Asian Journal of Chemistry; Vol. 28, No. 4 (2016), 910-916

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2016.19653

Ion Association and Solvation Behaviour of Metal(II) Chlorides in Binary Mixtures of Methanol + Water: A Conductance Method

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Received: 6 October 2015; *Accepted*: 14 December 2015; *Published online*: 30 December 2015; AJC-17715

Molar conductances of N-[benzoylamino)thioxomethyl]histidine Ni(II) chloride and N-[benzoylamino)thioxomethyl]histidine Mn(II) chloride have been studied in mole fraction (0.00 to 1.00) of methanol in water at varying temperature from 283.15-313.15 K. The limiting molar conductances ($\Lambda°$) and association constants (K_A) for ion pair formation in the mixed solvent systems have been evaluated using Shedlovsky technique. Gibbs energy ($\Delta G°$), enthalpy ($\Delta H°$), entropy ($\Delta S°$) and Arrhenius activation energy (E^a) for ion-association reaction were derived from the temperature dependence of ion association constant. Based on the composition dependence of Walden product ($\Lambda_o\eta_o$) and different thermodynamic properties ($\Delta G°$, $\Delta H°$, $\Delta S°$) and Arrhenius activation energy (E^a) of transport processes have been determined. The influence of the solvent composition on ion-association and solvation behaviour of ions was discussed in terms of ion-ion, ion-solvent and solvent-solvent interactions.

Keywords: Conductance, Association constant, Walden's product, Transition metal(II) chlorides.

INTRODUCTION

Behaviour of electrolytic solutions can be obtained by studying their thermodynamic and transport properties. The molecular interactions within the electrolytic solution can be studied in a better way by varying the properties of the solvents such as dielectric constant or viscosity which can be attained by using mixed solvent systems. The influence of the solvent mixtures on the ionic association of the electrolytes is due to the mode of solvation of the ions [1-5]. Solvent properties such as viscosity and the relative permittivity have been taken into consideration as these properties help in determining the extent of ion association and the solvent-solvent interactions. Conductance study is a very important tool in obtaining the information regarding the solvation and association behaviour of ions in solutions [6]. Conductivities of electrolytes in various pure and mixed solvent systems are of much interest to chemists. The electrical conductivity of electrolytes in mixed solvent solutions mainly depends upon the concentration of the electrolyte and also upon the viscosity of the solvent [7,8]. Here, we have investigated the conductance behaviour of two inorganic salts(transition metal salt) with commom anion *i.e.*, N-[benzoylamino)thioxomethyl]histidine Ni(II) chloride and N-[benzoylamino)thioxomethyl]histidine Mn(II) chloride in different mole fraction (0.0000, 0.0588, 0.1233, 0.1942, 0.2727, 0.3600, 0.4576, 0.5676, 0.6923, 0.8351 and 1.0000) of methanol in water at different temperatures ranging from 283.15, 288.15, 293.15, 298.15, 303.15, 308.15 and 313.15 K. Experimental results were treated by Shedlovsky equation to obtain the limiting molar conductance (Λ_o) and the association constant (K_A) which served further to calculate Walden product ($\Lambda_o\eta_o$) and other thermodynamic quantities of the ion association reaction ($\Delta G°$, $\Delta H°$, $\Delta S°$). The calculation was further extended to derive Arrhenius activation energy (E^a) for ion-association reaction and described accordingly.

EXPERIMENTAL

Double distilled water (specific conductivity $\approx 10^{-6}$ S cm^{-1}) was used throughout the work. KCl (Merck, India) was dried for 6 h at 393.15 K before use. Methanol (Merck, India, absolutely, 99.8 % pure) was used without further purification. The solutions of different concentrations (1×10^{-4} M) were carefully prepared by dissolving requisite amount of the salt in conductivity water. The transition metal chlorides selected for the present work, *i.e.*, N-[benzoylamino)thioxomethyl]-serine Ni(II) chloride and N-[benzoylamino)thioxomethyl]-serine Mn(II) chloride were synthesized according to the reported procedure [9]. All the viscosity, dielectric constant and density values were interpolated from literature values [10]. The electric conductivities were measured by Orion Star A112 Conductivity Benchtop meter with Epoxy 2 cell (K = 1.0) digital conductivity bridges with a dip type immersion

conductivity cell were used. Conductivity measurements were carried out over the temperature range of 283.15-313.15 K. The temperature control in the ranges of 283.15-313.15 K was made by using refrigerated water bath and Circulator-Cole-Palmer, Polystat R6L and graduated thermometer. The measurements of weights were done by using a METTER Balance, model TB-214 (max = 210 g; d = 0.1 mg). All calculations were done on IBM-PC-AT/386 using a basic programmed as suggested by Shedlovsky.

RESULTS AND DISCUSSION

The specific conductance (κ, mS cm^{-1}) of the electrolytes solutions under investigation with a molar concentrations, in different solvents were measured. The molar conductances (Λ) for all studied solution system have been calculated using following equation [11]

$$\Lambda = 1000\,\kappa/c$$

where c is the molar concentration and κ is the measured specific conductance of the studied solutions. The experimental values of conductance measurements of Ni^{2+} and Mn^{2+} complexes in water + methanol mixtures were analyzed by using Shedlovsky extrapolation technique [12].

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

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

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

$$Z = \left(\frac{\alpha\Lambda_o + \beta}{\Lambda_o^{s/z}}\right)(C\Lambda)^{1/2};\ \alpha = \frac{17.147\times 105W}{(DT)^{3/2}}$$

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

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:

$$\tau = \Lambda S(z)/L_o$$

$f_{\pm}$ is the activity coefficient of the free ions and was calculated using equation:

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

where,

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

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 [13]. 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 5 Å and d (Å) is given by Akhadov [14]

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

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,

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

where 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 *vs.* $c^{1/2}$, λ^o is obtained from the literature at 25 °C and at other temperatures it was obtained by using the following equation [15]

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

where 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 eqn. 2 for the above chosen complex salts. From the linear plot of 1/ΛS (Z) *vs.* C $\Lambda f_{\pm}^2$ S(Z); Λ_o and K_A was evaluated from the intercept $1/\Lambda_o$ and the slope K_A/Λ_o^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.

The results showed that the limiting molar conductances (Λ_0) increase as the temperature increases but decrease as the mass fraction of methanol in the solvent mixtures increases up to 50 % of methanol. This trend in limiting molar conductances can be well described by the viscosity behaviour of the solvent media. The viscosity of methanol-water mixtures passes through a maximum at about 50 % of methanol. It is interesting to note that the Λ_0 values of salts decrease up to this mole fraction and then increase in methanol rich region at all temperatures. The limiting molar conductances (Λ_0) follow the order: $Ni^{2+} > Mn^{2+}$ complexes suggesting that solvation increases the ionic sizes of cations in such away that the sizes of the solvated cations follows the crystallographic radii of the transition metal ions in aqueous methanol solutions. The values of K_A follows the order: $Ni^{2+} < Mn^{2+}$ complexes for all the solvent composition and experimental temperature, *i.e.*, with increasing methanol content the association equilibrium shifts to the right of the above order as a result of decrease in mixture permittivity.

Walden product ($\Lambda_0\eta_0$) for the transition metal(II) chlorides is given in Tables 1 and 2. The variations of Walden products with concentration are common and they can be attributed to change in ion-solvation and ion-solvent interaction. The value of $\Lambda_0\eta_0$ would be constant only if the effective radius of the ions were the same in different media. The increase of Walden product indicates the weak solvation of ions which attains a maximum value at 50 % of methanol and decrease of Walden product indicates an increase of the hydrophobic solvation with increasing concentration of

TABLE-1
VALUES OF LIMITING MOLAR CONDUCTANCE (Λ_o), ASSOCIATION CONSTANT (K_A), WALDEN PRODUCT ($\Lambda_o\eta_o$) AND EFFECTIVE RADIUS r (Å) FOR N-[(BENZOYLAMINO)THIOXOMETHYL]HISTIDINE NICKEL(II) CHLORIDE IN METHANOL + WATER MIXTURES AT 283.15-313.15 K

$X_{Methanol}$	Λ_o (S cm^2 mol^{-1})	K_A (dm^3 mol^{-1})	$\Lambda_o\eta_o$	r	Λ_o (S cm^2 mol^{-1})	K_A (dm^3 mol^{-1})	$\Lambda_o\eta_o$	r
	T = 283.15 K				T = 288.15 K			
0.0000	260.33	589.12	339.21	5.53	284.97	507.75	324.30	5.68
0.0588	240.24	628.14	388.47	4.83	252.49	545.63	365.10	5.05
0.1233	223.63	671.55	438.99	4.27	235.08	576.41	414.21	4.45
0.1942	212.29	704.79	462.79	4.05	222.96	609.04	436.78	4.22
0.2727	203.28	739.11	475.68	3.94	213.54	638.55	439.47	4.19
0.3600	191.73	771.45	477.60	3.93	202.16	670.62	459.51	4.01
0.4576	197.34	813.75	422.31	4.44	207.78	703.34	404.96	4.55
0.5676	207.98	862.33	411.80	4.55	218.04	738.03	368.27	5.00
0.6923	216.46	899.84	318.20	5.89	228.42	771.45	298.54	6.17
0.8351	231.10	938.66	245.20	7.65	242.81	809.77	234.31	7.86
1.0000	247.95	998.02	171.58	10.93	262.46	851.74	163.51	11.27
	T = 293.15 K				T = 298.15 K			
0.0000	300.52	434.14	301.12	6.01	317.32	377.32	282.73	6.30
0.0588	264.89	467.49	331.91	5.46	279.03	409.01	306.37	5.81
0.1233	246.86	495.05	374.24	4.84	258.78	428.73	340.55	5.23
0.1942	230.03	524.23	386.45	4.69	245.77	451.55	354.89	5.02
0.2727	219.15	551.16	387.90	4.67	236.52	478.39	355.25	5.01
0.3600	216.32	580.64	388.94	4.66	227.09	502.14	356.99	4.99
0.4576	218.73	609.15	367.69	4.92	229.65	526.93	335.52	5.31
0.5676	225.58	637.37	341.30	5.31	240.53	555.51	322.07	5.53
0.6923	236.88	667.66	282.36	6.41	251.41	581.38	271.77	6.55
0.8351	248.41	696.91	217.11	8.34	268.69	607.77	216.30	8.23
1.0000	273.10	735.62	163.04	11.11	287.98	643.24	156.66	11.36
	T = 303.15 K				T = 308.15 K			
0.0000	333.14	329.73	265.85	6.59	350.59	290.62	252.42	6.82
0.0588	292.62	356.37	287.35	6.09	307.16	311.69	268.77	6.41
0.1233	272.18	376.36	311.65	5.62	284.79	331.46	287.35	5.99
0.1942	253.57	397.04	323.30	5.42	270.58	349.43	300.61	5.73
0.2727	245.06	418.68	325.68	5.38	260.66	367.65	301.58	5.71
0.3600	240.65	439.73	328.01	5.34	253.08	388.52	303.19	5.68
0.4576	242.08	462	307.20	5.70	256.04	409.15	295.47	5.83
0.5676	251.96	487.95	298.32	5.87	265.23	429.32	280.61	6.14
0.6923	265.24	512.44	255.69	6.85	276.31	452.64	240.94	7.15
0.8351	281.62	535.76	204.46	8.56	295.03	473.68	198.56	8.68
1.0000	302.74	568.18	154.40	11.44	314.74	498.97	154.22	11.69
	T = 315.15 K							
0.0000	356.22	254.64	232.97	7.28				
0.0588	324.14	273.23	257.04	6.59				
0.1233	298.07	292.73	268.86	6.30				
0.1942	277.77	309.12	274.71	6.17				
0.2727	275.24	328.03	276.07	6.14				
0.3600	266.47	345.76	278.46	6.09				
0.4576	270.89	364.01	270.08	6.28				
0.5676	277.87	383.62	262.87	6.45				
0.6923	288.46	401.84	226.15	7.50				
0.8351	308.75	417.46	191.43	8.86				
1.0000	330.51	441.84	150.71	12.74				

methanol. The variation of Walden product with X_{MeOH} is due to an electrochemical equilibrium between the cations with the solvent molecules on one hand and the selective solvation of ions on the other with the change in composition of the mixed solvents and the temperature of the solution.

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, water-methanol interactions become stronger and in turn producing maximum Walden product. As the methanol content increases, progressive disruption of water structure occurs and the ions become solvated with the other component of the solvent mixture. The effective radius(*r*) of ion or solute can be calculated as

$$\Lambda_0\eta_0 = 1/6\ \pi rT$$

It has been possible to derive the values of r for the cation of Ni^{2+} complexes. The calculated values of r decrease with increase in methanol content upto $X_{MeOH} = 0.36$ and thereafter

TABLE-2
VALUES OF LIMITING MOLAR CONDUCTANCE (Λ_o), ASSOCIATION CONSTANT (K_A), WALDEN PRODUCT ($\Lambda_o\eta_o$) AND EFFECTIVE RADIUS r (Å) FOR N-[(BENZOYLAMINO)THIOXOMETHYL]HISTIDINE MANGANESE(II) CHLORIDE IN METHANOL + WATER MIXTURES AT 283.15-313.15 K

$X_{Methanol}$	Λ_o (S cm^2 mol^{-1})	K_A (dm^3 mol^{-1})	$\Lambda_o\eta_o$	r	Λ_o (S cm^2 mol^{-1})	K_A (dm^3 mol^{-1})	$\Lambda_o\eta_o$	r
	T = 283.15 K				T = 288.15 K			
0.0000	228.82	603.41	298.15	6.29	242.83	519.36	276.34	6.67
0.0588	213.24	634.34	344.81	5.44	227.35	552.22	328.75	5.60
0.1233	192.81	681.22	378.49	4.95	205.26	592.63	361.67	5.09
0.1942	181.34	712.01	395.32	4.74	192.58	621.77	377.26	4.88
0.2727	170.87	742.52	399.84	4.68	184.15	649.29	378.98	4.86
0.3600	162.05	776.62	403.67	4.64	172.38	688.51	391.82	4.70
0.4576	166.35	833.75	355.99	5.27	177.04	731.42	345.05	5.34
0.5676	174.11	871.04	344.74	4.43	185.39	769.44	313.12	5.88
0.6923	186.16	915.46	273.66	6.85	198.42	809.83	259.33	7.10
0.8351	200.54	955.24	212.77	8.81	214.09	842.69	206.60	8.92
1.0000	221.62	1019.15	153.36	12.22	240.32	892.81	149.72	12.30
	T = 293.15 K				T = 298.15 K			
0.0000	258.65	451.76	259.17	6.99	274.67	394.78	244.73	7.27
0.0588	241.45	484.91	302.54	5.98	257.55	421.57	282.79	6.30
0.1233	212.53	513.85	322.20	5.62	231.81	449.08	305.06	5.84
0.1942	198.26	540.45	333.08	5.44	217.06	473.96	313.43	5.68
0.2727	192.67	563.79	341.03	5.31	209.67	495.57	314.92	5.65
0.3600	190.68	604.54	342.84	5.28	201.53	535.38	316.81	5.62
0.4576	187.41	649.67	315.04	5.75	198.76	578.15	290.39	6.13
0.5676	196.80	682.85	297.76	6.08	208.61	605.84	279.33	6.37
0.6923	210.89	718.03	251.38	7.20	223.59	632.71	241.70	7.37
0.8351	227.71	749.05	199.02	9.10	242.71	664.72	195.38	9.11
1.0000	249.23	797.62	148.79	12.35	270.05	705.87	146.91	12.46
	T = 303.15 K				T = 308.15 K			
0.0000	289.93	348.43	231.36	7.57	308.44	309.31	222.08	7.76
0.0588	272.62	374.82	267.71	6.54	287.89	332.42	251.90	6.84
0.1233	240.64	399.73	275.53	6.36	257.31	357.32	259.63	6.64
0.1942	221.94	420.62	282.97	6.19	234.82	373.83	260.89	6.60
0.2727	213.08	441.81	283.18	6.18	225.78	395.72	261.23	6.59
0.3600	209.23	475.47	285.18	6.14	219.08	422.75	262.46	6.56
0.4576	210.12	515.71	266.64	6.57	222.74	457.43	257.04	6.70
0.5676	220.17	540.86	260.68	6.72	232.86	482.19	246.37	6.99
0.6923	236.72	567.18	228.20	7.67	251.43	505.41	219.25	7.86
0.8351	257.16	590.48	186.70	9.38	272.96	527.61	183.70	9.40
1.0000	286.06	624.63	145.89	12.55	296.04	562.15	145.06	12.62
	T = 315.15 K							
0.0000	325.44	275.85	212.84	7.96				
0.0588	295.04	296.71	233.97	7.24				
0.1233	265.75	317.88	239.71	7.07				
0.1942	244.33	336.16	241.64	7.01				
0.2727	242.76	353.28	243.49	6.96				
0.3600	234.39	379.62	244.94	6.92				
0.4576	237.68	411.62	236.97	7.15				
0.5676	243.02	431.81	229.90	7.37				
0.6923	261.84	453.67	205.28	8.27				
0.8351	289.21	473.59	179.31	9.45				
1.0000	317.09	504.15	144.59	12.76				

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. 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.*

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

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 *vs.* 1/T and are shown in Tables 3 and 4.

The negative values of $\Delta G°$ and $\Delta H°$ (Tables 3 and 4) can be explained by considering the participation of specific covalent interaction in the ion-association process. But the binding entropy ($\Delta S°$) between the ions was found to be negative to unfavoured the ion-association process and thus

TABLE-3
THERMODYNAMIC PARAMETERS ΔG° (kJ mol^{-1}), ΔH° (kJ mol^{-1}), ΔS° (kJ K^{-1} mol^{-1}), E^a (kJ mol^{-1}) AND 10^{-3} A FOR N-[(BENZOYLAMINO)THIOXOMETHYL]HISTIDINE NICKEL(II) CHLORIDE IN METHANOL + WATER MIXTURES AT DIFFERENT TEMPERATURES

	283.15 K	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
				X_1 = 0.0000			
ΔG°	-15.02	-14.93	-14.81	-14.71	-14.62	-14.53	-14.43
ΔH°	-24.25						
10^3 ΔS°	-32.60	-32.35	-32.22	-32.00	-31.78	-31.53	-31.37
E^a	7.07						
10^{-3}A	5.46						
				X_1 = 0.0588			
ΔG°	-15.17	-15.10	-14.99	-14.91	-14.81	-14.71	-14.61
ΔH°	-24.04						
10^3 ΔS°	-31.33	-31.02	-30.89	-30.62	-30.44	-30.27	-30.12
E^a	7.21						
10^{-3}A	3.90						
				X_1 = 0.1233			
ΔG°	-15.33	-15.23	-15.13	-15.03	-14.95	-14.87	-14.79
ΔH°	-23.51						
10^3 ΔS0	-28.90	-28.73	-28.60	-28.45	-28.24	-28.03	-27.85
E^a	7.48						
10^{-3}A	3.59						
				X_1 = 0.1942			
ΔG°	-15.44	-15.36	-15.27	-15.16	-15.09	-15.00	-14.93
ΔH°	-23.12						
10^3 ΔS°	-27.12	-26.92	-26.80	-26.71	-26.51	-26.33	-26.15
E^a	7.75						
10^{-3}A	4.28						
				X_1 = 0.2727			
ΔG°	-15.55	-15.48	-15.39	-15.30	-15.22	-15.14	-15.09
ΔH°	-22.89						
10^3 ΔS°	-25.91	-25.73	-25.60	-25.46	-25.31	-25.16	-24.92
E^a	7.99						
10^{-3}A	6.56						
				X_1 = 0.3600			
ΔG°	-15.65	-15.59	-15.51	-15.42	-15.34	-15.28	-15.22
ΔH°	-21.62						
10^3 ΔS°	-21.07	-20.91	-20.83	-20.80	-20.71	-20.58	-20.43
E^a	8.29						
10^{-3}A	7.89						
				X_1 = 0.4576			
ΔG°	-15.78	-15.71	-15.63	-15.54	-15.47	-15.41	-15.36
ΔH°	-20.36						
10^3 ΔS°	-16.18	-16.14	-16.13	-16.17	-16.14	-16.06	-15.98
E^a	8.11						
10^{-3}A	8.53						
				X_1 = 0.5676			
ΔG°	-15.92	-15.82	-15.74	-15.67	-15.61	-15.53	-15.49
ΔH°	-19.09						
10^3 ΔS°	-11.21	-11.33	-11.42	-11.48	-11.50	-11.54	-11.49
E^a	8.03						
10^{-3}A	7.16						
				X_1 = 0.6923			
ΔG°	-16.02	-15.93	-15.85	-15.78	-15.73	-15.67	-15.61
ΔH°	-14.81						
10^3 ΔS°	4.26	3.89	3.56	3.26	3.03	2.79	2.57
E^a	7.89						
10^{-3}A	7.04						
				X_1 = 0.8351			
ΔG°	-16.12	-16.05	-15.96	-15.89	-15.84	-15.78	-15.71
ΔH°	-12.62						
10^3 ΔS°	12.35	11.89	11.39	10.97	10.62	10.27	9.88
E^a	7.39						
10^{-3}A	5.73						
				X_1 = 1.0000			
ΔG°	-16.26	-16.17	-16.09	-16.03	-15.99	-15.92	-15.86
ΔH°	-21.26						
10^3 ΔS°	21.19	20.50	19.89	19.36	18.90	18.36	17.89
E^a	6.91						
10^{-3}A	4.87						

TABLE-4
THERMODYNAMIC PARAMETERS ΔG° (kJ mol^{-1}), ΔH° (kJ mol^{-1}), ΔS° (kJ K^{-1} mol^{-1}), E^a (kJ mol^{-1}) AND 10^{-3} A FOR N-[(BENZOYLAMINO)THIOXOMETHYL]HISTIDINE MANGANESE(II) CHLORIDE IN METHANOL + WATER MIXTURES AT DIFFERENT TEMPERATURES

	283.15 K	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
				X_1 = 0.0000			
ΔG°	-15.08	-14.98	-14.90	-14.82	-14.76	-14.69	-14.63
ΔH°	-26.22						
10^3 ΔS°	-39.36	-39.00	-38.61	-38.23	-37.82	-37.40	-37.00
E^a	8.18						
10^{-3}A	5.15						
				X_1 = 0.0588			
ΔG°	-15.19	-15.13	-15.08	-14.99	-14.94	-14.88	-14.82
ΔH°	-25.84						
10^3 ΔS°	-37.60	-37.17	-36.72	-36.41	-35.96	-35.57	-35.18
E^a	8.43						
10^{-3}A	5.36						
				X_1 = 0.1233			
ΔG°	-15.36	-15.30	-15.22	-15.14	-15.10	-15.06	-15.00
ΔH°	-25.46						
10^3 ΔS°	-35.67	-35.27	-34.94	-34.61	-34.17	-33.74	-33.39
E^a	8.81						
10^{-3}A	5. 57						
				X_1 = 0.1942			
ΔG°	-15.47	-15.41	-15.34	-15.28	-15.23	-15.18	-15.15
ΔH°	-24.84						
10^3 ΔS°	-33.11	-32.72	-32.41	-32.08	-31.70	-31.35	-30.95
E^a	9.10						
10^{-3}A	5.74						
				X_1 = 0.2727			
ΔG°	-15.56	-15.52	-15.44	-15.39	-15.35	-15.33	-15.28
ΔH°	-23.96						
10^3 ΔS°	-29.65	-29.30	-29.06	-28.76	-28.39	-28.02	-27.72
E^a	9.33						
10^{-3}A	6.05						
				X_1 = 0.3600			
ΔG°	-15.67	-15.66	-15.61	-15.58	-15.54	-15.49	-15.47
ΔH°	-23.23						
10^3 ΔS°	-26.70	-26.28	-25.99	-25.67	-25.37	-25.10	-24.79
E^a	9.53						
10^{-3}A	6.54						
				X_1 = 0.4576			
ΔG°	-15.84	-15.80	-15.79	-15.77	-15.74	-15.70	-15.68
ΔH°	-22.57						
10^3 ΔS°	-23.78	-23.49	-23.14	-22.81	-22.52	-22.31	-22.01
E^a	9.20						
10^{-3}A	5.94						
				X_1 = 0.5676			
ΔG°	-15.94	-15.92	-15.91	-15.88	-15.86	-15.83	-15.80
ΔH°	-20.12						
10^3 ΔS°	-14.77	-14.56	-14.36	-14.21	-14.04	-13.92	-13.79
E^a	8.95						
10^{-3}A	5.64						
				X_1 = 0.6923			
ΔG°	-16.06	-16.05	-16.03	-15.99	-15.98	-15.95	-15.93
ΔH°	-14.73						
10^3 ΔS°	4.69	4.57	4.44	4.23	4.14	3.97	3.83
E^a	8.63						
10^{-3}A	5.44						
				X_1 = 0.8351			
ΔG°	-16.16	-16.14	-16.13	-16.11	-16.08	-16.06	-16.05
ΔH°	-12.21						
10^3 ΔS°	13.94	13.64	13.39	13.09	12.78	12.50	12.24
E^a	8.26						
10^{-3}A	5.25						
				X_1 = 1.0000			
ΔG°	-16.31	-16.28	-16.23	-16.21	-16.20	-16.18	-16.15
ΔH°	-10.09						
10^3 ΔS°	21.96	21.48	21.14	20.70	20.24	19.91	19.53
E^a	7.97						
10^{-3}A	5.01						

favouring ion solvation process. The value of E^a increases with increase in X_1 upto about $X_1 = 0.36$ 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 (Tables 3 and 4).

The values of these thermodynamic parameters in all solvent mixtures at all temperature are given in Tables 3 and 4. As expected that the values of $\Delta G°$ become more negative at higher percentage of methanol which indicate that ion-pair association are favoured with lowering dielectric constant of the medium. The free energy change ($\Delta G°$) for association processes is evaluated from the relation, $\Delta G° = -RT \ln K_A$ [16,17]. The heat of association ($\Delta H°$) is obtained from the slope of the plot of log K_A *vs.* 1/T. The entropy change is calculated from Gibbs-Helmholtz equation, $\Delta G° = \Delta H° - T\Delta S°$.

$\Delta H°$ values obtained are found to increase with the composition of the mixed solvents. The negative values of $\Delta H°$ indicate that ion association processes are exothermic in nature in all solvents at all temperatures. A positive entropy change is 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 [18-20].

Conclusion

Conductivity measurement of Ni^{2+} and Mn^{2+} complexes in 0-100 % MeOH-water mixtures at 283.15-313.15 K have been reported. The conductivity data have been analyzed using Shedlovsky equation. As the composition of MeOH in mixed solvents increased, the K_As for both the complex are found to increase. As expected that the values of $\Delta G°$ become more negative at higher percentage of methanol which indicate that ion-pair association are favoured with lowering dielectric constant of the medium. The values of E^a increased with increase in X_1 upto about $X_1 = 0.36$ (50 % of methanol) and thereafter decreased rapidly. It shows 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 $X_1 = 0.36$.

ACKNOWLEDGEMENTS

The authors are thankful to Science and Engineering Research Board (SERB- DST), New Delhi, India for financial support under the Scheme of Young Scientist Fast Tract (No. SR/FT/CS-68/2012).

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