Mechanism and Cyclic Voltammetry of $Cu(en)_2X_2.nH_2O$ Complexes in Some Nonaqueous Solvents

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Abstract:

The electrochemical studies of solid 2.0 X 10^{-3}M $Cu(en)_2X_2.nH_2O$ (n=0 for X=ClO_4^-, NO_3^-, SCN^-, and n=1for Br^-) in dimethylsulfoxide, acetonitrile , and dimetylformamide /0.1M tetrabuthylammonium perchlorate , have been carried out by cyclic voltammetry. The electrode process shows two electro reduction and two chemical steps(CECE) mechanism. The reduction potentials of $Cu(en)_2(ClO_4)_2$ shift in the order DMF→ DMSO → AN contrary to one's expectation. For $Cu(en)_2(NO_3)_2$ and $Cu(en)_2(SCN)_2$, the reduction potentials are more negative in DMSO relative to DMF as expected. In DMF, the reduction potentials Epc_1 shift anodically in the order: $Cu(en)_2(ClO_4)_2$ → $Cu(en)_2(NO_3)_2$ → $Cu(en)_2(SCN)_2$ indicating that Epc_1 is also dependent on the nature of the anion, X

Keywords: $Cu(en)_2X_2.nH_2O$, Nonaqueous Solvent, Voltammogram, CECE mechanism, Reduction potential

1. Introduction

Ethylenediamine is a classic chelate ligand. Many of its metal complexes have been investigated and their structures solved (Monchak, et al 2009). Nature of the solvent has considerable influence on the composition and stability of complexes formed (Pandey and Dugar, 2001) and the choice of the medium in which to carry out various chemical process is difficult due to the lack of knowledge of the general regularities of the influence of solvent on the thermodynamic characteristics and kinetic of the reaction (Shamin, 1995).

The growing interest on copper complexes with various N- donor ligands especially di-amines, comes mainly from their capability of combining structural flexibility, mimicking of protein active sites, ease of preparation and stabilization of both oxidation states of the metal usual in biological systems(Dias et al, 2010).

Complexes of the type $Cu(en)_2X_2$(X=ClO_4^-, NO_3^-, Br^-, SCN^-, en=ethylenediamine), has been synthesized and their structure studied (Brown and Lingafelter, 1964; Proctor, et al, 1968). Continued interest in these complexes centres mainly on spectral (Cannas, et al, 1973; Subramanian and Jolicoeur, 1974; Sastry, and Asadullah, 1979; Hinge, et al , 2012). and thermal(Shamin, 1995; Langfelderova', 1983; Suresh, et al, 1991) methods with little or no attention on the electrochemical methods.

The study of metal complexes in non-aqueous solvents has attracted much attention (Pandey, and Dugar, . 2001) due to the wide spread of non-aqueous solvents in wide range of pure and applied chemistry which leads to quick development of science and technology(Saeid et al, 2011).

The study of homogeneous chemical reactions coupled to oxidation-reduction processes at electrode surface is a major subject in electrochemistry as well other scientific fields. In particular the common use of homogenous reactions involving the electro generated species has been extensively examined by means of different electrochemical techniques such as cyclic voltammetry(A'ngela] , et al,2009) specially for the electro reduction/oxidation of metal complexes(Nigoric and Kujundzic , 2002).

This paper is a result of cyclic voltammetry of complexes of $Cu(en)_2X_2$(X = ClO_4^-, NO_3^-, Br^-, and SCN^-), in order to determine their electrode mechanism in dimethylsulfoxide (DMSO), acetonitrile(AN), and dimethylformamide (DMF) solvents

2. Experimental

2.1 Material

The oxidation reduction potentials where obtained with a BAS Model CV-IB (Indiana USA) cyclic voltammograph instrument having an electrochemical cell with a three electrodes system. The working electrode was a glassy carbon electrode (GCE). Platinum wire was used as auxiliary electrode, while a saturated calomel electrode (SCE) as reference electrode with $E^o = 0.242V$ vs NHE. The voltammograms were recorded on an X-Y recorder. Ethylenediamine and Tetrabuthylammoniumphosphate (TBAP) were obtained from Aldrich (USA). DMSO, AN, DMF were spectroscopy grade and were used as such. The copper salts were of analytical reagent grade

2.2 Synthesis

The complexes under study were prepared according to known methods, viz $Cu(en)_2X_2$ (X= ClO_4^-, NO_3^-, Br^-) (Proctor, et al; 1968), $Cu(en)_2(SCN^-)_2$; (Brown and Lingarfelter ,1964).

2.3. Electrochemical methods

All the cyclic voltammetric experiments were done in an inert atmosphere achieved by purging the cell solutions with nitrogen gas for about 20 minutes and maintained over the cell solution during the recording of the voltammograms. The nitrogen gas was purified by bubbling through alkaline vanadous sulphate solution and passing through a calcium sulphate drying tube before bubbling through the cell solution(s).Freshly prepared solutions were used in carrying out the experiments at $25^0C\pm1^0C$ in 0.IMTBAP supporting electrolyte.

3.Results and discussion:

3.1. In dimethylsulfoxide

$2.0 \times 10^{-3}MCu(en)_2X_2$ (X=ClO_4^-, NO_3^-) complexes show similar cyclic voltammogram (CV) features (figure 1) in the potential window +40 to -0.70± 0.2V. Two cathodic peaks c'' and c_1 at $\approx$ -450 and -580 mV $\pm$- 5mV with corresponding anodic peak a_1 at -485 $\pm$ 5mV with scan rate 25mVs^{-1}. The redox couple (c_1/a_1) was at best slow electron transfer, attributed to $Cu(en)_2^{2+/+}$. The cathodic peak c_1'' may be attributed to irreversible reduction of some other copper (II)-en complex species present in solution. At potential limit of -0.75V, the CV of $Cu(en)_2(ClO_4)_2$ shows two new anodic peaks a_2(broad) at $\approx$ -280mV and a_1' at -30mV (figure 2). Expanding the potential window to -1.20V, the CV is characterised by the reduction peaks at -0.585mV (c_1) and -1.05V (c_2) followed by three oxidation peaks a_1, a_2, and a_1' at -485, -350 and +50mV respectively (figure 3). The irreversible reduction peak c_2 involves $Cu^{+/0}$ reduction and deposited copper metal at the electrode surface is also demonstrated by the significantly intense anodic peak, a_1'. Anodic peaks a_2 and a_1' may be attributed (Jiang, et al, 2010) to the electrochemical oxidation of Cu(0) to Cu(I) species and to the electrochemical oxidation of Cu(I) to Cu(II) species , respectively.

The CV for $Cu(en)_2(NO_3)_2$ shows similar features as observed for per chlorate analogue, except that the cathodic peak c_2 shifted anodically and the anodic peak, a_2 is not observed. The anodic peak, Epa_1' depended on the switching potential $_\lambda$ (figures 1 and 2).

The CV for $Cu(en)_2Br_2.H_2O$ with scan rate 25mVs^{-1} (fiqure4 A) shows an oxidation peak +330mV (a_1) in the cathodic scan from +100 to -500mV and a reduction peak at -70mV (c_1') in the anodic scan from +100 to -200mV. This clearly shows that peaks c_1' and a_1' are dependent of each other. Further scanning from + 0.10 to -0.85V exhibits an irreversible peak c_1''at $\approx$ -440mV and a redox couple Epc_1 = -550 and Epa_1 = -440mV (figure 4). These clearly demonstrate the presence of at least two electro active copper (II)-en complex species in solution.

On the positive- going scan in the potential window +0.10 to + 0.60V, the CV for $Cu(en)_2(SCN)_2$ with scan rate 25mVs^{-1} exhibits a redox couple, a_1'/c_1' (Epa_1' = +310mV and Epc_1' = +200mV), while on the negative going scan in the potential window from + 0. 10 to -0.80V shows one irreversible reduction peak at -85mV (c_1)

and a redox couple c_1/a_1 with Epc_1 = -520 and Epa_1 = -400mV. The CV features are observed throughout the cyclic voltammetric time scale 10 to 300mVs^{-1}.

DMSO is a highly polar versatile solvent which displays high salt solubility to produce well conducting solutions with a wide electrochemical widow.

3.2. In Dimethylformamide

The CVs for 2.0 x 10^{-3}M(en)$_2$(SCN)$_2$ with scan rate 10 and 25mVs^{-1} in the potential window +0.20 to 0.80V shows an irreversible reduction peak c_1 at -470mv. However, in the positive Cu(en)$_2^+$ appears to be chemically very unstable in DMF as compared to that in DMSO.

The CV for Cu(en)$_2$(ClO$_4$)$_2$ and Cu(en)$_2$(NO$_3$)$_2$ show a redox couple with reduction potentials Epc_1, = -580 and -530mV respectively. In the case of nitrate complex, a second anodic peak a1' at +40mV is observed at v ≤ 10mVs^{-1}suggesting mechanism involving one-electron charge transfer followed by chemical reaction (EC mechanism) (Nicholson, and Shain, 1964) for the latter.
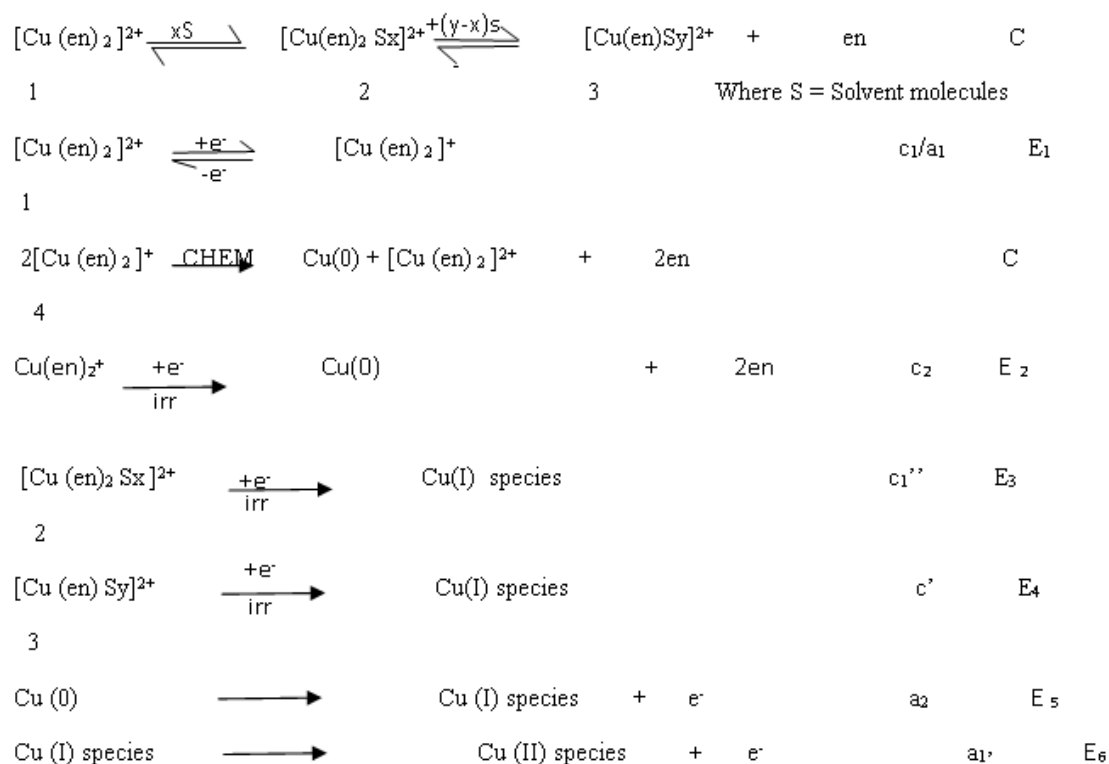
3.3.In acetonitrile

The CVs for Cu(en)$_2$(ClO$_4$)$_2$ exhibit redox couple Epc_1 =-610 and Epa_1 = - 445mv only, with scan rate ≥ 50mVs^{-1} in the potential window -0.40 to -0.70V. At potential window > -0. 70V, a remarkable current increase is detected. The positive scan from – 0.80V, however, shows a considerable hysteresis in the current followed by the oxidation peak a_1 and a new oxidation peak a_2 at - 240mV which may be attributed to the electro-oxidation of copper(0) to copper(I) species.

3.4.Analysis of CV responses

The first couple c_1/a_1 with different scan rates show the following (Nicholson, and Shain, 1964). With increasing of scan rate , both anodic and cathodic current increases and the cathodic peak potentials have shifted towards negative values, while anodic peak potential move towards more positive values. This observation suggests that the electrode process is diffusion controlled in DMSO, DMF and AN. The peak potential separation ΔEp increases with increasing scan rate, demonstrating that the electrode process is quasi-reversible. The peak current ratio (Ipa_1/ Ipc_1) is less than unity, indicating that the electron-transfer is followed by chemical reaction. Also, the plot of Ipc_1/C vs $v^{1/2}$ (figure 6) is linear but with a large positive intercept in all the solvents, this also demonstrates that the electrode process is not fully diffusion controlled and that the electron transfer is followed by chemical reaction(EC mechanism)(Nicholson, and Shain, 1964; Prasad, 1994).

The effect of various organic solvents on the electronic spectra of mixed copper(II) chelates with N,N,N,'N,'-tetramethylethylenediamine(tmen) and bidentate ligand of type en, glycine, oxalate or acac as studied (Fukuda , and Sone, 1972) shows an approximately linear relation between frequency of absorption maxima, vmax and donor number (DN) of the solvent, and , the larger the coordination ability of the solvent, the corresponding vmax value, the order or change being CH_3NO_2 >$C_2H_4Cl_2$> CH_3COCH_3> C_6H_5CN > CH_3CN >MeOH >H_2O>DMF >DMSO. This solvent effect has been explained by assuming the coordination of the solvent molecules above and below the chelate cation which is in solution. On the basis of these observations, the following reaction pathway may be proposed to explain the observed electrochemical data:

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$$[Cu(en)_2]^{2+} \xrightarrow{xS} [Cu(en)_2 Sx]^{2+} \xrightarrow{+(y-x)s} [Cu(en)Sy]^{2+} + en \qquad C$$

$$\underset{1}{} \qquad\qquad \underset{2}{} \qquad\qquad \underset{3}{} \qquad \text{Where S = Solvent molecules}$$

$$[Cu(en)_2]^{2+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [Cu(en)_2]^+ \qquad\qquad c_1/a_1 \qquad E_1$$

$$\underset{1}{}$$

$$2[Cu(en)_2]^+ \xrightarrow{CHEM} Cu(0) + [Cu(en)_2]^{2+} + 2en \qquad C$$

$$\underset{4}{}$$

$$Cu(en)_2^+ \xrightarrow[irr]{+e^-} Cu(0) \qquad\qquad\qquad + 2en \qquad c_2 \qquad E_2$$

$$[Cu(en)_2 Sx]^{2+} \xrightarrow[irr]{+e^-} Cu(I)\ species \qquad\qquad c_1'' \qquad E_3$$

$$\underset{2}{}$$

$$[Cu(en)Sy]^{2+} \xrightarrow[irr]{+e^-} Cu(I)\ species \qquad\qquad c' \qquad E_4$$

$$\underset{3}{}$$

$$Cu(0) \longrightarrow Cu(I)\ species + e^- \qquad a_2 \qquad E_5$$

$$Cu(I)\ species \longrightarrow Cu(II)\ species + e^- \qquad a_1' \qquad E_6$$

The above reaction pathway duly suggest a two electroduction and two chemical steps (CECE) mechanism

3.5 Solvent and Counterion effect

The donor number (donocity) of these solvents increases in the order AN (14.1)<D MF <DMSO(29.8)(Laoire, at al ,2010). On the basis of the donor number of these nonaqeous solvents, it is expected that the reduction potential of $Cu(en)_2^{2+/+}$ in DMSO should be most negative, however, a comparison of reduction potential (Epc_1) of $Cu(en)_2(ClO_4)_2$ in different nonaqueous solvents reveals that a shift of ($\Delta Epc_1 = 20mV$) occurs from DMF$\rightarrow$ DMSO $\rightarrow$AN contrary to one's anticipation.

In the case of $Cu(en)_2(NO_3)_2$ and $Cu(en)_2(SCN)_2$ however, Epc_1 in DMSO are negative relative to that in DMF as expected. In DMF, the reduction potential (Epc_1) shifts anodically in the order: $Cu(en)_2(ClO_4)_2 \rightarrow Cu(en)_2(NO_3)_2 \rightarrow Cu(en)_2(SCN)_2$ indicating that Epc_1 is also dependent on the nature of the anion.

4. Conclusion

The electrochemical behaviour of these complexes in nonaqueous solvents (DMSO, DMF and AN) is rather complex as it comprises several reactions, namely, the electroxidation and electro reduction of copper(0), copper(I) and copper(II) species preceded or followed by chemical reaction.

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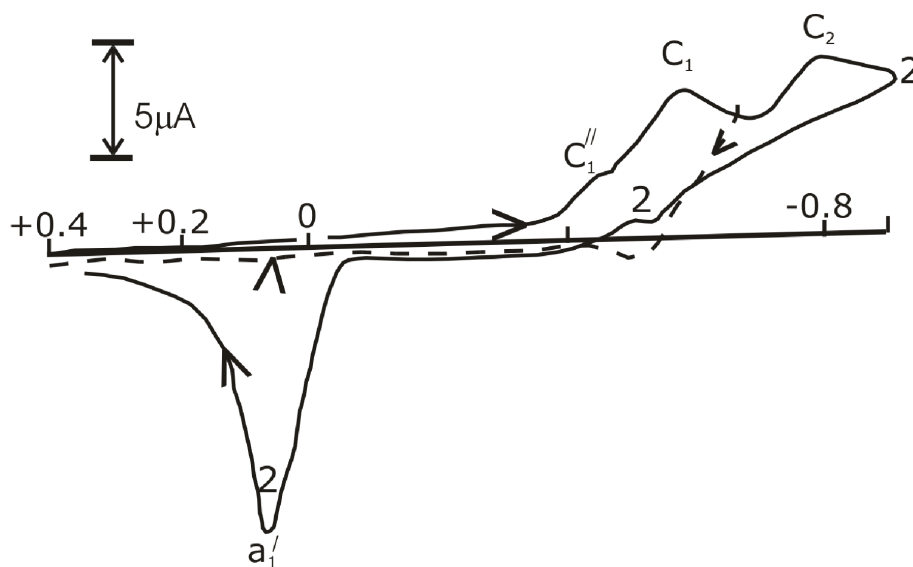

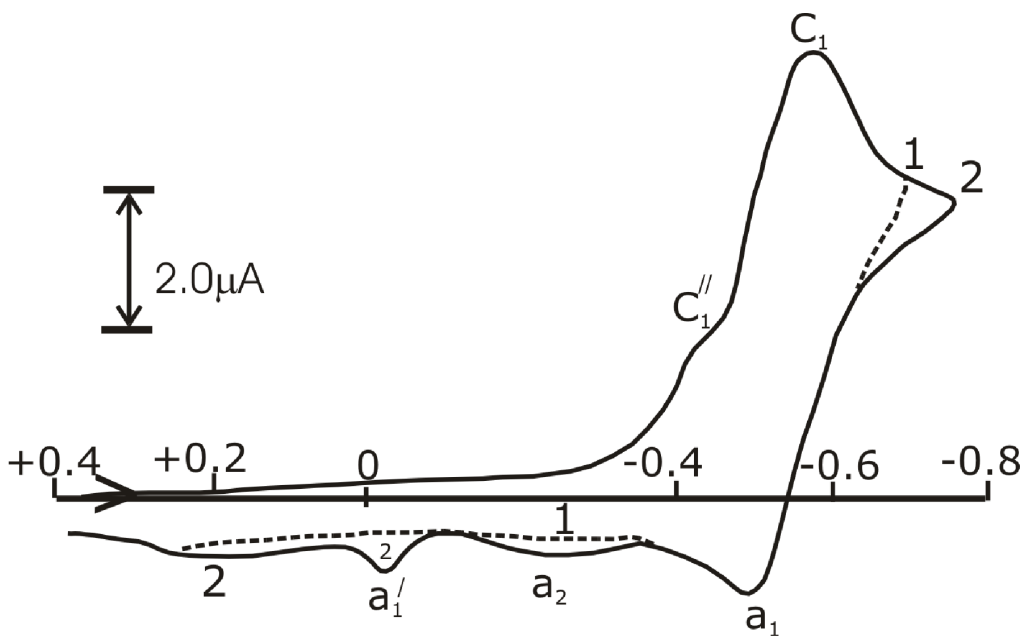FIGURE 1:   CV of 2.0 x 10 $^{-3}$M Cu(en)$_2$(NO$_3$)$_2$ in DMSO at 25 mVs^{-1}

FIGURE 2:   CV of 2.0 x 10 $^{-3}$M Cu(en)$_2$(ClO$_4$)$_2$ in DMSO at 25 mVs^{-1}

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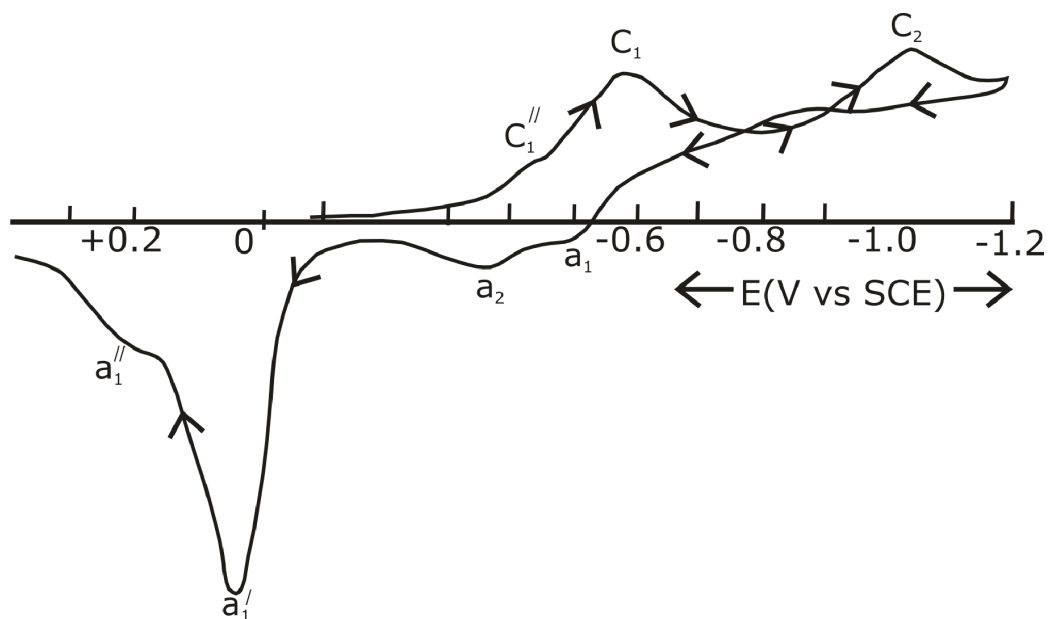
FIGURE 3:   CV of 2.0 x 10^{-3}M Cu(en)$_2$(ClO$_4$)$_2$ in DMSO at 25 mVs^{-1}
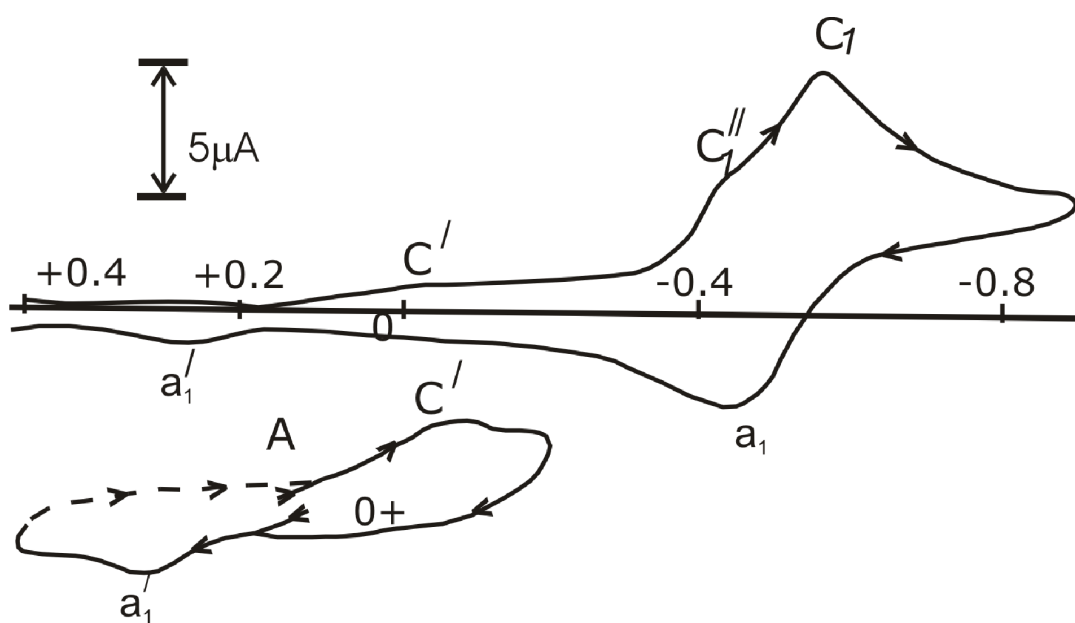
FIGURE 4 and 4A: Cvs of 2.0 x 10^{-3}M Cu(en)$_2$ Br$_2$.H$_2$O in DMSO at 25 mVs^{-1}
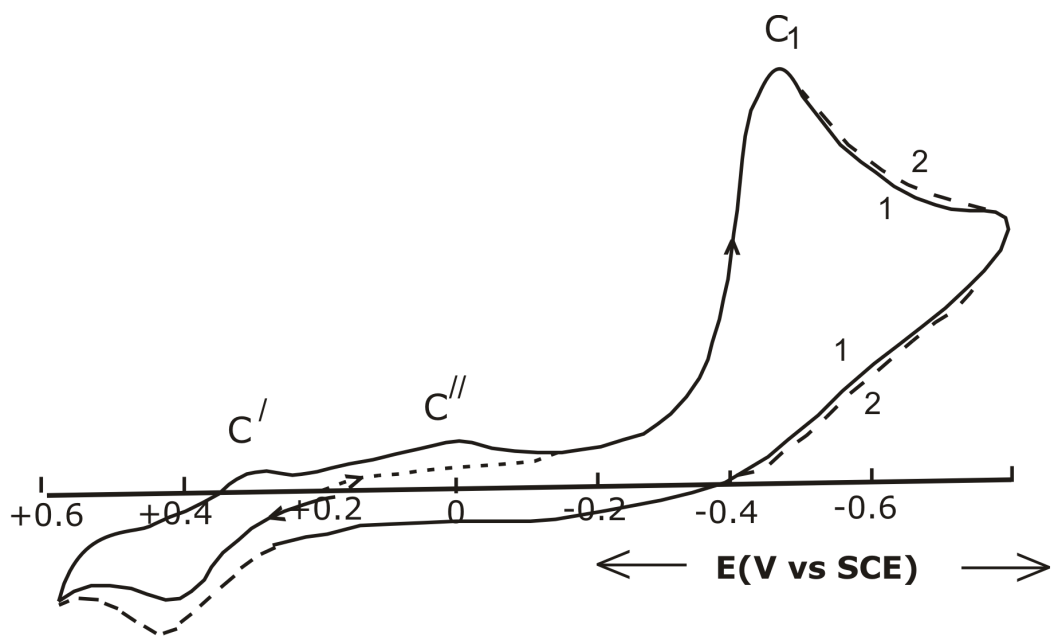
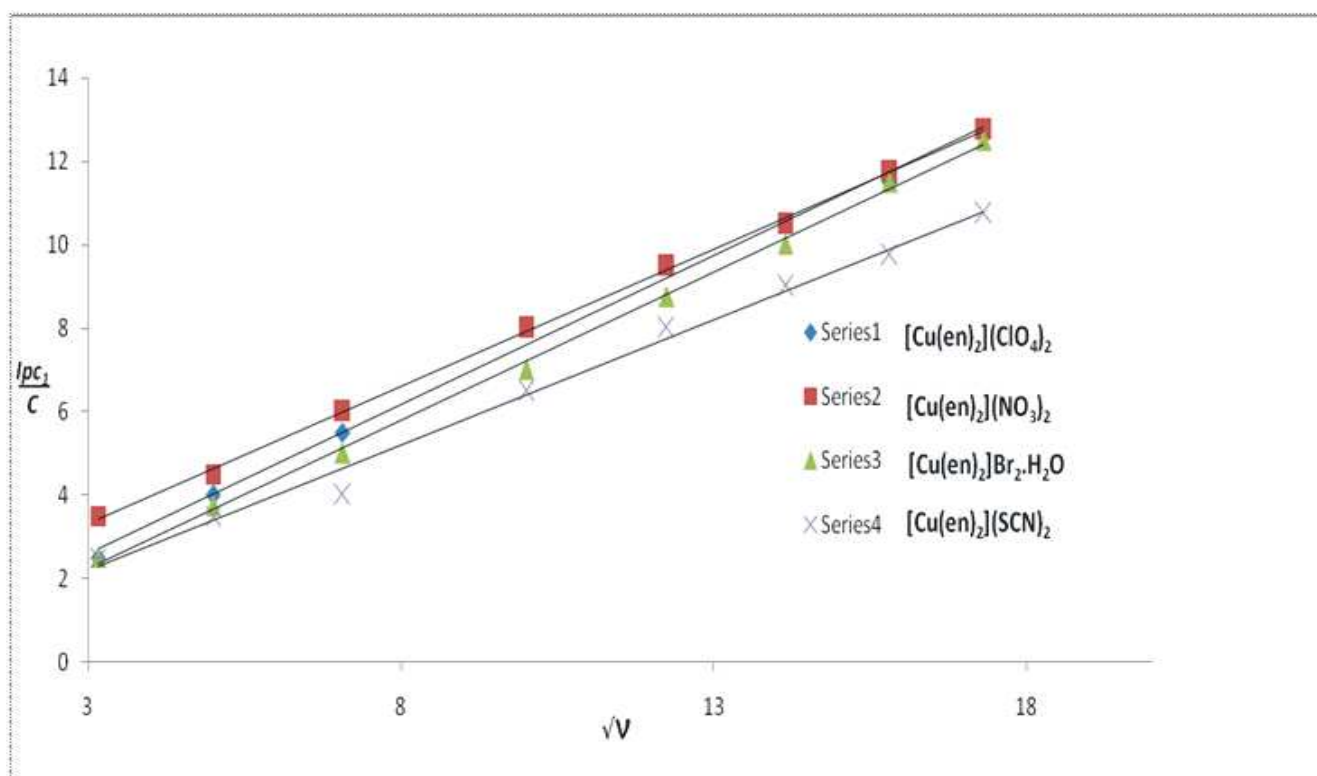FIGURE 5: CV of 2.0×10^{-3}M Cu(en)$_2$ (SCN)$_2$ in DMSO at 25 mVs^{-1}

FIGURE 6: Plot of Ipc$_1$ vs v$^{1/2}$ for 2.0X10^{-3}M Cu(en)$_2$X$_2$ in DMSO

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