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Journal of Advanced Chemical Sciences

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Effect of Substituted Thiocarbamido-1-Naphthols on Stability Constant using Cu(II), Cd(II) and Cr(III) Metal Ions in 70% Ethanol-Water Mixture

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ARTICLE DETAILS

Article history:

Received 13 November 2016

Accepted 24 November 2016

Available online 30 December 2016

Keywords:

5-Amino-1-Naphthol (L₁)5-Phenylthiocarbamido-1-Naphthol (L₂)5-p-Chlorophenylthiocarbamido-1-Naphthol (L₃)

Stability Constant

ABSTRACT

The present work highlighted the effect of substituent's on proton-ligand and metal-ligand stability constant of 5-amino-1-naphthol (L₁), 5-phenylthiocarbamido-1-naphthol (L₂) and 5-p-chloro -phenyl thiocarbamido-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-amino-1-naphthol (L₁), 5-phenylthiocarbamido-1-naphthol (L₂) and 5-p-chlorophenyl-thiocarbamido-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 studied from resultant estimated pK and log K values.

1. Introduction

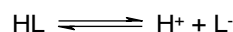
Thiocarbamido, hydroxyl, amino and benzenoid nucleus possessing molecule create their own important in various field of pharmaceutical and medicinal sciences. These types of drugs effectively used against various diseases. Several modern theories and concept are concerning to physical as well as chemical study of benzenoid, non-benzenoid, heteroacycles and heterocycles. Aminonaphthols and thiocarbamido nucleus containing heterocycles possesses pharmaceutical, medicinal agricultural industrial and biotechnological significances [1-5]. 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].

The study of substituted thiopyrimidine complexes in mixed solvents media pH-metrically had been carried out by many researchers [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). Stability constant and Formation constant of some metal complexes was studied [12-13]. There has been considerable interest in the study of binary ternary and quaternary complexes by pH-metric method [14-17]. Thakur et al was investigated stability study of complexation of trivalent rare earth metals with isoniazid: thermodynamic aspect. [18]. Some more authors 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-amino-1-naphthol(L₁), 5-phenylthiocarb amido-1-naphthol (L₂) and 5-p-chlorophenylthio- carbamido-1-naphthol(L₃) have not been reported in literature. Hence this study made an interest to study the stability constant of complexes form by interaction of 5-amino-1-naphthol, 5-phenylthiocarbamido-1-naphthol and 5-p-chlorophenylthiocarbamido-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.

2. Experimental Methods

All chemicals used are of AR grade. 5-amino-1-naphthol (L₁), 5-phenyl -thiocarbamido-1-naphthol (L₂) and 5-p-chlorophenylthiocarbamido-1-naphthol (L₃) was synthesized in the laboratory. The stock solution of ligands 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 0.1 N NaOH solution. The ionic strength of all the solutions was maintained constant i.e. 1 M 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,

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

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

3. Results and Discussion

3.1 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 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 Eq. (2) and (3),

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

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,

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

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 (Figs. 1-9).

Table 1 Proton-Ligand Stability constant (pK)

Ligand System	pK	
	Half integral method	Point wise method
L ₁ 5-amino-1-naphthol	9.20	7.76
L ₂ 5-phenylthiocarbamido-1-naphthol	10.55	10.62
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
L ₁ +Cu(II)	5.48	5.75	0.27	0.9530
L ₁ +Cr(III)	5.42	6.22	0.8	0.8713
L ₁ +Cd(II)	5.22	5.58	0.36	0.9354
L ₂ +Cu(II)	5.39	6.05	0.66	0.8909
L ₂ +Cr(III)	5.72	6.45	0.73	0.8868
L ₂ +Cd(II)	5.36	6.15	0.79	0.8715
L ₃ +Cu(II)	5.35	6.15	0.8	0.8699
L ₃ +Cr(III)	5.81	6.52	0.71	0.8911
L ₃ +Cd(II)	5.43	6.41	0.98	0.8471

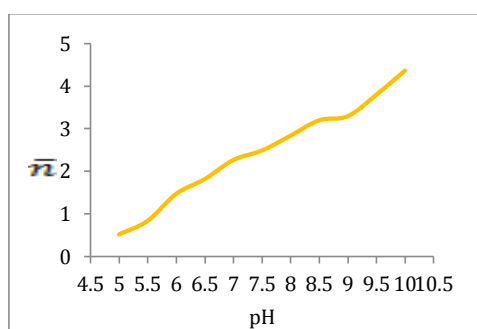


Fig. 1 Plot between \bar{n} vs pH System-L₁+Cu(II)

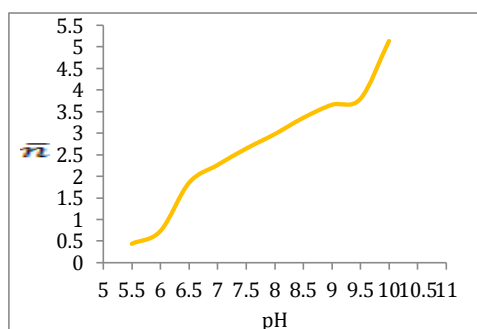


Fig. 2 Plot between \bar{n} vs pH System-L₁+Cr(III)

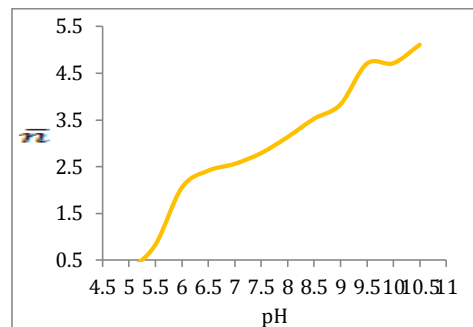


Fig. 3 Plot between \bar{n} vs pH System-L₁+Cd(II)

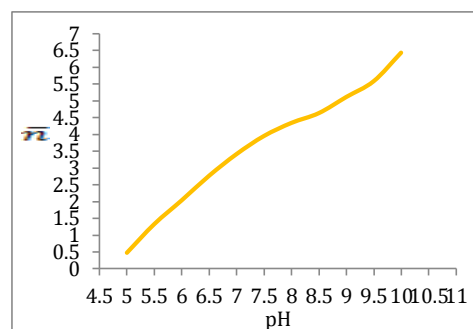


Fig. 4 Plot between \bar{n} vs pH System-L₂+Cu(II)

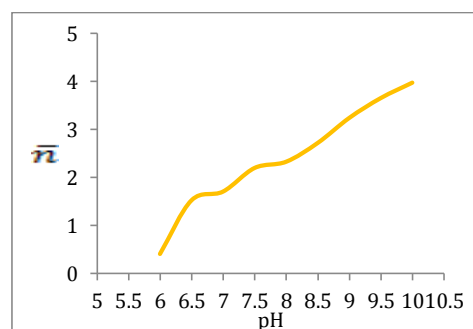


Fig. 5 Plot between \bar{n} vs pH System-L₂+Cr(III)

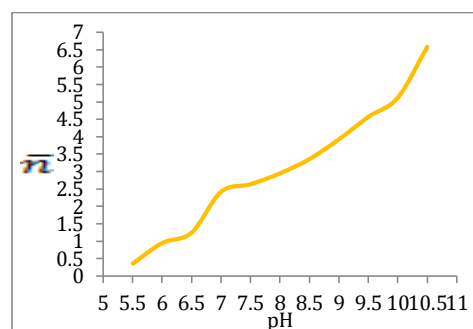


Fig. 6 Plot between \bar{n} vs pH System-L₂+Cd(II)

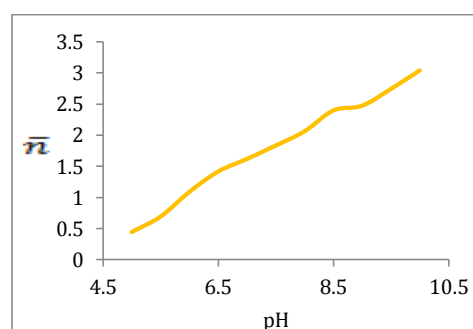


Fig. 7 Plot between \bar{n} vs pH System-L₃+Cu(II)

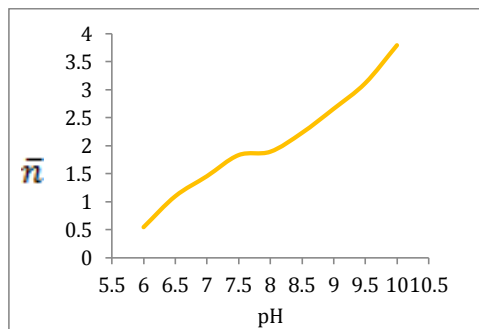


Fig. 8 Plot between \bar{n} vs pH System- L_3 +Cu(II)

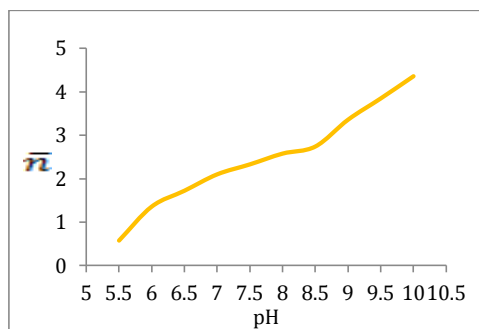


Fig. 9 Plot between \bar{n} vs pH System- L_3 +Cr(III)

4. 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 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 (L_2) greater than pK ligand L_1 and L_3 . The lower pK values of ligand L_1 lower than L_2 and L_3 . L_2 has greater pK values because of -phenyl group while L_3 has electron realizing-Cl group to phenyl ring which decrease the activity of ligand (L_3). L_1 form more stable complex. Observation of Table 2 showed that less difference between $\log K_1$ and $\log K_2$ values indicates the complex formation between metal ion and ligand occurring simultaneously. Values of $\log K_1$ and $\log K_2$ (Table 2) decided the stability of complexes.

For L_1 the difference between the values of $\log K_1$ and $\log K_2$ is higher with Cu(II) complex than Cd(II) and Cr(III). It indicates that Cu(II) forms more stable complex with ligand-1 than Cd(II) and Cr(II), in case of 5-phenylthiocarbamido-1-naphthol (L_2) 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) 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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