



P-ISSN 2349-8528
E-ISSN 2321-4902
IJCS 2014; 2(4): 01-05
© 2014 IJCS
Received: 21-10-2014
Accepted: 18-11-2014

A.A. Ramteke
Department of chemistry,
Govt. V.I.S.H.,
Amravati 444604 (M.S) India.

S.P. Chavan
Department of chemistry,
Devchand College,
Arjunnagar, Dist. Kolhapur
591237 (M.S) India.

S.D. Patil
Department of chemistry,
Devchand College,
Arjunnagar, Dist. Kolhapur
591237 (M.S) India.

M.L. Narwade
Department of chemistry,
Govt. V.I.S.H.,
Amravati 444604 (M.S) India.

Effect of ionic strength on the stability constants of complexes of 3-(4-chlorophenyl)-4-(3-pyridine)-5-(2-hydroxy phenyl)-pyrazole with Cu (II), Tb (III), and Nd (III) metal ions

A.A. Ramteke, S.P. Chavan, S.D. Patil, M.L. Narwade

Abstract

The determined the stability constants of the complexes of chloro pyrazoles with some metal ions and see the effect of various ionic strengths on the stability constants. The interactions of Cu (II), Tb (III) and Nd (III) metal ions with ligand i.e. 3-(4-chlorophenyl)-4-(3-pyridine)-5-(2-hydroxy phenyl)-pyrazole at various ionic strengths in 70% dioxane-water medium has been investigated by Calvin-Bjerrum p^H metric technique at 27 °C. The obtained data was used to study the correct mechanism of the complexation reaction and the results were used to show the linear relationship.

Keywords: Stability constants, Ionic strength, Complexes, Substituted chloro pyrazoles, Metals.

1. Introduction

In view of analytical applications, it was an interest to know the physico-chemical properties and influence of ionic strengths on complex equilibria. The properties of individual ions in a solution cannot be measured independently, because a solution is electrically neutral. It demands that each ion is accompanied by an ion of the opposite charge so activity coefficients of aqueous ions have to be estimated. The ionic strength is an electrical current proceed by the ions of an inert salt in solution. It affects proton-ligand stability constants (p^K) and metal ligand stability constant ($\log k$). To understand the thermodynamic properties of electrolytic solution, the knowledge of both, the long range interaction forces and short range interactions between the ions and solvent molecules is necessary. The net effect of interionic attractions and repulsion is decreasing the free energy of solute as compared to that of uncharged particles and hence activity coefficient decreases. The forces between the ions and solvent dipoles tend to hold the solvent in the solution with a consequent decrease in the solvent vapor pressure from ideal value and corresponding increases in activity coefficient of the state Debye – Huckel ^[1] have given a theory ion-ion interactions of the dilute solution. The electrostatic forces present among the charged solute species in an aqueous electrolyte solution rely on the charges of the species (higher the charges, greater the electrostatic force) and the total concentration of the species, both these factors are included in the ionic strength of an aqueous solution.

In the present paper describe, the interactions of Cu (II), Tb (III) and Nd(III) metal ions with ligand 3 - (4 - chlorophenyl) - 4 - (3 - pyridine) - 5 - (2 - hydroxy phenyl) - pyrazole at various ionic strengths in 70% dioxane-water medium have been investigated by Calvin-Bjerrum p^H metric technique at 27 °C. The various ionic strength data were used to study the correct mechanism of the complexation reaction. The thermodynamic properties of electrolyte solutions can be studied from long range interactions forces between ion and solvent molecules. Some studies on stability constant were reported ^[2, 3]. Recently, Ramteke *et al* ^[4] have studied the stability constants of complexes of chloro substituted pyrazoles and pyrazoline with Cu (II), Ni (II), Co (II) and Nd (III) metal ions in 70% dioxane-water mixture at 0.1 M ionic strength. Yadav *et al* ^[5] have studied the formation constants and thermodynamic parameters of some tri-ligand quaternary complexes (1:1:1:1; MLL'L'') using potentiometric technique.

Correspondence:
A.A. Ramteke
Department of chemistry,
Govt. V.I.S.H.,
Amravati 444604 (M.S) India.

2. Materials and Methods

2.1. Theory

A concept introduced by G.N. Lewis and Randall [6] in 1921, is used for calculating activity coefficients. The ionic strength is obtained by the following formula.

$$IS = \frac{1}{2} \sum Z_i^2 C_i \dots \dots \dots (1)$$

Where, Z_i = the charge (positive/negative) of i^{th} species, C_i = Concentration of i^{th} species and

IS = A quantitative measure of how 'ionic' a solution is.

According to the theory developed by the Debye-Huckel the mean activity coefficient $\log F (\pm)$ of an electrolyte dissociating into cations of valency Z_1 , and anions of valency Z_2 are given by,

$$\log F_{\pm} = - \frac{A |Z_1 Z_2| \sqrt{\mu}}{1 + B a \sqrt{\mu}} \dots \dots \dots (2)$$

Where, A and B involve the absolute temperature and dielectric constant of the medium and 'a' equation due to Guntelberg [7] for aqueous solution assumes to form.

$$\log F_{\pm} = - \frac{A |Z_1 Z_2| \sqrt{\mu}}{1 + \sqrt{\mu}} \dots \dots \dots (3)$$

After Debye-Huckel proposed their theory, Bjerrum suggested much simpler information and his theory develops from the consideration factor which determines the actual ionic association or more particularly the formation of ions pairs under the influence of columbic forces. The long range ions pairs not considered by Bjerrum have been discussed in a careful analysis of the whole theory by Fuoss and Krovs [8]. For slightly charged ions, may represent ionic association as –



Where, C^+ and A^- is the ion pair and CA is an undissociated molecule with non-polar bond.

The former being produced by columbic forces and later by electronic linkage, Bjerrum's theory cannot be expected to be valid if undissociated molecules with non-polar linkages are formed. Equation (3) gives a pair representation of the behavior of a number of, electrolytes up to $\mu = 0.1 \text{ M}$ [9]. At every low value of $\sqrt{\mu}$ i.e. in very dilute solutions, the term $B a \sqrt{\mu}$ will ultimately become negligible as compared to unity and equation (2) will be reduced to as

$$\log f_{\pm} = -A |Z_1 Z_2| \sqrt{\mu} \dots \dots \dots (4)$$

This is Debye-Huckel limiting law, according to which $\log f_{\pm}$ approaches linearly in the square root of concentration at high dilutions.

2.2. Chemicals

The ligand was synthesized by known literature methods [10]. The purity of these compounds was verified by TLC, and structures were confirmed by NMR, IR and melting points. All chemicals were used AR grade like KNO_3 , HNO_3 and NaOH . The stock solution of the ligand 3 – (4 – chlorophenyl) – 4 – (3 – pyridine) – 5 – (2 – hydroxy phenyl) – pyrazole (0.1 M) was prepared by dissolving the requisite quantity of the ligand in a minimum volume of dioxane subsequently diluted to the final volume and this stock solution of ligand was used to prepared the 0.02 M, 0.04 M, 0.06 M, 0.08 M of ionic strength solutions. Nitrates of Cu (II), Tb (III) and Nd (III) metal ions were used to prepare metal solutions (0.01 M) and

standardized by the EDT A titration method as discussed in literature [11]. The ionic strength (0.02, 0.04, 0.06, 0.08 and 0.1 mol/dm^3) was maintained constant by using 1 M potassium nitrate solution. The carbonate free sodium hydroxide solution (0.1057 mol/dm^3) was prepared and standardized by oxalic acid titration method.

2.3. Apparatus and procedure

All pH-metric titration were carried out at 27 °C in an inert atmosphere by bubbling oxygen free nitrogen gas through an assembly containing the electrodes in order to prevent atmospheric oxidation using carbonate free NaOH . The pH of the solution measured using with EQUIP-TRONICS digital pH meter (model EQ-610) equipped with a combined glass electrode and magnetic stirrer (accuracy ± 0.005 units). The instrument could read pH in the range 0.00-14.00 in the steps of 0.005. This pH meter has built in internal electronic voltage supply with temperature compensator covering the range 0 to 100°C. The pH meter was switched on half an hour before starting the titration for the initial warm up of the instruments. Before taking any reading, the electrodes were washed with distilled water and dried with filter paper. The readings were recorded only when the instrument registered a steady value for at least one minute. The pH meter was standardized before each titration with a buffer solution of pH 4.00 and 9.20, prepared from a Qualigens buffer tablets. The following three solutions were titrated separately against standard carbonate free NaOH (total volume 25 mL). a) Free HNO_3 (2.5 ml) + KNO_3 (2.5 mL). b) Solution a + ligand solution (5 mL). c) Solution b + metal solution (1 mL). The ligand was acidified with HNO_3 in a 70% dioxane-water medium and the ionic strength was kept constant by added the KNO_3 . The ligand was titrated against standard NaOH (carbonate free) using Calvin-Bjerrum and Calvin-Wilson pH titration methods [12, 13]. The pH meter reading was taken after fixing interval until a stable reading was obtained and then curves of pH verses ml of alkali were plotted (Fig.1). The proton-ligand constant were calculated from the pH values obtained from the titration using the Irving-Rossotti method [14].

3. Results and Discussion

In the present investigation, the dependence of stability constants on the ionic strength of the medium was examined by taking a fixed concentration of metal nitrates and nitric acid during pH – metric titrations. The systems have been studied at 0.02 M, 0.04 M, 0.06 M, 0.08 M and 0.1 M ($M = \text{mol/dm}^3$) ionic strengths by varying the concentrations of potassium nitrate. In addition to potassium nitrate, the titrating system is contained of ions from nitric acid, metal nitrate and sodium hydroxide. The total ionic strength of the medium is calculated by following expression,

$$\mu = \frac{1}{2} \sum C_i Z_i^2 \dots \dots \dots (5)$$

Where, C_i and Z_i are the concentration and valency of metal ion respectively. The stability constants for the following systems were determined at 0.02 M, 0.04 M, 0.06 M, 0.08 M and 0.1 M ionic strengths, the pK value of ligand 3 – (4 – chlorophenyl) – 4 – (3 – pyridine) – 5 – (2 – hydroxy phenyl) – pyrazole and log K values for the systems 1) Cu (II) – L, 2) Tb (III) – L, 3) Nd (III) – L. The pK and log K values for various systems at various ionic strengths are presented in the table no. 1, 2 and 3. It may be inferred from the experimental data that increases the ionic strength of the system that causes decrease in pK and log K values. Gupta *et al* [15] has determined stability constants of transition metal complexes with

salicylamide at various ionic strengths in 75% methanol-water mixture. The values of stability constants have been found to increase with the decreasing of ionic strength. Recently, Naik *et al* [16] have obtained stability constants of metal complexes of substituted pyrazole with some lanthanide metal ions in 70% dioxane-water mixture. Ionic strength dependence of formation constants, protonation and complexation of aspartic acid with dioxovanadium (V) has been studied by Vadi *et al* [17]. In the present paper, the data of pK and log K values are employed to calculate the thermodynamic constants with the help of Bronsted equation [18]. For the complexation reaction involved ions on the reactant and the product sites, Bronsted equation was used in the form.

$$\log K = \log K^0 + A \Delta Z^2 \sqrt{\mu} \quad \text{----- (6)}$$

$$pK = pK^0 - A \Delta Z^2 \sqrt{\mu} \quad \text{----- (7)}$$

Where, ΔZ^2 is the difference in the square of the charges of product and reactant ion. Newton and Arcand [19] have used a similar formula for the study of complex formed between Ce (III) and sulphate ions. For this purpose, values of pK and log K are plotted against $\sqrt{\mu}$ plots are generally linear up to 0.1 M ionic strength [20]. The data obtained of pK and log K values could be utilized to study thermodynamic dissociation constants at zero ionic strength and to know the mechanism of complexation equilibria. The validity of Bronsted equation for various systems is tested by plotting graphs between pK and log K Vs $\sqrt{\mu}$. The representative graphs for some systems are presented in figures 1 and 4. The plots of pK Vs $\sqrt{\mu}$ gave straight line over entire range of ionic strengths for a ligand and log K Vs $\sqrt{\mu}$ gave slightly deviation in the straight lines over entire range of ionic strengths for a ligand, which shows Bronsted relation is valid for the dissociation equilibria. The values of ΔZ^2 were calculated from the slopes of straight lines. The value of A was taken equal to 0.5161 [21]. The values of the magnitude of Debye Huckel constant and slopes are obtained from each plot. The different possible reactions and observed and expected values of ΔZ^2 for corresponding dissociation or association equilibria are represented in table no. 3. The observed ΔZ^2 values are represented in the table no. 4, in all these cases, are different than expected. These values do not therefore, give conclusive evidence regarding the magnitude of the charge of the reacting species except the information that these are oppositely charged. The variation of pK and log K with $\sqrt{\mu} / (1+\sqrt{\mu})$ gives straight line. The representative graphs for some systems are represented in figure 2, and figure 5. The variation of pK and log K Vs $\sqrt{\mu} / (1+\sqrt{\mu}) - 0.3\sqrt{\mu}$ are represented in representative figure 3, and figure 6. This plot gives linear relationship without any improvement in the magnitude of ΔZ^2 . This discrepancy may be due the fact that the values for closest distance approach 'a' is fixed ($3.33A^0$). Thermodynamic stability constants ($pK^0/\log K^0$) obtained from various plots are listed in table no. 3. It can be seen from above data that the agreement of the thermodynamic constants obtained from various plots for a particular system is approximately the same. Narwade, Naik [22] and Thakare [23] have reported similar thermodynamic constant from various plots for some substituted pyrazoles.

Table 1: Proton – ligand stability constants at various ionic strength for 3 – (4 – chlorophenyl) – 4 – (3 – pyridine) – 5 – (2 – hydroxy phenyl) – pyrazole as a ligand

Ionic strength (μ)	$\sqrt{\mu}$	$\sqrt{\mu}/(1+\sqrt{\mu})$	$\sqrt{\mu}/(1+\sqrt{\mu}) - 0.3\sqrt{\mu}$	p ^K of Ligand
0.02	0.1414	0.1238	0.0813	10.97
0.04	0.2000	0.1666	0.1066	9.84
0.06	0.2449	0.1967	0.1232	8.81
0.08	0.2828	0.2204	0.1355	7.14
0.10	0.3162	0.2402	0.1454	6.18

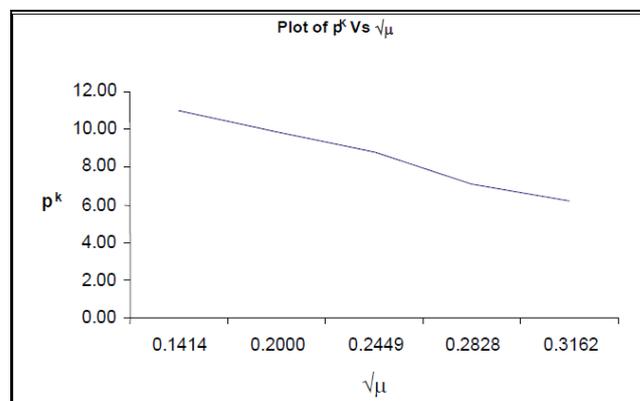


Fig 1: Plot of proton – ligand stability constants against ionic strength of ligand

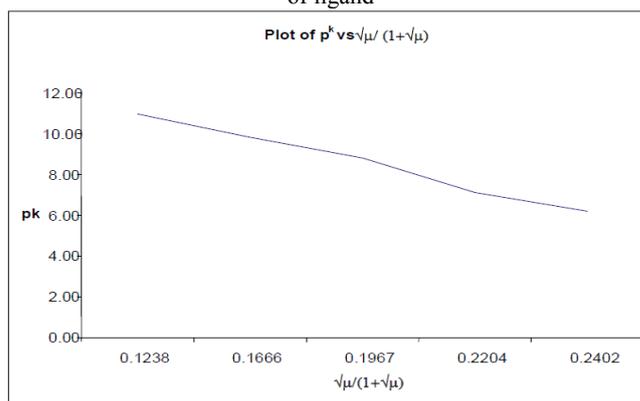


Fig 2: Plot of proton – ligand stability constants against ionic strength of ligand

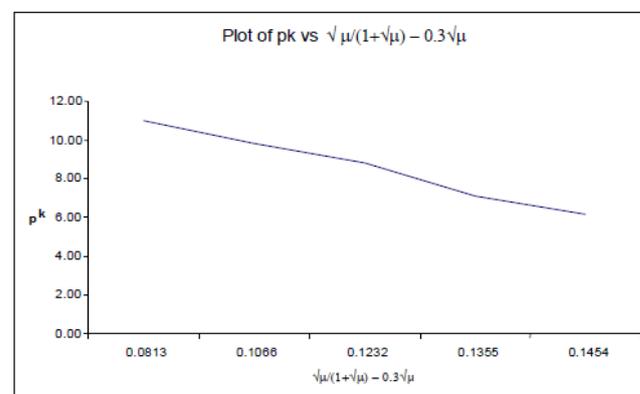


Fig 3: Plot of proton – ligand stability constants against ionic strength of ligand

Table 2: Log K values of Cu (II), Tb (III) and Nd (III) with 3 – (4 – chlorophenyl) – 4 – (3 – pyridine) – 5 - (2 – hydroxy phenyl) – pyrazole as a ligandat various ionic strengths

Ionic strength (μ)	$\sqrt{\mu}$	p^K	Cu (II) – ligand		Tb (III) – ligand		Nd (III) – ligand	
			log K ₁	log K ₂	log K ₁	log K ₂	log K ₁	log K ₂
0.02	0.1414	10.97	8.0864	6.0253	8.2529	6.1469	8.6355	6.4216
0.04	0.2000	9.84	7.6053	6.8435	7.6848	6.8943	7.8241	6.9143
0.06	0.2449	8.81	7.3927	6.8235	7.5740	6.8733	7.6944	6.9143
0.08	0.2828	7.14	6.2068	5.6355	6.2878	5.6656	6.3674	5.3206
0.10	0.3162	6.18	4.7649	4.0719	4.8241	4.1038	4.8543	4.1553

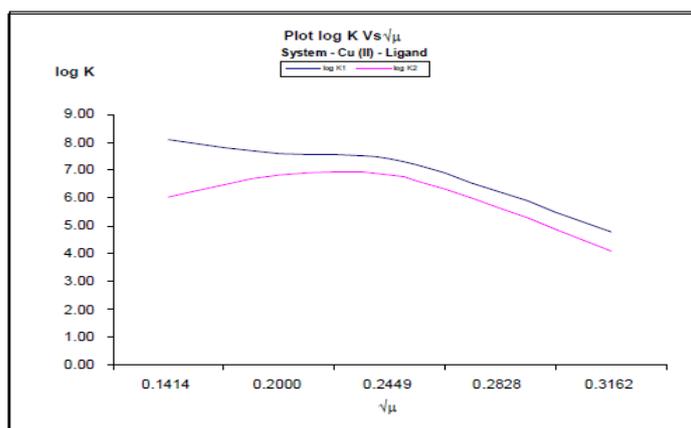


Fig 4: Plot of log K values of complex of Cu (II) with ligand against various ionic strengths of ligand

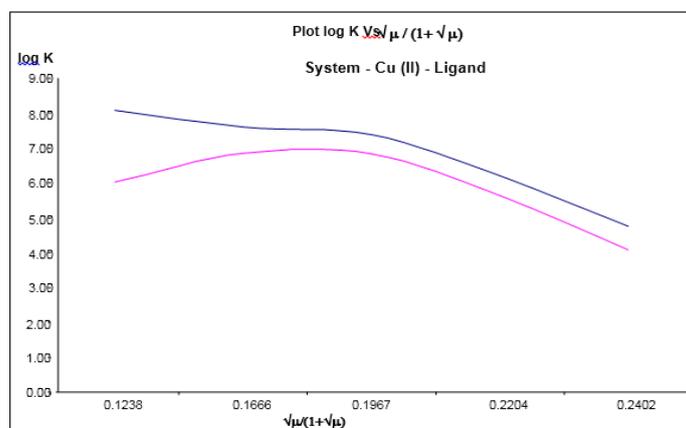


Fig 5 Plot of log K values of complex of Cu (II) with ligand against various ionic strengths of ligand

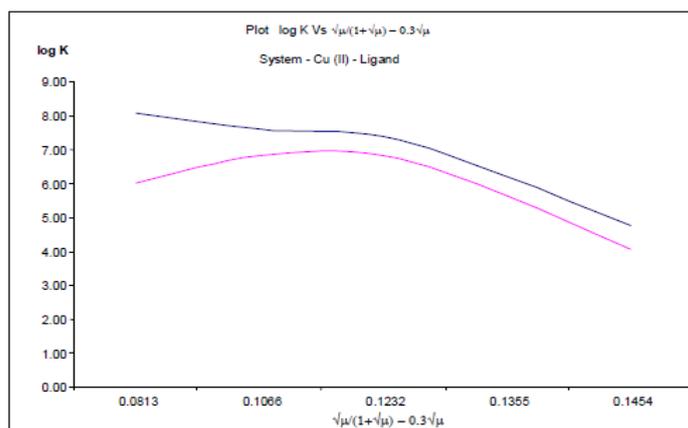


Fig 6 Plot of log K values of complex of Cu (II) with ligand against various ionic strengths of ligand

Table 3: Thermodynamic dissociation and association constants (pK^0 and $\log K^0$) at zero ionic strength of complexes of Cu (II), Tb (III) and Nd (III) metals with 3 – (4 – chlorophenyl) – 4 – (3 – pyridine) – 5 - (2 – hydroxy phenyl) – pyrazole as a ligand (L)

Plots	pK^0	Cu (II) \rightarrow L		Tb (III) \rightarrow L		Nd (III) \rightarrow L	
		$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$
p^k Vs $\sqrt{\mu}$	11.45	--	--	--	--	--	--
p^k Vs $\sqrt{\mu}/(1+\sqrt{\mu})$	11.50	--	--	--	--	--	--
p^k Vs $[\sqrt{\mu}(1+\sqrt{\mu})]-0.3\sqrt{\mu}$	11.40	--	--	--	--	--	--
$\log K_1$ Vs $\sqrt{\mu}$	--	8.37	--	8.63	--	9.10	--
$\log K_1$ Vs $\sqrt{\mu}/(1+\sqrt{\mu})$	--	8.39	--	8.59	--	9.09	--
$\log K_1$ Vs $[\sqrt{\mu}(1+\sqrt{\mu})]-0.3\sqrt{\mu}$	--	8.37	--	8.58	--	9.18	--
$\log K_2$ Vs $\sqrt{\mu}$	--	--	5.74	--	5.80	--	6.12
$\log K_2$ Vs $\sqrt{\mu}/(1+\sqrt{\mu})$	--	--	5.71	--	5.71	--	6.11
$\log K_2$ Vs $[\sqrt{\mu}(1+\sqrt{\mu})]-0.3\sqrt{\mu}$	--	--	5.58	--	5.69	--	6.17

Table 4: Probable Reaction Mechanism and Determination of ΔZ^2 values for ligand 3 – (4 – chlorophenyl) – 4 – (3 – pyridine) – 5 - (2 – hydroxy phenyl) – pyrazole

System	Constants	Reaction Equilibrium	ΔZ^2	
			Expected	Observed
Ligand – L	pK	$HL \leftrightarrow H^+ + L^-$	2.00	-11.12
Cu (II) \rightarrow L	$\log K_1$	$L^- + Cu^{2+} \leftrightarrow (CuL)^+$	- 4.00	-49.28
	$\log K_2$	$(CuL)^+ + L^- \leftrightarrow CuL_2$	- 2.00	-3.82
Tb (III) \rightarrow L	$\log K_1$	$L^- + Tb^{3+} \leftrightarrow (TbL)^{2+}$	- 6.00	-54.87
	$\log K_2$	$(TbL)^{2+} + L^- \leftrightarrow (TbL_2)^+$	- 4.00	-34.29
Nd (III) \rightarrow L	$\log K_1$	$L^- + Nd^{3+} \leftrightarrow (NdL)^{2+}$	- 6.00	-52.08
	$\log K_2$	$(NdL)^{2+} + L^- \leftrightarrow (NdL_2)^+$	- 4.00	-47.68

4. Conclusion

In this paper, the obtained data shows that, the value of pK and $\log K$ were found to decrease with increasing the ionic strength. It is found value of pK value decrease with an increase in the ionic strength that is in accordance with the Debye-Huckel theory. The systems of complexes of Cu(II), Tb (III) and Nd (III) metal ions with ligand (L) 3 – (4 – chlorophenyl) – 4 – (3 – pyridine) – 5 - (2 – hydroxy phenyl) – pyrazole at various ionic strength (The systems has been studied at 0.02, 0.04, 0.06, 0.08 and 0.10 mol/dm³ ionic strengths by varying the concentrations of potassium nitrate, the titrating system contained ions form acid, metal nitrate and sodium hydroxide) in dioxane-water mixture medium have been investigated by the Calvin-Bjerrum pH metric technique at 27 °C. The $\log K$ values for various systems at various ionic strengths are presented in the Table no 2. The ionic strength data was used to study the correct mechanism of the complexation shows in the table no. 4. It may infer from the experimental data that increases the ionic strength of the system and causes a decrease in $\log K$ values. The thermodynamic dissociation constants are evaluated at $\sqrt{\mu}=0$ from plots $\sqrt{\mu}$ vs $\log K$ showed in the representative figure no. 4.

5. Acknowledgement

The authors are thankful to the Govt. Vidarbha Institute of Science and Humanities, Amravati, Department of chemical technology, S.G.B. University, Amravati (M.S) India for providing laboratory facilities during the research work.

6. References

- Debye P, Huckel E, Physik Z, 1923; 24:185.
- Narwade ML, Gudadhe, Jamode VS, Acta. Ciencia Indica, 1985; XI C, 4: 234.
- Gupta RD, Manku GS, Bhat AN, Jain BD *et al*, J. of the less common metals, 1969; 18(2):139-147; 2003.

- Ramteke AA, Narwade ML. Archives of Applied Science Research 2013; 5(1):231-237.
- Yadav SS, Saxena RS. J Chem Ind Chem Soc 2009; 86(2):168–170.
- Lewis GN, Randoll M. J Am Chem Soc 1921; 43:1112.
- Guntelberg H. Z Phys Chem 1926; 123:199.
- Fuoss RM, Kravs CA. J Am Chem Soc 1933; 55:1919.
- Robinson RA, Stoke RH. Electrolyte Solutions, Edn 2, Butterworths 1959, 230.
- Bhuyar AD. Ph. D. Thesis in Chemistry SGB Amaravati University, Amaravati, 2008.
- Naik AB, Narwade ML. 2009; 35(12):932-937.
- Arrhenius S. Z Phys Chem 1887; 1:631.
- Ackermann T. Discuss Faraday Soc 1957; 24:180.
- Maringna C. Ann Chem (Paris) 1871; 22:415.
- Gupta A, Pannu BS. Asian J Chem 1994; 6(1):174.
- Naik AB, Narwade ML. Russian J Coordination chem 2009; 35(12):932-937.
- Vadi M, Zare Z, Nasiri Kh. Russian J of In org Chem 2007; 52(5):816-819.
- Amin ES. Solvent effects on reaction rates and mechanism. Academic Press, New York, 1966, 24.
- Newton TW, Archand GM. J Am Chem Soc 1953; 2449.
- Laidter EJ. "Chemical Kinetics" McGraw Hill Book Co., 1965, 221.
- Robinson RA, Stoke RH. "Electrolyte Solutions" Edn 2, Butterworths, 1959, 468.
- Naik AB, Ph D. Thesis in chemistry, SGB Amaravati Univ Amaravati 2007.
- Thakare VJ, Ph D. Thesis in chemistry, SGB Amaravati Univ Amaravati 2007.