International Journal of Sciences & Applied Research

www.ijsar.in

To study the interaction of 2-methyl thiocarbamidophenol and 2-tolyl thiocarbamidophenol with Cu(II), Co(II), Cd(II) and Ni(II) by pH-Metric method

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Abstract

In this research paper, the interaction between Cu(II), Co(II), Cd(II) and Ni(II) with L_2 and L_4 have been studied by pH-metric technique at 0.1 M ionic strength in 70% ethanol-water mixture with the use of Irving-Rossotti and Calving-Bjerrum method. The data obtain were used to estimate the value of proton-ligand stability constant (pK) and metal ligand stability constant (logK). It showed that the metal ions form 1:1 and 1:2 complexes with L_2 and L_4.

Keywords: Stability constant, 2-methyl thiocarbamidophenol, 2-tolyl thiocarbamidophenol, pH-metry

Introduction

From many decades in the organic chemistry several organic compounds were synthesized in laboratory by various chemist and their co-workers. The synthesized compounds contain benzonoide, non-benzonoide molecules. In drug chemistry the main goal of chemist to check the physical and chemical properties of synthesized compound. The pH-metric studies give the important and useful information about solute-solute, solute-solvent, solvent-solvent interaction. In the literature it was reported that the proton-ligand stability constant, metal-ligand stability constant, log K and pK values affects drug activity, drug effect and drug stability. This investigation discovers the power of synthesized drugs, stability of drugs and modernized the well known old drugs. There are many research have been carried out to study the stability of drugs. The formation constant and solubility constant of Th(V) complexes with some substituted pyrazolines was studied by Narwade*et al*[1]. Gudadhe*et al*[2] investigated the stability constant of Cu(II) with substituted isoxazoline in 70% dioxane-water mixture. The stability constant of some substituted pyrazoline, isoxazoline and diketones was studied by Tekade*et al*[3]. Ali Asagar*et al*[4] have investigated metal-ligand stability constant of some transition metal ions with some substituted pyrazoline and isoxazoline pH-metrically. The stability constant of Pr(III) complexes with substituted pyrazolines was studied by Meshram*et al*[5]. The studies of proton and

metal-ligand stability constant of Pr(III),Nd(III) and Gd(III) complexes of substituted Schiff's bases and dibromochalcones was done by Khambre and Narwade[6]. Naik A.B. *et al*[7] have studied the substituted pyrozoles with some lanthanides metal ions and the influence of ionic strength on complex equilibria in a 70% dioxane-water mixture. Ramteke*et al*[8] have studied stability constant of the complexes of chlorosubstitutedpyrozoles and pyrazolines with Cu(II), Ni(II), Co(II) and Nd(II) metal ions in 70% dioxane- water mixture at 0.1 M ionic strength. Murhekar*et al*[9] have investigated the formation constant of lanthanides metal ion chelates with some substituted pyrozoles in different solvent compositions. Das *et al*[10] have investigated the effect of ionic strength on the stability constant of complexes of Fe(III) with salicyclic acid and its derivatives. Majlesi*et al*[11] have studied the stability constant of tugesten(VI) and molybdenum(VI) with nitrilotriacetic acid and glutamic acid at different ionic strength. Sharma *et al*[12] have investigated the effect of ionic strength and solvent effect on thermodynamic parameters. The stability constant of mixed ligand complexes of bio-molecules and amino acids with Ni(II) was studied by Shankarwar*et al*[13]. Meshram*et al*[14] have studied the formation constant of Al(III), Cr(III) and Fe(III) complexes with some substituted isoxazoline, pyrazole and pyrazoline pH-metrically. Rawate G.D[15] have investigated the stability constant and thermodynamic properties of complexation of ibuprofen with Co(II) and Zn(II) pH-metircally.

Experimental Method

The pH-metric titrations were carried out with EQ-614 pH meter equipment. The entire chemicals were used of AR grade. The stock solutions of ligands were prepared by dissolving required amount of ligands in 70% ethanol water mixtures. The following three sets of solution were titrated against standard NaOH solution.

i) Perchloric acid (1 X 10^{-2} M) {Free Acid}, ii) Perchloric acid (1 X 10^{-2} M) {Free Acid}, and ligand (20X10^{-4} M) , iii) Perchloric acid (1x 10^{-2} M) {Free Acid), the ligand (20x10^{-4} M) and metal salt (4x10^{-4}M) (Ionic quality of the solution was kept up constant at (U = 0.1M) by including a proper measure of 1m KNO3 solution) for deciding the portrayed constants in the present research work. The readings were recorded for each 0.2ml addition. The graph was plotted between volume of alkali (NaOH) and pH. The ligands involved in the present work may be consider as monobasic acid having only one dissociable H^+ ion from phenolic -OH group and it can be therefore represented as HL. The dissociating equilibrium can be shown as HL.

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

By the Law of mass action, we have,

$K = [HL] / ([H^+] [L^-])$ …… (1)

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

Results and discussion

Determination of proton-ligand stability constant ($\bar{n}_A$)

To determine proton-ligand stability constant the plotted graph between volume of NaOH and pH of the solution were used (represent the replacement of H^+ ions from functional group of ligands with respect to pH value). Between the titration curves of free acid and acid + ligand horizontal difference (V2-V1) were measured accurately. It was used to calculate formation number $\bar{n}_A$ at various pH values and fixed ionic strength μ = 0.1M using Irving and Rossotti's equation.

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

Where, V^0 is the initial volume of solution.

E^0 and T_L^0 are initial concentrations of the free acid and ligand respectively.
V_1 and V_2 are the volume of alkali of normality N.

γ is the replaceable proton from the ligand.

The information of $\bar{n}_A$ at various pH along with the horizontal difference for some representative system are represented by in Table 1. The metal ligand formation number $\bar{n}$ is estimated by Irving and Rossotti's equation.

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

Symbolizations have the same meaning as given in earlier equation. The horizontal differences (V_3-V_2) between metal complex (A+L+M) and reagent (A+L) curve is used to evaluate the value of $\bar{n}$ using Irving Rossotti's equation

Table 1: Proton ligand Stability Constant (pK).

Ligand	pK (Half Integral Method)	pK (Pointwise Calculation Method)
Ligand (L_2)	5.22	5.11
Ligand(L_4)	4.54	4.92

The pK values were calculated from the formation curves between pHVsnA observing the pH at which nA=0.5 (halif integral method) and pointwise calculation method showed in Table 1.
It is observed that the order of pK values of ligands is found to be as pK ligand 2 >pK ligand 4. The reduction of pK values of ligand 4 may be due to inductive effect of methyl group which is substituted at para position of phenyl ring.
The stepwise formation constants of Cu(II), Co(II), Cd(II) and Ni(II) with ligand L_2 and ligand L_4 in ethanol-water mixture were determined. The values of logK1 and logK2 were calculated from the formation curves (nVspL) using half integral method. The most accurate values were calculated by pointwise calculation method which is denoted by Table 2.

Conclusion

The titration curves shows the departure between acid + ligands (A+L) curves and acid + ligand + metal (A+L+M) curves for all system started from pH = 4.8. This specified the origin of complex formation with the color changes from colorless to faint yellow in the pH range from 4.8 to 11 during titration indicates the complex formation between metal and ligand.

Table 2: Metal-Ligand Stability Constants.

System	LogK1	LogK2	Log K1- Log K2	Log K1 / Log K2
L2+Cu(II)	4.73	3.41	1.32	1.387
L2+Co(II)	4.15	3.05	1.1	1.361
L2+Cd(II)	3.91	3.09	0.82	1.265
L2+Ni(II)	3.92	3.05	0.87	1.285
L4+Cu(II)	4.61	3.45	1.16	1.336
L4+Co(II)	4.72	3.61	1.11	1.307
L4+Cd(II)	4.79	3.41	1.38	1.405
L4+Ni(II)	4.98	3.15	1.83	1.581

Table 2 indicates that the difference between $logK_1$ and $logK_2$ values provides information about complex is formed between metal ion and ligand. The value of $logK_1$ and $logK_2$ indicates the stability of complexes.

In the case of 2-methylthiocarbamidophenol (L_2) the difference between the value of $logK_1$ and $logK_2$ is higher with Cu(II) complex than Co(II), Cd(II) and Ni(II) complexes. Cu(II) forms more stable complex with L_2 than Co(II),Cd(II) and Ni(II). While in the case of 2-tolyl thiocarbamidophenol (L_4) the difference between the values of $logK_1$ and $logK_2$is higher with Ni(II) complex than Cu(II),Co(II) and Cd(II) complexes.Ni(II) forms more stable complex with L_4. The information obtained from above investigations is helpful to study the drug effect and drug activity of newly synthesized compound.

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