



ISSN Print: 2394-7500  
 ISSN Online: 2394-5869  
 Impact Factor: 5.2  
 IJAR 2015; 1(13): 640-642  
 www.allresearchjournal.com  
 Received: 19-10-2015  
 Accepted: 18-11-2015

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## To study the stability of complexes of substituted Thiocarbamidonaphthols with Different Transition metal ions in 70% mixed Solvent Media

**D.T. Tayade, A.B. Wadekar**

### Abstract

The interactions of Cu(II), Cd(II) and Cr(III) metal ions with 5-phenylthiocarbamido-1-naphthol(L<sub>2</sub>) and 5-p-chlorophenylthiocarbamido-1-naphthol (L<sub>3</sub>) have been studied at 0.1 M ionic strength in 70 % ethanol-water mixture by Bjerrum method as adopted by Calvin and Wilson. It is observed that Cu(II), Cd(II) and Cr(III) metal ions simultaneously form the 1:1 and 1:2 complexes with ligands (L<sub>2</sub> and L<sub>3</sub>). 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 substituents were studied from estimated data (pK & log k).

**Keywords:** Substituted thiocarbamido-1-naphthol, stability constant, pH-metry.

### Introduction

Thiocarbamide, amino, hydroxyl, benzenoid and non-benzenoid nucleus possessing molecule showed various applications in pharmaceutical and medicinal sciences. Such group of drugs can be 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. Recently 5-amino-1-naphthol was successfully condensed with various isothiocyanates in acetone mediums to obtain 5-phenylthiocarbamido-1-naphthol and 5-p-chlorophenylthiocarbamido-1-naphthol. The manifold research work has been done on the study of metal and nitrogen heterocyclic ligands containing complexes. Stability constant of mixed-ligand alkaline earth metal complexes with metal ions was studied by Banarjee *et al.* Many researchers studied the effect of transition metal on a stability of complex by pH metrically. There is also carried out investigation of stability constant of ligand with lanthanide metals. The investigation of interaction between to various metal ions and ligands carboxylic acids, oximes, phenols etc. provide the valuable information concerned to the mode of storage and transport of metal ions in biological kingdom. Activated complex form by the interaction of reacting molecules as well as polarized electrons from ligands towards the metal. The formation constant and free energy change value help to know the relation between stability and basicity of the ligands. 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. The metal-ligand stability constants of some lanthanides with some substituted sulphonic acids studied by Narwade *et al.* The metal-ligand stability constants of some  $\beta$ -diketones was investigated by Bodkhe *et al.* Investigation of mixed ligand complexes of alkaline earth metals, Mg(II), Ca(II), Sr(II) and Ba(II) with 5-nitrosalicylaldehyde and  $\beta$ -diketones was carried out by Prasad *et al.* Recently, interaction between some lanthanide and radioactive metal ion with substituted Schiff's bases at 0.1 M

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ionic strength pH metrically investigated by Thakur *et al.* Proper knowledge of stability constant enormously helpful 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. Bearing all these in mind to designed this research scheme. In present work an attempt has been made to study the interactions between Cu(II), Cd(II) and Cr(III) and 5-phenylthiocarbamido-1-naphthol and 5-p-chloro- phenylthiocarbamido-1-naphthol (L<sub>2</sub> and L<sub>3</sub>) at 0.1 M ionic strength pH metrically in 70% ethanol-water mixture.

**Experimental Section**

All chemicals used are of AR grade. The ligands (L<sub>2</sub>) & (L<sub>4</sub>) were synthesized in the laboratory by reported protocol. The stock solutions of the ligand was prepared by dissolving required amount of ligand in a of 70% (ethanol + water) mixture.

**General procedure**

Types of Titrations

- i) Free acid HNO<sub>3</sub> (0.01 M)
- ii) Free acid HNO<sub>3</sub> (0.01 M) and ligand (20 x 10<sup>-4</sup>M)
- iii) Free acid HNO<sub>3</sub> (0.01 M) and ligand (20 x 10<sup>-4</sup>) and metal ion (4 x 10<sup>-4</sup>M) against standard 0.1N NaOH solution. The ionic strength of all the solutions was maintained constant 1M by adding appropriate amount of KNO<sub>3</sub> 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<sup>+</sup> 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 (representing the replacement of H<sup>+</sup> ions from functional group of ligand with respect to pH value). The horizontal difference (V<sub>2</sub>-V<sub>1</sub>) 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, 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<sup>0</sup> is the initial volume of the solution. E<sup>0</sup> and T<sub>L</sub><sup>0</sup> are initial concentrations of the mineral acid and ligand respectively. V<sub>1</sub> and V<sub>2</sub> are the volumes of alkali of normality N during the acid and ligand titration at given pH.  $\gamma$  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.

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

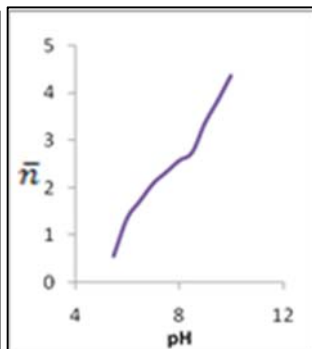
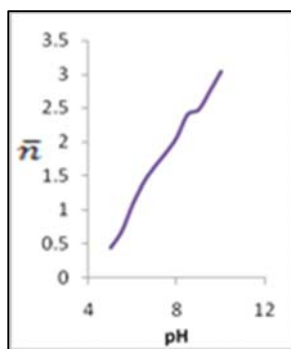
Where, the notations have the same meaning as given in earlier equation. The horizontal difference (V<sub>3</sub>-V<sub>2</sub>) between the metal complex (A+M+L) and reagent (A+L) curve is used to evaluate the value of n using Irving Rossotti's equation.

**Table 1:** Proton-Ligand Stability constant (pK)

Ligand	System	pK	
		Half integral method	Point wise method
L <sub>2</sub>	5-Phenylthiocarb amido-1-naphthol	10.55	10.62
L <sub>4</sub>	5-p-chlorophenyl thiocarbamido-1-naphthol	9.80	8.98

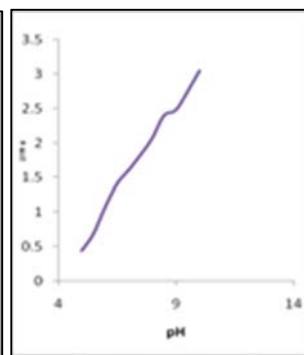
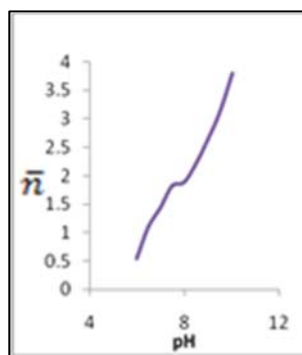
**Table 2:** Metal-ligand stability constant (log K)

System	Log K <sub>1</sub>	Log K <sub>2</sub>	$\Delta$ Log K	LogK <sub>1</sub> /Log K <sub>2</sub>
Cu(II)+L <sub>2</sub>	5.39	6.05	0.66	0.8909
Cd(II)+L <sub>2</sub>	5.36	6.15	0.79	0.8715
Cr(III)+L <sub>2</sub>	5.72	6.45	0.73	0.8868
Cu(II)+L <sub>3</sub>	5.35	6.15	0.8	0.8699
Cd(II)+L <sub>3</sub>	5.43	6.41	0.98	0.8471
Cr(III)+L <sub>3</sub>	5.81	6.52	0.71	0.8911



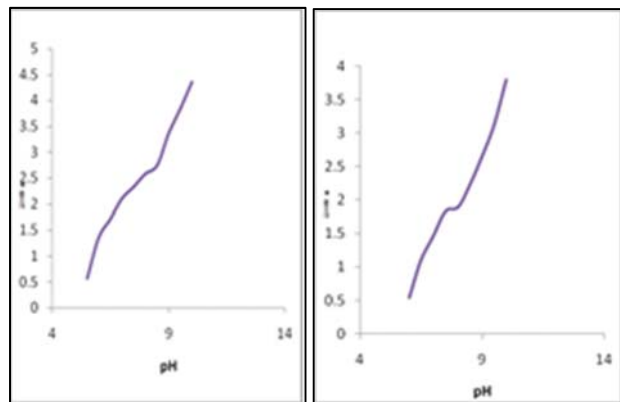
**Fig 1:** Plot between  $\bar{n}$  vs pH System- L<sub>2</sub>+Cu(II)

**Fig. 2:** Plot between  $\bar{n}$  vs pH System-L<sub>2</sub>+Cr(III)



**Fig 3:** Plot between  $\bar{n}$  vs pH system L<sub>2</sub>+Cd(II)

**Fig 4:** Plot between  $\bar{n}$  vs pH system L<sub>3</sub>+Cu(II)



**Fig 5:** Plot between  $\bar{n}$  vs pH System- $L_3$ +Cr(III)

**Fig 6:** Plot between  $\bar{n}$  vs pH System-  $L_3$ +Cd(II)

### 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 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 ligands are found to be pK of ligand ( $L_2$ ) greater than pK ligand ( $L_3$ ). The lower pK values of ligand ( $L_3$ ) because ( $L_3$ ) has electron realizing -Cl group to phenyl ring which decrease the activity of ligand ( $L_3$ ) to form more stable complex. 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) the stability of complexes was decided.

For 5-phenylthiocarbamido-1-naphthol ( $L_2$ ) the difference between the values of log  $K_1$  and log  $K_2$  is higher with Cd(II) complex than Cu(II) and Cr(III). It indicates that Cd(II) forms more stable complex with Ligand-2 than Cu(II) and Cr(II). while for 5-p-chloro-phenylthiocarbamido-1-naphthol ( $L_3$ ) the difference between the values of log  $K_1$  and log  $K_2$  is higher with Cr(III) complex than Cu(II) and Cd(II) complexes. Cr(III) forms more stable complex with  $L_3$  than Cu(II) and Cd(II) metal ions.

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