CHAPTER - VI

MIXED - LIGAND COMPLEXES INVOLVING DIPEPTIDES AND AROMATIC AMINES : EFFECT OF π - ACIDITY OF THE AROMATIC AMINES ON THE DEPROTONATION OF THE PEPTIDE GROUP IN THE TERNARY COMPLEX

INTRODUCTION

Ternary complexes of copper(II) involving 2, 2' - bipyridyl as one of the ligands have been extensively studied [1], since coordination sites of bipyridyl are similar to that of imidazole. Investigations of ternary copper(II) complexes containing an imidazole group as binding site is of special interest, since it is suggested that in several copper(II) proteins the binding of the imidazole group of histidine with copper(II) brings in interesting electronic, ESR spectral and electrochemical properties in the copper proteins.

One of the interesting observations in the studies of mixed-ligand complexes, containing aromatic tertiary amines, is the high stability of such complexes [1-9]. This was attributed to Π-back bonding from the metal ion to the aromatic amine [3,5,9]. If a complex MA is considered, where A is an aromatic tertiary amine like 2, 2' bipyridyl, $N \longrightarrow M$ σ bond formation results in the shift of electron density from ligand to metal. Because of the increase in electron density over the metal ion, it behaves as a better Π - electron donor. The tertiary amine having vacant Π^* - antibonding orbitals can behave as a better Π^* - acceptor on donation of N electron pair to the metal ion. This facilitates Π^* - bond formation between the filled $d\Pi$ orbitals of the metal and vacant Π^* - antibonding orbitals over the amine ligand. Thus, there is a synergic stabilisation of $N \longrightarrow M$ σ bond and $M \longrightarrow A$ Π^* bond. The $d\Pi$ - $p\Pi^*$ interaction does not allow the electron density over the metal ion to increase significantly. In other words, the electronegativity of $[MA]^{+2}$ is almost same as $[M(H_2O)_n]^{+2}$ and hence log $K^{MA}_{MAL} \approx K^{M}_{ML}$, L being secondary ligands.

The M $\longrightarrow$ A π interaction results in the shift of π electron density from metal to ligand. This results in an increase in class A character of a transition metal ion, on coordination with an aromatic amine. This brings in discriminating behaviour [5,10,12] in MA towards the secondary ligand L coordinating through $O^- - O^-$, $N - O^-$ or N - N coordination sites, as observed by Sigel and coworkers [5,10] and Bhattacharya and coworkers [11,12]. This has been explained in terms of electron repulsion [12,13,14]. In the formation of the binary complexes, there is repulsion between the metal dπ electrons and additional lone pairs of electrons present over the $O^- - O^-$ coordinating ligand. In the ternary complex, M$\longrightarrow$A π bonding reduces the electron density over the metal ion and hence the lone pair of electrons over L has to face less repulsion, while combining with MA^{+2} than with the free metal ion. The effect is maximum in case of $O^- - O^-$ coordinating ligands, like pyrocatechol ion with lone pair of electrons over both O^-. This results in $K^{\text{Cu bipy}}_{\text{Cu bipy cat}} > K^{\text{Cu}}_{\text{Cu cat}}$ or the positive value of $\triangle \log K$ [10,11].

Bhattacharya and coworkers [11,12,14,15] have observed that the tendency of mixed-ligand formation follows the order 2(2' pyridyl) benzimidazole $>$ 2, 2' bipyridyl $\approx$ 1,10 - phenanthroline $>$ 2(2' pyridyl) imidazoline. Because of the benzimdazole part, which is a better π - acceptor than pyridine, Cu $\longrightarrow$ A π interaction is greater in the complexes containing 2 (2' pyridyl) benzimidazole. This results in greater stabilization of the ternary complex. The saturated imidazole ring part in 2(2'pyridyl) imidazoline cannot have π interaction with the metal ion and hence results in less stable ternary complexes. Similar observations have been made in the series of complexes consisting 2, 2'-bipyridyl, 1, 10-phenanthroline

and 5 - nitro - 1, 10-phenanthroline as primary ligands [16].

Sigel etal [17,18] studied the ternary systems Cu(bipy) L and Cu(bipy) (L-H) where L = glycylglycine, glycyl-L-alanine, L-alanylglycine, L-alanyl-L-alanine, glycyl-L-leucine, L-leucylglycine, glycyl-L-isoleucine, L-isoleucylglycine, glycylsarcosine, sarcosylglycine, glycyl-L-proline and L-prolylglycine. Crystal structure analysis [19] of the $CuAL_{-H}$ (A=1, 10-phenanthroline, L=glycylglycine) ternary species indicate that the amide deprotonated glycylglycine is tridentate with a weak coordination from the third carboxylate end.

The present chapter comprises of the study of copper(II) ternary complexes involving the dipeptides (A), glycylglycine (gg), glycyl-L-alanine (ga) and glycyl-L-leucine (gl) and the tertiary aromatic amines (L), 5-nitro-1, 10-phenanthroline (Nphen), 2(2' pyridyl benzimidazole) (bpyz), 1,10-phenanthroline (phen) and 2(2' pyridyl imidazoline) (pyz). The effect of increasing π - acidity of the aromatic amines on the deprotonation of the dipeptide in the ternary complex has been discussed. The values have been compared with that of copper (II) - dipeptide - ethylenediamine (en) complex. Cyclic voltammetric studies of the binary Cu-en and ternary Cu-gg-en complex have been carried out and the general features of the cyclic voltammograms have been discussed.

EXPERIMENTAL

The dipeptides used were of the same quality as detailed in the previous chapters. The amines, ethylenediamine (Fluka AG), 1, 10-phenanthroline (BDH) and 5-nitro-1,10-phenanthroline (Sigma Co.) were of Analar grade. The ligands 2 (2'-pyridyl) imidazoline and 2,(2'-pyridyl) benzimidazoline were prepared by the known method [20] and their purity checked by TLC. The titrations were carried out using a digital pH-meter with an accuracy of ± 0.01, in 50% water-dioxan (1:1, v/v) medium at a constant ionic strength I = 0.2 M $NaClO_4$ and at 30°C.

The proton - ligand formation constant and the formation constants of binary and ternary complexes were refined using the SCOGS computer program. The values of the proton-ligand formation constant of the dipeptides and the formation constant of the binary copper (II) complexes are same as given in Chapter-IIA. In case of the aromatic amines and ethylenediamine, the proton-ligand formation constants and formation constants of the binary copper (II) complexes were also refined under identical conditions and the values were found to be in agreement with the values reported earlier [15,16].

The refined values were used as fixed paramters for the refinement of formation constants of 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 1:1:1 and 1:1:2 ratios were prepared and titrated against standard alkali:

(i) 0.02M $HClO_4$, 0.004M ligand A, 0.004M ligand L, 0.004M metal perchlorate and 0.168M $NaClO_4$;

(ii) 0.02M $HClO_4$, 0.004M ligand A, 0.008M ligand L, 0.004M metal perchlorate and 0.164M $NaClO_4$.

The values of the formation constants of the mixed ligand species are shown in Table 6.1. The titration curves for all the ternary systems under study are shown in fig.6.1 to fig.6.5. The distribution of the ternary complexes as a function of pH for the system Cu-gg-Nphen is shown in fig.6.6.

Cyclic voltammetric studies were carried out on a EG & G PARC Electrochemistry System as detailed in Chapter-III. Cyclic voltammograms were recorded in the potential range +0.2V to -0.6V in aqueous solution (ca. $1x10^{-3}$M) at different pH with $NaClO_4$ as supporting electrolyte. The cyclic voltammograms for different complexes at different pH are shown in figs 6.7 and 6.8. The relevant CV data for all complexes are collected in table 6.2.

Table 6.1 : Formation constants of the mixed-ligand complexes in 50% water-dioxane(1:1 v/v) medium at I = 0.2M $NaClO_4$ and 30°C with standard deviations ($\sigma\sim\beta$) in parentheses.

Complexes	$\log K^{CuA}_{CuAL}$	$\triangle \log K$	$\log K^{CuA}_{CuAL_{-H}L}$
Cu-gg-Nphen	5.49 (0.02)	-0.74	7.00 (0.03)
Cu-gg-bpyz	5.79 (0.04)	-0.44	-
Cu-gg-phen	5.52 (0.05)	-0.71	7.43 (0.06)
Cu-gg-pyz	5.50 (0.02)	-0.73	7.59 (0.02)
Cu-gg-en	6.01 (0.06)	-0.22	7.97 (0.08)
Cu-ga-Nphen	6.03 (0.02)	-0.44	6.93 (0.03)
Cu-ga-bpyz	6.07 (0.01)	-0.40	-

(Contd. Table 6.1)

Cu-ga-phen	6.00	-0.47	7.40
	(0.03)		(0.04)
Cu-ga-pyz	6.04	-0.43	7.56
	(0.02)		(0.02)
Cu-ga-en	5.95	-0.52	8.26
	(0.03)		(0.06)
Cu-gl-Nphen	5.96	-0.86	7.34
	(0.02)		(0.02)
Cu-gl-bpyz	6.31	-0.51	-
	(0.02)		
Cu-gl-phen	5.84	-0.98	7.83
	(0.03)		(0.03)
Cu-gl-pyz	5.78	-1.04	8.03
	(0.02)		(0.03)
Cu-gl-en	6.34	-0.48	8.20
	(0.05)		(0.08)

Table 6.2 : Cyclic Voltammetric data[a] on Copper (II) - Ethylenediamine (en) and Copper (II) - en - glycylglycine (gg) complexes.

Complex	pH	E^1_{red}	E^2_{red}	E^1_{ox}	E^2_{ox}
Cu - en	4.06	-0.08	-	-0.03	-
	5.03	-0.15	-0.35	-0.04	b
	7.07	-0.15[c]	-0.38	-0.06	b
Cu - gg - en	4.06	-0.09	-	-0.02	-
	5.03	-0.15	-0.35	-0.04	b
	7.12	-0.14[c]	-0.47	-0.06	b

a. All potentials are in Volts ; Scan rate = 0.05 Vs^{-1}

b. Broad peak, difficult to measure precisely.

c. Peak appears only in second and subsequent scans.

Fig 6.1 Potentiometric titration curves of 50% (v/v) water - dioxan solutions containing metal ions, gg, ga or gl and Nphen (each 4.0×10^{-3} M).
(1) Cu^{2+} + gg + Nphen.
(2) Cu^{2+} + ga + Nphen.
(3) Cu^{2+} + gl + Nphen.

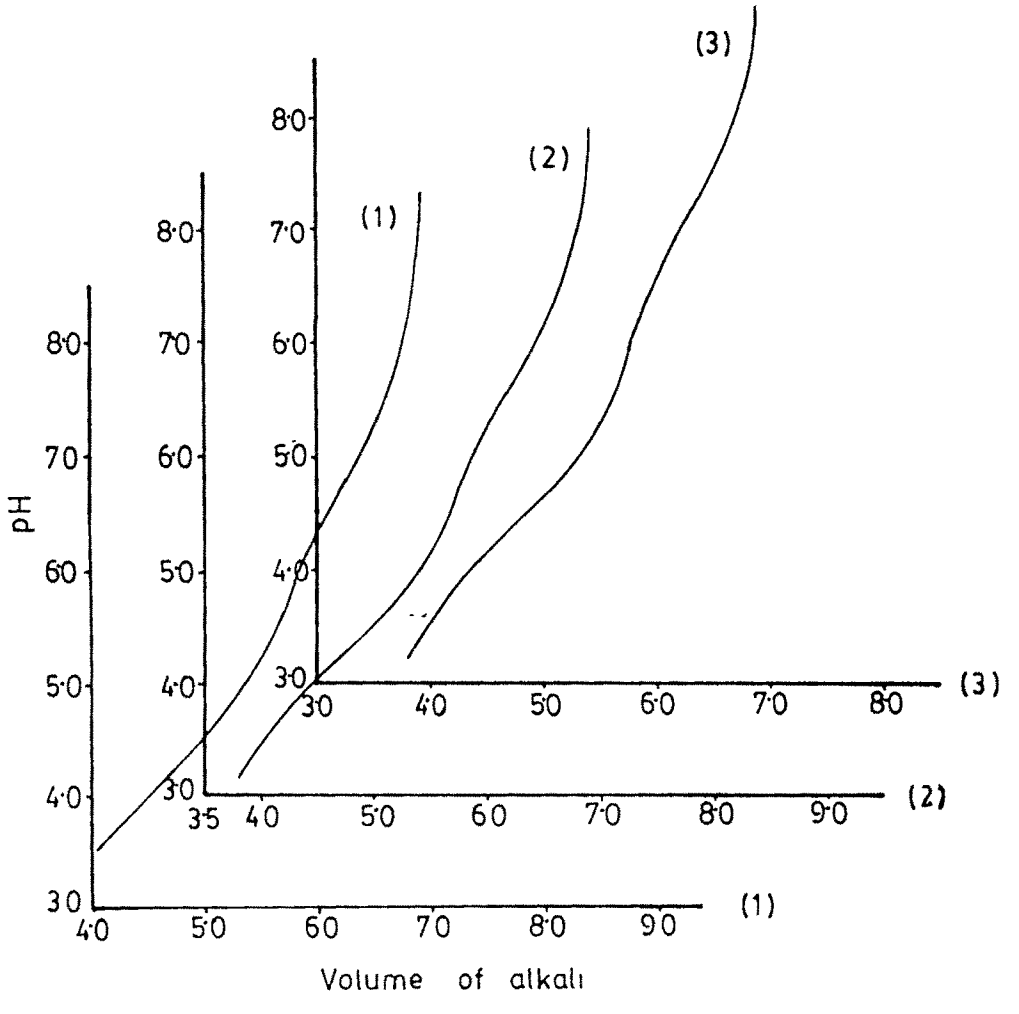


Fig. 6.2 Potentiometric titration curves of 50% (v/v) water - dioxan solutions containing metal ions, gg, ga or gl and bpyz (each 4.0 x 10^{-3} M).
(1) Cu^{2+} + gg + bpyz.
(2) Cu^{2+} + ga + bpyz.
(3) Cu^{2+} + gl + bpyz.

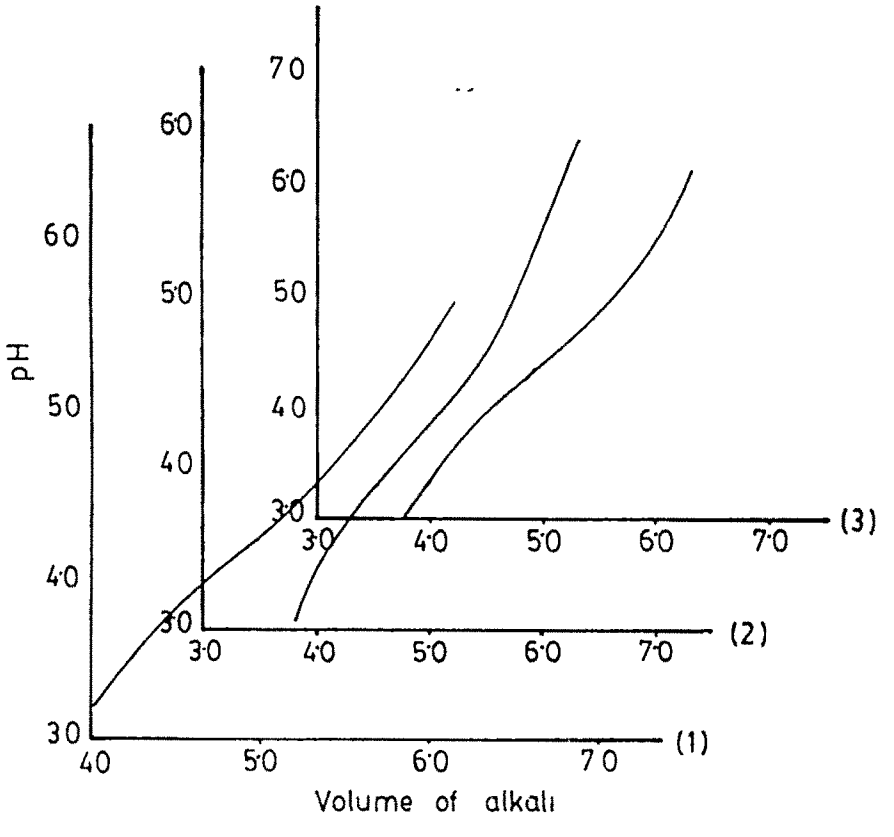


Fig. 6.3 Potentiometric titration curves of 50% (v/v) water - dioxan solutions containing metal ions, gg, ga or gl and phen (each 4.0×10^{-3} M).
(1) Cu^{2+} + gg + phen.
(2) Cu^{2+} + ga + phen.
(3) Cu^{2+} + gl + phen.

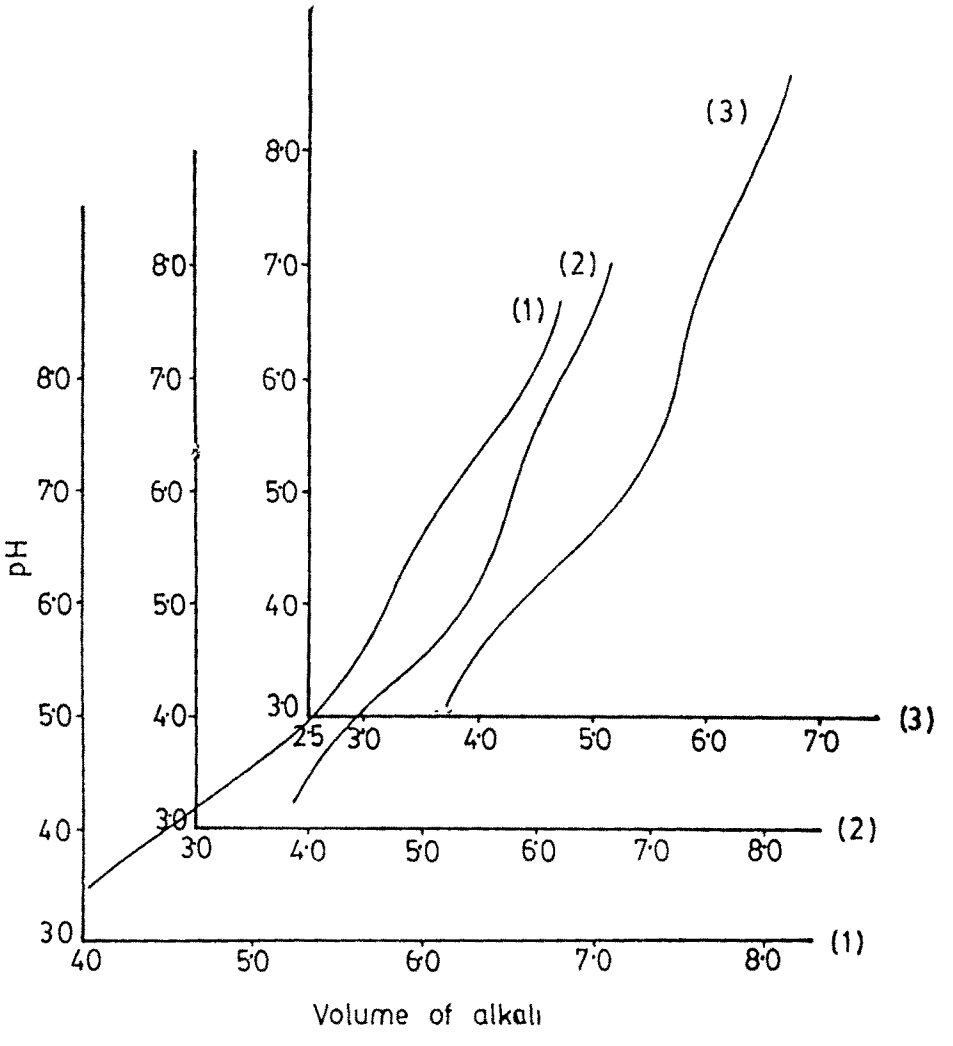


Fig. 6.4 Potentiometric titration curves of 50% (v/v) water - dioxan solutions containing metal ions, gg, ga or gl and pyz (each 4.0 x 10^{-3} M).
(1) Cu^{2+} + gg + pyz.
(2) Cu^{2+} + ga + pyz.
(3) Cu^{2+} + gl + pyz.

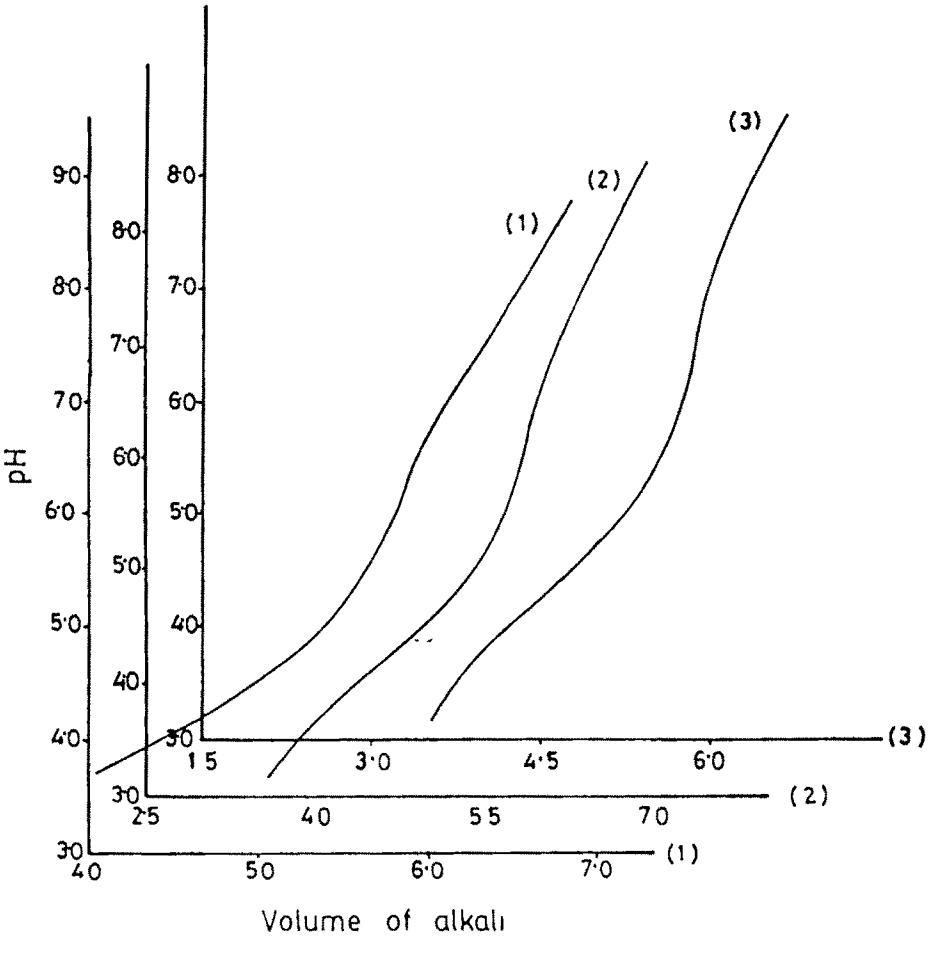
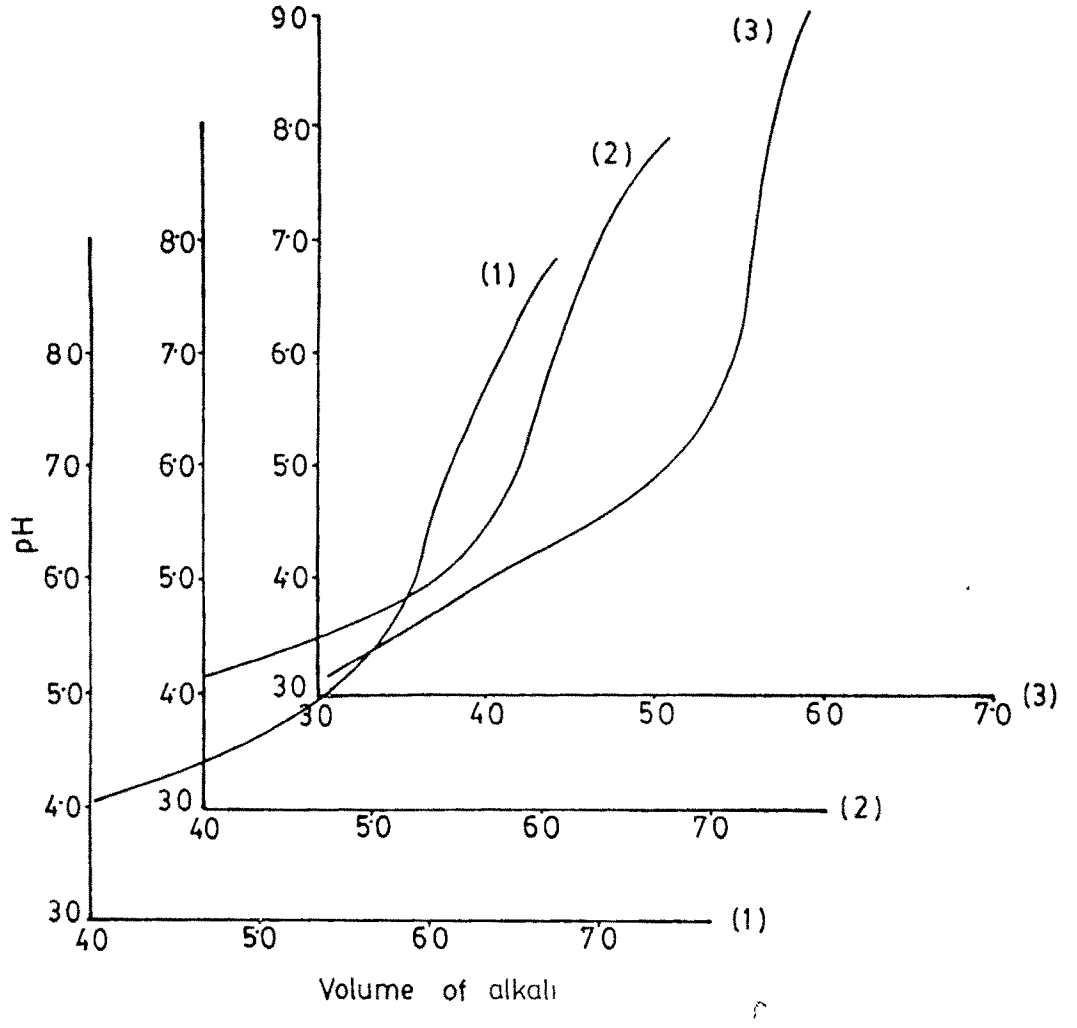


Fig. 6.5 Potentiometric titration curves of 50% (v/v) water - dioxan solutions containing metal ions, gg, ga or gl and en (each 4.0×10^{-3} M).
(1) Cu^{2+} + gg + en.
(2) Cu^{2+} + ga + en.
(3) Cu^{2+} + gl + en.



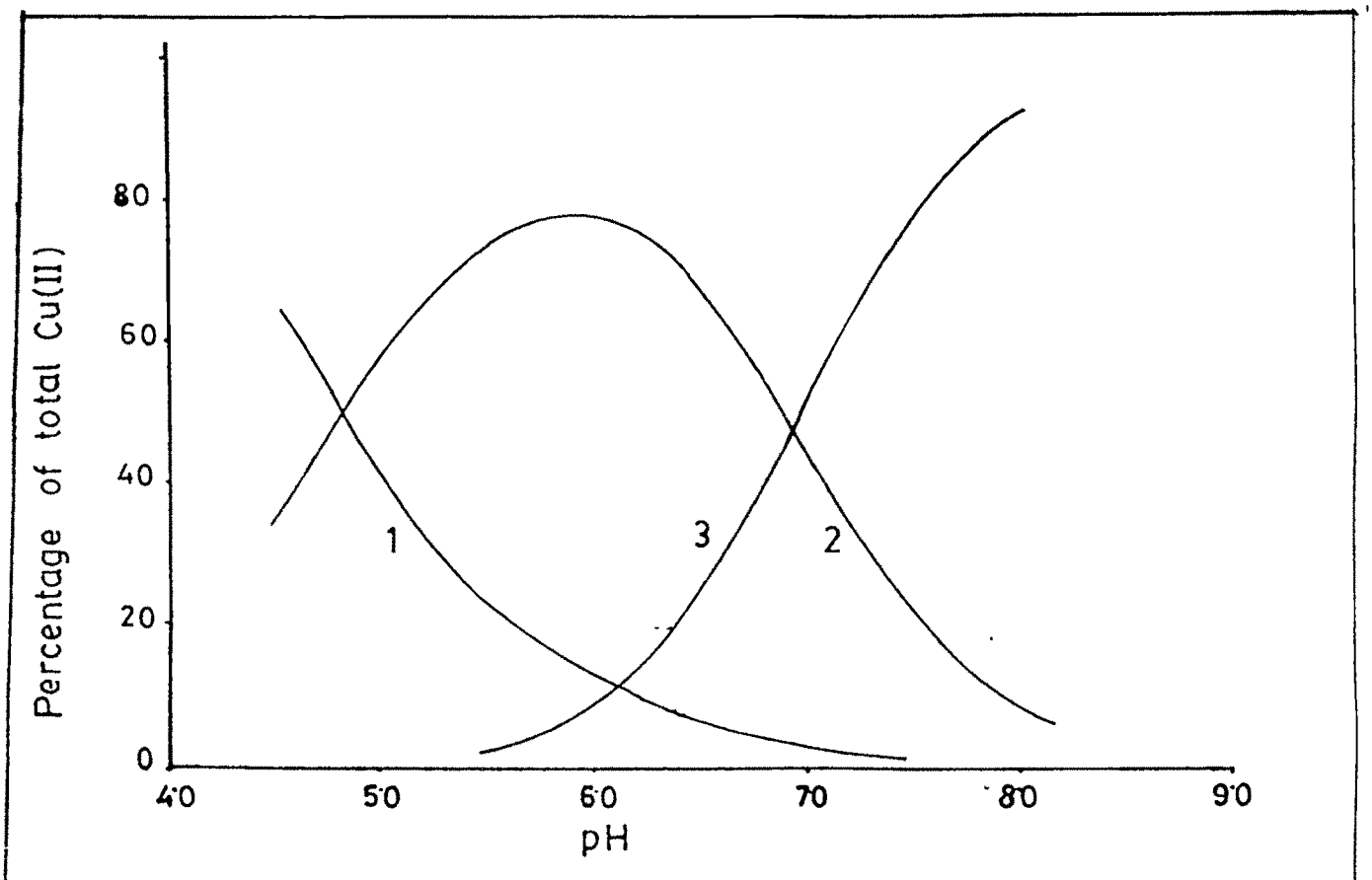


Fig. 6.6 Species distribution for Cu(II) - Nphen(A) - ga(L) system at M:A:L ratio of 1:1:1.

1) Unbound Cu(II) 2) CuAL 3) $CuAL_{-H}$

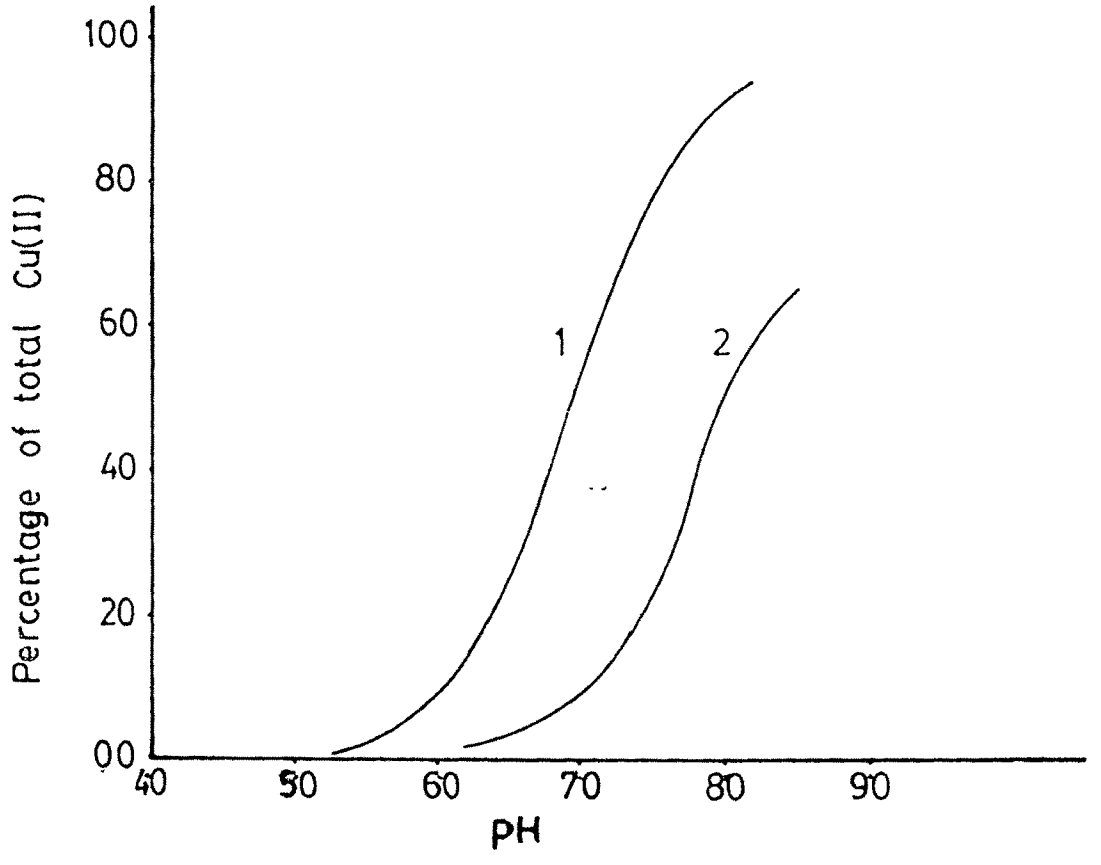


Fig 67 Species distribution curves for
1) Cu-Nphen-gg$_{-H}$ 2) Cu-en-gg$_{-H}$

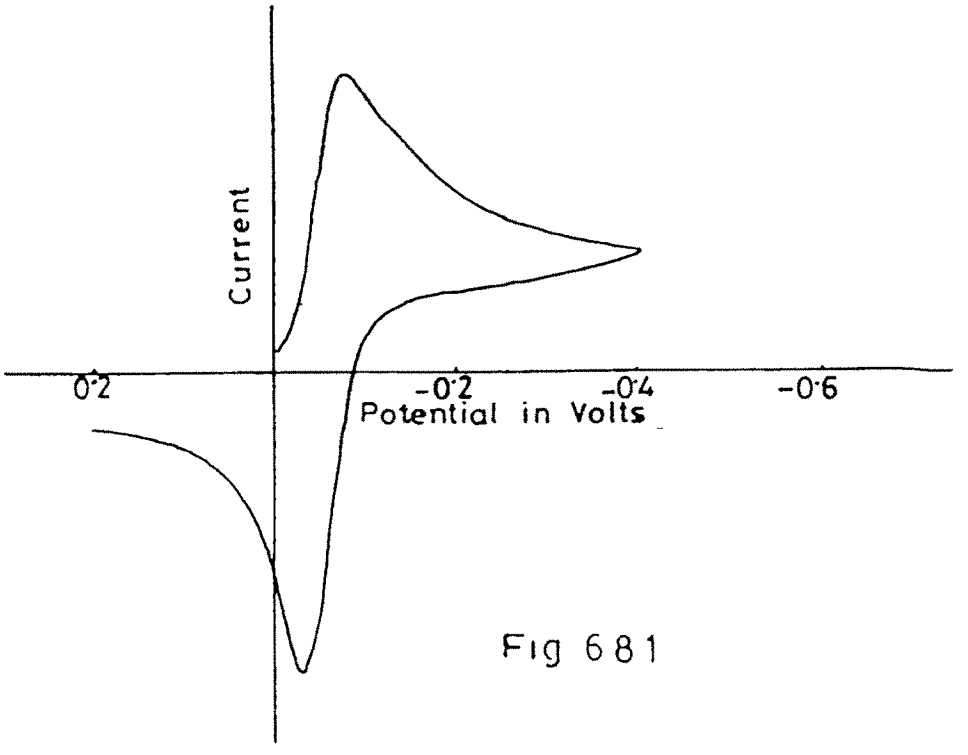


Fig 6 8 1

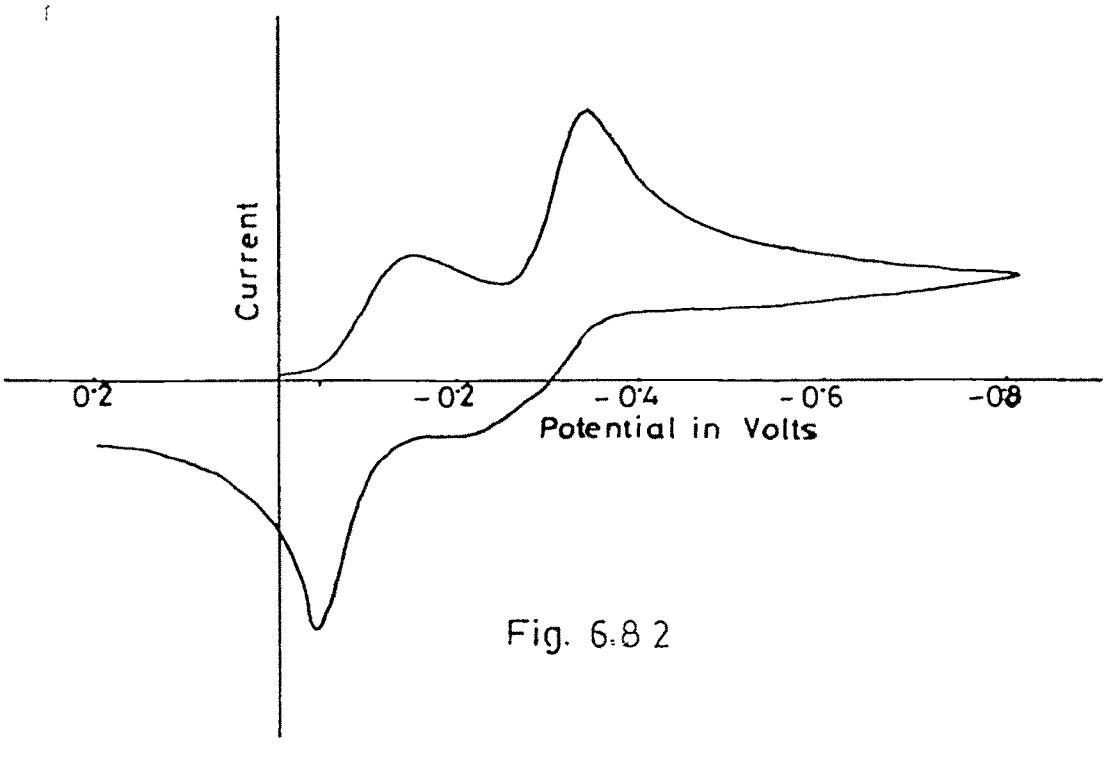


Fig. 6.8 2

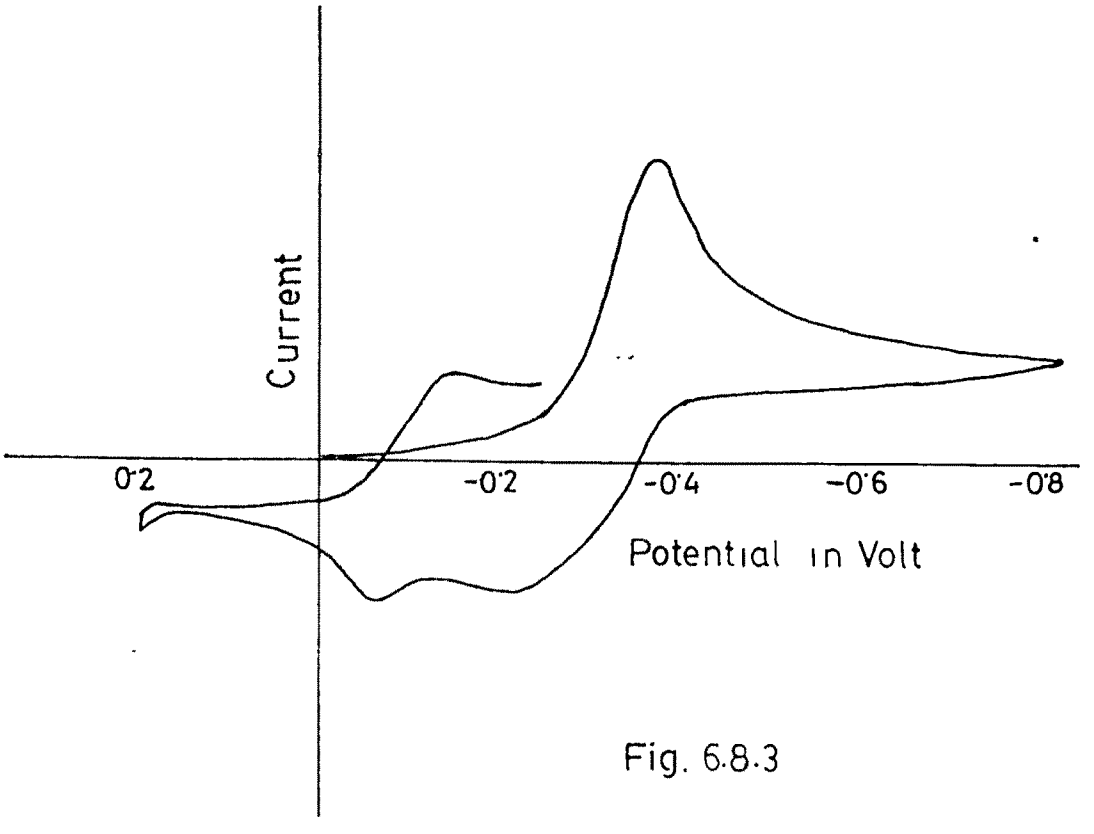


Fig. 6.8.3

Fig. 6 8 Cyclic Voltammograms of Cu(II) en Complex at scan rate = 0·05 Vs^{-1} and at various pH

6 8.1) pH = 4·06 6 8 2) pH = 5·03 6 8 3) pH = 7·07

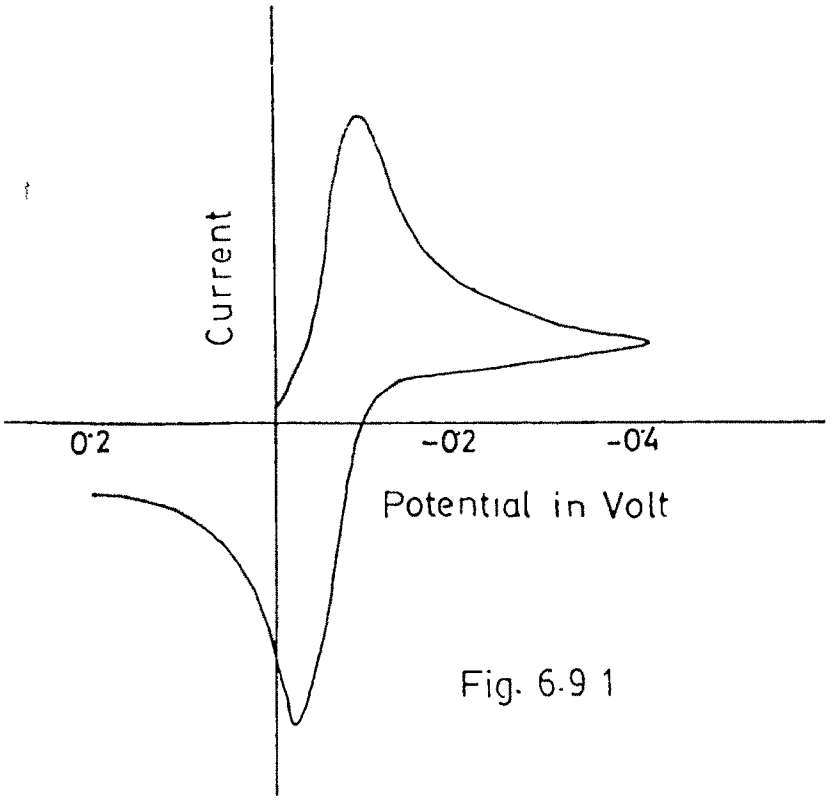


Fig. 6.9 1

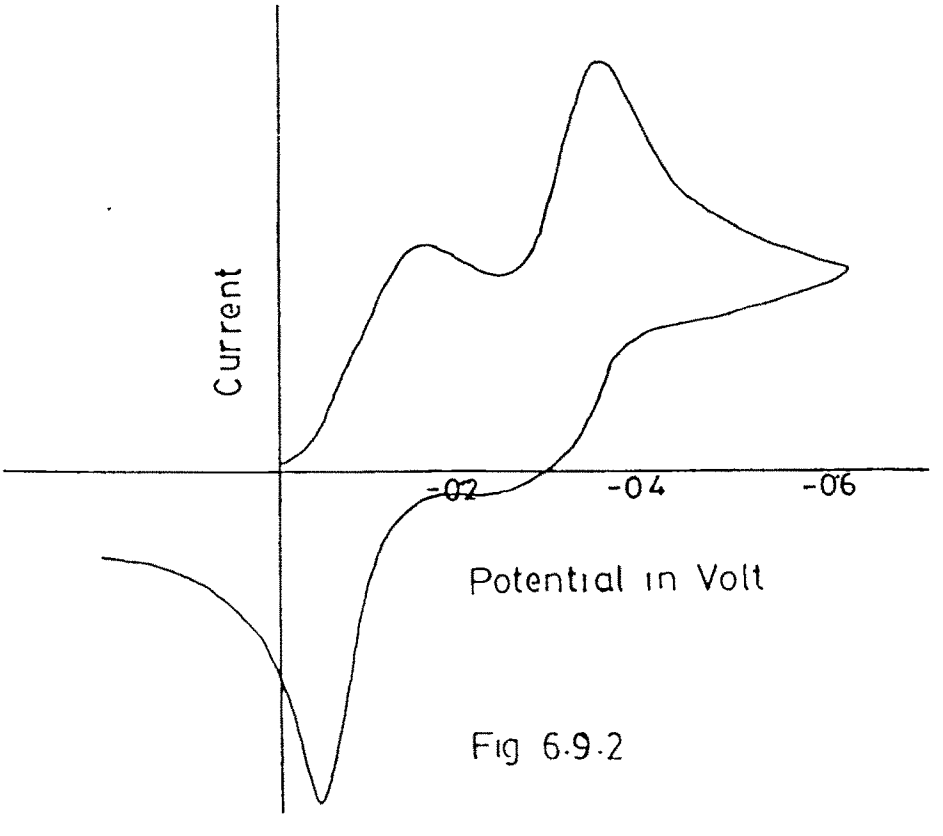


Fig 6.9.2

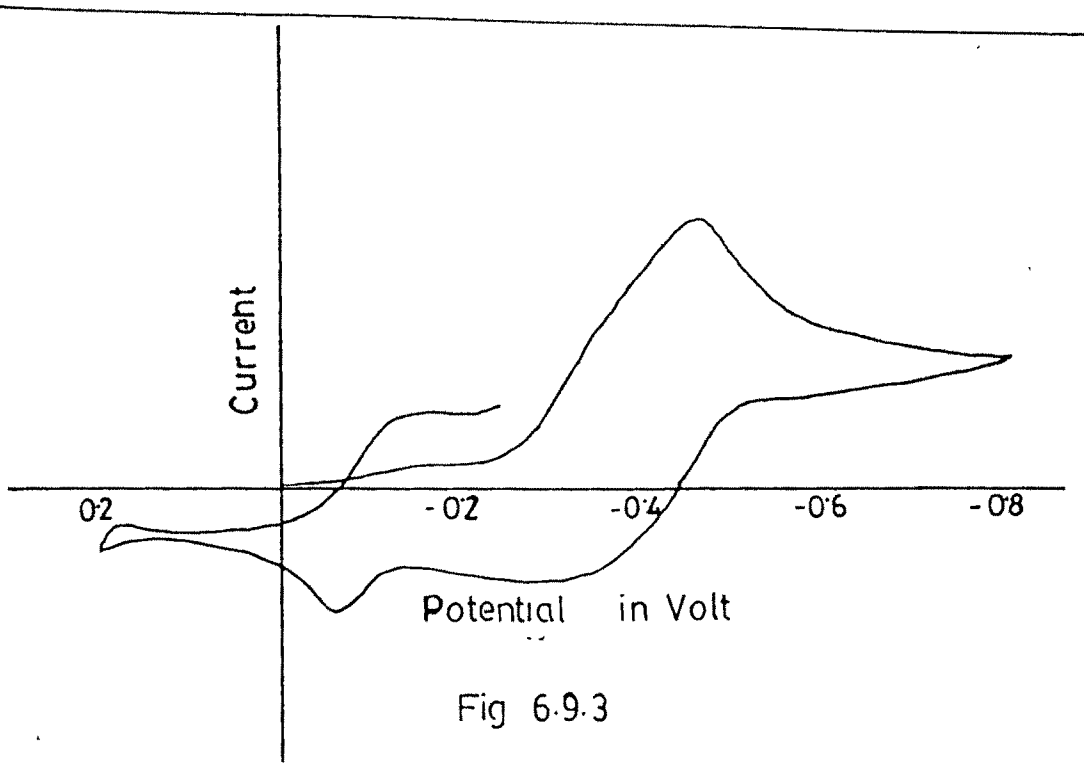


Fig 6.9.3

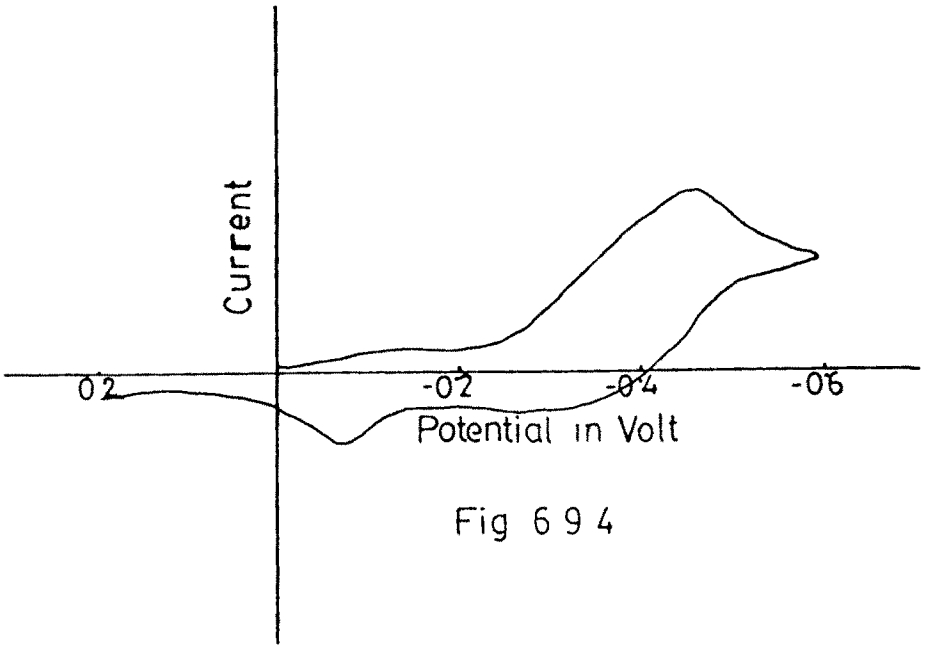


Fig 6 9 4

Fig 6 9 Cyclic Voltammograms of Cu(II)en gg Complex at scan rate = 0 05 Vs^{-1} and at various pH 6.9.1) pH = 4·06 6 9 2) pH = 5·03 6 9 3) pH = 7·12 6 9.4) **pH** = 7·12 ; scan rate = 0·02 Vs^{-1}

RESULTS AND DISCUSSIONS:

Species distribution curves show the formation of the two mixed-ligand species in different pH ranges (fig.6.6). The species CuAL is formed in the pH range 4.5-6.5 whereas the deprotonated ternary species $CuA_{-H}L$ starts forming at a pH $\sim$ 6.5 and its concentration increases with the increase in pH.

Formation and Stability of CuAL Complexes :

The equilibrium constant for the above ternary species can be represented by the equations given below :

$$Cu + A + L \rightleftharpoons CuAL \qquad (6.1)$$

$$K^{Cu}_{CuAL} = \frac{[CuAL]}{[Cu][A][L]} \qquad (6.2)$$

It was observed that $\triangle \log K = (\log K^{CuA}_{CuAL} - \log K^{Cu}_{CuL})$ for this ternary complex is negative for all the systems under study, as expected from statistical considerations. Increase in the Π - acidity of the aromatic amines has no effect on the $\triangle \log K$ values of the ternary CuAL complexes. This is because the dipeptide in this ternary complex is coordinated through amino nitrogen and oxygen of the amide group i.e. it has N-O coordination sites. None of the coordination sites have any additional lone pair of electrons. During the formation of ML binary complex, there is no repulsion between

the metal dΠ electrons and ligand electrons and hence no release of repulsion in the formation of the ternary complex, ▬ observed in the case of ternary complexes involving aromatic amines and secondary ligand having $O^- - O^-$ or $O^- - N$ coordination sites such as catechol or amino acids [10-14].

Formation and stability of $CuA_{-H}L$ Complex :

For the ternary complex $CuA_{-H}L$, only the protonation constant can be worked out. The protonation constant is represented by the equations shown below :

$$CuA_{-H}L + H \rightleftharpoons CuAL \qquad (6.3)$$

$$K^{CuA_{-H}L}_{CuAL} = \frac{[CuAL]}{[CuA_{-H}L]\ [H]} \qquad (6.4)$$

Hence, the deprotonation of the dipeptide in different ternary complexes involving aromatic amines with different Π-acidity can be compared. It was observed that increase in the Π-acidity of the aromatic amines has marked influence on the deprotonation of the dipeptide in the ternary complex. For each of the dipeptides it was observed that the deprotonation is more in case of ternary complexes with aromatic amines, compared to ethylenediamine (en). Deprotonation is maximum for the ternary complexes involving 5-nitro-1, 10-phenanthroline (Nphen). The order in which deprotonation is favoured in the ternary complexes is en < pyz < phen < Nphen, which is also the order of increasing Π-acidity of the amines. Thus it

is observed that Π-acidic ligands favour N-N^- coordination of the dipeptide to N-O coordination, in the ternary complex. This is because of the fact that a metal, when bound to a Π-acidic ligand, possess more class A character due to $d\Pi$-$p\Pi$ back bonding and becomes a hard acid. Hence during the formation of a ternary complex it will prefer a ligand, which is a hard base i.e. the dipeptide coordinated from N-N^- coordination sites, rather than N-O coordination sites. Nphen, being most Π-acidic, favours deprotonation of the dipeptide in the ternary complex to the maximum extent. Ethylenediamine has no Π-acidity, hence deprotonation of the dipeptide is not facilitated in Cu-dipeptide-en complexes.

Species distribution curves (fig.6.7) show the formation of the deprotonated $CuA_{-H}L$ species at a lower pH in case of CuANphen complex compared to the corresponding en complex, supporting the fact that Nphen favours deprotonation of the dipeptide, whereas en does not.

A comparison of the deprotonation of the dipeptide A in the binary complex CuA_{-H} with that in the ternary complex $CuA_{-H}L$ reveals, that deprotonation of the peptide N-H bond is very much reduced in the ternary complex, compared to the binary complex. This is because the deprotonated dipeptide is tridentate and in the binary complex coordinates through amino nitrogen, peptide nitrogen and carboxylate oxygen, the three atoms occupying the three equatorial positions. In the ternary complex two of the equatorial positions will be occupied by the amine, so that the dipeptide has to occupy one axial and two equatorial positions or the amine has to occupy one axial and one equatorial position. Occupation

of the axial position destabilizes the copper(II) complexes, because of Jahn-Teller distortion. This may inhibit the coordination from the peptide nitrogen.

Cyclic Voltammetry of Cu-en Complexes :

The general features of cyclic voltammograms of Cu-en system is disccussed below :

i) At a low pH ($\sim$ 4.06), a single reduction peak at about -0.08V is observed during the cathodic scan (fig.6.8.1). During the reverse scan a corresponding oxidation peak is observed at about -0.03V. Potentiometric studies reveal the presence of free Cu^{+2} ions and binary Cu-en species, in solution, at this pH. As the redox potential of Cu(II)en is not very different from Cu^{+2} the reduction and oxidation peaks are attributed to the combination of electrode process.

$$Cu^{+2} \underset{-2e}{\overset{+2e}{\rightleftharpoons}} Cu^{\circ} \quad \text{and}$$

$$Cu(II)en \underset{-e}{\overset{+e}{\rightleftharpoons}} Cu(I)en$$

ii) At an intermediate pH ($\sim$ 5.03) a reduction peak at about -0.15V is observed during the forward scan. The reverse scan gives an oxidation peak at about -0.04V (fig.6.8.2). The electrode process corresponding to the above reduction and oxidation peaks are as follows :

$$Cu(II)en \underset{-e}{\overset{+e}{\rightleftharpoons}} Cu(I)en$$

Another reduction peak at about -0.35V was also observed during the first forward scan. This is attributed to the reduction of the bis binary complex

$$Cu(II)en_2 \underset{-e}{\overset{+e}{\rightleftharpoons}} Cu(I)en_2$$

During the reverse scan, a broad peak is observed in the potential range -0.12V to -0.30V. It is evident that this board peak is not only due to oxidation of $Cu(I)en_2$ complex alone but due to overlapping of the oxidation potentials of more than one species. It is possible that $Cu(I)en_2$ being highly unstable, a fraction of it may break into $Cu(I)en(H_2O)_2$. Overlapping of the oxidation peaks of $Cu(I)en_2$ and $Cu(I)en(H_2O)_2$ results in peak broadening.

iii) At a higher pH ($\sim$ 7.07) a single reduction peak at about -0.38V is observed (fig.6.8.3). This is attributed to the reduction of $Cu(II)en_2$ to $Cu(I)en_2$. On reverse scan a broad peak is observed in the potential range -0.12V to -0.30V, which is due to oxidation of the species $Cu(I)en_2$ and $Cu(I)en(H_2O)_2$ as already discussed.

During the reverse scan an oxidation peak is also observed at about -0.06V, which is identical to the oxidation peak of free $Cu^{\circ} \xrightarrow{-2e} Cu^{+2}$. However, initially there were no free copper ions present in the solution at such high pH. The species $Cu(I)en_2$ formed by the reduction of $Cu(II)en_2$ species, being unstable may undergo disproportionation.

$$Cu(I)en_2 \longrightarrow Cu(0) + Cu(II)en_2$$

During the reverse scan this electrogenerated Cu(0) gets oxidized to Cu^{+2} at -0.06V and hence the corresponding peak is observed. However the reduction peak for free Cu^{+2} was not observed from the second cathodic scan onwards which was observed in the case of Cu-amino acid complexes [21] or Cu-dipeptide complexes [22]. This may be because the electrogenerated Cu^{+2} combines with free en present in the solution forming Cu(II)en and no free Cu^{+2} ion is left in the solution at the pH ($\sim$ 7.07). The formation of Cu(II)en complex is evident from the fact that the peak corresponding to the reduction of this complex to Cu(I)en is observed from the second scan onwards, though there is no corresponding peak in the first cycle, as there is no Cu(II)en in the solution at that pH, as shown by potentiometric studies.

Cyclic Voltammetry of Cu(II) ggen complex :

i) At a low pH ($\sim$4.06) a single reduction peak is observed at -0.09V during the forward scan (fig.6.9.1). The reverse scan gives an oxidation peak at about -0.02V. Potentiometric studies show the presence of free Cu^{+2} (31.8%) Cu(II)gg (22.8%) and Cu(II)en (28.7%). Hence the redox peaks observed are attributed to the electrode process

$$Cu^{+2} \underset{-2e}{\overset{+2e}{\rightleftharpoons}} Cu^{\circ}$$

$$Cu(II)en/Cu(II)gg \underset{-e}{\overset{+e}{\rightleftharpoons}} Cu(I)en/Cu(I)gg$$

ii) At an intermediate pH ($\sim$ 5.03), a reduction peak is observed at -0.15V and the corresponding oxidation peak is observed at

-0.04V (fig.6.9.2). Another reduction peak is also observed at -0.35V. Corresponding oxidation peak observed during the reverse scan is broad in the potential range -0.16V to -0.32V. Potentiometric studies show the presence of the binary complexes Cu(II)gg (2.5%), $Cu(II)gg_{-H}$ (29.2%), Cu(II)en (27.5%)and the ternary complex Cu(II)ggen (39.6%) at this pH. The reduction - oxidation peaks observed at less negative potential are attributed to the redox proccess

$$Cu(II)en/Cu(II)gg \underset{-e}{\overset{+e}{\rightleftharpoons}} Cu(I)en/Cu(I)gg$$

Whereas, the peaks observed at higher negative potential is attributed to the reduction of the deprotonated binary complex $Cu(II)gg_{-H}$, bis binary complex $Cu(II)en_2$ and the ternary complex Cu(II)ggen.

$$Cu(II)gg_{-H}/Cu(II)en_2/Cu(II)ggen \underset{-e}{\overset{+e}{\rightleftharpoons}} Cu(I)gg_{-H}/Cu(I)en_2/Cu(I)ggen$$

iii) At a higher pH ($\sim$ 7.12) a single reduction peak is observed at about -0.47V (fig.6.9.3). Potentiometric studies reveal the presence of the deprotonated ternary species $Cuengg_{-H}$ as the major species at this pH. Hence the reduction peak is attributed to the process $Cu(II)gg_{-H}en \xrightarrow{+e} Cu(I)gg_{-H}en$. Reverse scan gives a very broad oxidation peak in the potential range -0.20V to -0.40V. $Cu(I)engg_{-H}$ being unstable, a fraction of it may decompose into $Cu(I)en(H_2O)_2$ and $Cu(I)gg_{-H}$. The overlapping of the oxidation potentials of all these species causes peak broadening.

Another oxidation peak is also observed at -0.06V which is due to the oxidation of electrogenerated Cu(0) formed by the disproportionation of Cu(I)ggen species as observed in case of binary Cu(II)-en system. The reduction peak for free Cu^{+2} was not observed from the second cathodic scan onwards. This may be because the electrogenerated Cu^{+2} combines with free en present in the solution forming Cu(II)en complex as discussed in the case of Cu-en system.

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