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Ion pair formation and thermodynamic parameters of N-[(benzoyl-amino) thioxomethyl] histidine cobalt (II) chloride in water + methanol mixtures at different temperatures-A conductance study

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ABSTRACT

The conductivities of N-[(benzoyl-amino) thioxomethyl]-histidine cobalt (II) chloride complex were measured in various methanol (M) + water (W) mixtures, i.e., $X_{methanol}$ = 0.0000-1.0000 at varying temperatures from 283.15 to 313.15K. The limiting molar conductance (Λ_0) and the association constant (K_A) were estimated 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 ($\Lambda_0\eta_0$). Ion association constants calculated for the given complex salt in methanol-water mixtures increased, depending on the percentage of methanol. This was equivalent to the ion-association constants increasing with a decrease in the dielectric constant of the mixtures. Thermodynamic parameters (Gibb's free energy, enthalpy, entropy and Arrhenius activation energy) were estimated from the temperature dependence of the ion- association constant. The results have been discussed in terms of ion-ion, ion-solvent and solvent-solvent interactions.

Key words: Electrical conductance, Shedlovsky technique, N-[(benzoyl-amino) thioxomethyl]-histidine cobalt (II) chloride, thermodynamic parameters, Walden product, Arrhenius activation energy.
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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 [1,2]. It should be emphasized that the formation of an ion pair is due only to the so-called 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 [3,4]. It is clear therefore that any charged molecule in solution, under certain conditions, can form an ion-pair, with an ion of oppositely charge. In any solution of an electrolyte there is always the possibility that the ions of the electrolyte might not be fully dissociated in solution. Ion pairing results when the electrostatic interaction between two oppositely charged ions become sufficiently large for the two ions to move around as one entity, the ion-pair [5]. The extent of association into ion-pairs depends on many factors, with the most important being the nature, charges and sizes of the ions, the characteristics of the solvent and the temperature. Walden noted that the product of the equivalent conductance at infinite dilution and the viscosity of the solvent were approximately constant and independent of the nature of the solvent. This conclusion is known as Walden's Rule [6] and may be expressed as:

$\Lambda_o\eta_o \approx$ constant for a given electrolyte in solvent

Since Λ_o is the sum of the conductances of the constituent ions it follows that $\Lambda_o\eta_o$ should be approximately constant for a given ion in all solvents. If Stoke's law were obeyed, the values of $\Lambda_o\eta_o$ would be constant only if the

effective radius of the ions were same in different media. Since there are reasons for believing that most ions are solvated in solution, the dimension of the moving unit will undoubtedly vary to some extent and exact constancy of $\Lambda_o\eta_o$ not be expected. For small ions the value of $\Lambda_o\eta_o$ will depend to some extent on the fundamental properties of the solvent as well as on the effective size of the ion and for large ions such as tetraethyl ammonium and picrate ions, the $\Lambda_o\eta_o$ are much more nearly constant than in the case of other ions. Bag, Rajen and Rajmuhon [7] had determined the degree of ionic association in methanol + water mixed solvent interactions of conductance of α-alanine bis (biguanide) cobalt (III) bromide at different temperatures. The temperature dependence of ion-association constants is important because the standard enthalpies of ion association provide the interaction between the ions than the association constant at certain fixed temperature. The conductivity values were analyzed using Shedlovsky technique [8]. The Λ_0 value increased with increase in temperature in methanol + water mixtures. This is due to the fact that the increased thermal energy results in bond breaking and variation in vibrational, rotational and translational energy of the molecules leads to higher frequency and higher mobilities of ions. The observed association constants (K_A) are found to increase with increase in mole fraction of methanol which indicates an increased association as methanol is added to water, and dielectric constant is particularly property of the solvent that influences the association [9]. The lower the dielectric constant of the medium, the higher is the electrostatic attraction between the ions and hence the greater is the value of association constant (K_A). The values of ΔS^0 are negative in all solvents. This indicates that the association process is exothermic in nature and the process will occur spontaneously at all temperatures [10]. The variation of Walden product with the mole fraction of methanol at different temperature, it decreases with increase in mole fraction of methanol. This indicates an increase in hydrophobic solvation. As the methanol content increases, progressive disruption of water structure occurs and ions become solvated with the other components of the solvent mixture (viz. methanol). Further, this effect will be more in case of a solution at higher temperature [11].

The present work aims at determining the molar conductance values of the solutions of the title electrolyte in methanol + water mixtures at 283.15-313.15 K to examine the validity of Shedlovsky technique. The K_A and Walden products for Co^{II} complex have been evaluated in these solvents at experimental temperatures. The limiting molar conductance (Λ_o) and association constant (K_A) for different mole fractions, i.e., 0.0000, 0.0588, 0.1233, 0.1942, 0.2727, 0.3600, 0.4576, 0.5676, 0.6923, 0.8351 and 1.0000 have been calculated using Shedlovsky method. These computed values have been discussed qualitatively the nature of ion-ion, ion-solvent and solvent-solvent interactions of the Co^{II} complex in M-W mixed solvents. Temperature dependence of the K_A has also been studied to get the thermodynamic parameters, viz. ΔG^0, ΔS^0, ΔH^0 and E^a as a function of the solvent composition.

MATERIALS AND METHODS

N-[(benzoyl-amino) thioxomethyl] histidine copper (II) chloride was prepared by following reported procedure [12]. The purity of the sample was determined by conventional chemical analysis and spectral measurements. The values are in good agreement with the literature values. Methanol was treated by the standard procedure. 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 of the electrolyte in solvent mixtures. All the viscosity, dielectric constant and density values were interpolated from literature values [13]. For preparing aqueous solution of methanol X_{MeOH} = 0.0000-1.0000, water of specific conductance of order $2x10^{-6}$ Scm^{-1}were used. The electric conductivities were measured by EUTECT- PC-700 Conductivity Bench top meter with Epoxy 2 cell (K=1.0) digital conductivity bridge (accuracy ± 0.1%) with a dip type immersion conductivity cell were used. The observed conductivities were connected for the conductivity solvent. The experiment was performed between 10-40 ℃. The temperature was controlled was made by using refrigerated Bath and Circulator - Cole-Palmer, Polystat R6L with the help of thermometer.

The limiting molar conductances (Λ_0) and ion association constants (K_A) have been computed using Shedlovsky method [8]. Shedlovsky method involves the linear extrapolation using equation (1):

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

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 [14]

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

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

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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)

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

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

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. 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 [15]

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

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,

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

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 Onsager plot of Λ versus $c^{1/2}$, λ^o is obtained from [16] the literature at 25°C and at other temperatures it was obtained by using the following equation:

$$\lambda_t^0 = \lambda_{25}^0 [1 + \alpha'(t - 25)] \qquad (4)$$

α' is constant. Using these values of Λ_o, $\lambda^o.$, 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 [17] . The procedure was repeated using these new values of Λ_0 and K_A. All calculations were carried out by IBM-PC-AT/386.

RESULTS AND DISCUSSION

From the experimental data, the values of Λ_0 increased invariable with increase in temperature in all solvents irrespective of X_{MeOH}, indicating less solvation or higher mobility of ions (Fig.1). 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 [18]. The variation of $\Lambda_0\eta_0$ and η with mole fraction of methanol is shown in Fig.1. The viscosity of M + W mixtures increases upto $X_{MeOH} = 0.3600$ and thereafter it decreases. Values of Λ_0 of salts decrease upto this mole fraction and then increase in methanol rich region at all temperatures as expected from Walden rule (Table 1). The maximum in η versus mole fraction indicates maximum interaction between water and methanol in such solvent mixtures. $\Lambda_0\eta_0$ increases upto mole fraction of 0.3600 in methanol and then decreases. If change in solvation is reflected by the variation in $\Lambda_0\eta_0$ [16], the increase of the Walden product indicates the weak solvation of the ions. The decrease of the product indicates an 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 [15]. Then effective radius(r) of ion or solute can be calculated as

$$\Lambda_0\eta_0 = 1/6\ \pi r T \qquad (5)$$

It has been possible to derive the values of r for the cation of Co^{II} complexes. From the calculated values of r decrease with increase in methanol content upto $x_{MeOH} = 0.36$ and thereafter increase in methanol rich regions. The smaller $\Lambda_0\eta_0$ values in methanol rich region may be due to the large effective radius of the cation, whereas the maximum values of $x_{MeOH} = 0.36$ correspond to minimum values of r. The Walden products in these are solvents increase and then decrease after passing through a maximum [19,20]. It is thus apparent that its variation with the solvent composition is due to an electrochemical equilibrium between the cations with the solvent molecules on one hand and the selective solvation of ions of the mixed solvents and temperature of the solution. Since the conductance

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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.,

$$\Lambda_o = A.e^{-E^a/RT} \text{ or } ln\ \Lambda_o = ln\ A - E^a/RT \tag{6}$$

Where A is the frequency factor, R the ideal gas constant and E^a is Arrhenius activation energy of transport processes. E^a values can be computed from the slope of the plot of log Λ_o versus $1/T$ are shown in Table 2.

Table-1: The values of limiting molar conductance (Λ_0), association constant (K_A), Walden product ($\Lambda_0\eta_0$) and effective radius r (Å) obtained by Shedlovsky technique for N-[(benzoyl-amino)thioxomethyl]histidine cobalt (II) chloride have been measured in various methanol+ water mixtures at 283.15-313.15K

	283.15K				288.15K			
$x_{methanol}$	Λ_0 Scm^2mol^{-1}	K_A dm^3mol^{-1}	$\Lambda_0\eta_0$	r	Λ_0 Scm^2mol^{-1}	K_A dm^3mol^{-1}	$\Lambda_0\eta_0$	r
0.0000	280.10	633.93	364.97	5.131	303.19	303.19	345.03	5.333
0.0588	250.29	662.26	407.72	4.593	265.01	265.01	383.20	4.802
0.1233	231.83	673.00	455.08	4.115	244.07	244.07	430.05	4.279
0.1942	213.34	680.17	465.08	4.026	223.14	223.14	437.13	4.209
0.2727	201.13	703.35	470.64	3.979	214.36	214.36	440.15	4.181
0.3600	188.91	727.62	483.04	3.877	205.59	205.59	446.81	4.118
0.4576	196.86	772.72	421.28	4.445	211.46	211.46	412.14	4.465
0.5676	204.80	809.14	405.50	4.618	217.33	217.33	367.07	5.013
0.6923	216.58	842.92	319.67	5.858	228.62	228.62	298.81	6.158
0.8351	228.82	911.03	242.78	7.713	240.68	240.68	232.26	7.923
1.0000	249.96	951.52	171.47	9.921	261.26	261.26	166.68	10.039

	293.15K				298.15K			
$x_{methanol}$	Λ_0 Scm^2mol^{-1}	K_A dm^3mol^{-1}	$\Lambda_0\eta_0$	r	Λ_0 Scm^2mol^{-1}	K_A dm^3mol^{-1}	$\Lambda_0\eta_0$	r
0.0000	318.04	463.72	318.68	5.676	327.34	383.42	291.66	6.097
0.0588	273.77	491.52	343.03	5.273	291.28	411.65	319.83	5.560
0.1233	251.48	516.32	381.24	4.744	267.09	426.53	351.49	5.059
0.1942	233.20	528.67	391.78	4.617	242.88	439.32	354.06	5.023
0.2727	225.39	542.75	398.94	4.533	237.66	463.55	358.26	4.963
0.3600	222.68	588.01	400.38	4.518	232.46	489.01	365.43	4.866
0.4576	229.51	615.01	385.81	4.688	240.56	517.17	351.46	5.060
0.5676	236.41	644.20	357.69	4.799	248.71	544.05	330.02	5.388
0.6923	247.84	666.59	295.43	1.223	260.82	582.42	281.95	6.307
0.8351	259.21	721.40	226.55	7.984	271.48	628.29	218.54	8.137
1.0000	280.38	777.45	165.70	10.149	293.53	699.35	162.32	10.956

	303.15K				308.15K			
$x_{methanol}$	Λ_0 Scm^2mol^{-1}	K_A dm^3mol^{-1}	$\Lambda_0\eta_0$	r	Λ_0 Scm^2mol^{-1}	K_A dm^3mol^{-1}	$\Lambda_0\eta_0$	r
0.0000	340.99	343.07	272.11	6.427	363.16	284.92	261.48	6.580
0.0588	299.14	337.98	293.76	5.954	310.15	291.57	271.38	6.340
0.1233	277.43	355.06	317.66	5.506	289.25	305.84	291.85	5.895
0.1942	255.73	371.29	321.45	5.441	268.36	319.18	298.15	5.771
0.2727	249.87	384.54	330.08	5.298	264.41	335.84	305.92	5.624
0.3600	244.02	397.70	334.01	5.236	260.49	352.61	312.07	5.514
0.4576	249.40	430.79	316.49	5.526	268.67	363.71	310.05	5.549
0.5676	254.82	463.61	301.71	5.797	277.22	389.31	293.30	5.866
0.6923	265.68	495.69	256.12	6.829	289.20	418.13	252.18	6.823
0.8351	277.13	539.20	201.20	8.693	300.01	456.28	200.56	8.579
0.0000	379.88	253.71	248.44	6.815	321.56	536.49	151.02	11.393

	313.15K			
$x_{methanol}$	Λ_0 Scm^2mol^{-1}	K_A dm^3mol^{-1}	$\Lambda_0\eta_0$	r
0.0000	379.88	253.71	248.44	6.815
0.0588	330.59	250.73	262.16	6.458
0.1233	309.23	258.65	278.93	6.070
0.1942	288.08	273.43	284.91	5.942
0.2727	285.71	298.35	287.57	5.887
0.3600	283.06	307.92	295.80	5.724
0.4576	285.95	333.40	285.09	5.939
0.5676	288.87	357.41	273.27	6.196
0.6923	299.38	385.73	234.71	7.214
0.8351	312.11	418.00	193.51	8.749
1.0000	331.68	460.03	149.59	11.318

Table-2: Thermodynamic parameters ΔG^0(kJmole^{-1}), ΔH^0(kJmol^{-1}), ΔS^0(kJK^{-1}mol^{-1}), E^a (kJmol^{-1}) and 10^{-3} A of Shedlovsky techniques for N-[(benzoyl-amino)thioxomethyl]histidine cobalt (II) chloride have been measured in various methanol+ water mixtures at different temperatures

$X_{methanol}$	283.15K					288.15K		293.15K	
	ΔG^0	ΔH^0	$10^3 \Delta S^0$	E^a	10^{-1}A	ΔG^0	$10^3 \Delta S^0$	ΔG^0	$10^3 \Delta S^0$
0.0000	-14.07	-34.02	-35.14	8.68	5.35	-13.91	-34.82	-13.81	-34.82
0.0588	-14.11	-27.74	-34.01	8.93	5.56	-13.96	-33.77	-13.84	-33.77
0.1942	-14.35	-22.84	-29.72	9.40	5.94	-14.35	-29.61	-14.16	-29.47
0.3600	-14.81	-21.23	-26.31	9.83	6.54	-14.81	-26.16	-14.64	-26.87
0.5676	-15.43	-20.12	-23.68	8.71	5.84	-15.25	-23.47	-15.06	-23.41
0.8351	-13.81	-19.21	-19.07	8.16	5.45	-13.64	-18.92	-13.46	-18.77
1.0000	-12.62	-17.69	-17.90	7.87	5.21	-12.23	-17.75	-12.23	-17.63

$X_{methanol}$	298.15K		303.15K		308.15K		313.15K	
	ΔG^0	$10^3 \Delta S^0$	ΔG^0	$10^3 \Delta S^0$	ΔG^0	$10^3 \Delta S^0$	ΔG^0	$10^3 \Delta S^0$
0.0000	-13.63	-34.84	-13.46	-34.83	-13.27	-34.88	-12.94	-35.38
0.0588	-13.86	-33.62	-13.49	-33.57	-13.32	-33.56	-13.06	-33.57
0.1942	-14.94	-29.32	-13.96	-29.54	-13.67	-29.31	-13.45	-29.34
0.3600	-14.42	-26.27	-14.25	-26.59	-14.07	-26.45	-13.85	-26.36
0.5676	-14.84	-23.25	-14.62	-23.27	-14.43	-23.23	-14.23	-23.17
0.8351	-13.32	-18.59	-13.14	-18.41	-13.03	-18.25	-12.87	-18.08
1.0000	-12.07	-17.47	-11.91	-17.32	-11.76	-17.08	-11.62	-16.87

Table 2, shows that the values of E^a increases with increase in X_1 upto about X_1=0.3600 and thereafter decreases rapidly. It follows that in water rich region upto X_1=0.36, the chosen complex ion requires higher activation energy for transport processes as 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 mobilities of the ions in the solutions and hence lower Λ_0 values. Beyond X_1=0.36, as the activation energy decreases the Λ_0 values increases with X_1 (Fig.2). The experimentally determined of K_As (table 1) of the complex are found to increase with increase in x_1 which indicate an increased association as methanol is added to water. Large values of K_A and exothermic ion pair formation indicates the presence of specific short range interaction between ions which is again indicated by positive value of enthalpy change (Table 2). As expected that the values of ΔG^0 become more negative at higher percentage of methanol which indicate that ion pair association are favored with lowering dielectric constant of the medium.
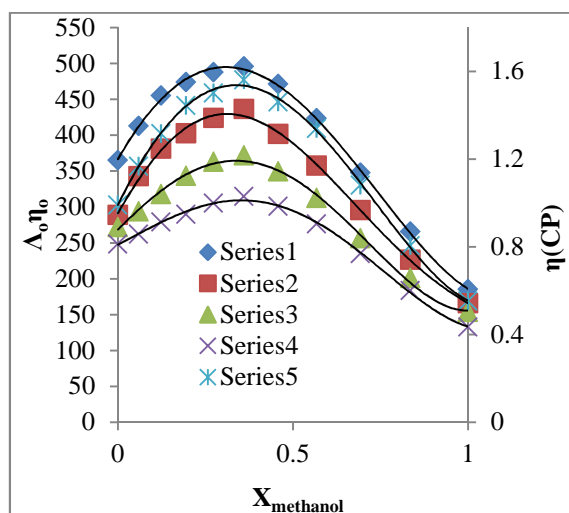

Fig.1. The value of Walden product ($\Lambda_o\eta_o$) and viscosity (η) for Co^{II} as a function of $X_{methanol}$ in methanol + water solvents.(Series1→283.15K, series2→293.15K, series3→288.15, series4→303.15K, series4→313.15K, series5→η(at 25^0 C)
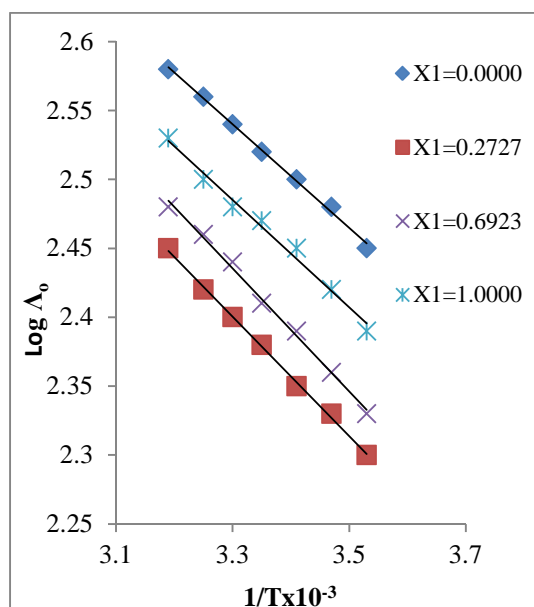

Fig.2. Plot of log Λ_o vs 1/T for Co^{II} complex in different mole fractions at temperatures 283.15-313.15K.

The free energy change (ΔG^0) for association processes is evaluated from the relation [14] $\Delta G^0 = -RT\ ln\ K_A$. The heat of association (ΔH^0) is obtained from the slope of the plot of log K_A versus $1/T$. ΔH^0 values obtained are found to

increase with the composition of the mixed solvents (Fig.3). The entropy of change is calculated from Gibbs-Helmholtz equation, $\Delta G^0 = \Delta H^0 - T\Delta S^0$. The values of these thermodynamic in nature in all solvent mixtures at all temperature are given in Table 2. At all temperatures, ΔG^0 values become more negative with increase in X_1 indicating that the ion pair formation is favored with lowering of permittivity of the medium.

CONCLUSION

The experimentally determined of K_As of the complex are found to increase with increase in X_1 which indicate an increased association as methanol is added to water. Large values of K_A and exothermic ion pair formation indicates the presence of specific short range interaction between ions which is again indicated by positive value of enthalpy change. As expected that the values of ΔG^0 become more negative at higher percentage of methanol which indicate that ion-pair association are favored with lowering dielectric constant of the medium. The values of E^a increased with increased in X_1 upto about $X_1=0.3600$ and thereafter decreased rapidly. It follows that in water rich region upto $X_1=0.36$, the chosen complex ion requires higher activation energy for transport processes as methanol content in the mixed solvent increases but reverse is the case beyond $X_1=0.3600$.

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