ION ASSOCIATION OF [Co(GLY)(AEUH)₂]I₂ IN METHANOL + WATER MIXTURES AT DIFFERENT TEMPERATURES

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ABTRACT
Electrical Conductance of glycine bis-1-amidino-O-ethylurea cobalt(III) iodide have been measured in various methanol(M) + water(W) mixtures at 283.15-318.15K. The limiting molar conductance (Λ_0) and the association constant (K_A) have been analyzed by Shedlovsky technique for the electrolytes. The influence of the mixed solvent composition on the solvation of ions has been discussed based on the composition dependence of the Walden product ($\Lambda_0\eta_0$). For this chosen salt, limiting equivalent conductances have been increased with raise in temperature and also ion association constants have been increased with increase in the mole fractions of methanol. Based on the K_A and temperature dependence Λ_0, the thermodynamic parameters viz., changes in free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) and Arrhenius activation energy (E^a) of transport processes have been determined. The results have been discussed in terms of ion-ion, ion-solvent and solvent-solvent interactions.

Keywords: *Electrical Conductance, Shedlovsky Technique, Cobalt(III) Complex, Thermodynamic Parameters, Walden Product, Arrhenius Activation Energy*

INTRODUCTION
Ion-pairs may be defined as a neutral species formed by electrostatic attraction between oppositely charged ions in solution, which are often sufficiently lipophilic to dissolve in non-aqueous solvents (Quintanar-Guerrero, 1997; Doelker, 1997). It should be emphasized that the formation of an ion pair is due only to outer sphere interaction and even though this molecular interaction can be written according to the mass action law, no chemical bond of any kind is formed. The general notation A^+, B^- is used to describe an ion-pair product which exists as stable, thermodynamically distinct species and not as a transient, continuously exchanging association.
It is clear therefore that any charged molecule in solution, under certain conditions, can form an ion-pair, with ions of oppositely charge.
Bjerrum *et al.,* (1926) had first introduced the concept of ion pairs into the evaluation of the enter-ionic forces in electrolytic solutions. The tendency of ions to associate into ion pair depends on the balance between the electrostatic forces and thermal energy. Ion pair formation refers to the association of cations and anions in solution. The significance influence of dielectric constants on the ion-pairing process of an electrolyte has been revealed by many workers (Bag *et al.,* 2000 and 2001; Singh *et al.,* 2009). The theories of conductance have revealed one feature in common that the solvent is assumed as a continuum of permittivity D and viscosity. 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. Concerning ion solvent interactions this model is at best a doubtful approximation. Fous *et al.,* (1949 and 1955) have developed a model which permits treatment of long and short range interionic effects.

MATERIALS AND METHODS
The chosen complex was prepared according to the report procedure (Dutta *et al.,* 1968*)*. For preparing aqueous solution of methanol X_{MeOH} = 0.0000-1.0000, water of specific conductance of order 2×10^{-6} Scm⁻¹ were used. The electrical conductivities were measured by Systronic-306 digital conductivity bride (accuracy ± 0.1%) with a dip type immersion conductivity cell was used. Conductivity measurements were carried out over the temperature range 10-45⁰C. Methanol (Merk) was treated by the standard

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procedure *[8]*. All the dielectric constants and viscosities were obtained from literature (Hodgman *et al.,* 1956; Timmermann, 1957; Akhadov, 1981). The temperature control in the ranges 10 -45^{0}C were made by using water bath and circular –Model D8-G of HAAKE Mess-Technik Gmbtlu. Co. Germany. The measurements of weights were done by using a METTER Balance, Model-AE- 260, Delta Range. All calculations were done on IBM-PC-AT/386 using a basic programmed.

The experimental data of conductance measurements were analyzed by using Shedlovsky equation. Shedlovsky equation (Shedlovsky, *et al.,* 1956) is given by

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

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

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

$$S(z) = \left(\frac{z}{2}\sqrt{1 + \left(\frac{z}{2}\right)^2}\right)^2 \; ; Z = \left[\frac{\propto \Lambda_o + \beta}{\Lambda_o^{S/z}}\right](C\Lambda)^{1/2} \; ; \propto = \frac{17.147x105W}{(DT)^{3/2}}$$

$$w = z_+z_-\frac{2q}{1+q^{1/2}} \qquad ; q = \frac{z_+z_-}{z_++z_-} x \frac{\lambda_++\lambda_-}{z_+\lambda_-+z_-\lambda_+} ; \beta = \frac{151.47}{\eta(DT)^{1/2}}$$

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)

$$-\log f_\pm = \frac{Az_+z_-\mu^{1/2}}{1+BR\mu^{1/2}} \tag{3}$$

where $A = \frac{1.8247x10^6}{(DT)^{3/2}}$; $B = \frac{0.5029x10^{10}}{(DT)^{1/2}}$; $\mu = \frac{1}{2}\sum_i (c_i\tau_i)z_i^2$

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 [24]. 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 [2]

$$d = 1.183\left(M/\rho\right)^{1/3} \tag{4}$$

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

$$M_{avg} = \frac{M_1M_2}{X_1M_2 + X_2M_1}$$

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 Onsager plot of Λ versus c$^{1/2}$, λ^o is obtained from the literature at 25°C and at other temperatures it was obtained by using the following equation (Glasstone, 1941)

$$\lambda_t^0 = \lambda_{25}^0[1 + \alpha'(t - 25)] \tag{5}$$

α$^{'}$ is constant. Using these values of Λ_o, λ^o_-, λ^o_+, z, s(z) and r values were calculated. 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 $1/\Lambda_0$ 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-AT/386.

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RESULTS AND DISCUSSION

From the experimental data, the values of Λ_0 increased invariable with increase in temperature (Table 1) in all solvents irrespective of X_{MeOH}, indicating less solvation or higher mobility of ions. This is attributed to the fact that increased in thermal energy results in greater bond-breaking in vibrational, rotational and translational energies of the molecules that lead to higher frequency and hence higher mobility of ions. In this case, the values of Walden product $\Lambda_0\eta_0$ increase with increase in x_1 upto about 0.36 and thereafter it decreases rapidly and is shown in Figure 1. Then effective radius r of ion or solute can be calculated as $\Lambda_0\eta_0 = 1/6\ \pi r T$. It has been possible to derive the values of r for the cation of the octahedral Co^{III} complex. As evident from Table 1, the values of r decrease with increase in methanol upto $x_1 = 0.36$ and thereafter increase in methanol rich region. In this case, the values of Walden product $\Lambda_0\eta_0$ increase with increase in x_1 upto about 0.36 and thereafter it decreases rapidly and is shown in Figure 1. The smaller $\Lambda_0\eta_0$ value in water rich region may be due to the large effective radius of the cation whereas maximum value of $\Lambda_0\eta_0$ corresponds to minimum value of r. It is interesting to note that the Λ_0 values of the solute decreases upto $x_1 = 0.36$ and then increases in methanol rich region at temperatures from 10 to 45 ºC, indicating maximum methanol-water interaction in the region $x_1 = 0.36$. The variation of $\Lambda_0\eta_0$ with x_1 is due to an electrochemical equilibrium between the cations with the solvent molecules on one hand and the change in composition of the mixed solvents and the temperature of the solution. Since the conductance of an ion depends on its mobility, it is reasonable to treat the conductance data similar to the one that employed for rate processes taking place with change of temperature i.e., $\Lambda_0 = Ae^{E_a/RT}$ or $\ln\Lambda_0 = \ln A - E_a/RT$, where A is the frequency factor and E_a is Arrhenius activation energy of transport processes (Dash *et al.,* 1998). E_a values are computed from the slope of the plot of $\log \Lambda_0$ versus $1/T$ are recorded in Table 2 which shows that the values of E_a increase with increase in x_1 upto $x_1 = 0.36$ and thereafter decreases rapidly. It follows that in water rich region upto $x_1 = 0.36$ the Co(III) complex ion requires higher activation energy for the transport processes as the methanol content in the mixed solvent increases but reverse is the case beyond $x_1 = 0.36$. A reaction which requires higher activation energy is slow at ordinary temperatures indicating the lower Λ_0 values. Beyond $x_1 = 0.36$, as the activation energy decreases the Λ_0 values increases with x_1.
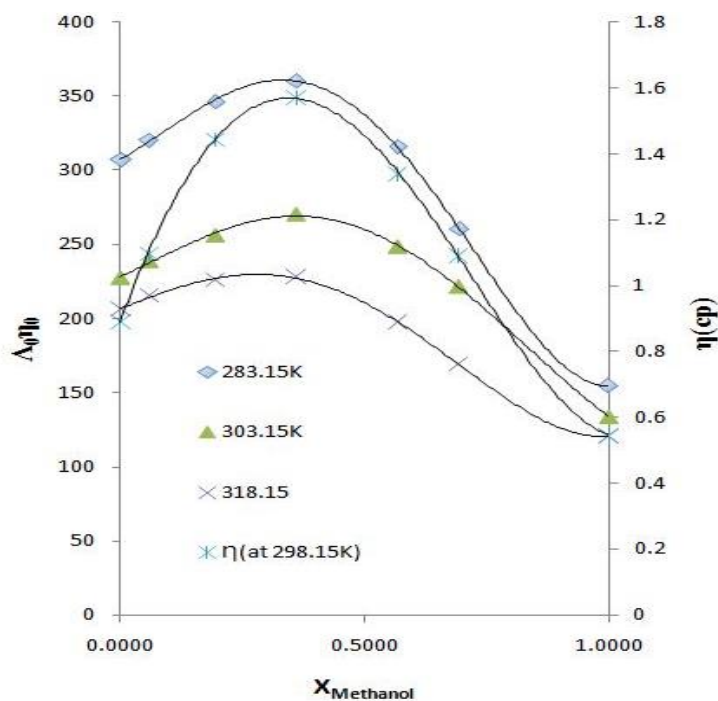

Figure 1: The Walden product ($\Lambda_0\eta_0$) and viscosity as a function of $X_{Methanol}$ in methanol+water mixture

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The experimentally determined K_{AS} (Table 1) are found to increase with the increase in mole fractions of methanol which indicate an increased association as methanol is added to water. The values of ΔG^0, ΔH^0 and ΔS^0 at different temperatures in different mixed solutions are shown in Table 2 and Table 3. The values of ΔG^0 for association is calculated from the relation, $\Delta G^0 = -RT \ln K_A$. The heat of association (ΔH^o) is obtained from the slope of the plot of log K_A *vs.* $1/T$. The ΔH^o values obtained are found to increase systematically with the composition of the mixed solvent. The negative values of ΔH^o indicate that ion association processes are exothermic in nature in all solvents at all temperatures. At a particular temperature ΔG^0 becomes more negative with increase in X_1. This shows that ion pair association is more favored with lowering of dielectric constant of the medium. The entropy change (ΔS^0) is calculated from the Gibbs-Helmholtz, $\Delta G^0 = \Delta H^o - T\Delta S^o$. Positive entropy change is explained on the assumption that the ice-berg structure around the cation is broken when association takes place leading to an increase in the degree of disorderliness (De *et al.,* 1975).

Table 1: The values of limiting molar conductances (Λ_0), association constant (K_A), Walden Product ($\Lambda_0\eta_0$) and effective radius (r) obtained by Shedlovsky technique for glycine bis-1-amidino-O-ethylurea cobalt (III) iodide in methanol + water mixtures at different temperatures

x_{MeOH}	Λ_0 (Scm² mol⁻¹)	K_A (dm³ mol⁻¹)	$\Lambda_0\eta_0$	r (Å)	Λ_0 (Scm² mol⁻¹)	K_A (dm³ mol⁻¹)	$\Lambda_0\eta_0$	r (Å)
	283.15K				**288.15K**			
0.0000	235.52	680.51	306.88	06.11	252.44	550.81	286.27	06.43
0.0588	201.96	767.62	320.57	05.74	214.16	633.17	309.68	05.95
0.1942	159.02	847.39	346.66	05.41	166.77	709.25	326.70	05.64
0.3600	144.88	945.71	360.90	05.19	164.97	829.86	341.98	05.39
0.5676	159.49	1080.14	315.79	05.94	176.87	922.85	298.73	06.17
0.6923	170.68	1165.12	261.92	07.44	188.35	1074.65	246.17	07.48
1.0000	225.84	1269.85	154.93	12.10	234.12	1194.75	149.37	12.23
	293.15K				**298.15K**			
0.0000	260.95	460.26	261.47	06.92	275.09	388.66	245.11	07.26
0.0588	222.17	529.75	278.38	06.50	227.32	434.67	249.60	07.13
0.1942	177.02	601.43	297.39	06.09	184.98	501.80	267.11	06.67
0.3600	169.18	688.19	304.19	05.95	174.36	563.97	274.09	06.50
0.5676	179.78	787.14	289.99	06.25	185.17	666.54	247.94	07.18
0.6923	201.53	947.87	240.22	07.53	207.85	746.84	224.69	07.92
1.0000	246.01	1072.50	145.39	12.52	253.58	864.46	137.95	12.94
	303.15K				**308.15K**			
0.0000	295.77	317.44	227.58	07.42	310.27	270.28	223.39	07.71
0.0588	243.30	370.68	238.92	07.33	266.84	308.62	233.49	07.38
0.1942	203.87	430.08	256.26	06.83	228.00	355.81	253.31	06.80
0.3600	198.56	479.18	270.64	06.47	221.33	436.28	265.15	06.50
0.5676	210.05	551.98	248.69	07.04	228.26	500.89	241.50	07.13
0.6923	229.95	636.37	221.67	07.90	240.52	655.42	209.73	08.21
1.0000	261.63	762.54	133.43	13.12	266.74	774.56	130.70	13.23
	313.15K				**318.15K**			
0.0000	327.44	225.87	214.15	07.91	346.12	170.11	206.29	08.09
0.0588	280.53	261.23	223.46	07.59	316.48	230.82	215.84	07.73
0.1942	235.43	315.54	235.43	07.20	270.13	297.74	226.09	07.38
0.3600	231.98	395.02	242.42	07.00	237.02	376.54	228.49	06.96
0.5676	233.05	484.95	232.35	07.29	251.60	456.02	197.76	08.44
0.6923	246.45	610.84	193.22	08.78	256.63	576.14	169.63	09.84
1.0000	280.24	718.25	127.79	13.34	317.74	667.35	121.06	13.78

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Table 2: Thermodynamic parameter ΔH^0, E_a and 10^{-3} A of Shedlovsky technique for glycine bis-1-amidino-O-ethylurea cobalt (III) iodide in methanol + water mixtures at different temperatures

$X_{methanol}$	ΔH^0 (kJmol^{-1})	E_a (kJmol^{-1})	$10^{-3}A$
0.0000	-29.45	08.33	08.13
0.0588	-26.17	09.17	09.77
0.1942	-23.55	10.49	13.27
0.3600	-21.67	10.68	13.68
0.5676	-18.99	09.31	08.43
0.6923	-15.89	08.79	07.24
1.0000	-13.71	06.51	03.55

Table 3: Thermodynamic parameters ΔG^0 and ΔS^0 of Shedlovsky technique for glycine bis-1-amidino-O-ethylurea cobalt (III) iodide in methanol + water mixtures at different temperatures

$X_{methanol}$	ΔG^0 (kJ mol^{-1})	$10^3\Delta S^0$ (kJ K^{-1}mol^{-1})	ΔG^0 (kJ mol^{-1})	$10^3\Delta S^0$ (kJK^{-1}mol^{-1})	ΔG^0 (kJ mol^{-1})	$10^3\Delta S^0$ (kJK^{-1}mol^{-1})	ΔG^0 (kJ mol^{-1})	$10^3\Delta S^0$ (kJK^{-1}mol^{-1})
	10^0C			15^0C	20^0C		25^0C	
0.0000	-15.34	-49.83	-15.12	-49.66	-14.93	-49.53	-14.79	-49.17
0.0588	-15.45	-38.25	-15.45	-37.20	-15.27	-37.18	-15.07	-37.23
0.1942	-15.89	-27.05	-15.73	-27.14.	-15.61	-27.09	-15.42	-27.27
0.3600	-16.16	-19.46	-16.11	-19.30	-15.94	-19.55	-15.70	-20.02
0.5676	-16.43	-09.04	-16.28	-09.02	-16.39	-09.24	-16.10	-09.69
0.6923	-16.91	02.65	-16.64	02.67	-16.73	02.87	-16.72	02.78
1.0000	-16.89	11.12	-16.94	11.21	-16.89	10.85	-17.01	11.07
	30^0C			35^0C	40^0C		45^0C	
0.0000	-14.51	-49.16	-14.33	-49.06	-13.79	-50.00	-13.58	-49.88
0.0588	-14.92	-37.14	-14.69	-37.25	-14.51	-37.23	-14.42	-36.93
0.1942	-15.27	-27.31	-15.05	-27.58	-14.99	-27.34	-14.38	-28.82
0.3600	-15.56	-20.17	-15.58	-19.76	-15.59	-19.42	-15.72	-18.70
0.5676	-15.90	-10.19	-16.05	-09.54	-16.13	-09.13	-16.20	-08.77
0.6923	-16.66	02.54	-16.63	02.40	-16.73	02.68	-16.81	02.89
1.0000	-17.07	11.08	-17.05	10.84	-17.15	10.99	-17.24	11.10

Conclusion

Association constant values increase with the increase in mole fraction of methanol. Λ_0 values increase linearly with the increase in temperatures. The smaller $\Lambda_0\eta_0$ value in water rich region may be due to the large effective radius of the cation whereas maximum vcalue of $\Lambda_0\eta_0$ corresponds to minimum value of *r*. Ion association process is exothermic in nature. Ion salvation is minimum in the mixture whose viscosity is maximum. In water rich region upto $x_1 = 0.36$ the Co(III) complex ion requires higher activation energy for the transport processes as the methanol content in the mixed solvent increases but reverse is the case beyond $x_1 = 0.36$. On the another hand, in methanol-rich region ion association processes are less energy consuming and more stabilized than in water rich region.

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