



**RESEARCH ARTICLE**

**STUDIES ON INTERACTION BETWEEN CU(II), NI(II) AND CO(II) METAL IONS AND HYDROXY-SUBSTITUTED CHALCONEIMINES, AT 0.1 M IONIC STRENGTH PH METRICALLY**

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**ABSTRACT**

The interaction of Cu(II), Ni(II) And Co(II) metal ions with 2-hydroxy -5-bromo-N-(Phenyl)chalconeimines (L<sub>1</sub>) and 2-hydroxy -5-Bromo - N- (O- nitro phenyl ) Chalconeimine (L<sub>2</sub>) have been studied at 0.1 M ionic strength (26 ± 0.1 °C) in 70% Dioxane- water mixture by Bjerrum method as adopted by Calvin Wilson. It is observed that Cu(II), Ni(II) And Co(II) metal ions form 1:1 and 1:2 complexes with ligands (L<sub>1</sub> & L<sub>2</sub>). The data obtained were used to estimate and compare the value of proton- ligand stability constant (pK) and metal- ligand stability constant (log k). The effect of substituent was studied from estimated data (pk & logk).

**Key words:**

2-Hydroxy-5- Bromo-  
substituted chalconeimine,  
Dioxane – water mixture,  
stability constant.

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**INTRODUCTION**

Considerable research work has been done in the past, on the study of complexes [1, 2]. The studies in metal-ligand complexes in solution of a number of metal ions with carboxylic acids, oximes, phenols etc. would be interesting which throw light on the mode of storage and transport of metal ions in biological kingdom. With the view to understand the bi-inorganic chemistry of metal ions, Banerjee *et al* [3] have synthesized a number of mixed-ligand alkaline earth metal complexes. Bjerrum's [4] dissertation has taken the initiative to develop the field. Metal complexation not only brings the reacting molecules together to give activated complex [5] but also polarized electrons from the ligand towards the metal. The relation between stability and basicity of the ligands is indicated by the formation constant and free energy change value. Bulkier group increases the basicity of ligands as well as stability. The stability of complexes is determined by the nature of central metal atom and ligands. The stability of complexes is influenced by the most important characteristics like degree of oxidation, radius and electronic structure. Irving and Williams [6] had studied the order of stability of metal complexes of transition metal ions by

comparing the ionic radius and second ionisation potential of metal ions, as it is valid for most nitrogen and oxygen donor ligands. Narwade *et al* [7] have investigated metal-ligand stability constants of some lanthanides with some substituted sulphonic acids. Many workers [8-23] have reported their results on metal-ligand stability constants. Bodkhe *et al* [24] have reported the metal-ligand stability constants of some b-diketones. Tekade *et al* [25] investigated stability constants of some substituted pyrazolines, isoxalline and diketone. Speciation of binary complexes of Ca (II), Mg (II) and Zn (II) with L-glutamic acid in DMSO water Mixtures has been studied [26]. Thakur *et al* [27,28] have studied the interactions of hydroxy-1-3-propanediones with Cr(III) and La(III) metal ions and Metal-ligand stability constants of Th(III), Sm(III), and Nd(III) and Pr(III) metal ion complexes with 2-mercapto-4-substituted phenyl-6-substituted phenyl pyrimidines at 0.1 M ionic strength pH metrically . Narwade *et al* [29] have investigated the Metal-ligand Stability Constants of Cu (II) Complexes and Measurement of Viscosity, Refractivity Index with some substituted Pyrazoles and Diketones at 0.1M Strength. Shivaraj *et al* [30] have studied formation constants and thermodynamic parameters of bivalent metal ion complexes with 3-amino-5-ethyl isoxazole Schiff bases and N, N, N, O

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and O, O donor ligands in solution. Thakur *et al* [31, 32] have studied The Influence of dielectric constants of medium on the complex equilibria of substituted hydroxy-1, 3-propanediones with Cr (III) metal ions and Studies on Interaction Between Cu (II), Cr (II) and Ni (II) Metal Ions At 0.1 M Ionic Strength pH metrically. Recently Tayade *et al* [33] have studied the interactions between divalent transition metal ions and some substituted imidazolinone at 0.1 ionic strength pH metrically. In present work an attempt has been made to study the interaction between Cu(II), Ni(II) and Co(II) and substituted hydroxyl chalconeimines, at 0.1 M ionic strength, pH metrically in 70 % dioxane water mixture.

### Experimental Section

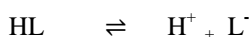
The chemicals used in the present work were of AR grade. Substituted hydroxy **chalconeimines**, (ligand 1 & 2) were synthesized by literature method in laboratory and their purity was checked by IR, NMR and M.P. techniques before used. The solutions of ligands were prepared in purified 70 % dioxane-water mixture and standardized by pH metric technique. Systronic microprocessor based instrument with accuracy  $\pm 0.01$  units with glass and saturated calomel electrode as used for the titrations. It was calibrated by buffer solution of pH 7.00 and 9.20 at  $28 \pm 0.1$  OC, before processing the titrations. Titrations were carried out in an inert atmosphere by bubbling a constant flow of nitrogen gas. The experimental procedure involved the titrations of:

1. Free acid HClO<sub>4</sub> (0.01 M)
2. Free acid HClO<sub>4</sub> (0.01 M) and ligand (20 x 10<sup>-4</sup> M)
3. Free acid HClO<sub>4</sub> (0.01 M) and ligand (20 x 10<sup>-4</sup>) and metal ion (4 x 10<sup>-4</sup> M) against standard NaOH solution.

The ionic strength of all the solutions was maintained constant (0.1 M) by adding appropriate amount of NaClO<sub>4</sub> solution. All the titrations were carried out in 70 % dioxane-water mixture and the reading were recorded for each 0.1 ml addition. The graphs of volume of alkali (NaOH) against pH were plotted.

### RESULT AND DISCUSSION

The extent of deviation may be the dissociation of -OH group. Substituted hydroxy Chalconeimines, may be considered as a monobasic acid having one replaceable H<sup>+</sup> ion from phenolic -OH group and can be represented as-HL. The dissociating equilibria can be shown as



By the law of mass action, we have,

$$K = \frac{[H^+][L^-]}{[HL]} \quad \text{----- (1)}$$

Where, the quantities in bracket denotes the activities at species at equilibrium. The titration data were used to construct the curves [acid curve (A), acid + ligand curve (A+L) and acid +

ligand + metal ion curve (A+L+M)] between volumes of NaOH against pH. The proton-ligand formation number  $n_A$  were calculated by Irving and Rossotti expression (Table1)

$$n_A = \frac{(E_0+N)(V_2-V_1)}{(V_0+V_1)T_L^0} \quad \text{-----(1)}$$

where  $n$  denotes the number of dissociable protons, N is the concentration of sodium hydroxide (0.145 mol.dm<sup>-3</sup>), (V<sub>2</sub>-V<sub>1</sub>) is the measure of displacement of the ligand curve relative to acid curve, where V<sub>2</sub> and V<sub>1</sub> are the volume of alkali added to reach the same pH reading to get accurate values of (V<sub>2</sub>-V<sub>1</sub>): the titration curves were drawn on an enlarged scale: E<sub>0</sub> and T<sub>L</sub><sup>0</sup> are the resultant concentration of perchloric acid and concentration of Ligand, respectively. V<sub>0</sub> is the initial volume of reaction mixture (50 cm<sup>3</sup>). Proton-Ligand stability constant pk values (Table 1) of Ligand were calculated by algebraic method point wise calculation and also estimated from formation curves  $n_A$  Vs pH (Half integral method) by noting pH at which  $n_A = 0.5$  [Bjerrum 1957]. Metal-Ligand stability constants (log k) (Table 2&3) were determined by the half integral method by plotting  $n$  Vs pL. The experimental  $n$  values determined using expression

$$n = \frac{(E_0+N)(V_3-V_2)}{(V_0+V_2)T_M^0} \quad \text{-----(2)}$$

Where N, E<sub>0</sub>, V<sub>0</sub> and V<sub>2</sub> have same significance as in equation (1), V<sub>3</sub> is the volume of NaOH added in the metal ion titration to attain the given pH reading and T<sub>M</sub><sup>0</sup> (4 x 10<sup>-4</sup> mol dm<sup>-3</sup>) is the concentration of metal ion in reaction mixture.

**Table 1** Proton-Ligand stability constants (pK)

Sr.No.	System	pK	
		Half Integral method	Pointwise Calculation
1.	L <sub>1</sub> : 2'-hydroxy-5'-Bromo-N-(phenyl)Chalconeimine[HBNPCI]	10.4930	10.3170
2.	L <sub>2</sub> : 2'-hydroxy-5'-Bromo-N-(O-nitro-phenyl)Chalconeimine[HBN2NPCI]	6.9883	6.0000

**Table 2** Metal-ligand stability constants (log K)

System	Metal Ligand Stability Constants	
	log K1	log K2
Cu(II)- ligand - 1	10.6708	9.7558
Ni (II)-ligand-1	10.6156	9.5309
Co (II) - ligand -1	9.4798	4.9878
Cu(II) - ligand - 2	7.0314	6.5885
Ni (II)-ligand -2	6.3881	6.0244
Co (II) - ligand - 2	6.7834	5.9315

**Table 3** Metal-ligand Stability Constants (log K)

System	Metal Ligand Stability Constants	
	Log K <sub>1</sub> - log K <sub>2</sub>	log K <sub>1</sub> / log K <sub>2</sub>
Cu(II)- ligand - 1	0.9150	1.0938
Ni(II) - ligand - 1	1.0847	1.1138
Co(II) - ligand - 1	4.492	1.9005
Cu(II) - ligand - 2	0.4429	1.0672
Ni(II) - ligand - 2	0.3637	1.0637
Co(II) - ligand - 2	0.8519	1.1437

## CONCLUSION

From the titration curves, it is observed that the departure between (acid + ligand) curve and (acid + ligand + metal) curve for all systems started from pH = 2.9 this indicated the commencement of complex formation. Also change in colour from yellow to orange in the pH range from 3.9 to 9.6 during titration showed the complex formation between metal and ligand.

The order of pK values of ligands is found to be as pK ligand (L<sub>1</sub>). > pK ligand (L<sub>2</sub>).

The decrease in pK value of ligand (L<sub>2</sub>) is attributed to presence of electron withdrawing –NO<sub>2</sub> group.

From the table 2 and 3, it is observed that the difference between log K<sub>1</sub> and log K<sub>2</sub> values are not sufficiently large that indicates the simultaneous formation of complex between metal ion and ligand. The values of log K<sub>1</sub> and log K<sub>2</sub> (table 2) for Cu(II)-L<sub>1</sub>, Co (II)-L<sub>1</sub>, Ni (II)-L<sub>1</sub> complexes are comparatively higher than Cu (II)-L<sub>2</sub>, Co (II)-L<sub>2</sub> and Ni (II)-L<sub>2</sub>. It indicates that Cu (II), Co (II), Ni (II) forms more stable complexes with ligand (L<sub>1</sub>) than complexes with ligand (L<sub>2</sub>).

The higher value of ratio (log K<sub>1</sub> / log K<sub>2</sub>) for Co (II)-L<sub>1</sub> and Ni (II)-L<sub>1</sub> and CO-L<sub>2</sub> ligand (L<sub>1</sub> and L<sub>2</sub>) complexes indicate the more stepwise complex formation as compare to Cu (II)-L<sub>1</sub> and Ni (II)-L<sub>2</sub> complexes.

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