International Journal of Basic and Applied Chemical Sciences ISSN: 2277-2073 (Online)
An Open Access, Online International Journal Available at http://www.cibtech.org/jcs.htm
2015 Vol. 5 (4) October-December, pp.11-18/Singh and Lalmuanzuali

Research Article

THERMODYNAMICS STUDIES OF METAL PERCHLORATES IN METHANOL + WATER MIXTURES AT DIFFERENT TEMPERATURES

***Mohondas Singh N. and Olivia Lalmuanzuali**
Department of Chemistry, School of Physical Sciences, Mizoram University
Aizawl-796004, Mizoram, India
** Author for Correspondence*

ABSTRACT

Electrical conductance of pentaammine chloronickel (II) perchlorate in different mass fraction (X_{MeOH} = 0.0000-1.0000) at different temperatures from 288.15-308.15K were studied. The limiting molar conductance (Λ_0) and ion association constant (K_A) of pentaammine chloronickel (II) perchlorate in methanol-water solutions at different temperatures were evaluated by Shedlovsky technique. It is evident that the values of (Λ_0) increase regularly with the increase in temperature indicating higher mobility of the ions in the solvent system studied. The free energy (ΔG^0), enthalpy (ΔH^0), entropy (ΔS^0) and Arrhenius activation energy (E^a) for ion-association reaction were derived from the temperature dependence of ion association constant. The influence of the mixed solvent composition on the solvation of ions have been discussed based on the composition dependence of the Walden product ($\Lambda_0\eta_0$).The effective radius r (Å) decreases with increase in methanol and thereafter increase in methanol rich regions. The results have been interpreted in terms of ion-ion, ion-solvent and solvent-solvent interactions.

Keywords: *Pentaammine Chloronickel (II) Perchlorate, Electrical Conductance, Shedlovsky Technique, Thermodynamic Parameters, Walden Product, Arrhenius Activation Energy*

INTRODUCTION

The concept of ion association in electrolyte solutions was introduced by (Bjerrum *et al.,* 1926) so as to improve Debye-Huckel theory. According to this concept, electrolyte is considered to be a mixture of free ions and ion clusters which are assumed to be taken part in chemical equilibrium according to the corresponding mass action law (Debye *et al.,* 1923). The phenomenon of ion association has an important effect in thermodynamic, transport, dielectric and other properties of electrolyte solutions. Several experimental techniques have been applied to study the thermodynamic and various interactions in electrolytic solutions (Yokoyama *et al.,* 1994; Das *et al.,* 1995; Parmar *et al.,* 1996; Ue *et al.,* 1996; Ue *et al.,* 1997; Seleem *et al.,* 2002).

Ion pairing between the metal ions and ligands has usually investigated by means of conductance technique (Ue *et al.,* 1995; Bakr *et al.,* 1999; Bakr *et al.,* 2001). The conductance behavior of many electrolytes in mixed solvent systems is reported to be influenced by number of factors like density, viscosity, dielectric constant of the medium, ion solvent interactions and solvent-solvent interactions. Ion-solvent interactions stabilize the ion by solvating it. The solvation of dissolved ions determines many of the properties of electrolyte solutions, including their redox potential, complexation and kinetic behaviour. Conductance studies in binary solvent mixtures not only give an idea about ion-solvent and solvent-solvent interactions but also the preferential solvation of an ion.

Methanol is polar solvents and often used to dissolve salts. They have high dielectric constant and high polarity. Alcohols associate in liquids by hydrogen bond. Perchlorates are often used in electrochemical studies as an inert additive for maintaining constant ionic strength since the perchlorate anion is one of the least prone to complex formation and has no effect on chemical equilibria. The ion association of perchlorates in non aqueous solvents with lower dielectric solvents may be significant and must be taken into account. Thus in this study, it was attempted to obtain some information on the association of perchlorate in methanol solutions at different temperatures ranging from 15-35^{0}C by Shedlovsky technique. The thermodynamic functions (ΔH°, ΔG°, ΔS° and E^a), effective radius (r) and Walden product ($\Lambda_0\eta_0$) were calculated and compared according to interactions of solvent at different temperatures.

MATERIALS AND METHODS

The Inorganic salt selected for the present work i.e., pentaammine chloronickel (II) perchlorate salt synthesized according from the literature (Schlessinger *et al.*, 1962). The purity of the sample was checked through conventional analysis and spectral measurements. 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 x10^{-3}) M were carefully prepared by dissolving requisite amount of the sample in conductivity water of low specific conductance (< 2x10^{-6} S cm^{-1}) and conductivity measurements were carried out over the temperature range of 15°C – 35° C. All the dielectric constants and viscosities were obtained from literature (Lalrosanga *et al.*, 2011). The temperature control in the ranges of 15-35^{0}C were made by using thermostat (Polystat R6L, Cole-Parmer) and thermometer. The measurements of weights were done by using a METTER Balance, model TB-214(max=210g; d=0.1mg). All calculations were done on IBM-PC-AT/386 using a basic programmed. The observed conductivities were corrected for the conductivity of the solvent. The accuracy of the temperature of the thermostat was ± 0.01^{0}C

The molar conductances (Λ) for studied solution system have been calculated using following equation (El Dossoki, 2010)

$$\Lambda = 1000\,\kappa / c \qquad (1)$$

Where c is the molar concentration and κ is the measured specific conductance of the studied solutions. The experimental values of conductance measurements of pentaammine chloronickel (II) perchlorate salt in mixed solvent after solvent correction were analyzed by using Shedlovsky extrapolation technique:

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

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)

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

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 (Shedlovsky *et al.*, 1956). 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]

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

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 *et al.*, 1942)

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

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 (Nelson *et al.*, 2005). 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 DISCUSSIONS

The observed limiting molar conductances and association constants of pentaammine chloronickel (II) perchlorate at 15-35^{0}C in Methanol-water mixtures are presented in Table I. The Walden product and effective radius are calculated and discuss below.

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 Pentaammine chloronickel(II) perchlorate have been measured in various methanol +water mixtures at 283.15K-303.15K

Xmethanol	Λ_0 Scm^{2}mol^{-1}	K_A dm^{3}mol^{-1}	$\Lambda_0\eta_0$	r	Λ_0 Scm^{2}mol^{-1}	K_A dm^{3}mol^{-1}	$\Lambda_0\eta_0$	r
	T=288.15K				**T=293.15K**			
0.0000	260.74	420.11	344.88	5.341	279.05	350.21	317.83	5.697
0.0588	245.53	449.23	500.91	3.677	268.20	362.26	464.18	3.901
0.1942	238.64	460.41	537.83	3.244	245.00	380.00	500.03	3.621
0.3600	214.12	485.53	551.94	3.163	220.23	398.43	563.81	3.404
0.5676	221.00	521.34	462.76	3.980	238.42	400.23	445.83	4.062
0.8351	232.33	540.36	363.00	5.074	242.44	413.05	337.16	5.370
1.0000	240.23	562.21	350.11	6.974	257.70	427.32	246.97	7.331
	T=298.15K				**T=303.15K**			
0.0000	290.74	324.98	294.69	6.042	300.70	300.24	274.27	6.386
0.0588	279.56	394.76	420.54	4.234	282.22	315.66	380.39	4.604
0.1942	263.44	420.68	455.77	3.906	278.69	337.40	423.54	4.134
0.3600	243.16	451.57	483.69	3.303	255.30	358.08	487.43	3.719
0.5676	251.30	473.90	412.18	4.320	265.53	379.29	377.44	4.638
0.8351	267.83	498.62	319.45	5.574	274.47	385.82	293.64	5.963
1.0000	270.13	532.32	232.33	7.663	298.51	409.23	218.11	8.026
	T=308.15K							
0.0000	325.85	273.07	249.01	6.916				
0.0588	305.25	286.56	348.36	4.945				
0.1942	282.48	308.40	383.52	4.492				
0.3600	263.88	322.28	439.53	4.239				
0.5676	281.84	337.72	350.41	4.916				
0.8351	290.41	340.82	276.21	6.238				
1.0000	310.73	371.52	217.70	7.911				

From Table 1, 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 (Figure 1).

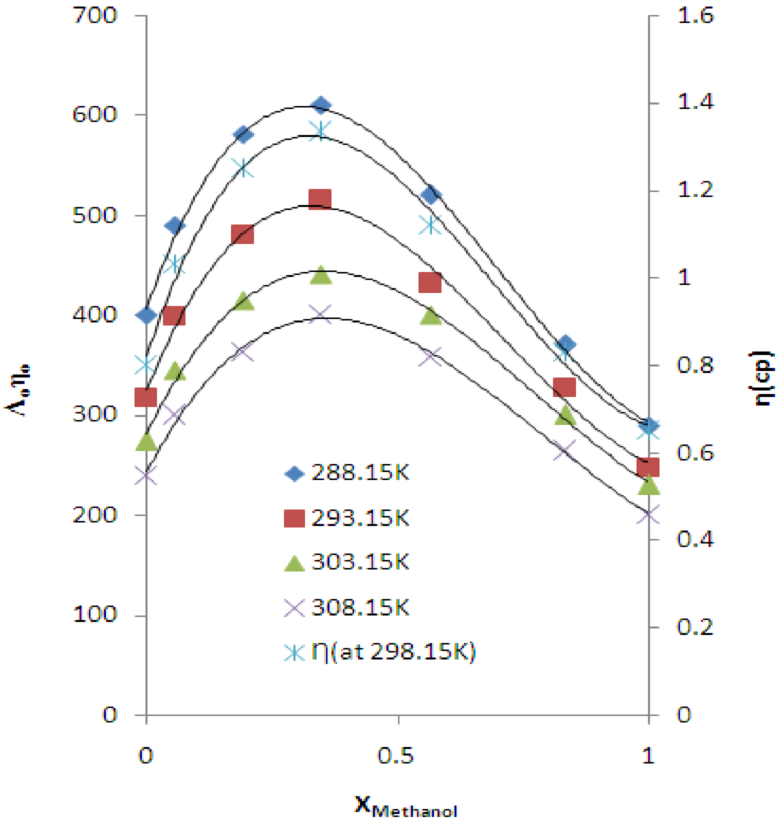

Figure 1: The value of Walden product $\Lambda_o\eta_o$ and (η) for Ni (II) Complex as a function of X_{MeOH} in methanol + water solvents

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. The viscosity of M + W mixtures increases upto X_{MeOH} = 0.36 and thereafter it decreases. Values of Λ_0 of salts decrease up to this mole fraction (X_{MeOH} = 0.36) and then increase in methanol rich region at all temperatures as expected from Walden rule (Table I).If change in solvation is reflected by the variation in $\Lambda_0\eta_0$ (Singh *et al.*, 2008), the increase of the Walden product indicates the weak salvation of the ions. The decrease of the product indicates an increase of the hydrophobic salvation 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. Then effective radius(*r*) of ion or solute can be calculated as

$$\Lambda_0\eta_0 = 1/6\ \pi rT \qquad (7)$$

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 (Bag *et al.*, 2001). 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 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.,

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

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 2: Thermodynamic parameters ΔG°(KJ mole-1), ΔH°(KJ mole-1), ΔS°(KJ mole-1), Ea(KJ mole-1) and 10-3 A of Shedlovsky techniques for Pentaammine chloronickel (II) perchlorate have been measured in various Methanol + water mixtures at different temperatures.

	15°C	**20°C**	**25°C**	**30°C**	**35°C**
X_1=0.0000					
ΔG°	-14.47	-14.28	-14.27	-14.22	-14.16
ΔH°	-23.54				
10^{-3}xΔS°	-30.33	-31.58	-31.09	-30.74	-30.43
E^a	7.67				
10^{-3}A	2.74				
X_1=0.0588					
ΔG°	-14.62	-14.59	-14.55	-14.51	-14.45
ΔH°	-23.25				
10^{-3}xΔS°	-29.95	-29.54	-29.18	-28.83	-28.56
E^a	7.80				
10^{-3}A	2.96				
X_1=0.1942					
ΔG°	-14.67	-14.42	-14.27	-14.22	-14.16
ΔH°	-23.06				
10^{-3}xΔS°	-29.12	-29.47	-29.48	-29.16	-28.88
E^a	8.12				
10^{-3}A	3.16				
X_1=0.3600					
ΔG°	-14.78	-14.59	-14.27	-14.20	-14.16
ΔH°	-22.86				
10^{-3}xΔS°	-28.04	-28.21	-28.81	-28.56	-28.23
E^a	8.38				
10^{-3}A	3.43				
X_1=0.5676					
ΔG°	-14.89	-14.87	-14.84	-14.80	-14.75
ΔH°	-22.62				
10^{-3}xΔS°	-26.83	-26.44	-26.09	-25.79	-25.54
E^a	8.10				
10^{-3}A	3.21				
X_1=0.8351					
ΔG°	-15.17	-15.13	-14.84	-14.51	-14.45
ΔH°	-22.31				
10^{-3}xΔS°	-24.78	-24.49	-25.05	-25.72	-25.50
E^a	7.90				
10^{-3}A	3.00				
X_1=1.0000					
ΔG°	-15.45	-15.43	-15.41	-15.38	-15.34
ΔH°	-22.10				
10^{-3}xΔS°	-23.08	-22.75	-22.44	-22.17	-21.94
E^a	7.73				
10^{-3}A	2.81				

The values of E^a increase with increase in X_1 up to about X_1=0.36 and thereafter decreases rapidly. It follows that in water rich region up to 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. 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 favoured with lowering dielectric constant of the medium.

The free energy change (ΔG^0) for association processes is evaluated from the relation $\Delta G^0 = -RT \ln K_A$. 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 (Figure 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 favoured with lowering of permittivity of the medium.

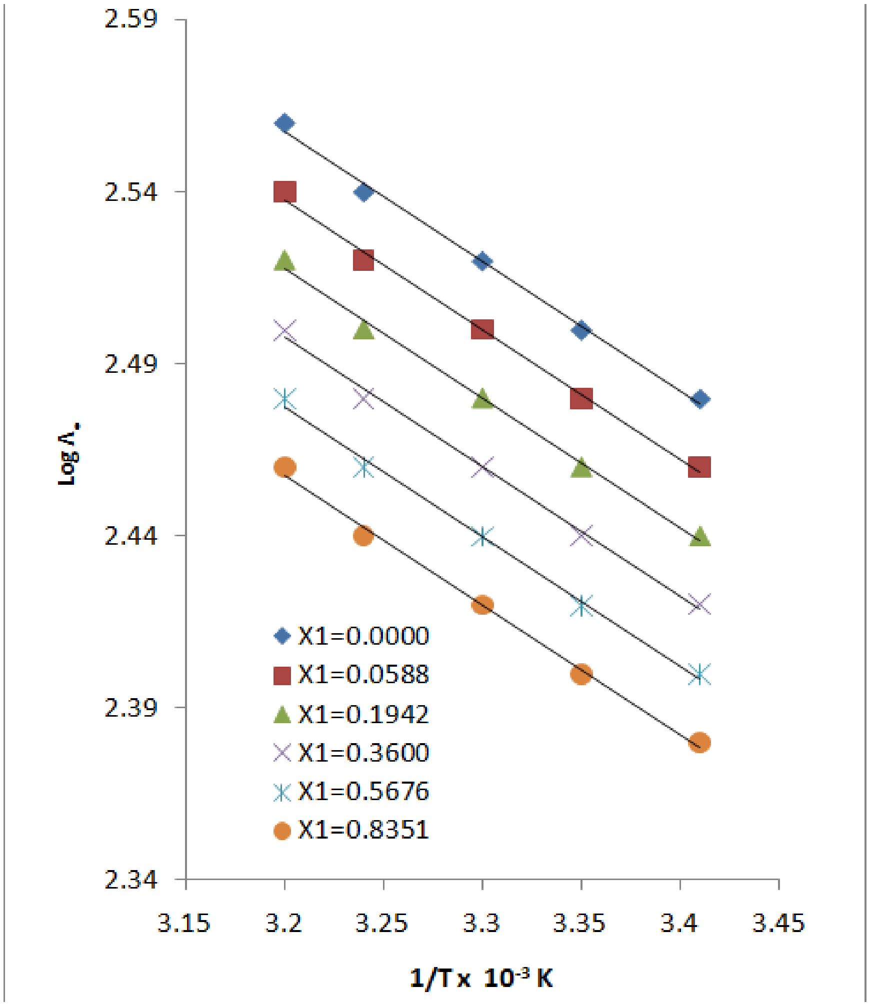

Figure 2: Lok Λ_o vs 1/T for Ni (II) Complex in different mole fraction at temperature 288.15-308.15K

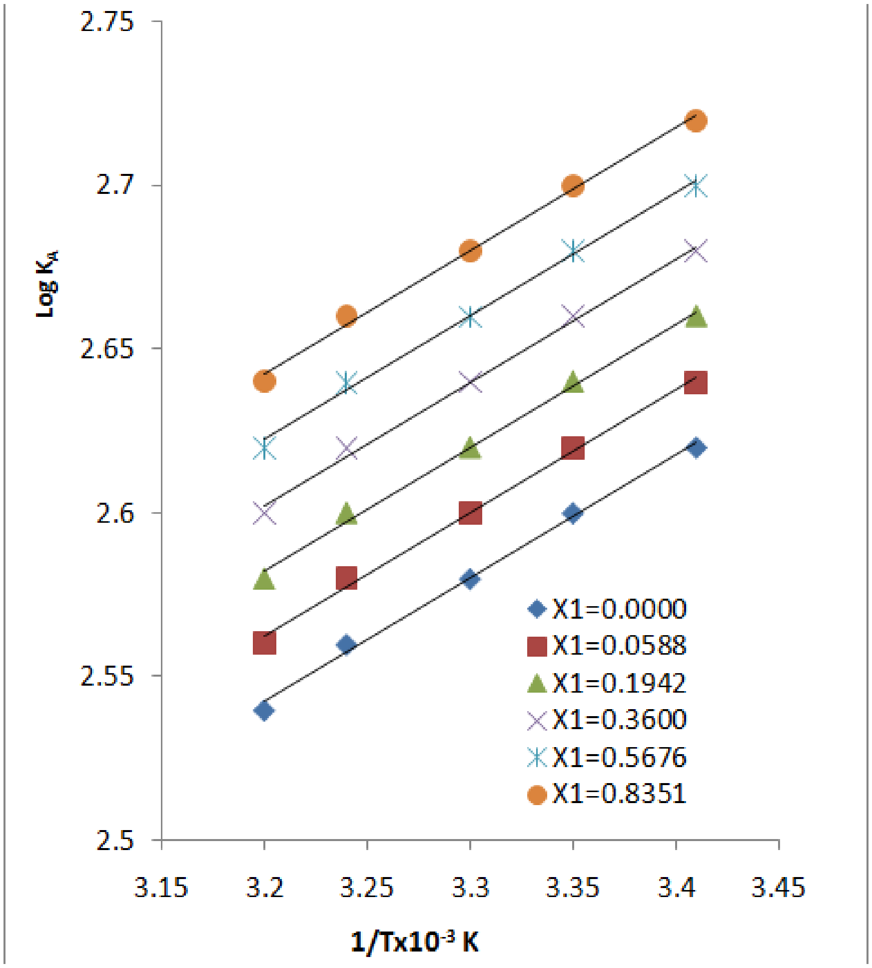

Figure 3: Lok K_A vs 1/T for Ni(II) Complex in different mole fraction at temperature 288.15-308.15K

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 favoured with lowering dielectric constant of the medium. 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

ACKNOWLEDGEMENT

The authors grateful to Science and Engineering Research Board (SERB- DST), New Delhi for financial support under the Scheme of *Young Scientist Fast Tract (Vide* No.SR/FT/CS-68/2011).

REFERENCES

Bag GC, Singh NM and Singh NR (2001). Ion Pair Association Constant of diammine bis-1-amidino-O-Methylurea Cobalt (III) monochloride in Acetonitrile + Water Mixtures at Different Temperatures- A Conductance Study. *Indian Journal of Chemistry A* **40** 500-504.

Bakr MF (2001). Thermodynamic study of ion-pairing of some transition metal perchlorates in urea-water mixtures from conductivity measurements. *Journal of the Chinese Chemical Society* **48** 1087-1091.
Bakr MF and Mohamed AA (1999). Ion-Solvent interaction of biunivalent electrolytes in dioxane-water mixtures from conductivity data at different temperatures. *Journal of the Chinese Chemical Society* **46** 899-904.
Bjerrum N, Mat-Fys Medd and Ionic Association I (1926). Influence of Ionic Association on the Activity of Ions at a Moderate Degrees of Association. *Det Kongelige Danske Videnskabernes Selskab* **7** 1- 48.
Das B and Hazra DK (1995). Conductometric, viscometric, and spectroscopic investigations on the salvation phenomena of alkali-metal ions and ion pairs in 2-methoxyethanol. *The Journal of Physical Chemistry* **99** 269 -273.
Debye P, Huckel E and Physik Z (1923). The interionic attraction theory of deviations from ideal behavior in solution. *Zeitschrift für Physik* **24** 185-187.
El-Dossoki FI (2010). Effect of hydrogen bond,relative permittivity and temperature on the transport properties and the association behavior of some 1:1 electrolyte in some binary mixed solvents. *Journal of Molecular Liquids* **151** 1-8.
Glasstone S (1942). *An Introduction to Electrochemistry* (EWP, New Delhi) **1** 61-65.
Lalrosanga and Singh NM (2011). Ion Pair formation of $CoCl_2.6H_2O$ and $[Co(NH_3)_5Cl]Cl_2$ in Aqueous Medium at Different Temperatures – A Conductance Method. *Asian Journal of Chemistry* **233** 1120-1122.
Nelson JB and Essington ME (2005). The association constants of H^+ and Ca^{2+} with 2-keto-D-gluconate in aqeous solutions. *Journal of Solution Chemistry* **34**(7) 789-800.
Parmar ML and Gupta VK (1996). A study on the conductometric determination of ion-association constants and Walden product for some Transition Metal sulphate in aqueous Urea solutions. *Journal of Indian Chemical Society* **73** 512-515.
Schlessinger GG (1962). *In Inorganic laboratory Preparations* (Chemical Publishing Company, Inc) **1** 1-8.
Seleem HSM, El-Behairy M, Mashaly MM and Mena HH (2002). Thermodynamics of complexation of isotin-3-thio-semicarbazone (HIT) and other related derivatives with some metal ions. *Journal of the Serbian Chemical Society* **67**(4) 243-256.
Shedlovsky T and Kay RK (1956). The ionization constant of acetic acid in water-methanol mixtures at 25^0C from conductance measurements. *The Journal of Physical Chemistry* **60** 151-155.
Singh NM, Singh TD, Yaiphaba N and Singh NR (2008). Ion pair formation and thermodynamics of glycine bis-1-amidino-O-methylurea cobalt (III) halides in water + methanol mixed solvents at different temperatures. *Asian Journal of Chemistry* **20**(3) 1750-1760.
Ue M (1996). Ionic radius of $(CF_3SO_2)_3C^-$ and applicability of Stokes law to its Propylene carbonate solution. *Journal of the Electrochemical Society* **143**(2) L270-L272.
Ue M (1997). Solution Chemistry of Organic Electrolytes. *Progress in Batteries and Battery Materials* **16** 332-349.
Ue M and Mori S (1995). Mobility and ionic association of lithium salts in a propylene carbonate-ethyl methyl carbonate mixed solvent. *Journal of the Electrochemical Society* **142**(8) 2577-2581.
Yokoyama H, Hiramoto T and Shinozaki K (1994). Conductometric study of ion association between Tris (oxalato) chromaste (β) and Alkali metal ions at temperatures from 0 to 50^0C. *Bulletin of the Chemical Society of Japan* **67**(8) 2086-2092.