

## Binary and Ternary Copper(II) Complexes of Some Amino Acids and Glycylglycine

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The electrode behaviour and spectral characteristics of binary and ternary complexes of copper(II) with glycylglycine and some amino acids have been investigated in aqueous 0.3M sodium perchlorate medium. For ternary complexes, glycylglycine(GG) was used as a primary ligand and amino acid—glycine (Gly) L- $\alpha$ -alanine ( $\alpha$ -Ala), DL- $\alpha$ -aminobutyric acid ( $\alpha$ -Aba), DL-n-valine (n-Val), DL-valine (Val), L-serine (Ser) or L-threonine (Thr)—as a secondary one. From a suitable analysis of the polarographic and spectral data, the stoichiometry and stereochemistry of the complex species formed at different pH values have been ascertained. A probable mechanism for the electro-reduction of the complexes has been proposed. The anomalous behaviour of glycine complexes has been rationalized on the basis of the steric factors.

### INTRODUCTION

The solution studies of mixed-ligand complexes have received much attention recently, following the recognition that these play an important role in biological processes<sup>1-3</sup>. The mixed-ligand complexes formed by biologically active ligands like amino acids and peptides may serve as model systems for the study of the more complicated phenomena occurring in biological systems. Thus the enzyme-metal ion-substrate complex formed as an intermediate in the enzymatic reactions in the presence of a metal ion, is a kind of mixed ligand complex and the reaction itself is regarded as ligand-ligand interaction assisted by the co-operative action of the central metal ion. A well known example for such systems is the carboxypeptidase, a peptide complex whose crystal structure has been studied by X-ray analysis.<sup>4</sup>

The study of electrode behaviour of co-ordination compounds at the dropping mercury electrode (d.m.e) under varying experimental conditions<sup>5-11</sup> has been proved useful in indicating the ways in which such factors control the nature of the reducible species in solution and hence indicate the ways in which the electrochemical behaviour may change from one condition to another.

Keeping the above ideas in view, the aims of the present paper are to investigate the polarographic and electronic spectral behaviour of (1) the binary systems of copper(II) with amino acids—glycine (Gly), L- $\alpha$ -alanine ( $\alpha$ -Ala), DL- $\alpha$ -aminobutyric acid ( $\alpha$ -Aba), DL-nor-valine (n-Val) DL-valine (Val), L-serine (Ser) and L-threonine (Thr) and (2) mixed-ligand

systems with glycylglycine (GG) as primary ligand and one of the present amino acids as secondary ligand at the d.m.e. under varying experimental conditions such as pH, temperature, ligand concentration and depolarizer concentration.

## EXPERIMENTAL

Polarograms were recorded with a recording polarograph (systronics model-1632) and recorder model-1501 with a three electrode set up. A constant temperature water bath accurate to  $\pm 0.2^\circ\text{C}$  was used for all measurements. A calomel electrode and a platinum electrode were used as reference electrode and counter electrode respectively. All the pH measurements, with an accuracy of 0.05 pH unit, were made with a Naina digital pH-meter model NIG-333 using glass electrode. Buffer solution prepared from buffer powder of pH 4.00 and of pH 9.0 was used for calibration purposes before each reading. Spectral measurements were made with the Beckman model-26 spectrophotometer under the same conditions in which the polarographic waves were recorded, except the concentrations which were higher for spectral studies.

The amino acids-glycine, L- $\alpha$ -alanine, L-serine, L-threonine were purchased from Romali, and DL-valine, DL-nor-valine, DL $\alpha$ -aminobutyric acid from B.D.H. (Biochemical). The peptide glycylglycine was a sigma product. Analar grade copper-chloride was used for maintaining metal ion concentration. The solution of  $\text{CuCl}_2$  was standardized iodometrically with hypo, using potassium iodide and starch indicator. The sodium perchlorate used was of E-Merk (AnalaR grade). All the reagents were used without any further purification. Triton X-100 was purchased from Rhom and Haas, Company, Philadelphia.

### Procedure

#### *Binary Systems*

Polarographic measurements have been performed in conductivity water at  $25 \pm 0.2^\circ\text{C}$  for systems Cu(II): A (A is amino acid) in the ratio 1 : 1 and 1 : 2 in the pH range 4–10. The effect of ligand concentration has also been seen for the system Cu (II): A in the ratio 1 : 1, 1 : 2, 1 : 4, 1 : 5, 1 : 6, at pH 6.00 and 1 : 2, 1 : 10, 1 : 20, 1 : 40, and 1 : 60 at pH 8.00.

#### *Ternary Systems*

All the polarographic measurements were carried out in conductivity water at different pH values (pH 6–10) and temperatures. The effect of varying concentrations of depolarizer has also been investigated at pH 9.50. The Cu(II): B: A ratio was maintained 1 : 1 : 1 (B is GG). At pH

6.00 studies have also been made for Cu(II) : B : A, 1 : 1 : 1, 1 : 2 : 1, 1 : 1 : 1, 1 : 2 : 2, 1 : 10 : 1, 1 : 1 : 10.

The polarographic measurements have in general, been performed (both in binary and ternary systems) at a constant copper(II) concentration of  $1 \times 10^{-3}M$ , at a constant ionic strength of 0.3M of base electrolyte using 0.001% Triton X-100 as a maximum suppressor. The dissolved oxygen in the test solution was removed by bubbling purified nitrogen for fifteen minutes in each case. A nitrogen atmosphere was maintained over the solution during the actual experiment. In each system, the pH was maintained using dilute solutions of NaOH and HCl. The electronic spectral studies were made at a constant Cu(II) concentration of 0.01M.

## RESULTS AND DISCUSSION

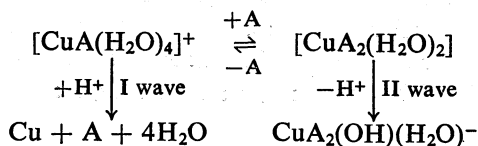
Oldham and Parry's<sup>12</sup> equation (1) which is valid for  $0 \leq x \leq 1$  for irreversible diffusion controlled waves:

$$-E_{d.e.} = E_{1/2} + (2.303RT/n\alpha F) \log \left\{ \frac{X(5.5 - X)}{5(1 - X)} \right\} \quad (1)$$

Where  $X = i_E/i_{lim}$  ( $i_E$  = current at potential  $E$ ,  $i_{lim}$  is limiting current) has been used to determine  $n\alpha$  and  $E_{1/2}$  values. The higher values of slope of the log plot than the theoretical values of  $2.303 RT/\alpha nF$  indicate the irreversible nature of the electrode process. The criterion of diffusion controlled nature of the wave is the constancy of  $i_d/h^{1/2}_{corr.}$  value at different heights of mercury column.

### Binary Cu(II):A systems

For Cu(II) : A (A is amino acid) 1 : 1 system, the appearance of a single well defined, diffusion controlled, reversible polarographic wave at pH 4.00 may be attributed to the reduction of only a single species, probably to  $[CuA(H_2O)_4]^+$ . The splitting of a single wave into two on changing the pH to 4.50 may be due to  $[CuA(H_2O)_4]^+$  species being in equilibrium with  $[CuA_2(H_2O)_2]$  in the bulk of the solution as shown in scheme I.



Scheme I

The first wave seems to be due to the electro-reduction of  $[CuA(H_2O)_4]^+$  together with  $[Cu(H_2O)_6]^{2+}$  species as their  $E_{1/2}$  values are nearly the same and the second wave due to the electro-reduction of  $[CuA_2(H_2O)_2]$  species. The probability of stepwise reduction may be ruled out on the basis of

the unequal heights of the waves. The heights of the waves vary with the change of pH in such a way that it seems probable that at higher pH  $[\text{CuA}_2(\text{H}_2\text{O})_2]$  species predominates (Fig. 1). At pH 6.50 the solution begins to become turbid and at pH 7.0 the precipitate settle down. With further increase of pH, the first wave disappears and only second wave remains with an  $i_d$  value approximately half of total wave height of the

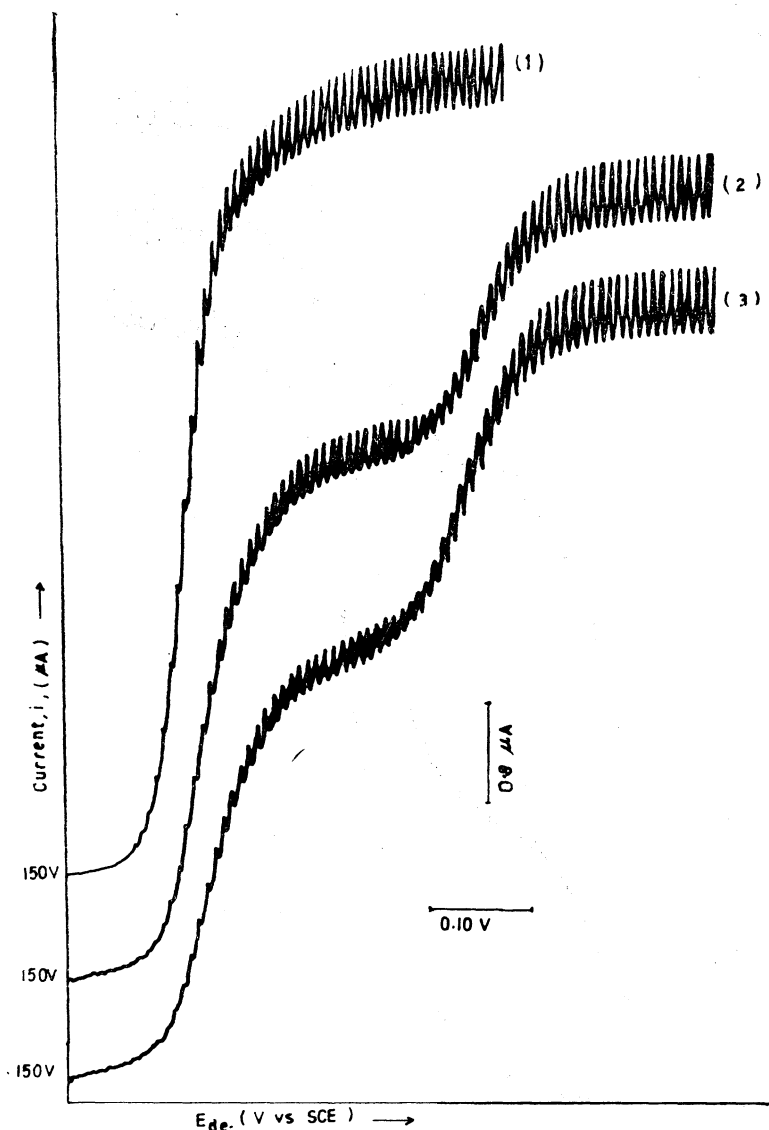


Fig. 1. Influence of pH on the nature of the reduction wave of Cu(II) : Gly (1 : 1)  
(1) pH 4.00, (2) pH 5.00, (3) pH 6.00

double wave indicating reduction of only  $[\text{CuA}_2(\text{H}_2\text{O})_2]$  species at higher pH. To get support for the above proposition attempts were made to investigate the effect of varying concentrations of ligand at 6 pH value. It has been found that the height of second wave increases and that of the first decreases showing predominance of  $[\text{CuA}_2(\text{H}_2\text{O})_2]$  at higher ligand concentrations as expected. At a ligand concentration of Cu(II) : A, 1 : 6 only a single wave appears showing the reduction of only a single species (Fig. 2).

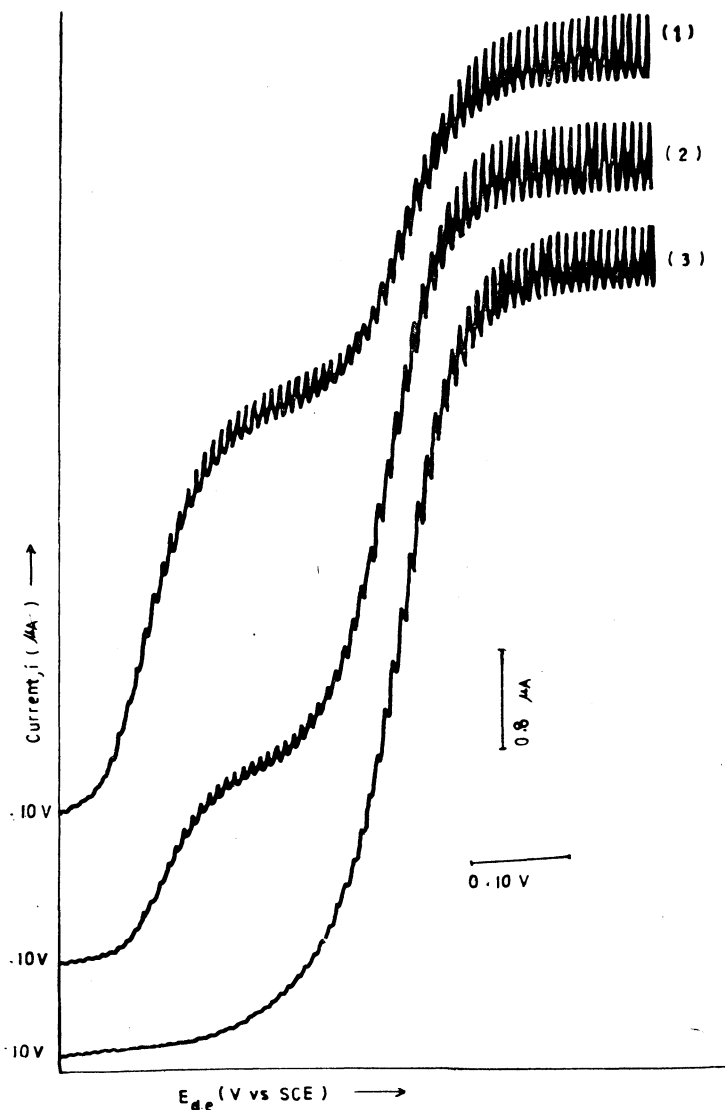


Fig. 2. Influence of free ligand concentration on the height of the wave of Cu(II) : Gly (1) 1 : 1, (2) 1 : 2, (3) 1 : 4

In case of Cu(II) : A, 1 : 2, a double wave appears at pH 4.00, perhaps due to the presence of two species viz.,  $[\text{CuA}(\text{H}_2\text{O})_4]$  and  $[\text{CuA}_2(\text{H}_2\text{O})_2]$  in equilibrium. It is also supported by the increase in the wave height of second wave with ligand concentration at pH 4.00. Similar trend is found with increasing pH which indicates the predominance of  $[\text{CuA}_2(\text{H}_2\text{O})_2]$  at higher pH values. (In case of Cu(II) (n-val) precipitation takes place at pH 6.00). With increasing pH, the  $E_{1/2}$  of first wave shifts towards negative potential while that of the second wave towards the positive potential. The plot of  $E_{1/2}$  vs pH for first wave, exhibits the involvement of one  $\text{H}^+$  ion in the electrode process. However, the plot of  $E_{1/2}$  vs pH for second wave reveals a release of one  $\text{H}^+$  ion (Fig. 3 and scheme I). At

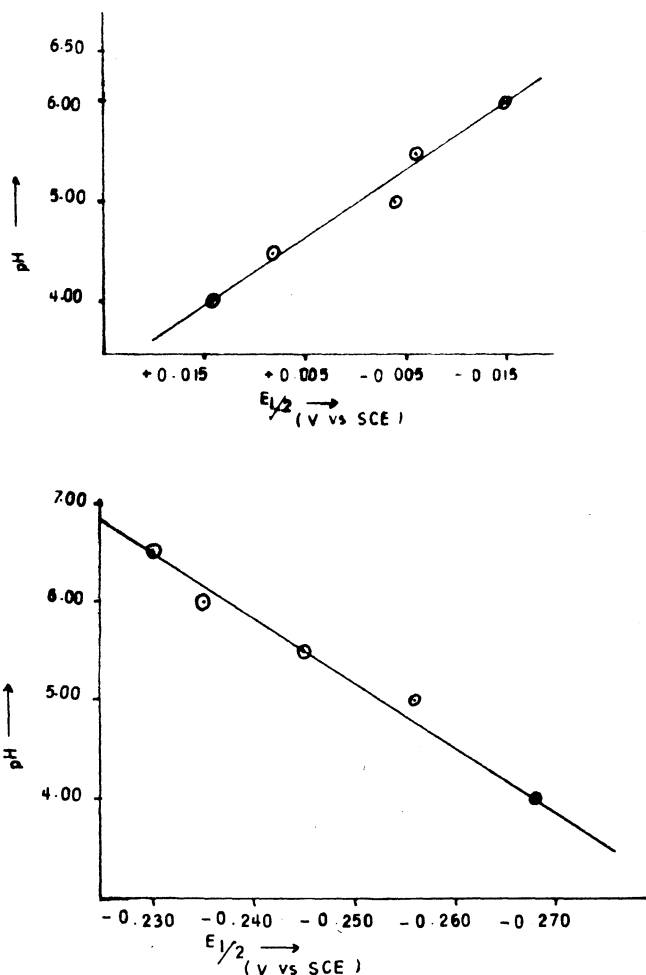


Fig. 3. Influence of pH on the half wave potential of Cu(II) : Gly (1 : 2) (a) for first wave (b) for second wave

pH 8.00 a single well defined, diffusion controlled, irreversible wave appears indicating the reduction of only  $[\text{CuA}_2(\text{H}_2\text{O})_2]$  species. The linear plot of  $E_{1/2}$  vs  $-\log A$  with slope value of 0.124 gives  $j = 4.06$  (where  $j =$  co-ordination number) indicating a co-ordination number four. This confirms the possibility of the existence of  $[\text{CuA}_2(\text{H}_2\text{O})_2]$  species.

TABLE 1

POLAROGRAPHIC PARAMETERS OF BINARY 1 : 2, Cu(II) : AMINO ACID COMPLEXES AT DIFFERENT pH, T = 25°C,  $[\text{NaClO}_4] = 0.3\text{M}$ ,  $[\text{Triton X-100}] = 0.001\%$ ,  $[\text{Cu}^{2+}] = 1 \times 10^{-3}\text{M}$ ,  $h_{\text{corr}} = 83.0 \text{ cm}$ ,  $m = 1.316 \text{ mg sec}^{-1}$ ,  $t = 3.8 \text{ sec}$

Complex	pH	$i_d(\mu\text{A})$	$-E_{1/2}$ (V vs SCE)
Cu(II)(Gly)	8.00	5.80	0.223
	9.00	5.80	0.228
	9.50	5.76	0.231
	10.00	5.68	0.236
Cu(II)( $\alpha$ -Ala)	8.00	5.20	0.216
	9.00	5.08	0.220
	9.50	5.06	0.224
	10.00	4.96	0.228
Cu(II)( $\alpha$ -Aba)	8.00	5.72	0.205
	9.00	5.64	0.207
	9.50	5.64	0.216
	10.00	5.64	0.222
Cu(II)(Val)	8.00	5.00	0.219
	9.00	4.80	0.226
	9.50	4.80	0.230
	10.00	4.72	0.233
Cu(II)(Ser)	8.00	5.88	0.205
	9.00	5.88	0.216
	9.50	5.86	0.220
	10.00	5.78	0.225
Cu(II)(Thr)	8.00	5.62	0.215
	9.00	5.62	0.222
	9.50	5.60	0.224
	10.00	5.60	0.227

The electronic spectra of Cu(II) : A, 1 : 1, complexes give a single absorption band at  $13600 \text{ cm}^{-1}$  ( $\epsilon = 26$ ) at pH 4.00 (Table 2). The aquocopper(II) complex absorbs at *ca.*  $12500 \text{ cm}^{-1}$ . This shift from  $12500 \text{ cm}^{-1}$  to  $13600 \text{ cm}^{-1}$  may be taken as an evidence for co-ordination of the

TABLE 2  
SPECTRAL CHARACTERISTICS OF BINARY, 1 : 1 AND 1 : 2 Cu(II) :  
AMINO ACID COMPLEXES

Complex	pH	$\nu_{\max}(\text{cm}^{-1})$	$\epsilon$	
Cu : Gly,	1 : 1	4.00	13330	26
	1 : 2	8.00	16000	50
Cu : $\alpha$ -Ala,	1 : 1	4.00	13500	25
	1 : 2	8.00	16200	51
Cu : $\alpha$ -Aba	1 : 1	4.00	13570	26
	1 : 2	8.00	16300	52
Cu ; n-Val,	1 : 1	4.00	—	—
	1 : 2	8.00	ppt	
Cu : Val,	1 : 1	4.00	13880	26
	1 : 2	8.00	16260	48
Cu : Ser,	1 : 1	4.00	13700	26
	1 : 2	8.00	16130	48
Cu : Thr	1 : 1	4.00	13880	26
	1 : 2	8.00	16180	48

copper(II) ion with the amino acid. Thus the species reduced at d.m.e. at pH 4.00 may be  $[\text{CuA}(\text{H}_2\text{O})_4]^+$ . The electronic spectra of Cu(II) : A, 1 : 2 complexes at pH 8.00 with varying concentrations of ligand always gives a characteristic spectrum of tetragonally distorted octahedral<sup>13, 14</sup> species with  $\nu_{\max} \approx 16240 \text{ cm}^{-1}$  and molar extinction coefficient *ca* 50 (Table 2). It is evident, therefore, that the bis species has the composition  $[\text{CuA}_2(\text{H}_2\text{O})_2]$ .

#### Ternary Cu(II) : GG : A systems

This has been established in our earlier paper<sup>15</sup> that the peptide group of GG is deprotonated at pH 6.25. From a close examination of polarograms (Fig. 4) of different species reduced at d.m.e. and from perusal of the results obtained (Table 3) one may conclude that the appearance of a double wave in the case of ternary Cu(II) : GG : A, 1 : 1 : 1 complexes may be due to the reduction of two species, probably  $[\text{CuA}_2]$  and  $[\text{CuGG-HA}]$ . In case of n-Val and Val complexes a prewave also appears at pH 6.00, these three waves may be attributed to the reduction of three species  $[\text{CuA}]$ ,  $[\text{CuA}_2]$  and  $[\text{CuGG A}]$  respectively. The prewave can not be attributed to the adsorption of the species, as there is no adsorption shown by electro capillary curve, nor to the reduction of  $[\text{CuGG}]$  or  $[\text{Cu}(\text{GG})_2]$  as their  $E_{1/2}$  values are much different<sup>15</sup>. This is also supported by the fact that on addition of ligand, A, the first wave disappears and the height of the



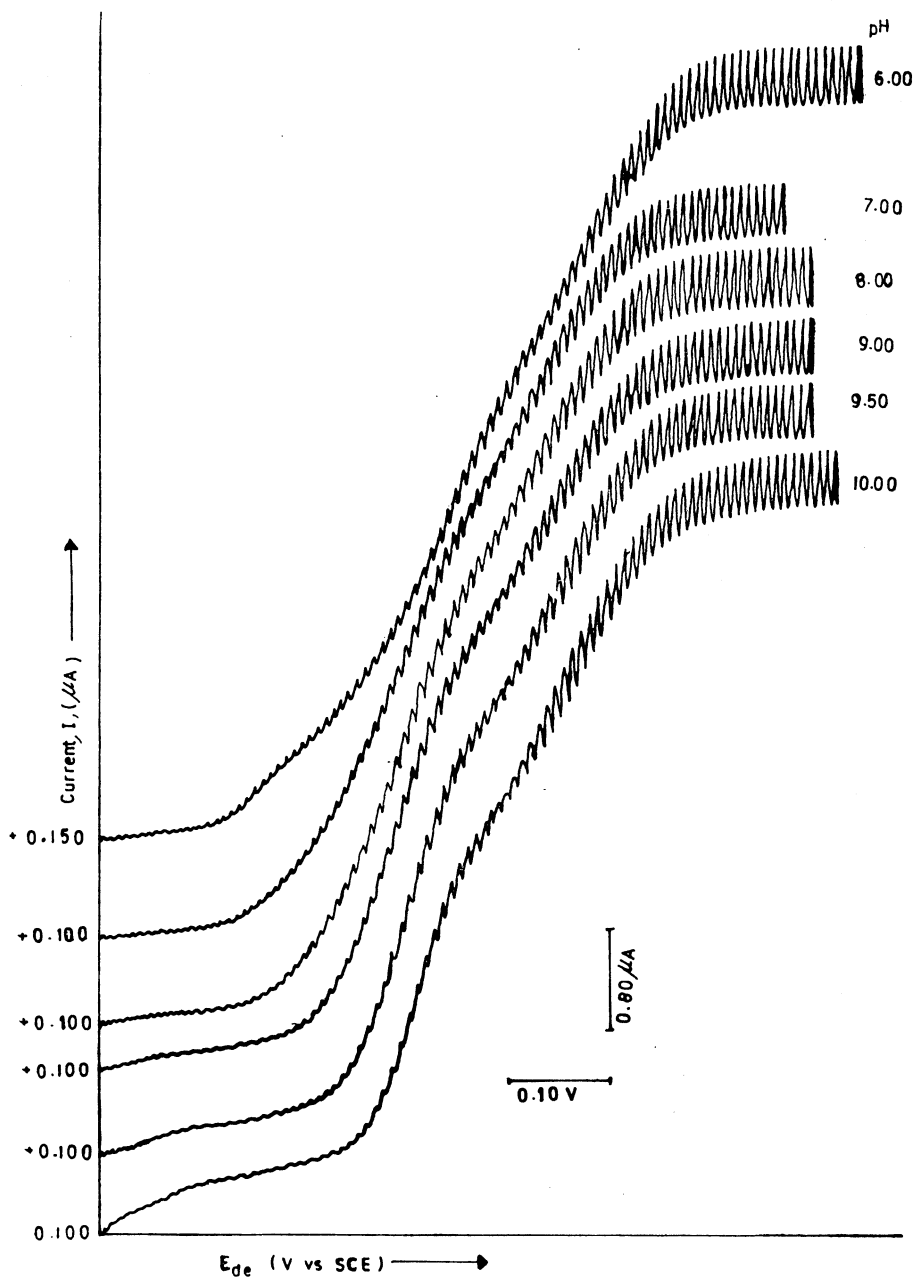


Fig. 4. Influence of pH on polarograms of Cu(II) : GG ; Val (1 : 1 : 1)

TABLE 3  
 POLAROGRAPHIC PARAMETERS OF TERNARY Cu(II) COMPLEXES AT  
 DIFFERENT pH, T = 25°C, [NaClO<sub>4</sub>] = 0.3M, [Cu<sup>2+</sup>] = [Ligand A] =  
 [Ligand B] = 1 × 10<sup>-3</sup>M, [Tritox X-100] = 0.001% h<sub>corr</sub> = 83 cm,  
 m = 1.316 sec<sup>-1</sup>, t = 3.8 sec

Complex		i <sub>d</sub> (μA)		-E <sub>1/2</sub> (V vs SCE)	
		I	II	I	II
[Cu(II)(GG)(Gly)]	8.00	2.24	3.44	0.168	0.337
	9.00	2.08	3.52	0.185	0.346
	9.50	1.80	3.68	0.196	0.355
	10.00	1.80	3.60	0.215	0.368
[Cu(II)(GG)(α-Ala)]	8.00	1.88	3.52	0.158	0.325
	9.00	1.84	3.50	0.173	0.334
	9.50	1.84	3.48	0.188	0.345
	10.00	1.52	3.72	0.205	0.354
[Cu(II)(GG)(α-Aba)]	8.00	2.60	3.56	0.160	0.326
	9.00	2.52	2.60	0.162	0.330
	9.50	2.20	3.04	0.174	0.334
	10.00	2.00	3.16	0.182	0.337
[Cu(II)(GG)(n-Val)]	8.00	2.88	3.44	0.163	0.331
	9.00	2.52	3.52	0.175	0.338
	9.50	2.28	3.68	0.190	0.344
	10.00	2.28	3.68	0.207	0.358
[Cu(II)(GG)(Val)]	8.00	2.92	2.52	0.165	0.335
	9.00	2.86	2.56	0.177	0.346
	9.50	2.64	2.72	0.193	0.352
	10.00	2.64	2.96	0.205	0.364
[Cu(II)(GG)(Ser)]	8.00	2.32	3.36	0.155	0.326
	9.00	2.16	3.36	0.170	0.331
	9.50	2.04	3.40	0.180	0.335
	10.00	1.80	3.76	0.200	0.343
[Cu(II)(GG)(Thr)]	8.00	2.44	3.76	0.157	0.330
	9.00	2.44	3.84	0.172	0.337
	9.50	2.40	3.84	0.185	0.344
	10.00	1.32	4.32	0.205	0.348

second wave increases. However, on addition of the ligand, GG, the second wave remains unaffected and the height of third wave increases. At pH 7.00 the double wave is observed which may be attributed to the reduction of  $[\text{CuA}_2]$  and  $[\text{CuGG-HA}]$  species. However, the polarograms are ill-defined perhaps, due to less difference in the reduction rate of the species. The increase in the height of second wave at pH 7.00 shows the predominance of  $[\text{CuGG-HA}]$  species at higher pH.

For ternary complexes  $\text{Cu(II)} : \text{GG} : \text{A}$ , 1 : 1 : 10 at pH 6.00 only a single wave has been observed which indicates the reduction of only single species that may be  $[\text{CuA}_2]$ , as shown by the morphology of the wave. However, for  $\text{Cu(II)} : \text{GG} : \text{A}$ , in the ratio, 1 : 10 : 1, the double wave remains, but the second wave may not be attributed to the reduction of  $[\text{Cu(GG)}_2]$  species<sup>15</sup>. This supports the fact that the metal binding by small ligands such as amino acids is significant even when peptides and proteins are also present and must be taken into account in any physiological studies of metal protein interactions.

TABLE 4  
POLAROGRAPHIC PARAMETERS OF TERNARY  $\text{Cu(II)}$  COMPLEXES AT  
DIFFERENT TEMPERATURES, pH = 9.50,  $[\text{NaClO}_4] = 0.3\text{M}$ ,  
 $[\text{Triton X-100}] = 0.001\text{M}$ ,  $[\text{Cu}^{2+}] = [\text{Ligand A}] = [\text{Ligand B}] = 1 \times 10^{-3}\text{M}$

Complex	Temp. °C	$i_d(\mu\text{A})$		$-E_{1/2}(\text{V vs SCE})$	
		I	II	I	II
$[\text{Cu(II)(GG)(Gly)}]$	25	1.80	3.68	0.196	0.355
	35	2.08	4.08	0.205	0.375
	45	2.44	4.62	0.209	0.389
$[\text{Cu(II)(GG)(}\alpha\text{-Ala)}]$	25	1.84	3.48	0.188	0.345
	35	2.24	3.96	0.195	0.369
	45	2.44	4.28	0.200	0.382
$[\text{Cu(II)(GG)(}\alpha\text{-Aba)}]$	25	2.20	3.04	0.174	0.334
	35	2.72	3.20	0.188	0.349
	45	3.20	3.56	0.189	0.379
$[\text{Cu(II)(GG)(n-Val)}]$	25	2.28	3.68	0.190	0.347
	35	2.96	4.04	0.203	0.371
	45	3.64	4.34	0.205	0.385
$[\text{Cu(II)(GG)(Val)}]$	25	2.64	2.72	0.193	0.352
	35	3.24	2.80	0.204	0.381
	45	4.20	2.64	0.206	0.405
$[\text{Cu(II)(GG)(Ser)}]$	25	2.04	3.40	0.180	0.335
	35	2.28	3.92	0.189	0.361
	45	2.48	4.40	0.203	0.379
$[\text{Cu(II)(GG)(Thr)}]$	25	2.40	3.84	0.185	0.344
	35	2.64	4.40	0.200	0.378
	45	2.88	4.88	0.205	0.395

From the perusal of Table-5, the electro reduction appears to be more difficult at higher temperatures, since  $E_{1/2}$  shifts towards more negative potentials with increase in temperature. The polarograms become kinetically controlled at higher temperatures. This has also been supported by the non-linear nature of the plot of  $E_{1/2}$  vs  $T$ , which shows that the mechanism of electro-reduction of these complexes changes with temperature<sup>11</sup>. An increase in the diffusion current of both the waves with temperature may be due to increase of diffusion coefficient,  $D$  at higher temperatures.

TABLE 5  
SPECTRAL CHARACTERISTICS OF TERNARY Cu(II) COMPLEXES OF  
AMINO ACIDS AND PEPTIDES

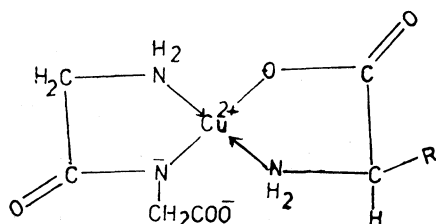
Complex	pH	$\nu_{\max}(\text{cm}^{-1})$	$\epsilon$
[Cu(II)(GG)(Gly)]	6.00	15750	58
	8.00	16000	64
	9.50	16000	68
[Cu(II)(GG)( $\alpha$ -Ala)]	6.00	—	—
	8.00	—	—
	9.50	16130	54
[Cu(II)(GG)( $\alpha$ -Aba)]	6.00	15870	68
	8.00	16260	70
	9.50	16260	72
[Cu(II)(GG)(n-Val)]	6.00	—	—
	8.00	Precipitate	—
	9.50	—	—
[Cu(II)(GG)(Val)]	6.00	15820	58
	8.00	16130	64
	9.50	16130	64
[Cu(II)(GG)(Ser)]	6.00	15820	60
	8.00	16130	64
	9.50	16130	65
[Cu(II)(GG)(Thr)]	6.00	15870	56
	8.00	16130	62
	9.50	16130	64

Diffusion current has been found to be proportional to the concentration of the depolarizer, indicating that there is no association or dissociation of the complex in aqueous medium. A negative shift of  $E_{1/2}$  with concentration of the depolarizer supports the irreversible nature of the electrode process.<sup>16</sup>

Although polarographic studies show the existence of two species viz.  $[\text{CuA}_2]$  and  $[\text{CuGG-HA}]$  in the solution, but the electronic spectra of ternary Cu(II) : GG : A, 1 : 1 : 1 complexes give only a single asymmetric absorption band at  $16000\text{cm}^{-1}$  ( $\epsilon \sim 65$ ) (Table 5) from which the ternary complexes seem to be tetragonally distorted octahedral in geometry. In

addition, it may be inferred from these observations that the mode of co-ordination of the  $\alpha$ -amino acids in the ternary complexes studied is the same as in the binary complexes. As  $\alpha$ -amino acids are effective bidentate ligands, hence the carboxylate group of binary complex of GG is replaced from the tetragonal plane in the ternary complexes. The single asymmetric absorption band may be due to the overlapping of the two expected bands because of less difference in maximum absorption of the two species. Gergely *et al.*<sup>17</sup> have used pH-metric studies to determine the stability constants of ternary complexes of amino acids and peptides. They have explained their results on the basis of the penta co-ordinated Cu(II) complexes. The amino acid was assumed to occupy the equatorial and one axial position. However, present electronic spectral studies in visible region do not support the presence of penta-co-ordinated Cu(II) as the values of ( $\epsilon \sim 65$ ) and  $\nu_{\max}$  *ca.* 16000  $\text{cm}^{-1}$  (Table 5) are consistent with the data for tetragonally distorted octahedral complexes. The electronic spectra in the pH range 6.00 to 9.50 show a slight intensification of absorption band with increase of pH. This increase in band intensity may be attributed to the lowering of symmetry (distortion of octahedral geometry) which, in turn, may be attributed to the deprotonated peptide linkage, resulting in shorter Cu-N bond.

It follows from the experimental results, described in the preceding sections that the ternary complex, formed at pH 6.25 comprises a deprotonated peptide as shown in I, with a local symmetry,  $C_{2v}$ —



I

where for Gly : R = —H,  $\alpha$ -Ala : R = —CH<sub>3</sub>,  $\alpha$ -Aba : R = —CH<sub>2</sub>CH<sub>3</sub>, n-Val : R = —CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, Val : R = —CH<sub>2</sub>(CH<sub>3</sub>)<sub>3</sub>, Ser : R = —CH<sub>2</sub>(OH), Thr : R = —CH(OH)CH<sub>3</sub>

The Tables 1 and 2 show that the half-wave potential of the complex of glycine is abnormally higher than those of the other amino acids ( $\alpha$ -Ala,  $\alpha$ -Aba, n-Val; Val, Ser, Thr). This abnormal behaviour may be attributed to the steric factors<sup>18</sup>. Bulky substituents on  $\alpha$ -carbon atom may distort the bond angle between the two bonds which participate in chelation, as the chelate ring is essentially planar<sup>18</sup>, the bulky substituents on  $\alpha$ -carbon atom may create a strain in the chelate ring and the chelate may be less

rigid. Since glycine has no bulky substituent on  $\alpha$ -carbon atom it can form strainless chelates. The lower value of  $E_{1/2}$  of Ser complex may be attributed to the presence of electron withdrawing —OH group adjacent to the  $\alpha$ -carbon atom. However, the value of  $E_{1/2}$  of  $\alpha$ -Aba complex has been found to be lowest in this series.

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