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PH-metric studies on 2-p-chlorophenyl thiocarbamidophenol with different transition metal ions in 70% mixed solvent media

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Abstract
Stability constant is an effective parameter in pharmacodynamics and pharmacokinetic study of molecules. The medicinal properties of any molecule are checked after synthetic process for that various physical methodologies are used. Late work highlight pH-metric investigation of proton-ligand and metal-ligand stability constant of 2-p-Chlorophenylthiocarbamidophenol with various transition metal ion at 0.1 M ionic strength in 70% ethanol-water mixture by Irving-Rossotti method. It is observed that different transition metal ions forms 1:1 complex with 2-p-Chlorophenyl - thiocarbamidophenol. The information acquired was used to estimate and compare the values of proton –ligand stability constant (pK) and metal-ligand stability constants (logk). The effects of substituent's were studied from the evaluated information (pK and logk).

Keywords: 2-p-chlorophenyl thiocarbamidophenol, stability constant, pH-metry

1. Introduction
Every days thousands number of new compounds are synthesized and determination of anatomical, physiological and pharmacological activities of any molecule is essential for knowing its significances and application in medicinal, pharmaceutical agricultural and industrial sciences. Drug activity, drug effect, transmission of drug and absorption of drug these are very much important factors directly influence by the stability of molecule. The stability of molecules during this study can be easily determined from the values of stability constants. The formation of complex can also be determined from these values, hence pH-metric measurements created its own importance in life, medicinal and pharmaceutical, agricultural and industrial sciences. Physical and chemical properties are varied due to complexation. Composition as well as conformation of complex formation can be measured from study of various physicochemical properties by pH-metric method. pH-metric technique has a great significance in measurements of stability constant and confirmation of complex formation in solution. pH-metric technique evaluates the stability constant [1-5]. The studies of stability constant of mixed ions were also done[6]. The metal ligand selectivity and strength of metal-ligand bond depends on stability constant[7]. The study of stability constant of binary and ternary complexes of phenytoin sodium drug and glutamine by mazahar farooqui *et al* [8]. Formation constant and thermodynamic parameters of trifluoperazine metal complexes was studied pH metrically [9]. Y.K. Meshram *et al* [10] have reported the stability constants of transition metal complexes with substituted ketones. Mane *et al*[11]studied the proton-ligand and metal-ligand stability constant of maleic acid and glycine with Mn(II),Cu(II),Fe(III),Ni(II) and UO_2(II). Formation constant of bivalent metal ion complexes with 3-amino 5-methyl isoxazole schiff bases have been studied by Martell[12]. The study of 2-p-Chlorophenylthiocarbamidophenol with different transition metal ions has not yet reported in literature. It's being interesting to study the proton-ligand stability constant and metal ligand stability constant of 2-p-Chloro - phenylthiocarbamide phenol with different transition metal ions in 70% ethanol-water mixture by pH-metric method.

2. Experimental Section
In this research work all AR grade chemical are used. Required amount of ligand was dissolved in 70% ethanol water mixture to form the stock solution of ligand.

3. General Procedure

Types of Titrations i) Perchloric acid (1 X 10^{-2} M) {Free Acid},ii) Perchloric acid (1 X 10^{-2} M) {Free Acid}, and ligand (20X10^{-4} M), iii) Perchloric acid (1x 10^{-2} M) {Free Acid), the ligand (20x10^{-4} M) and metal salt (4x10^{-4}M) were done against standard NaOH solution (0.1N) in 70 % ethanol-water mixture. (Ionic quality of the solution was kept up constant at (U = 0.1M) by including a proper measure of 1m KNO3 solution) for deciding the portrayed constants in the present research work. The readings were recorded for each 0.2ml 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.

$$HL \rightleftharpoons H^+ + L^-$$

By the Law of mass action, we have,

$$K = [HL] / ([H^+] [L^-]) \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where the quantities in bracket denote the activities of the species of the equilibrium.

4. Result and Discussion

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

To determine proton-ligand stability constant the plotted graph between volume of NaOH and pH of the solution were used (represent the replacement of H^+ ions from functional group of ligands with respect to pH value). Between the titration curves of free acid and acid + ligand horizontal difference (V2-V1) were measured accurately. It was used to calculate formation number $\bar{n}_A$ at various pH values and fixed ionic strength μ = 0.1M using Irving and Rossotti's equation.

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

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.γis 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.

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

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_3)	2-p-chlorophenyl -thiocarbamidophenol	4.53	4.96

Table 2: Metal ligand Stability Constant (log K)

System	LogK1	LogK2	Log K1- Log K2	Log K1 / Log K2
L3+Cu(II)	4.25	3.21	1.04	1.324
L3+Co(II)	4.51	3.45	1.06	1.307
L3+Cd(II)	4.45	3.01	1.44	1.478
L3+Ni(II)	4.15	3.17	0.98	1.309

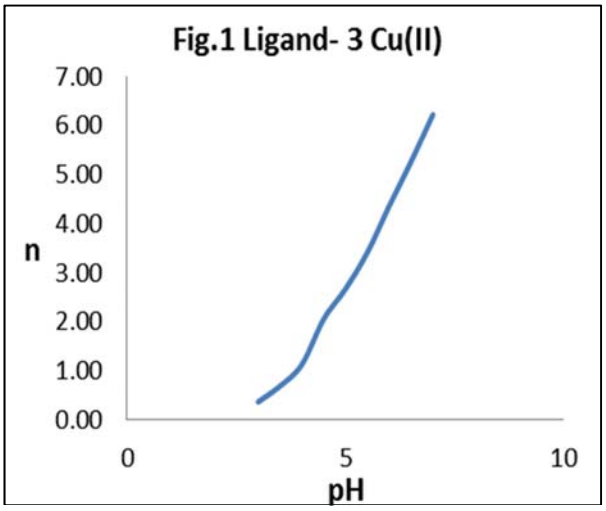

Fig 1: Plot between $\bar{n}$ vs pH system – L_3 + Cu (II)

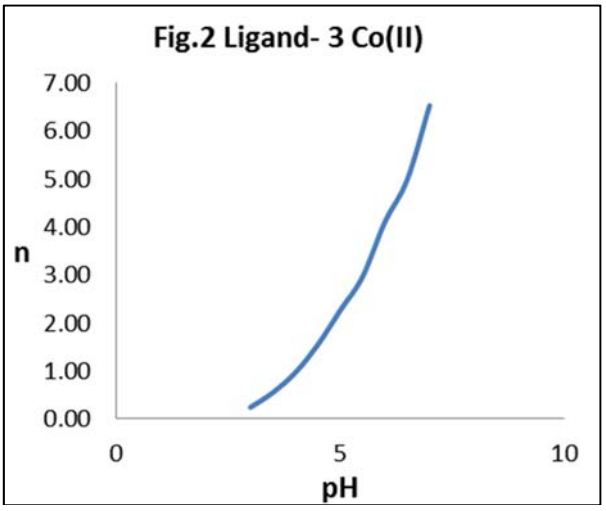

Fig 2: Plot between $\bar{n}$ vs pH system – L_3 + Co(II)

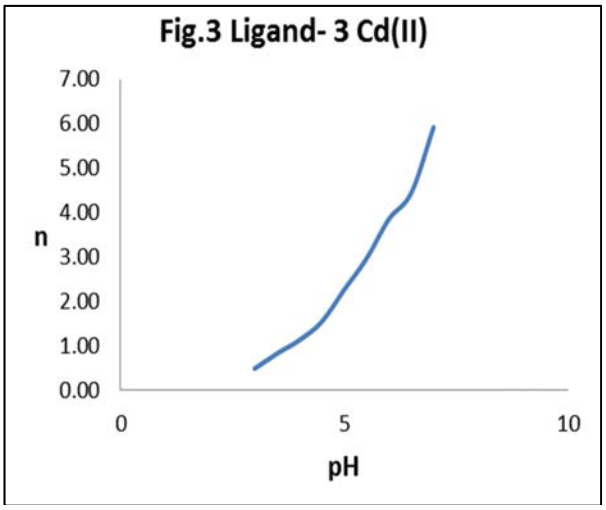

Fig 3: Plot between $\bar{n}$ vs pH system – L_3 + Cd(II)

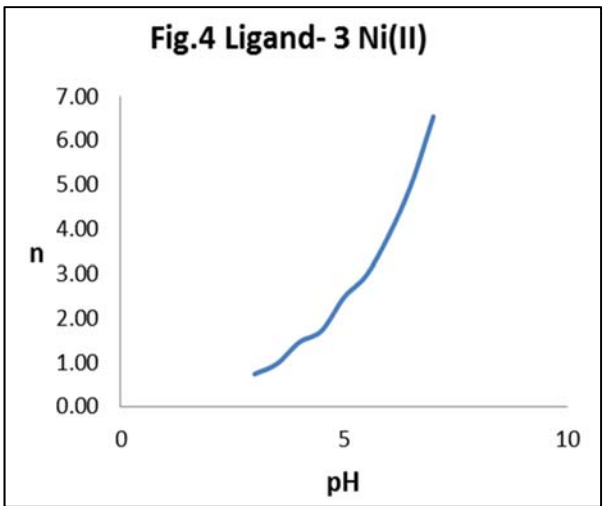

Fig 4: Plot between $\bar{n}$ vs pH system – L_3 + Ni (II)

5. Conclusion

The titration curves shows the departure 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. To form the more stable complex the order of pK values of ligand (L_3) provides attributed towards deprotonation of ligand which have good activity. From table 1 we can conclude that L_3 having good pK values. Table 2 indicates that the difference between $\log K_1$ and $\log K_2$ values provides information about complex is formed between metal ion and ligand. The value of $\log K_1$ and $\log K_2$ indicates the stability of complexes.

While in the case of 2-p-chlorophenylthiocarbamidophenol (L_3) 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_3 than Cu (II), Co (II) and Ni(II). The information obtained from above investigations is helpful to study the drug effect and drug activity of newly synthesized compound.

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