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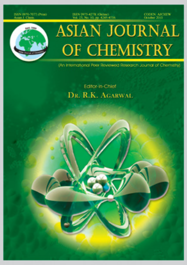

Ion Pair Formation of 1-Amidino-O-ethylurea Nickel(II) Chloride and 1-Amidino-O-ethylurea Nickel(II) Bromide in Aqueous Medium at Different Temperatures- A Conductance Method

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Aqueous solutions of 1-amidino-O-ethylurea nickel(II) chloride and 1-amidino-O-ethylurea nickel(II) bromide have been investigated at different temperatures (303-318 K) by conductance method over wide range of salt concentrations. The limiting equivalent conductances (Λ_0) and ion association constants (K_A) for various compositions have been calculated using Shedlovsky method. For both electrolytic salts, the limiting equivalent conductances increased linearly with increased in temperature and the ion association constants values increased with rise in temperature. Based on the K_A values and temperature dependence of Λ_o, the thermodynamic parameters *viz*., free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) have been determined. 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. 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 $[Ni(AEUH)_2]Cl_2$ are always greater than those values of complex $[Ni(AEUH)_2]Br_2$. The values of the K_As for these two complexes increase with rise in temperature. The higher K_A values in 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 $[Ni(AEUH)_2]Cl_2$ is greater than that of the charge density of $[Ni(AEUH)_2]Br_2$.

Key Words: Conductance, Ion-pair, Shedlovsky equation, Thermodynamic parameters, 1-Amidino-O-ethylurea nickel(II) chloride and 1-amidino-O-ethylurea nickel(II) bromide.

INTRODUCTION

The conductometric method is well suited to investigate the ion-ion and ion-solvent interactions in electrolyte solutions[1]. Several experimental techniques have been applied to study the thermodynamic and various interactions in electrolytic solutions[2,3]. Electrolytic conductivity is a very useful classical experimental technique to determine transport as well as equilibrium properties of dilute electrolytic solutions. Because of its relative simplicity and versatility, the measurements of the conductivity of electrolyte solutions which can be carried out to a high precision, remains an important tool to obtain information about electrolytes in different solvents[4]. The theory of conductance has revealed one feature in common that the solvent is assumed as a continuum of permittivity (D) and viscosity (η). This assumed when we discuss the strong ion-solvent interaction, since the size of solvent molecules are comparable to those of solute molecules, since the sizes are also considered as a rigid uniformly charged unpolarizable sphere. In the solvent of low dielectric constant, where the potential energy of the anion and cation is large to the mean thermal energy kT, it is expected that the association of ions as non-conducting pairs[5]. As the dielectric constant is increased the extent of association should decrease but it should never become zero because there is non-zero chance that anion and cation contact will occur[6].

In the present study, conductances of the *bis*-1-amidino-O-methylurea nickel(II) chloride and 1-amidino-O-ethylurea nickel(II) bromide have been measured in aqueous medium at 303-318 K. The conductance data in all cases have been analyzed by Shedlovsky extrapolation method[7] to obtain limiting molar conductance (Λ_0) and association constant (K_A) values for the electrolytes. These results were discussed in terms of association constant (K_A) and also the approach of linear Gibb's energy relationship LGER[8] can be applied to the association process at various temperatures to discuss the thermodynamic features of metal-ion complexes. The effect of temperature on the Stokes'radius for the complex cation has been discussed in the light of Walden product. Based on the K_A values and temperature dependence of Λ_0, the thermodynamic parameters, ΔG^o, ΔH^o and ΔS^o were evaluated by investigating the process over a certain temperature range.

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 solvents[9-11]. 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 Eutect Instrument-pc 510 digital conductivity bridges with a dip type immersion conductivity cell (cell constant 0.99) were used. The solutions of different concentrations (1.5×10^{-4}) M were carefully prepared by dissolving requisite amount of the sample in conductivity water (*i.e.*, double distilled water) of low specific conductance ($< 2 \times 10^{-6}$ S cm^{-1}). Conductivity measurements were carried out over the temperature range 30-45 ºC. All the dielectric constants and viscosities were obtained from literature. The temperature control in the range of 30-45 ºC were made by using water bath and thermometer. The measurement of weights were done by using a Mettler Balance, model TB-214 (max = 210 g; d = 0.1 mg) delta range.

RESULTS AND DISCUSSION

The experimental data of conductance measurements were analyzed by using Shedlovsky equation. Shedlovsky equation[12] is given by

$$\frac{1}{\Lambda S(Z)} = \frac{1}{\Lambda_0} + \left(\frac{K_A}{\Lambda_0}\right)(C\Lambda f_{\pm}^2 S(Z)) \qquad (1)$$

where Λ is molar conductance at a concentration C (g mol dm^{-3}), Λ_0 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,

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

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

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

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

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

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

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

$$\tau = \frac{\Delta S(Z)}{\Delta_0}$$

$f_{\pm}$ is the activity coefficient of the free ions and was calculated as

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

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

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

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

R is the maximum centre to centre distance between the ions in the ion-pair. There exists at present no method of determining the value of R precisely[13]. 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 5 Å and d (Å) is given by[14].

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

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) were introduced as input in computer programme. The mean activity coefficient f was determined by eqn. 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_0 and K_A was evaluated from the intercept $1/\Lambda_0$ 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 (ΔGº) was calculated from the equation:

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

The enthalpy change of association (ΔHº) was obtained from the slope of log K_A *versus* 1/T. The change of association entropy (ΔSº) was calculated from the Gibbs-Helmholtz equation:

$$\Delta S^{o} = \frac{(\Delta H^{o} - \Delta G^{o})}{T}$$

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. 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 $[Ni(AEUH)_2]Cl_2$ are always greater than those values of complex $[Ni(AEUH)_2]Br_2$ and $[Ni(AEUH)_2]Cl_2$ is most prone to the variation in vibrational, rotational and translational with temperature.

TABLE-1
VALUE OF LIMITING MOLAR CONDUCTANCE Λ_0 (Scm^3) AND ASSOCITION CONSTANT K_A (dm^3 mol^{-1}) OBTAINED BY SHEDLOVSKY TECHNIQUE FOR 1-AMIDINO-O-ETHYLUREA NICKEL(II) CHLORIDE IN AQUEOUS SOLUTION AT DIFFERENT TEMPERATURES

	303 (K)	308 (K)	313 (K)	318 (K)
L_0	262.005	270.442	286.622	311.052
K_A	8043.403	8596.936	9027.04	9502.479

TABLE-2
VALUE OF LIMITING MOLAR CONDUCTANCE Λ_0 (Scm^3) AND ASSOCIATION CONSTANT K_A (dm^3 mol^{-1}) OBTAINED BY SHEDLOVSKY TECHNIQUE FOR 1-AMIDINO-O-ETHYLUREA NICKEL(II)BROMIDE IN AQUEOUS SOLUTION AT DIFFERENT TEMPERATURES

	303 (K)	308 (K)	313 (K)	318 (K)
Λ_o	219.810	250.860	268.058	293.205
K_A	6295.558	6460.089	6638.082	6895.711

The values of the K_As for these two complexes increase with rise in temperature (Tables 1 and 2). The higher K_A values in the case of simple salt compared to complex 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 $[Ni(AEUH)_2]Cl_2$ is greater than that of the charge density of $[Ni(AEUH)_2]Br_2$. The free energy change (ΔG^o) for association is calculated from the relation $\Delta G^o = -RT \ln K_A$. The heat change of association (ΔH^o) is obtained from the slope of the plot of log K_A *versus* 1/T (Fig. 1). The entropy change (ΔS^o) is calculated from the Gibbs-Helmholtz equation $\Delta G^o = \Delta H^o - \Delta S^oT$. The values of thermodynamic functions are given in Tables 3 and 4. The negative value of ΔH^o indicates that ion association processes are exothermic at all temperatures[15].

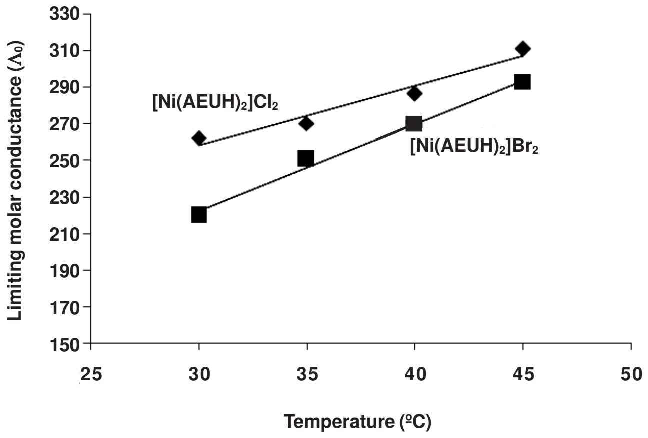

Fig. 1. A comperative limiting molar conductances of $[Ni(AEUH)_2]Cl_2$ and $[Ni(AEUH)_2]Br_2$ in aqueous solution at different temperatures

Out of these two complexes, negative values of ΔG^o is more in $[Ni(AEUH)_2]Cl_2$ 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 disorderliness[16].

TABLE-3
THERMODYNAMIC PARAMETERS ΔG^o (kJ mol^{-1}), ΔH^o (kJ mol^{-1}) AND ΔS^o (kJ K^{-1} mol^{-1}) OBTAINED BY SHEDLOVSKY TECHNIQUE FOR 1-AMIDINO-O-ETHYL UREA NICKEl(II) CHLORIDE IN AQUEOUS SOLUTION AT DIFFERENT TEMPERATURES

	303 (K)	308 (K)	313 (K)	318 (K)
ΔG^o	-22.659	-23.203	-23.707	-24.221
ΔH^o	-0.466	–	–	–
10^{-3} ΔS^o	73.237	73.827	74.255	74.709

TABLE-4
THERMODYNAMIC PARAMETERS ΔG^o (kJ mol^{-1}), ΔH^o (kJ mol^{-1}) AND ΔS^o (kJ K^{-1} mol^{-1}) OBTAINED BY SHEDLOVSKY TECHNIQUE FOR 1-AMIDINO-O-ETHYL UREA NICKEL (II) BROMIDE, $[Ni(AEUH)_2]Br_2$ IN AQUEOUS SOLUTION AT DIFFERENT TEMPERATURES

	303 (K)	308 (K)	313 (K)	318 (K)
ΔG^o	-22.041	-22.470	-22.907	-23.374
ΔH^o	-0.254	–	–	–
10^{-3} ΔS^o	71.897	72.202	72.489	72.597

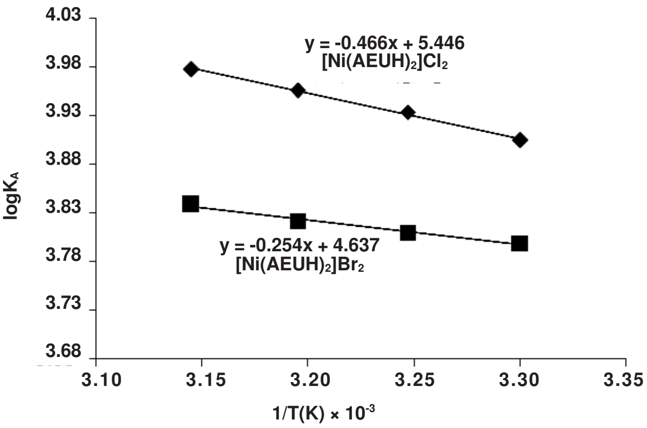

Fig. 2. Plots of log K_A *versus* 1/T (K) for $[Ni(AEUH)_2]Cl_2$ and $[Ni(AEUH)_2]Br_2$ in aqueous medium

The free energy change (ΔG^o) for association is calculated from the relation $\Delta G^o = -RT \ln K_A$. The heat of association (ΔH^o) is obtained from the slope of the plot of log K_{AS} *versus* 1/T (Fig. 2). The entropy change (ΔS^o) is calculated from the Gibbs-Helmholtz equation, $\Delta G^o = \Delta H^o - \Delta S^oT$. The values of thermodynamic functions are given in Tables 3 and 4. The positive values of ΔS^o and negative values of ΔH^o indicate that ion association process will occur spontaneously at all temperatures[17]. The negative value of ΔH^o indicates that ion association processes are exothermic at all temperatures[18].

Conclusion

The limiting equivalent conductance (Λ_0) increased linearly with the increased in temperature and the association constant (K_A) values increased with rise in temperature. Both the reactions are exothermic which is determined by the negative values of ΔH^o. The nickel(II) complexes show ion-pair association within the experimental different temperature ranges; which is supported by negative values of ΔG^o. The K_A values for 1-amidino-O-ethylurea nickel(II) chloride is better than 1-amidino-O-ethylurea nickel(II) bromide and found in the order: 1-amidino-O-ethyl urea nickel(II) chloride > 1-amidino-O-ethyl urea nickel(II) bromide.

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