CHAPTER - V

INTERLIGAND INTERACTIONS IN MIXED - LIGAND COMPLEXES INVOLVING DIPEPTIDES AND AUXINS

INTRODUCTION

Auxins are the growth hormones in plants which regulate cell enlargement. In the biological systems, auxins may coordinate with the metal ions found in vivo and hence study of metal complexes of auxins is important.

Proton-ligand and metal-ligand complexes of Mn(II) with indole acetic acid were determined pH-metrically at 30°, 35° and 40°C in 50% (1:1,v/v) water-dioxane medium of ionic-strength 0.1 M KNO_3. It was found that 1:1 and 1:2 metal-ligand complexes are formed [1].

Complexation of Ce(III), Pr(III), Nd(III) or Sm(III) with indole acetic acid (IAA), indole propionic acid (IPA), indole butyric acid (IBA) and 1-napthalene acetic acid (NAA) was studied pH-metrically in 50% aqueous acetone medium (I = 0.01 M $NaClO_4$) at 28° and 38°C [2].

As stated in Chapter-I, mixed chelation occurs commonly in biological fluids, as large number of potential ligands are likely to compete for the metal ions found in biological systems. Hence study of mixed-ligand complexes with auxins as one of the ligand is of significance.

Ternary complexes of Co(II), Ni(II) and Cu(II) with 2,2' - bipyridyl (bpy) or 1,10 - phenanthroline (phen) (primary ligands) and plant auxins such as Indole acetic acid (IAA), Indole propionic acid (IPA) and Indole butyric acid (IBA) (secondary ligands) have been studied in solution [3] using pH titration technique in order to test the complexation hypothesis of growth regulating activities of these plant auxins. The

general order of stability of the complexes with reference to auxins is IAA $\rangle$ IPA $\rangle$ IBA. The higher stability of these ternary complexes has been explained on the basis of intramolecular aromatic ring stacking between the aromatic rings of bipy or phen and indole moiety of the auxins. Sigel etal [4] studied the system [CuAL], where A = 1, 10 - phenanthroline and L = auxins such as indole acetic acid and indole propionic acid. Stability of the ternary complexes has been attributed to stacking interactions between coordinated phenanthroline and the non-coordinated indole part of the auxin.

In the biochemical systems auxins may coordinate with the metalloproteins, which act as enzymes. It was therefore, thought interesting to investigate the possibility of intramolecular interactions in ternary complexes involving auxins. [Copper (II) - dipeptide - auxin] ternary complexes have been studied in this chapter, where the dipeptides (A) gg, ga and gl are the same as discussed in previous chapters. The auxins (L) used for the present study are indole acetic acid (IAA), indole propionic acid (IPA) and indole butyric acid (IBA). The possibility of intramolecular hydrogen bonding between the two ligands have been discussed.

EXPERIMENTAL

The auxins, indole acetic acid (Riedel-De), indole propionic acid (Riedel-De) and indole butyric acid (Merck) were of A.R. grade. The dipeptides were of same quality as discussed in chapter IIA. The metal perchlorate, sodium perchlorate, sodium hydroxide and perchloric acid solutions were prepared and standardized in the same way as detailed in chapter IIA.

Titrations were carried out in 50% (1:1, v/v) water-dioxane medium using a pH-meter DIGICHEM 8201 with an accuracy of ± 0.01. The values of the formation constants were refined using the computer program SCOGS.

The values of the proton-ligand formation constant of the dipeptides and formation constant of their binary complexes with copper(II) was same as given in chapter IIA. In case of auxins, the proton-ligand formation constant and formation constant of binary complexes with copper (II) were also refined under indentical conditions. The formation constants calculated are given in Table 5.1. Their values are found to be similar to those reported in literature [4]. These values were used as fixed parameter for the refinement of the formation constants of the mixed-ligand complexes.

For the determination of the formation constants of the ternary complexes, the following sets of solutions (50 c.c.) having Cu:A:L in the ratio 1:1:1 and 1:1:2 were prepared and titrated against standard alkali:

(i) 0.02M $HClO_4$, 0.006M metal perchlorate, 0.006M ligand A, 0.006M ligand L and 0.162M $NaClO_4$.

(ii) 0.02M $HClO_4$, 0.006M metal perchlorate, 0.006M ligand A, 0.012M ligand L and 0.156M $NaClO_4$.

The evaluation of the formation constants of ternary complexes was done by taking into account the simultaneous existence of the species AH_2, AH, A, LH, L, Cu, CuA, CuA_{-H}, CuL, CuL_2, CuAL and $CuA_{-H}L$. These constants were refined by the computer program SCOGS and values are shown in Table 5.2.

The titration data have been shown in fig.5.1 to fig. 5.3. The distribution of various binary and ternary complexes, formed during the course of titration, has been shown in fig. 5.4 and fig.5.5 as a function of pH.

Table 5.1 : Proton-ligand formation constants of the Auxins and their corresponding binary constants in 50% water - dioxane (1:1, v/v) medium at 0.2 M $NaClO_4$ and 30°C with standard deviation in parentheses.

Ligands	pK^H_1	$logK^{Cu}_{CuL}$	$logK^{CuL}_{CuL_2}$
Indole acetic acid (IAA)	5.95	2.86	2.57
	(0.03)	(0.03)	(0.02)
Indole propionic acid (IPA)	6.00	2.73	2.68
	(0.09)	(0.08)	(0.07)
Indole butyric acid (IBA)	6.15	2.68	2.91
	(0.02)	(0.07)	(0.04)

Table 5.2 : Formation constants of mixed-ligand complexes in 50% water-dioxane (1:1, v/v) medium, I = 0.02M $NaClO_4$ at 30°C. Standard deviations ($\sigma \sim \beta$) are given in parentheses.

Complexes	$\log K^{Cu}_{CuAL}$	$\Delta \log K$	$\log K^{CuA_{-H}L}_{CuAL}$
Cu-gg-IAA	9.82	+0.73	5.28
	(0.15)		(0.08)
Cu-gg-IPA	10.13	+1.14	5.49
	(0.11)		(0.09)
Cu-gg-IBA	9.85	+0.94	5.50
	(0.14)		(0.09)
Cu-ga-IAA	11.26	+1.93	5.85
	(0.07)		(0.09)
Cu-ga-IPA	11.24	+2.04	6.13
	(0.07)		(0.10)
Cu-ga-IBA	11.17	+2.02	6.30
	(0.10)		(0.17)
Cu-gl-IAA	10.31	+0.63	5.91
	(0.11)		(0.13)

(Contd. Table 5.2)

Cu-gl-IPA	10.12	+0.57	5.60
	(0.08)		(0.06)
Cu-gl-IBA	10.19	+0.69	6.01
	(0.07)		(0.07)

Fig. 5.1 Potentiometric titration curves of 50% (v/v) water - dioxan solutions containing metal ions, gg, ga or gl and IAA (each 6.0×10^{-3} M).
(1) Cu^{2+} + gg + IAA.
(2) Cu^{2+} + ga + IAA.
(3) Cu^{2+} + gl + IAA.

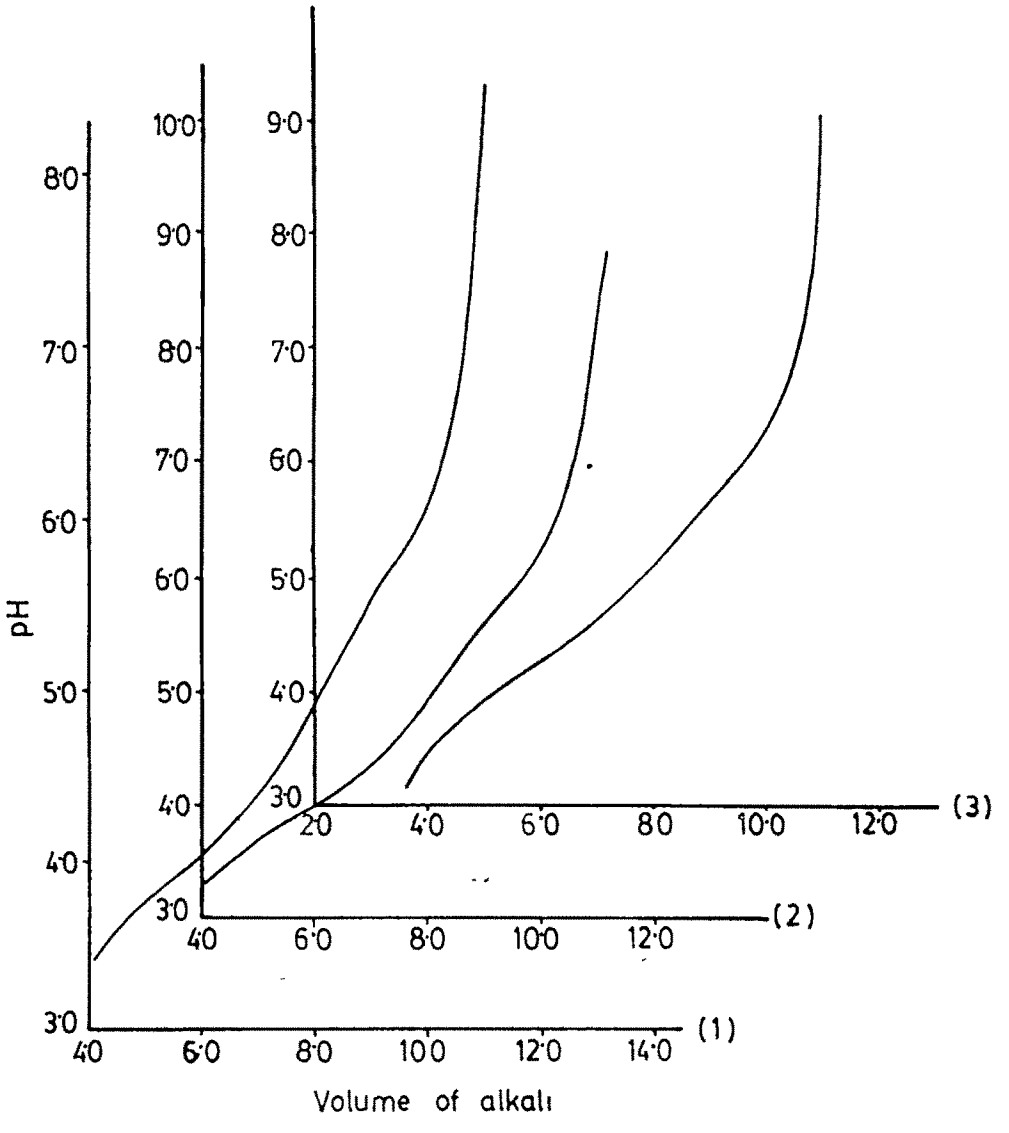


Fig. 5.2 Potentiometric titration curves of 50% (v/v) water - dioxan solutions containing metal ions, gg, ga or gl and IPA (each 6.0×10^{-3} M).
(1) Cu^{2+} + gg + IPA.
(2) Cu^{2+} + ga + IPA
(3) Cu^{2+} + gl + IPA.

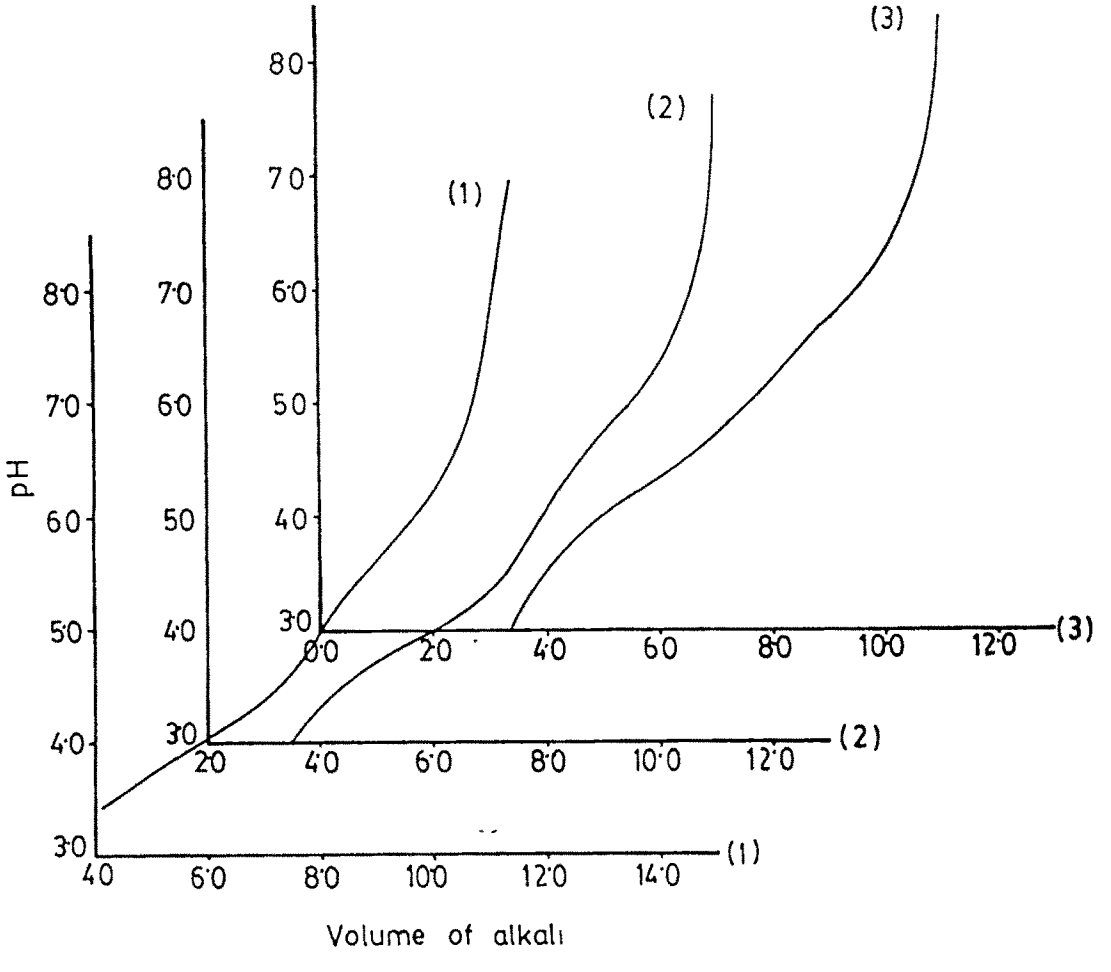
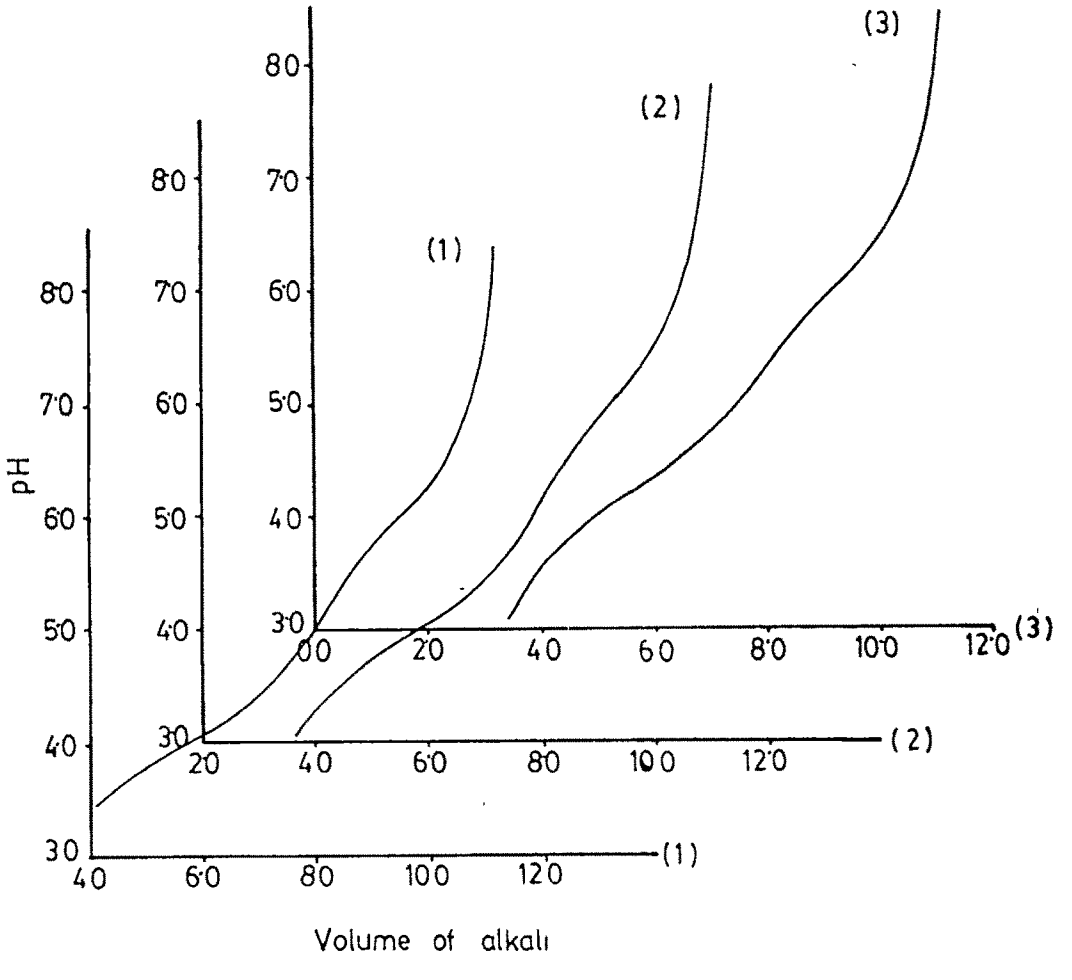


Fig 5.3 Potentiometric titration curveys of 50% (v/v) water - dioxan solutions containing metal ions, gg, ga or gl and IBA (each 6.0×10^{-3} M).
(1) Cu^{2+} + gg + IBA.
(2) Cu^{2+} + ga + IBA.
(3) Cu^{2+} + gl + IBA.



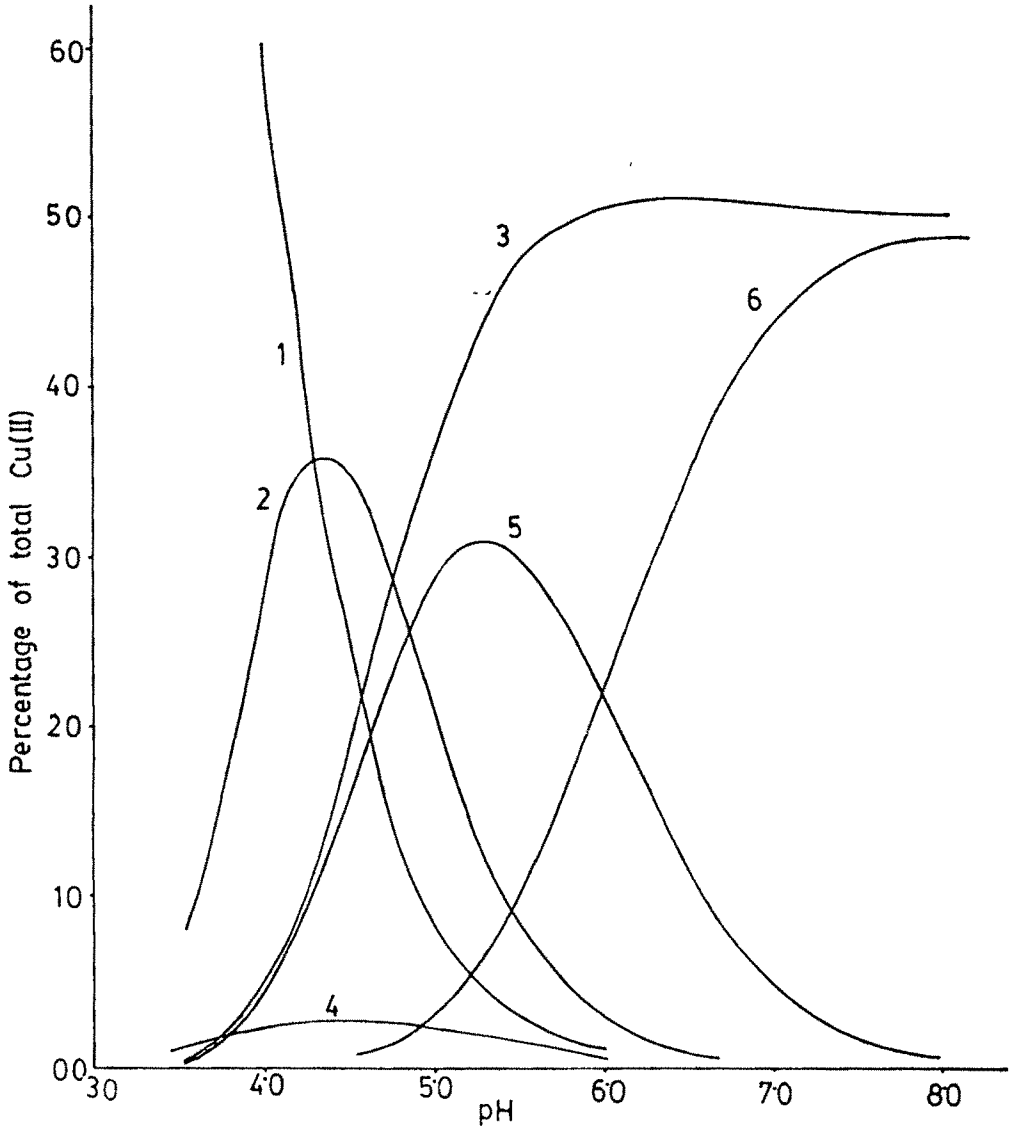


Fig. 5.4 Species Distribution for the Copper(11) - Glycyl - L - leucine (A) - Indole butyric acid (L) Ternary system at Metal : A : L ratio of 1:1:2 ; (1) Unbound Copper(11), (2) [CuA], (3) [CuA_{-H}), (4) [CuL), (5) [CuAL] and (6) [$CuA_{-H}L$].

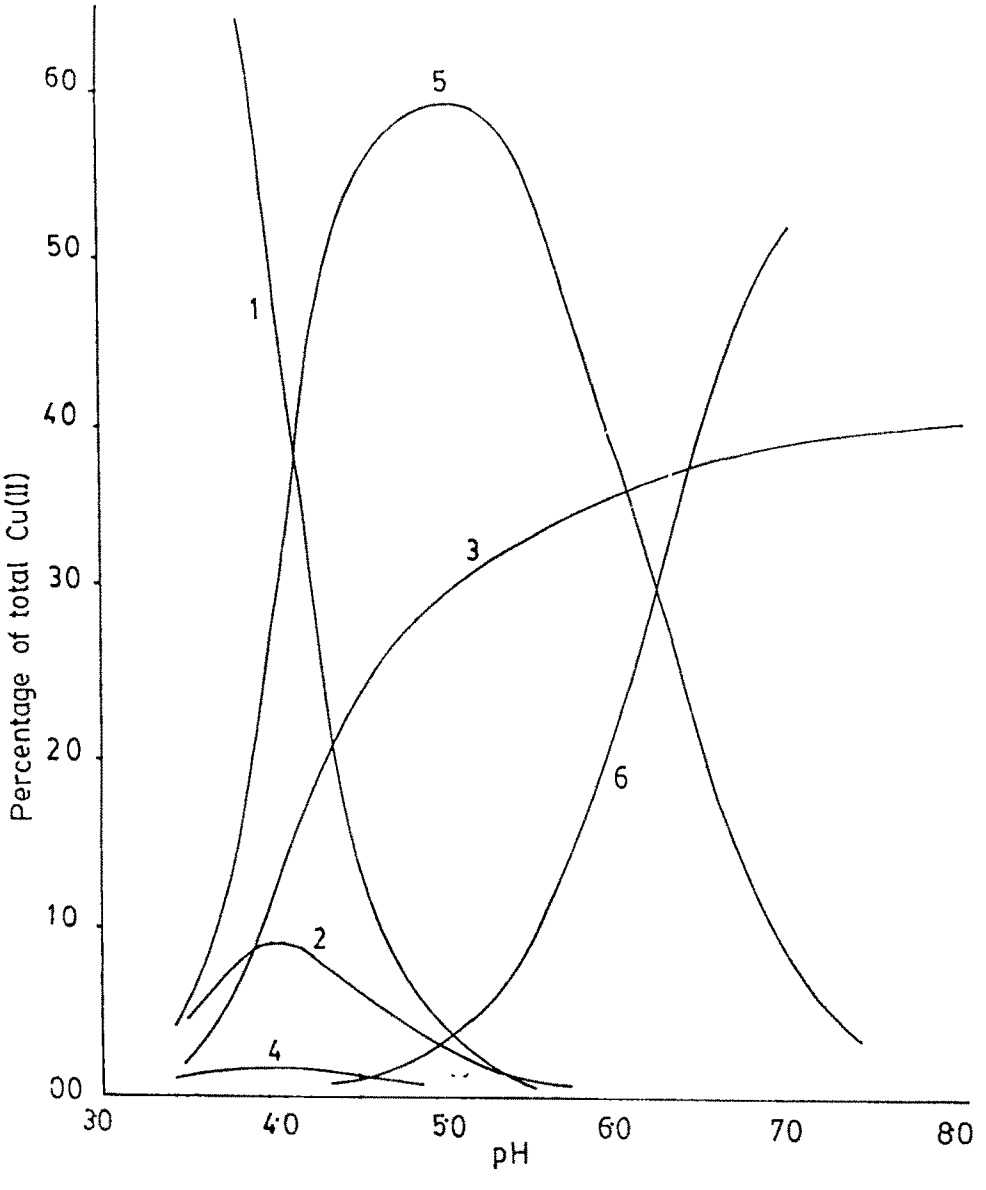


Fig. 5.5 Species Distribution for the Copper(11) - Gylcyl - L - alanine (A) - Indole butyric acid (L) Ternary system at Metal : A : L ratio of 1:1:2 ; (1) Unbound Copper(11), (2) [CuA], (3) [CuA_{-H}] (4) [CuL], (5) [CuAL] and (6) $CuA_{-H}L$.

RESULTS AND DISCUSSIONS

The formation of the two ternary species CuAL and $CuA_{-H}L$ at different pH ranges is shown in the species distribution curves. The complex CuAL starts forming at a pH $\sim$ 3.5 and attains a maximum concentration at pH $\sim$ 5.5. The ternary species $CuA_{-H}L$ starts forming at a pH $\sim$ 5.0 and its concentration increases with the increase in pH. Since the ligand L is a monodentate ligand, there is a possibility of formation of the complex species $CuAL_2$. However, it was found that the concentration of the above species did not exceed 0.1% of the total metal concentration in all the ternary systems under study. Hence this species has not been considered in the present study.

Formation and Stability of CuAL Complex :

In the ternary complex CuAL, the dipeptide is coordinated through amino nitrogen and peptide oxygen, the carboxylate group remaining free and uncoordinated. The auxins coordinate through their carboxylate end. The constant for the ternary species correspond to the following equlibria:

$$Cu + A + L \rightleftharpoons CuAL \qquad (5.1)$$

$$K^{Cu}_{CuAL} = \frac{[CuAL]}{[Cu]\ [A]\ [L]} \qquad (5.2)$$

Since both the ligands, dipeptide A and auxin L, coordinated to copper(II) in the ternary complex CuAL, are monoanions, it is expected that $\triangle$ logK

should be negative due to electrostatic repulsion between the two ligands in the ternary complex. However, $\triangle$ logK values were found to be positive for all the (Cu - dipeptide - auxin) complexes under study. The high stability of the ternary complexes is due to possible hydrogen bonding between the indole -NH of auxin and free carboxylate group of the dipeptide (fig.5.6).

Comparison of the $\triangle$ logK values of CuAL complexes where A= gg, ga and gl reveals that $\triangle$ logK is more positive for (CugaL) complexes than (CuggL). This is, probably, because the $-CH_3$ group, adjacent to the carboxylate group of ga, increases the electron density on the carboxylate oxygen, thereby making possible the formation of a strong hydrogen bond with the indole moiety of auxins. The (CuglL) complexes are relatively less stable compared to (CuggL) because the bulky $-CH_2CH(CH_3)_2$ group in the neighbourhood of free carboxylate in dipeptide (gl) hinders its participation in the formation of hydrogen bond with non-coordinated indole moiety of the auxins.

Formation And Stability of $CuA_{-H}L$ Complexes :

The formation of the ternary complex $CuA_{-H}L$ is represented by the equation :

$$CuA_{-H}L + H \rightleftharpoons CuAL \qquad (5.3)$$

$$K^{CuA_{-H}L}_{CuAL} = \frac{[CuAL]}{[CuA_{-H}L][H]} \qquad (5.4)$$

The constant $K^{CuA_{-H}L}_{CuAL}$ gives the protonation constant of the ternary complex $CuA_{-H}L$. Hence deprotonation of the dipeptide A in the ternary complex can be compared with the deprotonation of A in the binary complex CuA. It was observed that deprotonation of the dipeptide occurs at a higher pH in the ternary complex compared to binary complex. This can be accounted for by considering that the dipeptide coordinating from the peptide N^- forms a dianion with negative charges on peptide nitrogen and carboxylate oxygen. There is a possibility of strong repulsion between the auxin monoanion and dipeptide dianion. This inhibits the coordination of the dipeptide from the peptide N and hence deprotonation of peptide -NH is reduced, in the ternary complex.

It was also observed that the deprotonation of the dipeptide A is favoured i.e. it occurs at a lower pH in (Cu-dipeptide-auxin) complex compared to (Cu-dipeptide-amino acids) complex, where deprotonation occurs at a high pH. This is because the auxins being monodentate, there is no Jahn-Teller distortion destabilising the [Cu-dipeptide-auxin] complexes as observed for [Cu-dipeptide - amino acid] complexes with one bindentate amino acid and another tridentate dipeptide. Hence the deprotonation of [Cu-dipeptide-auxin] complex is more and occurs at relatively lower pH compared to [Cu-dipeptide-amino acid] complex. This results in higher protonation constant value of [Cu-dipeptide$_{-H}$-amino acid] complex compared to [Cu-dipeptide$_{-H}$-auxin] complex.

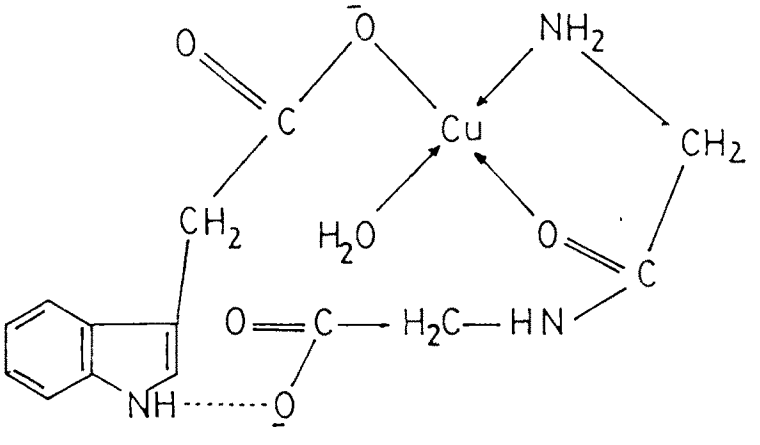


Fig. 5.6

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