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Study of redox behavior of Cu(II) and interaction of Cu(II) with lysine in the aqueous medium using cyclic voltammetry

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ABSTRACT

Potassium chloride (0.1 M) and acetate buffer of different pH are used to study the redox behavior of Cu(II) ions in absence and presence of lysine amino acid. The potential window +1500 mV and -1000 mV was used to study the redox properties at solid glassy carbon electrode. Silver/silver chloride is used as a reference electrode and the counter electrode used is Pt. One pair of cathodic and anodic peaks for the Cu(II)/Cu(0) system is showed in cyclic voltammograms indicating the presence of two-electron transfer. The interaction between metal and ligand is supported by the shift of peak potential and charge transfer rate constant (k_s) values. Concentration effect of Cu(II) ions and solution pH effect on the interaction was also studied. The quasi-reversible process is indicated by a higher value of peak current ratio and peak potential separation (ΔE).

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1. Introduction

Copper is an important metal which plays a vital role in many biological processes inside human and animal bodies. Complexes of Cu(II)-amino acids have received greater attention in recent years as they proved to be powerful agents against bacterial activity such as *Escherichia coli, Staphylococcus aureus*, and used for humans and animals as nutritious provides, etc. [1,2]. Structural units of proteins are natural occurring twenty amino acids, which are chemical species essential to perform a large number of vital functions [3]. Transition metals-amino acids complexes in peptides and proteins are consumed in several biological processes such as oxygen conveyer, electron oxidation, and transfer. The active sites of enzymes which are very specific, forms divalent metal ions complexes in these processes [4]. Due to an inability of a human to synthesize amino acid lysine inside the body, lysine is considered to be one of the very important essential amino acids. This reason makes lysine be used as a food dietary supplement and as a drug. Lysine can be destroyed at high temperatures and in bad storage conditions. Many techniques are used for determination of lysine such as chromatography, spectrophotometry, and fluorimetry but each technique has its defect such as long time, high cost and inaccurate results. We choose cyclic voltammetry technique for this present study due to its efficiency in examining the redox behavior of electroactive ions. It is well known that potentiometric and spectroscopic techniques take large and special attention, due to the ability to determine accurate values for the stability constants from potentiometric techniques and due to the ability of different spectroscopic methods analysis to give large variety of structural information [5,6] among the plans that can be applied for the study of complexation. However, these techniques have a limitation that makes their application not possible once a large concentration of the ligand is present (e.g. to prevent complex precipitation), this defect make these techniques are less sensitive at high concentrations. Voltammetry techniques can be an alternative suitable solution in such situation. The redox behavior of metal ion Cu(II) and its interaction with lysine is investigated in the aqueous medium in the current study.

2. Experimental

2.1. Chemicals

The chemicals used in the present study were copper sulfate (Oxford Co., India), lysine amino acid (Cambrian Co.), potassium chloride (MERCK, Germany), sodium acetate

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(Oxford Co., India), acetic acid (Sigma-Aldrich) and 99.997% nitrogen (Talkha Co.).

2.2. Instrumentation

This study was carried out using DY2000, DY2000EN multichannel potentiostat for voltammetry measurements, magnetic stirrer, and its magnetic bar that coated by Teflon tape, a pH meter (±0.03) and an electrochemical cell that is consisting of three electrodes inserted in Pyrex glass with Teflon cap. The three electrodes used were a Pt wire that used as a counter electrode, silver/silver chloride that used as a reference electrode and solid glassy carbon disk that used as working electrode. The glassy carbon electrode (GCE) surface was polished to a mirror state using 1.00-0.03 µm alumina powder. The GCE was washed ultrasonically with absolute alcohol and double-distilled water, respectively, after rinsing thoroughly with water again to remove any adhering alumina particles. Deoxygenation of solutions was performed using high purity nitrogen before each electrochemical experiment. Three measurements were repeated and the average value of each parameter is quoted for discussion. The data were analyzed using origin software.

3. Results and discussion

Cu (II) redox behaviors, in the presence and absence of lysine have been determined in different supporting electrolytes using cyclic voltammetry.

3.1. Cu(II) electrochemical behavior in 0.1 M potassium chloride

Cyclic voltammetry behavior of Cu (II) (6×10^{-3} M) scan between 1500 to -1000 mv is introduced in Figure 1. The addition of copper ions to the basic electrolyte shows a noticeable change of the redox behavior. Cathodic scan shows two reduction peaks that are observed at 0.411 V and 0.0063 V, respectively, which reflect the reduction of copper ions according to reaction:

$$Cu^{2+} + e^- \rightarrow Cu^+ \quad (1)$$

$$Cu^+ + e^- \rightarrow Cu \quad (2)$$

Two prominent anodic peaks were observed when the scan was reversed at around 0.085 V and 0.247 V corresponding to oxidation of copper according to reaction:

$$Cu \rightarrow Cu^+ + e^- \quad (3)$$

$$Cu^+ \rightarrow Cu^{2+} + e^- \quad (4)$$

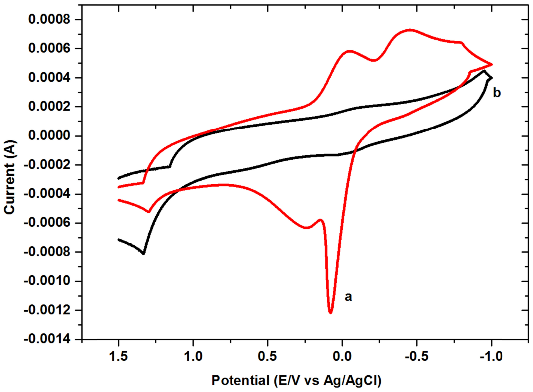

Figure 1. Cyclic voltammograms of (a) 6×10^{-3} M $CuSO_4$ in 0.1 M KCl electrolyte and (b) 0.1 M KCl at 0.1 V/sec.

3.2. Effect of concentration change

Changing copper ions concentrations has a great effect on redox behavior. $CuSO_4$ CVs of various concentrations (6×10^{-3}, 4×10^{-3}, 3×10^{-3} and 1×10^{-3} M) in 0.1 M potassium chloride at 100 mV/s are shown in Figure 2 and 3 that show the variation of anodic peak current against concentration for $CuSO_4$. There is a successive linear increase in the central wave with increasing the amount of copper ions that may be due to the presence of a large amount of electroactive species by increasing concentration [7,8]. This increasing of peak current with concentration increase also gives the indication that the system may be diffusion controlled [9,10]. From the relation between anodic peak current, we can obtain three linear ranges from 0.001 to 0.003, 0.003 to 0.004 and from 0.004 to 0.006 with a very good linear correlation r^2 = 0.98. The sensitivity of electrode is found to be 0.001 A.M^{-1} obtained from the slope of the plot. The detection limit is found to be 8 µM that calculated from concentration that gave signal similar to the basic electrolyte.

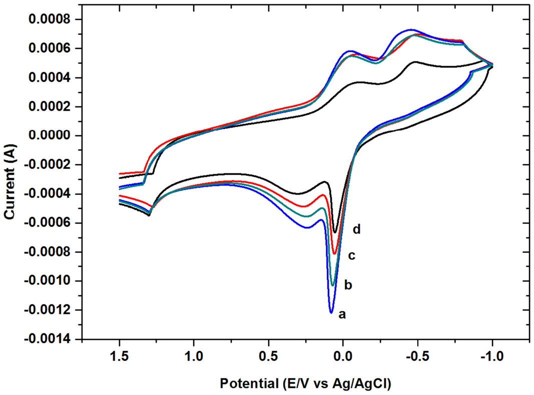

Figure 2. Cyclic voltammograms of (a) 6×10^{-3}, (b) 4×10^{-3}, (c) 3×10^{-3} and (d) 1×10^{-3} M $CuSO_4$.

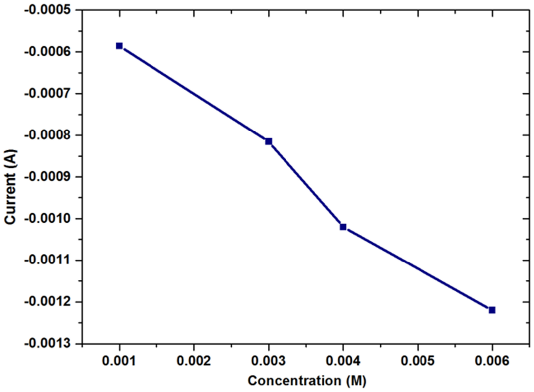

Figure 3. Anodic peak current variations with concentration.

3.3. Effect of pH change

The variation of reduction properties with pH variation was studied. The CVs of $CuSO_4$ in acetate buffer of pH = 3, 4, and 5 at 100 mV/s are introduced to study pH effect. In Figure 4, the CVs are compared. At pH range from 3 to 5, the GCE show electro catalytic activity. Variation of pH against anodic peak current is shown in Figure 5. The best resolution for peak current is observed at pH = 5. Comparable CVs at pH = 3, 4 and 5 indicates that redox behavior of copper ions on GCE is pH dependent.

Table 1. Current-potential data, peak potential separation, peak current ratio of the voltammogram of 0.1 M $CuSO_4$ in 0.1 M KCl at different scan rates.

ν(V/s)	$\nu^{1/2}$	E_{pa} (v)	E_{pc} (v)	$-i_{pa}$ (mA)	i_{pc} (mA)	$\Delta E = E_{pc} - E_{pa}$ (v)	i_{pa}/i_{pc}
0.10	0.316	0.044	0.462	0.670	0.518	0.418	1.293
0.05	0.223	0.054	0.371	0.594	0.359	0.317	1.654
0.02	0.141	0.044	0.289	0.489	0.255	0.245	1.917
0.01	0.100	0.034	0.257	0.402	0.200	0.223	2.010

Peak potential by increasing hydrogen ions concentrations (pH) is moved to lower potentials. These results indicate that this electrode shows a very good response to copper ions at low concentrations and different pH values and the best detection at pH = 5. The dependence of redox properties on pH variation can be suggested as follow:

$$E^0 = -56.1pH + 1.203\ (r^2 = 0.9765) \qquad (5)$$

This value is very close to the theoretical value that equal to 59.1 mV/pH at 298 K.

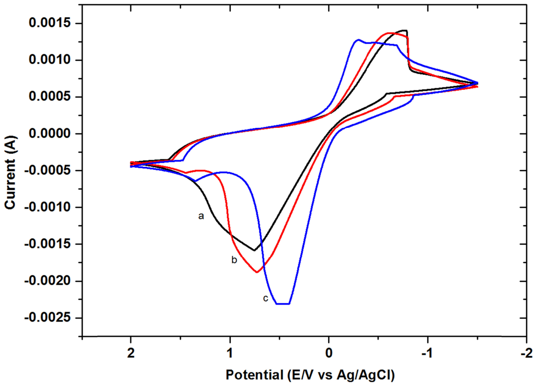

Figure 4. Cyclic voltammograms of 6×10^{-3} M Cu(II) in acetate buffer of pH = 3 (a), pH = 4 (b) and pH = 5 (c) at 100 mV/s.

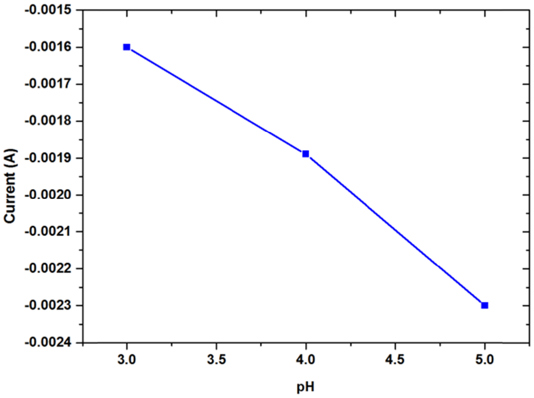

Figure 5. Anodic peak current variation with pH changes for the cyclic voltammograms of 6×10^{-3} $CuSO_4$ in acetate buffer.

3.4. Effect of scan rate on redox behavior

The effect of scan rate on redox behavior of was studied. Cyclic voltammograms of the Cu(II) solution were recorded at different scan rates ranging from 100-10 mV/s and shown in Figure 6. The peak potential separation, current-potential data, peak current ratio of the voltammograms at mentioned scan rates is recorded in Table 1. By increasing the scan rate, the cathodic peaks potentials are increased while for the anodic peaks, the peak potentials are decreased. As shown in Figure 7 that is a plot of ΔE_p *vs.* scan rate, with increasing the scan rate the peak potential separation (ΔEp) increases because the cathodic peak shifts toward negative potential and that of anodic toward positive potential but the value of formal redox potential [$E^0 = (E_{pc} + E_{pa})/2$] is almost constant and is almost independent of scan rate. This may be due to the decrease of iR (ohmic potential) or due to slow kinetics of electron transfer [11,12].

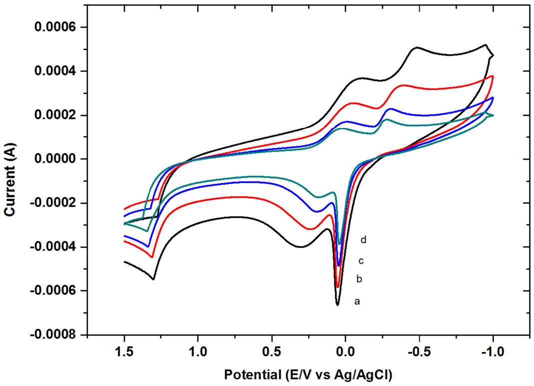

Figure 6. Cyclic voltammograms of 1×10^{-3} $CuSO_4$ in 0.1 M KCl at (a) 100, (b) 50, (c) 20 and (d) 10 mV/s.

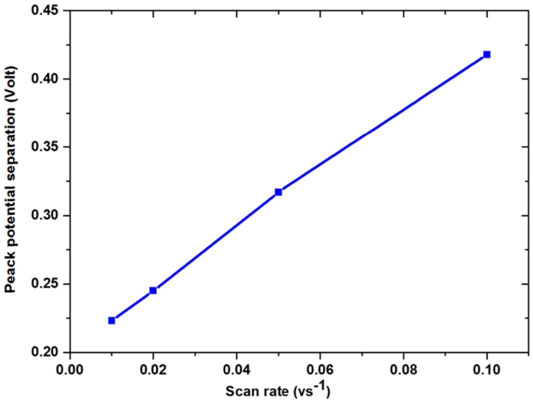

Figure 7. Peak potential separation variations with changing scan rate for the cyclic voltammograms of 1×10^{-3} M $CuSO_4$.

The process is adsorptive controlled as shown in Figure 8 in which the cathodic and anodic peak currents increase almost linearly with square root of scan rate (SQRT). The dependency of anodic and cathodic peak currents on scan rates is also indicating that the process is surface and diffusion controlled. In the electrochemical process the currents for adsorbed and desorbed ions are proportional to $\nu^{1/2}$ and ν, severally.

Figure 9 is a plot of log i *vs.* log v and shows a linear relation indicating that the process is diffusion controlled [13,14]. Each charge transfer and mass transport is controlling the peak current [15]. The system is quasi-reversible and this can be approved by the peak current quantitative relation that is found to be over than unity.

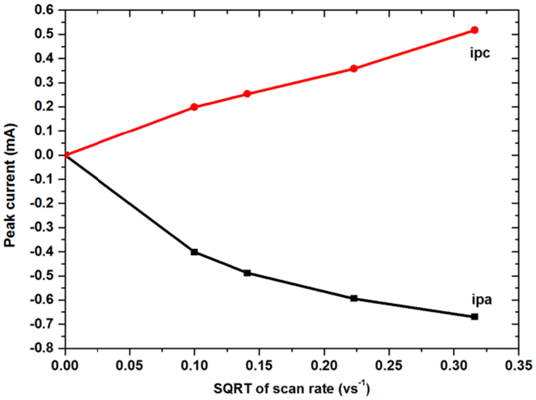

Figure 8. Peak current variation with SQRT of scan rate for the voltammogram of 1×10^{-3} M $CuSO_4$.

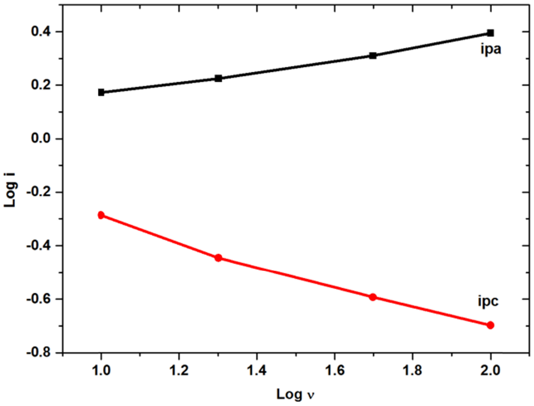

Figure 9. log i *vs.* log ν plot for the CV of 1×10^{-3} M $CuSO_4$.

3.5. Cu (II) electrochemical behavior in presence of lysine in 0.1 M potassium chloride

Cu(II) redox behavior in the presence of lysine was studied in 0.1 M potassium chloride at room temperature within the same conditions (potential window and same electrode) that was used for Cu(II) free ions. The given voltammogram in Figure 10 demonstrate that both the anodic and cathodic peak position of the voltammogram of 6×10^{-3} M $CuSO_4$ in the presence of 6×10^{-3} M lysine moves toward left with respect to those of 6×10^{-3} M $CuSO_4$. Additionally, the peak intensity has been modified. This behavior of position and intensity confirms the Cu-amino acid interaction. In the voltammogram of metal-amino acid interaction, there is a cathodic peak at potentials -314.14 mV and anodic peak at 129.6 mV.

3.6. Effect of pH change

Figure 11 shows the CVs of Cu(II) in the presence of lysine in acetate buffer of pH = 3, 4 and 5 at 100 mV/s. The anodic peak current is changed with pH change as indicated in Figure 12. As seen in the figure, the redox behavior is changed. There is a peak shift to right with respect to that for free a Cu(II) ion. The resolution of redox properties at different pH values is decreased by the addition of lysine. This may result from the copper lysine interaction.

3.7. Effect of scan rate

Figure 13 shows a number of CVs of 6×10^{-3} M $CuSO_4$ in the presence of 6×10^{-3} M lysine in 0.1 M potassium chloride at different scan rates. CVs show almost similar behavior like that of the free Cu(II) ion. It is observed that by increasing the scan rate, there is a negative potential shift for cathodic peaks and positive potential shift for anodic peaks. Table 2 shows the parameters that obtained from Figure 13. The peak potential separation increases by increasing the scan rate as in Figure 14 shows in which peak potential separation is plotted against scan rate. This may be due to the decrease of iR (ohmic potential) or slow kinetics of electron transfer [11,12]. Cathodic and anodic peaks current increases almost linearly with SQRT of scan rate as in Figure 15, which proves that the process is adsorptive controlled. The dependency of peak currents on scan rates is indicating that the redox process is surface and diffusion controlled. In the electrochemical process, the peak currents for adsorbed and desorbed ions are proportional to $\nu^{1/2}$ and m, severally [16]. The process is diffusion controlled as indicated by a linear plot of log i *vs.* log ν (Figure 16) [13,14]. Each mass transfer and charge transport is controlling the peak current [15]. The system is quasi-reversible indicated by peak current ratio that is found to be much over than unity [9,10]. The process is adsorptive controlled as shown in Figure 15.

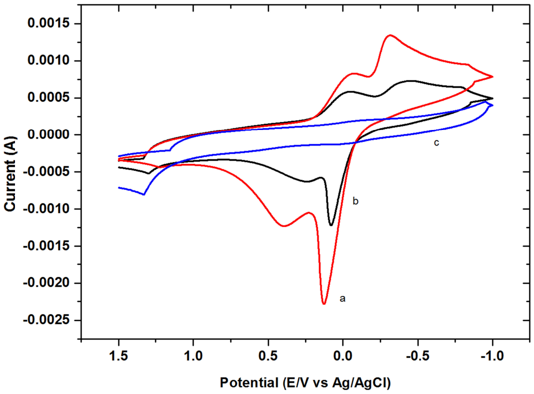

Figure 10. Cyclic voltammograms of (a) 6×10^{-3} M $CuSO_4$ in presence of 6×10^{-3} M lysine, (b) 6×10^{-3} M $CuSO_4$, and (c) 6×10^{-3} M lysine in 0.1 M KCl at 100 mV/s.

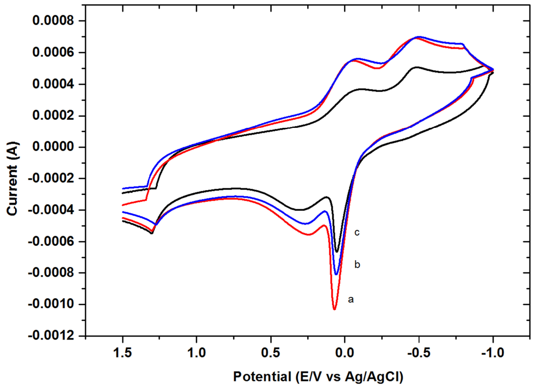

Figure 11. CVs of 6×10^{-3} M $CuSO_4$ in the presence of 6×10^{-3} M lysine in acetate buffer of pH = 3 (c) (black), 4 (b) (blue), and 5 (a) (red) at 100 mV/s.

3.8. Charge transfer rate constants (ks) and diffusion coefficient (D)

The diffusion coefficients were calculable from a series of electrochemical analysis. The diffusion coefficient (D) will be determined from the cathodic peak current equation of a reversible or quasi-reversible system as in equation (6) [17].

$$i_p = (2.69x10^5)n^{3/2}AD^{1/2}v^{1/2}C \qquad (6)$$

Table 2. Current-potential data, peak potential separation, peak current ratio of the voltammogram of 0.1 M $CuSO_4$ in 0.1 M potassium chloride in the presence of lysine at different scan rates.

ν (V/s)	$ν^{1/2}$	E_{pa} (v)	$-E_{pc}$ (v)	$-i_{pa}$ (mA)	i_{pc} (mA)	$ΔE = E_{pc} - E_{pa}$ (v)	i_{pa}/i_{pc}
0.10	0.316	0.117	0.310	0.002	0.0010	0.193	2.000
0.05	0.223	0.109	0.261	0.001	0.0010	0.152	1.000
0.02	0.141	0.085	0.220	0.001	0.0007	0.135	1.428
0.01	0.100	0.065	0.168	0.001	0.0005	0.103	2.000

Table 3. Current-potential data, diffusion coefficient, D and the charge-transfer rate constant, k_s, for M(II) and M(II)-lysine interaction on GCE *.

ID	ν ($V.s^{-1}$)	E_{pc} (v)	i_{pc} (mA)	Diff. Coff. ($Cm^{-2}.S^{-1}$)	Charge transfer rate constant (log K_S)
Cu(II) in KCl	0.10	0.462	0.5180	0.90998	4.1485
	0.05	0.371	0.3590		
	0.02	0.289	0.2550		
	0.01	0.257	0.2000		
Cu(II)-lysine in KCl	0.10	-0.310	0.0010	2.23×10^{-6}	-3.0877
	0.05	-0.261	0.0010		
	0.02	-0.220	0.0007		
	0.01	-0.168	0.0005		

* T = 298 K, n = no of electron transferred = 2, R = 8.314 J/K.mol, F = 96,500, A = surface area of the electrode = 2.01 cm^2, Conc. = 1 mM.

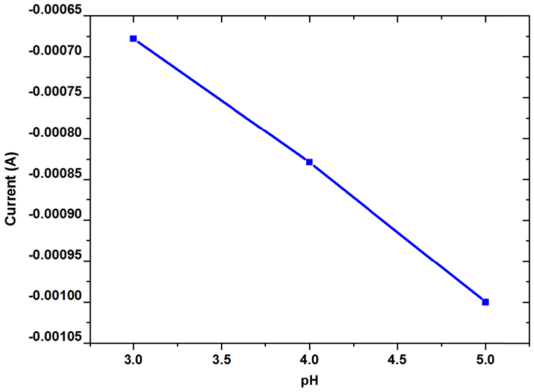

Figure 12. Variation of anodic peak current with pH in the interaction of $CuSO_4$ with lysine in acetate buffer.

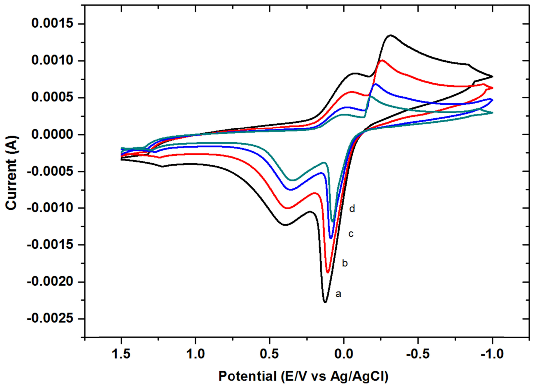

Figure 13. Cyclic voltammograms of 6×10^{-3} M $CuSO_4$ in presence of 6×10^{-3} M lysine in 0.1 M KCl at (a) 100, (b) 50, (c) 20 and (d) 10 mV/s.

where A (cm^2) is the surface area of electrode, C (mmol/L) is the sample concentration, D (cm^2/s) is the diffusion coefficient, ν (V/s) is the potential scan rate, F is the Faraday constant and has its usual value, n is the number of transferred electrons, and T is the absolute temperature in K. Diffusion and charge transfer kinetics are the major factors that affect the reduction process. The charge transfer rate constant (k_S) associated with both diffusion coefficient and transfer coefficient, can be described as equation (7) [18].

$$K_S = 2.18 \left[\frac{D(\alpha n_\alpha)F\nu}{RT}\right]^{1/2} exp \left[\frac{\alpha^2 nF(E_{PC}-E_{pa})}{RT}\right] \quad (7)$$

From results of the heterogeneous charge transfer rate constant k_s (Table 3), it is observed that free Cu(II) ions have greater value than that of the Cu-lysine system at 298 K temperature that predicts the reduction of charge transfer velocity as a result of Cu(II)-lysine amino acid interaction [19-25].

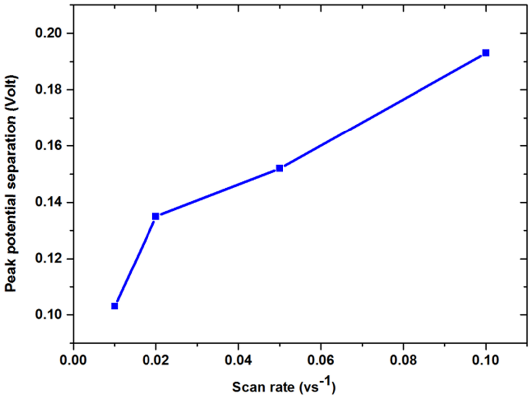

Figure 14. Variation of peak potential separation with scan rate for coordinated Cu(II) ions.

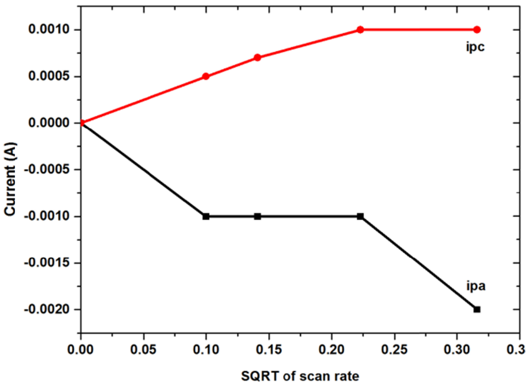

Figure 15. Peak current variations with SQRT of scan rate for complexed Cu(II) ions.

4. Conclusions

Cyclic voltammetry technique provides good information about the electrochemical behavior of studied material. In the present work he redox behaviors of Cu(II) in absence and presence of lysine have been studied in potassium chloride and in acetate buffer. In all cases the redox processes of Cu(II)/Cu(0) system is diffusion controlled and/or adsorptive controlled. Additionally, the values of peak current quantitative relation and peak potential separation powerfully support that the electron transfer processes are quasi-reversible. The heterogeneous charge transfer rate constant (ks) for Cu(II) in the presence of essential amino acid lysine is smaller than that within the absence of the ligand which confirms the interaction between metal ion and ligand in all the electrolytic systems.

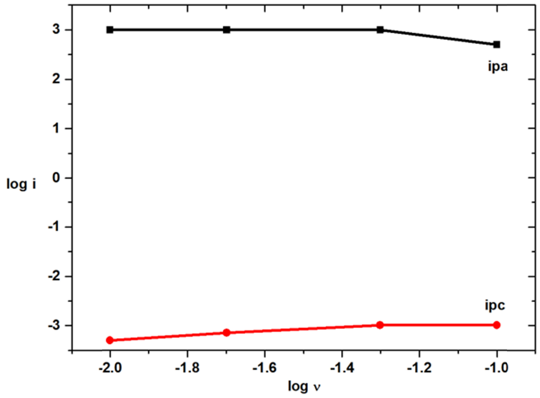

Figure 16. Log i *vs.* log ν plot for the CVs of 6×10^{-3} M $CuSO_4$ in the presence of 6×10^{-3} M lysine.

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