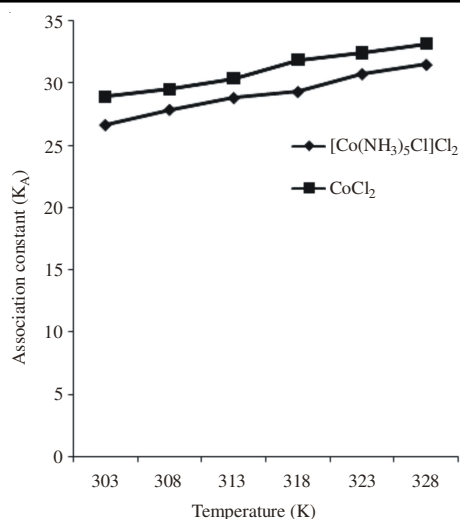


Fig. 1. Temperature dependence of ion association constants for $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$

The negative value of ΔH° indicates that ion association processes are exothermic in nature¹⁹. Out of these two complexes, negative values of ΔG° is more in cobalt(II) chloride hexahydrate and this complex is more favoured in ion-pair formation. A positive entropy change is broken when association takes place leading to an increase in the degree of disorderliness²⁰.

Evaluation of thermodynamic parameters: The free energy change (ΔG°) for association process is calculated from the relation, $\Delta G^\circ = -RT \ln K_A$. The heat of association (ΔH°) is obtained from the slope of the plot of $\log K_A$ versus $1/T$ (Fig. 2) and the entropy change (ΔS°) is then calculated from the Gibbs-Helmholtz equation, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. The values of these thermodynamic functions are given in Tables 3 and 4. The negative value of ΔH° indicates that ion-association processes are exothermic in nature²¹. The positive values of ΔS° and negative values of ΔH° indicates that ion association process will occur spontaneously at all temperatures.

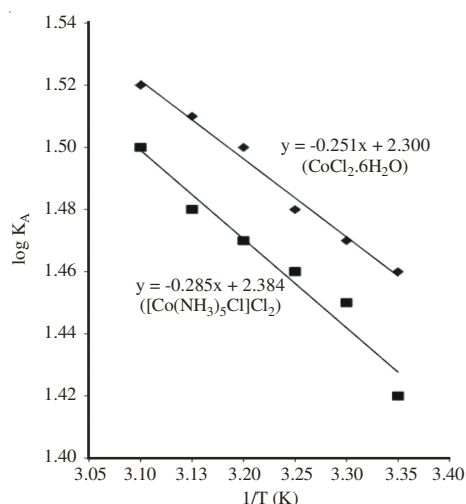


Fig. 2. Plot of $\log K_A$ versus $1/T$ for $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ in aqueous medium

Conclusion

The limiting equivalent conductance (Λ_0) increased linearly with the increase in temperature and the association constant (K_A) values increase with rise in temperature. Both the reactions are exothermic in nature which is determined by negative

TABLE-3
THERMODYNAMIC PARAMETERS ΔG° (KJ mol⁻¹), ΔH° (KJ mol⁻¹) AND ΔS° (KJ K⁻¹ mol⁻¹) OBTAINED BY SHEDLOVSKY TECHNIQUE FOR COBALT(II) CHLORIDE HEXAHYDRATE IN AQUEOUS SOLUTIONS AT DIFFERENT TEMPERATURES

| | 298 K | 303 K | 308 K | 313 K | 318 K | 323 K |
|---------------------------------|---------|---------|---------|---------|---------|---------|
| ΔG° | -8.34 | -8.53 | -8.74 | -9.01 | -9.20 | -9.40 |
| ΔH° | -251 | - | - | - | - | - |
| $10^{-3} \times \Delta S^\circ$ | -242.66 | -242.47 | -242.26 | -241.99 | -241.80 | -241.60 |

TABLE-4
THERMODYNAMIC PARAMETERS ΔG° (KJ mol⁻¹), ΔH° (KJ mol⁻¹) AND ΔS° (KJ K⁻¹ mol⁻¹) OBTAINED BY SHEDLOVSKY TECHNIQUE FOR PENTAAMINECHLOROCOBALT(III) CHLORIDE IN AQUEOUS SOLUTIONS AT DIFFERENT TEMPERATURES

| | 298 K | 303 K | 308 K | 313 K | 318 K | 323 K |
|---------------------------------|---------|---------|---------|---------|---------|---------|
| ΔG° | -8.14 | -8.34 | -8.60 | -8.93 | -9.05 | -9.26 |
| ΔH° | -285.00 | - | - | - | - | - |
| $10^{-3} \times \Delta S^\circ$ | -276.86 | -276.62 | -276.40 | -276.07 | -275.95 | -275.74 |

values of ΔH° . The chosen metal complexes show ion-pair association within experimental different temperatures ranges; which is supported by negative values of ΔG° . The K_A values for cobalt(II) chloride hexahydrate are better than pentaaminechlorocobalt(III) chloride and found in the order: $\text{CoCl}_2 \cdot 6\text{H}_2\text{O} > \text{Co}[(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$.

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