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PH-METRICALLY STUDY THE INTERACTION OF 5-P-CHLOROPHENYL -THIOCARBAMIDO-1-NAPHTHOL AND CU(II), CD(II) AND CR(III) COMPLEXES IN 70% ETHANOL-WATER MEDIUM

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ABSTRACT

Recent work highlights the study of proton-ligand and metal- ligand stability constant of 5-p-Chlorophenylthiocarbamido-1-naphthol with Cu (II), Cd(II) and Cr(III) metal ions at 0.1 M ionic strength in 70% ethanol-water mixture by Irving–Rossotti titration technique. Present work revels that 5-p-Chlorophenylthiocarbamido-1-naphthol form 1:1 and 1:2 complexes. The values of proton-ligand stability constant (pK) and metal-ligand stability constants (log k) were calculated and compared from resultant data. Variation in pK and log K values also studied during this work. This work plays a supporting role toward development of new drugs.

KEYWORDS: 5-p-Chlorophenylthiocarbamido-1-naphthol, stability constant, pH-metrically.

INTRODUCTION

Thiocabamido, hydroxyl, amino and benzenoid nucleus possessing molecule create their own important in various field of pharmaceutical and medicinal sciences. These types of drugs effectively used against various diseases. Several modern theories and concept are concerning to physical as well as chemical study of benzenoid, non-benzenoid, heteroacycles and heterocycles. Aminonaphthols and thiocarbamido nucleus containing heterocycles possesses pharmaceutical, medicinal agricultural industrial and biotechnological significances. Evaluate the stability constant by pH-metric titration method.[1-5] It is also well known that some medicinal drugs exhibit increased activity when administered as metal complexes. The manifold research work has been done on the study of metal and nitrogen and sulphur atoms containing ligands.[6-7] Stability constant of mixed ions was also studied.[8] References indicates that the metal ligand stability constants and proton ligand stability constants of Cu(II)-salicylic acid complex have been studied.[9] Stability constant of lanthanide ions with some substituted sulphonic acid spectrometrically investigated by Narwade and Khobragade.[10] Mane et al [11] evaluated the proton - ligands and metal- ligands stability constant of maleic acid and Glycine with Mn(II), Cu(II), Fe(III), Ni(II) and UO_2(II). Formation constants of bivalent metal ion complexes with 3-amino 5-methyl isoxazole sciff bases have been studied by Martell.[12] Formation constant of substituted pyrazoles complexes with some lanthanide metal ions studied by Martel and Smith.[13] There has been considerable interest in the study of binary ternary and quaternary complexes by pH – metric method[14-17] determined log K value of chalcones pyridine carboxylic acids and hydroxyl ethyl benzene. Study of stability constants of 5-p-Chlorophenylthiocarbamido-1-naphthol and Cu(II), Cd(II) and Cr(III) metal ion complexes have not reported in literature. Thus it was interest to study stability constant of complexes from the interaction of 5-p-Chlorophenyl- thiocarbamido-1-naphthol with Cu(II), Cd(II) and Cr(III) metal ions by pH-metrically in 70% ethanol-water mixture.

MATERIALS AND METHOD

All AR grade chemicals used during this work. Stock solutions of ligand was prepared by 70% (ethanol + water) mixture. Titrations of (i) free acid (0.01 M), (ii) free acid (0.01 M) and ligand (20 x 10^{-4}M) and (iii) free acid (0.01 M), ligand (20 x 10^{-4}) and metal ion (4 x 10^{-4}M) against standard 0.1N NaOH solution. The ionic strength of all solutions was maintained 1M by adding appropriate amount of KNO_3 solution. All titrations were carried out in 70% (ethanol-water) mixture and readings ware recorded for each 0.2 ml addition. The graph of volume of alkali added (NaOH) against pH were plotted. The ligand involved in present work is 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 equillibria can be shown as,

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

By the law of mass action, we have,

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

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

RESULT AND DISCUSSION

pH-metric Measurement

Proton-Ligand Stability Constant ($\bar{n}_A$) & Metal-ligand stability constant ($\bar{n}$)

The plots between volume of NaOH and pH of the solution were used to determine the proton ligand stability constant (representing the replacement of H^+ ions from functional group of ligand with respect to pH value). 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 μ = 0.1 M using Irving and Rossotti's equation 2 and 3;

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

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. 'γ' 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;

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

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
L_3	5-p-chlorophenylthiocarbamido-1-naphthol	9.80	8.98

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

System	log K_1	log K_2	Δ log K	log K_1/log K_2
Cu(II) + L_3	**5.35**	**6.15**	**0.8**	**0.8699**
Cd(II) + L_3	**5.43**	**6.41**	**0.98**	**0.8471**
Cr(III) +L_3	**5.81**	**6.52**	**0.71**	**0.8911**

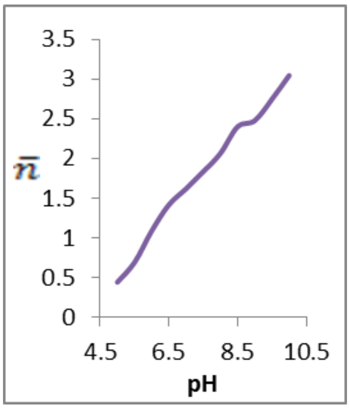

Fig. 1

Plot between $\bar{n}$ vs pH

System-L_3+Cu(II)

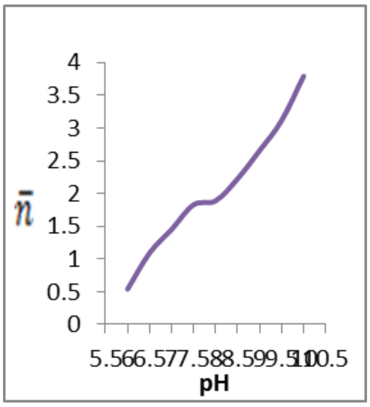

Fig. 2

Plot between $\bar{n}$ vs pH

System-L_3+Cd(II)

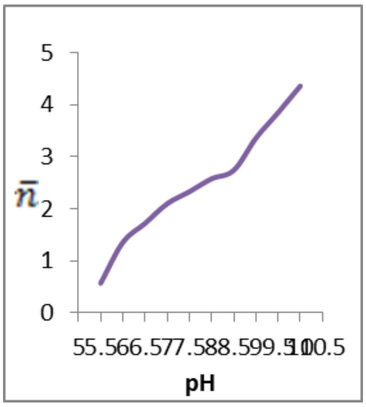

Fig. 3

Plot between $\bar{n}$ vs pH

System- L_3+Cr(III)

CONCLUSION

From the 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 indicated the commencement of complex formation. The order of pK values of ligand give attributed toward deprotonation of ligand having good activity to form the more stable complex. **Table 1** revels that L_3 has good pK value. **Table 5** showed that less difference between log K_1 and log K_2 values indicated 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. Difference between log K_1 and log K_2 is smaller in some of the systems. It seems, therefore, both the 1:1 and 1:2 complexes are formed simultaneously and not in a stepwise process. **Table 2** revel that log K_1 and log K_2 difference is higher For 5-p-Chloro-phenylthiocarbamido-1-naphthol (L_3) with Cd(II) complex than Cu(II) and Cr(III) complexes. Thus Cd(II) forms more stable complex with L_3 than Cu(II) and Cr(III) metal ions. This investigation helps to study of drug activity and drug effect of newly synthesized drugs.

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