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pH-metric study of substituted thiocarbamidonaphthols complexes with different transition metal ions in 70% mixed solvent media

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ABSTRACT

The interactions of Cu(II), Cd(II) and Cr(III) metal ions with 5-phenylthiocarbamido-1-naphthol(L_2) and 5-ptolylthiocarbamido-1-naphthol (L_4) 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 form 1:1 and 1:2 complexes with ligands (L_2 and L_4). The values of proton-ligand stability constant (pK) and metal-ligand stability constants (log k) were estimate and compared from resultant data. The effect of substituent's were studied from estimated data (pK & log k).

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

INTRODUCTION

Molecule containing thiocabamido, amino, hydroxyl, benzenoid and non-benzenoid nucleus showed various applications in pharmaceutical and medicinal sciences. These types of drugs are very effective in various diseases. Several modern theories and concept are concerning to physical as well as chemical study of benzenoid, nonbenzenoid, heteroacycles and heterocycles. Aminonaphthols and thiocarbamido nucleus containing heterocycles possesses pharmaceutical, medicinal agricultural industrial and biotechnological significances [1-5]. Recently 5amino-1-naphthol was successfully condensed with various isothiocyanates in acetone mediums to obtain 5phenylthiocarbamido-1-naphthol and 5-p-tolylthiocarbamido-1-naphthol. The manifold research work has been done on the study of metal and nitrogen heterocyclic ligands containing complexes[6-7]. Stability constant of mixed-ligand alkaline earth metal complexes with metal ions was studied by Banarjee et al [8]. Many workers study the effect of transition metal on a stability of complex by pH metrically [9-11]. Also there is a investigation of stability constant of ligand with lanthanide metals [12-15]. The studies of metal-ligand complexes in solution having number of metal ions with ligands carboxylic acids, oximes, phenols etc. would be interesting which throw a light on the mode of storage and transport of metal ions in biological kingdom. Metal complexation not only brings the reacting molecules together to give activated complexes [16] but also polarized electrons from the ligands towards the metal. The relation between stability and basicity of the ligands is indicated by the formation constant and free energy change value. 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. Narwade et al have

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investigated metal-ligand stability constants of some lanthanides with some substituted sulphonic acids[17]. Bodkhe et al have reported the metal-ligand stability constants of some β -dikctones[18]. Prasad et al have studied mixed ligand complexes of alkaline earth metals, Mg(II). Ca(II), Sr(II) and Ba(II) with 5-nitrosalicyladehyde and β -diketones [19]. Recently, Thakur et al studied the interaction between some lanthanide and radioactive metal ion with substituted Schiff's bases at 0.1 M ionic strength pH metrically and spectrophotometrically[20]. Reliable information of stability constant is of great importance 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. 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-tolylthiocarbamido-1-naphthol (L₂ and L₄) at 0.1 M ionic strength pH metrically in 70% ethanol-water mixture.

MATERIALS AND METHODS

All chemicals used are of AR grade. The ligands (L_2) & (L_4) 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 HNO₃ (0.01 M)

ii) Free acid HNO₃ (0.01 M) and ligand (20 x 10^{-4} M)

iii) Free acid HNO₃ (0.01 M) and ligand (20×10^{-4}) and metal ion (4×10^{-4} M) against standard 0.1N NaOH solution. The ionic strength of all the solutions was maintained constant 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 may be 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.

$$HL = H^+ + L$$

By the law of mass action, we have,

$$K = [HL] / ([H^+] [L^-])$$

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^+ 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 equation [1,2]

$$\bar{\mathbf{n}}_{\mathbf{A}} = \gamma - \left\{ \frac{(\mathbf{V}_2 - \mathbf{V}_1)(\mathbf{N} + \mathbf{E}^\circ)}{(\mathbf{V}^\circ + \mathbf{V}_1)\mathbf{T}_{\mathbf{L}}^\circ} \right\}$$
(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.

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(1)

$$\bar{n} = \frac{(V_3 - V_2) (N + E^0)}{(V^0 + V_2) \bar{n}_A T_M^0}$$
(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	рК		
		Half integral method	Point wise method	
L2	5-Phenylthiocarbamido-1-naphthol	10.55	10.62	
L4	5-Tolvlthiocarbamido-1-naphthol	10.02	9.25	





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System	Log K ₁	Log K ₂	Δ Log K	Log K1/Log K2
$Cu(II) + L_2$	5.39	6.05	0.66	0.8909
$Cd(II) + L_2$	5.36	6.15	0.79	0.8715
$Cr(III) + L_2$	5.72	6.45	0.73	0.8868
$Cu(II) + L_4$	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

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

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 ligands are found to be pK of ligand (L₂) > pK ligand (L₄). The more pK values of ligand (L₂) is attributed because (L₄) has electron realizing methyl group which decrease the activity of ligand to form the more stable complex. Observation of Table 2 shows 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) the stability of complexes was decided.

For 5-phenylthiocarbamido-1-naphthol (L2) 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). And for 5-tolylthiocarbamido-1-naphthol (L₄) the difference between the values of log K_1 and log K_2 is higher with Cu(II) complex than Cd(II) and Cr(II) complexes. Cu(II) forms more stable complex with L₄ than Cd(II) and Cr(II) metal ions.

REFERENCES

- [1] Barnes D.M., Jianguo Ji, Fickes M.G., J. Am. Chem. Soc., 2002, 124, 13097-13105.
- [2] Cyril V., Milam M.. Chem. Abstract., 1977, 86, 190015.
- [3] Ghaigy A.G.. Siess Patent, 1965, 393, 344.
- [4] Bossinger S.D. and Tekeshi E.. Chem. Abstract., 1972, 77, 343590.
- [5] Seidal M., Betiver E.F., African Patent, 1964, 68, 03, 47.
- [6] Irving H. and Rossotti H., J. Chem. Soc., 1954, 2904.

[7] Martell A.E. and Calvin M., Chemistry of metal chelate compounds. Prentice Hall. Inc. England. Cliffs. N. J.

- **1962**.
- [8] Banarjee A. K and Rao T.V.R., J. Indian Chem. Soc., 1968, 63, 480.
- [9] Meshram Y.K., Khan R.F., Ind. J. Applied Res., 2014, 4(3), 37.
- [10]Khobragade V.B. Narwade M.L., JCPR, 2013, 5(10), 189.
- [11]Majlesi K., Nezaieneyad K., J. Serb chem. Soc, 2013, 78(10), 1547.
- [12]Bendi R.R., Bull chem. Soc, ethhiop, 2011, 25(1), 43.
- [13]Janrao D.M., Pathan J., Sci. chem. Commun., 2014, 4(1), 11.
- [14]Ramteke A., Narwade M.L., Arch Applied Sci. Res, 2013, 5(1), 231.
- [15] Thakur S.V., J. Chem., Bio & Phys Sci., 2014, 4(1), 01.
- [16] Irving H and William R.J.P., J. Chem. Soc., 1953, 3192.
- [17] Narwade M.L., Chincholkar M.M. and Sathe S.W., J. Indian Chem. Soc., 1985, 62, 194.
- [18] Bodkhe P.S., Patil K.N., Narwade M.L. and Doshi A.G., Asian J. Chem., 2003, 15(3 & 4) 1739-1743.
- [19] Prasad R.N., Agrawal M, Ratnani R. and Sarswal K., J. Indian Chemical Soc, 2005, 82, 137 139,.
- [20] Thakur S.D., Munot K.P., Raghuvanshi P.B., Tayade D.T.. Acta Ciencia Indica, 2010, XXXC(3), 425.