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Voltammetric Study of Cu(II) in Presence of Aspartic Acid and L-Phenyl Alanine at Different pH Media

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Abstract- The voltammetric study of Cu (II) in presence of aspartic acid (Aa) and L-phenyl alanine (Pa) respectively has been carried out in buffer solution of different pH, scan rate and variation of Aa or Pa concentration. Cu(II) in presence of Aa and Pa has been found to undergo two anodic peaks follows two step two electron transfer anodic reaction. The peak positions of the voltammogram of Cu(II) in presence of Aa or Pa shifted with respect to that of uncoordinated Cu(II). The peak current of Cu(II) with ligands (Aa, Pa) decrease significantly compared with that of uncoordinated Cu(II) in the same experimental conditions. These behaviors may ascribe the formation of complex of Cu(II) with Aa and Cu(II) with Pa. The linear behavior of peak current with the square root of scan rate of Cu complexes indicates that the electrochemical processes are diffusion controlled. The effects of pH of Cu-Aa and Cu-Pa complexes were studied by varying pH from 3.5 to 5.5. The oxidation peak current increases with the decrease in pH. At higher pH (pH>7) the complexes were almost electroinactive. This attributed that the electrochemical oxidation of the complexes are facilitated in lower pH media. The slope of the plots of E_p against pH of Cu-Aa and Cu-Pa complexes are 35-39 mV, indicates that the oxidation of Cu-Aa and Cu-Pa complexes proceeded via $2e^-/2H^+$ processes. The complexes were formed by the addition of Aa or Pa into Cu(II) and the maximum interaction has been found for 1:3 molar ratio at pH 3.5. The mode of interaction of Aa and Pa with Cu(II) has been found to be similar.

Keywords- Cyclic voltammetry, Differential pulse voltammetry, pH effect, Aspartic acid, L-Phenylalanine, Cu Complexes

1. INTRODUCTION

A noticeable rising interest in the design of electroactive metal ligand complexes such as medicinal compounds, drugs and their derivatives has been found to be essential for living organisms. Metal ligand complexes with amino acids, imidazole derivatives, indole derivatives, pyridine derivatives, Schiff bases etc. exemplified remarkable biological activity as well as electrochemical activity [1-6]. The ligands containing N/S/O- sites afford potential binding sites for metal ions. Their coordinating properties are important to understand the role of the metal ions in biological systems.

Essential transition metals such as Cu, Zn, Fe, Mn etc. are present in biological bodies that serve as metalloenzyme or as enzymatic activators. Copper(II) is one of the biologically important chemical species that functions as a co-factor in metalloenzymes and metalloproteins [7]. It is also regarded as an essential component of different organs such as blood, bones, teeth, nerves, etc. Its imbalance may result anemia, Wilson disease etc., and a number of other diseases in animals [8]. Its redox behavior may play a vital role to maintain its biological activities in association with different biomolecules especially with electron donor atoms at different pH.

Electrochemical redox reaction of Cu(II) in different supporting electrolytes media in the acidic pH range [9-13] and basic medium [14,15] has been investigated because of its application in electrolysis, microelectronics, electroplating, sensors, batteries and biochemical catalytic systems [16]. The mechanism and kinetic behavior of the reduction of aquo-Cu(II) have been investigated using a number of electrochemical techniques, such as dc polarography [17], ac polarography [18-20], hydrodynamic voltammetry[21-23], chronoamperometry at constant potential [24], and coulometry [25,26]. Cyclic voltammetric study of Cu(II) in presence of some ligands have also been investigated [27-29].

In order to understand the issue of interaction of Cu(II) with aspartic acid and phenylalanine at different pH, an experimental aspect of redox interaction in terms of electrochemical current potential curves analysis is necessary. To the best of our knowledge, both cyclic voltammetric and differential pulse voltammetric studies of Cu(II) with aspartic acid and phenylalanine at different pH, different scan rate and variation concentration of ligands has not been analyzed.

2. EXPERIMENTAL

Copper (II) chloride, Aspartic acid (Aa), L-Phenylalanine (Pa), Acetic acid, Sodium acetate, Potassium chloride were of analytical grade (E-Merck). Cu(II) in presence of Aa and Pa solutions of different concentrations were prepared in different pH by using acetate or phosphate buffer solutions. The buffer solutions were prepared by dissolving acetic acid and sodium acetate in deionized water.

Platinum disks of 1.6 mm in diameter (BASi) were used as a working electrode for voltammetry. The electrode surface was polished with 0.05 µm alumina before each run. The auxiliary electrode was a platinum coil. The reference electrode was an Ag|AgCl electrode. The working electrode was then polished on this surface by softly pressing the electrode against the polishing surface in the end for 5-10 minutes. The electrode was then thoroughly washed with deionized water. At this point the electrode surface would look like a shiny mirror. The potentiostat was µStat 400 (DropSens, Spain). Nitrogen gas was bubbled from the one-compartment cell before electrochemical run.

3. RESULTS AND DISCUSSION

3.1 Redox behavior of Cu-Aspartic acid (Aa) and Cu-L-Phenylalanine (Pa)

The redox behavior of Cu(II) in presence of aspartic acid (Aa) and L-phenyl alanine (Pa) in buffer solution of different pH was carried out by Cyclic voltammetry (CV) and Differential pulse voltammetry (DPV). Figure 1 shows the CV of uncoordinated Cu(II) (solid bold line), Cu(II) in presence of Aa (solid line) and Pa (dotted line) in buffer solution of pH 3.5 at scan rate 0.1 V/s. It shows that Cu (II) with Aa, the anodic peaks appeared at -0.08 V and 0.22 V and the corresponding cathodic peak at 0.09 V. On the other hand, uncoordinated Cu(II) shows anodic peaks at -0.15 V and 0.31 V and a cathodic peak at 0.18 V in the same experimental condition (Figure 1). Pure Aa and Pa are electrochemically inactive in the different pH and potential range investigated. From the Figure 1, it is seen that the peak positions of the voltammogram of Cu(II) in presence of Aa or Pa is shifted with respect to that of only Cu(II). With the addition of Aa into Cu(II) the anodic first oxidation peak shifts positively towards 0.04 V and second oxidation peak shift 0.1 V negatively and reduction peak shift negatively 0.09 V. The first and second oxidation peaks of uncoordinated Cu(II) are sharp but Cu(II) in presence of ligands (Aa, Pa) the peaks are found to be broad. The peak current decreases significantly compared with that for free Cu(II) in the same experimental conditions. These behavior may be ascribed the formation of Cu– Aa and Cu-Pa complexes. Similar voltammetric behavior of Cu(II) and Mn(II) with ascorbic acid and L-leucine were reported [30-31].

Figure 2 (a) shows the CV of Cu(II) in presence of Aa at different scan rates in buffer solution of pH 3.5. The peak current of both the anodic and cathodic peaks increases with the increase of scan rate. Figure 2 (b) shows plots of the two kinds of the anodic and one cathodic net peak currents of Cu(II)-Aa for first cycle against the square-root of the scan rates where the net current means the second peak subtracted from the first one by the scan-stopped method [18]. The nearly proportionality of the anodic and the cathodic first scan peaks suggests that the peak current of the reactant at each redox reaction is controlled by diffusion process. For second cycle, anodic and cathodic peak current is not fully linear behavior of i_p

vs. square root of scan rate suggest that second cycle peak current is affected by chemical complications or polymerization. For uncoordinated Cu(II), the anodic and cathodic peak current for redox reaction is also controlled by diffusion.

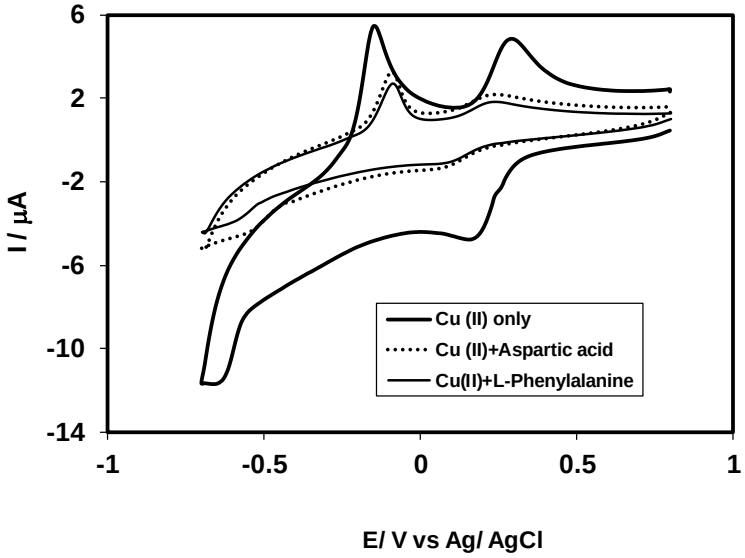


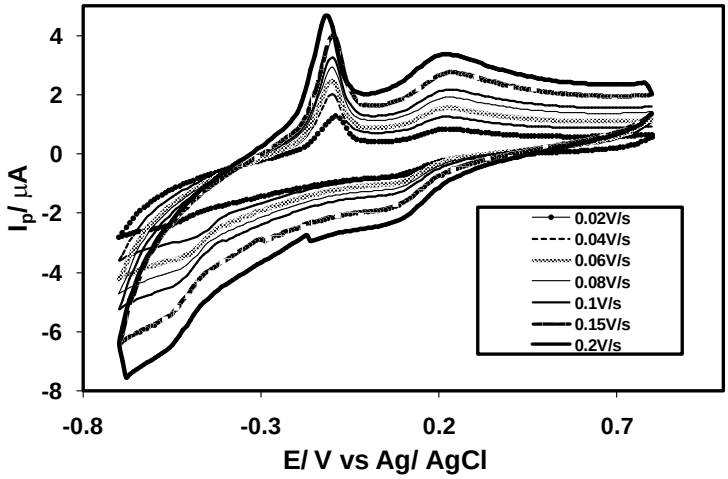
Fig. 1. Comparison of cyclic voltammogram of 2 mM Cu(II), 2 mM Cu(II)+6 mM aspartic acid (1:3), 2 mM Cu(II)+6 mM L-phenyl alanine (1:3) in buffer solution of pH 3.5 at scan rate 0.1 V/s

The second corresponding peak current ratios (I_{pa}/I_{pc}) of Cu(II)-Aa are close to one and independent of scan rate (Table 1). It indicates that voltammetric reactions of Cu(II)-Aa are reversible at any scan rate. From the Table 1, it is seen that the corresponding peak potential difference is >0.1 V which is higher than theoretical one electron transfer reaction. The measured value is sometimes higher due to uncompensated solution resistance between the reference and working electrodes and non-linear diffusion [19]. The corresponding peak potential separation increases with the increase in scan rate. It indicates that there is a limitation due to charge transfer kinetics or Ohmic potential (iR) drop [20].

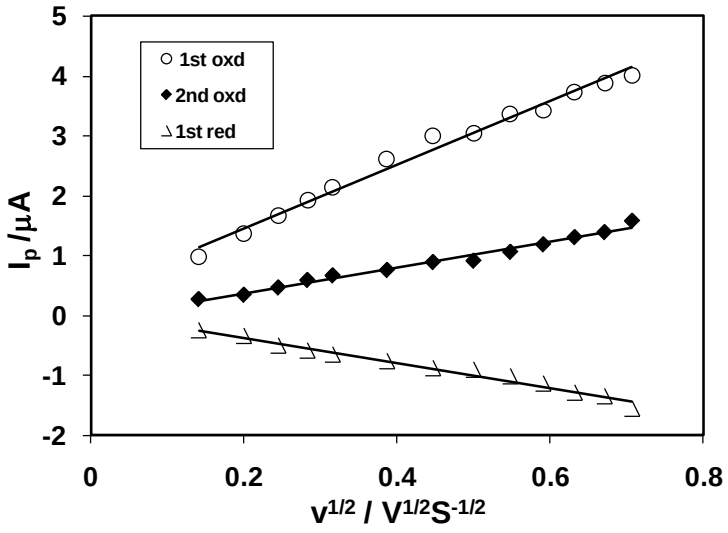
3.2. pH effect of Cu-Aspartic acid (Aa) and Cu-L-Phenylalanine (Pa)

Figure 3 shows the voltammogram of Cu-Aa in buffer solution of different pH (3.5, 4.5 and 5.5) at scan rate 0.1 V/s. The peak position of the redox couple is found to be dependent upon pH. The peak current is plotted against pH as shown in figure 3(a). From the figure it is seen that the oxidation peak current increased with the decrease in pH. The maximum peak current is obtained at pH 3.5. At higher pH (pH>7) the complexes are almost electroinactive.

This indicates that the electrochemical oxidation of Cu-Aa is facilitated in acid media and hence the rate of electron transfer is faster. The coordination sites of the ligands molecules are increased with decreasing pH that may be favored for the formation of more Cu-Aa complex. In the pH range studied, with the increase of pH, the anodic and cathodic peak potential shifted negatively.



(a)



(b)

Fig. 2. (a) Cyclic voltammogram of 2 mM Cu(II)+6 mM aspartic acid (1:3) in buffer solution of pH 3.5 at different scan rate. (b) Plots of peak current versus square root of scan rate of 2 mM Cu(II)+6 mM aspartic acid (1:3) in same condition

Table 1. Peak potential (E_{pa}), corresponding peak potential difference (ΔE), peak separation ($\Delta E_{1/2}$), peak current Ip (μA), corresponding peak current ratio (I_{pa}/I_{pc}) of Cu(II)+aspartic acid (1:3) in aqueous buffer solution (pH=3.5) at different scan rate

v/Vs^{-1}	E_{pa1} /V	E_{pc1} /V	E_{pa2} /V	ΔE = E_{pc1}~E_{pa2}	$\Delta E_{1/2}$/V	I_{pa1} /μA	I_{pc1} /μA	I_{pa2} /μA	I_{pa}/ I_{pc}
0.02	-0.09	0.06	0.23	0.17	0.32	0.978	-0.252	0.277	1.099
0.04	-0.10	0.08	0.23	0.15	0.33	1.370	-0.346	0.348	1.006
0.06	-0.10	0.07	0.22	0.15	0.32	1.660	-0.508	0.469	0.923
0.08	-0.10	0.07	0.23	0.16	0.33	1.918	-0.591	0.592	1.001
0.10	-0.10	0.07	0.23	0.16	0.33	2.138	-0.658	0.668	1.015
0.15	-0.10	0.05	0.24	0.19	0.34	2.607	-0.768	0.757	0.986
0.20	-0.10	0.06	0.24	0.18	0.34	2.995	-0.885	0.888	1.003
0.25	-0.09	0.01	0.24	0.23	0.33	3.051	-0.910	0.910	1.000
0.30	-0.09	0.03	0.25	0.22	0.34	3.367	-1.020	1.056	1.035
0.35	-0.06	0.02	0.26	0.24	0.32	3.420	-1.141	1.180	1.034
0.40	-0.07	0.03	0.26	0.23	0.33	3.740	-1.293	1.299	1.005
0.45	-0.07	0.07	0.26	0.19	0.33	3.878	-1.353	1.382	1.021
0.50	-0.07	0.10	0.26	0.16	0.33	4.012	-1.561	1.569	1.005

Figure 3(b) shows the plot of oxidation peak potential, E_p values against pH. The slopes of the plot was determined graphically as the anodic peak 39 mV/pH at 0.1 V/s, which is close to the theoretical value for a two-electron, two-proton transfer process (5). This indicates that the oxidation of the Cu-Aa proceeded via the $2e^-/2H^+$ processes. This also suggests that during the reaction not only electron but also protons are released from the Cu-Aa complex. For Cu(II) in presence of L-phenylalanine similar voltammetric behaviors were found.

3.3. Composition effect of Cu-Aspartic acid (Aa) and Cu-L-Phenylalanine (Pa)

Figure 4 (a) shows the variation of voltammogram pattern by the addition of Aa into fixed concentration of Cu(II) (1:1 to 1: 3) at pH 3.5. The first anodic peak shifted positively and second anodic peak shifted negatively upon addition of Aa which indicates the formation of Cu-Aa complex. The peak separation potential, ΔE decreases with the increase of Aa composition. This ascribed that the redox interaction of Cu(II)-Aa is lower than only Cu(II). With the increasing of Aa composition of 1:1 to 1:3, the first and second anodic peak current decreases (shown in Figure 4(b)). After further addition of Aa, the anodic and cathodic peak

current is almost unchanged. This is due to the availability of Cu(II) is limited for the binding of Aa in solution. By the addition of L-Phenylalanine into Cu(II) similar effects were found.

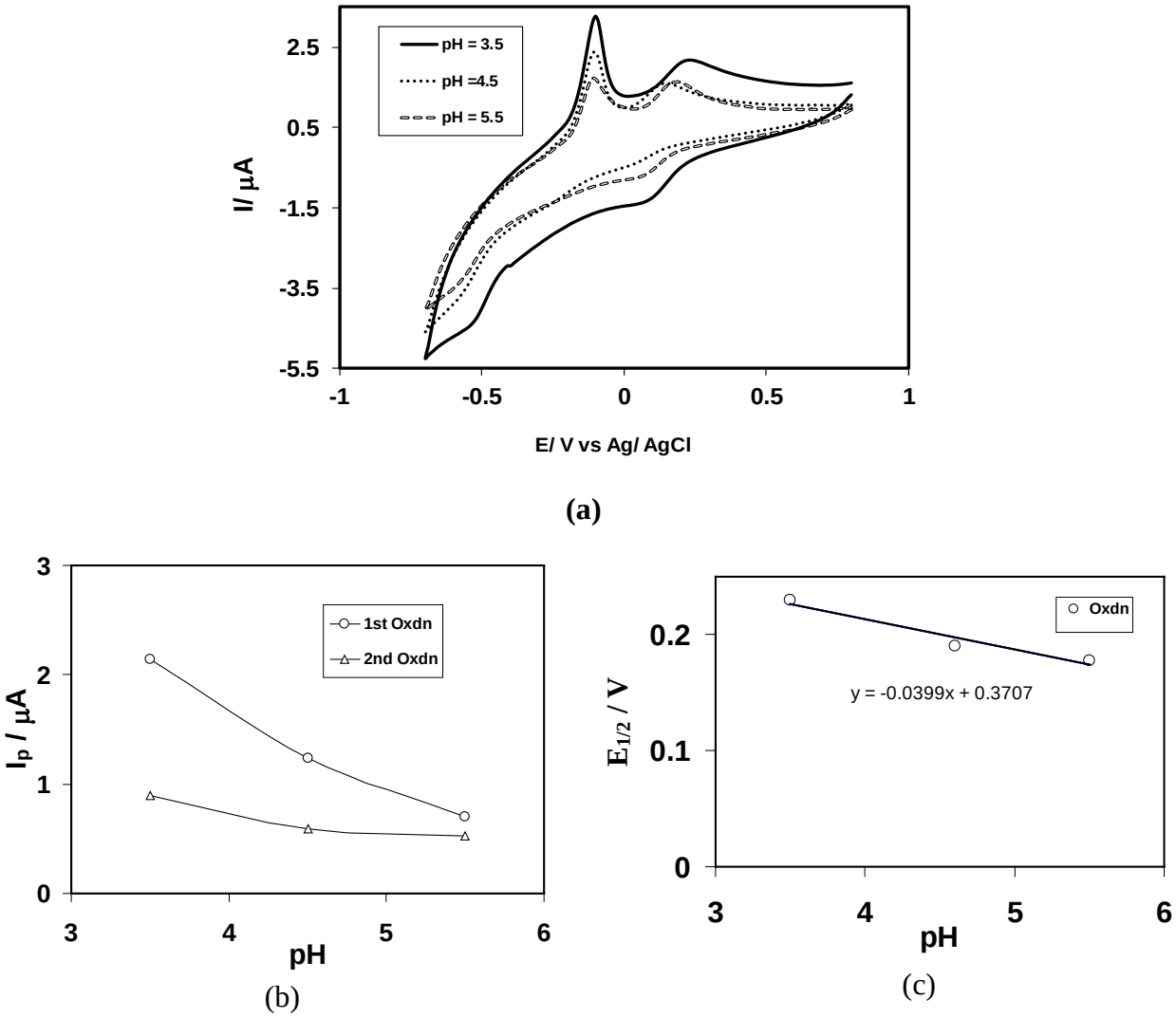
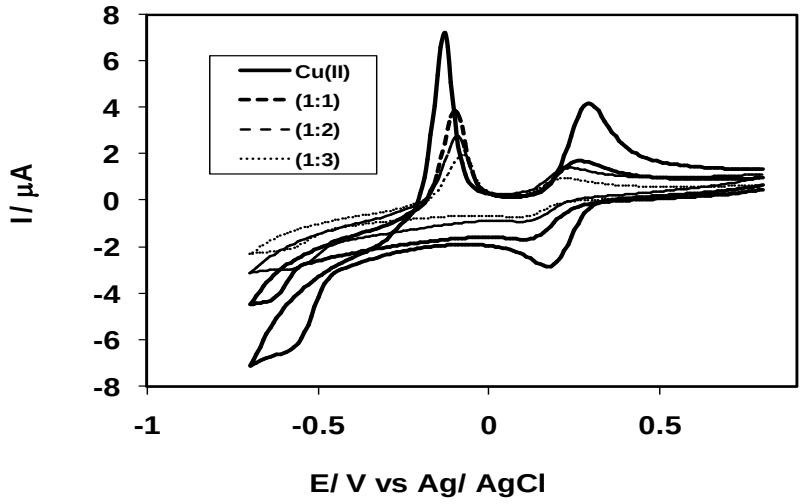


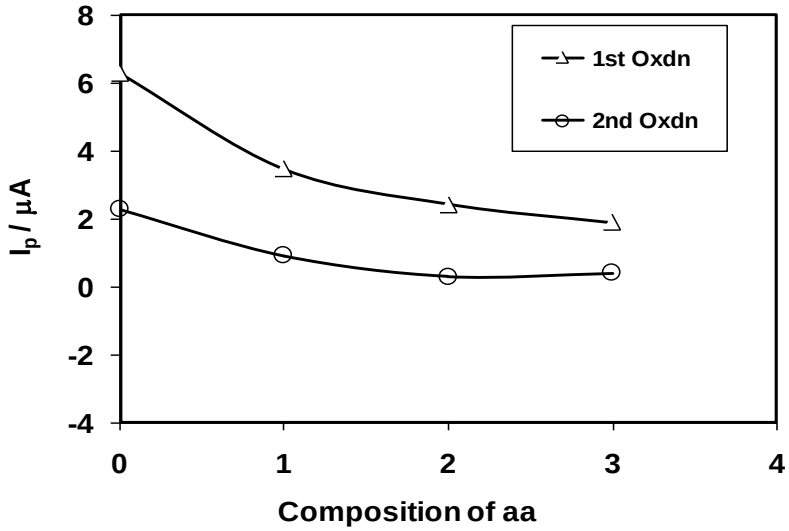
Fig. 3. (a) Comparison of Cyclic voltammogram 2 mM Cu(II)+6 mM aspartic acid (1:3) in different pH (3.5, 4.5, 5.5) at scan rate 0.1 Vs^{-1}. b) Plots of peak current, I_p *vs* pH of 2mM Cu(II)+6 mM aspartic acid (1:3) in same condition. c) Plots of peak potential, E_p *vs* pH of 2mM Cu(II)+6 mM aspartic acid (1:3) in same condition

Figure 5(a) shows the cyclic voltammograms of increase of concentrations of both the Cu(II) and Aa simultaneously at 0.1 Vs^{-1} scan rate. The intensity of the first and second anodic peaks and cathodic peak increases with increasing of Cu(II)+Aa concentration. Figure 5(b) shows the plots of peak currents against concentration of both Cu(II)+Aa species. The relation between Cu(II)+Aa concentration (2,3,4 and 5 mM) and cyclic voltammetric anodic peak current (Ip) is linear. By the increase in concentration, there is a gradual linear increase

in peak current, which may be due to the presence of a large amount of electroactive species at higher concentration. Similarly the cyclic voltammogram of different concentrations of the Cu(II)+Pa at 0.1 Vs^{-1} scan rate shows the intensity of the anodic and cathodic peak current increases with increasing of concentration.

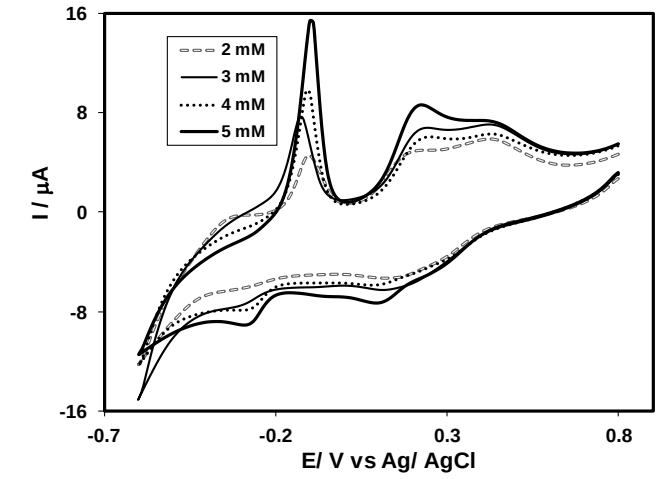


(a)

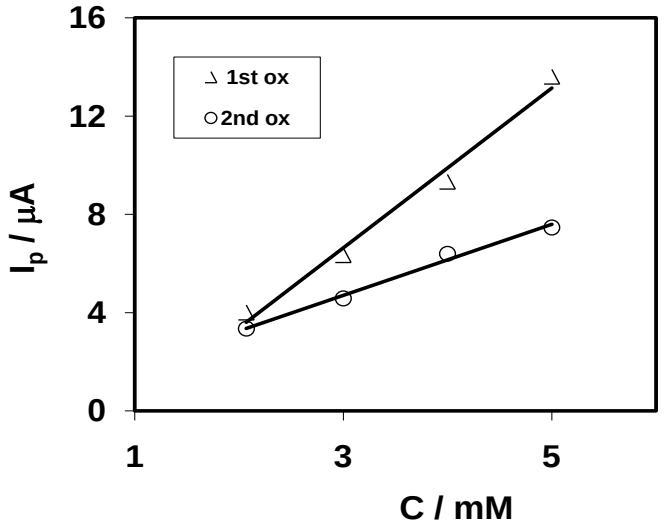


(b)

Fig. 4. a) CV of composition change of aspartic acid (2 mM-6 mM) with the fixed composition of 2 mM Cu (II) at (1:0), (1:1), (1:2) and (1:3) at pH 3.5 and scan rate 0.05 Vs^{-1}. b) Plots of anodic peak current versus composition of aspartic acid at same condition of CV



(a)



(b)

Fig. 5. (a) Cyclic voltammogram of different concentration of Cu(II)+aspartic acid (2-5 mM) in buffer solution of pH 3.5 at scan rate 0.1 V/s. (b) Plots of peak current versus concentration of Cu(II)-aspartic acid (2-5 mM) in same condition

3.4. DPV of Cu-Aspartic acid (Aa) and Cu-L-Phenylalanine (Pa)

Figure 6 shows the Differential pulse voltammogram (DPV) of Cu(II) in presence of Aspartic acid (Aa) and L-Phenylalanine (Pa) in aqueous buffer solution (pH=3.5) at E_{puls} 0.02 V, t_{puls}=20 ms and scan rate 0.1 V/s. It is observed that the first anodic peak positions of the DPV of Cu(II) with aspartic acid was shifted positively from -0.18 V to -0.10 V and the second anodic peak from 0.32 V to 0.17 V with respect to that of only Cu(II). The peak current decreases significantly compared with that for free Cu(II) in the same experimental conditions. This indicate that the formation of complexation of free Cu(II) with aspartic acid.

The anodic peak potential difference (ΔEp) of Cu-Aa in buffer solution of pH 3.5 at 0.1 V/s is almost 0.27 V which is lower than only Cu(II) in aqueous solution (0.48 V). Similarly, In Cu-Pa system, the first anodic peak was shifted from -0.18 to -0.14 V and second anodic peak from 0.30 V to 0.23 V with respect to only Cu(II). The redox interaction of Cu-Aa and Cu-Pa is lower than only Cu(II) in aqueous solution. The first anodic peak current of DPV of Cu(II), Cu-Aa and Cu-Pa are 21.8 µA, 3.55 µA and 3.45 µA respectively. The peak currents of Cu-Aa and Cu-Pa systems are significantly lower than uncoordinated Cu(II) in the same experimental conditions. These behaviors also attributed the formation of complex of Cu(II) with ligands (Aa, Pa). The DPV data is fully consistent with CV data.

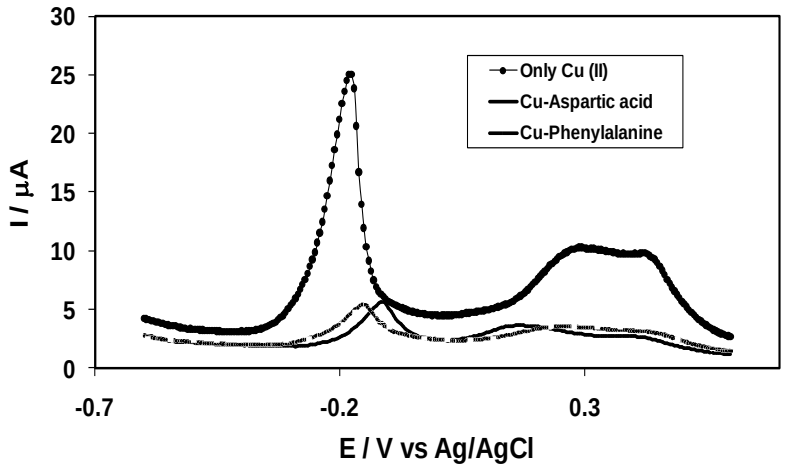
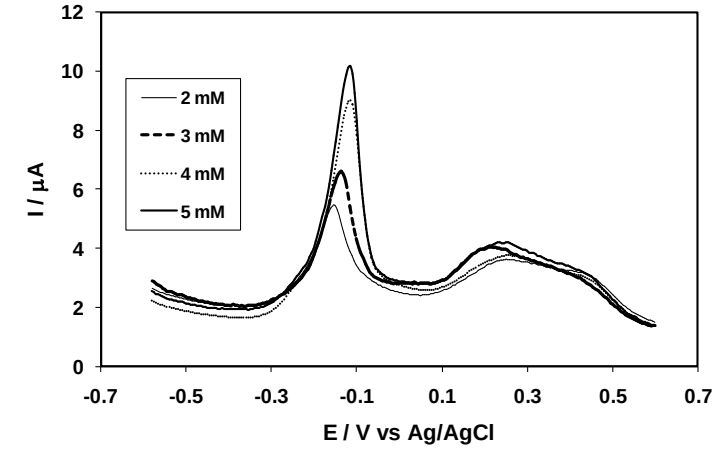


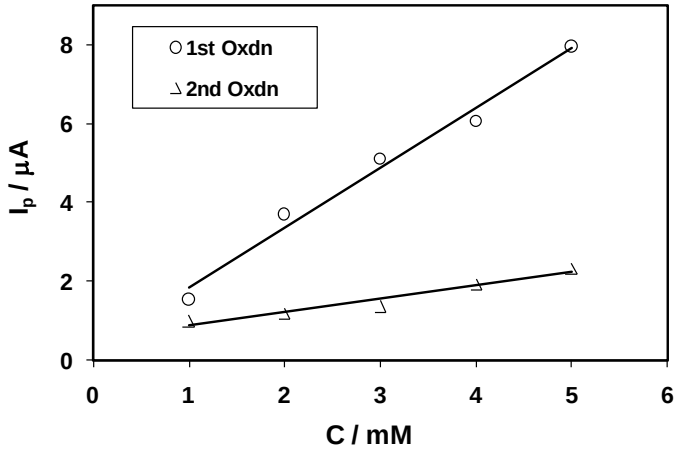
Fig. 6. Differential pulse voltammogram (DPV) of 2 mM Cu(II), 2 mM Cu(II)+6 mM aspartic acid (1:3) and 2 mM Cu(II)+6 mM L-phenylalanine (1:3) in buffer solution of pH 3.5 at *E*puls 0.02 V, tpuls 20 ms and scan rate 0.1 V/s

3.5. Concentration effect of DPV of Cu-Aa

Figure 7 (a) shows the DPV of different concentrations of the Cu(II)-Aa in buffer solution of pH 3.5 at 0.1 Vs^{-1} scan rate. The intensity of the anodic peak current increases with increasing of Cu(II)-Aa concentration. The effect of concentration can be shown by recording the DPV at each concentration (2, 3, 4 and 5 mM) and plotting i_p *vs*. concentration for either the anodic peak or the cathodic peak (Figure 6(b)). The relation between Cu(II) concentration and anodic peak current (Ip) is linear. The DPV pattern of Cu and Cu-ligands are fully consistent with CV pattern.



(a)



(b)

Fig. 7. (a) Differential pulse voltammogram (DPV) of different concentration of Cu(II)-aspartic acid (2-5 mM) in buffer solution of pH 3.5 at *E*puls 0.01 V, tpuls 10 ms and scan rate 0.1 V/s. (b) Plots of peak current versus concentration of Cu(II)-aspartic acid (2-5 mM) in same condition

4. CONCLUSION

Voltammetric studies were used to investigate the interaction behavior of biologically important Cu(II) with Aa or Pa . The interaction studies have been carried out in variation of Cu(II) concentration, Aa or Pa concentration, pH and scan rate. By the addition of Aa or Pa into Cu (II) both the cathodic and anodic peak potentials were shifted. The peak current decreases significantly compared with that of free Cu(II) in the same experimental condition. The shifted of peak potentials or decrease of current suggested the formation of Cu- Aa or Cu -Pa complex. The complex was formed either by the addition of Aa or Pa into Cu(II) or by the addition of Cu(II) into Aa or Pa. The intensities of the peak current were increased with

increasing both the concentrations of metal ions as well as ligands. The peak current of Cu-Aa or Cu -Pa complexes increases with the decrease of pH. The maximum peak current was obtained at pH 3.5. The electrochemical oxidation of Cu- Aa or Cu -Pa complexes is facilitated in acid media. The oxidation of the Cu- Aa or Cu -Pa complex proceeded via the $2e^-/2H^+$ processes. A linear behavior of i_p *vs*. square root of scan rate plot indicated that the electrochemical processes of Cu- Aa or Cu -Pa complex are diffusion controlled.

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