pH-Metric Study of 2-Phenyl Thiocarbamidophenol with Cu(II), Co(II), Cd(II) and Ni(II) Metal Ions at 0.1 M Ionic Strength.

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ABSTRACT

The interaction of Cu(II), Co(II), Cd(II) and Ni(II) with 2-phenyl thiocarbamidophenol have been studied at 0.1 M ionic strength. It is observed that Cu(II), Co(II), Cd(II) and Ni(II) forms 1:1 complex with 2-phenyl thiocarbamidophenol. The result obtained for pK and logK are used to see the effect of substituent which has been studied pH-metrically by Calvin-Bjerrum titration technique.

INTRODUCTION

Coordination compounds played an important role in biological activities for removal of unwanted and toxic metals from living organism. The application of coordination chemistry is varied in the field of biology, biochemistry, medicine, agriculture, organometallic chemistry, and solid state chemistry, pharmaceutical. The metal ion complexes as catalysts are invariably involved in various industrial processes. Stability constant is well-known medium for solution chemist, biochemist and chemist. The knowledge of stability constant is useful for correct interpretation of complex. In analytical and separation procedure the stability constant is used. Literature survey reveals that since many decades there has been lot of research done on the study of metal complexes[1-2]. Many workers studied the effect of transition metals on stability of complex by pH-metrically[3-6]. Wadekar *et al.*[7] have studied the stability constant of substituted thiopyrimidine. Frau *et al.*[8] have investigated the theoretical calculation of stability constant and pK_a values of metal complexes in solution. Zaid *et al.*[9] studied the stability constant of biologically active molecules by using pH-metric technique. The investigation of metal-ligand stability constant of Th(III), Sm(III), Nd(III) and Pr(III) metal ion complexes with 2-mercapto-4-substituted phenyl-6-substituted phenyl pyrimidines at 0.1 M ionic strength by Thakur *et al.*[10]. The determination of stability constant of metal-ligand equilibria with special reference to Schiff base and transition element have been studied by Jadhav *et al.*[11]. The proton-ligand stability constant with dichloro substituted pyrazolines, isoxazolines, pyrazoles and isoxazoles has been studied by Deshmukh[12]. The stability of metal complexes heterocyclic compounds was studied by Clark and Willeford[13]. The metal-ligand stability constant of 3-[3-(2-hydroxy-5-methylaryl] pyrazol-5-yl]-5-thiazolo[2,3-*C*]-S-triazol-5-(6*H*)one with transition metals in 70% ethanol-water mixtures has been reported Agrawal[14]. Nandurkar *et al.*[15] has studied the stability constants of Cu(II), Co(II), Ni(II), Mn(II) complexes with substituted pyrazoles in DMF as a solvent by using pH-meter.

This present work described the interaction of 2-phenyl thiocarbamidophenol with Cu(II), Co(II), Cd(II) and Ni(II) metal ions at 0.1M ionic strength.

EXPERIMENTAL METHOD

The ligand was synthesized by known literature method**.** pH-metric titration was carried out with EQ-614 pH meter equipment. The AR grade chemicals were used. The stock solutions

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of ligands were prepared by dissolving required amount of ligands in 70% ethanol-water mixtures. The solutions involved in the experimental procedure for pH-metric titration are:

i) Perchloric acid (1×10^{-2} M) {Free Acid},

ii) Perchloric acid (1×10^{-2} M) {Free Acid}, and ligand (20×10^{-4} M),

iii) Perchloric acid (1×10^{-2} M) {Free Acid), the ligand (20×10^{-4} M) and metal salt (4×10^{-4}M) (Ionic quality of the solution was kept up constant at (U = 0.1M) by including a proper measure of 1m KNO_3 solution) for determining the described 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 considered 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.
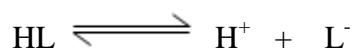
$$HL \rightleftharpoons H^+ + L^-$$

By the Law of mass action, we have,

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

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

RESULT AND DISCUSSION

Determination of proton-ligand stability constant ($\bar{n}_A$)

The plot between volume of NaOH and pH of the solution were used to determine the proton-ligand stability constant (represent the replacement of H^+ ions from functional group of ligands with respect to pH value). The horizontal difference (V_2-V_1) was measured accurately between the titration curves of free acid + ligand. 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.

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

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 volumes of alkali of normality N.

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γ 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.

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

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 are used to evaluate the value of $\bar{n}$ using Irving Rossotti's equation.

Table 1: Proton ligand Stability Constant (pK)

Ligand	pK (Half Integral Method)	pK (Pointwise Calculation Method)
Ligand (L$_1$)	7.50	7.76

The pK values were calculated from the formation curves between pH Vs $\bar{n}_A$ observing the pH at which nA=0.5 (half integral method) and point wise calculation method showed in **Table 1.**

Table 2: Metal-Ligand Stability Constants

System	LogK1	LogK2	Log K1- Log K2	Log K1 / Log K2
L1+Cu(II)	4.73	3.41	1.32	1.387
L1+Co(II)	4.15	3.05	1.1	1.361
L1+Cd(II)	3.91	3.09	0.82	1.265
L1+Ni(II)	3.92	3.05	0.87	1.285

The stepwise formation constants of Cu(II), Co(II), Cd(II) and Ni(II) with ligand L$_1$ in ethanol-water mixture were determined. The values of logK1 and logK2 were calculated from the formation curves (n Vs pL) using half integral method. The most accurate values were calculated by pointwise calculation method which is denoted by **Table 2.**

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CONCLUSION

The titration curves show 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. **Table 2** indicates that the difference between $logK_1$ and $logK_2$ values provides information about complex is formed between metal ion and ligand. The value of $logK_1$ and $logK_2$ indicates the stability of complexes.

In the case of 2-phenylthiocarbamidophenol (L_1), the difference between the value of $logK_1$ and $logK_2$ is higher with Cu(II) complex than Co(II), Cd(II) and Ni(II) complexes. Cu(II) forms more stable complex with L_1 than Co(II), Cd(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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