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Synthesis and Evaluate pK and Log K of 1(4-Aminophenyl)-2(p-Chlorophenyl thiocarbamido)-1-Ethanol with Cr(III), Cd(II) and Cu(II) ions pH-metrically

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Abstract

Present work deals with synthesis and evaluation of pK and Log K of 1(4-Aminophenyl)-2(p-Chlorophenyl thiocarbamido)-1-Ethanol with Cr(III), Cd(II) and Cu(II) ions pH-metrically. In present work studied proton-ligand stability constant (pK) and metal -ligand stability constant (log K) by interacting 1(4-Aminophenyl)-2(p-Chlorophenyl thiocarbamido)-1-Ethanol with Cr(III), Cd(II) and Cu(II) metal ions at 0.1 M ionic strength in 75 % ethanol-water mixture by Bjerrum method as adopted by Calvin and Wilson, It is observed that Cr(III), Cd(II) and Cu(II) metal ions form 1:1 with ligands [L]. The values of proton-ligand stability constant (pK) and metal-ligand stability constants (log k) were estimated and compared from resultant data. The effects of substituents were studied from estimated data (pK & log k).this work helps to understand solute-solute, solute-solvent and solvent-solvent interaction.

Keywords: 1(4-Aminophenyl)-2(p-Chlorophenyl thiocarbamido)-1-Ethanol [L], Proton ligand stability constant, Metal-Ligand stability constant, H-metrically investigation.

1. Introduction

Molecule containing thiocabamido, amino, hydroxyl, benzenoidand 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, non-benzenoid, heteroacycles and heterocycles. Aminonaphthols and thiocarbamido nucleus containing heterocycles possesses pharmaceutical, medicinal agricultural industrial and biotechnological significances [1-5]. The manifold research work has been done on the study of metal and nitrogen heterocyclic ligands containing complexes [6-15].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

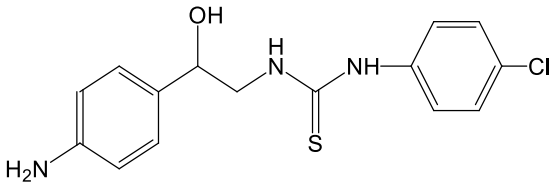
increases the basicity of ligands as well as stability. The stability of the complexes is determined by the nature of central metal atom and ligand. The stability of complexes is influenced bythe most important characteristics degree of oxidation, radius and electronic structure. Irving and Williams 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. Stability and complexation by lingands and various metal ions were evaluated by many researchers [17-20]. 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 synthesis and evaluation of pK and Log K of 1(4-Aminophenyl)-2(p-Chlorophenylthiocarbamido)-1-Ethanol with Cr(III), Cd(II) and Cu(II) ions pH-metrically.

2. Research Methodology

2.1 Synthesis

Synthesis of 1(4-aminohenyl)-2(p-chlorophenylthiocarbamido)-1-ethanol

4-(2-amino-1-hydroxyehtyl) aniline and p-chlorophenyl isothiocynate are reflux in acetone medium for 2 hrs to obtained 1(4-aminophenyl)-2(p-chlorophenyl thiocarbamido)-1-ethanol. After completion of reaction, to isolated 1(4-aminophenyl)-2(p-chlorophenyl thiocarbamido)-1-ethanol from solvent. After distillation of acetone the product is isolated which is recrystallized from ethanol to get white colour crystalline solid with m.p. 85^0C.



1(4-aminophenyl)-2(p-chlorophenyl thiocarbamido)-1-ethanol

2.2. pH-Metric Analysis:

All chemicals used are of AR grade. The stock solutions of the ligand [L] was prepared by dissolving required amount of ligand in a of 75% (ethanol + water) mixture.

General procedure:

Types of Titrations

i) Free acid HNO_3 (0.01 M)

ii) Free acid HNO_3 (0.01 M) and ligand (20 x 10^{-4}M)

iii) Free acid HNO_3 (0.01 M) and ligand (20 x 10^{-4}) and metal ion (4 x 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 KNO_3 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.

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

By the law of mass action, we have,

$$K = [HL] / ([H^+] [L^-]) \quad \ldots\ldots\ldots (1)$$

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

3. 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 (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

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

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. □ □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

$$\bar{n} = \left\{\frac{(V_3 - V_2)(N + E^\circ)}{(V^\circ + V_2)\bar{n}_A T_M^\circ}\right\} \quad \ldots\ldots\ldots (3)$$

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)

System	pK		Diff.
	Half integral method	Point wise method	
1(4-Aminophenyl)-2(p-Chlorophenylthiocarbamido)-1-Ethanol (L)	7.95	8.15	0.20

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

System	Log K_1	Log K_2	Δ Log K	Log K1/ Log K2
Cr(III) + L	6.25	6.85	0.6	0.912409
Cd(II) + L	5.56	6.2	0.64	0.896774
Cu(II) +L	4.85	5.74	0.89	0.844948

Fig. 1 Plot between $\bar{n}$ vs pH
System- L-Cr(III)

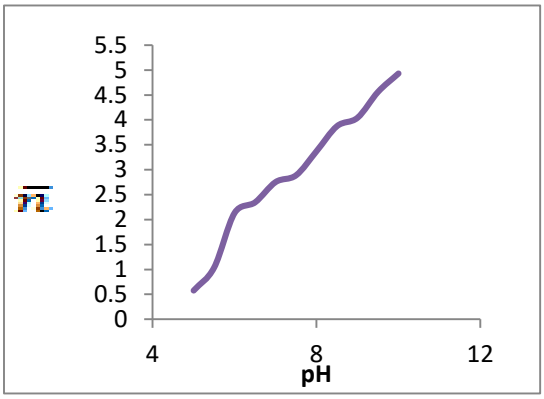


Fig. 2 Plot between $\bar{n}$ vs pH
System- L-Cd(II)

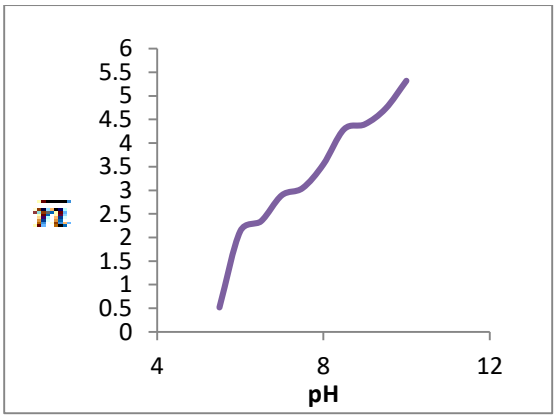
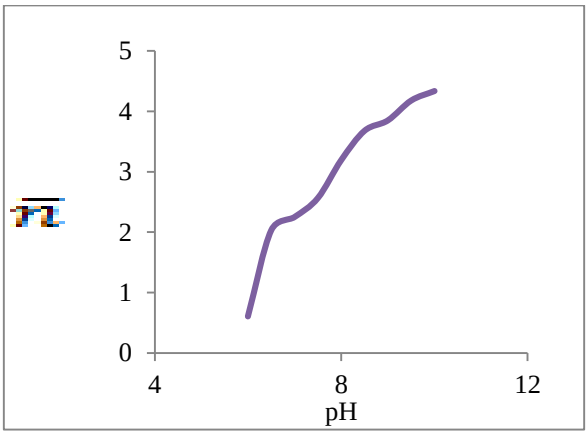


Fig. 3. Plot between $\bar{n}$ vs pH
System -L+Cu(II)



4. Conclusion

During this work ethanol water mixture solvent give good result. Metal salts soluble in ethanol as well as water but ligand soluble in organic solvent. For 1(4-Chlorophenyl)-2(P-Tolylthiocarbamido)-1-Ethanol the difference between the values of log K_1 and log K_2 is higher with Cr(II) complex than Cd(II) and Cu(II) complexes Cr(III) metal ion forms more stable complex with L than Cd(II) and Cu(II) metal ions. Proton ligand stability value in good range their difference in negligible.

Observation of Table-2 showed that less difference between log K1 and log K2 values indicates complex formation between metal ion and ligand occurring simultaneously and 1:1 complexation occurs in between to above metal ions and L. This work helps to understand proton ligand stability and metal ligand stability constant of 1(4-Aminophenyl)-2(p-Chlorophenyl thiocarbamido)-1-Ethanol (L). Present work useful to understand solute(L)-solute(M) interaction, Solute(L)-Solvent(E-W) interaction and Solute(M)-Solvent(E-W) interaction,

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