Potentiometric Formation of Binary and Ternary Complex of Cu(II) with Tridentate Schiff Base and Dipeptide as Primary and Secondary Ligand.

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Abstract

The stability of 1:1:1 ternary chelates of bivalent Cu(II) metal ion with Schiff Base ligand4-hydroxy-3(1-{2-[(4-chlorobenzylideneamino) o-phenylimino) ethyl)-6methyl-2H-pyran2one- as primary ligand (L_1) and DL- Alanyl Glycyl (R_1), Glycyl- DL-Valine (R_2) as secondary ligand (R1) have been carried out in 60% (v/v) THF-Water medium pH metrically at 30° C and 0.1 M $NaClO_4$ ionic strength. The stability constants of ternary complexes ML and MR are also determined under similar experimental conditions. The stability constants of ternary complexes are evaluated and their relative stabilities compared to the corresponding binary complexes are evaluated and their relative stabilities compared to the corresponding binary complexes are expressed in terms of statistical parameter Δ logk, K_R,K_L and K_r values. The species distribution curves are used to explain the variation in concentration of these as function of pH. The pH have been discussed by Irving-Rossotti technique and evaluated by using the computer SCOGS program.

Kewords: Tridentate ligand, Schiff Bases, Potentiometry, Binary complex, Ternary complex

Introduction

A dipeptide is an organic compound derived from two amino acids. The constituent amino acids can be the same or different. When different, two isomers of the dipeptide are possible, depending on the sequence. Dipeptides play an important role in human body.[1-5] Due to coordination sites dipeptides form coordination compounds Dipeptides have coordination sites. Although research work on dipeptides have been carried out by many researchers. [6-8] The reactions of dipeptides with metal ions are of biochemical importance. To determine tendency of dipeptides with metal ions to form metal complex in liquid media is the measure of protonation constants and stability constants. Potentiometric technique is electro analytical technique to determine protonation and stability constants. It is well known that proton transfer plays an important role in the reaction in aqueous solution such as complex formation acid and base catalysis and enzymatic reaction.[9] There for in the present study the ternary complex formation of Cu(II) metal complexes with Schiff base ligand.

Experimental

Material and Methods: In the present investigation THF, NaOH used Titrations were obtained from E. Merk. THF was further purified by known literature method [10]. 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 [10]. A standard 0.2N NaOH solution was used for titrations. Standard solutions of AR grade $HClO_4$, $NaClO_4$ (1.0M) were prepared and standardized by known methods [10]. DHA and o-Phyne Experimental procedure by potentiometric titration technique performed in inert atmosphere (nitrogen) at ionic strength of 0.1 M ($NaClO_4$). The ligand solution (0.1M) was prepared in distilled THF.

Procedure

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 $HClO_4$ → A

2). Free $HClO_4$ + Ligand (L) → A + L

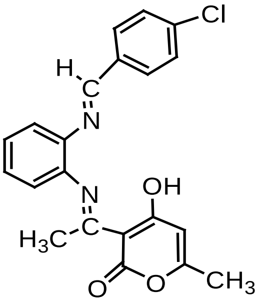
3).Free $HClO_4$ + Primary Ligand (L) + Metal ion (M) → A + L+M

4).Free $HClO_4$ +Secondary Ligand (R) →A + R

5).Free $HClO_4$ +Secondary Ligand (R) + Metal ion (M) →A + R+M.

6).Free $HClO_4$ + Primary Ligand (L) + Secondary Ligand (R) + Metal ion (M) →A +L+ R+M.

Detection Method: 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.



4-hydroxy-3(1-{2-[(4-chlorobenzylideneamino) phenylimino) ethyl) - 6-methyl-2H-Pyran2-one

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 [13]. 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

Results and Discussion

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 [13]. The concentration of these species were plotted against pH values to study complexing equilibria and predominance of mixed ligand complexes over binary complexes.

$$M + R + L \rightleftharpoons MRL$$

$$\beta_{111} \rightleftharpoons [MRL]\ [M]^{-1}\ [R]^{-1}[L]^{-1}$$

Cu (II)-L-R_1/R_2 Systems

It can be seen from (Fig.1) for Cu(II)-L-R_1 system, that the mixed ligand curve coincide with A+L up to pH 3 and then deviates. It was observed that the theoretical composite curve remains towards left of the experimental mixed ligand titration curve. This confirms the formation of ternary complex. Similarly the theoretical composite curve of Cu (II)-L-R_2 system lies towards left of the experimental mixed ligand titration curve (Fig.2). This confirms the formation of its ternary complex. The mixed ligand curve coincide with A+L curve up to pH 3.8 and then deviates. Non super impossible nature of the composite curve over mixed ligand curve confirms the formation of ternary complex.

$$C_1 = H_2L + H$$

$$C_2 = H_2L \rightleftharpoons HL + H \ldots\ldots.(1a)$$

$$C_3 = HL \rightleftharpoons H + L \quad \ldots\ldots\ldots(1b)$$

$$C_4 = H_2R \rightleftharpoons HR + H \ldots\ldots \ (2a)$$

$$C_5 = HR \rightleftharpoons H + R \ldots\ldots\ldots\ \ldots(2b)$$

$$C_6 = M + L \rightleftharpoons ML \ldots\ldots.\ (3a)$$

$$C_7 = ML + L \rightleftharpoons ML_2 \quad \ldots(3b)$$

$$C_8 = M + R \rightleftharpoons MR \ldots\ldots\ldots(4a)$$

$$C_9 = MR + R \rightleftharpoons MR_2 \ldots\ldots(4b)$$

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

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

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

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

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

RESULT AND DISCUSSION

Cu(II)-L-R_1 System

To study the effect of coordinating nature of primary ligand we have selected the ligand L (Schiff base) which is tridentate in nature. The system under study consists of tridentate Schiff base as primary ligand and DL- Alanyl Glycyl (R_1), Glycyl- DL-Valine (R_2) as secondary ligands. These systems differ from previously discussed systems [13] only by the presence of tridentate Schiff base (L) in place of tetradentate Schiff base. The complexation behavior of these ligand systems is studied for Cu (II) metal ions. Therefore, the changes in different parameters in complexation equilibria in these systems may be considered due to the change in primary ligand from tetradentate to tridentate one. This change in the systems shows many interesting features which are discussed in this part. The values of log k_1, and log k_2 of the copper complex of primary tridentate ligand in Cu(II)-L-R_1 system are found to be relatively lower than that of the tetradentate ligand. Hence the binary complexes of copper (II) with ligand L seems to the comparatively less stable than L_4 complexes. However, inspite of the lower stability of binary complexes the ternary complexes of this ligand show higher stability. Particularly the $ß_{111}$ value of Cu(II)-L-R_1 system is notably higher than that of the Cu(II)-L-R_1 system. This observation leads to the conclusion that the structure of ligand L is more favorable for the formation of ternary complex in presence of secondary ligand R_1 .The formation of ternary complex in this system also takes place through simultaneous equilibria. Higher positive values of K_L and K_r indicate that the formation of ternary complex is favored than binary ones. The tendency towards ternary complex formation is evaluated by comparing Δlogk values depicted in (Table.1) Similar to the previously presented systems, the Δlog k values in this system is also negative which shows higher stability of binary complexes than the ternary once.

The percentage distribution curves of F_M, F_L and F_R of Cu-L-R_1 system are shown in (Fig.5-7). The initial percentage of free metal is extremely small at pH 3.2 and then it sharply reaches to about zero value. The percentage of free primary ligand F_L, though it is very small, increases slightly up to pH 7.4. However the behavior of free ligand F_R shows considerable difference than the system containing L_4 as primary ligand. It increases to 19.3 percent up to pH 7.4 indicating the change in formation equilibria of ternary complex in this system.

The distribution of species diagram depicted in (Fig.3) showed that the predominant species present at pH 3.2 are, R(C_4) and ML (C_5) whereas the ternary species is 12.3 percent at this initial pH. The concentration of ternary species then continuously increases and touches to maxima around pH 5.4 and then remains nearly constant. Thus more than 80% of the metal ion is present in the form of ternary complex, at this pH. Remaining i.e. about 20% of metal ion is shown to the present as the complex ML (C_5).

The curve (C_4) showed that the presence of R at concentration 76 at initial pH sharply decreases with increasing pH and at last reaches to 8.6 percent. The concentration of species L represented by C_2 also decreases with increasing pH indicating the possibility of formation of ternary complex by equilibria (5).

The nature of the two curves C_4 and C_5 corresponding to R and ML show that the initial percentage of these two species is maximum i.e. 76 and 82 respectively decreases sharply up to pH 5.4 where the ternary complex formation also reaches to maximum value. It is evident from this observation that the formation of ternary complex mainly takes place by the reaction $ML + R \rightleftarrows MLR$ (reaction 7). Formation of MLR by disproportionation reaction (11) is also possible to small extent. From the above observations it is seen that the major reaction of ternary complex formation in this system is altogether different than the previously discussed systems. In earlier systems the formation of ternary complex was favored by reaction (6) whereas in this system it is favored by reaction (7).

Cu(II) -L-R_2 System

The system Cu(II)-L-R_1 differs from previously discussed Cu(II)-L–R_2 by only the presence of secondary ligand. Instead of the secondary ligand R_1, ligand R_2 has been used to study its effect on the system. The difference between the formation mechanisms of ternary complex in these systems is found to be very interesting. The formation of ternary complex in this system is also by simultaneous equilibria. The stability constant of ternary complex is approximately same as that of the Cu(II)-L-R_1 complex. The values of K_L and K_R in these systems are also nearly similar to the previous system. The negative values of $\Delta\log k$ also show identical mechanism. The Kr value in Cu(II)-L-R_1 system was absent whereas in this system it is 0.14 indicating the less stability of ternary complex compared to overall value of 1:2 binary complexes of primary and secondary ligands.

The drastic difference in the formation mechanisms of ternary complex in those two systems could be seen from their speciation curves. The percentage distribution of F_M, F_L and F_R shows different concentrations (Fig.8-10) than that shown in Cu-L_2-R_4 system (Fig.5-7). The concentration of free meal ion is very small and reaches to minimum value at pH 6.4, similar to the preceding system. However, the percentage of F_L and F_R are negligibly small initially and increases slowly to attain maximum value though very small. The concentration of F_R is 3.8 percent at pH 6.4, whereas the percentage of same species in previous system was 19.3. From the (Fig.4) it can be observed that the predominant species at initial pH is the ternary complex itself which has concentration about 55%. This indicates that the formation of ternary complex is already completed to more than 50%, while it was only about 12% in the previous system. The concentration of ternary complex then increases continuously up to pH 5.4 attains maximum value of 95.5% and then remains nearly constant. From the speciation curve it is found that all other species are reaching to their minimum concentration value up to pH 5.5. These observations lead to the conclusion that the ternary complex may be formed mainly by reaction (5). The disproportionation reaction (II) may also have a considerable role in the formation of ternary complex. This indicates that the reaction (11) is more favorable in this complex equilibrium than in the case of previous system. In this system the ternary complex is formed to maximum extent showing that 99% of the metal ion is present in the form of ternary complex.

Conclusion

The system under study consists of tridentate Schiff base as primary ligand and DL- Alanyl Glycyl (R_1), Glycyl- DL-Valine (R_2) as secondary ligands. The present study include the stability of 1:1:1 ternary chelates of bivalent Cu(II) metal ion with Schiff base ligand 4-hydroxy-3(1-{2-[(4-chlorobenzylideneamino) o-phenylimino)ethyl)-6methyl -2H-pyran2one- as primary ligand(L_1) and DL-Alanyl-DL-Phenylalanine as secondary ligand (R_1) have been carried out in 60% (v/v) THF-Water medium pH metrically at 30° C and 0.1 M$NaClO_4$ ionic strength. Here the ternary complexation takes place in a stepwise method. The values of k_R and k_L values in Cu(II)-L-R_1 system are considerably higher than those in the system Cu(II)-L-R_2. Comparison of these values show additional stability of ternary complex in Cu(II)-L-R1 system. The Δlogk values in both the systems are negative. The lower values of Δlogk towards negative side in Cu(II)-L-R_1 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 μ= 0.1 M NaClO$_4$)

Ligands(L) /peptide(R_1 ,R_2)	**pK_1**	**pK_2**	**pK_3**	**logk_1**	**Logk_2**	**logβ**
Ligand (L)	3.02	9.97	10.59	9.97	7.47	17.44
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 (R_1,R_2)

Dipeptides	**logβ_{20}**	**β_{02}**	**β_{11}**	**k_L**	**k_R**	**k_r**	**Δlogk**
DL-Alanyl glycine(R_1)	17.4501	6.05	15.5209	5.5457	9.4709	-	-0.5043
Glycyl valine(R_2)	17.4501	12.4988	15.407	5.4318	7.7817	0.14128	-2.1935

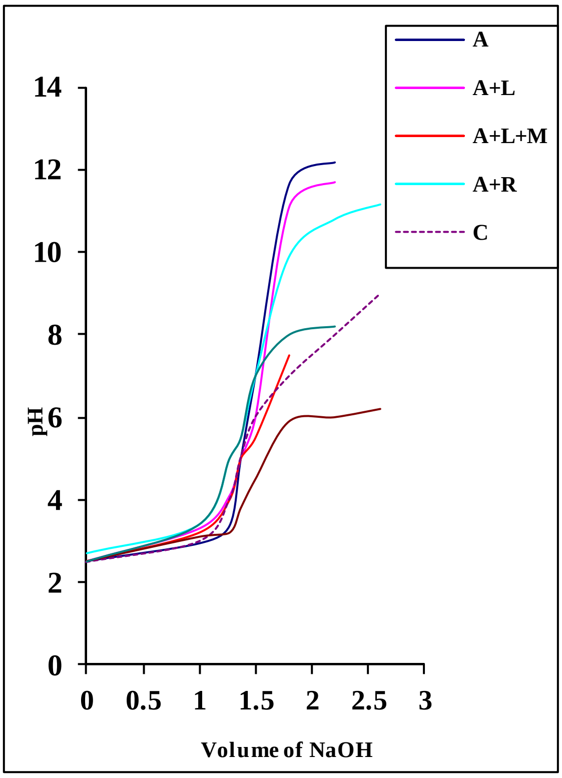


Fig. 1 pH titration curve of Ternary Complex formation of

L-R$_1$-.Cu (II) system in 60% THF- water at 30°C

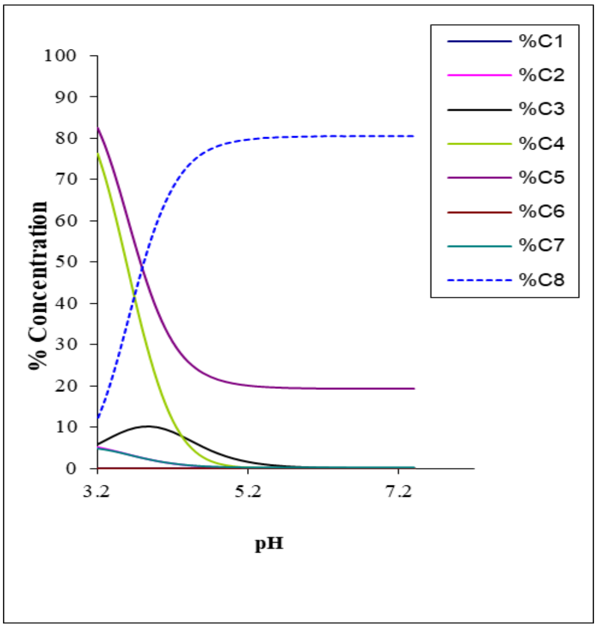


Fig.3. Percentage Distribution curve of L-R$_1$-.Cu (II) -

system in 60%THF-water at 30°C

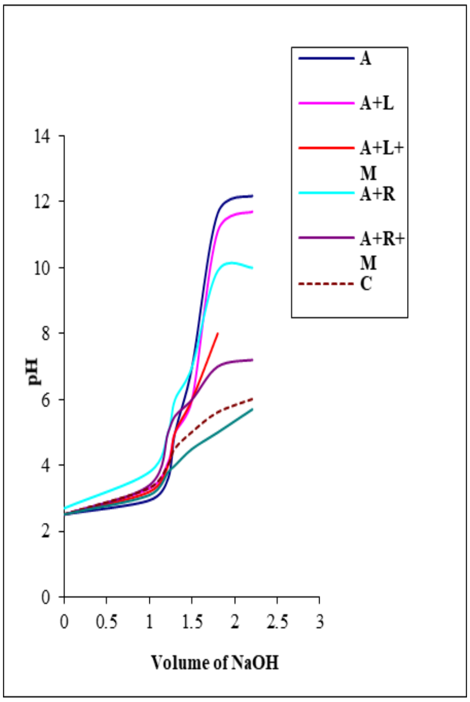


Fig. 2 pH titration curve of Ternary Complex formation of L-R$_2$-.Cu (II)

system in 60%THF-water at 30°C -

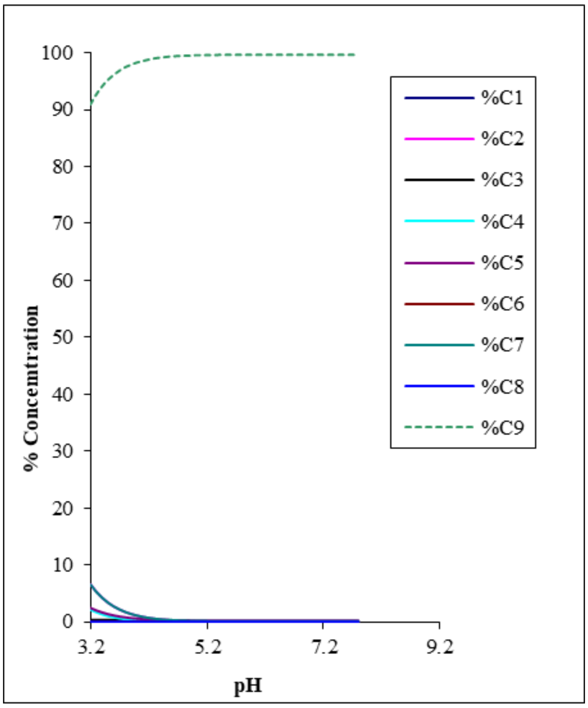
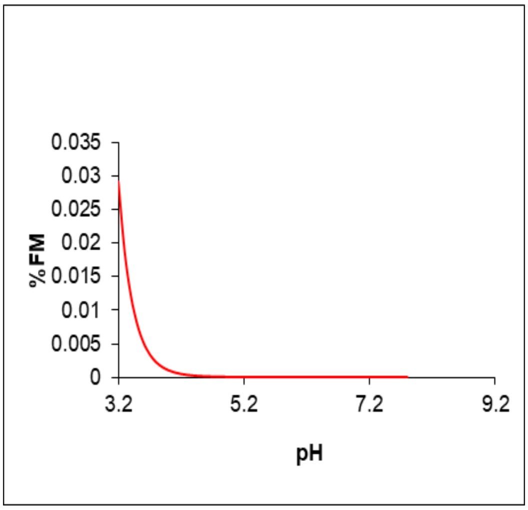


Fig.4. Percentage Distribution curve of L-R$_2$-.Cu (II)

L-R$_1$-.Cu (II) system in 60%THF-water at 30°C



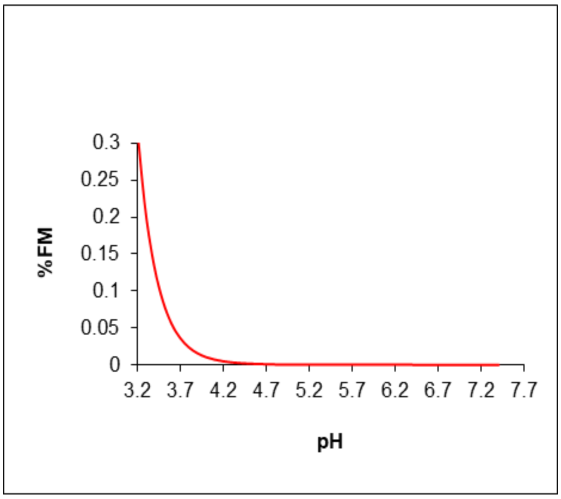
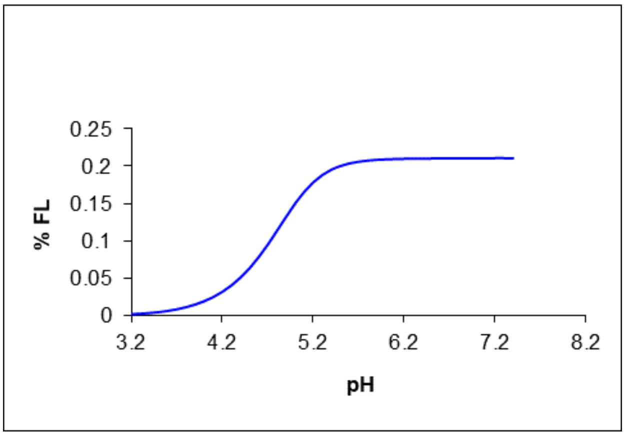


Fig 5 Plot of % F_M vs pH in LR_1Cu System.

Fig 8 Plot of % F_M vs pH in LR_2Cu System.



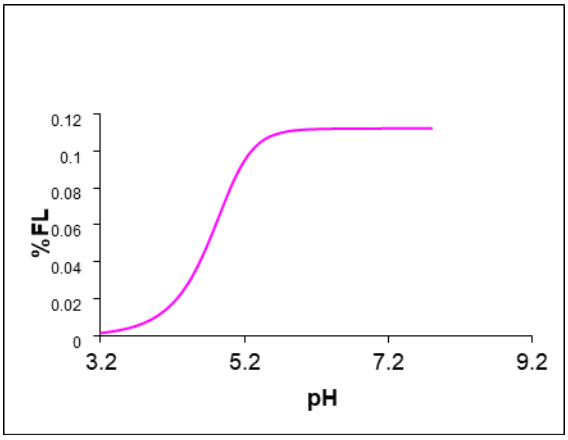
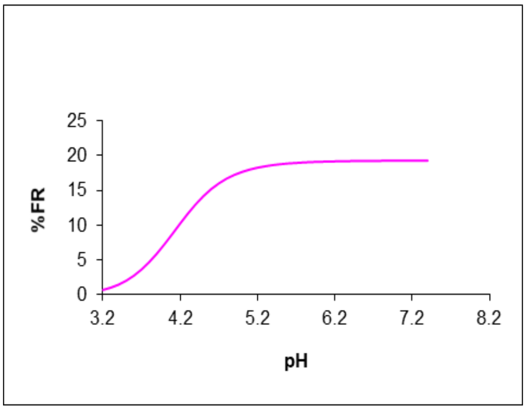


Fig 6 Plot of % F_L vs pH in LR_1Cu System.

Fig 9 Plot of % F_L vs pH in LR_2Cu System.



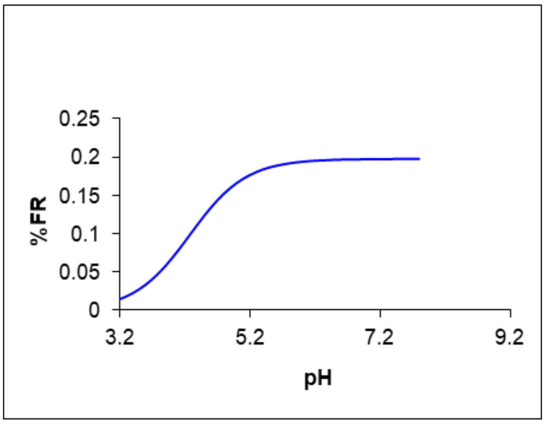


Fig 7 Plot of % F_M vs pH in LR_1Cu System.

Fig 10 Plot of % F_R vs pH in LR_2Cu System.

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