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Ion Pair Formation of Hexamine Nickel (II) Chloride and Tris-Ethylene Diamine Nickel (II) Chloride in Aqueous Medium at Different Temperatures

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ABSTRACT

Conductance of complex of hexamine nickel (II) chloride and tris-ethylenediamine nickel (II) chloride have been measured in aqueous medium at different temperature ranges 25-50^{0}C (steps of 5^{0}C) in the concentration range 8.6-3.4 x 10 ML^{-1}. The limiting equivalent conductance (Λ_0) and association constant (K_A) for complex in aqueous medium have been evaluated using Shedlovsky technique. The limiting equivalent conductance increased linearly with the increase in temperature and the association constant values increased with rise in temperature. The limiting equivalent conductance and the ion association constant values for hexamine nickel (II) chloride were found to be higher than those in tris-ethylenediamine nickel (II) chloride. The standard Gibbs energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) of the ion pairing process were calculated from the temperature dependence of the ion association constants. Both the associations are exothermic in nature which is supported by negative values of ΔH^0. The negative values of ΔG^0 indicated that the chosen metal complexes show ion-pair association within experimental different temperature ranges.
Keywords: Conductance, Shedlovsky technique, hexamine nickel (II) chloride, tris-ethylenediamine nickel (II) chloride, ion-association.

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INTRODUCTION

The ion pair formation in aqueous solution refers to the association of cations and anions present in the electrolytic solution. Ion pair formation process is a kind of very important chemical reaction whose theoretical and experimental studies are significant to the revealing of the microscopic dynamics of gas phase, liquid-phase reaction and the upper-space atmospheric reaction. The ion of the pair together formed an ionic dipole on which the net charge is zero. Within the ionic cloud, the locations of such ion-pairs are completely random, since, being uncharged, they are not acted upon the Coulombic field of the central ion. Furthermore, on the average, a certain fractions of the ions in the electrolytic solution will be stack together in the form of ion-pairs [1].

The conductance and viscosity measurements provide valuable information regarding the ion-ion and ion-solvent interactions [2]. Bag, Mohondas and Rajmuhon [3] had studied ion association of cobalt (II) complexes in different solvent mixtures at different temperatures. The conductance method is widely used methods for investigation of physic-chemical nature of ion pair formation of simple and complex salts [4, 5]. Recently, Mohondas and his co-workers [6] had studied ion pair formation and thermodynamics of glycine bis-1-amidino-O-methylurea cobalt (II) halides in water + methanol mixed solvents at different temperatures.

The present work reports the comparative studies of conductometric properties and thermodynamic properties of hexamine nickel (II) chloride and tris-ethylenediaamine nickel (II) chloride in water at different temperatures ranges 25-50^{0}C. The data were analyzed by using Shedlovsky method. The K_As and Λ_0 have been evaluated in these solvents at the experimental temperatures. The thermodynamic parameters viz., ΔH^0, ΔS^0 and ΔG^0 for the formation have been studied from the values of ion association constant at various temperatures.

EXPERIMENTAL

Complex of hexamine nickel (II) chloride and tris-ethylenediamine nickel (II) chloride was prepared by following the reported procedure [7,8]. The purity of the sample was determined by conventional chemical analysis and spectral measurements. The values were in good agreement with the literature values. Water of specific conductance of the order < 2 × 10^{-6} S cm^{-1} was used. The electrical conductivities were measured by Eutect Instrument – pc 510 digital conductivity bridges with a dip type immersion conductivity cell were used. The solutions of different concentrations (8.6 – 3.4 x 10^{-3}) were carefully prepared by dissolving requisite amount of the sample in conductivity water (i.e., double distilled water) of low specific conductance (< 3x 10^{-6} Scm^{-1}). Conductivity measurements were carried out over the temperature range 25^0 C - 50^0 C. All the dielectric constants and viscosities were obtained from literature. The temperature controls in the range of 25 - 50^0 C were made by using water Bath and thermometer. The measurements of weights were done by using a METTER 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 metal complexes, i.e., [Ni (NH$_3$)$_6$] Cl$_2$ and [Ni (en)$_3$]Cl$_2$ in aqueous medium by Using Shedlovsky extrapolation Technique[9]. Shedlovsky equation is given by

$$\frac{1}{\Lambda S(Z)} = \frac{1}{\Lambda_o} + \left(\frac{K_A}{\Lambda_o}\right)\left(C\Lambda f_{\pm}^{2} S(Z)\right) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Where Λ is molar conductance at a concentration C (g.mol.dm^{-3}), Λ_0 is the limiting molar conductance and K$_A$ the observed association constant. The other symbols are given by Z and λ are the valence and conductance of the ions respectively, excluding their signs, 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,

$$S(Z) = \left[\frac{Z}{2} + \sqrt{1 + \left(\frac{Z}{2}\right)^2}\right]^2, \quad Z = \left[\frac{\alpha\Lambda_o + \beta}{\Lambda_o^{\frac{3}{2}}}\right](C\Lambda)^{\frac{1}{2}}$$

$$\alpha = \frac{17.147 X 10^5 W}{(DT)^{\frac{3}{2}}}$$

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

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

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

z and λ are the valence and conductance of the ion respectively, excluding their signs, 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

$$\tau = \Lambda S(Z)/\Lambda_0$$

f± is the activity coefficient of the free ions and was calculated as

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

where

$$A = \frac{1.8247 X 10^6}{(DT)^{3/2}}$$

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

$$\mu = \frac{1}{2}\sum_i (C_i \tau_i) Z_i^2$$

R is the maximum centre to centre distance between the ions in the ion-pair. There exists at present no method of determining the value of R precisely [10]. In order to treat the data in our 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 $5A^0$ and d (A^0) is given by Akhadov [11] and Lacour et al. [12]

$$d = 1.183(M/\rho)^{1/3} \tag{3}$$

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

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

The Change of free energy for the association process (ΔG^0) was calculated from the equation:

$$\Delta G^0 = -2.303RT\log_{10}K_A \tag{4}$$

The enthalpy change of association (ΔH^0) was obtained from the slope of log K_A vs. 1/T. The change of association entropy (ΔS^0) was calculated from the Gibbs- Helmholtz equation:

$$\Delta S^0 = (\Delta H^0 - \Delta G^0)/T \tag{5}$$

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 ions [13]. 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 [14]. Values of Λ_0 for [Ni $(NH_3)_6$] Cl_2 are always greater than those values of complex [Co $(NH_3)_5Cl$] Cl_2 is most prone to the variation in vibrational, rotational and translational energy levels with temperature.

TABLE: 1. The value of limiting molar conductance Λ_0 Scm^3 and association constants K_A (dm^3 mol^{-1}) obtained by Shedlovsky technique for hexamine nickel (II) chloride in aqueous solution at different temperatures.

	303 K	308 K	313 K	318 K	323 K
K_A	124.24	149.41	174.33	194.62	216.84
Λ_0	66.80	70.04	77.70	82.01	86.15
Log K_A	2.09	2.17	2.24	2.29	2.34

TABLE: 2.The value of limiting molar conductance Λ_0 (Scm^3) and association constant K_A (dm^3 mol^{-1}) obtained by Shedlovsky technique for tris-ethylenediamine nickel (II) chloride in aqueous solution at different temperatures.

	303 K	308 K	313 K	318 K	323 K
K_A	119.49	141.62	162.11	168.69	207.32
Λ_0	55.05	59.79	65.04	70.32	76.49
Log K_A	2.08	2.15	2.21	2.27	2.32
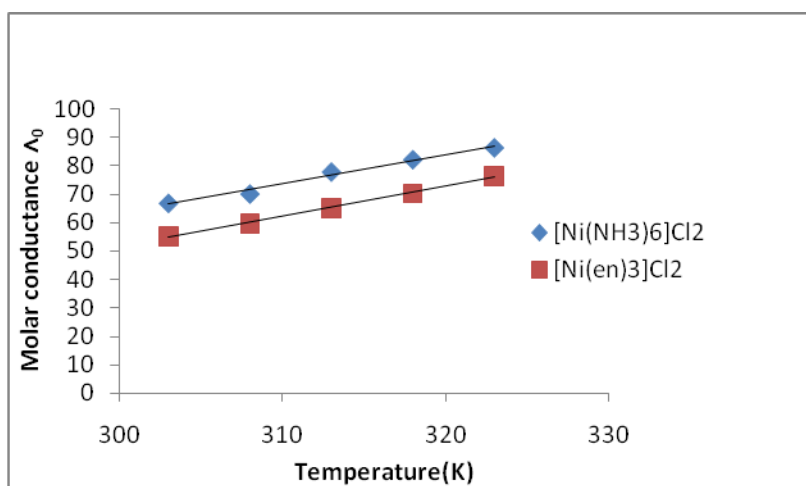
Fig. 1: Comperative molar conductance for [Ni(NH₃)₆]Cl₂ and Ni(en)₃]Cl₂
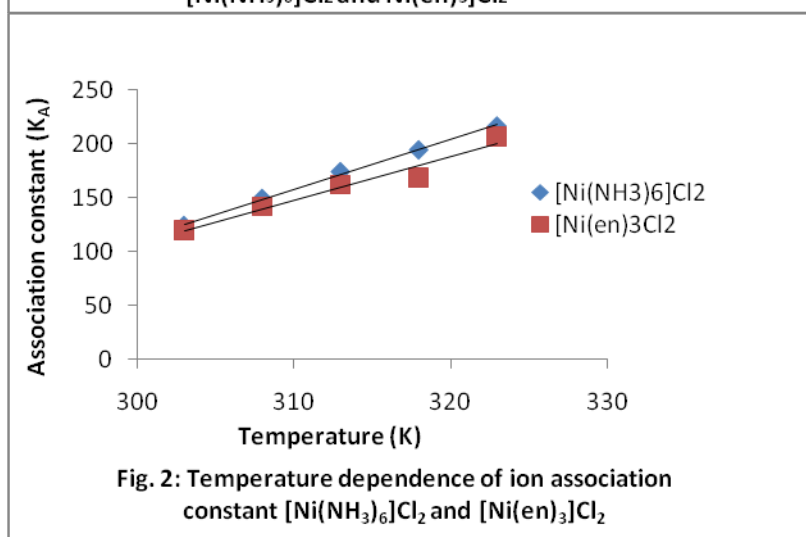
Fig. 2: Temperature dependence of ion association constant [Ni(NH₃)₆]Cl₂ and [Ni(en)₃]Cl₂

Fig 3. $LogK_A$ Vs 1/T for
$[Ni(NH_3)_6]Cl_2$ and $[Ni(en)_3]Cl_2$
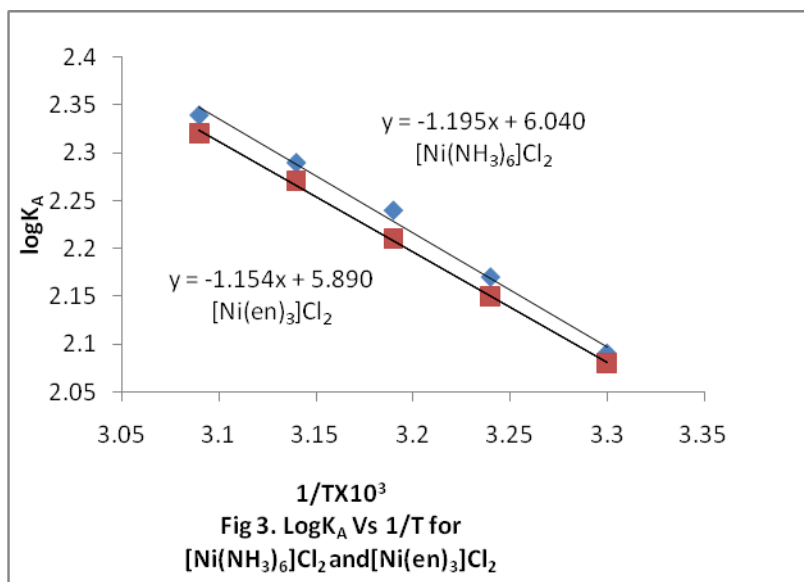
The values of the K_As for these two complexes increase with rise in temperature (Table 1 & 2). The higher K_A values in the case of simple salt compared to complexes salt may be ascribed to the more coulombic type of interaction (specific short-range interaction) between the nickel ion and chloride ion. This is so because the charge density of Ni^{+2} ion is greater than that of the charge density of $[Ni (en)_3] Cl_2$ ion.

Evaluation of Thermodynamic Parameters: The free energy change (ΔG^0) for association is calculated from the relation $\Delta G^0 = - RT \ln K_A$. The heat of association (ΔH^0) is obtained from the slope of the plot of log K_A vs 1/T (fig.1). The entropy change (ΔS^0) is calculated from the Gibbs-Helmholtz equation, $\Delta G^0 = \Delta H^0 - \Delta S^0 T$. The values of thermodynamic functions are given in table 3 & 4. The positive values of ΔS^0 and negative values of ΔH^0 indicate that ion association process will occur spontaneously at all temperatures [15]. The negative value of ΔH^0 indicates that ion association processes are exothermic in nature [16].

TABLE: 3. Thermodynamic parameters ΔG^0 (kJ mol^{-1}), ΔH^0 (k J mol^{-1}) and ΔS^0 (k J K^{-1} mol^{-1}) obtained by Shedlovsky technique for Hexamine nickel (II) chloride In aqueous solutions at different temperatures.

	303 K	308 K	313 K	318 K	323 K
ΔG^0	-5.23	-5.51	-5.46	-6.00	-6.22
ΔH^0	-1240.00				
10^{-3}x ΔS^0	-4075.15	-4008.08	-3944.22	-3880.50	-3819.75

TABLE- 4. Thermodynamic parameters ΔG^0 (k J mol^{-1}) , ΔH^0 (kJ mol^{-1}) and ΔS^0 (kJK^{-1} mol^{-1}) obtained by Shedlovsky technique for tris-ethylenediamine nickel (II) chloride in aqueous solutions at different temperatures.

	303 K	308 K	313 K	318 K	323 K
ΔG^0	-5.28	-5.57	-5.83	-6.05	-6.27
ΔH^0	-1200.00				
10^{-3}x ΔS^0	-3977.82	-3878.02	-3815.24	-3754.56	-3695.76

Out of these two complexes, negative values of ΔG^0 is more in hexamine nickel (II) chloride and this complex is more favored in ion – pair formation. A positive entropy change is broken when association takes place leading to an increase in the degree of disorderliness [17].

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 values of ΔH^0. The chosen metal complexes show ion – pair association within experimental different temperatures ranges; which is supported by negative values of ΔG^0. The K_A values for hexamine nickel (II) chloride are better than tris-ethylenediamine nickel (II) chloride and found in the order:

$$[Ni\,(NH_3)_6]Cl_2 > [Ni\,(en)_3]Cl_2$$
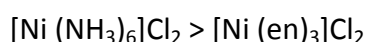
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