













formation is evaluated by comparing  $\Delta \log k$  values depicted in (Table.1) Similar to the previously presented systems, the  $\Delta \log k$  values in this system is also negative which shows higher stability of binary complexes than the ternary one.

The percentage distribution curves of  $F_M$ ,  $F_L$  and  $F_R$  of Cu-L-R<sub>1</sub> 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<sub>4</sub> 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<sub>4</sub>) and ML (C<sub>5</sub>) 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 be present as the complex ML (C<sub>5</sub>).

The curve (C<sub>4</sub>) 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<sub>2</sub> also decreases with increasing pH indicating the possibility of formation of ternary complex by equilibria (5).

The nature of the two curves C<sub>4</sub> and C<sub>5</sub> 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  $ML + R \rightleftharpoons MLR$  (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<sub>2</sub> System**

The system Cu(II)-L-R<sub>1</sub> differs from previously discussed Cu(II)-L-R<sub>2</sub> by only the presence of secondary ligand. Instead of the secondary ligand R<sub>1</sub>, ligand R<sub>2</sub> 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<sub>1</sub> complex. The values of K<sub>L</sub> and K<sub>R</sub> in these systems are also nearly similar to the previous system. The negative values of  $\Delta \log k$  also show identical mechanism. The K<sub>r</sub> value in Cu(II)-L-R<sub>1</sub> 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<sub>M</sub>, F<sub>L</sub> and F<sub>R</sub> shows different concentrations (Fig.8-10) than that shown in Cu-L<sub>2</sub>-R<sub>4</sub> system (Fig.5-7). The concentration of free metal ion is very small and reaches to minimum value at pH 6.4, similar to the preceding system. However, the percentage of F<sub>L</sub> and F<sub>R</sub> are negligibly small initially and increases slowly to attain maximum value though very small. The concentration of F<sub>R</sub> 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-pyran-2-one- 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 MNaClO<sub>4</sub> 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- $R_1$  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- $R_1$  system indicate the extra stabilization of ternary complex of this system than the previous system.

Table 1. 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  $\mu = 0.1 \text{ M NaClO}_4$

Ligands(L) /peptide( $R_1, R_2$ )	pK <sub>1</sub>	pK <sub>2</sub>	pK <sub>3</sub>	logk <sub>1</sub>	Logk <sub>2</sub>	log $\beta$
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	log $\beta_{20}$	$\beta_{02}$	$\beta_{11}$	$k_L$	$k_R$	$k_T$	$\Delta \log k$
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

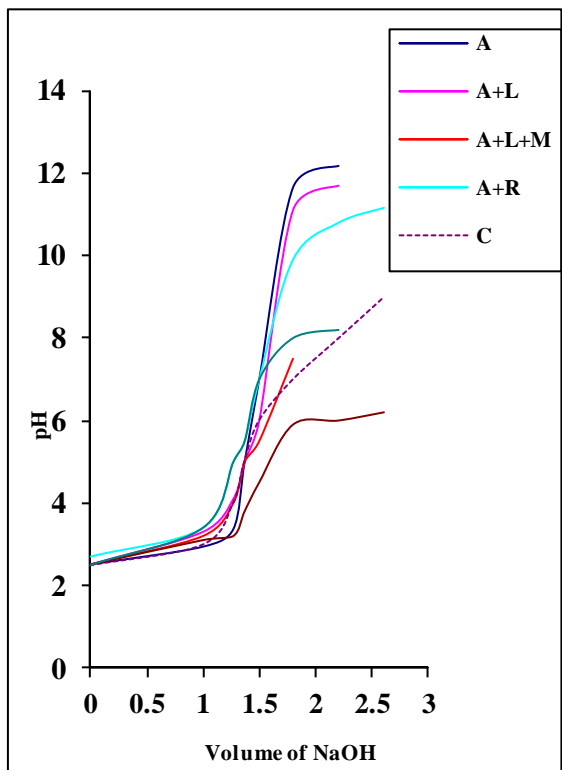


Fig. 1 pH titration curve of Ternary Complex formation of

L-R<sub>1</sub>-Cu (II) system in 60% THF- water at 30°C

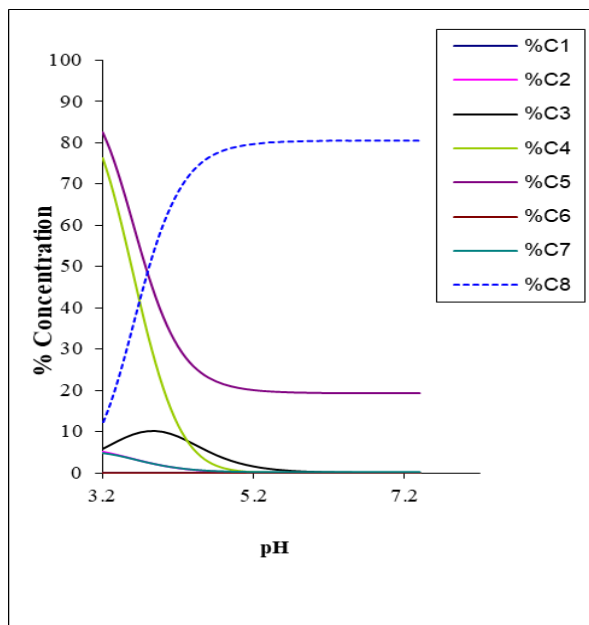


Fig.3. Percentage Distribution curve of L-R<sub>1</sub>-Cu (II) -

system in 60% THF-water at 30°C

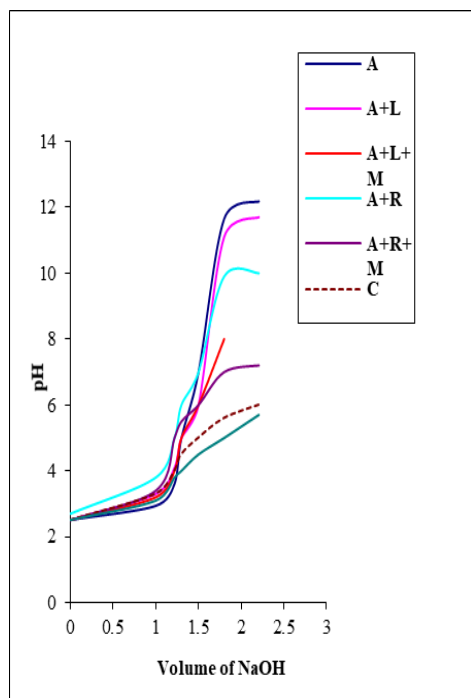


Fig. 2 pH titration curve of Ternary Complex formation of L-R<sub>2</sub>-Cu (II)

system in 60% THF-water at 30°C -

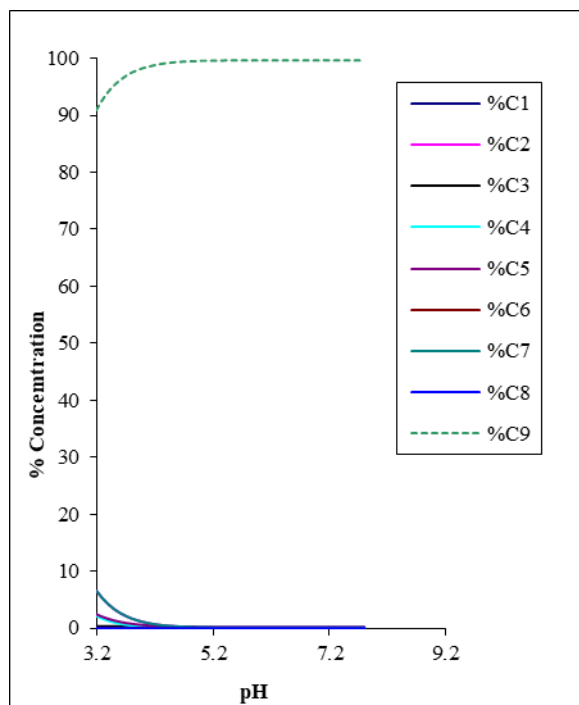


Fig.4. Percentage Distribution curve of L-R<sub>2</sub>-Cu (II)

L-R<sub>1</sub>-Cu (II) system in 60% THF-water at 30°C

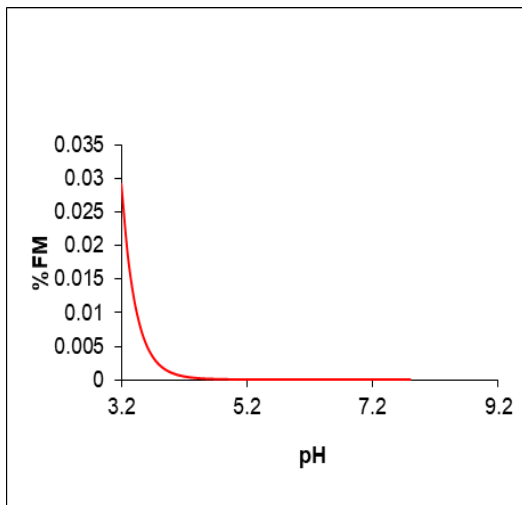


Fig 5 Plot of %  $F_M$  vs pH in  $LR_1Cu$  System.

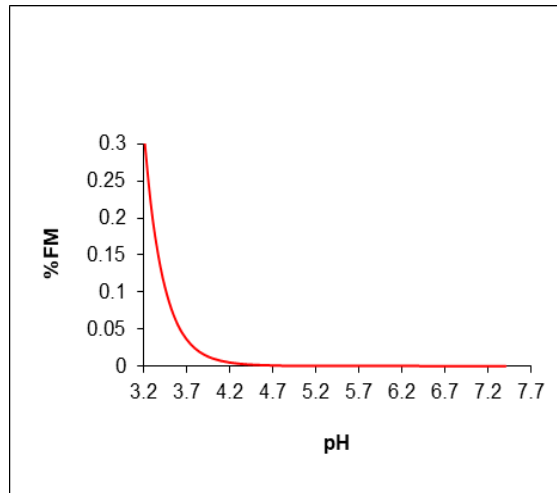


Fig 8 Plot of %  $F_M$  vs pH in  $LR_2Cu$  System.

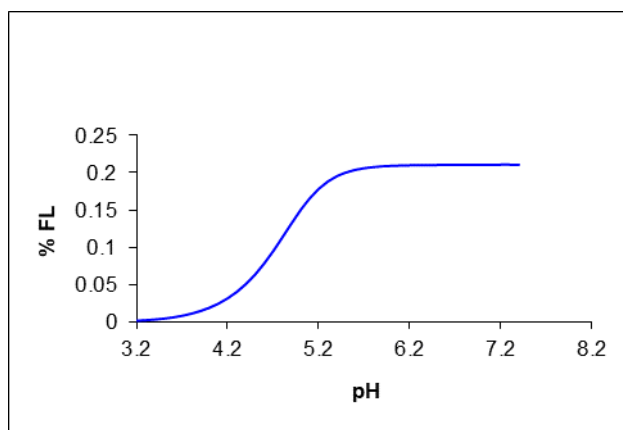


Fig 6 Plot of %  $F_L$  vs pH in  $LR_1Cu$  System.

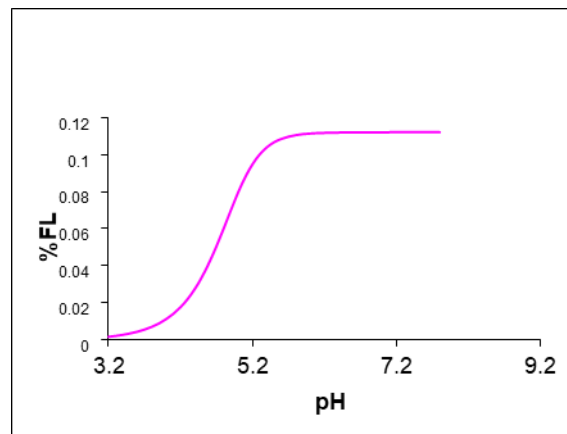


Fig 9 Plot of %  $F_L$  vs pH in  $LR_2Cu$  System.

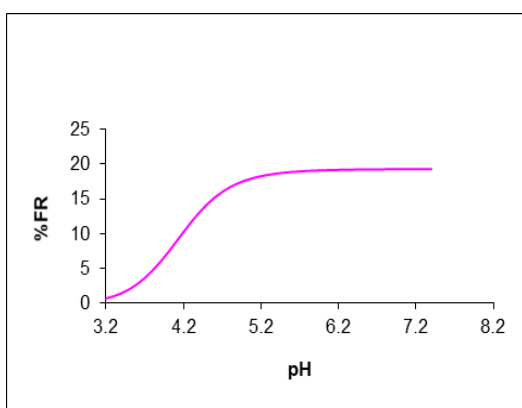


Fig 7 Plot of %  $F_M$  vs pH in  $LR_1Cu$  System.

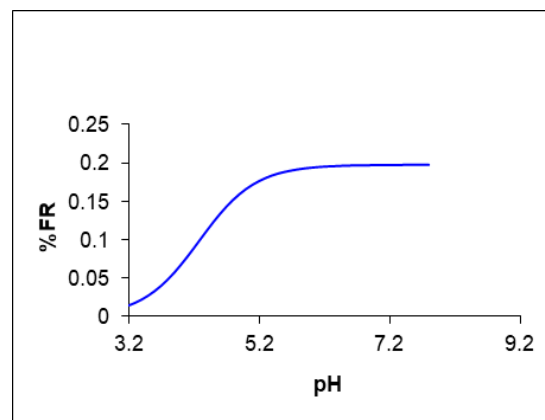


Fig 10 Plot of %  $F_R$  vs pH in  $LR_2Cu$  System.

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