

Electrochemical Behaviour of N₂O₂ Schiff base Cu(II) Complex in Non Aqueous Media at the Surface of Solid Electrode

V. Krishna¹ and S. Kondaiah

¹Department of Chemistry, Malla Reddy Engineering College (Autonomous), Maisammaguda
Dulapally, Secunderabad

ABSTRACT: The Electrochemical behaviour of newly synthesized Schiff base Cu(II) complex with O₄ donor group was investigated in a different non aqueous media using TEABF₄ and DMSO as a aprotic solvent at the surface of solid electrode(platinum) using TEABF₄ as a supporting electrolytes. Electrochemical behaviour studied by cyclic voltametry. It has been found that the compound exhibited one or two quasireversible oxidation peaks and the charge transfer coefficient (α) and diffusion coefficient (D) for this compound in solvent was obtained. The effect of scan rate and dielectric constant of solvent on the redox behaviour of compound was evaluated.

Keywords: Schiff Base; Electrochemical Behaviour; Solid Electrodes; Cyclic Voltametry

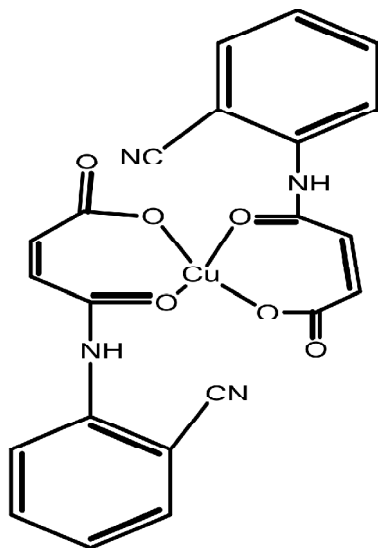
INTRODUCTION

Amide group contains two potential donor atoms the Oxygen and Nitrogen for coordination with metal ions. The coordination Chemistry of complexes contaminating amide group has been an important study in the recent years in view of structure and stability in-vivo reactions. It is also known that N & O atoms play a key role in the coordination of metals at the active sites of numerous metallo biomolecules. Chelating ligands containing N & O donor atoms show broad biological activity and are of special interest because of variety of ways in which they are bonded to metal ions. In the literature survey, there are papers in the synthesis, characterization and study of the electrochemical behaviour of new carboxamide ligands and there compounds at the surface of the solid electrodes and media. These were also found to possess pronounced biological activity [1, 2]. These are reported to exhibit potential antitumor activity [3]. At well et al [4] recently described new class of DNA interacting antitumor drugs based on N – [2 – (dimethylamino) ethyl] – 9 – amino acridine 4 – carboxamide [5] and various substituent's of carboxamide in order to impart them invivo activity [6,7]. Present work deals with the synthesis and characterization of complex of carboxamide ligand derived from maleic anhydride and 2-aminobenzonitrile and a

brief study of electrochemical behaviour of the ligand and the complex. A series of carboxamide ligands were synthesized but the cyclic voltametric data recorded for the sodium salt of carboxyamide in aqueous solutions at different P^H's reveals that only the derivatives of maleic amide compounds are electrochemically active and give two successive irreversible reduction waves at -1.2 V and -1.7 V, where as succinic amide and benzamide derivatives do not undergo any electrochemical reduction. From the above statement i.e. the absence of any electrochemical response for the succinamide and benzamide derivatives it can be concluded that the two irreversible reduction waves observed are due to electrochemical reduction of -C=C- of maleic amide derivatives but not due to the other possibilities of electrochemical reductions across the carbonyl C=O or azometanine C=N of the amide and carboxylate moiety, because succinamide and benzamide derivatives which also contain these centres donot respond in this range. The electrochemical reduction potentials of carbonyl and nitrile groups in all these compounds might be more negative than the hydrogen evolution potential.

EXPERIMENTAL

All the chemicals and solvents used for the synthesis were of analar grade and were obtained



Structure of Complex

commercially. Methanol was distilled, the solvents like petroleum ether and diethyl ether were distilled and stored over sodium-wire, and the double distilled water used throughout is obtained by re distilling demineralized water. The deuterated solvents, d_6 -DMSO, CD_3OD , Aldrich chemical company. The new ligands prepared are characterized by elemental analysis, IR, HNMR and MASS spectral data, the purity of the compounds is tested by TLC.

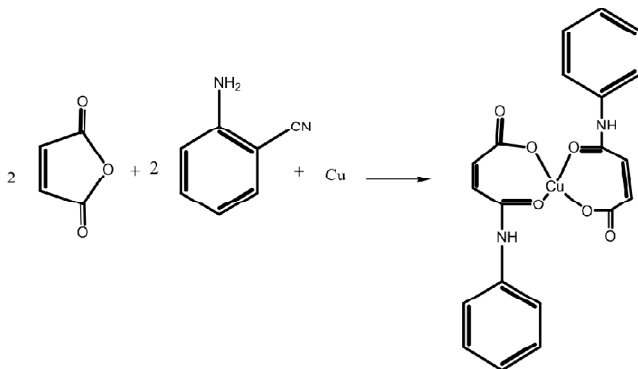
Elemental analysis were carried out by using a Perkin Elmer C,H,N analyses 2400 analytische chemie der technische universitat Berlin, germany). IR spectra of the ligands and their metal complexes were recorded in KBr pellets or Nuzol on Perkin Elmer-283 spectrophotometer. The scanning rate was 6 minutes in the range of 4000-600 cm^{-1} . The FTIR spectra were recorded on JASCO FT/IR 5300 spectrophotometer at University of Hyderabad, the scanning rate was 4 minutes in the range of 4000-400 cm^{-1} . PMR spectra were recorded at Technical University Berlin using Bruker 80 si instrument and University of Hyderabad using Jeol 100 MHz FT NMR spectrometer. The ESR spectra of Cu(II) complexes in solid state at room temperature were recorded on Jeol-JES FE -3X model at University of Hyderabad. The MASS spectra of all the ligands were recorded using a Varian MAT CH-7 instrument at 70.e.v. at T.U.Berlin. Cyclic voltametric studies were carried out on EG and G Princeton applied research corporation's PARC model 264 A3 polarographic analyzer/stripping

voltameter comprising of PARC model 303 A electrode system.

SYNTHESIS OF LIGAND

Preparation of 2-carboxy (N-benzonitrile) maleic amide (CBnMAH): 9.8 gm (0.1mol) of maleic anhydride was taken in 20 ml of chloroform, 11.8gm (0.1M) of 2-amino benzonitrile was taken in 20ml of chloroform are taken in a 100ml round bottom flask and was refluxed on water bath for 30 minutes, light yellow colored product was obtained and filtered, washed with chloroform and recrystallised from methanol. The melting point of the product is 130°C(yield 85%).

Preparation of metal complex (Cu(BnMA)₂): 20 ml of ethanolic solution containing 0.5 gm of cupric acetate was added to 50ml of ethanolic solution containing 1.08 gm CBnMAH. A green colored solid was separated and digested on water bath for 30 minutes. The isolated product was washed with ethanol and dried in vacuo (yield 85%).



RESULTS & DISCUSSION

Electrochemical Studies

Normal pulse, differential pulse polarographic and cyclic voltammetric studies were carried out on EG and Princeton Applied Research Corporation's PARC model 264 A₃ polarographic analyzer. The three electrodes are stationery mercury drop working electrode, platinum wire auxillary electrode and Ag/Agcl reference electrode. Controlled Potential Coulometry (CPC) was performed with the help of PARC model 173 potentiostat coupled with PARC model 179 integrated. A coulometric cell of three electrode configurations consisting of a mercury pool cathode, a platinum wire counter electrode, separated from main solution by a glass frit and

SCE as reference electrodes were used. A typical electrochemical run, followed in the cyclic voltammetry, normal pulse polarography, differential pulse polarography and fast polarography involved the transfer of 1ml of $10^{-3}M$ stock solution of electroactive species followed by the addition of 4ml of appropriate buffer of supporting electrolyte ($1 \times 10^{-1}M$) Nitrogen was purged for 4 minutes before the electrochemical run was recorded.

P^H metry was done using Elico Model L1-120 Digital pH meter which was periodically calibrated with well known buffer. The electrochemical studies Cu(II) complexes were performed on PARC model 173 cyclic voltammetry, consisting of potentiostat, a function generator and a voltammetry 0150 X-Y recorded. The three electrodes used were working platinum electrode (BAS), auxillary electrode (Pt wire) and reference electrode is an aqueous saturated calomel electrode (SCE). In each electrochemical run 1mmol of the complexe was dissolved in dimethyl sulphoxide containing 0.1M tetraethyl ammonium tetra fluoro borate supporting electrolyte. DMSO was used as electrochemical solvent, without any further any purification tetraethyl ammonium tetra fluoro borate ($TEABF_4$) Aldrich supporting electrolyte was dried for 6h at $50^\circ C$ under reduced pressure before use. A stream of 99.99% of pure nitrogen was followed continuously during the experiments in order to purge the space above solution.

Effect of scan Rate on C.V. Profiles

At lower scan rates in C.V. the second wave is faint whereas it becomes more prominent as the scan rate increases. This can be seen from the C.V. profile as shown in Fig. 1. The dependence of peak current on the scan rate for the first and second waves is shown in Fig. 2. From the curve it is obvious that the supply of reducing species to the electrode surface resulting in the first wave is diffusion controlled, whereas that giving the second wave is governed by the kinetics of generation of reducible species. Further, the potential scan was held at an intermediate potential between the two peak potentials and scanned even faster forward in the negative direction, no second peak is observed. This phenomenon is shown in Fig. 3. For a representative sample, these results indicate an ECE mechanism which suggests that the reducible species responsible for the second curve which is generated from post first wave and that is chemically unstable.

The differential pulse polarogram recorded for the sample solution gave two peaks. From the relation:

$$W_{1/2} = 90.12/n$$

Where $W_{1/2}$ is the width in mv at half height of the peak, the number of electrons "n" is calculated and found that both the waves are corresponding to each one electron transfer process. This fact is further confirmed by the controlled potential coulometry performed at two set of potentials one after the first peak and other after the second. The number of electrons obtained from the first set is one, whereas from the second is two, confirming the above conclusions. Based on the above investigations and the derived data, the following scheme of ECE mechanism can be suggested for the present studied systems.

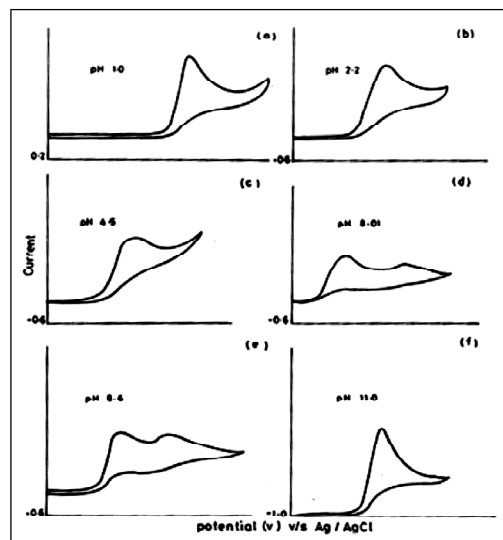


Figure 1: Cyclic Voltammograms of CBnMAH (2×10^{-3}) at different Ph values (Scan rate 50 mV S^{-1})

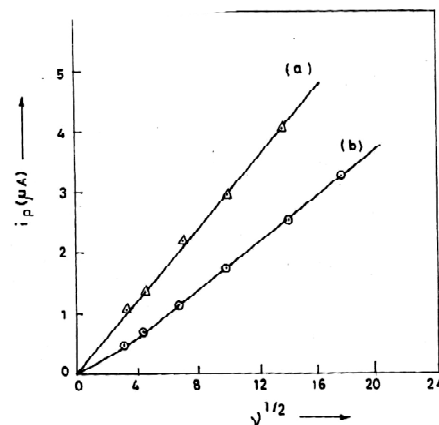


Figure 2: Plot showing the effect of scan rate on peak currents of C.V. profiles of CBnMAH in 8.01 pH ammoniacal buffer at a Scan rate 50 mV S^{-1}

Table 1
Successive Electron Transfer Reduction Potentials of Carboxamide at P^H 8.01

Carboxy amide	1 st peak				2 nd peak			
	<i>Tast</i>	<i>NPP</i> ^b	<i>DPP</i> ^b	<i>C.V.</i> ^b	<i>Tast</i>	<i>NPP</i>	<i>DPP</i>	<i>C.V.</i>
	<i>E</i> _{1/2}	<i>E</i> _{1/2}	<i>Ep</i>	<i>Ep</i>	<i>E</i> _{1/2}	<i>E</i> _{1/2}	<i>Ep</i>	<i>Ep</i>
CBnMAH	-1.260	-1.255	-1.255	-1.250	-1.705	-1.700	-1.705	-1.695

a. All potentials in volts versus Ag/AgCl reference electrode.

b. NPP normal pulse polarography; DPP Diffusion pulse polarography; CV Cyclic voltametry; *E*_{1/2} half Wave potential; *Ep* peak potential

c. No reduction transfer below -1.90 V where hydrogen evolution commences.

Table 2
Diffusion Coefficients of Carboxamide (L) in aqueous 8.01 P^H buffer at room Temperature

Maleic amide	<i>Ilkovic</i> ^b	Normal ^c pulse	<i>D</i> ₀ ^a X 10 ⁶		<i>Mean</i>	<i>[i_d(n)/i_d(T)]^e</i>
			<i>Randles</i> ^d sevick			
CBnMAH	1.609	1.616	1.604	1.609	1.609	3.195

a in cm²; b- From equation 1; c- From equation 2; d- from equation 4; e- From equation 3

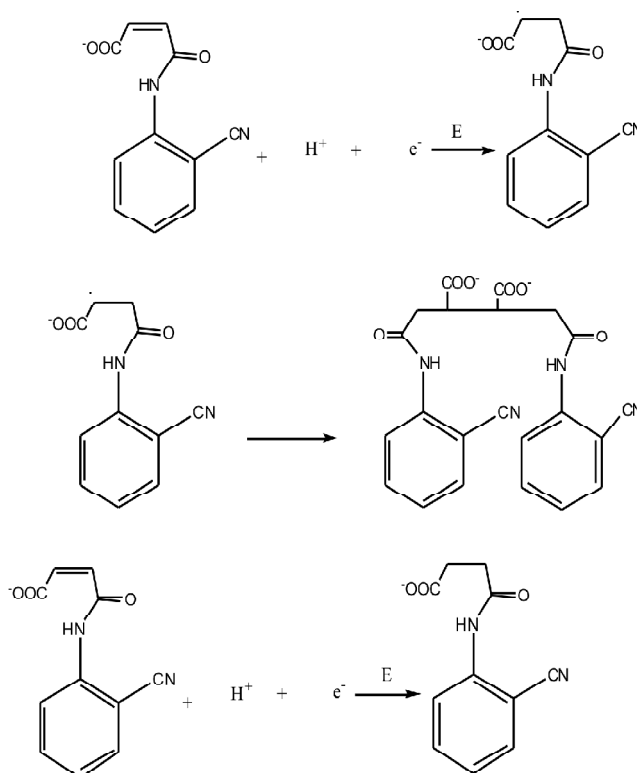
Table 3
Coulometric data of Carboxamides in aqueous media at Hg electrode

Maleicamide	<i>p</i> ^H	Potential applied	Moles of ligand Taken	Total No. of Coulombs registered	No. of Electrons permole ligand
CBnMAH	0.1 M HCl	-0.8 V	3.24 X10 ⁻⁵	6.254	2

Scheme of ECE Mechanism

The first electrochemical reduction wave observed at -1.20 V is due to the electron transfer step (a) and second reduction wave at -1.70 V is due to (c). the free radical produced by (a) is unstable and undergoes a chemical dimerisation shown at step (b) rather slowly expending the free radical reactant for step (c) hence the low intensity of second wave at low scan rates. Hence the low intensity of second wave at low scan rate is increased the electrochemical potential for the electron transfer process at step (c) is quickly reached before the free radical generated from (a) is depleted through step (b) and hence the improvement in peak height of the second wave at faster potential scan is observed as shown in Fig. 4.

This mechanism is in good agreement that of electrochemical reduction of maleic acid reported in literature [8]. Soon after the electrolysis at -1.80.V was over the solution is slowly acidified, resulting on the succinic equivalent of L^{•-}, confirming the mechanistic step at (a), (b) and (c). Also after the completion of electrolysis at -



Scheme of ECE mechanism

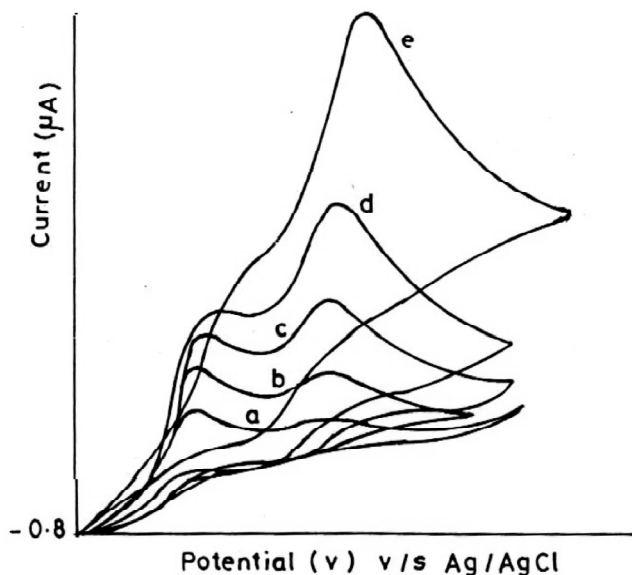


Figure 4: C. V. profiles of CBnMAH at different scan rates ($mV S^{-1}$), a) 20 b) 50 c) 100 d) 200 e) 500

1.80 V the solutions is acidified to obtain a colorless powder that is insoluble in water but soluble in alkaline media with an intake of two equivalents of base. This observation confirms the mechanistic step at (b). Diffusion coefficients for maleic amide derivatives are calculated assuming that the first electron transfer step in Table 1 (a) is diffusion controlled (followed by two fast protonation steps in quick succession). From the fast polarography, diffusion Coefficient, D_0 of the reducible species can be calculated using the relation [9].

$$I_d(T) = 708 n D_0^{1/2} C_0 m^{2/3} T^{1/6} \quad (1)$$

Where $i_d(T)$ - limiting current in microamperes from the fast polarography, n - the number of electrons involved in the electron transfer, C_0 is the bulk concentration of oxidant in millimoles per litre, 'm' mass of mercury in $mg sec^{-1}$, T is the sampling interval which in this instrument is drop time in seconds. After the first electron transfer process is nearly diffusion controlled As evident from the linearity of plots i_p of versus $V^{1/2}$ in cyclic voltammetry, where $V^{1/2}$ is the scan rate. Usage of equation (1) for the diffusion coefficients of L is justified. Diffusion coefficients thus calculated are collected in Table 2.

From normal pulse polarography [9] also the D_0 s are calculated are calculated using the relationship.

$$i_d(n) = Nn F A D^{1/2} C_0^*/\pi^{1/2} \Delta T \quad (2)$$

where $i_d(n)$ = diffusion current in normal pulse polarogram, F = Faraday constant in coulombs, A = the drop area in cm^2 , ΔT = pulse duration in seconds. The D_0 s calculated are collected in Table 2. The relationship between $i_d(T)$ and $i_d(n)$ is given by:

$$\frac{i_d(T)}{i_d(n)} = \frac{(3T)^{1/2}}{7\Delta T} \quad (3)$$

if drop time T is same in both experiments under similar studied experimental conditions. In the present experimental conditions T is 1 second, and ΔT is 40 m sec. The ratio turns out ideally about 3.273. The close agreement is found between the expected and observed values.

Further proof for the fact that the first electron transfer is diffusion controlled comes from the close agreement of D_0 s calculated from equation 1,2, with those obtained from the Randles sevcik equation pertaining to cyclic voltammetry as:

$$i_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} v^{1/2} C \quad (4)$$

where i_p is peak current, V = the scan rate in mv per second D_0 calculated from the C.V. technique are collected in Table 2.

In the pH above 9.4, the derivatives of maleicamides do not undergo successive electron transfer process but undergo a one step two electron irreversible reduction process at higher negative potentials [-1.90 V]. The plausible scheme type reduction may not be seen due to the poor concentration of H^+ ions at pH's greater than 9.4 which might have been observed by the over whelming hydrogen evolution current. However, hydrogen evolution process is shifted to beyond -2.00 V in basic media.

Electrochemical Studies of Cu(II) Complexes

The oxidation of Cu(II) / Cu(III) is well known [10-12] in many mononuclear, tri- and tetrapeptide complexes with potentials varying from +0.4 to +1.0 V. Here, we wish to report the redox behavior of Cu(II) complexes. Typical cyclic Voltammograms of $[Cu(CBnMA)_2]$ at different scan rates are shown in Fig. 5. The relevant cyclic voltammetric data for $[Cu(CBnMA)_2]$ complex is collected in Table 4.

All the complexes show distinct redox couple in positive potential range. The anodic peak observed around at +0.4 V is due to the Oxidation of Cu(II) to Cu(III), and the cathodic peak at 0.10

V is due to the reduction of Cu(III) to Cu(II). All the Cu(II) complexes show quasireversible response [13] with E^0 near + 0.3 V vs S.C.E. The E^0 values for the couple Cu (II)/Cu(III) reported in literature [14, 15] is in the range of +0.35 V to 1.0 V vs S.C.E. However, the present complexes exhibit Cu (II)/Cu (III) quasireversible couple at potentials in the range of +0.25 - 0.35 V. The observed and relative ease with which the present complexes are oxidized to Cu(III) equivalents may be attributed to the fact that the Cu(II) systems reported in literature possess their metal ions in a relatively more shielded environment by the ligand framework whereas our complexes .Have an open structure with distorted square planar geometry. This causes the complexes to lose the electrons relatively at lower anodic potentials. Apart from quasireversible nature, the i_{pa}/i_{pc} ratio is 1.0 within experimental error for different scan rates. The ratio $i_{pc}/V^{1/2}$ is practically constant and the peak separation " E_p " increases slowly within an increase in scan rate. At higher scan rate the cyclic voltammograms approach reversibility this can be seen from the convergence of the ratio i_{pa}/i_{pc} to 1.0 at higher scan rates. This may be due to the fact that at higher scan rates the proposed following conformational isomerisation reaction is superceded by the reconversion of Cu(III) to Cu(II).

To identify the possible ligand oxidations the corresponding Ni(II) and Co(II) complexes are subjected to cyclic voltammetric investigations. None of these complexes showed any well defined peaks in the region -1.0 v to + 1.0 v, only a broad anodic peak appears at 1.0v, but on scan reversal no peak appears. This indicates that the oxidized species undergo rapid chemical decomposition once generated electrochemically. We, therefore assign this quasireversible response to the redox reactions. On scanning further on either side none of the Cu(II) complexes showed any well defined cyclic voltammetric response. However, when scanned in negative direction beyond -0.9 V a broad peak appears and on scan reversal an intense peak centering around -0.2 V appears, which is attributable to [16] the oxidation of copper deposited at the electrode, as the data shown in table -3.6.4.

In controlled potential coulometric tests 0.000 V it can be ascertained that one mole of electrons per mole of the substrate is spent in the reduction of Cu(III) \rightleftharpoons Cu(II) during this process the

solution turns from pale green to orange color in Table 3.

On the basis of above results it can be concluded that the Cu(II) complexes show a quasireversible Cu(III)/Cu(II) couple, while Ni(II) and Cu(II) complexes do not show any well defined peaks in the cyclic voltammograms. The generation of Cu(III) in the cyclic voltammetric time scale may be associated with strong equatorial ligation by Oxygen/Nitrogen donor atoms [17, 18]. The absence of reversibility in case of Cu(II) complexes generated from the ligands of phthalic anhydride origin as evident from elongation of the cathodic peak may be attributed to the stabilization of Cu(III) system due to conformation of isomerization of electro generated Cu(II) complex.

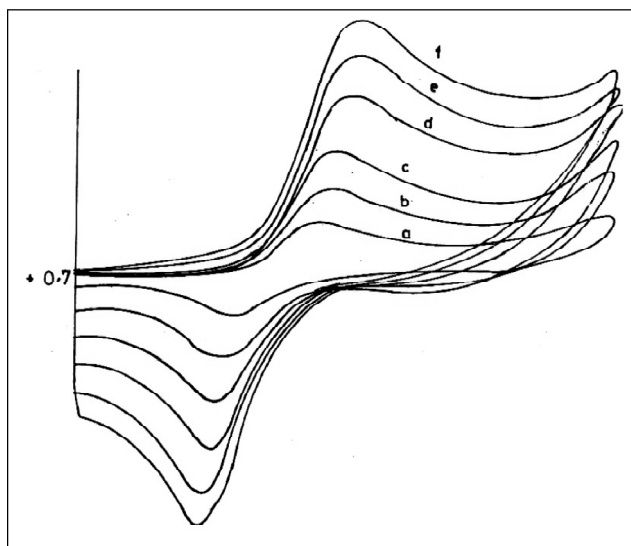


Figure 5: Cyclic Voltammogram of $[Cu(CBNMA)_2]$ in DMSO ($1 \times 10^{-3} M$) at different scan rates ($mV S^{-1}$), a) 20 b) 50 c) 100 d) 200 e) 500

Table 4
Cyclic Voltammetric data of $[Cu(CBNMA)_2]$ in DMSO ($1 \times 10^{-3} M$) and TEABF₄ (0.1M)

Scan rate (mv)	$E_{pc(v)}$	$E_{pa(v)}$	$^*E_p(mv)$	$E^0(v)$	i_{pa}/i_{pc}
20	0.157	0.364	189	0.251	0.67
50	0.140	0.367	222	0.251	0.82
100	0.125	0.380	255	0.252	0.97
200	0.090	0.400	310	0.245	1.00
300	0.070	0.425	355	0.247	1.01
400	0.069	0.433	364	0.251	1.00

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