Electrochemical Properties of Copper Complex of Furdap Amide in Non-Aqueous Medium

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The electrochemical behavior of Cu (II)-Furdap amide complex has been investigated by the use of several electrochemical methods in DMSO on platinum electrode. The number of electrons transferred was calculated by bulk electrolysis and rotating disc electrodes. The reversibility tests were applied to elucidate the reaction mechanism. It was found that the Cu (II)- Furdap complex is reduced with quasi-reversible reaction. The mechanism of the electrode reaction was confirmed by simulation experiments. The standard heterogeneous rate constant (7×10^{-4} cm s^{-1}), the charge transfer coefficient (0.5), and the diffusion coefficient (1.7×10^{-6} cm^2 s^{-1}) were found by simulation study.

1. INTRODUCTION

Amides are very important compounds for pharmaceutics. Aspirin contains acetaminophen derivative of amide as antipyretic and analgesic. Amide ligands act as a chelating agent forming monomeric, dimeric and polymeric complexes [1]. Because they lose their amide protons in alkaline solution and the complex formation takes place on more basic amide nitrogen [2]. It is important to elucidate the reactions of the compounds contain amide for the peptide and protein chemistry. Since the conjugation of the free electron pair located on nitrogen atom and the π bond between carbon and oxygen atoms on the carbonyl group amides have distinctive chemical and physical properties. The amide linkages are an essential building unit in proteins, which has attracted much attention because of its high resistance to hydrolysis. This fact is of crucial importance in biological systems, since it permits for the building of peptides (amides) from relatively simple amino acid precursors [3].

Ethoxylated fatty amide was used as corrosion inhibitors for carbon steel [4]. Multidentate mono or bis amide ligands and their metal complexes have been widely studied by potentiometric and

spectrophotometric measurements and crystal structure analysis for a long time [5]. However, there are several studies on the electrochemical investigation of amides or amide containing complexes. Some of them are Mo(IV) catecholamide sidepore complexes [6], Ru(II) phorphyrine [7], thiophene amides [8] and buzepide methiodide [9]. In another study the stabilizing effect of amide containing L_1 $(L_1+H)^-$ and $(L_1{}')^-$ ligands on oxidation of Cu(II) in aqueous media was investigated with the use of cyclic voltammetry [10]. It is reported in this study that two different complexes obtained Cu $(L_1+H)NO_3$ and Cu $(L_1{}')OAc$ showed unexpectedly different cyclic voltammetric behavior. The complex obtained with the reduction of copper nitrate salt showed a quasi reversible behavior at a less positive potential while the complex formed by the use of copper acetate gave an irreversible oxidation reaction. This showed that the compound with two coordinated amide nitrogen atoms is more easily oxidized than the one with only one coordinated amide nitrogen atom [10].

In our previous study the electrochemical behaviors of Zn (II)-Furdap amide complex was investigated in DMSO [11]. It was found that the complex reduced with a quasi reversible mechanism. The number of electron transferred was found as one. On the other hand, there was no oxidation peak observed corresponding to the reduction of ligand, there was a corresponding oxidation peak appeared for the complex. Besides, the kinetic parameters like standard rate constant (k_s), transfer coefficient (α) and diffusion coefficient (D) of the reduction mechanism of the complex were calculated [11].

This study is related to electrochemical properties of Cu (II)-Furdap complex. The complex was synthesized and characterized as literature [12] firstly and then the electrochemical reduction of this complex was investigated using cyclic voltammetry, chronoampherometry, bulk electrolysis. The number of electron transferred was estimated and the reaction kinetics was elucidated.

2. EXPERIMENTAL

2.1. Preparation of Furdap ligand and Cu (II)-Furdap complex

To a solution of furan-2-carbonyl chloride (0.036 mol) in dichloromethane (20 cm^3), 1,3-diaminopropane (0.018 mol) in dichloromethane (10 cm^3) was added drop wise with cooling in an ice bath. The reaction mixture was stirred magnetically under reflux for a day. The precipitate was dissolved in a 30 mL of MeOH by heating and the solvent was evaporated to half of its original volume. The solution was filtered warm to remove impurities and left for crystallization at room temperature. After a week, crystals were collected then washed with MeOH and dried in air [12].

The Cu (II)-Furdap complex was prepared by the addition of hot solution (40 °C) of the CuCl$_2$ in 25 mL MeOH to the hot solution (40 °C) of ligand in the same solvent (25 mL) at the same mol ratio. The resulting mixture was stirred under reflux whereupon the complex was precipitated. It was collected by filtration and washed with diethyl ether [12].

2.2. Instrumentation and electrochemical techniques

All the electrochemical studies were carried out with CH Instruments Model 660C Electrochemical Analyzer equipped with a BAS C3 Cell Stand and BAS RDE-2 Rotating Disc

Electrode. The working electrode was platinum disc (BAS Model MF 2013) electrode, the counter electrode was a Pt wire and the reference electrode was Ag|Ag$^+$. The platinum micro electrode (BAS Model MF 2005) and platinum rotating disc electrode were also used as a working electrode in related experiments. The electrochemical techniques used are cyclic voltammetry (CV), chronoramperometry (CA) and bulk electrolysis (BE).

2.3. Reagents

Tetrabutylammonium tetrafluoroborate (TBATFB), dimethylsulfoxide (DMSO), silver nitrate (AgNO$_3$) and were purchased from Merck Chemical. All other chemical compounds used in this study were reagent grade commercial products. The water used was obtained from Milipore water purification system with an outlet resistivity of 18 MΩ·cm. The experimental solutions were purged with nitrogen for at least 10 min just before the voltammetric experiments and throughout the hydrodynamic experiments like RDE and BE. The ligand and complex solutions were prepared from 10^{-3} M stock solutions.

3. RESULTS AND DISCUSSION

## 3.1. Cyclic voltammetry studies

The cyclic voltammetric behavior of copper (II) complex of Furdap was studied in anhydrous DMSO at room temperature. The cyclic voltammograms of Cu (II)-Furdap complex and free Furdap ligand were compared first. Then the electrochemical reduction of Cu (II)-Furdap complex was investigated by cyclic voltammetry.

The current-potential curves for 1 mM solutions of Furdap ligand and its copper(II) complex using 0.1 M TBATBF in DMSO are presented in Fig. 1 and Fig. 2 respectively.
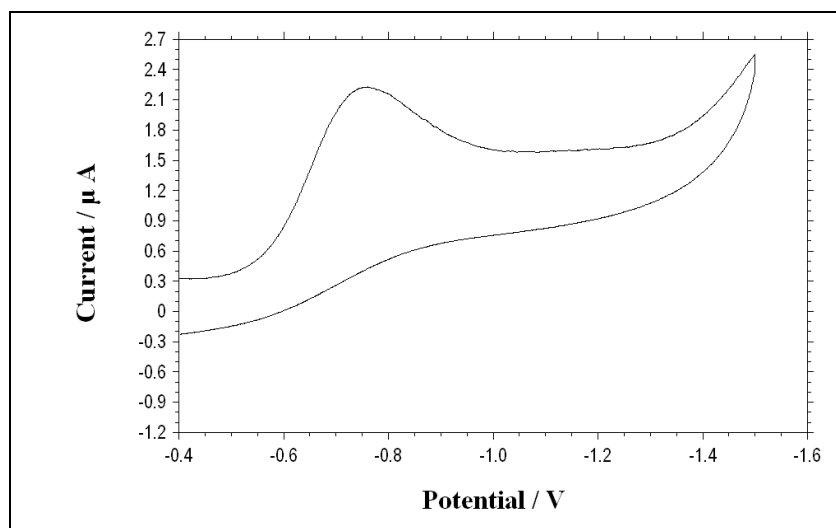
Figure 1. Cyclic voltammogram of 1 mM Ligand 0.1 M TBATFB in DMSO on Pt electrode, v=0.1 V s^{-1}, (vs. Ag|Ag$^+$ electrode).

The voltammetric behavior of free ligand is characterized by one reduction peak in this medium at a platinum surface (Fig. 1). The peak potential is about -0.8 V (vs. Ag|Ag$^+$) at a scan rate $v=$ 0.1 Vs^{-1}. The peak height corresponds to a one-electron reduction. There appears no oxidation peak in the reverse scan. It is seen that the free ligand reduces irreversibly with one electron transfer on platinum surface. The cathodic peak is for the reduction of Furdap ligand to the anion radical. In contrast to free ligand, the Cu (II)-Furdap complex undergoes a quasi-reversible process at the platinum surface. The complex gives one electron transfer redox system at -0.55 V (vs. Ag|Ag$^+$) which occurs at 0.25 V more positive potential than free ligand. The oxidation peak is also observed in the reverse scan for the complex (Fig. 2). These results indicate that the reductions of free ligand and the complex take place differently.
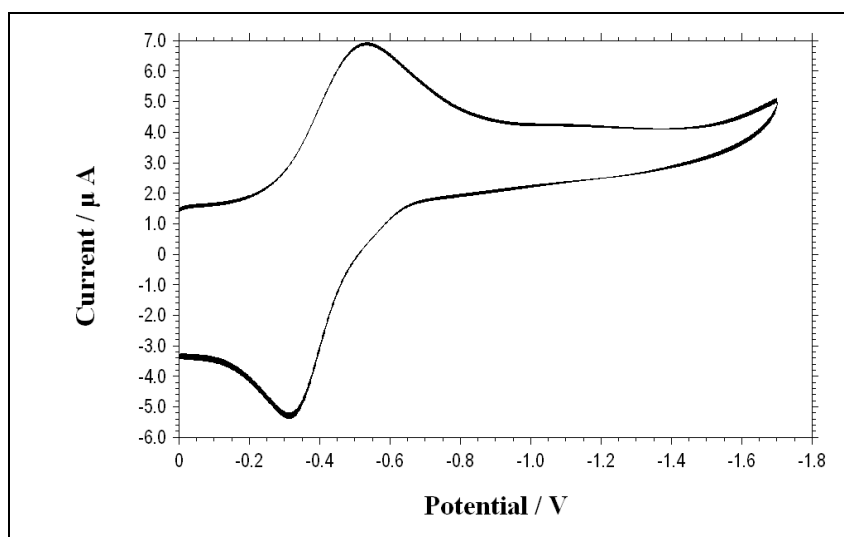

Figure 2. Cyclic voltammogram of 1 mM Cu (II)-Furdap complex in 0.1 M TBATFB in DMSO on Pt electrode, v=0.1 V s^{-1}, (vs. Ag|Ag$^+$ electrode).

*3.1.1. Reversibility test*

From the cyclic voltammogram of free ligand it can be concluded that the ligand reduces irreversibly. On the contrary it cannot be concluded for copper complex because of the oxidation peak. In order to indicate the reversibility of electron transfer reaction of the complex different peak current values corresponded with different scan rates were plotted.

Fig. 3 shows the i_p-$v^{1/2}$ graph of Cu (II)-Furdap complex for cathodic ($i_p{}^c$) peak currents. As seen from the graph the peak currents obtained at different scan rates were observed to change linearly with square root of scan rate. This behavior supports the reversibility of electron transfer reaction for the complex. However when we investigated the change between the peak potential and scan rate we determined that peak potential shifts to more negative values with the increase in scan rate (Fig. 4). In addition to this result the ΔE_p value is higher than 60 mV. As a result it is found that the complex is reduced in quasi-reversible way.
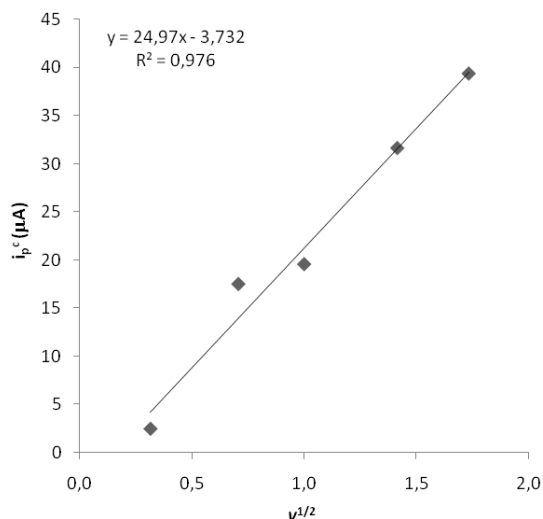
Figure 3. The i_p-$v^{1/2}$ graph of Cu (II)-Furdap complex.
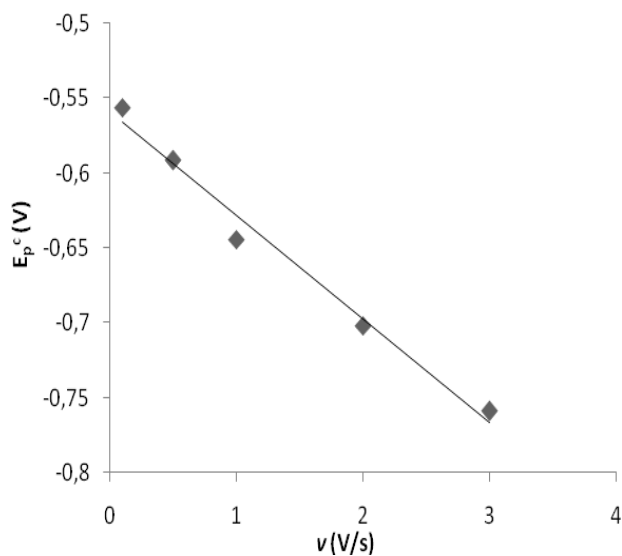
**Figure 4.** The change in E_p^c values of Cu (II)-Furdap complex with the scan rate.

3.1.2. Adsorption test

It can also be determined by cyclic voltammetry whether the complex adsorbed on the electrode surface or not. In Fig. 5, the log i_p-log v graph is shown for purpose of investigating the existence of adsorption in the electrode reaction of Cu (II)-Furdap complex. Since the slope of the graph depicted in Fig. 4 is greater than 0.5 but not equal to 1. It is concluded that the complex are weakly adsorbed upon the surface [13].
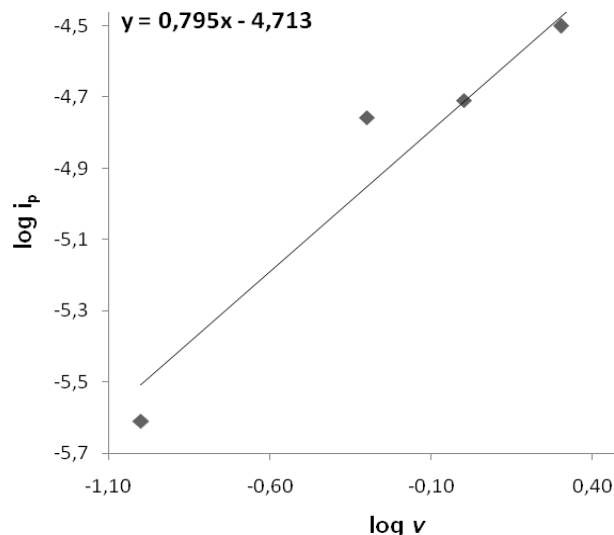
Figure 5. The dependence of log i_p to log v for Cu (II)-Furdap complex in DMSO (0.1 M TBATFB).

On the other hand the presence of adsorption was also designated by the multicycle voltammetry [14]. Fig. 6 shows the consecutive cyclic voltammetry of 1 mM Cu (II)-Furdap complex at a platinum electrode. As shown in Fig. 6, the current decreases to almost half of that of the first scan due to the complete coverage of the electrode surface by the Cu (II)-Furdap complex molecules. Moreover a post peak appeared from the second scan.
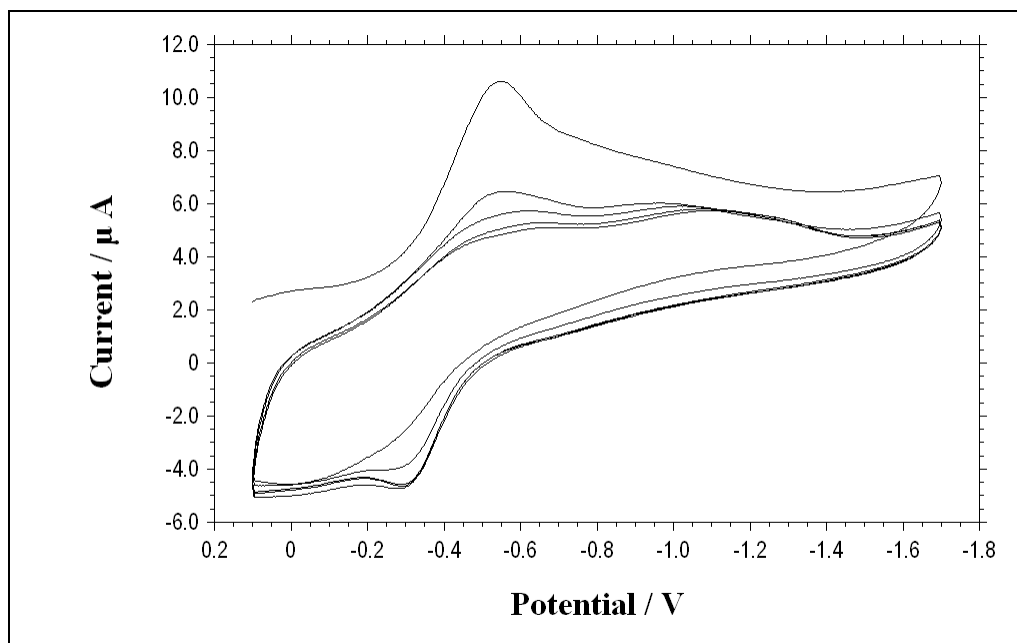
Figure 6. Consecutive CV experiment of 1 mM Cu (II)-Furdap complex in DMSO (0.1 M TBATFB) at Pt electrode at scan rate of 0.2 V s^{-1} with 5 cycle, (vs. Ag|Ag^{+} electrode).

### 3.2. Determination of the number of electrons transferred

A controlled potential coulometric experiment was carried out at the potential of the cathodic peak for the reduction of Cu (II)-Furdap complex to acquire the charge consumption in the one-electron reduction process. The number of electrons transferred was determined by bulk electrolysis using a platinum fence electrode. Controlled potential coulometric experiments showed that about 1.20 mole of electron consumed for each mole of Cu (II)-Furdap complex. The number of electrons (n) transferred was estimated by the help of Faraday laws and taken as 1 (one) within an experimental error.

In addition the controlled potential coulometric experiment mentioned above, the number of electron transferred was also determined with the use of rotating disc electrode by the help of Koutecky-Levich equation [15].

$$\frac{1}{I} = \frac{1}{I_k} + \frac{1}{0.620nF\pi r^2 D_0^{2/3} \vartheta^{-1/6} w^{1/2} C^0}$$

Koutecky-Levich

Fig. 7 shows the effects of rotation rate on the voltammetric current for the reduction of Cu (II)-Furdap complex. From the slope of the line shown in Fig. 8, the number of electron transferred was calculated as 1.3 and can be accepted as 1 (one) within an experimental error.
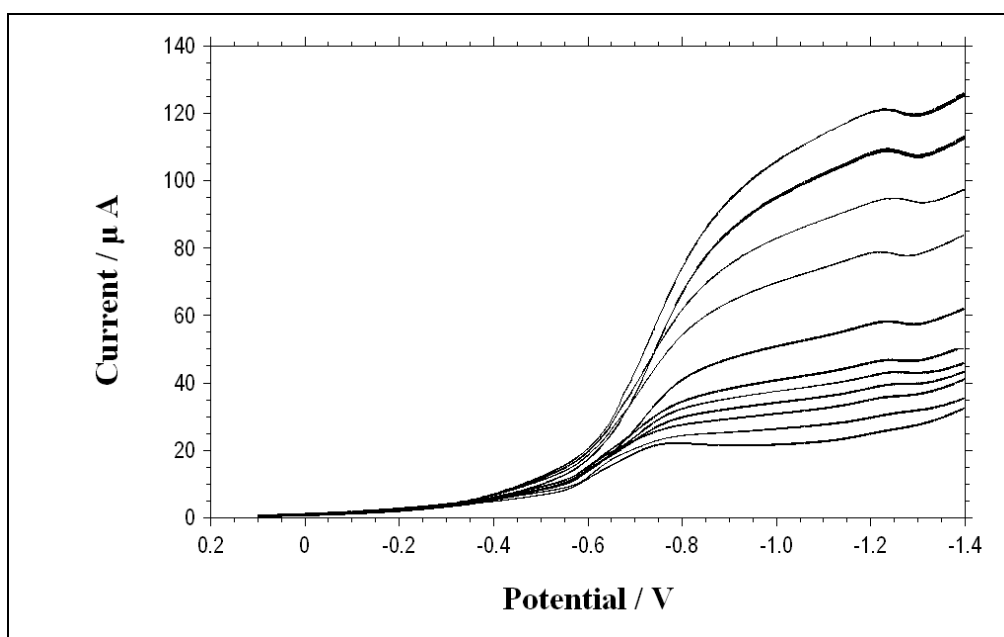
Figure 7. The voltammetric i-E curves of Cu (II)-Furdap complex for several rotation rates at rotating GC disc electrode in DMSO (0.1 M TBATFB).
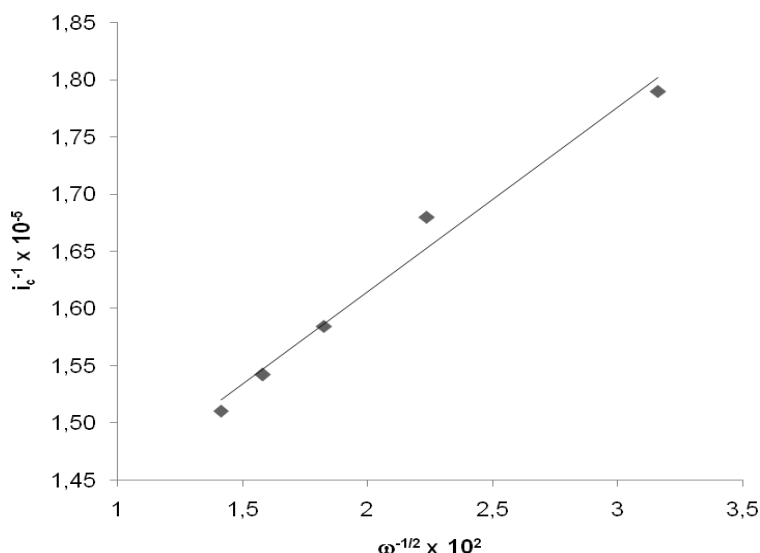
Figure 8. The change in current with rotation rate ($\omega^{-1/2}$) for 1 mM Cu (II)-Furdap complex in DMSO (0.1 M TBATFB).

3.3. Mechanism of the electrode reaction of Cu (II)-Furdap

The cyclic voltammogram of Cu (II)-Furdap represents a redox couple (Fig. 2). Cu (II)-Furdap molecule is reduced at -0.55 V (vs. Ag|Ag^{+}) by accepting electron and this electrochemical product is then oxidized at -0.31 V (vs. Ag|Ag^{+}) by losing this electron. The reversibility test shows that this redox system occurs at quasi-reversible conditions. On the other hand the adsorption test reveals that Cu (II)-Furdap molecules adsorb on platinum surface weakly. Consequently it was understood from this result that the peak observed in cyclic voltammogram is diffusion controlled not an adsorption peak [13]. Besides the number of electron transferred were found as 1 from both controlled potential coulometric and rotating disc electrode experiments in experimental error. It was also determined from cyclic voltammetry study that there was not any homogenous chemical reaction followed by electrochemical step. For this reason the electrode reaction mechanism for Cu (II)-Furdap compound is a one electron quasi-reversible electrochemical reaction.

From all of the results reported so far and considering the structure of Cu (II)-Furdap complex, the overall reaction describing the electrode reaction of Cu (II)-Furdap compound in DMSO is given in Scheme 1 below.
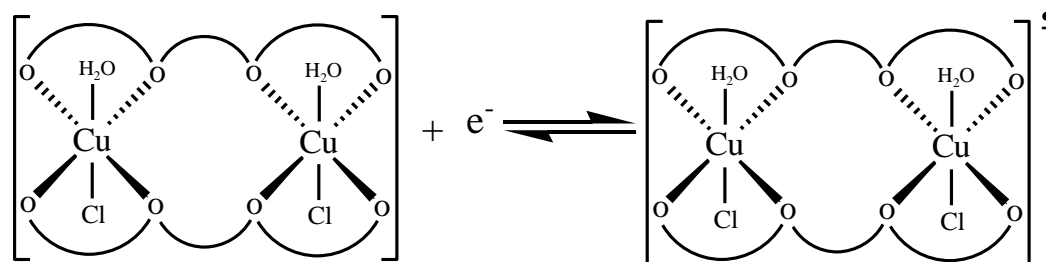

Scheme 1. Proposed mechanism for electroreduction of copper complex of Furdap.

3.4. Digital simulation and kinetics

Digital simulation of cyclic Voltammetry study is widely used application for estimating the reaction kinetics [11, 14 and 16]. After the all experimental studies mentioned above a theoretical study was executed in order to prove the proposed mechanism of the electrode reaction of Cu (II)-Furdap complex compound and to detect the kinetic parameters such as the heterogeneous rate constant (k_s), the electron transfer coefficient (α) and the diffusion coefficient (D) for the complex by using the digital simulation property of CHI660C software for cyclic voltammetry. In this study all of the experimental condition such as concentration (C), parameters of cyclic voltammetry, electrode area (A), standard potential of the redox system (E^0) and the type of mechanism were taken as the same. For these conditions the best theoretical voltammogram was determined by substituting the kinetic values (Fig. 9).
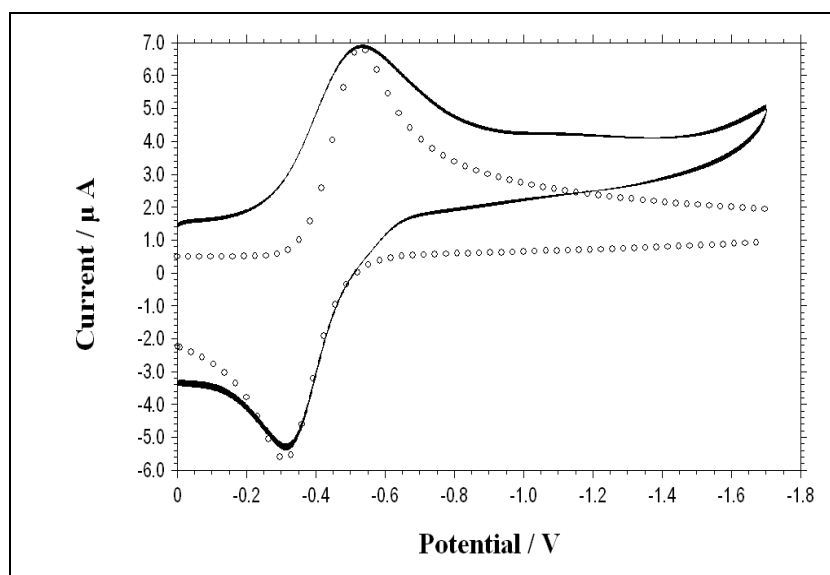
Figure 9. The experimental and theoretical voltammograms of Cu (II)-Furdap complex for 1 mM Cu (II)-Furdap solution in 0.1 M TBATFB at 0.1 V s^{-1} scan rate.

It can be seen from Fig. 9 that very good simulation curve was obtained. The difference between cathodic and anodic peak potential was adjusted by changing the k_s values. On the other hand D values affect the peak currents of those peaks. The cathodic and anodic peak shapes were differentiated by depending on the α.

All of the data used in and found from the digital simulation study for obtaining the best fitting cyclic voltammogram are listed in Table 1.

Table 1 Conditions and reaction kinetics for the digital simulation study.

Mechanism	System	Concentration (M)	D (cm^{2}s^{-1})	T (°C)	A (cm^2)	k_0 (cms^{-1})	E^0 (V)	α
A + e = B	Diffusive	1×10^{-3}	1.7×10^{-6}	25	0.07065	7×10^{-4}	-0.44	0.5

4. CONCLUSIONS

The electrochemical reductions of Furdap ligand and Cu (II)-Furdap complex were investigated at platinum surface in DMSO medium. The free ligand reduces irreversibly when the complex behaves a one-electron quasi-reversible redox system. The reduction potentials of the ligand and its copper complex are -0.80 V (vs. Ag|Ag$^+$) and -0.55 V (vs. Ag|Ag$^+$) respectively. It can be fairly understood from these potential values the reduction of complex is easier than that of the ligand. Since the ligand reduces irreversibly the reorganization energy of the electrode reaction is higher [17]. Even though the copper complex form of Furdap molecule has a more stable structure than free ligand form the electrochemical reduction of complex is easier. If we take a glance at the reduction mechanism for Cu (II)-Furdap complex in Scheme 1 it can be noticed that both the complex and the electrochemical product of the reaction are very similar. It can be expected that the reorganization energy of this reaction is smaller than that of free ligand [17]. As a conclusion the ligand and the complex show different behavior in this medium. The simulation study is beneficial in the evaluation of the electrode mechanism and determination of reaction kinetics.

References

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