

# STUDIES IN STABILITY OF COMPLEXES OF SUBSTITUTED THIOCARBAMIDO PHENOLS WITH Cu(II), Co(II), Cd(II) AND Ni(II) IN 65% ETHANOL-WATER MIXTURES.

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## Abstract

The solution studies the proton–ligand stability constant  $pK$  and metal ligand stability constants  $\log k$  of binary (1:1) complexes of Cu(II), Co(II), Cd(II) and Ni(II) with substituted thiocarbamido phenols have been studied at 0.1 M ionic strength in 65% ethanol-water mixture by Bjerrum method as adopted by Calvin and Wilson. It is observed that Cu(II), Co(II), Cd(II) and Ni(II) metal ions form 1:1 and 1:2 complexes with ligands (L1 & L3). The information acquired was used to estimate and compare the values of proton –ligand stability constant ( $pK$ ) and metal-ligand stability constants ( $\log k$ ). The effects of substituents were studied from the evaluated information ( $pK$  and  $\log k$ ).

**Key Words :** Substituted thiocarbamidophenols, stability constant, pH-metry

## Introduction

In organic chemistry, from many years new compounds has been discovered by many researchers and their co-workers. Mostly hetrocyclic, benzonoide and non-benzonoide molecules containing compounds achieve great importance in medicinal, pharmaceutical, industrial and agricultural fields. Now-a-days number of researchers used various research methods and techniques to study the physical and chemical properties of newly synthesized compounds. Recently aminophenol is reacted with various isothiocyanates to obtained 2-phenyl thiocarbamidophenol (L<sub>1</sub>) and 2-p-chlorophenyl thiocarbamidophenol (L<sub>2</sub>) respectively. The study of Cu(II), Ni(II) and Zn(II) metal complexes with new Schiff bases contain cyclobutane and thiazole groups in 60% dioxane-water mixture pH-metrically by Y.Altun *et al*<sup>(1)</sup>. The knowledge of stability constant of complex is foremost requirement to study the co-ordination compound in solution and to study the stability constant, metal-ligand reaction in water and biological system<sup>2</sup> is determined. Larson<sup>3</sup> examined the linear relationship between the stability constant of silver (I) ion complex and organic amines. The structure, reactivity and analytical application of complexes can be explained by measuring the stability constant. When the reacting molecules interact with metal ion to form complex then the formation constant and free energy changes explain the relationship between stability and basicity of ligands. The stability and basicity of ligands increases due to presence of bulky group in the complex. The high charge and the small size of ligand lead to the formation of stable complexes. The stability of complexes is greatly increased by chelating ligands. This is known as chelate effects. The chelating ligand forms stable complex. Thus larger value of stability constant ( $k$ ) is favored by larger negative

enthalpy and positive entropy charges.  $Pk_a$  values of new phenacyl piperidine derivative in aqueous medium at room temperature by S.Zafar *et al*<sup>4</sup>. J.Pathan *et al*<sup>5</sup> investigated stability constant of metal complexes by pH-metric method. To eliminate unwanted and toxic metal from living organism chelating agents are very useful factor in biological system. This gives importance to study of determination of stability constant of metal complexes. Thermo dynamical stability of complexes of rare earth metal ions with substituted pyrazole was studied by A.B.Naik and M.L.Narwade<sup>6</sup>. Tayade *et al*<sup>7</sup> had studied the stability constant of Cu(II) chelates with some substituted s-triazines. D.T.Tayade and A.B.Wadekar<sup>8</sup> investigated the stability of complexes of substituted thiocarbamidonaphthols with different transitions metal ions in 65% mix solvent media. All these things are taken into consideration this research scheme is designed. In this present work, an attempt has been made to study the interactions between Cu(II), Cd(II), Co(II) and Ni(II) and 2-phenylthiocarbamidophenol ( $L_1$ ) and 2-p-chlorophenyl thiocarbamidophenol ( $L_2$ ) at constant ionic strength pH-metrically in 65% ethanol water mixtures.

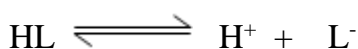
### Experimental Section

In this research work all AR grade chemical are used. In the laboratory the ligands ( $L_1$ ) and ligands ( $L_2$ ) were synthesized by above instructions. Required amount of ligand was dissolved in 65% ethanol water mixture to form the stock solution of ligand.

### General Procedure

#### Types of Titrations

- i) Perchloric acid ( $1 \times 10^{-2}$  M) {Free Acid},
- ii) Perchloric acid ( $1 \times 10^{-2}$  M) {Free Acid}, and ligand ( $20 \times 10^{-4}$  M) and
- iii) Perchloric acid ( $1 \times 10^{-2}$  M) {Free Acid}, the ligand ( $20 \times 10^{-4}$  M) and metal salt ( $4 \times 10^{-4}$  M) were carried out against standard NaOH solution (0.1N) in 65 % ethanol-water mixture. (Ionic quality of the solution was kept up constant at ( $U = 0.1$ M) by including a proper measure of 1m  $KNO_3$  solution) for deciding the portrayed constants in the present research work. The readings were recorded for each 0.2 ml addition. The graph was plotted between volume of alkali (NaOH) and pH. The ligands involved in the present work may be consider as monobasic acid having only one dissociable  $H^+$  ion from phenolic -OH group and it can be therefore represented as HL. The dissociating equilibrium can be shown as HL.



By the Law of mass action, we have,

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

where, the quantities in bracket denote the activities of the species of the equilibrium.

## Result and Discussion

### Calculation of Proton-Ligand Stability Constant ( $\bar{n}_A$ )

To determine proton-ligand stability constant graph between volume of NaOH and pH of the solution were plotted which are used to determine the replacement of H<sup>+</sup> ions from functional group of ligands with respect to pH value. Between the titration curves of free acid and acid + ligand horizontal difference ( $V_2 - V_1$ ) were measured accurately. It was used to calculate formation number  $\bar{n}_A$  at various pH values and fixed ionic strength  $\mu = 0.1M$  using Irving and Rossotti's equation.

$$\bar{n}_A = \gamma - \left\{ \frac{(V_2 - V_1)(N + E^0)}{(V^0 + V_1)T_L^0} \right\} \dots\dots\dots(2)$$

where,  $V^0$  is the initial volume of solution.  $E^0$  and  $T_L^0$  are initial concentrations of the free acid and ligand respectively.  $V_1$  and  $V_2$  are the volume of alkali of normality  $N$  during the acid and ligand titration at given pH.  $\gamma$  is the replaceable proton from the ligand. The information of  $\bar{n}_A$  at various pH along with the horizontal difference for some representative system are represented by in **Table 1**. The metal ligand formation number  $\bar{n}$  is estimated by Irving and Rossotti's equation.

$$\bar{n} = \frac{(V_3 - V_2)(N + E^0)}{(V^0 + V_2)\bar{n}_A T_M^0} \dots\dots\dots(3)$$

Symbolizations have the same meaning as given in earlier equation. The horizontal differences ( $V_3 - V_2$ ) between metal complex (A+L+M) and reagent (A+L) curve is used to evaluate the value of  $\bar{n}$  using Irving Rossotti's equation

**Table 1:** Proton ligand Stability Constant (pK)

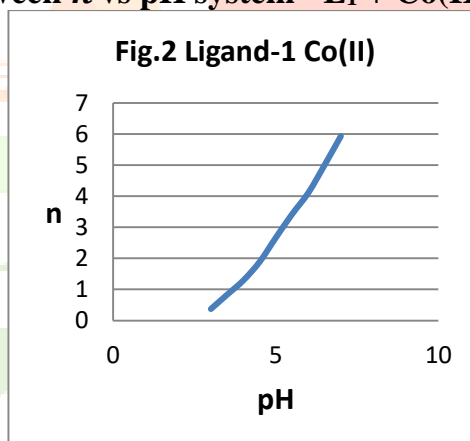
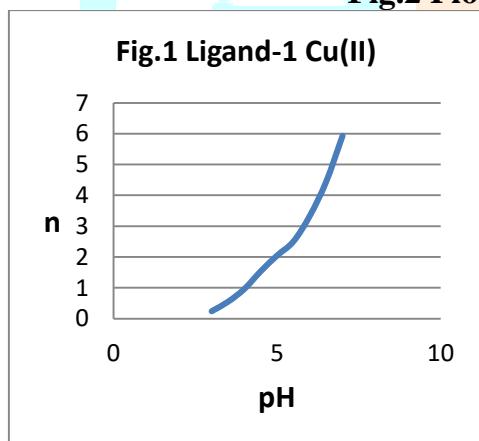
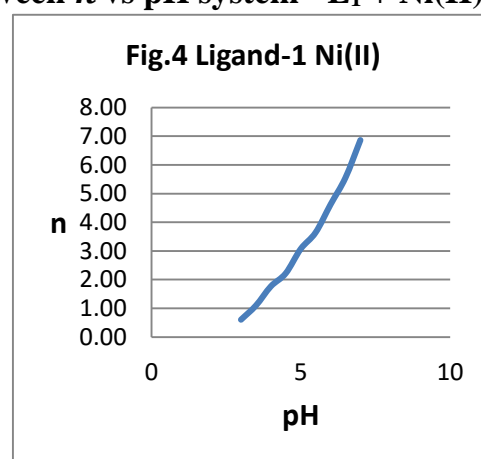
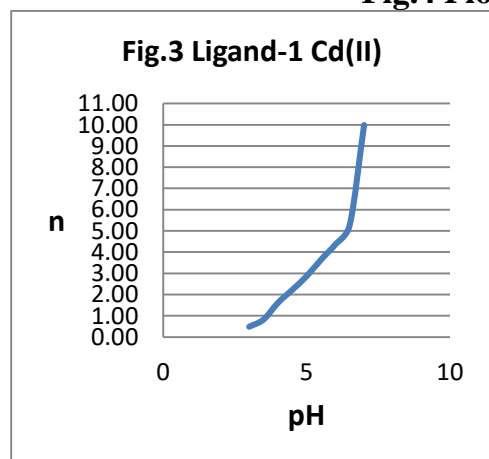
Ligand	System	pK (Half Integral Method)	pK (Pointwise Calculation Method)
Ligand (L <sub>1</sub> )	2-Phenylthio-carbamidophenol	4.55	5.03
Ligand (L <sub>2</sub> )	2-p-Chlorophenyl thiocarbamidophenol	4.49	4.92

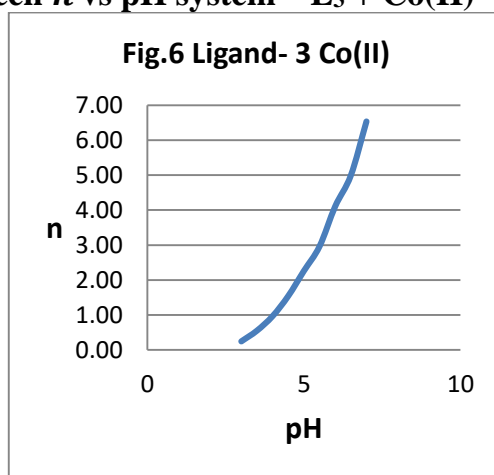
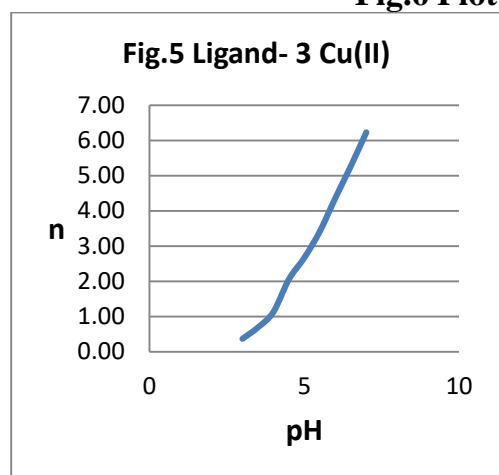
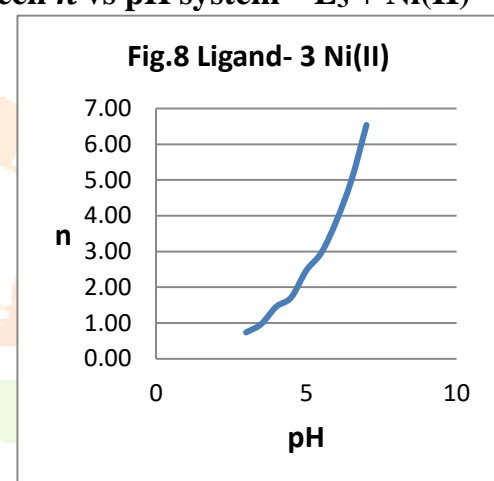
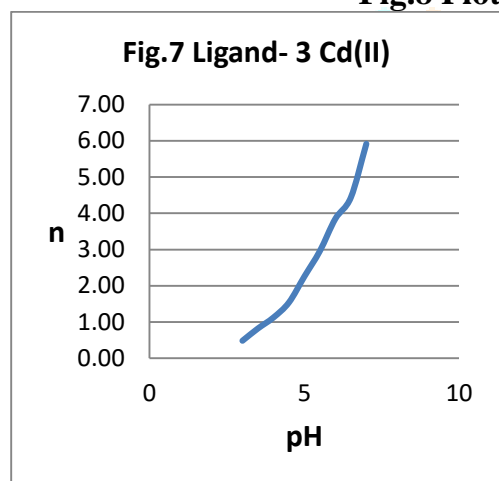
The pK values were calculated from the formation curves between pH Vs  $\bar{n}_A$  observing the pH at which  $\bar{n}_A = 0.5$  (half integral method) and pointwise calculation method shown in **Table 1**. It is observed that the order of pK values of ligands is found to be as pK L<sub>1</sub> > pK L<sub>2</sub>. The reduction of pK values of L<sub>2</sub> may be due to -I and +R effect of chloro group which is substituted at para position of phenyl ring.

**Table 2 : Metal ligand Stability Constant (logK)**

System	LogK1	LogK2	Log K1- Log K2	Log K1 / Log K2
L1+Cu(II)	4.42	3.41	0.99	1.292
L1+Co(II)	4.19	3.12	1.05	1.38
L1+Cd(II)	3.92	3.08	0.82	1.268
L1+Ni(II)	3.79	2.98	0.78	1.264
L3+Cu(II)	4.22	3.18	1.02	1.322
L3+Co(II)	4.49	3.42	1.04	1.305
L3+Cd(II)	4.42	2.97	1.42	1.476
L3+Ni(II)	4.12	3.14	0.96	1.307

The stepwise formation constants of Cu(II), Co(II), Cd(II) and Ni(II) with ligand L<sub>1</sub> and ligand L<sub>2</sub> in ethanol-water mixture were determined. The values of logK<sub>1</sub> and logK<sub>2</sub> were calculated from the formation curves ( $\bar{n}$  Vs pH) using half integral method. The most accurate values were calculated by pointwise calculation method which is denoted by **Table 2**.

**Fig.1 Plot between  $\bar{n}$  vs pH system - L<sub>1</sub> + Cu(II)****Fig.2 Plot between  $\bar{n}$  vs pH system - L<sub>1</sub> + Co(II)****Fig.3 Plot between  $\bar{n}$  vs pH system - L<sub>1</sub> + Cd(II)****Fig.4 Plot between  $\bar{n}$  vs pH system - L<sub>1</sub> + Ni(II)**

**Fig.5 Plot between  $\bar{n}$  vs pH system – L<sub>3</sub> + Cu(II)****Fig.6 Plot between  $\bar{n}$  vs pH system – L<sub>3</sub> + Co(II)****Fig.7 Plot between  $\bar{n}$  vs pH system – L<sub>3</sub> + Cd(II)****Fig.8 Plot between  $\bar{n}$  vs pH system – L<sub>3</sub> + Ni(II)**

The metal-ligand formation number ( $\bar{n}$ ) is calculated from above given equation (3). In **Fig.1** to **Fig.8** the graph is plotted between ( $\bar{n}$ ) and its corresponding pH. The Irving-Rossotti equation is used to decide the value of  $\bar{n}$  for Cu(II), Co(II), Cd(II) and Ni(II) system for ligand L<sub>1</sub> and ligand L<sub>4</sub>.

### Conclusion:

Observations from titration curve presented the disappearance between acid + ligands (A+L) curves and acid + ligand + metal (A+L+M) curves for all system started from pH = 4.8. This specified the origin of complex formation with the color changes from colorless to faint yellow in the pH range from 4.8 to 11 during titration indicates the complex formation between metal and ligand. The pK values of ligand (L<sub>1</sub>) greater than pK ligand (L<sub>2</sub>) are found to be in order of pK values of ligands. The lower pK value of ligand (L<sub>2</sub>) because (L<sub>2</sub>) has electron releasing –Cl group to phenyl ring which decreases the activity of ligand (L<sub>2</sub>) to form more stable complex. We can see that the difference between logK<sub>1</sub> and logK<sub>2</sub> is less which indicates the formation of complex between ligands and metal ions which occurring simultaneously (**Table 2**). The stability of complexes was decided by the values of log K<sub>1</sub> and log K<sub>2</sub>.

For 2-phenylthiocarbamidophenol (L<sub>1</sub>) the difference between the values of logK<sub>1</sub> and logK<sub>2</sub> is higher with Co(II) complex than Cu(II), Cd(II) and Ni(II) which indicates that Co(II) forms more stable complex with ligand-1 than Cu(II), Cd(II) and Ni(II), while in the case of 2-p-

chlorophenylthiocarbamidophenol ( $L_2$ ) the difference between the value of  $\log K_1$  and  $\log K_2$  is higher with Cd(II) complex than Cu(II), Co(II) and Ni(II) complexes. Cd(II) forms more stable complex with  $L_2$  than Cu(II), Co(II) and Ni(II).

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