NOTE

pH-Metric Study of Metal-Ligand Stability Constants of Cu(II) and Fe(III) Complexes with Substituted Pyrazole and Isoxazole

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The interaction of Cu(II) and Fe(III) with 3-(2-hydroxy-3,5-dichlorophenyl)-4-benzoyl-5-(2'-furyl)-1-phenylpyrazole (L_1) and 3-(2-hydroxy-3,5-dichlorophenyl)-4-anisoyl-5-(2'-furyl) isoxazole (L_2) have been studied by Bjerrum method as adopted by Calvin and Wilson. The stability constant of 1 : 1 and 1 : 2 complexes of Cu(II) and Fe(III) have been studied at constant temperature ($27 \pm 0.1°C$) and 0.1 M ionic strength in 70% dioxane-water mixture. It is observed that formation of 1 : 1 and 1 : 2 complexes is occurring simultaneously.

Key Words : pH-metric study, Cu(II), Fe(III), Metal-ligand stability constants, Substituted pyrazole, Isoxazole.

Since the last 45 years, considerable research work has been done on the study of complexes in solution[1-3]. Coordination compounds play an important role in numerous chemical and biological systems like separation of lanthanides, water softening, ion exchange resins, electroplating, dyeing antioxidants, photosynthesis in plants, removal of undesirable and harmful metals from living organisms, etc. Metal complexation not only brings the reacting molecules together to give activated complex[4] but also polarize 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 the ligands as well as stability. The stability of the complexes is determined by the nature of central metal atom and the ligands and depends on the same characteristics of the ligands as considered for the cation as complexes reacted with monoatomic ligands.

Synthesis of 3-(2-hydroxy-3,5-dichlorophenyl)-4-benzoyl-5-(2'-furyl)-1-phenylpyrazole (L_1) and 3-(2-hydroxy-3,5-dichlorophenyl)-4-anisoyl-5-(2'-furyl) isoxazole (L_2) was done by the treatment of phenyl hydrazine hydrochloride on chromones and hydroxylamine hydrochloride on chromones respectively.

The purity of these compounds was checked by TLC, m.p. and spectral analysis. The solutions of purified ligands were prepared in 70% dioxane-water mixture and standardized by pH-metric techniques.

(L_1)

(L_2)
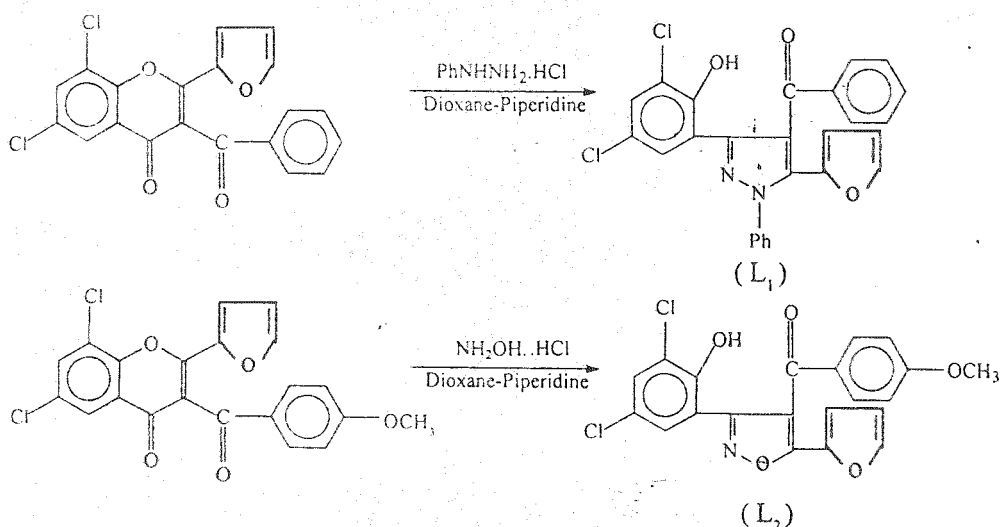
The experimental procedure involved potentiometric titration of:
1. Free acid (0.01 M),
2. Free acid (0.01 M) and ligand (20×10^{-4} M)
3. Free acid (0.01 M), ligand (20×10^{-4} M) and metal ion (4×10^{-4} M) against standard NaOH solution.

The ionic strength of all the solutions was maintained constant (0.01 M) by adding appropriate quantity of 1 M KNO$_3$ solution.

The titrations were carried out in a 100 mL pyrex glass beaker kept in an ice-cold water bath maintained at constant temperature ($27 \pm 0.1°C$). Nitrogen gas was purged for chemically inert atmosphere. The readings were recorded for each addition of 0.2 mL. The graphs of volume of alkali against pH were plotted.

The ligands used in the present investigation were monobasic acids having only one dissociable H$^+$ ion from OH group and can therefore be represented as

$$HL \rightleftharpoons H^+ + L^-$$
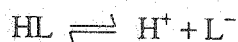
The titration curves of the acid and the ligand deviate at about pH 2.5 and then increase up to pH 7.5. The deviation between acid curve from ligand for all the systems shows the dissociation of H$^+$ ions from —OH groups of the ligands.

Proton-ligand formation numbers ($\bar{\eta}_A$) were calculated by the Irving and Rossotti expression

$$\bar{\eta}_A = \gamma - \frac{(E° + N)\,\Delta V}{(V_0 + V_2)T_L^0}$$

where V_0 = initial volume of solution (50 mL), N = normality of sodium hydroxide, T_L^0 = concentration of ligand in 50 mL solution, $E°$ = initial concentration of free acid (HNO$_3$), γ = number of dissociable protons from ligand.

$$(V_3 - V_2) = \Delta V - \text{volume of alkali consumed by acid and ligand}$$
on the same pH.

The pK$_a$ values for both systems were calculated by half integral calculations which are presented in Table-1 and metal-ligand stability constants are presented in Table-2.

TABLE-1
PROTON-LIGAND STABILITY CONSTANTS

System	pK
3(2-hydroxy-3,5-dichlorophenyl)-4-benzoyl-5-(2'-furyl) 1-phenylpyrazole (L_1)	7.25
3(2-hydroxy-3,5-dichlorophenyl)-4-anisoyl-5-(2'-furyl)-isoxazole (L_2)	6.40

TABLE-2
METAL-LIGAND STABILITY CONSTANTS (log k)

System	Metal-ligand stability constantsts	
	$\log k_1$	$\log k_2$
Cu(II) L_1	7.74	5.50
Fe(III) L_1	7.39	3.64
Cu(II) L_2	6.38	3.49
Fe(III) L_2	6.92	4.39

Conclusion

The deviation between ligand curves and metal-ligand curves indicates a commencement of complex formation between ligand and metal ions. The change in colour of complex solution from light yellow to bright yellow between the pH range 2.5–7.5 also indicated by the complex formation.

From Table-1 the order of pK values of the ligands is found to be as

$$pK_{L_1} > pK_{L_2}$$

This may be due to the fact of the presence of —OCH_3 electron withdrawing group in ligand 2. The reduction in pK values may be due to the effect of electron withdrawing group of ligands. It is seen from Table-2 that the difference between $\log k_1$ and $\log k_2$ values is sufficiently large which shows the stepwise complex formation between ligand and metal ions. From Table-2 it is observed that the values of metal-ligand stability constants are greater for Cu(II) complex than Fe(III) for L_1. It means that Cu(II) forms more stable complex than Fe(III) with L_1 whereas Fe(III) forms more stable complex than Cu(II) with L_2.

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