



pH-Metric Study of 4-Phenylthiocarbamidophenol Complex with Cu (II), Cd(II), Co(II) and Ni(II) Metal Ions In 70% Ethanol-Water Solvent System

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ABSTRACT

The metal ions Cu(II), Cd(II), Co(II) and Ni(II) interacted with ligand 4-phenylthiocarbamidophenol have been studied at 0.1 M ionic strength in 70 % ethanol-water mixture by Bjerrum method as adopted by Calvin and Wilson. It was observed that Cu(II), Cd(II) and Cr(III) metal ions form 1:1 complexes with ligand 4 phenylthiocarbamidophenol. The values of proton-ligand stability constant (pK) and metal-ligand stability constants (log k) were estimate and compared from resultant data. The effects of substituent were studied from estimated data (pK & log k).

Keywords: 4-phenylthiocarbamidophenol; Stability constant; pH-metry.

INTRODUCTION

Last decades it was observed that thiocarbamido and phenyl nucleus containing compound frequently used as drugs in medicinal and pharmaceutical chemistry. These are the most excellent drug for various serious diseases. Hence it's a great challenge before chemist to synthesize such drugs which include phenyl in addition to thiocarbamido in the similar molecule. It has been observed in literature that drug have biological and pharmacological activities like rate of passing drug through cell membrane depends on pK values [1-3].

Many workers study the effect of transition metal on a stability of complex by pH metrically [4-6]. Banarjee *et al* studied [7] the stability constant of ligand and alkaline earth metal complexes. It is also investigation of stability constant of ligand with lanthanide metals [8-11]. The studies of metal-ligand complexes in solution having number of metal ions with ligands carboxylic acids, oximes, phenols would be interesting which throw a light on the mode of storage and transport of metal ions in biological kingdom. Metal complexation not only brings the reacting molecules together to give activated complexes but also polarized electrons from the ligands towards the metal [12]. 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 the complexes is determined by the nature of central metal atom and ligand. The stability of complexes is influenced by the most important characteristics degree of oxidation, radius and electronic structure. Irving and Williams had studied the order of stability of metal complexes of transition metal ions by comparing the ionic radius and second ionization potentials of metal ions, as it is valid for most nitrogen and oxygen donor ligands. Narwade *et al* having investigated metal-ligand stability constants of some lanthanides with some substituted sulphonic acids [13]. Bodkhe *et al* have reported the metal-ligand stability constants of some β -diketones [14]. Prasad *et al* have studied mixed ligand complexes of alkaline earth metals, Mg(II), Ca(II), Sr(II) and Ba(II) with 5-nitrosalicylaldehyde and β -diketones [15].

The stability constant is great importance in analytical and separation procedure to remove undesirable and harmful metals from living organism, chelating agents are very much useful in biological systems. This gives importance to the study of determination of stability constant of metal complexes. In present work an attempt has been made to study the interactions between Cu(II), Cd(II), Co(II) and Ni(II) metal ions with 4-phenylthiocarbamidophenol at 0.1 M ionic strength pH metrically in 70% ethanol-water solvent.

EXPERIMENTAL SECTION

All chemicals used are of AR grade. The ligand 4-phenylthiocarbamidophenol was synthesized in the laboratory by reported protocol. The stock solutions of the ligand was prepared by dissolving required amount of ligand in of 70% (ethanol + water) solvent.

General procedure

Types of titrations:

- i) Free acid HNO₃ (0.01 M),
- ii) Free acid HNO₃ (0.01 M) and ligand (20 x 10⁻⁴M),
- iii) Free acid HNO₃ (0.01 M) and ligand (20 x 10⁻⁴) and metal ion (4 x 10⁻⁴M) against standard 0.1N NaOH solution.

The ionic strength of all the solutions was maintained constant 1M by adding appropriate amount of KNO₃ solution. All the titrations were carried out in 70% (Ethanol-water) mixture and the reading were recorded for each 0.2 ml addition. The graph of volume of alkali added (NaOH) against pH were plotted. The ligands involved in the present work may be considered as a monobasic acid having only one dissociable H⁺ ion from phenolic -OH group and it can therefore, be represented as HL. The dissociating equilibria can be shown as.



By the law of mass action, we have,

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

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

RESULT AND DISCUSSION

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

The plots between volume of NaOH and pH of the solution were used to determine the proton ligand stability constant. The horizontal difference ($V_2 - V_1$) was measured accurately between the titration curves of free acid and acid + ligand. It was used to calculate the formation number \bar{n}_A at various pH values and fixed ionic strength $\mu = 0.1$ M using Irving and Rossotti's equation 1 and 2

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

Where, V^0 is the initial volume of the solution. E^0 and T_L^0 are initial concentrations of the mineral acid and ligand respectively. V_1 and V_2 are the volumes of alkali of normality N during the acid and ligand titration at given pH is the replaceable proton from the ligand. The data of \bar{n}_A obtained at various pH along with the horizontal difference for some representative systems are represented in Table-1. The metal-ligand formation number (\bar{n}) is estimated by Irving-Rossotti's equation.

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

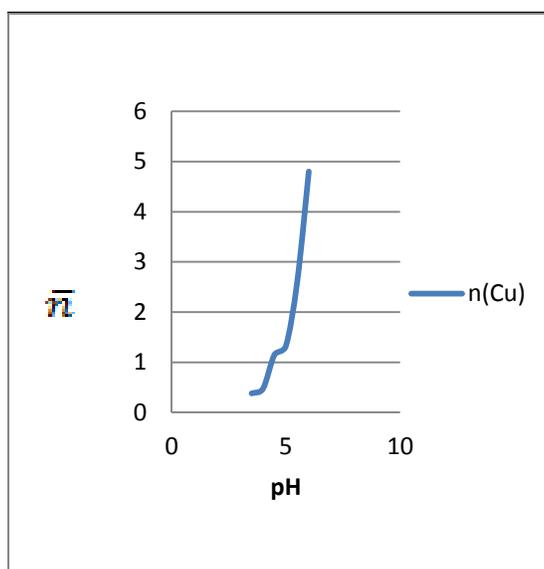
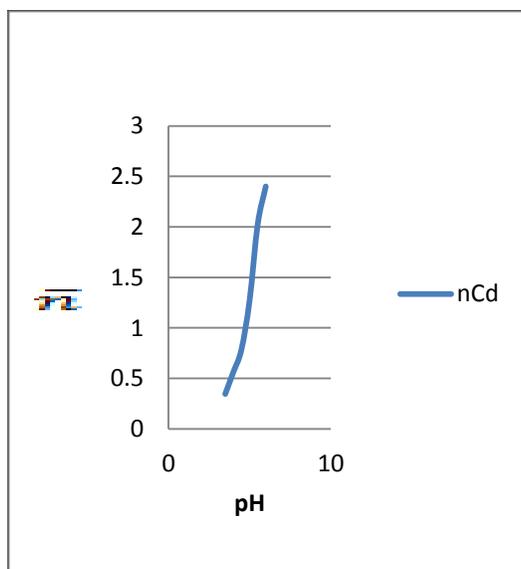
Where, the notations have the same meaning as given in earlier equation. The horizontal difference ($V_3 - V_2$) between the metal complex (A+M+L) and reagent (A+L) curve is used to evaluate the value of n using Irving Rossotti's equation.

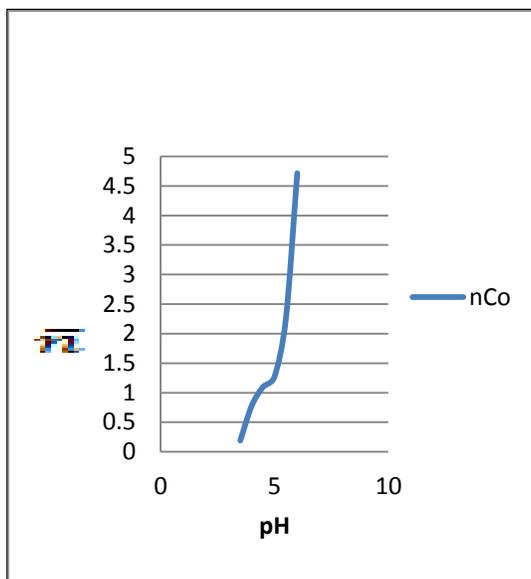
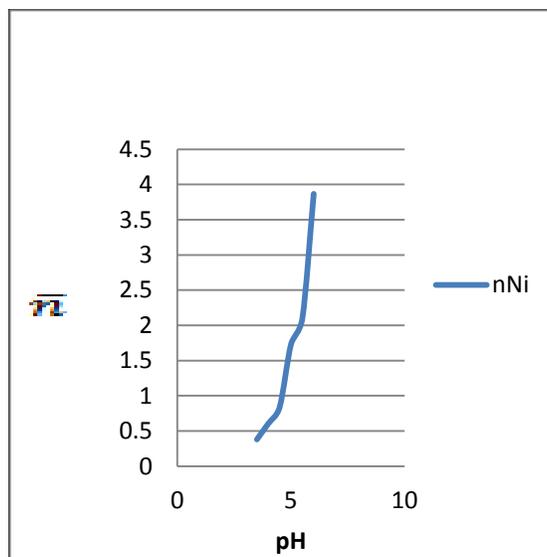
Table 1: Proton-Ligand Stability constant (pK)

Ligand	System	pK	
		Half integral method	Point wise method
L1	4-ethylthiocarbamidophenol	3.98	3.8671

Table 2: Metal-ligand stability constant (log K)

System	Log K ₁	Log K ₂	Log K ₁ -log K ₂	Log K ₁ /log K ₂
Cu(II)-L ₁	5.5	3.8	1.7	1.4475
Cd(II)-L ₁	5.6	4.39	1.211	1.276
Co(II)-L ₁	5.32	4	1.32	1.33
Ni(II)-L ₁	5.6	4.25	1.35	1.3176

Figure 1: Plot between \bar{n} vs pH System- L1+Cu(II)Figure 2: Plot between \bar{n} vs pH System-L1+Cd(II)

Figure 3: Plot between \bar{n} vs pH System- L1+Co (II)Figure 4: Plot between \bar{n} vs pH System-L1+Ni (II)

CONCLUSION

From the above titration curves, it is observed that the departure between acid + ligand (A+L) curve and acid + ligand + metal (A+L+M) curve for all systems started from pH = 4.5. This indicates the commencement of complex formation and also change in colour from colourless to purple in the pH range from 4.5 to 11 during titration showed the complex formation between metal and ligand. The order of pK values of ligand give attributed toward deprotonation of ligand having good activity to form the more stable complex. Observation of Table-2 shows that the less difference between $\log K_1$ and $\log K_2$ values indicates the complex formation between metal ion and ligand occurring simultaneously. The values of $\log K_1$ and $\log K_2$ (Table 2) decided the stability of complexes.

For 4-phenylthiocarbamidophenol (L1) the difference between the values of $\log K_1$ and $\log K_2$ is higher with Cu(II) complex than Co (II), Cd(II) and Ni(II) complexes. Cu(II) metal ion forms more stable complex with L1 than Co (II), Cd(II) and Ni(II) metal ions.

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