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INFLUENCE OF IONIC STRENGTH ON THERMODYNAMIC CONSTANT OF COMPLEXES OF CHLORO SUBSTITUTED PYRAZOLE WITH Cu (II), Tb (III), and Nd (III) METAL IONS

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ABSTRACT

In this paper, study 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 – (2 – furanoyl) – 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 27^0C. The obtained data was used to study the correct mechanism of the complexation reaction and the obtained results were used to study the thermodynamic constant.

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

INTRODUCTION

The nature of ionic strength is one of the important factors, which influences metal ligand stability constants. 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 ions and solvent molecules is necessary. 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, The theory ion -ion interactions of the dilute solution reported by Debye – Huckel[1]. The net effect of inter ionic attractions and repulsion is decrease the free energy of solute as compared to that of uncharged particles and hence activity coefficient decreases. 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 this research work, study the interactions of Cu (II), Tb (III) and Nd (III) metal ions with ligand 3-(4-Chlorophenyl) -4- (2- Furanoyl)- 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 27^0C. The various ionic strengths data was used to study the thermodynamic properties of electrolyte solutions can be studied from long range interactions forces between ion and solvent molecules. Recently, Ramteke *et al* have studied the stability constants of complexes of chlorosubstituted pyrazoles and pyrazoline with Cu (II), Ni (II), Co (II) and Nd (III) metal ions in 70% dioxane-water mixture at 0.1M ionic strength[2]. Yadav *et al* have studied the formation constants and thermodynamic parameters of some tri-ligand quaternary complexes using potentiometric technique[3].

EXPERIMENTAL

Chemicals

The ligand was synthesized by known literature methods[4]. 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-(2 – Furanoyl) – 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 EDTA titration method as discussed in literature[5]. 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.

Apparatus and procedure

All pH-metric titration were carried out at 27 ^{0}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 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^{0}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 minutes. 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.[6, 7] The pH meter reading were taken after fixed interval until 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[8].

RESULTS AND DISCUSSION

A concept introduced by G.N. Lewis and Randall in 1921, is used for calculating activity coefficients[9]. The ionic strength is obtained by the following formula.

$$IS = \frac{1}{2}\ Zi^2Ci \qquad (1)$$

Where, Zi = the charge (positive/negative) of ith species, Ci = Concentration of ith species and IS = A quantitative measure of how 'ionic' a solution is.

In the present investigation, the dependence of stability constants on the ionic strength of the medium was examined by taking 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=mol/dm^3) ionic strengths by varying the concentrations of potassium nitrate. The total ionic strength of the medium is calculated by following expression-

$$\mu = \frac{1}{2}\ \Sigma Ci\ Zi^2 \qquad (2)$$

Where, Ci and Zi are the concentration and valency of metal ion respectively. The stability constants for the 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 – (2 – furanoyl) – 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-1, 2 and 3. The results clearly show that increases the ionic strength of the system that causes decrease in pK and log K values. Recently, Ionic strength dependence of formation constants, protonation and complexation of aspartic acid with dioxovandium (V) has been studied by Vadi *et al*[10]. Ramteke and Narwade reported the stability constant of chlorosubstituted pyrazoles with Cu (II) Nd (III) and Tb (III) metal ions at 0.1 M Ionic strength by spectrophotometric technique and show the good agreement with the pH metric technique[11]. In this paper, the data of pK and log K values are employed to calculate the thermodynamic constants with the help of Bronsted equation[12]. Since the complexation reaction involved ions on the reactant and the product sites, Bronsted equation was used in the form-

$$\log K = \log K^0 + A\,\Delta Z^2 \sqrt{\mu} \qquad (3)$$

$$pK = pK^0 - A\,\Delta Z^2 \sqrt{\mu} \qquad (4)$$

Where, ΔZ^2 is the difference in the square of the charges of product and reactant ion.

Newton and Arcand have used a similar formula for the study of complex formed between Ce (III) and sulphate ions[13]. 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[14]. 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 slopes of straight lines. The value of A was taken equal to 0.5161[15].

The values of magnitude of Debye Huckel constant and slopes are obtained from each plot. In the different possible reactions, observed and expected values of ΔZ^2 for corresponding dissociation or association equilibria are represented in Table-3. The observed ΔZ^2 values are represented in the Table-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 value for closest distance approach 'a' is fixed ($3.33A^0$). Thermodynamic stability constants ($pK^0/\log K^0$) obtained from various plots is listed in Table-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 and Thakare have reported similar thermodynamic constant from various plots for some substituted pyrazoles[16, 17].

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

Ionic strength (μ)	√μ	√μ/(1+√μ)	√μ/(1+√μ) - 0.3√μ	p^K of Ligand
0.02	0.1414	0.1238	0.0813	11.58
0.04	0.2000	0.1666	0.1066	10.44
0.06	0.2449	0.1967	0.1232	9.96
0.08	0.2828	0.2204	0.1355	9.74
0.10	0.3162	0.2402	0.1454	8.46

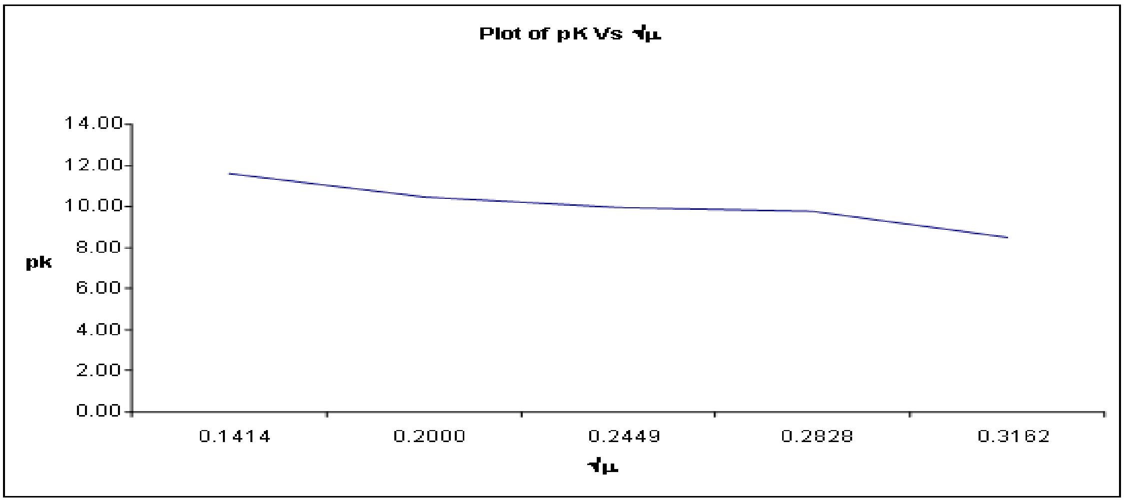

Fig.-1

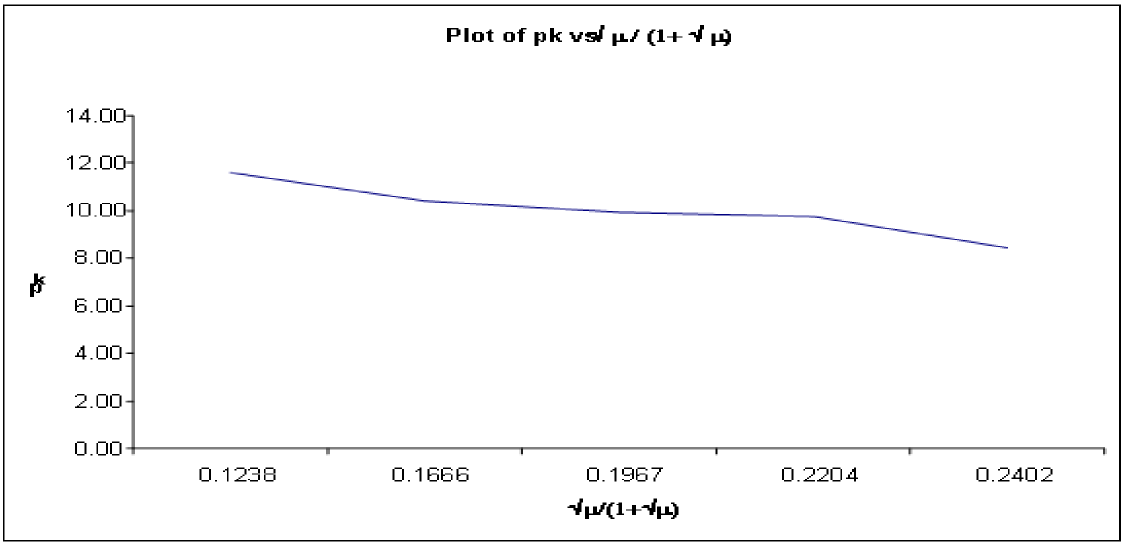

Fig.-2

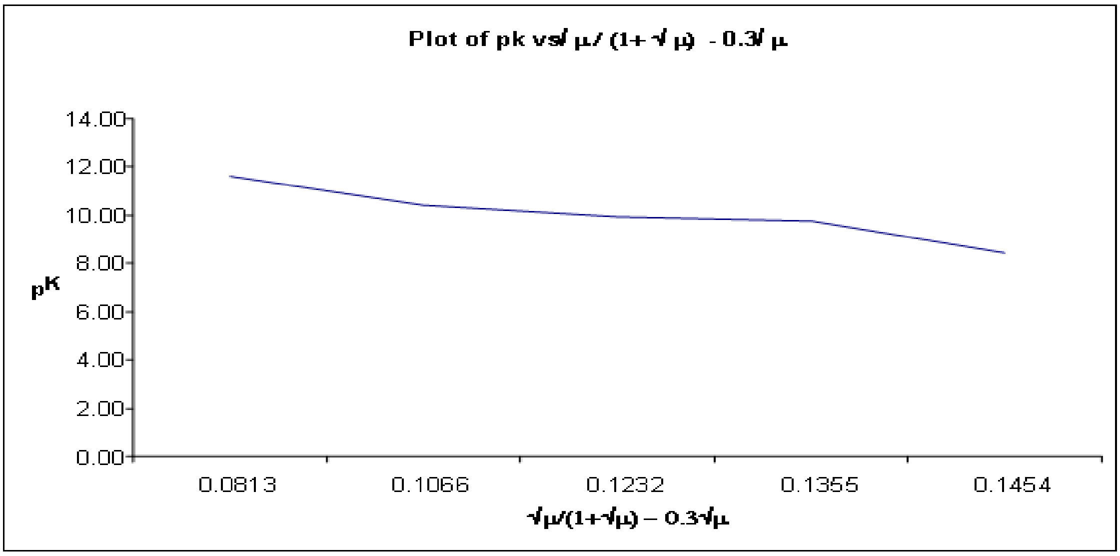

Fig.-3

Table-2: Log K values of Cu (II), Tb (III) and Nd (III) with 3 – (4 – Chlorophenyl) – 4 – (2 – Furanoyl) – 5 – (2 – hydroxy phenyl) – pyrazole as a ligand at 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	11.58	10.5855	8.4340	10.6551	8.6542	10.8041	8.8235
0.04	0.2000	10.24	9.9750	8.3345	10.0334	8.4440	10.1931	8.5038
0.06	0.2449	9.96	8.3243	6.7340	8.4133	6.7745	8.5453	6.8439
0.08	0.2828	9.74	8.6243	6.9841	8.7348	7.0334	8.8041	7.0969
0.10	0.3162	8.46	7.8842	6.2430	7.7962	6.2945	8.0645	6.3541

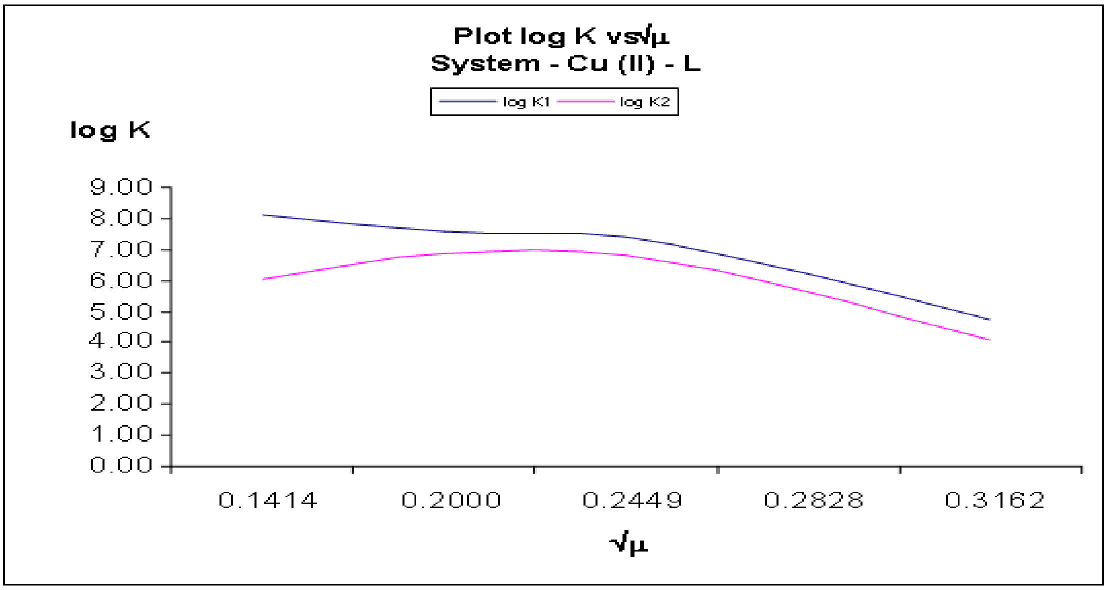

Fig.- 4

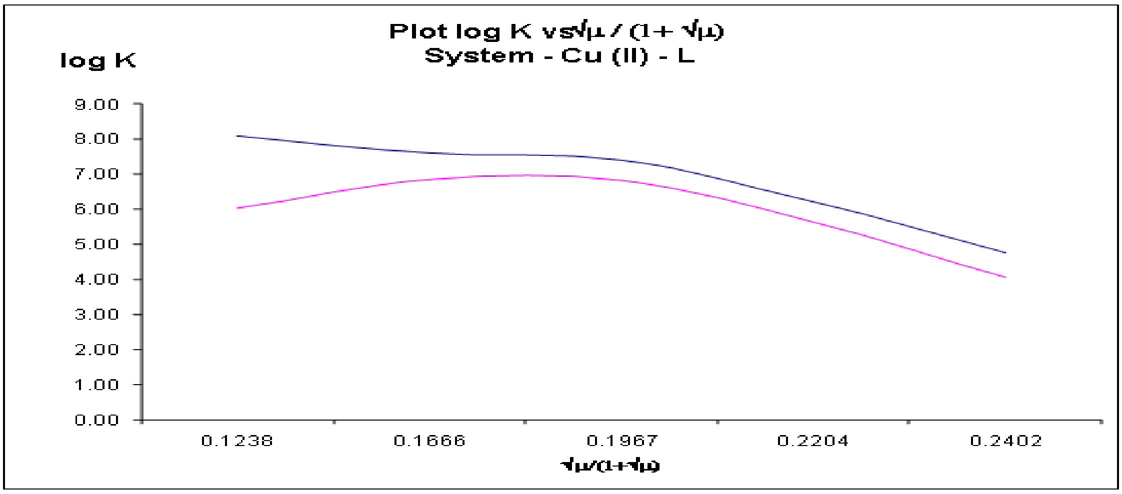

Fig.-5

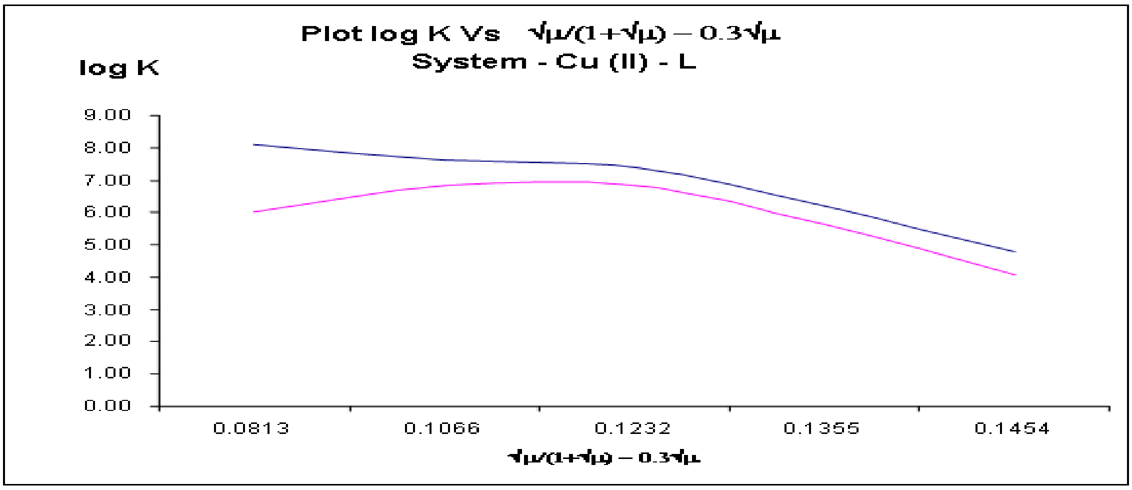

Fig.-6

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 – (2 – Furanoyl) – 5 – (2 – hydroxy phenyl) – pyrazole as a ligand (L)

Plots	pK^0	Cu (II) → L		Tb (III) → L		Nd (III) → L	
		$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$
p^K Vs $\sqrt{\mu}$	11.85	--	--	--	--	--	--
p^K Vs $\sqrt{\mu}/(1+\sqrt{\mu})$	12.06	--	--	--	--	--	--
p^K Vs $[\sqrt{\mu}(1+\sqrt{\mu})]-0.3\sqrt{\mu}$	12.05	--	--	--	--	--	--
$\log K_1$ Vs $\sqrt{\mu}$	--	8.31	--	8.59	--	9.16	--
$\log K_1$ Vs $\sqrt{\mu}/(1+\sqrt{\mu})$	--	8.52	--	8.60	--	9.19	--
$\log K_1$ Vs $[\sqrt{\mu}(1+\sqrt{\mu})]-0.3\sqrt{\mu}$	--	8.49	--	8.60	--	9.20	--
$\log K_2$ Vs $\sqrt{\mu}$	--	--	7.54	--	7.55	--	7.59
$\log K_2$ Vs $\sqrt{\mu}/(1+\sqrt{\mu})$	--	--	7.72	--	7.45	--	7.81
$\log K_2$ Vs $[\sqrt{\mu}(1+\sqrt{\mu})]-0.3\sqrt{\mu}$	--	--	7.80	--	7.62	--	8.28

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

System	Constants	Reaction Equilibrium	ΔZ^2	
			Expected	Observed
Ligand – L	log K_1	$L^- + Cu^{2+} \leftrightarrow (Cu)^+$	- 4.00	-72.92
Cu (II) → L	log K_2	$(CuL)^+ + L^- \leftrightarrow CuL_2$	- 2.00	-62.18
	log K_1	$L^- + Tb^{3+} \leftrightarrow (TbL)^{2+}$	- 6.00	-67.40
Tb (III) → L	log K_2	$(TbL)^{2+} + L^- \leftrightarrow (TbL_2)^+$	- 4.00	-59.42
	log K_1	$L^- + Nd^{3+} \leftrightarrow (NdL)^{2+}$	- 6.00	-64.17
Nd (III) → L	log K_2	$(NdL)^{2+} + L^- \leftrightarrow (NdL_2)^+$	- 4.00	-46.91
	log K_1	$L^- + Cu^{2+} \leftrightarrow (Cu)^+$	- 4.00	-72.92

CONCLUSION

The found result of pK and log K values, the decrease with increasing the ionic strength and this is in accordance with the Debye-Huckel theory. The log K values for various systems (i.e. Cu (II), Tb (III) and Nd (III) metal ions with ligand (L) 3 – (4 – Chlorophenyl) – 4 – (2 – furanoyl) – 5 – (2 – hydroxy phenyl) – pyrazole) at various ionic strengths are presented in the Table no 2. The obtained data was used to study the correct mechanism of the complexation shows in the table no. 4. It may inferred 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-4.

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