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Ion Association and Solvation Behaviour of Nickel(II) Complexes in Binary Mixtures of DMSO-H_2O at Different Temperatures

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Electrical conductance and solvation behaviour of [Ni(HL)(bipy)(H_2O)](NO_3)(ClO_4)(H_2O) and [Ni(HL)(dien)](ClO_4)$_2$(H_2O), where HL = 2-[(1)-pyridin-2-ylmethylidene]benzohydrazide in various compositions (0-100 %) of H_2O + DMSO in the temperature range 288.15 to 308.15 K have been studied by conductance measurement. The conductance data have been analyzed by Shedlovsky equation. The limiting molar conductance Λ_o has been decreased with the increase in the percentage of DMSO in the mixed solvent. This is due to increase in solvent-solvent interaction and increase in the dielectric constant. Owing to their high viscosity and molecular measurements of DMSO in water, lower specific conductance has been observed in H_2O + DMSO. The K_A values have been increased on increasing the temperature and increasing the percentage of DMSO in the mixed solvent presenting endothermic character of ionic association in this system. Activation energy of the rate process and related thermodynamic parameters have been evaluated and reported. Applying viscosity of the solvent/solvent mixture, Walden product $\Lambda_o\eta_o$ and effective radius r (Å) have been obtained and discussed. The results have been interpreted in terms of ion-solvent interactions and solvent-solvent interactions.

Keywords: Electrical conductance, Ion association, Nickel(II)complexes, Walden product.

INTRODUCTION

Electrical conductance of an electrolyte in mixed solvents is of value, as it gives information about the behaviour of ions in solution, ion-solvent interaction and solvent structural effects. Knowledge of electrolyte solution is found to be helpful for various electrochemical and technical investigations [1-4]. Dimethyl sulphoxide is a polar aprotic solvent that has applicable properties in electrochemical systems [5,6]. Attentiveness of dimethylsulfoxide is due to the broad use of DMSO-H_2O mixture as solvents and reaction media. Dimethyl sulfoxide has a polyfunctional molecule with a highly polar S=O group and two hydrophobic methyl groups. Unfinished negative charge on the oxygen atom of a DMSO molecule approved the formation of hydrogen bonds with water molecules, whereas the non-polar CH_3 groups may results in hydrophobic hydration and hydrophobic association of DMSO molecule [7]. Research [7,8] have shown that dimethyl sulfoxide gives hydrogen bonds with water molecules throughout the whole composition range. Perchlorates are applicable in electrochemical studies as an inert additive for maintaining constant ionic strength because the perchlorate anion is one of the least prone to complex formation and has no effect on chemical equilibrium. Ion association of perchlorates in non-aqueous solvents with lower dielectric solvents may be significant and must be taken into consideration. Here effect of temperature on the ion association behaviour of perchlorate complexes in mixed solvents were studied by measuring the electrical conductance of Ni(II) complexes at varying temperatures in 0-100 wt % DMSO-H_2O solvent mixtures. The conductance data were examined by Shedlovsky equation. The K_A values increase on increasing the temperature and increasing the percentage of DMSO in the mixed solvent presenting endothermic character of ionic association in this system. Thermodynamic parameters ($\Delta H°$, $\Delta G°$ and $\Delta S°$) were obtained from the temperature dependence of K_A for these complexes. These parameters are compared according to interactions of solvent at different temperatures.

EXPERIMENTAL

The inorganic salts selected for the present work, *i.e.*, [Ni(HL)(bipy)(H_2O)](NO_3)(ClO_4)(H_2O) and [Ni(HL)(dien)](ClO_4)$_2$ (H_2O) were synthesized according to the literature [9]. The electric conductivities were measured by Eutech Instruments, PC 700 with a dip type immersion conductivity cell were used. The solutions of different concentrations (1×10^{-3}) M were carefully prepared by dissolving requisite amount of the sample in conductivity water of low specific conductance ($< 2 \times 10^{-6}$

S cm^{-1}). All the dielectric constants and viscosities were obtained from literature [10]. The tempe-rature control in the ranges of 15-35 °C were made by using thermostat (Polystat R6L, Cole-Parmer) and thermometer. The measurements of weights were done by using a METTLER Balance, model TB-214 (max = 210 g; d = 0.1 mg). 0.1 M KCl solution in doubly distilled de-ionized water was prepared and used for calibrating the cell.

RESULTS AND DISCUSSION

The molar conductance (Λ) for studied solution system has been calculated using the following equation [11]:

$$\Lambda = 1000\ \kappa/c \tag{1}$$

where c is the molar concentration and κ is the measured specific conductance of the studied solutions. The experimental values of conductance measurements of nickel(II) complexes salts in mixed solvent after solvent correction were analyzed by using Shedlovsky extrapolation technique:

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

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

$$S(z) = \left(\frac{z}{2}\sqrt{1+\left(\frac{z}{2}\right)}\right)^2 ;\ Z = \left(\frac{\propto \Lambda_o + \beta}{\Lambda_o^{s/z}}\right)(C\Lambda)^{1/2} ;$$

$$\propto = \frac{17.147\times 105W}{(DT)^{3/2}} ;\ w = z_+z_- \frac{2q}{1+q^{1/2}} ;$$

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

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:

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

$f_{\pm}$ is the activity coefficient of the free ions and was calculated using eqn. 2:

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

$$\text{where } A = \frac{1.8247\times 10^6}{(DT)^{3/2}} ;\ B = \frac{0.5029\times 10^{10}}{(DT)^{1/2}} ;$$

$$\mu = \frac{1}{2}\sum\nolimits_i (c_i\tau_i)z_i^2$$

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 crystallographic radii of the ions, is approximately equal to 5 Å and d (Å) is given by eqn. [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 DMSO 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 [13]:

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

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) *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 [14]. The procedure was repeated using these new values of Λ_0 and K_A.

From Tables 1 and 2, the values of Λ_0 decrease invariable with increase in temperature in all the solvents irrespective of X_{DMSO}, indicating less solvation or higher mobility of ions [Fig. 1(a) & 1(b)]. 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 the ions. The dependence of viscosity on composition of the solvent is remarkable and that the maximum deviation of relative viscosity from additive behaviour (calculated under the assumption of additive behaviour of both binary systems) is achieved at X_{DMSO} = 0.09. Therefore, it follows that the most important is to investigate the influence of gradual replacement of water by DMSO on electrical conductivity and to compare it with behaviour of viscosity of the system. Values of Λ_0 of salts increase upto the mole fraction X_{DMSO} = 0.09 at all temperatures [Fig. 2(a) & 2(b)] as expected from Walden rule (Tables 1 and 2). If change of total solvation is reflected by the variation of $\Lambda_0\eta_0$ [15], the increase of the Walden product indicates the weak salvation of the ions. The decrease of the Walden product indicatives an increase of the hydrophobic salvation with increasing concentration of DMSO. The value of $\Lambda_0\eta_0$ would be constant only if r values were the same in different media. Since most ions are solvated in solution the constancy of the Walden product is not expected. As the DMSO content increases, progressive disruption of water structure occurs and the ions become solvated with the other component of the solvent mixture (*viz.* DMSO) [16]. Then effective radius (r) of the concerned ion can be calculated as:

$$\Lambda_0\eta_0 = 1/6\ \pi rT \tag{7}$$

The smaller $\Lambda_0\eta_0$ values in DMSO rich region may be due to the large effective radius of the cation, whereas the maximum values of X_{DMSO} = 0.09 correspond to minimum values of r [17,18]. It is thus apparent that its variation with

TABLE-1
VALUES OF LIMITING MOLAR CONDUCTANCE (Λ_o), ASSOCIATION CONSTANT (K_A), WALDEN PRODUCT ($\Lambda_0\eta_0$) AND EFFECTIVE RADIUS (r) OBTAINED BY SHEDLOVSKY TECHNIQUE FOR [Ni(HL)(bipy)(H_2O)](NO_3)(ClO_4)(H_2O) COMPLEX HAVE BEEN MEASURED IN VARIOUS DMSO + H_2O MIXTURES AT 288.15-308.15 K

X_{DMSO}	Λ_o (S cm^2 mol^{-1})	K_A (dm^3 mol^{-1})	$\Lambda_o\eta_o$	r (Å)	Λ_o (S cm^2 mol^{-1})	K_A (dm^3 mol^{-1})	$\Lambda_o\eta_o$	r (Å)	Λ_o (S cm^2 mol^{-1})	K_A (dm^3 mol^{-1})	$\Lambda_o\eta_o$	r (Å)
	288.15 K				293.15 K				298.15 K			
0.0000	398.40	13.26	525.25	3.51	294.61	17.06	385.34	4.70	266.42	21.51	354.15	5.03
0.0250	450.13	19.71	615.13	3.34	347.44	24.32	495.48	3.65	309.71	27.44	445.14	4.00
0.0900	542.32	25.36	789.89	2.33	486.54	30.10	676.74	2.67	436.52	33.17	638.37	2.80
0.1874	504.44	31.15	759.38	2.43	450.31	36.41	655.55	2.76	400.36	39.25	630.57	2.83
0.3499	470.36	38.36	673.02	2.74	422.71	42.23	574.19	3.15	382.49	46.28	540.00	3.30
0.6749	401.28	42.15	555.28	3.32	385.68	48.94	464.13	3.91	300.26	50.17	433.32	4.12
1.0000	354.42	48.43	433.45	4.26	290.57	53.17	349.13	5.18	206.49	56.29	312.98	5.68
	303.15 K				308.15 K							
0.0000	237.82	26.35	324.42	5.41	195.48	29.21	260.23	6.62				
0.0250	282.52	29.12	425.34	4.12	233.29	32.42	364.25	4.74				
0.0900	383.31	37.80	613.23	2.86	310.67	39.37	554.39	3.11				
0.1874	323.64	42.22	596.46	3.00	270.33	45.11	536.48	3.22				
0.3499	268.11	49.28	517.75	3.38	211.71	51.12	464.41	3.70				
0.6749	228.73	54.24	412.60	4.24	191.62	57.35	362.13	4.76				
1.0000	189.60	59.10	300.04	5.85	152.20	63.32	257.68	6.67				

TABLE-2
VALUES OF LIMITING MOLAR CONDUCTANCE (Λ_o), ASSOCIATION CONSTANT (K_A), WALDEN PRODUCT ($\Lambda_0\eta_0$) AND EFFECTIVE RADIUS (r) OBTAINED BY SHEDLOVSKY TECHNIQUE FOR [Ni(HL)(dien)](ClO_4)$_2$(H_2O) COMPLEX HAVE BEEN MEASURED IN VARIOUS DMSO + H_2O MIXTURES AT 288.15-308.15 K

X_{DMSO}	Λ_o (S cm^2 mol^{-1})	K_A (dm^3 mol^{-1})	$\Lambda_o\eta_o$	r (Å)	Λ_o (S cm^2 mol^{-1})	K_A (dm^3 mol^{-1})	$\Lambda_o\eta_o$	r (Å)	Λ_o (S cm^2 mol^{-1})	K_A (dm^3 mol^{-1})	$\Lambda_o\eta_o$	r (Å)
	288.15 K				293.15 K				298.15 K			
0.0000	354.86	29.40	505.12	3.65	265.96	36.40	370.21	4.88	229.31	43.81	341.00	5.00
0.0250	408.20	34.67	600.00	3.10	301.20	42.89	480.35	3.77	275.27	49.62	390.15	4.55
0.0900	595.22	39.70	749.76	2.46	442.16	56.73	635.61	2.85	378.42	56.92	487.68	3.65
0.1874	480.04	45.63	706.25	2.61	419.82	59.29	605.42	3.00	300.26	67.77	408.95	4.35
0.3499	408.42	52.90	609.89	3.02	352.64	63.81	518.06	3.50	246.29	73.63	352.50	4.98
0.6749	311.36	63.12	499.15	3.70	286.32	75.91	415.00	4.00	200.60	82.19	278.10	6.41
1.0000	205.28	69.71	390.32	4.72	196.68	79.31	320.00	5.65	102.45	86.40	191.62	9.26
	303.15 K				308.15 K							
0.0000	200.40	52.64	309.19	5.65	163.57	59.68	245.00	7.04				
0.0250	249.18	64.48	410.21	4.27	186.71	63.20	349.02	5.00				
0.0900	342.27	72.86	578.10	3.03	280.26	68.41	529.16	3.26				
0.1874	234.53	79.40	559.33	3.13	222.28	71.78	513.25	3.33				
0.3499	219.82	84.32	479.62	3.65	194.18	86.93	438.18	4.00				
0.6749	184.92	87.16	375.47	4.67	160.36	92.86	339.90	5.10				
1.0000	138.51	91.37	280.91	6.25	96.20	98.20	248.45	6.94				

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 on the other hand with the change of mixed solvent composition and 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.*,

$$\Lambda_o = A.e^{-E^a/RT} \quad \text{or} \quad \ln\Lambda_o = \ln A - E^a/RT \qquad (8)$$

where A is the frequency factor, R is the ideal gas constant and E^a is Arrhenius activation energy of transport processes. E^a values can be computed from the slope of plot of log A *versus* 1/T are shown in Tables 3 and 4.

The values of E^a increase with increase in X_1 throughout the mole fraction. The experimentally determined of K_As of the complex are found to increase with increase in x_1 which indicate an increased association as DMSO 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 $\Delta G°$ become more negative at higher percentage of DMSO 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 $\Delta G° = -RT \ln K_A$. The heat of association ($\Delta H°$) is obtained from the slope of the plot of log K_A *versus* 1/T. $\Delta H°$ values obtained are found to increase with the composition of the mixed solvents [Fig. 3(a) & 3(b)]. The entropy of change is calculated from Gibbs-Helmholtz equation, $\Delta G° = \Delta H° - T\Delta S°$. The values of these thermodynamic in nature in all solvent mixtures at all temperature are given in Tables 3 and 4.

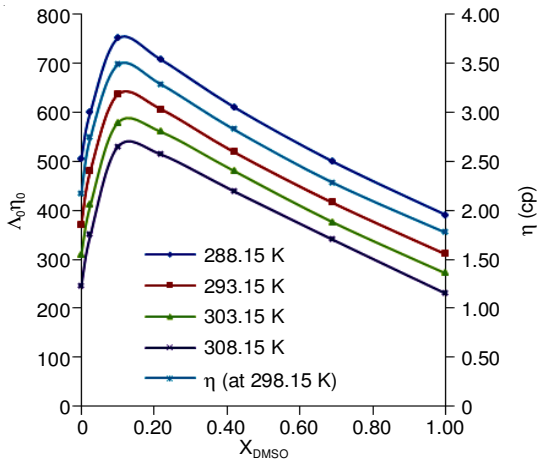

Fig. 1(a). Value of Walden product $\Lambda_o\eta_o$ and η for $[Ni(HL)(bipy)(H_2O)](NO_3)(ClO_4)(H_2O)$ complex in H_2O + DMSO solvents

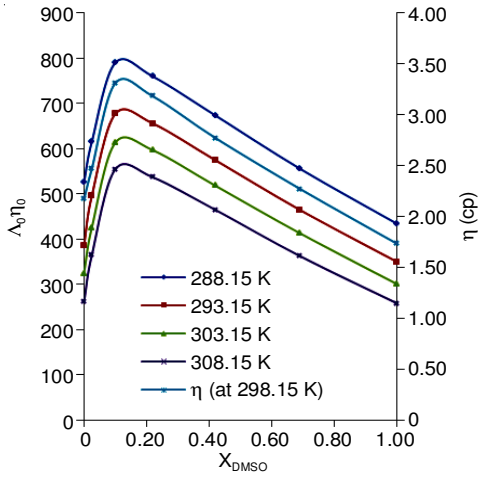

Fig. 1(b). Value of Walden product $\Lambda_o\eta_o$ and η for $[Ni(HL)(dien)](ClO_4)_2(H_2O)$ complex in H_2O + DMSO solvents

TABLE-3
THERMODYNAMIC PARAMETERS ΔG° (KJ mol^{-1}), ΔH° (KJ mol^{-1}), ΔS° (KJ mol^{-1}), E_a (KJ mol^{-1}) AND 10^{-3} A OF SHEDLOVSKY TECHNIQUES FOR $[Ni(HL)(bipy)(H_2O)](NO_3)(ClO_4)(H_2O)$ COMPLEX HAVE BEEN MEASURED IN VARIOUS DMSO + H_2O MIXTURES AT DIFFERENT TEMPERATURES

	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K
	$X_1 = 0.0000$				
ΔG°	-8.11	-8.76	-9.36	-9.98	-10.44
ΔH°	-1.60	-1.73	-1.87	-1.96	-2.08
$10^{-3} \times \Delta S°$	22.60	24.00	25.12	26.46	27.13
E^a	11.30				
$10^{-3}A$	2.88				
	$X_1 = 0.0250$				
ΔG°	-8.50	-9.15	-9.70	-10.51	-10.62
ΔH°	-1.78	-1.85	-1.94	-2.01	-2.15
$10^{-3} \times \Delta S°$	23.32	24.90	26.03	28.04	27.50
E^a	13.21				
$10^{-3}A$	3.02				
	$X_1 = 0.0900$				
ΔG°	-8.83	-9.82	-10.05	-10.80	-10.80
ΔH°	-1.84	-1.92	-2.07	-2.17	-2.27
$10^{-3} \times \Delta S°$	24.26	26.95	26.77	28.47	27.70
E^a	15.13				
$10^{-3}A$	3.16				
	$X_1 = 0.1874$				
ΔG°	-9.16	-9.93	-10.45	-11.03	-10.97
ΔH°	-1.96	-2.00	-2.16	-2.28	-2.36
$10^{-3} \times \Delta S°$	25.00	27.05	27.80	28.86	28.00
E^a	17.04				
$10^{-3}A$	3.31				
	$X_1 = 0.3499$				
ΔG°	-9.49	-10.10	-10.68	-11.14	-11.45
ΔH°	-2.05	-2.15	-2.24	-2.34	-2.49
$10^{-3} \times \Delta S°$	25.82	27.12	28.31	29.03	29.08
E^a	19.00				
$10^{-3}A$	3.47				
	$X_1 = 0.6749$				
ΔG°	-9.93	-10.55	-10.90	-11.26	-11.62
ΔH°	-2.17	-2.27	-2.32	-2.40	-2.52
$10^{-3} \times \Delta S°$	26.93	28.24	28.78	29.23	29.53
E^a	20.87				
$10^{-3}A$	3.63				
	$X_1 = 1.0000$				
ΔG°	-10.15	-10.66	-11.07	-11.38	-11.80
ΔH°	-2.25	-2.30	-2.48	-2.51	-2.68
$10^{-3} \times \Delta S°$	27.42	28.52	28.81	29.33	29.60
E^a	22.78				
$10^{-3}A$	3.80				

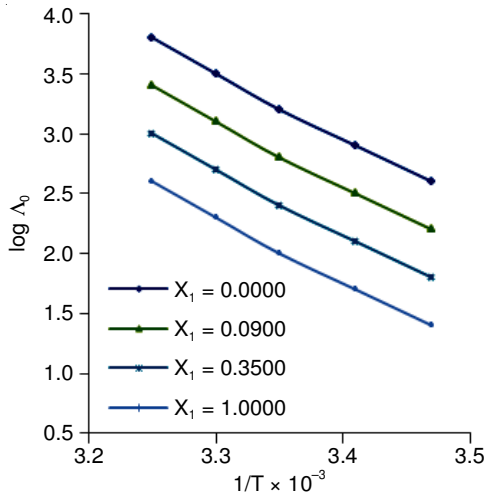

Fig. 2(a). log Λ_o *vs.* 1/T for [Ni(HL)(bipy)(H_2O)](NO_3)(ClO_4)(H_2O)

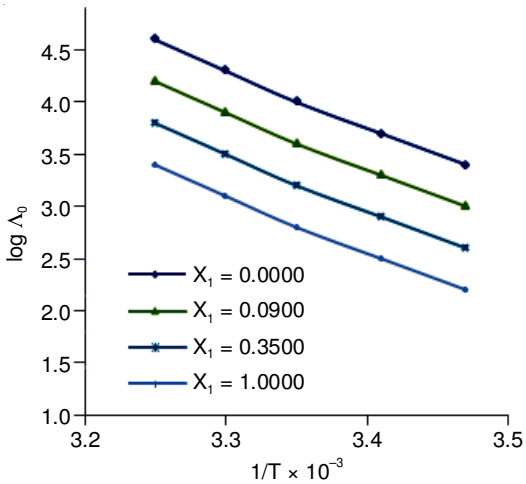

Fig. 2(b). log Λ_o *vs.* 1/T for Ni(HL)(dien)](ClO_4)$_2$(H_2O)

TABLE-4
THERMODYNAMIC PARAMETERS ΔG° (KJ mol^{-1}), ΔH° (KJ mol^{-1}), ΔS° (KJ mol^{-1}), E_a (KJ mol^{-1}) AND 10^{-3} A OF SHEDLOVSKY TECHNIQUES FOR [Ni(HL)(dien)](ClO_4)$_2$(H_2O) COMPLEX HAVE BEEN MEASURED IN VARIOUS DMSO + H_2O MIXTURES AT DIFFERENT TEMPERATURES

	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K
	X_1 = 0.0000				
ΔG°	-6.18	-6.90	-7.59	-8.24	-8.61
ΔH°	-1.30	-1.59	-1.78	-1.89	-2.06
10^{-3} × ΔS°	16.93	18.11	19.49	20.95	21.26
E^a	9.57				
10^{-3}A	4.47				
	X_1 = 0.0250				
ΔG°	-7.17	-7.74	-8.22	-8.47	-8.91
ΔH°	-1.52	-1.73	-1.82	-1.96	-2.18
10^{-3} × ΔS°	19.61	20.50	21.46	21.47	21.84
E^a	11.48				
10^{-3}A	4.68				
	X_1 = 0.0900				
ΔG°	-7.62	-8.31	-8.68	-9.17	-9.44
ΔH°	-1.73	-1.91	-1.97	-2.08	-2.28
10^{-3} × ΔS°	20.44	21.83	22.51	23.39	23.24
E^a	13.40				
10^{-3}A	4.90				
	X_1 = 0.1874				
ΔG°	-8.27	-8.76	-9.13	-9.40	-9.73
ΔH°	-1.86	-2.08	-2.04	-2.15	-2.39
10^{-3} × ΔS°	22.24	22.79	23.78	23.91	23.82
E^a	15.32				
10^{-3}A	5.13				
	X_1 = 0.3499				
ΔG°	-8.72	-9.09	-9.48	-9.87	-10.09
ΔH°	-1.94	-2.23	-2.12	-2.27	-2.48
10^{-3} × ΔS°	23.53	23.40	24.68	25.07	24.70
E^a	17.23				
10^{-3}A	5.37				
	X_1 = 0.6749				
ΔG°	-8.94	-9.54	-9.70	-10.04	-10.38
ΔH°	-2.09	-2.34	-2.23	-2.38	-2.57
10^{-3} × ΔS°	23.77	24.56	25.05	25.27	25.34
E^a	19.15				
10^{-3}A	5.62				
	X_1 = 1.0000				
ΔG°	-9.27	-9.65	-10.0	-10.27	-10.62
ΔH°	-2.15	-2.41	-2.35	-2.48	-2.69
10^{-3} × ΔS°	24.70	24.70	25.66	25.70	25.73
E^a	21.06				
10^{-3}A	5.89				

At all temperatures, ΔG^0 values become more negative with increase in X_1 indicating that the ion pair formation is favoured with lowering of permittivity of the medium.

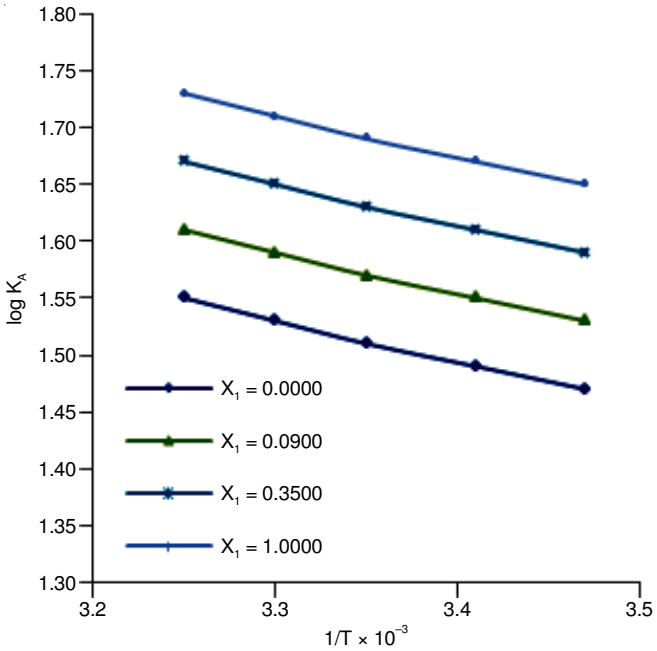

Fig. 3(a). log K_A *vs.* 1/T for $[Ni(HL)(bipy)(H_2O)](NO_3)(ClO_4)(H_2O)$

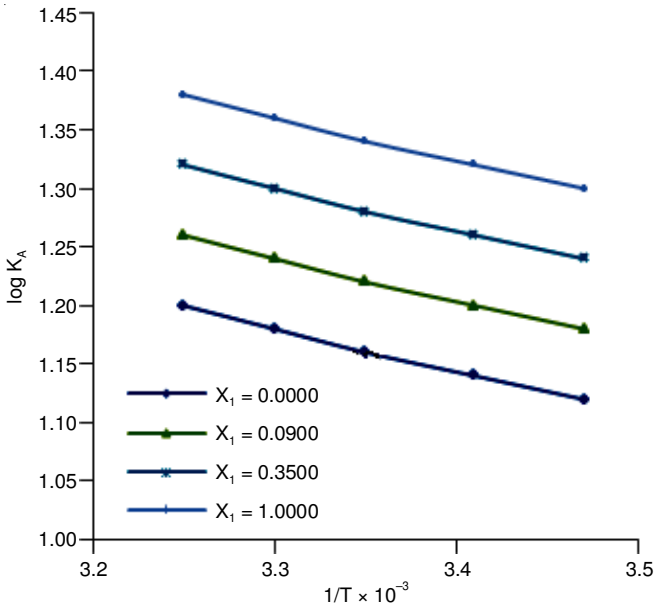

Fig. 3(b). log K_A *vs.* 1/T for $[Ni(HL)(dien)](ClO_4)_2(H_2O)$

Conclusion

The experimentally determined K_As of the complex are found to increase with increase in X_1 which indicate an increased association as DMSO 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 $\Delta G°$ become more negative at higher percentage of DMSO which indicate that ion-pair association are favoured with lowering dielectric constant of the medium. The value of E^a increases with increase in X_1 indicating that there is an increased association on adding DMSO in water. Therefore, among the two complexes it shows that in DMSO rich region $[Ni(HL)(bipy)(H_2O)](NO_3)(ClO_4)(H_2O)$ complex requires more higher activation energy processes as DMSO content in the mixed solvent increases.

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