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Study of Electric effect and Electrochemical behavior of Cu(II) metal and Cu(II)-Lysine Complexes at Different pH in absence of Strong Electrolyte (KCl)

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***Abstract**: This research was carried out to studied the electrochemical behavior of metals Cu(II) with Lysine (Lys) by Cyclic voltammetry (CV), Chronamperometry (CA), UV-Vis and FTIR spectroscopic techniques. Electrochemical and spectroscopic techniques reveal the interaction of Cu(II), with the ligands (Lys) that may be formed of metal-ligand complexes. Electrochemical studies have been carried out in variation of metal ion concentration, ligand concentration, buffer solution of different pH and different scan rate. In this study all the experiment is carried out only in aqueous buffer solution; KCl or other conventional supporting electrolytes are not used in the solution. The effect of pH of Cu(II)-Lys was studied by varying pH from 3.0 to 9.0. The maximum peak current was obtained at pH 4. This shows that the electrochemical oxidation of Cu(II)-is facilitated in acid media and consequently the rate of electron transfer is quicker. The slopes of the plots of E_p against pH of Cu-Lys metal ligand system was determined graphically as anodic peak 21-31 mV/pH at 0.1V/s, which is close to the theoretical value of 30 mV which indicates that the oxidation of all the studied metal-ligand systems proceeded via the $2e^-/2H^+$ processes. During the bulk electrolysis the electrosynthesized metal-ligand products were generated. UV-Vis and FTIR techniques were also used to confirm the interaction of Cu(II) with Lys.*

***Keywords:** Cyclic voltammetry, pH effect, Cu(II)-Lysine complex, Chronamperometry (CA), UV-Vis and FTIR.*

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I. Introduction

Metal-Ligand complexes have a metal center that is bound to ligands. The metal atoms serve as an electron pair acceptor, while the ligands perform as electron pair donors. The redox behavior of metal and ligand express a crucial mechanism in the metabolism of all living cells contributing in a great variety of anabolic and catabolic processes. Transition metal complexes are seen at the active sites of a great variety of redox-active proteins owing to their capacity of accessible in more than one stable oxidation state illustration them to function in detoxification, transport, catalysis and storage in biological processes [1]. Due to the physiological importance of metal-ligand complexes, there has been much attempt taken to know their redox behavior.

Many transition metal-ligand complexes have been synthesized and characterized, and they have become an important part of bioinorganic chemistry. One property of complexes with multiple ligands is that they may be mixed valence. The rate of electron transfer of the complexes depends upon the degree of charge localization, that is, the coupling between the mixed-valence centers. Coupling depends on several factors, including distance between mixed-valence centers and the environment surrounding each center. Robin and Day developed three broad categories describing the degree of interaction between mixed-valence centers. Class I compounds are described as having localized valences, where there is little or no communication between the mixed-valence centers. Class II compounds have some degree of communication between mixed-valence centers, with an activation energy barrier to electron transfer between the centers. Class III compounds are described as having completely delocalized charge, with no barrier to coupling between mixed-valence centers [1].

Electrochemical properties of polymetallic clusters, such as oligomers of ferrocene, often include cyclic voltammograms with multiple one-electron couples, the separation of which depends upon the degree of coupling between metal centers [2, 3]. Class I compounds, with completely localized valency, have one-electron couple at the same, or nearly the same, potential. As electron transfer between mixed-valence sites increases towards Class II and Class III regimes, the separation between couples also increases. Transition metal-ligand complexes may exhibit similar behavior, with the couples corresponding to either redox activity on the non-innocent ligands or the metal center. These complexes are unique in that it is the metal center of the complex that acts as the bridge between redox-active ligands, rather than ligands acting as a bridge between metal centers. Some of these complexes exhibit properties desirable in electrocatalysts, with multiple reversible redox couples within a narrow range of potential. These may supply or accept multiple electrons to catalyze redox reactions. One advantage of ligand-based redox chemistry is that it does not rely on oxidative additon/reductive elimination to transfer electrons, so the chemistry it facilitates does not have to be on substances that ligate with the metal. Furthermore, the narrow potential range of the redox couples mitigates the problem of chemically-active intermediates by allowing multiple electrons to be transferred nearly simultaneously [2,3].

It is known that O, N and S atoms take part a key role in the coordination of metals at the active place of many metallobiomolecules [4]. O, N, S sites having metal complexes was widely examined because they have antibacterial, anticancer, industrial, antifungal, herbicidal and antiviral applications [5-10]. They act as models for biologically important species and have applications in biomimetic catalytic reactions. Chelating ligands containing N, S and O donor atoms provide wide biological activity and are of particular attention as of the diversity of behavior in which they are bonded to metal ions. It is recognized that the existence of metal ions bonded to biologically active compounds may improve their activities [8-10]. The complexes of Fe(III), Co(II), Mn (II) , Cu(II) and Ni(II) ions with amines have been synthesized and analysis using diverse physico-chemical process, such as conductance measurements, elemental analysis, and UV-Vis, FTIR and NMR spectra. [11]. In order to understand the issue of interaction of Cu(II) with Lys 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, Cyclic voltammetry (CV), Chronamperometry (CA), UV-Vis and FTIR spectroscopic techniques and differential pulse voltammetric studies of Cu(II) with Lys at different pH, different scan rate and variation concentration of ligands has not been analyzed.

II. Experimental Method

The electrochemical behavior of Cu (II)-Lys at various pH has been investigated using controlled potential coulometry(CPC), Amerometry and cyclic voltammetry at glassy carbon (GC) or platinum electrode (Pt) or gold electrode. Details of the instrumentation are given in the following sections. The thoroughly cleaned glass pieces were dried in electric oven. The smaller pieces of apparatus were dried in an electric oven and stored in a desiccator, while larger pieces of apparatus were used directly from the oven.

III. Results And Discussion

Electrochemical behavior of Cu(II)-L-Lysine System

The electrochemical behavior of Cu (II) with L-Lysine (Lys) system in aqueous buffer solution was carried out by cyclic voltammetry (CV). Cyclic voltammogram of Cu (II) ion in presence of Lys at 0.1V/s at pH 4 is shown in Figure 1 (red line). Electrochemical experiments are performed in only aqueous buffer solution, KCl or other conventional electrolytes are not used as a supporting electrolyte. Buffer solution contains electrolyte that act as a supporting electrolyte. It is seen from the Figure, the anodic peak arises at 0.05V and the corresponding cathodic peak at -0.41V. In contrast, Cu (II) appears (green line) one anodic peak at 0.13V and two cathodic peaks at -0.28V and -0.11V in the identical experimental state. Pure Lys (blue line) displays electro-inactivity in the similar investigational condition (Figure 1). It is observed from the Figure, the peak point of the voltammogram of Cu-Lys is altered negatively as regards of only Cu (II). On the adding of Lys into Cu (II) the anodic oxidation peak moves left to 0.08V and reduction peak also shifts negatively 0.13V (Figure 1). The peak current also reduces considerably as regards with of free Cu (II) in the similar investigational conditions. This activity attributed the formation of Cu-Lys complex. Similar voltammetric properties of Cu (II) and Mn (II) with ascorbic acid were stated [12-14].

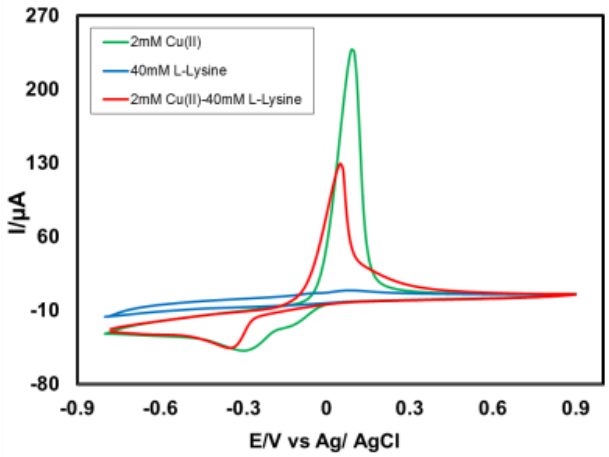

Figure 1: Cyclic voltammogram of 2 mM Cu(II) (green line), 40 mM L-Lysine (blue line) and 2 mM Cu(II) with 40 mM L-Lysine (red line) of GC electrode in buffer solution of pH 4 (without KCl solution) at scan rate 0.1 V/s (2^{nd} cycle).

The CV of Cu-Lys in buffer solution (pH 4) at different scan rates is shown in Figure 2. The peak current of the anodic and cathodic peak rises with the increasing of scan rate (Table 1). The cathodic peaks are moved in the direction of left and the anodic peak is altered slightly to the right direction with increasing in scan rate. Figure 3 shows plot of the anodic and cathodic net peak currents of Cu-Lys (second cycle) versus the square-root of the scan rates where the net current is measured by the scan-stopped method [15]. The almost proportionality of the redox peak current indicate that the peak current of the species is controlled by diffusion process. The CV of uncoordinated 2mM Cu (II) in aqueous solution at different scan rates is shown in Figure 4. Figure 5 demonstrates plots of the anodic and the cathodic net peak currents versus the square-root of the scan rates (Table 2). The proportionality of the anodic and the cathodic peaks also attributed that the peak current of the species at each redox reaction is governed by diffusion process.

Peak current ratios (I_{pa}/I_{pc}) of the corresponding peak of Cu-Lys are higher than one (Table 1). It suggests that redox reactions of Cu-Lys are not reversible. Peak potential difference (ΔE) of the corresponding peak is > 0.1 V. This is much higher than one electron transfer reaction. Sometimes higher values of ΔE are showed owing to uncompensated solution viscosity and the diffusion of the species is not linear [16]. The value of ΔE increases with the increasing of scan rate. This attributed that there is a restriction owing to charge transfer kinetics [17]. When current passage through the cell containing electrolytes need additional driving force to overcome the viscosity (solution resistance) of the ions to shift towards the electrode. The corresponding peak potential difference (ΔE) of Cu(II)- Lys is lower than Cu(II) in the similar investigational condition (Table 1-2).

pH effect of Cu-Lysine system

CV of Cu(II)-Lys in aqueous buffer solution (without additional supporting electrolyte) of various pH (3.0, 4.0, 5.0, 6.0 and 7.0) at 0.1V/s scan rate is shown in Figure 6. The peak point of the redox species is strongly influenced by pH and it is shifted negatively with the increase of pH. The peak current versus pH is plotted as shown in Figure 7. It is observed from the Figure, the oxidation peak current rises with the increasing of pH upto pH 4 then the peak current decreased (Table 3). At pH 7 the CV is shown electro-inactive. The highest peak current is found at pH 4 (Table 3). At elevated pH (pH >7) the Cu(II)-Lys complexes are nearly electroinactive. This ascribed that the redox reaction of Cu(II)-Lys systems is favored in acid media (pH<7). Therefore the rate of electron transfer is faster in acid media and the optimum condition is found to be pH 4. The coordination sites of the ligands are most active at pH 4 that may be facilitated for the formation of Cu(II)-Lys complex. With the increase of pH (pH>7), the coordination sites of the ligands may be deactivated, therefore the anodic and cathodic peak disappeared.

The plot of oxidation peak potential, E_p values versus pH is shown in Figure 8. The slope of the plot has been measured graphically as the anodic peak ~31mV/pH at scan rate 0.1V/s. This value is very close to the value for a two-electron transfer process [13]. This ascribed that the redox reaction of the Cu(II)-Lys carried on by means of the $2e^-$ processes. One step two electron transfer reaction may be occurred in the solution of without conventional supporting electrolyte as: Cu(II)-Lys +2e ↔ Cu(0) + Lys

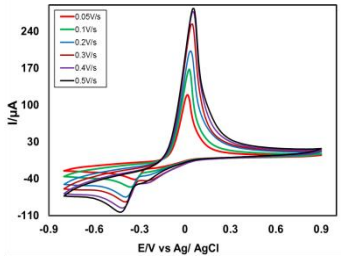

Figure 2: CV of 2 mM Cu(II) with 40 mM Lys (1:20) of GC electrode in buffer solution of pH 4 at scan rate 0.05 V/s to 0.5 V/s (2nd cycle).

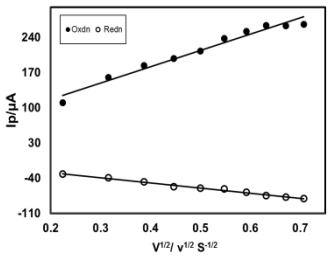

Figure 3: Plots of peak current (I_p) versus square root of scan rate ($v^{1/2}$) of 2 mM Cu(II) with 40 mM Lys of GC electrode in buffer solution (pH 4).

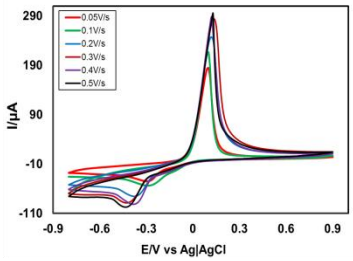

Figure 4: CV of 2 mM Cu(II) of GC electrode in buffer solution of pH 4 (without KCl solution) at scan rate 0.05 V/s to 0.5 V/s (2nd cycle).

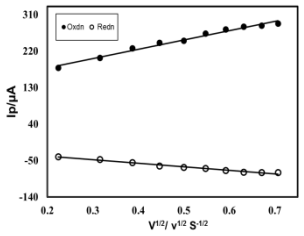

Figure 5: Plots of peak current (I_p) versus square root of scan rate ($v^{1/2}$) of 2 mM Cu(II) of GC electrode in buffer solution (pH 4) (2nd cycle)

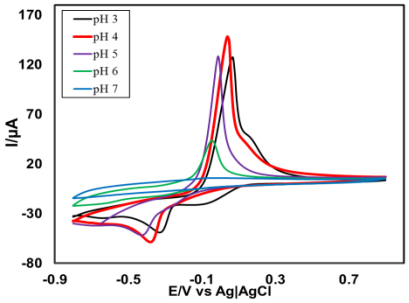

Figure 6: Cyclic voltammogram 2 mM Cu(II) with 40 mM L-Lysine of GC electrode in different pH (3, 4, 5, 6 and 7) (without KCl solution) at scan rate 0.1 V/s (2nd cycle).

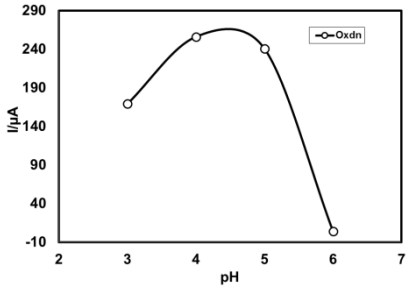

Figure 7: Plots of peak current vs pH (3, 4, 5 and 6) of 2 mM Cu(II) with 40 mM L-Lysine of GC electrode at scan rate 0.1 V/s (2nd cycle).

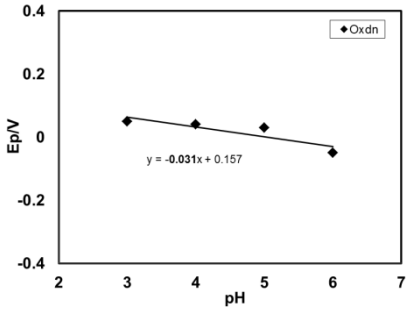

Figure 8: Plots of peak potential vs pH (3, 4, 5, 6 and 7) of 2 mM Cu(II) with 40 mM L-Lysine of GC electrode at scan rate 0.1 V/s (2nd cycle).

Table 1: Peak potential (E_p), corresponding peak potential difference (ΔE), peak current Ip (µA) and corresponding peak current ratio (I_{pa}/I_{pc}) of 2mM Cu (II) with 40mM L-Lysine (1:20) of GC electrode in buffer solution of pH 4 without conventional supporting electrolyte (SE) at scan rate 0.05 V/s to 0.5 V/s (2nd cycle).

ν/Vs^{-1}	E_{pa1} /V	E_{pc1} /V	$\Delta E = E_{pc1} \sim E_{pa1}$	I_{pa1} /µA	I_{pc1} /µA	I_{pa1}/I_{pc1}
0.05	-0.01	-0.31	0.30	109.74	-32.13	3.41
0.10	0.01	-0.35	0.36	159.91	-39.32	4.06
0.15	0.01	-0.35	0.36	183.67	-47.55	3.86
0.20	0.01	-0.38	0.39	198.25	-56.74	3.49
0.25	0.02	-0.38	0.40	212.79	-59.67	3.56
0.30	0.03	-0.38	0.41	237.98	-61.42	3.87
0.35	0.03	-0.38	0.41	251.93	-67.84	3.71
0.40	0.04	-0.40	0.44	263.37	-74.48	3.53
0.45	0.04	-0.40	0.44	263.17	-77.59	3.39
0.50	0.04	-0.41	0.45	265.62	-80.64	3.29

Table 2: Peak potential (E_p), corresponding peak potential difference (ΔE), peak current Ip (µA) and corresponding peak current ratio (I_{pa}/I_{pc}) of only 2mM Cu (II) of GC electrode in buffer solution of pH 4 without conventional SE at scan rate 0.05 V/s to 0.5 V/s (2nd cycle).

ν/Vs^{-1}	E_{pa1} /V	E_{pc1} /V	$\Delta E = E_{pc1} \sim E_{pa1}$	I_{pa1} /µA	I_{pc1} /µA	I_{pa1}/I_{pc1}
0.05	0.08	-0.28	0.36	178.15	-40.66	4.38
0.10	0.09	-0.28	0.37	202.76	-47.52	4.26
0.15	0.09	-0.35	0.44	226.91	-55.08	4.11
0.20	0.10	-0.35	0.45	239.72	-63.76	3.76
0.25	0.10	-0.41	0.51	245.14	-67.51	3.63
0.30	0.11	-0.41	0.52	262.83	-69.91	3.76
0.35	0.11	-0.38	0.49	272.87	-74.56	3.66
0.40	0.12	-0.38	0.50	280.19	-79.44	3.52
0.45	0.12	-0.42	0.54	282.30	-79.81	3.53
0.50	0.12	-0.42	0.54	287.240	-80.110	3.586

Table 3: Peak Current I_p (µA) and peak potential E_p (V) of 2 mM Cu (II) with 40 mM L-Lysine of GC electrode without conventional SE at scan rate 0.1 V/s in different pH media (2nd cycle)

pH	Peak Current, I_{pa} (µA)	Peak potential, E_{pa}(V)
3	169.30	0.05
4	256.30	0.04
5	240.88	0.03
6	4.150	-0.05

UV-Vis spectra Analysis of Cu (II) and Lysine

The electronic spectrum of the Cu (II)-Lys complex and only Lys are shown in Figure 9. In this Figure, it is seen that Cu (II)-Lys adduct shows a broad absorption spectrum at 265nm (red line). Uncoordinated Lys shows peak at 252nm. The wavelength shift of Cu(II)-Lys complexes from that of pure Cu (II) and pure Lys ascribed the formation of complexes [18].

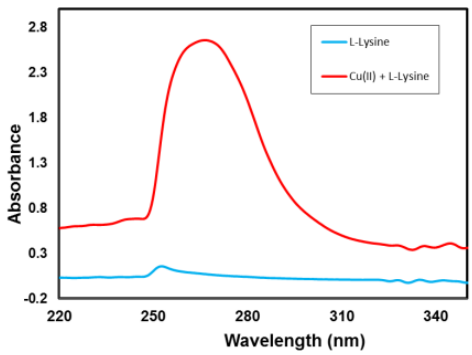

Figure 9: UV-Vis spectra of 0.2 mM L-Lysine (blue line) and 0.2 mM Cu(II)-Lysine (red line) in buffer solution of pH 4 (without KCl solution).

FTIR Spectral analysis of Cu (II)-Lysine complex

The FTIR spectrum of the vibrational modes of the Cu(II)-Lys complex and pure Lys were shown in Figure 10. The spectrum of Cu(II)-Lys is different from that of pure Lys specially in finger print region. The bending vibration of Cu (II)-Lys decreases enormously with respect to pure Lys suggesting that the formation of complexes of Cu(II) with Lys [19].

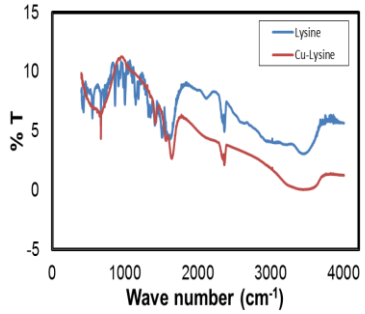

Figure 10: FTIR spectra of L-Lysine (blue line) and Cu(II)-Lysine (red line). Product Cu(II)-Lysine extracted from bulk electrolysis of Cu(II) with L-Lysine in buffer solution of pH 4.

IV. Conclusion

Cyclic voltammetry (CV), UV-Vis and FT-IR techniques were used to investigate the interaction behavior of biologically important metal ions such as Cu(II), with L-Lysine, in aqueous solution with various pH, and scan rates. Electrochemical and spectroscopic techniques reveal the interaction of metal (Cu,) with the ligands (Lys) that may be formed of metal-ligand complexes. L-Lysine, is electro-inactive ligand. The voltammogram of Cu(II)-ligand system is irreversible. From the voltammogram studies, it is seen that Cu (II) interacts with L-Lysine. The peak current of metal-ligand complexes increases with the decrease of pH indicating that at lower pH the metal-ligand complexes are highly electro-active. The electrochemical oxidation of the studied metal ligand complexes are facilitated in acid media. The slope of peak potential, E_p against pH of studied metal-ligands varies linearly and the slopes of the plot are close to 30 mV which indicates that the oxidation of the metal-ligand complexes proceeded via the $2e^-/2H^+$ processes. The peak current of the complexes at each redox reaction is controlled by diffusion process. The optimum condition of elelectrochemical reaction such as pH, composition of metal:ligands, scan rate are determined. The spectra of the studied pure metals and ligands were different from metal-ligand complexes indicating the complexation of metals with ligands. The behavior of electrode reaction of all the studied systems is electron transfer, chemical reaction and electron transfer (ECE) type.

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