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Conductometric Studies of the Ion Association of α-/β-Alanine *Bis*-Biguanide Cobalt(III) Iodide in Methanol + Water Mixtures at Different Temperatures

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The conductance behaviour of α-alanine *bis* biguanide cobalt(III) iodide and β-alanine *bis* biguanide cobalt(III) iodide have been measured in the concentration range (3.00-1.25) $\times 10^{-4}$ eqv.dm^{-3} in methanol + water mixtures at 10-35 ºC. The limiting equivalent conductances (Λ) and ion association constants (K_A) for various compositions have been calculated using Shedlovsky method. The limiting equivalent conductances (Λ_0) and ion association constants (K_A) for various composition have been calculated using Shedlovsky method. The Walden products were determined. Based on the composition dependence of the Walden products, the influence of the mixed solvent composition on the solvation of ions has been discussed. For both salts, limiting equivalent conductances increase with raise in temperature and also ion association constants increase with increase in the mole fraction of methanol. The thermodynamic parameters *viz.*, change in free energy (ΔGº), enthalpy (ΔHº) and entropy have been calculated from the values of association constants.

Key Words: Association constant, Shedlovsky equation, Thermodynamic parameters, α-/β-Alanine *bis*-biguanide cobalt(III) iodide.

INTRODUCTION

The significance influence of dielectric constants on the ion-pairing process of an electrolyte has been revealed by many workers[1-4]. The theories of conductance have revealed one feature in common that the solvent is assumed as a continuum of permittivity D and viscosity η. This assumption is hardly valid when discussing strong ion- solvent interaction, since the size of solvent molecules are comparable to those of solute molecules, since the size of solvent molecules are also considered as rigid uniformity charged unpolarizable sphere[5,6]. Concerning ion solvent interactions this model is at best a doubtful approximation. Fous[5,6] has developed a model which permits treatment of long and short range interionic effects.

In the present work, the conductance and thermodynamic parameters of α-/β-alanine *bis*-biguanide cobalt(III) iodide in water (H_2O) + methanol (MeOH) mixture at 283.15, 288.15, 293.15, 303.15 and 308.15 K were examined. The limiting equivalent

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conductances (Λ_0) and ion association constants (K_A) for different mole fraction *i.e.*, 0.0000, 0.1942, 0.3600 and 0.5676 have been calculated using Shedlovsky[7] method. These computed values have been used to discuss qualitatively the nature of the ion-ion, ion-solvent and solvent-solvent interactions of the complexes salt in water + methanol mixtures. Temperature variation of K_A and Λ_0 have been studied to obtained the thermodynamic parameters *i.e.*, change in free energy, entropy and enthalpy.

EXPERIMENTAL

α-Alanine *bis*-biguanide cobalt(III) iodide and β-alanine *bis* biguanide cobalt(III) iodide were prepared by following the reported procedure[8,9]. The purity of the sample was determined by conventional chemical analysis and spectral measurements. The values were in good agreement with the literature values. Methanol was treated by the standard procedure[10]. About 700 mL of crude methanol (qualigens) was treated with (10-13 g) CaO and was refluxed for 6 h. The mixture was kept undisturbed overnight and then distilled[11]. For preparing aqueous solution of methanol X_{MeOH} +0.0588, 0.1942, 0.3600 and 0.5676 water of specific conductance of the order $< 2 \times 10^{-6}$ S cm^{-1} was used. All the solution were prepared by dissolving weighed samples of the electrolyte in solvent mixtures. All the viscosity, dielectric constant and density values were interpolated fromm literature values[12]. The conductivity measurements were made at 1 KHz with a Systronics-306 digital conductivity cell with smooth electrode. The observed conductivities were connected for the conductivity solvent. The experiment was performed between 10-35 ºC. The temperature was controlled in a thermostatic bath- Model D-G of HAAKE Mess-technik.

RESULTS AND DISCUSSION

The conductivity values of α-/β-alanine *bis* biguanide cobalt(III) iodide (2:1 salts) were analyzed using Shedlovsky[7] technique. Shedlovsky method involves the linear extrapolation using eqn. 1:

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

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

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

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

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

$$W = z_+ z_- \frac{2q}{(DT)^{3/2}}$$

$$W = \frac{z_+ z_-}{z_+ + z_-} \cdot \frac{\lambda_+ + \lambda_-}{z_+ \lambda_- + z_- \lambda_+}$$

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

z and λ are the valence and conductance of the 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,

$$\tau = \Lambda S(Z)/\Lambda_o \qquad (2)$$

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

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

$$B = \frac{0.5029 \times 10^{10}}{(DT)^{1/2}}$$

$$\mu = 1/2 \sum_i (C_i \tau_i) Z_i^2$$

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[12]. In order to treat the data in our system the R value is assumed to be R = a+d, where a, the sum of the crystallographic radii of the ions, is approximately equal to 5 Å and d (Å) is given by Glasstone[13]:

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

where M is the molecular weight of the solvent and ρ the density of the solution. For mixed solvent M is replaced by the mole fraction average molecular weight,

$$M_{avg} = \frac{M_1 M_2}{X_1 M_2 + X_2 M_1}$$

X_1 is the mole fraction of methanol of molecular weight M_1 and X_2 that of water of molecular weight M_2.

As per Shedlovsky method, an initial value of Λ_o was obtained from the intercept of the linear Onsagar plot of Λ *vesus* $C^{1/2}$. λ^o is obtained from the literature at 25 ºC and at other temperatures it was obtained by using equation[14]:

$$\lambda_1^0 = \lambda_{25}^0[1+\alpha'(t-25)] \qquad (3)$$

where α' is constant.Using these values of Λ_0, λ_-^0, λ_+^0; Z,S(Z) and t values were calculated. The mean activity co-efficient $f_\pm$ was determined by eqn. 2. From the linear plot of 1/ΛS(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 ($K_A/\Lambda^2{}_0$), respectively. The procedure was repeated using these values of Λ_0 and K_A. All calculations were carried out on IBM PC-AT/386. The results of K_A and $\Lambda_0\eta_o$ at different temperatures are summarized in Table-1.

TABLE-1

VALUE OF LIMITING EQUIVALENT CONDUCTANCE Λ_O (S cm^2), ASSOCIATION CONSTANTS K_A (dm^{3}equiv^{-1}) AND WALDEN PRODUCT ($\Lambda_O\eta_O$) OBTAINED BY SHEDLOVSKY TECHNIQUE FOR α-ALANINE *BIS* BIGUANIDE COBALT(III) IODIDE IN METHANOL + WATER MIXTURES AT DIFFERENT TEMPERATURES

	Temperature (ºC)					
	10	15	20	25	30	35
			X_1 = 0.000			
Λ_o	210.57	228.76	241.14	256.24	265.97	287.22
K_A	435.57	307.78	328.88	293.36	323.56	372.83
$\Lambda_o\eta_o$	274.37	259.41	241.62	228.31	212.24	206.80
			X_1 = 0.0588			
Λ_o	176.34	186.78	208.24	226.20	241.08	262.69
K_A	490.78	420.89	367.05	334.26	374.59	432.97
$\Lambda_o\eta_o$	285.14	270.08	260.92	248.37	236.74	229.85
			X_1 = 0.1942			
Λ_o	135.03	143.22	164.15	179.96	193.79	208.53
K_A	583.60	50.35	417.79	373.42	422.97	515.44
$\Lambda_o\eta_o$	294.37	280.57	275.77	259.86	243.59	231.68
			X_1 = 0.3600			
Λ_o	122.55	141.18	156.30	168.14	181.97	196.95
K_A	678.72	565.85	478.18	406.33	480.96	561.72
$\Lambda_o\eta_o$	305.27	292.67	281.03	264.32	248.03	235.95
			X_1 = 0.5676			
Λ_o	127.53	137.42	151.89	168.19	186.99	201.60
K_A	737.47	616.46	528.47	462.18	529.21	660.40
$\Lambda_o\eta_o$	252.51	232.10	229.81	226.17	221.40	213.29

The values of log K_A are plotted *versus* temperature(t) in Fig. 1. These plots give smooth curve with a minima (t_{min}) generally at 25 ºC. The relative order of magnitude of log K_A for the complex salt depends on the temperature which can be reproduced by a quadratic equation[14].

$$\log K_A = p(t-t_{min})^2 + \log K_{A(min)} \tag{4}$$

where t_{min}, $\log K_{A(min)}$ are constant and p corresponds to the curvature of the parabola. The following expressions for the standard entropies and enthalpies ion association in salt solution ΔS^o and ΔH^o can be derived from the eqn. 4.

$$\Delta S^o = 2.303\ R\{\log K_{A(min)} + p(3t + 546.3)\ (t-t_{min})\}$$

$$\Delta H^o = 4.605\ pR\ (t + 273.15)^2\ (t-t_{min})$$

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

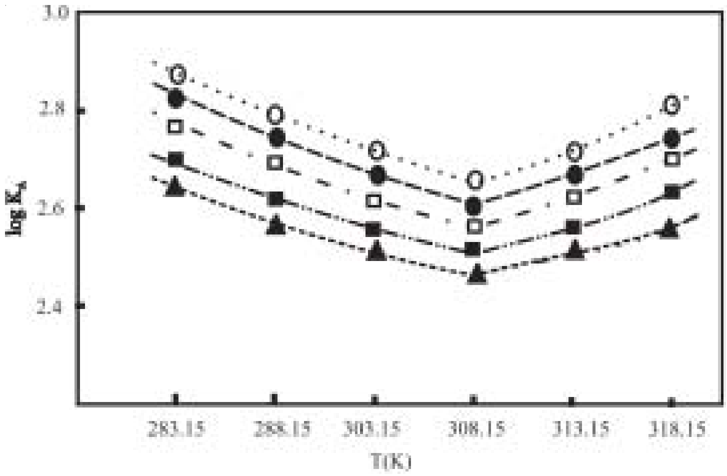

Fig. 1. Temperature dependence of the ion-association constants between [Co(α-alan)(BigH)$_2$]$^{2+}$ and I$^-$ in different mixed solvents of methanol + water: (▲) X = 0.0000, (■) X = 0.0588 (□) X = 0.1942, (●) X = 0.3600 and (○) X = 0.5676

The Λ_0 values for the electrolytes increases with rise in temperature in methanol + water mixtures. These are due to the fact that increased thermal energy results in bond breaking and variation in vibrational, rotational and translational energy of the molecules that leads to higher frequency and higher mobility of ions.

The variations of $\Lambda_o\eta_o$ and η with the mole fraction of methanol is shown in Fig. 2. The viscosity of methanol + water mixture increase upto $X_{MeOH} = 0.36$ in both cases and thereafter it decreases. Interestingly values of Λ_o of the salt decrease upto this mole fraction and then increase in methanol rich region at all the temperature *i.e.*, 10-35 ºC as expected from the Walden product rule. The maximum in η *versus* mole fraction indicates maximum interaction between water and methanol in such solvents. The Walden product ($\Lambda_o\eta_o$) increases upto the mole fraction of 0.36 in methanol and decreases. It's change in solvation is reflected by the variation in $\Lambda_o\eta_o$[15], the increase of the product indicates as increase of the hydrophobic solvation with increasing concentration of methanol. As the methanol content increases progressive disruption of water structure occurs and the ions become solvated with the other component of the solvent mixture (*viz.*, methanol). Further, the effect would be more in case of a solution at a higher temperature. These trends are observed in present experiment too (Fig. 2).

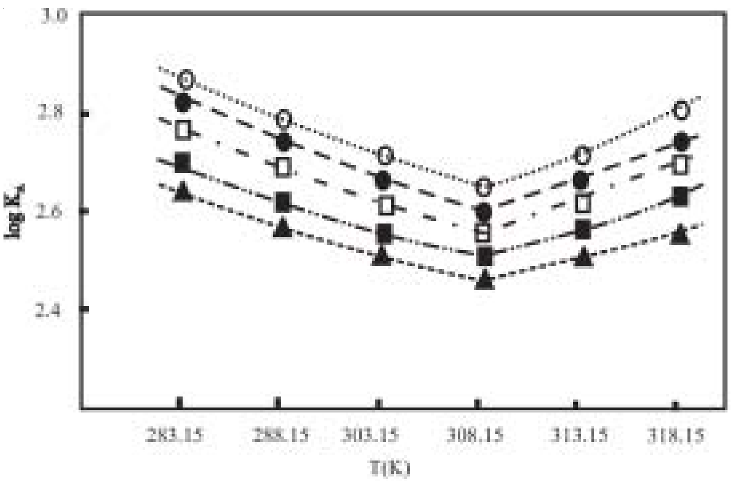

Fig. 2. Temperature dependence of the ion-association constants between [Co(β-alan)(BigH)$_2$]$^{2+}$ and I$^-$ in different mixed solvents of methanol + water: (▲) X = 0.0000, (■) X = 0.0588 (□) X = 0.1942, (●) X = 0.3600 and (○) X = 0.5676

Both salts, the K_As are found to increase in X_{MeOH} (linear plots) which indicates an increased associations when methanol is added to water. The smaller $\Lambda_o\eta_o$ values in water rich region may be due to the large effective radius of the solvated radius of the cation whereas maximum value of $\Lambda_o\eta_o$ at $X_{MeOH} = 0.36$ corresponds to minimum value of solvated radius of the cation. A noticeable decrease in the solvation size of other solutes in water rich mixtures has also been found previously by other[16,17]. The $\Lambda_o\eta_o$ in these binary mixed solvents of water increases and then decreases after passing through a maxima[18]. It is thus apparent that the variation of the Walden product with the solvent compositions is due to an electrochemical equilibrilium between the cations with the solvent molecules on one hand and the selective solvation of ions on the other with the change in the composition of the mixed solvents and temperature of the solution.

The values of ΔS°, ΔH° and ΔG° at different temperatures and in different solvents are shown in Tables 1 and 2. The values of the K_A of the complexes decrease with rise in temperature until the $K_{A(min)}$ is reached at t_{min} which is characteristics of the anions. Beyond t_{min}, these values increase gradually. The presence of t_{min} was explained due to the weak hydration of the anion related to their structure of breaking properties[18,19]. The increase in the K_A beyond t_{min} is supported by increase of entropy changes. A positive entropy change has explained on the assumption that the 'iceberg' structure around the cation is broken when association takes place leading to an increase in the degree of disorderliness[20].

TABLE-2
VALUE OF LIMITING EQUIVALENT CONDUCTANCE Λ_O (S cm^2), ASSOCIATION CONSTANTS K_A (dm^{3}equiv^{-1}) AND WALDEN PRODUCT ($\Lambda_O\eta_O$) OBTAINED BY SHEDLOVSKY TECHNIQUE FOR β-ALANINE *BIS* BIGUANIDE COBALT(III) IODIDE IN METHANOL + WATER MIXTURES AT DIFFERENT TEMPERATURES

	Temperature (ºC)					
	10	15	20	25	30	35
			X_1 = 0.000			
Λ_o	176.13	189.89	203.43	223.14	237.12	256.80
K_A	455.84	392.49	347.48	315.03	338.15	377.10
$\Lambda_o\eta_o$	229.50	215.34	203.84	198.82	189.22	184.90
			X_1 = 0.0588			
Λ_o	144.58	155.83	172.19	194.53	200.56	217.49
K_A	527.18	441.18	381.28	347.19	411.58	476.10
$\Lambda_o\eta_o$	233.79	225.33	215.75	213.59	196.95	190.30
			X_1 = 0.1942			
Λ_o	110.52	119.94	136.57	149.59	163.72	175.10
K_A	645.73	555.24	461.12	405.85	458.52	559.70
$\Lambda_o\eta_o$	240.93	234.96	229.44	216.10	205.80	194.34
			X_1 = 0.3600			
Λ_o	102.53	114.10	128.06	138.93	155.41	165.42
K_A	709.48	592.91	518.16	451.16	492.14	596.01
$\Lambda_o\eta_o$	255.40	236.53	230.79	218.40	211.82	198.17
			X_1 = 0.5676			
Λ_o	107.42	120.78	132.35	146.13	159.82	174.52
K_A	795.43	686.93	573.89	496.99	598.95	731.85
$\Lambda_o\eta_o$	212.69	204.00	200.25	195.68	189.23	184.64

As expected, the free energy changes become more negative at higher percentage of methanol which indicate the ion pair association are favoured with lowering of dielectric constant of the medium in both cases. The lowering of K_A values with rise in temperature upto t_{min} is reflected by negative ΔHº values. Since the reaction is exorthermic, at higher temperature, ion association decreases. Above t_{min}, K_A values increase with increase in temperature which is supported by positive ΔHº values as shown in Tables 3 and 4. Beyond t_{min} ion-assocciation is endothermic so ion-association increase with increase in temperature.

Conclusion

Both salts show minimum association constants $K_{A(min)}$ at 25 ºC, $\Lambda_o\eta_o$ are maximum at same mole fraction *i.e.*, X_{MeOH} = 0.36 in which η is maximum. At a particular temperature, solvated radius of cation is inversely proportional to $\Lambda_o\eta_o$. Solvent-solvent interaction is maximum where η of solvent mixture is maximum. With the increase in mole fraction of methanol, progressive disruption of water structure occurs and the ions become solvated with methanol. Further, thermodynamics parameters support the variation of K_A with temperature in both cases.

TABLE-3

THERMODYNAMICS PARAMETERS ΔG^o (kJ equiv^{-1}), ΔH^o (kJ equiv^{-1}) AND ΔS^o (kJ K^{-1}equiv^{-1}) OF α-ALANINE *BIS* BIGUANIDE COBALT(III) IODIDE IN METHANOL + WATER MIXTURES AT DIFFERENT TEMPERATURES

	Temperature (K)				
	283.15	288.15	293.15	303.15	308.15
X_1 = 0.000					
ΔG^o	-14.87	-14.75	-14.71	-15.25	-15.18
ΔH^o	-35.14	-32.33	-32.64	38.35	37.85
$10^3\ \Delta S^o$	-71.58	-62.02	-61.16	176.83	172.08
X_1 = 0.0588					
ΔG^o	-14.58	-14.44	-14.39	-14.95	-15.56
ΔH^o	-34.13	-31.79	-26.72	34.83	40.86
$10^3\ \Delta S^o$	-69.05	-60.21	-42.05	164.20	183.12
X_1 = 0.1942					
ΔG^o	-14.99	-14.89	-14.70	-15.25	-16.01
ΔH^o	-39.68	-40.63	-32.11	37.37	50.90
$10^3\ \Delta S^o$	-87.20	-89.32	-59.38	173.55	217.14
X_1 = 0.3600					
ΔG^o	-15.22	-15.18	-15.03	-156.58	-16.23
ΔH^o	-41.03	-45.71	-46.52	51.52	51.12
$10^3\ \Delta S^o$	-91.16	-105.97	-107.43	221.31	218.56
X_1 = 0.5676					
ΔG^o	-15.54	-15.36	-150.28	-15.82	-16.65
ΔH^o	-41.52	-38.63	-38.30	41.38	56.35
$10^3\ \Delta S^o$	-91.76	-80.73	-78.73	188.67	236.90

TABLE-4

THERMODYNAMICS PARAMETERS ΔG^o (kJ equiv^{-1}), ΔH^o (kJ equiv^{-1}) AND ΔS^o (kJK^{-1} equiv^{-1}) OF β-ALANINE *BIS* BIGUANIDE COBALT(III) IODIDE IN METHANOL + WATER MIXTURES AT DIFFERENT TEMPERATURES

	Temperature (K)				
	283.15	288.15	293.15	303.15	308.15
X_1 = 0.0000					
ΔG^o	-14.41	-14.30	-14.26	-14.68	-15.21
ΔH^o	-32.83	-30.33	-27.97	21.60	28.40
$10^3\ \Delta S^o$	-65.04	-55.61	-46.77	119.70	141.49
X_1 = 0.0588					
ΔG^o	-14.81	-14.58	-14.48	-15.19	-15.81
ΔH^o	-39.50	-33.06	-26.72	52.00	49.84
$10^3\ \Delta S^o$	-87.17	-64.12	-41.73	221.64	213.05
X_1 = 0.1942					
ΔG^o	-15.12	-15.00	-14.94	-15.46	-16.22
ΔH^o	-37.15	-43.26	-36.46	37.30	50.72
$10^3\ \Delta S^o$	-77.80	-97.63	-73.38	174.01	217.23

$X_1 = 0.3600$					
ΔG^o	-15.45	-15.29	-15.24	-15.63	-16.38
ΔH^o	-40.39	-37.57	-39.35	26.32	43.84
$10^3\ \Delta S^o$	-88.08	-77.33	-82.25	138.38	149.55
$X_1 = 0.5676$					
ΔG^o	-15.72	-15.64	-15.49	-16.13	-16.91
ΔH^o	-41.81	-44.70	-41.13	57.07	61.11
$10^3\ \Delta S^o$	-92.14	-100.83	-87.47	241.15	253.21

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