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Ion Pair Formation and Thermodynamics of Glycine *Bis*-1-Amidino-O-Methylurea Cobalt(III) Halides in Water + Methanol Mixed Solvents at Different Temperatures

N. MOHONDAS SINGH†, TH. DAVID SINGH, N. YAIPHABA and
N. RAJMUHON SINGH*
Department of Chemistry, Manipur University, Canchipur, Imphal-795 003, India
E-mail: rajmuhon@yahoo.co.in

Conductometric studies have been made for the solutions of glycine *bis*-1-amidino-O-methylurea cobalt(III) chloride, glycine *bis*-1-amidino-O-methylurea cobalt(III) bromide and glycine *bis*-1-amidino-O-methylurea cobalt(III) iodide in water and water + methanol mixtures at different temperatures ranging from 5-35 ºC. The conductance data in all cases have been analyzed by Shedlovsky method to obtain limiting molar conductances (Λ_o) data and ion association constants (K_A) values. The influence of the mixed solvent composition on the solvation of ions has been discussed based on the composition dependence of the Walden product ($\Lambda_o\eta_o$). The thermodynamics parameters *viz.*, changes in enthalpy, entropy and free energy for the ion pair formation have been calculated from the value of ion association constant at different temperatures. The results have been discussed in terms of ion-ion, ion-solvent and solvent-solvent interactions.

Key Words: Ion association constants, Thermodynamic parameters, Walden product, Glycine *bis*-1-amidino-O-methylurea cobalt(III) halides.

INTRODUCTION

Reliable values of single ion conductivities are useful for a variety of purposes, among them is investigation of ion solvent interactions[1]. The split of electrolyte conductivities into the ionic components ideally requires transference numbers, the accurate measurement of which presents serious experimental problems in many non-aqueous solvents. The conductance and viscosity measurements provide valuable information regarding the ion-ion and ion-solvent interactions[2]. Izonfuo and Obunwo[3] and Roy *et al.*[4] studied the conductance of alkali metal in different mixtures mixed solvents. Rajmuhon *et al.*[5-7] had studied the thermodynamic parameters and

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†Department of Chemistry, Mizoram University, Aizawl-796 009, India

Walden products of different complexes. Rajmuhon and *et al.*[8,9] also had determined the comparison of transition metal complexes among the halide groups.

The present work reports the comparative studies of conductometric properties, thermodynamic behaviour and Walden product of glycine *bis*-1-amidino-O-methylurea cobalt(III) chloride, glycine *bis*-1-amidino-O-methylurea cobalt(III) bromide and glycine *bis*-1-amidino-O-methylurea cobalt(III) iodide in water and water + methanol mixed solvents at different temperatures between 5 to 35 ºC. The data were analyzed using Shedlovsky method[10]. The K_As and Walden products have been evaluated in these solvents at the experimental temperatures. The thermodynamic parameters *viz.*, ΔHº, ΔSº and ΔGº for the formation have been studied from the values of ion association constant at various temperatures. The computed values have been used to discuss qualitatively the nature of different interactions.

EXPERIMENTAL

The octahedral Co(III) complexes *viz.*, glycine *bis*-1-amidino-O-methylurea cobalt(III) chloride, glycine *bis*-1-amidino-O-methylurea cobalt(III) bromide and glycine *bis*-1-amidino-O-methylurea cobalt(III) iodide were prepared by the reported procedure[11]. The purity of the samples 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[12]. Water of specific conductance of the order $< 3 \times 10^{-6}$ S cm^{-1} was used for preparing aqueous solutions of methanol with $X_{MeOH} = 0.0000, 0.0588, 0.1942, 0.3600$ and 0.5676. These solutions were prepared by dissolving weighed samples of the electrolyte in solvent mixtures (w/w). All the viscosity, dielectric constant, density and ion conductance values were interpolated from the literature values[13]. A Systronics conductivity meter 306 (accuracy ± 0.1 %) with a dip-type immersion conductivity cell with smooth electrode was used. The experiments were repeated 2-3 times for each concentration of the solution. The observed molar conductivities were corrected for the conductivity of the solvent concerned. The precision of the temperature measurement was ± 0.01 (Model DS-G HAAKE Mess-Technik).

RESULTS AND DISCUSSION

The experimental values of conductance measurements of 2:1 Co(III) complexes in water-methanol mixtures after correction were analyzed using Shedlovsky extrapolation technique[9]. Shedlovsky method involves the linear extrapolation equation

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

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

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

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

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

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

$$q = \frac{Z_+Z_-}{Z_+ + Z_-} \cdot \frac{\lambda_+ + \lambda_-}{Z_+\lambda_- + Z_-\lambda_+}$$

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

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,

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

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

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

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

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

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[14]. 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 *ca.* equal to 5 Å and d (Å) is given by[15]

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

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,

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

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 Onsagar plot of Λ *vs.* $C^{1/2}$. λ^o is obtained from the literature at 25 ºC and other temperatures it was obtained by using equation[16],

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

where α′ is constant. Using these values of Λ_0, λ^0_-; λ^0_+; Z,S(Z) and τ values were calculated. The mean activity co-efficient $f_\pm$ was determined by eqn. 2. From the linear plot of 1/Λ S(Z) *vs.* C Λ $f^2_\pm$ 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 these values of Λ_0 and K_A. All calculations were carried out on IBM PC-AT/386.

The results of K_A and $\Lambda_o\eta_o$ at different temperatures are summarized in Tables 1-3. As expected the order of K_A values are $Cl^- > Br^- > I^-$. The variation of Walden product ($\Lambda_o\eta_o$) for three salts with X_1 at 5, 10 and 20 ºC are shown in Figs. 4-6. In all these cases, the values of $\Lambda_o\eta_o$ increase with increase in X_1 upto about 0.36 and thereafter it decreases rapidly. The viscosity of water + methanol mixtures also passes through maximum about $X_1 = 0.36$. It is interesting to note that the Λ_o values of the solute decreases upto $X_1 = 0.36$ and then increases in methanol rich region at temperatures from 5 to 35 ºC, indicating maximum methanol-water interaction in the region $X_1 = 0.36$.

On the water-rich side there exists a region, where water structure remains more or less intact as methanol molecules are added interstitially into cavities in the structure. As more and more methanol is added the cavities are progressively filled, solvent-solvent interactions become stronger and in turn producing maximum Walden product. Further addition of methanol results in progressive disruption of water structure and the ions

TABLE-1

VALUE OF Λ_o (S cm^2), K_A (dm^3 mol^{-1}) AND $\Lambda_o\eta_o$ OBTAINED BY SHEDLOVSKY TECHNIQUE FOR GLYCINE *BIS*-1-AMIDINO-O-METHYLUREA COBALT(III) CHLORIDE IN METHANOL AND WATER MIXED SOLUTION AT DIFFERENT TEMPERATURES

	5 ºC	10 ºC	15 ºC	20 ºC	25 ºC	30 ºC	35 ºC
$X_1 = 0.0000$							
Λ_o	213.26	235.52	252.44	260.95	275.09	295.77	310.27
K_A	806.79	680.51	550.81	460.26	388.66	317.44	270.28
$\Lambda_o\eta_o$	324.16	306.88	286.27	261.47	245.11	236.02	223.39
$X_1 = 0.0588$							
Λ_o	187.30	201.96	204.16	222.17	227.32	243.30	266.84
K_A	903.20	767.62	633.17	529.75	434.67	370.68	308.62
$\Lambda_o\eta_o$	334.89	326.57	295.22	278.38	249.60	238.92	233.49
$X_1 = 0.1942$							
Λ_o	150.99	159.02	166.77	177.02	184.98	203.87	228.00
K_A	1006.33	847.39	709.25	601.43	501.80	430.08	355.81
$\Lambda_o\eta_o$	362.53	346.66	326.70	297.39	267.11	256.26	253.31
$X_1 = 0.3600$							
Λ_o	127.29	144.88	167.97	169.18	174.36	198.56	221.33
K_A	1131.20	945.71	829.86	688.19	563.97	479.18	417.28
$\Lambda_o\eta_o$	370.29	360.90	348.20	304.19	274.09	270.64	265.15
$X_1 = 0.5676$							
Λ_o	146.83	159.49	176.87	179.78	185.17	210.05	228.26
K_A	1241.79	1100.14	922.85	787.14	666.54	551.98	474.89
$\Lambda_o\eta_o$	333.45	315.79	298.73	289.99	247.94	248.69	241.50

TABLE-2

VALUE OF Λ_o, K_A, $\Lambda_o\eta_o$ OBTAINED BY SHEDLOVSKY TECHNIQUE FOR GLYCINE *BIS*-1-AMIDINO-O-METHYLUREA COBALT(III) BROMIDE IN METHANOL AND WATER MIXED SOLUTION AT DIFFERENT TEMPERATURES

	5 ºC	10 ºC	15 ºC	20 ºC	25 ºC	30 ºC	35 ºC
$X_1 = 0.0000$							
Λ_o	230.58	253.68	268.53	277.85	291.37	313.75	330.30
K_A	778.31	645.57	536.84	433.09	370.51	303.16	253.80
$\Lambda_o\eta_o$	350.48	330.55	304.51	278.41	259.61	250.37	237.82
$X_1 = 0.0588$							
Λ_o	200.64	215.29	224.41	241.55	249.41	260.45	280.92
K_A	863.05	722.43	607.31	500.20	401.49	338.35	282.17
$\Lambda_o\eta_o$	358.74	348.12	324.50	302.66	273.85	255.76	245.81
$X_1 = 0.1942$							
Λ_o	163.62	173.34	178.37	193.04	205.90	218.56	238.30
K_A	945.51	805.25	670.91	566.50	465.87	389.85	322.75
$\Lambda_o\eta_o$	392.85	377.88	349.43	324.31	297.32	274.73	264.75
$X_1 = 0.3600$							
Λ_o	139.14	155.79	172.84	182.59	194.14	210.62	233.22
K_A	1078.17	918.83	798.92	647.55	512.55	440.79	372.17
$\Lambda_o\eta_o$	404.76	388.07	358.30	328.30	305.19	287.20	279.40
$X_1 = 0.5676$							
Λ_o	155.10	167. 55	186.60	198.85	204.97	227.36	239.05
K_A	1166.44	1001.10	861.20	708.10	593.03	480.18	431.84
$\Lambda_o\eta_o$	352.23	331.75	315.17	300.86	274.45	269.19	252.91

TABLE-3

VALUE OF Λ_o, K_A, $\Lambda_o\eta_o$ OBTAINED BY SHEDLOVSKY TECHNIQUE FOR GLYCINE *BIS*-1-AMIDINO-O-METHYLUREA COBALT(III) IODIDE IN METHANOL AND WATER MIXED SOLUTION AT DIFFERENT TEMPERATURES

	5 ºC	10 ºC	15 ºC	20 ºC	25 ºC	30 ºC	35 ºC
			X_1 = 0.0000				
Λ_o	244.19	263.82	276.58	288.37	302.16	318.14	335.02
K_A	701.88	572.99	465.95	390.70	346.70	290.51	232.18
$\Lambda_o\eta_o$	371.17	343.76	313.64	288.95	269.22	253.87	241.21
			X_1 = 0.0588				
Λ_o	214.47	224.23	229.61	245.55	258.86	270.31	286.73
K_A	837.30	697.94	579.14	458.23	392.67	328.13	266.05
$\Lambda_o\eta_o$	383.47	362.58	332.02	307.67	279.84	265.44	250.89
			X_1 = 0.1942				
Λ_o	169.34	178.17	179.65	195.61	210.85	230.05	242.24
K_A	924.44	778.23	651.85	535.67	449.13	374.24	309.97
$\Lambda_o\eta_o$	406.59	388.41	351.93	328.62	304.47	289.17	269.13
			X_1 = 0.3600				
Λ_o	143.54	157.97	175.75	189.32	200.62	220.34	237.24
K_A	1022.85	864.18	731.35	605.98	488.91	421.38	357.59
$\Lambda_o\eta_o$	417.56	393.50	364.33	340.40	315.37	300.46	384.21
			X_1 = 0.5676				
Λ_o	170.18	168.96	188.93	201.10	211.56	231.28	241.16
K_A	1099.49	965.16	840.99	678.13	579.41	473.28	425.98
$\Lambda_o\eta_o$	386.48	334.54	319.10	304.26	283.28	273.84	255.15

TABLE-4

THERMODYNAMIC PARAMETERS ΔG^o (kJ mol^{-1}), ΔH^o (kJ mol^{-1}) AND ΔG^o (kK^{-1} J mol^{-1}) OF GLYCINE 1-AMIDINO-O-METHYLUREA COBALT(III) CHLORIDE IN METHANOL + WATER MIXTURES USING SHEDLOVSKY METHOD

	278.15K	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K
			X_1 = 0.0000				
ΔG^o	-15.50	-15.34	-15.12	-14.93	-14.79	-14.51	-14.34
ΔH^o	–	-31.33	–	–	–	–	–
$10^3\ \Delta S^o$	-56.91	-56.47	-56.26	-55.94	-55.48	-55.48	-55.14
			X_1 = 0.0588				
ΔG^o	-15.50	-15.67	-15.47	-15.27	-15.07	-14.92	-14.69
ΔH^o	–	-30.64	–	–	–	–	–
$10^3\ \Delta S^o$	-53.50	-52.87	-52.72	-52.43	-52.22	-51.86	-51.76
			X_1 = 0.1942				
ΔG^o	-15.98	-15.89	-15.72	-15.60	-15.41	-15.27	-15.05
ΔH^o	–	-29.79	–	–	–	–	–
$10^3\ \Delta S^o$	-49.65	-49.09	-48.83	-48.41	-48.23	-47.90	-47.83
			X_1 = 0.3600				
ΔG^o	-16.24	-16.16	-16.11	-15.94	-15.70	-15.56	-15.46
ΔH^o	–	-28.72	–	–	–	–	–
$10^3\ \Delta S^o$	-44.87	-44.36	-43.76	-43.60	-43.67	-43.41	-43.03
			X_1 = 0.5676				
ΔG^o	-16.46	-16.48	-16.38	-16.28	-16.10	-15.90	-15.81
ΔH^o	–	-27.35	–	–	–	–	–
$10^3\ \Delta S^o$	-39.15	-38.38	-38.07	-37.76	-37.73	-37.77	-37.45

TABLE-5

THERMODYNAMIC PARAMETERS ΔG^o, ΔH^o and ΔS^o OF GLYCINE 1-AMIDINO-O-METHYLUREA COBALT(III) BROMIDE IN METHANOL + WATER MIXTURES USING SHEDLOVSKY METHOD

	278.15K	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K
$X_1 = 0.0000$							
ΔG^o	-15.39	-15.23	-15.06	-14.82	-14.67	-14.40	-14.16
ΔH^o	–	-28.72	–	–	–	–	–
$10^3\ \Delta S^o$	-47.92	-47.64	-47.47	-47.42	-47.12	-47.24	-47.25
$X_1 = 0.0588$							
ΔG^o	-15.66	-15.51	-15.34	-15.16	-14.84	-14.69	-14.46
ΔH^o	–	-27.85	–	–	–	–	–
$10^3\ \Delta S^o$	-43.83	-43.83	-43.41	-43.29	-43.64	-43.41	-43.45
$X_1 = 0.1942$							
ΔG^o	-15.87	-15.78	-15.61	-15.44	-15.24	-15.03	-15.81
ΔH^o	–	-25.53	–	–	–	–	–
$10^3\ \Delta S^o$	-35.48	-34.58	-43.41	-43.29	-43.51	-34.64	-34.79
$X_1 = 0.3600$							
ΔG^o	-16.14	-16.05	-16.00	-15.77	-15.47	-15.32	-15.16
ΔH^o	–	-23.93	–	–	–	–	–
$10^3\ \Delta S^o$	-28.01	-27.09	-27.52	-27.84	-28.37	-28.40	-28.46
$X_1 = 0.5676$							
ΔG^o	-16.35	-16.26	-26.22	-16.00	-15.81	-15.56	-15.56
ΔH^o	–	-21.88	–	–	–	–	–
$10^3\ \Delta S^o$	-19.88	-19.85	-19.64	-20.06	-20.36	-20.85	-20.44

TABLE-6

THERMODYNAMIC PARAMETERS ΔG^o, ΔH^o and ΔS^o OF GLYCINE 1-AMIDINO-O-METHYLUREA COBALT(III) IODIDE IN METHANOL + WATER MIXTURES USING SHEDLOVSKY METHOD

	278.15K	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K
$X_1 = 0.0000$							
ΔG^o	-15.18	-14.96	-14.73	-14.54	-14.50	-.14.28	-13.98
ΔH^o	–	-26.81	–	–	–	–	–
$10^3\ \Delta S^o$	-41.81	-41.85	-41.92	-41.86	-41.29	-41.33	-41.64
$X_1 = 0.0588$							
ΔG^o	-15.55	-15.40	-15.23	-14.93	-14.79	-14.63	-14.28
ΔH^o	–	-25.53	–	–	–	–	–
$10^3\ \Delta S^o$	-35.89	-35.78	-35.75	-36.16	-36.02	-35.96	-36.51
$X_1 = 0.1942$							
ΔG^o	-15.82	-15.67	-15.50	-15.32	-15.13	-14.92	-14.69
ΔH^o	–	-23.57	–	–	–	–	–
$10^3\ \Delta S^o$	-27.83	-27.90	-28.01	-28.14	-28.31	-28.53	-28.82
$X_1 = 0.3600$							
ΔG^o	-16.03	-15.94	-15.78	-15.60	-15.36	-15.21	-15.50
ΔH^o	–	-22.98	–	–	–	–	–
$10^3\ \Delta S^o$	-24.99	-24.86	-24.99	-25.17	-25.56	-25.63	-25.73
$X_1 = 0.5676$							
ΔG^o	-16.19	-16.16	-16.11	-15.88	-15.76	-15.56	-15.52
ΔH^o	–	-20.89	–	–	–	–	–
$10^3\ \Delta S^o$	-16.90	-16.90	-16.59	-17.09	-17.21	-17.58	-17.43

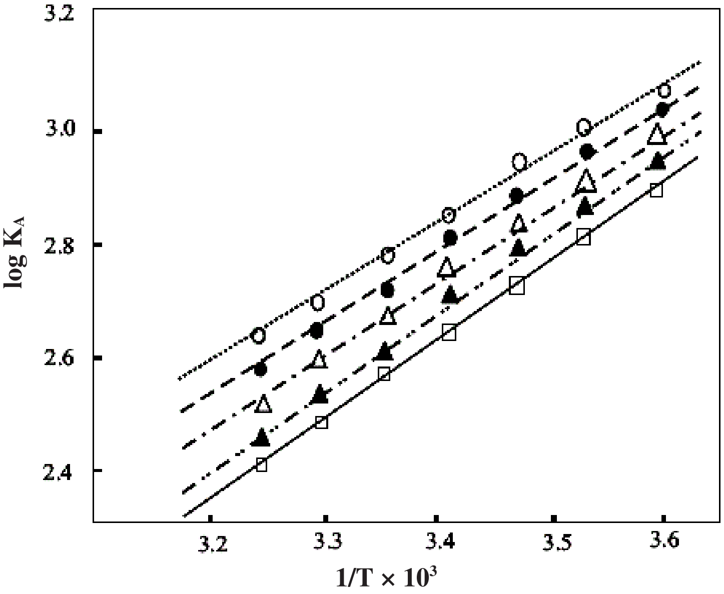

Fig. 1. Plot of log K_A *vs.* $1/T \times 10^3$ for $[Co(gly)(AMUH)_2]Cl_2$
..............$X_{0.5676}$, - - - - - -$X_{0.3600}$, —·—·— $X_{0.1642}$, —··—··—$X_{0.0588}$, ———$X_{0.0000}$

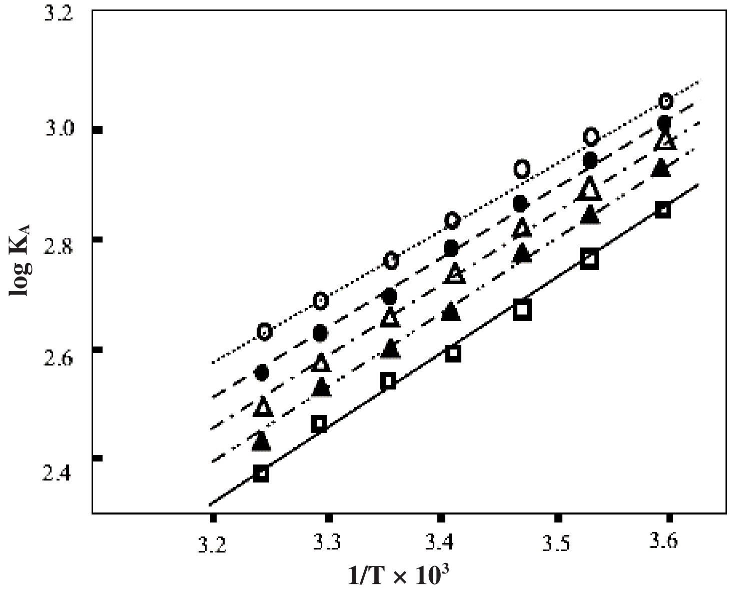

Fig. 2. Plot of log K_A *vs.* $1/T \times 10^3$ for $[Co(gly)(AMUH)_2]Br_2$
..............$X_{0.5676}$, - - - - - -$X_{0.3600}$, —·—·— $X_{0.1642}$, —··—··—$X_{0.0588}$, ———$X_{0.0000}$

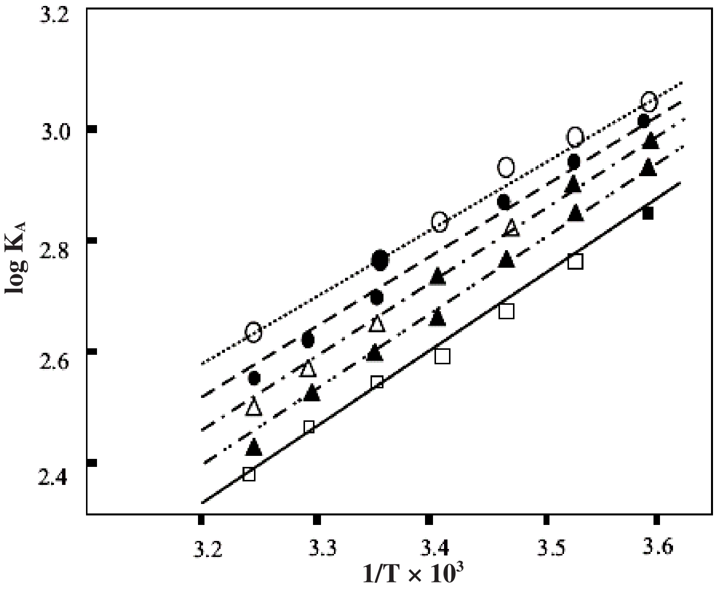

Fig. 3. Plot of log K_A *vs.* 1/T × 10^3 for $[Co(gly)(AMUH)_2]I_2$
..............$X_{0.5676}$, - - - - - -$X_{0.3600}$, — · — · — $X_{0.1642}$, —··—··—·$X_{0.0588}$, ———$X_{0.0000}$

become solvated with the other component of the solvent mixture (*viz.*, methanol). The effect would be more in case of a solution at a higher temperature. As expected, Λ_o values increase with rise in temperature linearly irrespective of the nature of the solvent. The free energy change (ΔG^o) for association is calculated from the relation[19], $\Delta G^o = -RT \ln K_A$. The heat of association (ΔH^o) is obtained from the slope of the plot of log K_A *vs.* 1/T shown in Figs. 1-3. The ΔH^o values obtained are found to increase systematically with the composition of the mixed solvent. The entropy change (ΔS^o) is 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 Tables 4-6. The negative values of ΔH^o indicates that ion association processes are exothermic in nature in all solvents at all temperatures. At a particular temperature ΔG^o becomes more negative with the increase in X_1. This indicates that ion-pair association is favoured with lowering of dielectric constant of the medium. A 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[20].

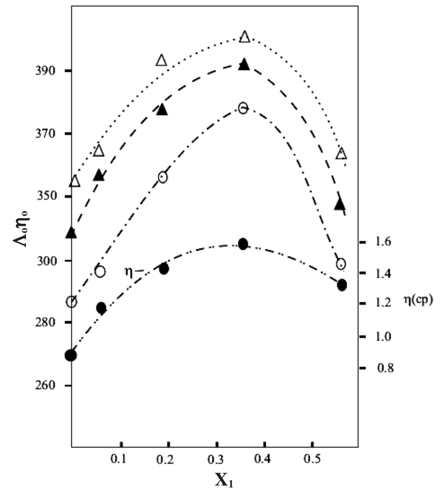

Fig. 4. Walden product $\Lambda_o\eta_o$ and viscosity as function of X_{CH_3OH} the mole fraction of methanol of $[Co(gly)(AMUH)_2]Cl_2$ in methanol + water mixture at; ....10 ºC, - - - - - -15 ºC, —·—·— 20 ºC, η at —··—··—·25 ºC

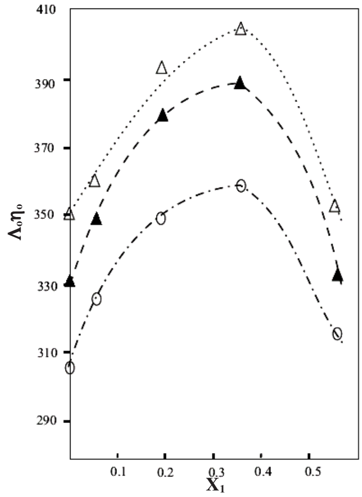

Fig. 5. Walden product $\Lambda_o\eta_o$ and viscosity as function of X_{CH_3OH} the mole fraction of methanol of $[Co(gly)(AMUH)_2]Br_2$ in methanol + water mixture at; ....10 ºC, - - - - - -15 ºC, —·—·— 20 ºC

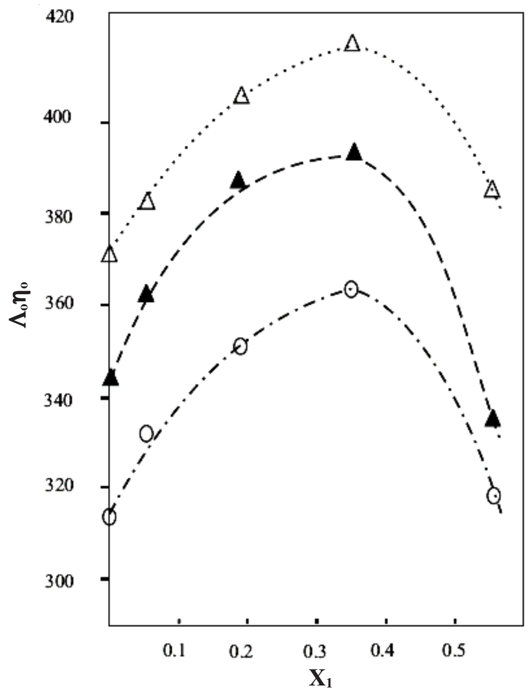

Fig. 6. Walden product $\Lambda_o\eta_o$ and viscosity as function of X_{CH_3OH} the mole fraction of methanol of $[Co(gly)(AMUH)_2]I_2$ in methanol + water mixture at; ....10 ºC, - - - - - -15 ºC, —·—·— 20 ºC

log K_As increase linearly with the increase in temperature. $\Lambda_o\eta_o$ is maximum at $X_1 = 0.36$ in which η is maximum. Ion-association process is exothermic in nature. Ion-solvation is minimum in the mixture whose viscosity is maximum. In methanol rich region ion association process are less energy-consuming and more stabilized than in water-rich region.

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