The Study on 1,10-Phenanthroline-copper Complex By CV-Thin Layer Spectroelectrochemistry

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The electrochemical behaviour of copper-1,10-phenanthroline (phen) complex in aqueous and in water-acetone mixed solutions was studied by CV-thin layer spectroelectrochemistry. In aqueous solution, $[Cu(II)(phen)_2]^{2+}$ complex electrochemically reduced to $[Cu(I)(phen)_2H_2O]^+$ with maximum absorption at 405nm, and followed by a reversible chemical reaction. The formal potential, E^0=0.078V, the number of electron transferred, n=1.0, and the equilibrium constant of the following chemical reaction, K=0.107 ($\pm$0.005), were determined. In water-acetone mixed solution, $[Cu(II)(phen)_2]^{2+}$ reduced to $[Cu(I)(phen)_2]^+$ with maximum absorption at 435 nm.

Keywords: CV-thin layer spectroelectrochemistry; copper-1,10-phenanthroline complex

1. INTRODUCTION

Copper, as one of essential life elements, takes part in the redox reaction as electron carriers such as plastocyanins of copper-proteins. since metal-phen complexes are found use as photo/redox-active components of supramolecular assemblies [1-4], DNA intercalators [5-6], DNA footprints [7], the studies on copper-1,10-phenanthroline (phen) complexes becomes increasing important. The damage of copper-phen complex on DNA [8, 9] has been used as a probe in a new vivo technique in studying interactions of DNA and proteins in whole cells [7]. Redox property is the characteristic behavior of copper-phen complex, it seems very simple, but something still keeps unclear up to now. The insight study on its electrochemical behavior will help us to understanding the processes happened in the biological chemistry.

Spectroelectrochemistry [10], combination of spectroscopy with electrochemistry, is a powerful tool in studies of mechanisms, thermodynamic and kinetic parameters of an electrode reaction. In this study, thin-lay cyclic voltammetric spectroelectrochemistry was used to study electrochemical behavior of copper-phen complex, the electrode reaction mechanism and some thermodynamic parameters were obtained.

2. EXPERIMENTAL

2.1. Chemicals and solutions

$CuSO_4 \cdot 5H_2O$, 1,10-phenanthroline and other reagents are all analytical pure. All solutions were prepared with MilliQ water. The solutions were deaerated with high-pure nitrogen for 15min before use. The copper-phen complex solutions were prepared by mixing 0.5 mM $CuSO_4$ solution with different concentration of phen solution (0.5, 0.75, and 1 mM) in pH 5.0 acetate buffer.

2.2. Apparatus

Spectroelectrochemical experiments were carried out on Perkin-Elmer Lambda 25 UV/VIS spectrometer (made in USA) and CHI620B (made in China) with homemade long optical path length thin layer cell (LOPTLC, thickness of the thin layer is 0.020 cm) [11]. A graphite carbon slice served as working electrode, a platinum wire as auxiliary electrode and a Ag/AgCl (KCl saturated) as reference electrode. All potentials are reported with respect with this reference electrode.

Graphite carbon electrode was polished to a mirror-like surface with 1.0, 0.3 and 0.05 micron α-alumina powder in sequence and washed in supersonic for one minute before use.

3. RESULTS AND DISCUSSION

3.1 Cyclic voltammetric studies of copper-phen complex

In pH 4.4 NaAc-HAc buffer solution, the CVs of Cu-phen complexes with different mol ratios of copper to phen in the range of +0.835V−-0.765V were recorded and shown in Fig.1. Cu(II) shows three reduction peaks at –0.165, -0.235 and –0.115 V and two oxidation peaks at 0.145 and 0.305 V as usual case (dashed line). In copper-phen solution with 1:1 and 1:1.5 mol ratios, CVs show one reduction peak at –0.165 V corresponding to the reduction of Cu(II) and two oxidation peaks at 0.145 and 0.205 V corresponding to the oxidation of Cu(I)-phen and free Cu(0) to Cu(I) (lines 1 and 2). In solutions with the mol ratios ≥2, the reduction peak at –0.165 V shifts to –0.115V, and the oxidation peak at 0.135 V disappears (line 3). The reduction peak current at –0.025 V increase and oxidation current at 0.135 V decreases with the increase of mol ratios and disappears at mol ratio ≥2. The CVs

indicate that both of copper (I) and copper (II) forms a 1:2 complex with phen, which are in accord well with references [9, 12].

In the solution with mol ratio of 1:2, Both of the redox peaks increase with scan rates and follow the diffusion controlled model with $i_{pc} = 3.54568 + 11.1493 \ v^{1/2}$ (R=0.9912, SD=0.1063) and $i_{pa} = 0.6012 + 21.48 \ v^{1/2}$ (R=0.9997, SD=0.0303), respectively. The reduction peak potential shifts to negative direction with scan rates (average 53 mV for 10 times of scan rate), and the ratio of peak currents, i_{pa}/ i_{pc}, goes up to 1 with the increase of scan rates, as shown in Fig.2. The results indicate that there is a reversible following chemical reaction [9] in the reduction process.
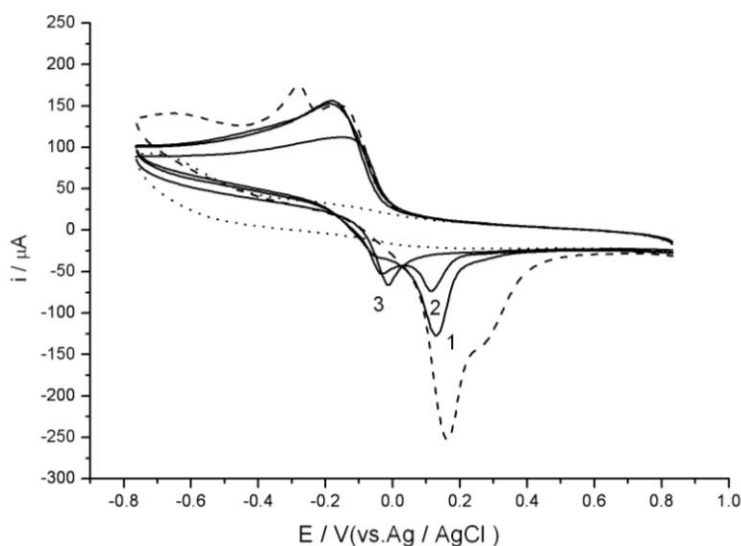

Figure 1. The CVs of copper-phen complex with different mol ratios in 0.2 mol/L NaAc-HAc buffer solution (pH=4.4). scan rate:60 mV/s; mol ratio of copper to phen: 1, 1:1; 2, 1:1.5; 3, 1: 2.The dot line: background; The dash line: CuSO$_4$ solution without phen.
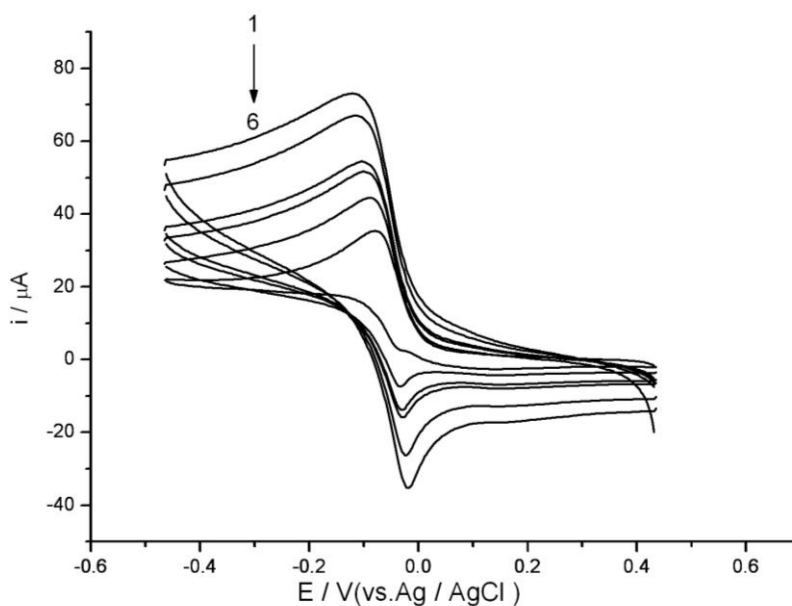

Figure 2. The CVs of Cu-phen complex at different scan rates. Scan rate (V/s): 1, 0.03; 2, 0.02; 3, 0.01; 4, 0.008; 5, 0.004; 6, 0.002.Other conditions are the same as in Fig.1.

3.2 Potential-step thin-layer spectroelectrochemical study of Copper-phen complex

The solution with 1:2 mol ratio of Cu(II) and phen was put into LOPTLC for the potential step spectroelectrochemical experiments. After the potential was applied to electrode, the absorption spectra were recorded in the range of 800 nm-380 nm, as shown in Fig.3.
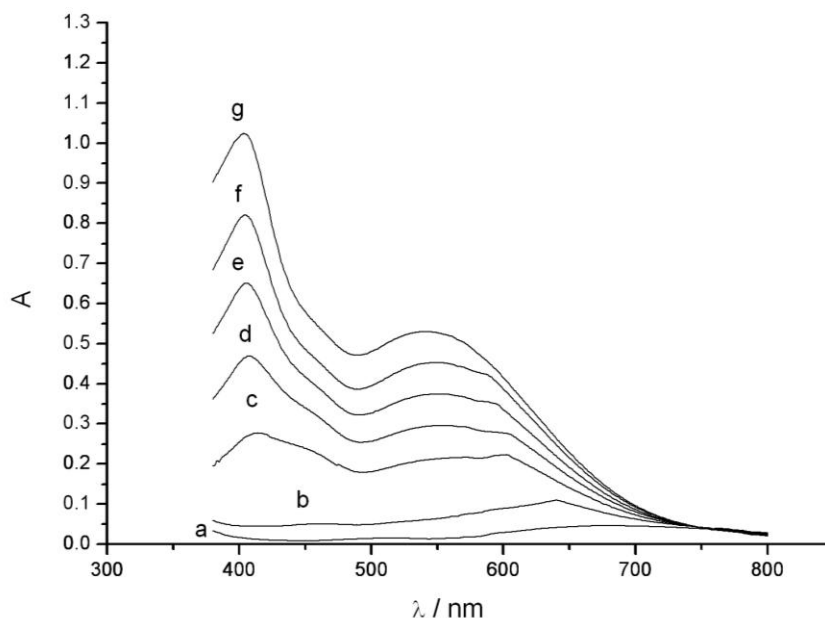

Figure 3. The absorption spectra of copper-phen complex at different potentials. Applied potential (E/V): a, open circuit; b, -0.060; c, -0.080; d, -0.100; e, -0.120; f, -0.150; g, -0.450. The experimental conditions are the same as in Fig.2.

At open circuit, Cu(II)-phen complex shows a small absorption peak at 680nm. With potential steps from –0.060 V to –0.450 V, The peak at 680 nm shifts to 545nm, and a new peak appears at 408 nm, and increases with the potential shift to negative direction. This peak is identical absorption of Cu(I)-phen complex corresponding to the reduction of Cu(II)-phen. Cu(I) coordinates with phen and forms a 1:2 complex, $[Cu(I)(phen)_2]^+$ with a absorption peak at 435 nm [9]. In our experimental conditions, this peak shows a 30 nm red shift, which indicates it is another complex.

Cu(I) is likely to coordinate with two phen and another coordination reagent to form mixed complexes. In aqueous solution, Cu(II) exists in the form of $[Cu(II)(H_2O)_6]^{2+}$, in which two of the six water molecules are apart away from Cu(II) [13] . During the addition of phen, the complex ion, $[Cu(II)(phen)_2(H_2O)_2]^{2+}$, may exits, which is corresponded to the absorption at 680 nm. With potential shifts to negative direction, the molecule is reduced into $[Cu(I)(phen)_2(H_2O)_2]^+$ with absorption at 405 nm. The following chemical reaction may be the loss of one water molecule, and forms a 5 coordination number complex.

Replacing NaAc-HAc with K_2SO_4 and HCOOH-HCOONa as supporting electrolyte and buffer system, the same spectra were obtained, indicating the only possible mixed coordination reagent is water molecule. In order to removing water molecules, small amount of acetone was added.

$$[Cu(II) (phen)_2H_2O]_2]^{2+} = [Cu(II) (phen)_2]^{2+} + H_2O \qquad (1)$$

$[Cu(II)(phen)_2]^{+2}$ shows a absorption peak at 661nm in open circuit. The peak at 661 nm shifts to 531 nm at −0.250 V, and a new peak at 435 nm appears during the electrochemical reduction process, which is in accord well with the reference [9,12] as shown in Fig.4.
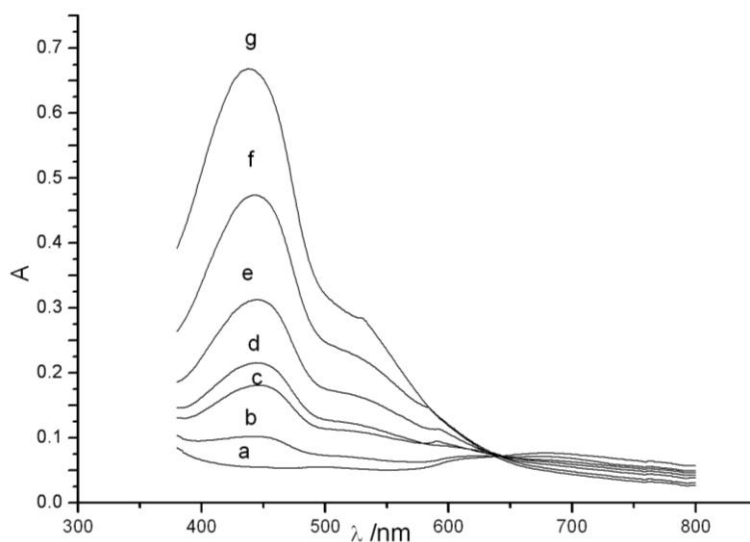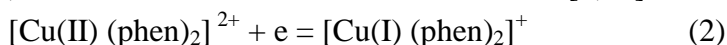
$$[Cu(II) (phen)_2]^{2+} + e = [Cu(I) (phen)_2]^{+} \qquad (2)$$

Figure 4. The absorption spectra of Cu-phen complex at different potentials in water- acetone mixed solution. Applied potential (E/V): a, open circuit; b, -0.070; c, -0.075; d, -0.090; e, -0.100; f, -0.140; g, -0.250. Other experimental conditions are the same as in Fig.2.

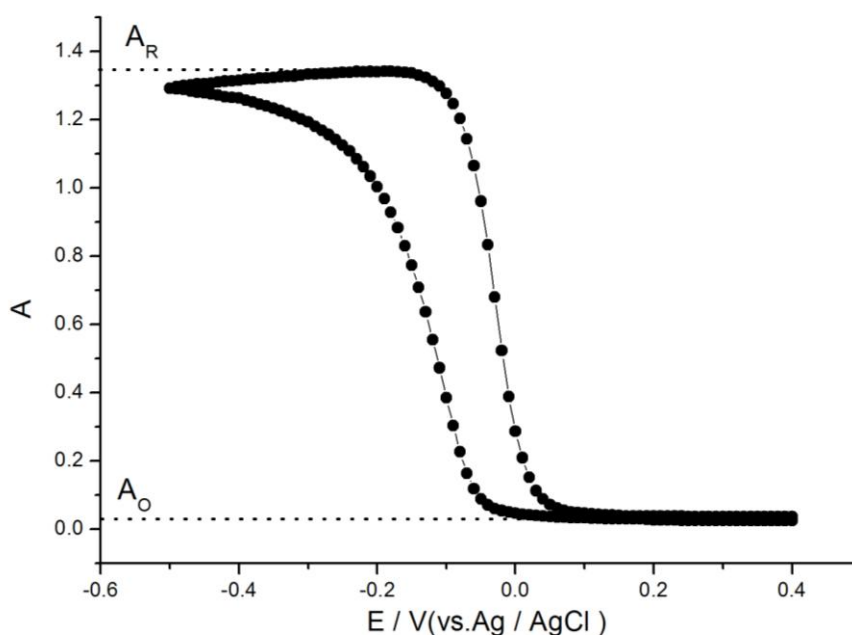*3.3 Cyclic voltammetryic thin-layer spectroelectrochemical studies of Copper-phen complex*

Figure 5. The absorbance-potential plot of copper-phen complex at 405nm. Scan rate:1.0 mV/s; T=283.15 K; time interval: 10 s. Other experimental conditions are the same as in Fig.3.

Under the same experimental conditions, at 1 mV/s potential scan rate, CV technique combined with thin layer spectroelectrochemistry, called CV thin layer spectroelectrochemistry, was performed. The absorbance at 405 nm was recorded with potential scanning as shown in Fig.5.

The curves are very similar, but the reduction curve at negative potential part is bended to potential axis, while the curve in oxidation process shows a simple Nernstian process. Nernstian plot of the oxidation process is a straight line over the all of potential range as shown in Fig.6. From the Nernstian plot, $E = E^{0'} + (0.059/n) \lg[(A_R-A)/(A-A_O)]$, where A_R and A_O is the absorbance (marked in Fig. 5) of the copper-phen complex solution applied with the low and high potential at which all the Cu species are changed to Cu(I) and Cu(II), respectively, n=1.06 and $E^{0'}$=-30mV (R= 0.9995, SD=0.00221) was obtained.
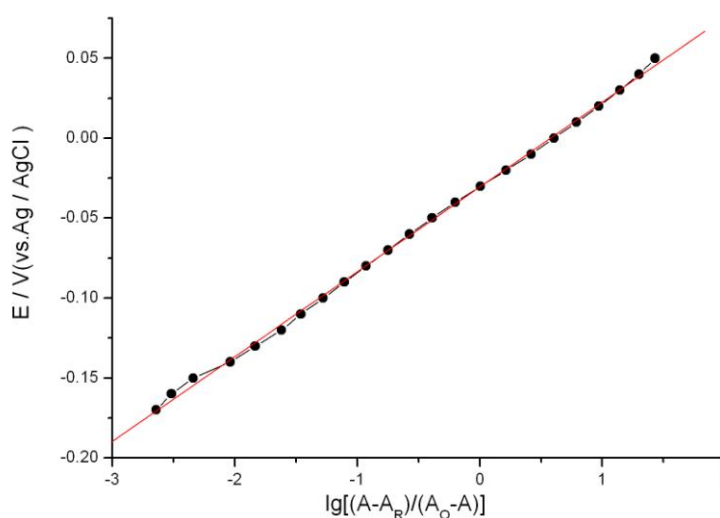

Figure 6. The Nernst graph of the oxidation process. The experimental data are from Figure 5
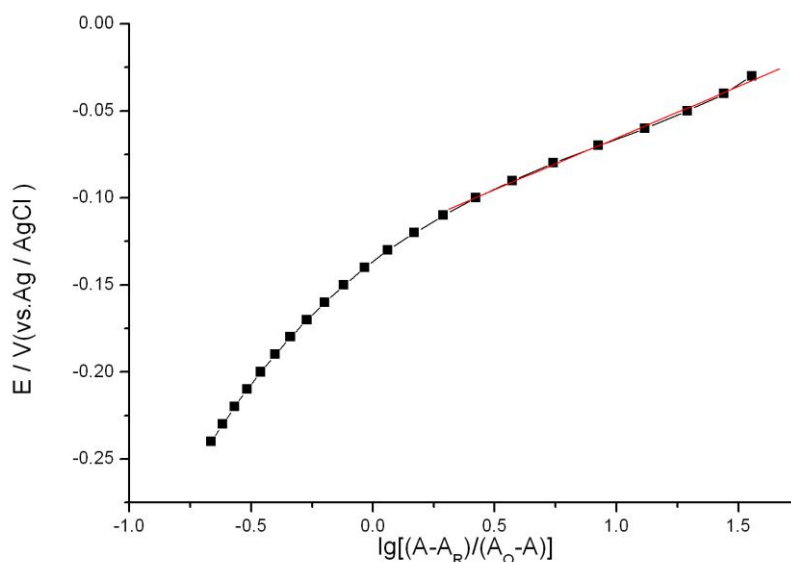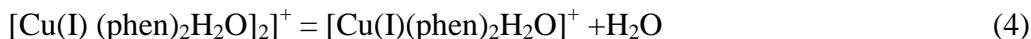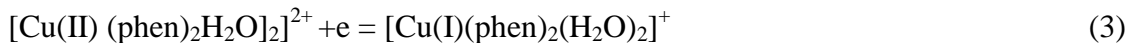

Figure 7. The Nernst plot in the reduction process. The experimental data are from Figure 5

The Nernstian plot in reduction process shows a straight line at potential range of –0.030 V − -0.100V, after that, the curve bends to logarithmic axis as shown in Fig.7. From the Nernstian plot, n= 0.95 and $E^{0'}$=-0.125 V were obtained (R=0.99836, SD=0.00151). Consideration of CV studies, there is a following chemical reaction in the reduction process. By non-linear fit of the reduction process, $E^{0'}$=-0.096(±2) V and K=0.107(±0.005) were obtained with total SD of 0.047.

The reduction process includes the following mechanism,

$$[Cu(II) (phen)_2 H_2O]_2]^{2+} + e = [Cu(I)(phen)_2(H_2O)_2]^+ \tag{3}$$

$$[Cu(I) (phen)_2 H_2O]_2]^+ = [Cu(I)(phen)_2 H_2O]^+ + H_2O \tag{4}$$

4. CONCLUSIONS

From the CV and CV thin-layer spectroelectrochemistry studies, some conclusions are as followings.

Cu (II) and Cu(I) react with phen and forms 1:2 complexes, which is in accord well with references.

Both of oxidation and reduction processes are diffusion controlled processes, with a following reversible chemical reaction in the reduction process.

The thin-layer potential step study of copper-phen complex shows the deferent components, $[Cu(I) (phen)_2(H_2O)_2]^+$ in aqueous solution with absorption peak at 405 nm, and $[Cu(I) (phen)_2]^+$ in water-acetone mixed solution with absorption peak at 435 nm, which is a irreversible transfer process.

The CV thin-layer spectroelectrochemical study of the Cu-phen complex shows EC mechanism in reduction process and a E mechanism in oxidation process, from which formal potential, $E^{0'}$, and electron transfer number, n, and following chemical reaction equilibrium constant were obtained.

The CV thin-layer spectroelectrochemistry is a useful tool in the study of reversible electrochemical process, especially in the following chemical reaction cases.

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