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Evaluation of association constant and thermodynamic parameters of [Cu(Me-AAUH)₂]Cl₂ complexes in aqueous medium

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ABSTRACT

Conductance measurements on aqueous solutions of bis-methyl 1-amidino-O-methylurea copper (II) chloride and bis-methyl 1-amidino-O-ethylurea copper (II) chloride have been investigated at different temperatures ranging from $25 - 50^{\circ}$ C over wide range of concentration from $1.13-1.80 \times 10^{\circ}$ ³N. The limiting molar conductance (Λ_0) data and ion association constants (K_A) values were estimated by analyzing conductivity data in term of Shedlovsky technique. The values of Λ_o 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 as well as K_A . The higher K_A values in the case of [Cu(Me-AMUH)₂]Cl₂ compared to [Cu(Me-AEUH)₂]Cl₂ may be ascribed to the more coulombic type of interaction (specific short-range interaction) between the [Cu (Me-AMUH)₂]²⁺ ion and Chloride ion. The thermodynamic parameters viz., changes in enthalpy (ΔH^0), entropy (ΔS^0) and free energy (ΔG^0) were estimated from the temperature dependence of the ion association constant.

Key words: Conductance, Shedlovsky equation, Thermodynamic parameters, Cu(II) complexes.

INTRODUCTION

The concept of ion pairs to the evaluation of the interionic forces in electrolytic solution was first introduced by Bjerrium [1]. 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] 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 ion. The phenomenon of ion pair formation is by itself of fundamental importance to the chemical field as it influences reaction rates or may be exploited in numerous chemical applications such as ion pair chromatography or ion selective electrodes. The temperature and concentration dependence of the electrolyte conductance has been proved as one of the most appropriate methods for studying ion-ion, ion-solvent and solvent-solvent interactions in solutions [3]. Electrolytic conductivity is a very useful classical experimental technique to determine transport as well as equilibrium properties of dilute electrolyte solutions. Because of its relative simplicity and versatility, the measurement of the conductivity of electrolyte solutions, which can be carried out to a very high precision, remains an important tool to obtain information about electrolytes in different solvents [4]. The conductometric method is well suited to

investigate the ion-ion and ion-solvent interactions in electrolyte solutions. Ion pair formation in solutions of alkali metal halides of small metal ions have been extensively investigated both in aqueous and aquo-organic solvent mixtures [5].

The present work reports the comparative studies of conductometric properties, thermodynamic behavior and Walden product of $[Cu(Me-AMUH)_2]Cl_2$ (*Bis-methyl 1-Amidino-O-Methylurea copper (II) chloride*) and $[Cu(Me-AEUH)_2]Cl_2$ (*Bis-methyl 1-Amidino-O-Ethylurea copper (II) chloride*) in water at different temperatures between 25 to 50 °C. The data were analyzed using Shedlovsky method to obtain the limiting equivalent conductivity and Association constant, Walden products have been evaluated. The thermodynamic parameters viz., changes in enthalpy (ΔH^0), entropy (ΔS^0) and free energy (ΔG^0) have been studied from the values of ion association constant at various temperatures.

MSTERIALS AND METHODS

The complexes *bis-methyl 1-amidino-O-methylurea copper (II) chloride)* and *bis-methyl 1-amidino-O-ethylurea copper (II) chloride* had been prepared from the literature [6,7]. The purity of the sample was checked through conventional chemical analysis and spectral measurements. The electric conductivities were measured by Orion Star A112 Conductivity Benchtop meter with Epoxy 2 cell (K=1.0) digital conductivity bridges with a dip type immersion conductivity cell were used. The solutions of different concentrations (1 x10⁻³) M were carefully prepared by dissolving requisite amount of the sample in conductivity water (ie, double distilled water) of low specific conductance (< $2x10^{-6}$ S cm⁻¹). Conductivity measurements were carried out over the temperature range of 25° C – 50° C. All the dielectric constants and viscosities were obtained from literature [8]. The temperature control in the ranges of $25-50^{\circ}$ C were made by using refrigerated water bath and circulator Model D8-G of HAAKE Mess-Technik) and graduated thermometer. The measurements of weights were done by using a METTER Balance, model TB-214(max=210g; d=0.1mg). All calculations were done on IBM-PC-AT/386 using a basic programmed.

The experimental data of conductance measurement of Cu(II) complexes in water after solvent corrections were analyzed by using Shedlovsky extrapolation equation[9] for 2:1 electrolytes:

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

where Λ is equivalent conductance at a concentration c (g.equiv.dm⁻³), Λ_0 the limiting equivalent conductance and K_A the observed association constant. The other symbols[10] are given by

$$S(z) = \left(\frac{z}{2}\sqrt{1 + \left(\frac{z}{2}\right)^2}\right)^2; \qquad Z = \left[\frac{\alpha A_0 + \beta}{A_0^{5/z}}\right] (C\Lambda)^{1/2} \quad ; \qquad \alpha = \frac{17.147 \times 105W}{(DT)^{3/2}}$$
$$w = z_+ z_- \frac{2q}{1 + q^{1/2}}; \qquad q = \frac{z_+ z_-}{z_+ + z_-} x \frac{\lambda_+ + \lambda_-}{z_+ \lambda_- + z_- \lambda_+} ; \qquad \beta = \frac{151.47}{\eta (DT)^{1/2}}$$

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,

$$\tau = \Lambda S(z) / \Lambda_o$$

 f_{\pm} is the activity coefficient of the free ions and was calculated using equation (2)

$$-\log f_{\pm} = \frac{Az_{\pm}z_{-\mu}^{1/2}}{1 + BR\mu^{1/2}}$$
where,
$$A = \frac{1.8247 \times 10^{6}}{(DT)^{5/2}}; \qquad B = \frac{0.5029 \times 10^{10}}{(DT)^{1/2}}; \qquad \mu = \frac{1}{2} \sum_{i} (c_{i}\tau_{i}) z_{i}^{2}$$
(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 [11]

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

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

From the linear plot of $1/\Delta S(z)$ versus $f_{\pm}^2 s(z)$; Λ_o and K_A were estimated from the intercept $(1/\Lambda_o)$ and slope (K_A/Λ_o^2) respectively. The values of K_A and Λ_o are calculated using eqn (1) by an iteration procedure. All calculations were done on IBM-PC-AT/386 using a basic programmed. 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:

$$\Delta G = -2.303 RT \log K_A$$

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:

$$\Delta S^0 = (\Delta H^0 - \Delta G^0)/T$$

(5)

(4)

RESULTS AND DISCUSSION

From Table 1 and 2, the values of Λ_o for the electrolytes increase invariably with increase in temperature first in aqueous medium, indicating less solvation or higher mobility of ions 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_o for [Cu (Me-AMUH)₂]Cl₂ are always greater than those values of complex [Cu (Me-AEUH)₂]Cl₂ and is most prone to the variation in vibrational, rotational and translational energy levels with temperature.

The values of K_A 's for these two complexes increase with rise in temperature (Table 1 and 2). The higher K_A values in the case of $[Cu(Me-AMUH)_2]Cl_2$ compared to $[Cu(Me-AEUH)_2]Cl_2$ may be ascribed to the more coulombic type of interaction (specific short-range interaction) between the $[Cu (Me-AMUH)_2]^{2+}$ ion and Chloride ion. This is so because the charge density of $[Cu (Me-AMUH)_2]^{2+}$ ion is greater than that of the charge density of $[Cu (Me-AMUH)_2]^{2+}$ ion.

	298 K	303 K	308 K	313K	318K	323K
K _A	283.44	301.27	319.34	327.85	343.17	361.70
Λ_0	154.63	165.44	174.98	186.10	195.38	206.61
logK _A	2.452	2.479	2.504	2.515	2.535	2.558

	298 K	303 K	308 K	313K	318K	323K
KA	260.66	280.52	300.99	318.07	338.85	357.59
Λ_0	148.54	159.52	168.95	180.25	191.12	200.24
logK _A	2.416	2.448	2.479	2.502	2.530	2.553

 $\label{eq:constraint} \begin{array}{l} \mbox{Table-3: Thermodynamic parameters $\Delta G^0(kJequiv^1), \Delta H^0(kJequiv^1)$ and $\Delta S^0(kJK^{-1}equiv^{-1})$ obtained by Shedlovsky technique for [Cu $(Me-AMUH)_2]Cl_2$ in aqueous solution at different temperatures $(Me-AMUH)_2]Cl_2$ in the set of the set o$

	298K	303 K	308 K	313 K	318 K	323 K
ΔG^0	-13.99	-14.45	-14.77	-15.07	-15.44	-15.82
ΔH^0	-0.39					
$10^3 \mathrm{x} \Delta \mathrm{S}^0$	45.64	46.39	46.70	46.90	47.31	47.77



The negative value of ΔH° indicates that ion association processes are exothermic at all temperature [12]. Out of these two complexes, negative values of ΔG° is more in [Cu (Me-AMUH)₂]Cl₂ compared to [Cu (Me-AEUH)₂]Cl₂ 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 [13].



$Table-4: Thermodynamic parameters \ \Delta G^0(kJequiv^{-1}), \ \Delta H^0(kJequiv^{-1}) \ and \ \Delta S^0(kJK^{-1}equiv^{-1}) \ obtained \ by \ Shedlovsky \ technique \ [Cu(MeAEUH)_2]Cl_2 \ in \ aqueous \ solution \ at \ different \ temperatures$

	298K	303 K	308 K	313 K	318 K	323 K
ΔG^0	-13.79	-14.20	-14.62	-15.00	-15.41	-15.79
ΔH^0	-0.53					
$10^3 \mathrm{x} \Delta \mathrm{S}^0$	44.49	45.14	45.76	46.23	46.79	47.25

The free energy change (ΔG°) for association 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 vs 1/T (fig. 2). The entropy change (ΔS°) is calculated from the Gibbs-Helmholtz equation $\Delta G^{\circ} = \Delta H^{\circ} - \Delta S^{\circ}T$. The values of thermodynamic function are given in table 3 and 4. The negative value of ΔH° indicates that ion association processes are exothermic at all temperature. The positive values of ΔS° and negative value of ΔH° indicates that ion association process will occur spontaneously at all temperatures [14].

CONCLUSION

The limiting equivalent conductance (Λ_o) increased linearly with the increase in temperature and the association constant K_A values increase with rise in temperature. Both the reactions are exothermic which is determined by negative values of ΔH^o . The copper(II) complexes show ion pair association within experimental obtained by the negative values of ΔG^o at different temperatures. The positive value of ΔS^o and negative value of ΔH^o indicates that the ion association process will occur spontaneously at all temperatures. The K_A values for both complexes are determined and found in order: [Cu (Me-AMUH)₂]Cl₂ > [Cu (Me-AEUH)₂]Cl₂.

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