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Research Article

**EVALUATE THE EFFECT OF SUBSTITUTED
THIOCARBAMIDO-1-NAPHTHOL ON STABILITY
CONSTANT BY USING Cu(II), Cd(II) AND Cr(III) METAL
IONS IN 70% ETHANOL-WATER MIXTURE**

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Department of Chemistry, Government Vidarbha Institute of Science and Humanities,
Amravati 444604.**Abstract:**

The present work deals with the study of proton -ligands and metal- ligands stability constant of 5-p-chlorophenylthiocarbamido-1-naphthol and 5-p-tolylthiocarbamido-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. 5-p-chlorophenylthiocarbamido -naphthol and 5-p-tolylthiocarbamido-1-naphthol form 1:1 complexes by interacting with Cu(II), Cd(II) and Cr(III) metal ions were found in present work. The values of proton-ligand stability constant (pK) and metal-ligand stability constants (log k) were evaluate and compared from resultant data. The effect of substituents were also studied from resultant estimated data on pK and log K.

Keywords: 5-p-chlorophenylthiocarbamido-1-naphthol, 5-p-Tolylthiocarbamido -1-naphthol, stability constant, pH-metry.

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INTRODUCTION:

Thiocarbamido, 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 [1-5]. Evaluate the stability constant by pH-metric titration method. 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 et al[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 UO₂(II). Formation constants of bivalent metal ion complexes with 3-amino 5-methyl isoxazole sciff bases have been studied [12]. Formation constant of the complexes of substituted pyrazoles with some lanthanide metal ions [13]. There has been considerable interest in the study of binary ternary and quaternary complexes by pH – metric method [14-17]. In the present work we investigate the stability constant of isoniazid drug with rare earth metal ions La(III),Ce(III),Nd(III),Sm(III), Gd(III),Tb(III) and Dy(III) using pH-metric technique by S.V.Thakur et al [18]. Evaluated the influence of transition metal on a stability of complex by pH metrically [19-20]. The stability constants of Cu(II), Cd(II) and Cr(III) with ligands 5-p- chlorophenylthiocarbamido-1-naphthol and 5-p-tolylthiocarbamido-1-naphthol have not reported in literature. Thus it was interest to study the stability constant of complexes form by

RESULTS AND DISCUSSION:

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

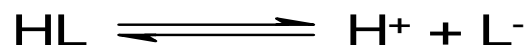
The plots between volume of NaOH and pH of the solution were used to determine the proton ligand stability constant (representing the replacement of H⁺ ions from functional group of ligand with respect to pH value). The horizontal difference (V₂-V₁) was measured accurately between the titration

interaction of 5-p-chlorophenylthiocarbamido -1-naphthol and 5-p-tolylthiocarbamido-1-naphthol with Cu(II), Cd(II) and Cr(III) metal ions at 0.1 M ionic strength pH-metrically in 70% ethanol-water mixture.

MATERIALS AND METHOD:

All chemicals used are of AR grade. 5-p-chlorophenylthiocarbamido-1-naphthol and 5-p-tolylthiocarbamido-1-naphthol (ligands) was synthesized in the laboratory. The stock solutions of ligands were prepared by 70% (ethanol + water) mixture.

Titration of (i) free acid (0.01 M), (ii) free acid (0.01 M) and ligand (20 x 10⁻⁴M) and (iii) free acid (0.01 M), 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 i.e. 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 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 equilibria can be shown as,



By the law of mass action, we have,

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

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

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

$$3; \bar{n}_A = \gamma - \left\{ \frac{(V_2 - V_1)(N + E^0)}{(V^0 + V_1)T_L^0} \right\} \quad \text{--- (2)}$$

Where, V⁰ is the initial volume of the solution. E⁰ and T_L⁰ 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;

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

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
L ₄	5-Tolythiocarbamido-1-naphthol	10.02	9.95

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
Cu(II) + L ₄	5.32	6.30	0.98	0.8444
Cd(II) + L ₄	5.54	6.45	0.91	0.8589
Cr(III) + L ₄	5.95	6.68	0.73	0.8907

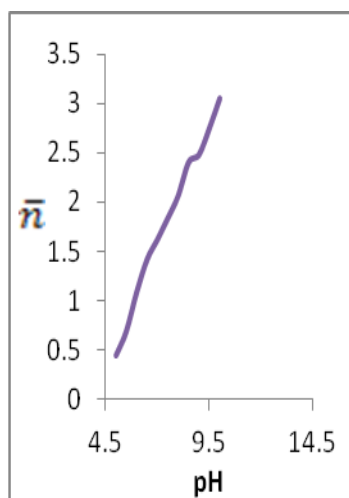


Fig. 1: Plot between \bar{n} vs pH System-L₃+Cu(II)

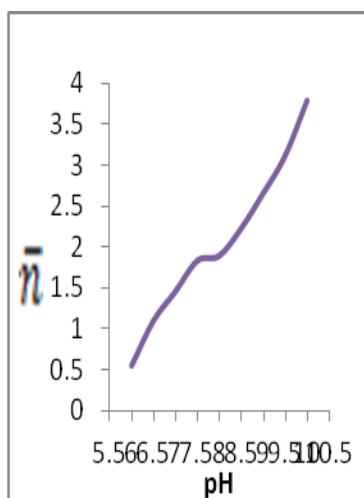


Fig. 2: Plot between \bar{n} vs pH System-L₃+Cd(II)

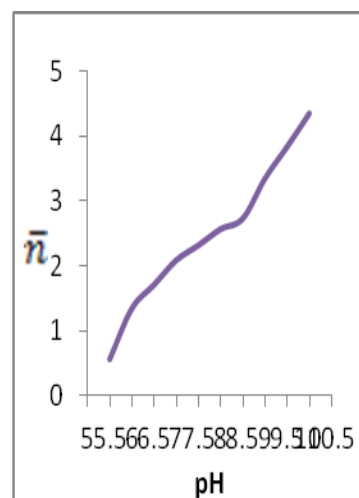


Fig. 3: Plot between \bar{n} vs pH System- L₃+Cr(III)

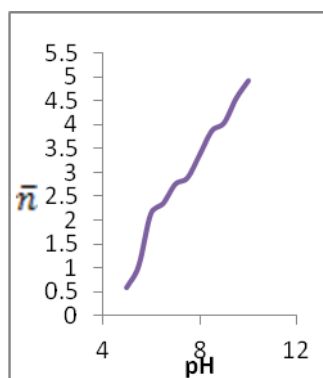


Fig. 4: Plot between \bar{n} vs pH
Ph System- L₄+Cu(II)

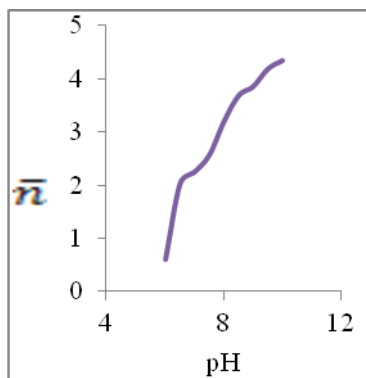


Fig. 5: Plot between \bar{n} vs pH
System-L₄+Cd(II)

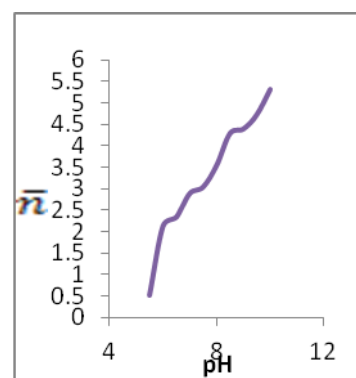


Fig. 6: Plot between \bar{n} vs
System- L₄+Cr(III)

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. Also change in color from colorless to purple in the pH range from 4.5 to 11 and 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. **Table 1** reveals that pK of ligand (L₄) greater than pK ligand (L₃). The lower pK values of ligand (L₃) because (L₃) has electron realizing -Cl group to phenyl ring which decrease the activity of ligand (L₃) to form more stable complex. Observation of **Table 2** showed that the less difference between log K₁ and log K₂ values indicates the complex formation between metal ion and ligand occurring simultaneously. The values of log K₁ and log K₂ (Table 2) decided the stability of complexes.

For 5-p-chloro-phenylthiocarbamido-1-naphthol (L₃) the difference between the values of log K₁ and log K₂ is higher with Cd(II) complex than Cu(II) and Cr(III) complexes. Cd(II) forms more stable complex with L₃ than Cu(II) and Cr(III) metal ions. While for 5-tolylthiocarbamido-1-naphthol the difference between the values of log K₁ and log K₂ is higher with Cu(II) complex than Cd(II) and Cr(III) complexes. Cu(II) forms more stable complex with 5-tolylthiocarbamido-1-naphthol than Cd(II) and Cr(III) metal ions.

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