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PH-Metric study of substituted thiocarbamidophenol complexes with different transition metal ions in mixed solvent media

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Abstract

The interaction of transition metal ions with L₂ and L₃ have been studied in 0.1 ionic strength at 70% ethanol-water mixture by Bjerrum method as adopted by Calvin and Wilson. It is observed that metal ions forms 1:1 and 1:2 complexes with L₂ and L₃. The data obtained were used to estimate and compare the values of proton-ligand stability constant (pK) and metal-ligand stability constant (logK).

Keywords: Substituted thiocarbamidophenols, stability constant, pH-metry

1. Introduction

Metal complexes used in various fields such as biological processes, pharmaceutical, analytical processes, separation technique. Metal complexes play a vital role in nature they have been extensively used in clinical application as antibacterial [1, 2], antiviral [3-5] and as anti-cancerous [6-8]. Chemistry of drugs attracts many researchers because of its application in medicinal [9]. Literature survey reveals that, over the last decades there has been tremendous work done on the study of metal complexes [10, 11]. The studies in metal-ligand complexes in solution of a number of metal ions with carboxylic acids, oximes, phenol etc. would be interesting which throw light on the mode of storage and transport of metal ion in biological kingdom. Gollapalli *et al* [12] investigate the formation of binary complexes of Co(II), Ni(II) and Cu(II) with L-Dopa in dioxane-water mixtures. Wadekar *et al* [13] studied the determination of stability constant of substituted imidazolinone drugs by pH-metric method. Stability constant of some rare-earth metal chelates was also determined [14]. pH-metric study of metal-ligand stability constant of cefadroxil with Cu²⁺ metal ion at 0.1 M ionic strength was done by Kamkhede [15]. Mosa *et al* [16] investigate the thermodynamic properties of some lanthanide metal ion complexes of newly mono- and dioximes in dioxane-water mixtures. Stability constant and stoichiometries of chromium and zirconium carboxylates complexes was studied by Omar and Ali [17]. The potentiometric studies on transition metal complexes of substituted derivative of coumarin were done by Hathi *et al* [18]. The stability constant of some a-amino acids-copper (II) and nickel (II) system in ethanol-water mixtures was studied by Dogan [19].

It's being interesting to study the interaction between the substituted thiocarbamidophenol and different transition metal ions in mixed solvent media.

2. Experimental section

In this research work all AR grade chemical are used. Required amount of ligands were dissolved in 70% ethanol- water mixture to form the stock solution of ligand.

2.1 General procedure

2.1.1 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) and
- iii) Perchloric acid (1x 10⁻² M) {Free Acid}, the ligand (20x10⁻⁴ M) and metal salt (4x10⁻⁴M) 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

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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.



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 of the equilibrium.

3. Result and Discussion

3.1 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 $\mu = 0.1M$ 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, V⁰ is the initial volume of solution. E⁰ and T_L⁰ are initial concentrations of the free acid and ligand respectively. V₁ and V₂ are the volume of alkali of normality N during the acid and ligand titration at given pH. γ is the replaceable proton from the ligand. The metal ligand formation number \bar{n} is estimated by Irving and Rossotti's equation.

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

Symbolizations have the same meaning as given in earlier equation. The horizontal differences (V₃-V₂) 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 ₂)	2-methyl thiocarbamidophenol	5.22	5.11
Ligand (L ₃)	2-p-chlorophenylthiocarbamidophenol	4.53	4.96

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 L₂ > pK L₃. The reduction of pK values of L₃ 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
L2+Cu(II)	4.73	3.41	1.32	1.387
L2+Co(II)	4.15	3.05	1.1	1.361
L2+Cd(II)	3.91	3.09	0.82	1.265
L2+Ni(II)	3.92	3.05	0.87	1.285
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

The stepwise formation constants of Cu (II), Co (II), Cd (II) and Ni (II) with ligand L₂ and ligand L₃ in ethanol-water mixture were determined. The values of logK₁ and logK₂ 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.

4. 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 (L₂) greater than pK ligand (L₃) are found to be in order of pK values of ligands. The lower pK

value of ligand (L₃) because (L₃) has electron releasing -Cl group to phenyl ring which decreases the activity of ligand (L₃) to form more stable complex. We can see that the difference between logK₁ and logK₂ 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 K₁ and log K₂. For 2-methylthiocarbamidophenol (L₂) the difference between the values of logK₁ and logK₂ is higher with Cu(II) complex than Co(II), Cd(II) and Ni(II) which indicates that Cu(II) forms more stable complex with ligand-2 than Co(II), Cd(II) and Ni(II). While in the case of 2-p-chlorophenylthiocarbamidophenol (L₃) the difference between the value of logK₁ and logK₂ is higher with Cd(II) complex than Cu(II), Co(II) and Ni(II) complexes. Cd(II) forms more stable complex with L₃ than Cu(II),Co(II) and Ni(II).

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