



Ternary complex formation equilibria of tetradentate Schiff base ligand with Cu(II) and dipeptides

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Abstract — Ternary complex formation equilibria of Cu(II), metal involving tetra dentate Schiff base ligand (L) 4-hydroxy-3-(1-{2-[4-chlorobenzylideneamino] phenylimino} ethyl) – 6 methyl-2H- Pyran-2-one as primary ligand and DL-Alanyl Glycyl (R₁), Glycyl- DL-Valine(R₂) dipeptides as secondary ligands have been carried out in 60% (v/v) THF-Water medium and ionic strength of 0.1 M (NaClO₄) investigated potentiometric ally. Ternary complexes are formed by simultaneous reactions. The stability constant of binary complexes ML, ML₂ are determined under similar experimental conditions. The species formed during ternary complexation such as concentration of total metal, total ligand, free metal, free ligand are discussed by Irving Rossottii technique calculated by using “SCOG” computer programme. The comparative study of Cu(II) ternary complexes is discussed.

Keywords- Ternary complexes, tetra dentate Schiff base ligand, dipeptides.

I. INTRODUCTION

The ligand involved in ternary complexation have the functional groups such as –COOH, NH₂ and CONH₂. Which are identical with those present in enzyme. Schiff base transition Metal Complexes have important and popular area for research due to their simple synthesis [1]. The importance of ternary metal complexes is from application of such complexes in many analytical and biological reactions [2,3]. Metal ternary complexes with Oxygen and nitrogen donor ligands show remarkable high stability [3-6] ONH, Schiff Life and its appearance are connected with specific and distinct macroscopic structures. Complexes of amino acids and peptides are involved in the exchange and transport mechanism of trace metal ions in the human body [6, 7]. Hence it is worthwhile to study ternary complexes of Cu(II) dipeptides MLR complexes Where M = (Cu) and L = Schiff bases & R = dipeptides. Copper is ubiquitous in plants and animals, and its redox chemistry is involved in a variety of biological oxidation processes. Copper usually binds to proteins (copper proteins) in living organisms. As ternary complexes containing Cu(II) as a metal are relatively well investigated. The stability of ternary complexes will help towards understanding of the driving forces that lead to the formation of such complexes in biological systems. In the present study Cu(II) metals is used.

In continuation of our earlier work [8-10] we have prepared tetra dentate Schiff base with known method.

II. EXPERIMENTAL

THF, NaOH used in present investigation Titrations were obtained from E. Merk. THF was further purified by known literature method [11]. All metal chlorides used for preparation of metal ion solutions obtained from their AR grade metal chlorides. These metal solutions were further standardize by known literature method [11]. A standard 0.2N NaOH solution was used for titrations. Standard solutions of AR grade HClO₄, NaClO₄ (1.0M) were prepared and standardized by known methods [11]. Experimental procedure by potentiometric titration technique performed in inert atmosphere (nitrogen) at ionic strength of 0.1 M (NaClO₄). The ligand solution (0.1M) was prepared in distilled THF. Schiff base used in present investigation found to be insoluble in water. THF: water (60:40) was used as a solvent for potentiometric studies. The potentiometric technique for study of the mixed ligand complexes include following titrations.

- 1). Free HClO₄ → A
- 2). Free HClO₄ + Ligand (L) → A + L
- 3). Free HClO₄ + Primary Ligand (L) + Metal ion (M) → A + L + M
- 4). Free HClO₄ + Secondary Ligand (R) → A + R
- 5). Free HClO₄ + Secondary Ligand (R) + Metal ion → A + R + M
- 6). Free HClO₄ + Primary Ligand (L) + Secondary Ligand (R) + Metal ion → A + L + R + M

The solutions were titrated pH metrically against (0.2N) NaOH. The commercial alcohol was distilled over freshly

ignited dry calcium oxide to obtain absolute alcohol. The fraction distilled at 78°C was collected after discarding 20 ml of distillate. Anhydrous methanol and super dry ethanol were obtained from commercial methanol and ethanol (AR) respectively by distillation after treatment with magnesium metal turnings and iodine [11]. All other solvents used during the entire research work were of AR grade

III. Apparatus

The titrations were carried out using Elico digital pH meter (model LI-127) equipped with a CL-51B combined electrode for pH measurements. Before titrations pH meter was calibrated against standard buffers (pH 4.02 and 9.18) readings were corrected for THF: water media. The pH and volume of NaOH piloted to determine protonation constants and stability constants of the Schiff bases and their complexes were determined. Throughout the experimental work glass distilled water was used. This was obtained by double distillation of deionised water in presence of crystals of potassium permagnate and potassium hydroxide pallets. For synthesis of Schiff bases, ethanol and methanol were used as commercial solvents. Structure of Ligand is as follow

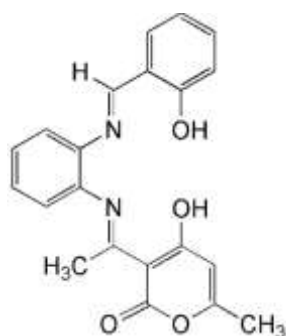
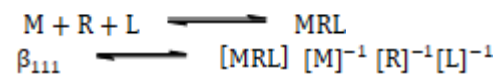


Figure1. 4-hydroxy-3-(1-(2-((4-hlorobenzylideneamino) phenylimino) ethyl) - 6 methyl-2H- Pyran2

IV. POTENTIOMETRIC MEASUREMENTS

The synthesis and characterisation of ligand is reported earlier [12]. Stock solutions of ligand (0.1M) was prepared in THF. The protonation constants of primary ligand (L) and secondary ligands DL- Alanyl Glycyl (R_1), Glycyl-DL-Valine (R_2) with Cu ions determined in 60% (v/v) THF:Water medium. The Irving-Rossetti technique was used after appropriate pH corrections determined by using method suggested by Van Uitert [12]. The protonation constant and metal- ligand stability constant of ligands is given in the (Table 1). The pH values of titrations were found in between pH 3 to 11 from pH metric data the stoichiometry, deprotonation and stability constants were calculated. Primary and secondary ligands form both 1:1 and 1:2 complexes with Cu(II) ions. Here two systems are represented in the above work. The Concentration of various species HL, L, R, CuL, CuR, CuLR, at different pH were obtained by using SCOGS computer programme [14, 15]. The concentration of these species were plotted

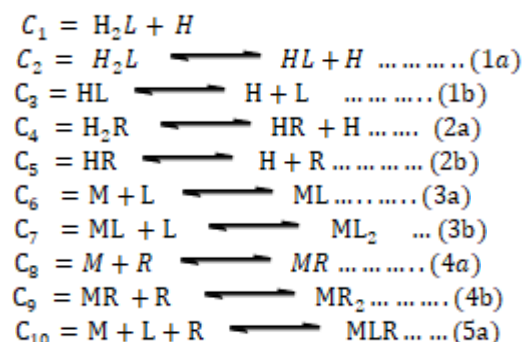
against pH values to study complexing equilibria and predominance of mixed ligand complexes over binary complexes. Equilibrium constant β_{111} for the reaction



The plots of systems i.e. Cu(II)-DL-Alanyl Glycyl (L), Cu(II)-Glycyl-DL-Valine (L), systems were presented (Fig.1-8). The possible equilibria in the ternary chelation was done by analyzing the graphs. The pH titration curves for systems Cu(II)-L- R_1/R_2 are represented in (Fig. 1-2).The precipitation pH of mixed ligand complex was about 7.2. The mixed ligand curves coincide with A+L curve .at pH 1.5 and then deviates. The mixed ligand curve from the theoretical composite curve towards left indicate the formation of ternary complex. The mixed ligand curve did not coincide with A+L+M and A+R+M metal complex titration curves, indicates the formation of 1:1:1 complex by a simultaneous equilibria.

In Cu(II)-L- R_2 system from (Fig.2)it was observed that the mixed ligand titration curve coincides with A+L curve at pH 3.8 and later on deviates.

Non super impossible nature of the composite curve over mixed ligand curve confirms the formation of ternary complex.



The relative stability of ternary complexes as compared to binary complexes indicated by $\Delta \log K$, K_r , K_R and K_L parameters. These parameters are defined by the equations.

$$V. \Delta \log K = \log \beta_{111} - \log K_{10} - \log K_{01}$$

$$VI. K_r = \beta_{111}^2 / K_{20} K_{02}$$

$$VII. K_R = \beta_{111} / K_{10}$$

$$VIII. K_L = \beta_{111} / K_{10}$$

V. RESULT AND DISCUSSION

i). Cu(II)LR₁ SYSTEM

The tetradentate Schiff base (L) as primary ligand forms both 1:1 and 1:2 complexes with Cu(II), while the secondary ligand, dipeptides, DL-Alanyl Glycyl (R_1) forms only 1:1 metal-ligand complex with copper. The curves of (F_M), (F_L) and (F_R) are shown in (Fig.5-7).

The initial percentage of free metal at pH = 3.2 is very less i.e. 3.6 which indicates the maximum consumption of metal ions in the complex formation at this pH. It sharply decreases up to pH 5.2 after which the concentration remains constant indicating the maximum complexation in the pH- range 3.2 to 5.2. The percentage of free ligands L and R₁, though extremely low (~0.03%) found to increase with increasing pH. The percentage of F_L and F_R reaches to 6 and 0.64 percent respectively at pH 5.5 and then remains constant. Due to the dissociation of excess ligands present in the system increase in free ligand concentrations.

The values of β₁₁₁, β₂₀, β₀₂, K_L, K_R, K_f and Δ logK are presented in (Table. 2). These values express relative stabilities of binary and ternary complexes.

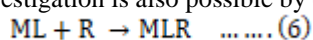
The comparative study of β₁₁₁ with the product of β₂₀ and β₀₂ i.e. K_R of the system confirm formation of ternary complexes over binary complexes of primary as well as secondary ligands. Since they show positive value. Relatively higher positive value of K_R than K_L reveals greater stability of ternary complexes with respect to the binary complexes of secondary ligand than that of primary ligand.

The binary 1:1, Cu(II)-L and Cu(II)-R₁ complexes are stable than ternary complex confirm by the negative Δlogk value. Further negative Δlogk value shows higher stability of binary complexes than the ternary one and may be due to the reduced number of co-ordination sides.

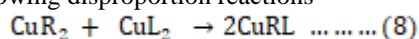
To understand the mechanism and extent of formation of ternary complex at different pH, the species distribution curves are most useful. The speciation diagram obtained for the system Cu (II)-L-R₁ is presented in (Fig. 3)

From the curve C₉, it can be observed that the initial concentration of ternary species is very less i.e. 5.54 percent. Above this pH, it increases very sharply to attain maximum value at pH 5.2 and then remains constant at about 93 percent for the whole pH range up to pH 7.2. Thus more than 93 percent metal ion is present in the form of ternary complex at pH 7.2.

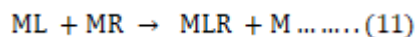
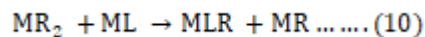
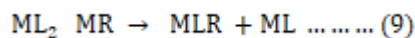
The reactions 1b and 2b represent the formation of HL(C₂) and R(C₅). There is continuous decrease in HL(C₂) and R(C₅) with increasing pH indicate the formation of Cu(II)-L-R by reaction (5). It can be seen from the (Fig.3) that the concentration of HL is 93% and that of R is about 4% at the initial pH 3.2 which sharply decrease up to pH 5.2. The ternary complex takes place to the maximum extent i.e. up to 92% in the same pH range which supports the possibility of reaction (5). The formation of CuLR in the present investigation is also possible by equilibria



The another way of characterizing the ternary complexes is by following disproportionation reactions



If primary ligand (L) and secondary ligand (R) form 1:1 and 1:2 complexes individually with the metal then disproportionation reaction is possible. Other disproportionation reactions are



The reaction 9 correspond to the system consisting of one ligand which forms only 1:1 complex and reaction 10 correspond to ligand which forms both 1:1 and 1:2 complexes. The reaction 11 represent the system containing primary and secondary ligands which form only 1:1 binary complexes of metal. This reaction is possible in sufficient concentration of ML and MR.

In addition to this, ternary complex may be formed by reaction 7. Since concentration of MR (C₈) decreases from 90 to 6.2%. However disproportionation reaction (11) cannot be ruled out. Since in the present system, primary ligand (L) forms both 1:1 as well as 1:2 complexes, while the secondary ligand(R) forms only 1:1 complex, the formation of MLR is also possible by the disproportionation reaction (9).

ii. Cu (II)-L (R₂) SYSTEM

In this system the primary ligand (L) and secondary ligand (R₂) form 1:1 and 1:2 metal ligand binary complexes. The species distribution diagram of this system (Fig.4). Show considerably high initial percentage i.e.77% of CuLR₂ species at pH 3.2. The initial percentage of the ternary complex of Cu(II)-L-R₁ system was comparatively very less. This observation indicates that the formation of ternary complex with Glycyl-Valine as a secondary ligand is more favorable at lower pH region and also it is stable. The curve C₁₀ representing the formation of ternary complex reaches to maximum at pH 4.2 i.e. 97 percent and then attains the value of more than98% Such a high stability of the 1:1:1 complex may be attributed to the more ligational property of the secondary ligand which forms both 1:1 and 1:2 metal complexes. Initial percentage values of HL and R (C₂ and C₅) are 4.6 and 16.63 respectively, decrease to nearly zero. The reaction (5) indicates ternary complex formation.

In addition with reaction (5) there is a possibility of formation of 1:1:1 complex by reaction (6). This can be justified from the observation that the concentration of R and ML decrease to minimum in the same pH region where ternary complex formation possible. The ternary complex formation by the disproportionation reaction (11). Since the concentration of ML and MR decreases to negligible value in this pH range. In this system the percentage distribution curves of free metal(F_M) and free ligands F_L, F_R (Fig8-9) show exactly similar trend as in case of Cu(II)-L-R₁ system .

From (Table.2) it can be found that the β₁₁₁ value of Cu(II)-L-R₂ system is considerably higher than that of Cu-

L-R₁ system. Comparison of these values suggests that the ternary complex of the system containing Glycyl-Valine as a secondary ligand are highly stable than the complex of the system, containing Alanyl-Glycyl.

The β_{111} value of Cu(II)-L-R₂ system is comparable with β_{20} indicate the equal possibility of formation of 1:1:1 and binary complexes of primary ligand. Whereas, the lower value of β_{02} than β_{111} indicate formation of ternary complex over the binary complex of secondary ligand which may be considered as additional support to the observed more stability of the ternary complex. In case of Cu(II)-L-R₁ system the β_{111} value was notably less than β_{20} . which also supports the observation that the ternary complex formed in this system at initial pH is very less more over similar to the previous system the higher values of β_{111} compared to β_{20} in this system indicate the preferential formation of ternary complex over binary complex of secondary ligand.

It is seen from the (Table.2) that the k_R and k_L values in Cu(II)-L-R₂ system are considerably higher than those in the system Cu(II)-L-R₁. Comparison of these values show additional stability of ternary complex in Cu(II)-L-R₂ system. The $\Delta \log k$ values in both the systems are negative. The lower values of $\Delta \log k$ towards negative side in Cu(II)-L-R₂ system indicate the extra stabilization of ternary complex of this system than the previous system

Table1. pK and logk values of Cu(II) chelates of ligand and dipeptides in 60% (v/v) THF-water medium at Temp: 30 °C and ionic strength $\mu = 0.1$ M NaClO₄

Ligands(L)/peptide(R ₁ , R ₂)	pK ₁	pK ₂	pK ₃	logk ₁	Logk ₂	log β
Ligand (L)	2.93	9.97	10.59	10.15	7.97	18.12
DL-Alanyl Glycyl(R ₁)	4.13	8.45	-	6.05	-	6.05
Glycyl-DL-Valine(R ₂)	4.33	8.59	-	7.62	4.87	12.49

Table. 2 Parameters of formations of mixed ligand complexes of Cu(II) with primary ligand (L) and dipeptides (R₁,R₂)

Dipeptides	log β_{20}	β_{02}	β_{11}	k_L	k_R	k_T	$\Delta \log k$
DL-Alanyl glycine(R ₁)	18.13	6.05	12.65	2.49	6.6	-	-3.55
Glycyl valine(R ₂)	18.13	12.49	17.02	6.87	9.40	0.15	-0.75

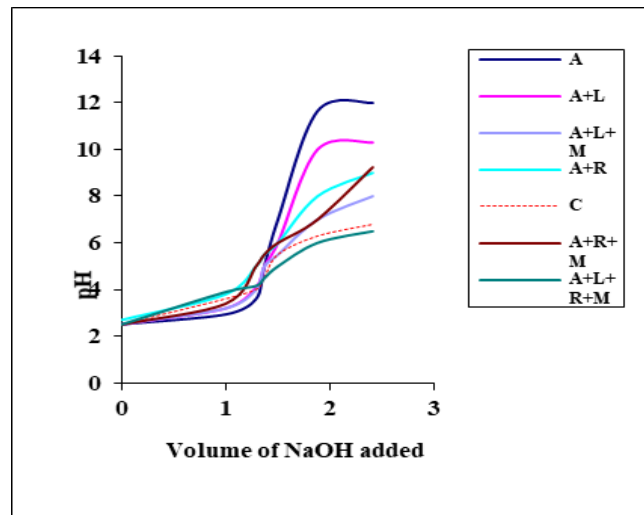


Figure. 1 pH titration curve of Ternary Complex formation of L-R₁-Cu (II) system in 60% THF-water at 30°C

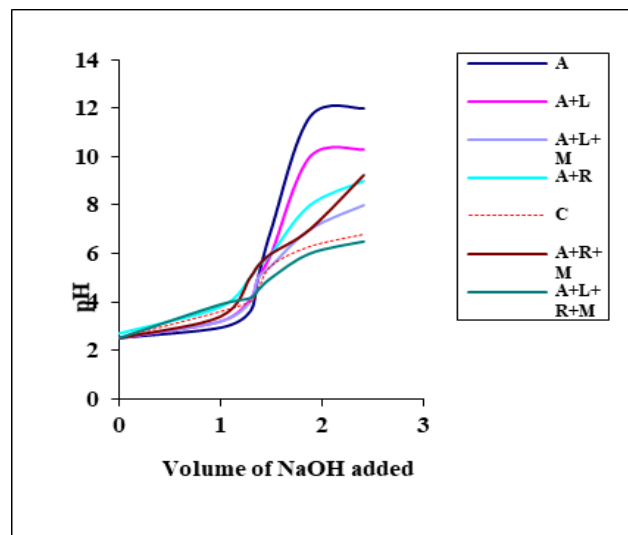


Figure 2 pH titration curve of Ternary Complex formation of L-R₂-Cu(II) system in 60% THF-water at 30°C

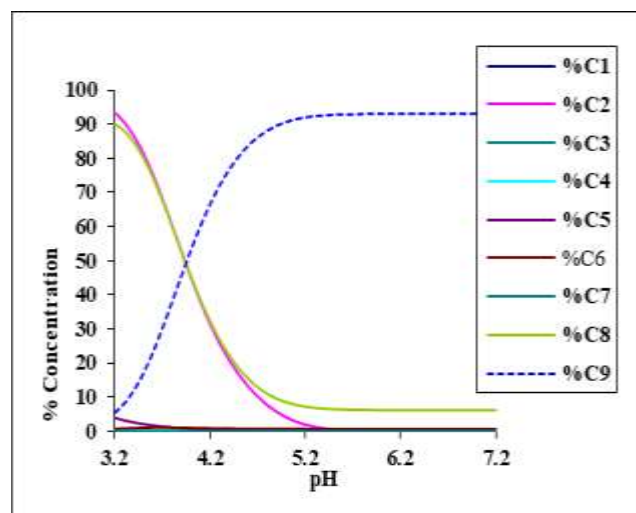


Figure 3 Percentage distribution curves of L-R₂-Cu(II) system L-R₂-Cu (II) system

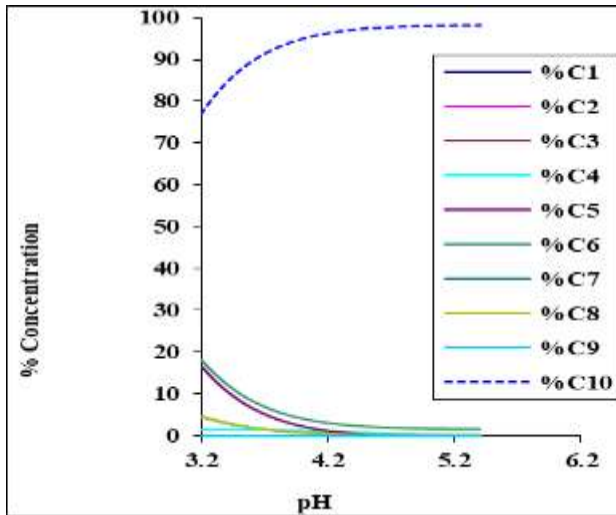


Figure 4 Percentage distribution curves of L-R₂Cu (II) system

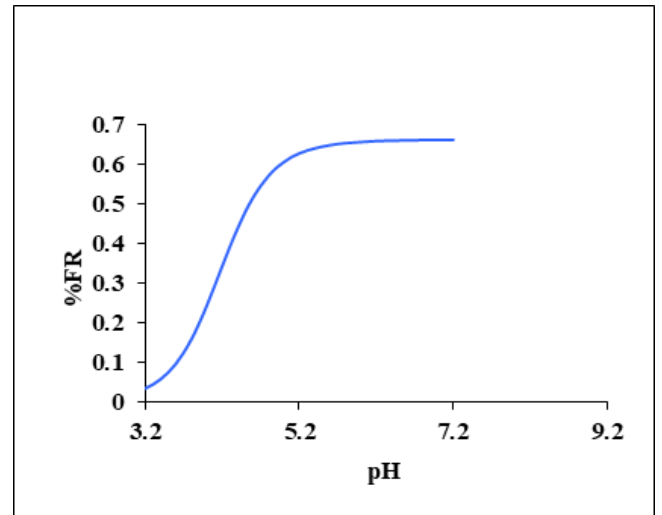


Figure.7 Plot of % F_R vs pH in LR₁Cu System.

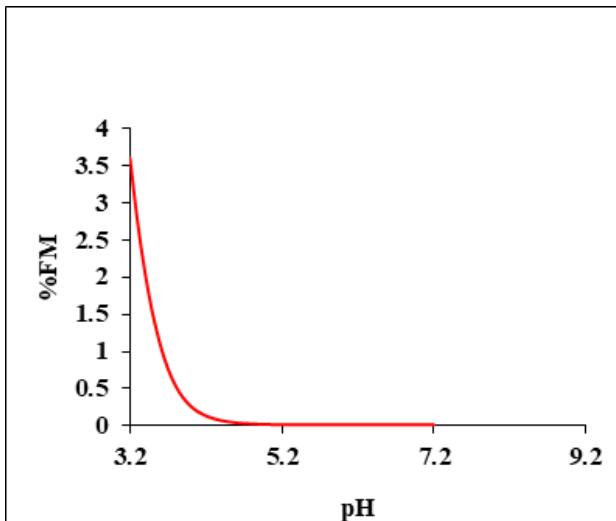


Figure 5 Plot of % F_M vs pH in LR₁Cu System.

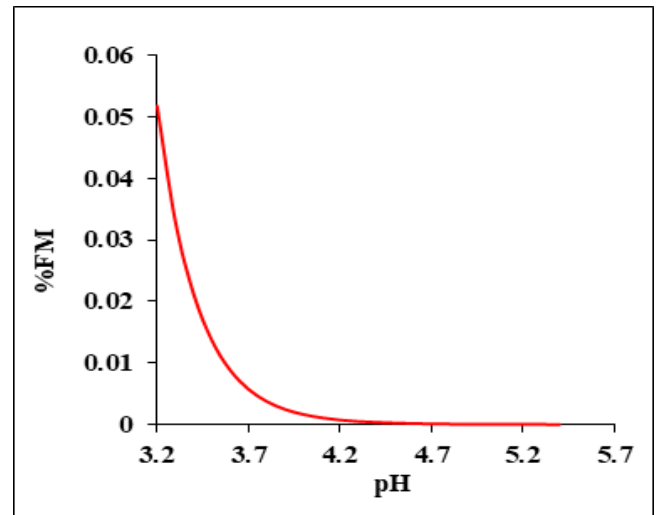


Figure 8 Plot of % F_M vs pH in LR₂Cu System.

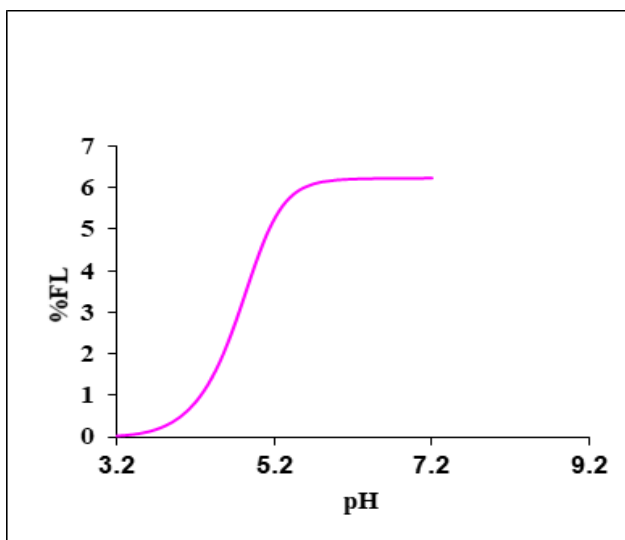


Figure 6. Plot of % F_L vs pH in LR₁Cu System

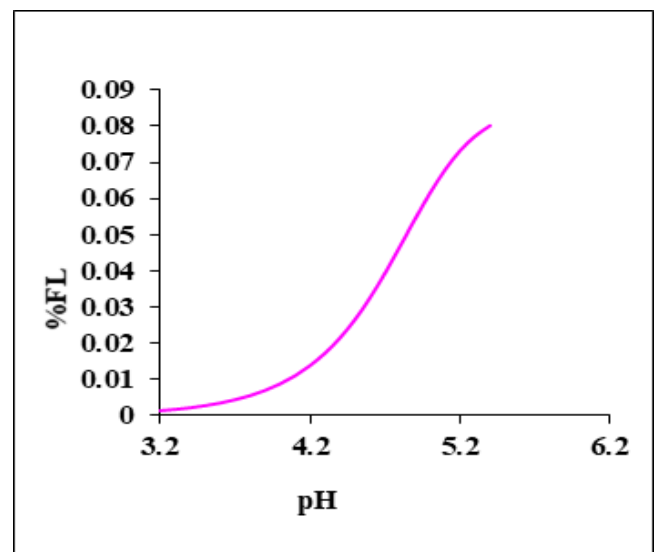


Figure 9 Plot of % F_L vs pH in LR₂Cu System

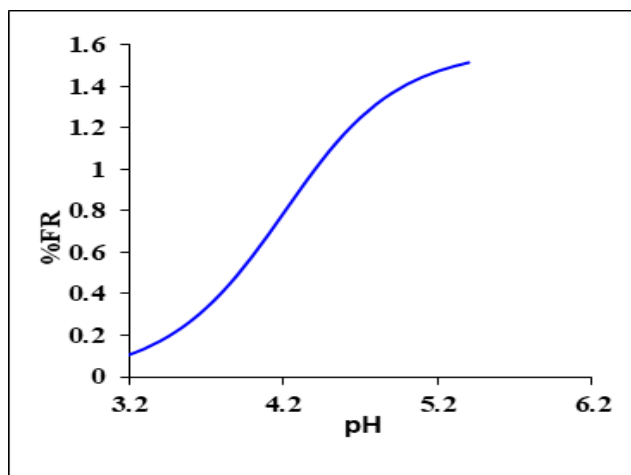


Figure 10 Plot of % F_R vs pH in LR₂Cu System.

VI. CONCLUSION

Present investigation include the study of - Ternary complex formation equilibria of Cu(II) metal involving tetra dentate Schiff base ligand (L) 4-hydroxy-3-(1-{2-[(4-chlorobenzylideneamino) phenylimino] ethyl} - 6 methyl-2H- Pyran-2-one as primary ligand and DL- Alanine Glycyl (R₁), Glycyl- DL-Valine(R₂).

Ternary complex formation takes place in a stepwise method. It is seen from the (Table.2) that the K_R and K_L values in Cu(II)-L-R₂ system are considerably higher than those in the system Cu(II)-L-R₁. Comparison of these values show additional stability of ternary complex in Cu(II)-L-R₂ system. The Δlogk values in both the systems are negative. The lower values of Δlogk towards negative side in Cu(II)-L-R₂ system indicate the extra stabilization of ternary complex of this system than the previous system.

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