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Ion Pair Association Constant of *Bis*-1-Amidino-O-methylurea Copper(II) Acetate in Aqueous Medium at Different Temperature: A Conductance Study

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Conductances of the *bis*-1-amidino-O-methylurea copper(II) acetate has been measured in aqueous medium at 278.15 to 313.15 K. The conductance data in all the cases have been analyzed by Shedlovsky equation to obtain Λ_o and K_A value for the electrolyte. 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_o the thermodynamic parameters have been determined. The results have been discussed in terms of ion-ion and ion-solvent interactions.

Key Words: Conductance, Ion pair, Shedlovsky equation, Walden product, Stokes' radii, *bis*-1-Amidino-O-methylurea copper(II) acetate.

INTRODUCTION

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 (and does) decrease, but it should never become zero because there is always a non-zero chance that anion-cation contacts will occur. Conductance of 1:1 electrolytes has been extensively studied[1] by using Shedlovsky equation[2]. 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 complex salt *bis*-1-amidino-O-methylurea copper(II) acetate in aqueous medium at 278.15 to 313.15 K using Shedlovsky equation by making suitable changes[3] in the functions α, β and μ. The equivalent conductance at infinite dilution (Λ_o), the association constants (K_A) and Walden products ($\Lambda_o\eta_o$) for the complex salt have been evaluated. The temperature variation of Stokes' radius for

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the cations and anions have been discussed. The computed values of Λ_o, K_A, $\Lambda_o\eta_o$ and r have been used to discuss quantitatively the nature of ion-ion and ion-solvent interactions. The thermodynamic parameters ΔG^o, ΔH^o and ΔS^o have also been calculated from the temperature variations of the association constants.

EXPERIMENTAL

Bis-1-Amidino-O-methylurea copper(II) acetate was prepared according to the reported procedure[4]. The purity of the sample was determined by conventional chemical analysis (calculated 15.36, 27.08 % and found 15.42, 27.20 % of Cu and N, respectively). Water of specific conductance of the order $< 2 \times 10^{-6}$ S cm^{-1} was used. All the solutions were prepared by dissolving weighed samples (METTLER AE 260, Delta range) of the electrolyte in water. The temperature was maintained by using refrigerated water bath and circulator (Model D8-G of HAAKE Mess-Technik. Accuracy ± 0.01 K). All the permittivity, viscosity and density values were taken from literature values[5]. Systronic-306 conductivity bridge (accuracy ± 0.l %) with a dip type immersion conductivity cell (cell constant 0.99) was used. The details of experimental procedure has been described in previous publication[6].

RESULTS AND DISCUSSION

Evaluation of Λ_o, K_A and $\Lambda_o\eta_o$: The experimental data of conductance measurements of 2:1 Cu(II) complex in water after solvent correction were analyzed using Shedlovsky equation:

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

where Λ is the equivalent conductance at a concentration C g.equiv.dm^{-3}, Λ_o the limiting equivalent conductance and K_A the observed association constant. The other symbols are given by

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

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

Since the salt is 2:1, the α and β values were modified as follows:

The Debye-Huckel-Onsager conductance equation[7] is :

$$\Lambda = \Lambda_o - \left[\frac{29.15(Z_+ + Z_-)}{(DT)^{1/2}\eta} + \frac{9.90 \times 10^5}{(DT)^{3/2}}\Lambda_o w\right]\sqrt{C(Z_+ + Z_-)}$$

For 2:1 salt $Z_+ = 2$ and $Z_- = 1$, then

$$\Lambda = \Lambda_O - \left[\frac{29.15 \times 3\sqrt{3}}{(DT)^{1/2}\eta} + \frac{9.90 \times 10^5 \sqrt{3}}{(DT)^{3/2}}\Lambda_O w\right]\sqrt{C}$$

$$= \Lambda_O - \left[\frac{151.47}{(DT)^{1/2}\eta} + \frac{17.147 \times 10^5}{(DT)^{3/2}}\Lambda_O w\right]\sqrt{C}$$

$$= \Lambda_O - (\beta + \alpha\Lambda_O)\sqrt{C}$$

$$\therefore \quad \alpha = \frac{17.147 \times 10^5}{(DT)^{3/2}} w \text{ and } \beta = \frac{151.47}{(DT)^{1/2}\eta}$$

where,

$$w = z_+ z_- \frac{2q}{1 + q^{1/2}} \text{ and } q = \frac{z_+ z_-}{z_+ + z_-} \cdot \frac{\lambda_+ + \lambda_-}{z_+\lambda_- + z_-\lambda_+}$$

z and λ are the valence and conductance of the ions respectively excluding their sign; D the permittivity of the medium; η the viscosity co-efficient of the medium. The degree of dissociation (τ) is related to S(Z) by the equation,

$$\tau = \frac{\Lambda S(Z)}{\Lambda_o}$$

$f_\pm$ is the mean activity coefficient of the free ions and was calculated using eqn. 2

$$-\log f_\pm = \frac{A Z_+ Z_- \mu^{1/2}}{1 + BR'\mu^{1/2}} \tag{2}$$

where $A = \frac{1.8247 \times 10^6}{(DT)^{3/2}}$, $B = \frac{0.5029 \times 10^{10}}{(DT)^{1/2}}$ and $\mu = \frac{1}{2}\sum_i (C_i \tau_i) Z_i^2$

R′ is the maximum centre to centre distance between the ions in the ion-pair. There exists at present no precise method[8] for determining the value of R′. In order to treat the data in present system, the R′ value is assumed to be R′ = a + d, where a is the sum of crystallographic radii of the ions approximately equal to 5 Å and d is the average distance corresponding to the side of a cell occupied by a solvent molecule. The distance d is given by[9]

$$d = 1.183(M/\rho)^{1/3} \text{ Å}$$

where M is the molecular mass of the solvent and ρ is the density of the solution. The values of association constant (K_A) and limiting equivalent conductance (Λ_o) have been calculated using eqn. 1 by an iterative procedure[10]. All the calculations have been carried out on IBM PC. The results of Λ_o, K_A and $\lambda_o\eta_o$ at different temperatures are collected in Table-1.

TABLE-1

VALUES OF LIMITING EQUIVALENT CONDUCTANCE Λ_O (Scm^2), ASSOCIATION CONSTANT K_A (dm^{3}g.equiv^{-1}), WALDEN PRODUCT $\Lambda_O\eta_O$, λ_O^+, λ_O^-, $\lambda_O^+\eta_O$, $\lambda_O^-\eta_O$ AND STOKES' RADII r^+ AND r^- (Å) AT DIFFERENT TEMPERATURES

	Temperature (K)							
	278.15	283.15	288.15	293.15	298.15	303.15	308.15	313.15
Λ_o	75.49	83.26	90.06	96.45	103.82	111.18	118.28	125.60
K_A	1384.73	1103.79	1034.13	799.57	775.35	682.35	529.91	434.58
$\Lambda_o\eta_o$	112.80	106.92	100.69	96.64	92.50	89.23	85.16	82.14
λ_o^+	50.95	54.63	57.34	59.64	62.92	66.19	69.20	72.43
λ_o^-,	24.54	28.63	32.72	36.81	40.90	44.99	49.08	53.17
$\lambda_o^+\eta_o$	77.44	71.18	65.02	59.76	56.06	52.82	49.82	47.37
$\lambda_o^-\eta_o$	37.30	37.30	37.10	36.88	36.44	35.90	35.34	34.77
r^+	2.12	2.30	2.52	2.74	2.92	3.10	3.29	3.46
r^-	2.20	2.20	2.21	2.22	2.25	2.28	2.32	2.36

As per Shedlovsky method, an initial value of Λ_o was obtained from the intercept of the linear regression of Λ *versus* $\sqrt{C}$. λ^o is obtained from the literature[10] at 298 K. At other temperatures it was obtained by using the equation

$$\lambda_t^0 = \lambda_{25}^0[1+\alpha'(t-25)]$$

where α' is constant for a given ion in the particular solvent for a narrow temperature range *e.g.* about 10^0 either side of 298 K. For conveniences, α' - value has been taken as 2×10^{-2} within the experimental temperature range.

Using the values of Λ_0, λ^0_- and λ^0_+; Z, S(Z) and τ values were calculated. From the linear plot of $1/\Lambda S(Z)$ *versus* $C\Lambda f_\pm^2 S(Z)$, Λ_0 and K_A were evaluated from the intercept ($1/\Lambda_0$) and the slope (K_A/Λ_0^2), respectively. The procedure was repeated using the new values of Λ_0 and K_A. From Table-1, it is evident that Λ_0 increases linearly with rise in temperature. The association constant, K_A and Walden product $\Lambda_o\eta_o$ gradually decreases with rise in temperature.

Size of ions: For a particle of macroscopic dimensions moving in an ideal hydrodynamic continuum, it is possible to calculate the frictional resistance in terms of the dimensions of the particle and the viscosity (η) of the medium. For a spherical particle, the result was obtained by Stokes[11] as:

$$r = 1/6\ \pi\eta u$$

'u' is expressed in terms of the limiting equivalent conductivity by the equation,

$$u = N\lambda/(|Z|\ F^2)$$

We have, $$r = (|Z|\ F^2)\ /\ (6\pi N\eta_o\lambda_o)$$

If we express 'r' in Å, η_o in poise and λ_o in S cm^2 equiv^{-1}

$$r = \frac{0.820|Z|}{\lambda_o\eta_o}$$

As evident from Table-1. $r_{CH_3COO^-}$ is found to be more or less constant with the variation of temperature. The Stokes' radius for the complex cations increase with increase of temperature which indicates that the cations become more hydrated as the temperature rises. Similar trends have been reported previously[12]. The monoatomic ions K^+, Rb^+, Cl^-, Br^-, I^- and ClO_4^-, NO_3^- are of similar mobility and show similar variation of the product $\Lambda_o\eta_o$ with temperature[13] in contrast to the approximate constancy $\Lambda_o\eta_o$ for the larger ions. In present experiment, it is also found that though $[Cu(AMUH)_2]^{2+}$ is a large polyatomic ion it does not show constancy of the product $\Lambda_o\eta_o$ with temperature as shown in Fig. 1. This suggests that there is some other effect operative in addition to ordinary viscous forces in determining the motion of the ions in water.

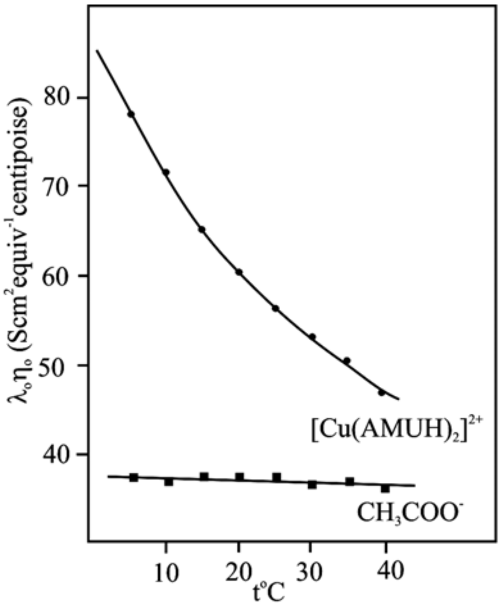

Fig. 1. Variation of Walden product $\lambda_o\eta_o$ with temperature (°C)

Evaluation of thermodynamic parameters: The free energy change (ΔG^o) for association process 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_A *versus* 1/T and the entropy change ΔS^o is then calculated from the Gibbs-Helmholtz equation, $\Delta G^o = \Delta H^o - T\Delta S^o$. The values of these thermodynamic functions are given in Table-2.

The negative value of ΔH^o indicates that ion-association processes are exothermic in nature. The positive values of ΔS^o and negative value of ΔH^o indicates that ion association process will occur spontaneously at all the temperatures. As expected, the variation of ΔG^o with temperature reveals that the ion association process is favoured at low temperature.

TABLE-2
THERMODYNAMIC PARAMETERS ΔG^o (KJ mol^{-1}), ΔH^o (KJ mol^{-1}) AND ΔS^o (KJ K^{-1} mol^{-1}) OF *BIS*-1-AMIDINO-O-METHYLUREA COPPER(II) ACETATE IN WATER USING SHEDLOVSKY METHOD

	Temperature (K)							
	278.15	283.15	288.15	293.15	298.15	303.15	308.15	313.15
ΔG^o	-16.71	-16.47	-16.59	-16.27	-16.49	-16.42	-16.04	-15.82
$\Delta H^o \times 10^5$	-1.61	-1.61	-1.61	-1.61	-1.61	-1.61	-1.61	-1.61
$\Delta S^o \times 10^2$	6.00	5.82	5.76	5.55	5.33	5.42	5.20	5.05

Conclusion

In this paper ion association of a complex salt, obtained from the reaction of *bis*-1-amidino-O-methylurea, copper(II) acetate and methanol, is described. Since the salt is 2:1, Shedlovsky equation is modified and Λ_0, K_A are obtained. Stokes' radii of the cation on the basis of Λ_0 are determined. The hydrated radius of $[Cu(AMUH)_2]^{2+}$ increases with rise in temperature instead of remaining constant. Ion association process is spontaneous and favoured at low temperature.

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