

Cyclic Voltammetry of Aqueous Copper (II)- Pentamethyldiethylenetriamine Systems at Various pH Values.

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Abstract: The redox behaviour of Copper(II)-pentamethyldiethylenetriamine(pmdt) system has been studied in aqueous 0.2M NaClO₄.6H₂O supporting electrolyte at glassy carbon electrode(GCE) at various pH and pmdt concentration values by means of cyclic voltammetry. The cyclic voltammetric parameters are calculated. The first couple Cu^{2+/+} showed a diffusion controlled, quasi-reversible, one electron charge transfer at GCE. The intensities of both cathodic and anodic peak current are increased with increasing scan rate consistent with Randles-Sevcik equation. The cyclic voltammograms indicated the presence of more than one complex specie in solution followed by complicated anodic response except for 1:100 Cu(II)-pmdt system at pH11.04. A linear behaviour of peak current versus square root of scan rate indicated that the electrochemical processes are diffusion controlled for 1:100 Cu(II)-pmdt at pH 7.10.

Keywords: Cyclic Voltammetry, Copper (II) Complex, pentamethyldiethylenetriamine, aqueous medium, quasi-reversible, diffusion-controlled.

I. 1.Introduction

Copper is an important trace element for plants and animals (Gaudin,1967; Seigel,1974) and is involved in mixed ligand complex formation in a number of biological processes(Patel et al 2004; Bjerrum, 1941;). Also, the synthesis of low molecular weight copper (II) complexes mimicking the SOD activity has been challenging to bioinorganic chemists and for many years efforts have been made to obtain compounds with high catalytic activity (Patel, 2003). Pentamethyldiethylenetriamine (PMDT) is a tridentate nitrogen donor ligand with donor groups suitably placed for forming 5-membered chelate rings. Such tridentate ligands are known to form stable mononuclear and binuclear copper (II)complexes which have been a subject of extensive studies(Patel, 2004) . Copper complexes are commonly air and moisture stable, having informative and easy to obtain UV-vis and EPR spectroscopic signatures. The stereochemical flexibility of copper (II)complexes also means that they adopt a wider range of coordination geometries shown for transition metal ion(Hathaway, 1984).

pH is an important factor influencing complex formation and stability. Most chelating agents are unstable in low pH whereas at high pH, metals tend to form insoluble hydroxides which are less accessible to chelating agent (Flora & Pachauri 2010). Electrochemical studies of Cu(II) reduction in various electrolytes in the acidic and basic pH range have been studied (Shaikh et al 2011). In nitrate and perchlorate media the Cu(II) reduction was pH dependent (Anderson & Shain 1976). In nitrate and chloride solution, copper reduction is complete in pH range pH 2<pH 4.5 (Mecucci & Scott).

Diethylenetriamines are highly caustic, soluble in ethyl alcohol, in water, and have almost the same physiological properties like ammonia (Quattara & Diaco 2006). Due probably to their high causticity, their electrochemical oxidation is not too much investigated.

Cyclic voltammetry offers several distinct advantages over some methods of analysis because of ease of and rapidity to work outside pH range of glass electrodes and to use non-protic media (Quattara & Diaco 2006). This in turn permits straight forward determination of kinetic parameters (Munoz et al 1988). As cyclic voltammetry is the most effective and versatile technique in the diagnosis of complex electrode mechanism (Shaikh, 2011), in the present study, this technique is employed to examine the electrochemical behaviour of Cu(II)-pmdt system in aqueous NaClO₄ medium under conditions of various pH and ligand concentrations.

II. Materials and Method

Analar grade copper perchlorate and sodium perchlorate were procured. Pentamethyldiethylenetriamine was obtained from Aldrich (USA). To adjust the pH of the solution, perchloric acid and sodium hydroxide (BDH) were used. The cyclic voltammetric data were obtained with BAS model CV-IB (Indiana, USA) cyclic voltammograph instrument having an electrochemical cell with a three electrode system. The working electrode was a glassy carbon electrode (GCE). Platinum wire was used as an auxiliary electrode, while a saturated calomel (SCE) as the reference electrode with E⁰=0.242V vs NHE. The voltammograms were recorded on an X-Y recorder. The pH of the working solutions were obtained with a digital

pH meter Model MD21 after calibration using pH 4.00, 7.00, and 10.00 commercial standard buffers. All the 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(s) 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 the cell solution(s). The glassy carbon electrode (GCE), was polished with fine alumina powder on wet polishing cloth for about 5 minutes. The shiny black mirror like electrode surface was then thoroughly washed with double distilled water. Fresh solutions of copper(II)-pmdt complexes were prepared by mixing the appropriate quantities of metal ion and ligand solutions to obtain 1:1, 1:2, 1:10, and 1:100 molar ratios, 1mM Cu(ClO₄)₂·6H₂O. The pH of the solutions was adjusted by controlled addition of sodium hydroxide or perchloric acid solution as required. All experiments were carried out at 25°C and all solutions were prepared in double distilled water

III. Results and Discussion

The cyclic voltammetric study of 1:1 mM Cu(II)-pmdt system at pH 7.10, 9.10 and 10.20 was investigated at GCE within the potential windows of +0.60 to -0.70V at 25mV/s. Figure 1 is the cyclic voltammogram (CV) at pH 7.10. A cathodic sweep with an initial potential of +0.30V shows one small irreversible reduction peak, c_1'' at -245mV and a quasi-reversible reduction peak, c_1 at -405mV which is followed by three oxidation peaks at -300mV(a_1), +185mV(a_1') and +455mV(a_1'') in the reverse sweep. The peak potentials are slightly changed in the second cycle. The appearance of two reduction peaks c_1'' and c_1 clearly demonstrates the presence of more than one Cu (II)-complex species in solution at pH 7.10. On increasing the scan rate to 100mV/s, the second oxidation peak a_1' broadened and the third a_1'' disappeared. This clearly shows that EC mechanism (Nicholson & Shain, 1964; Becker et al 1982; Harmalkar et al 1983; Pandeya et al 1994), is involved in the electrode process.

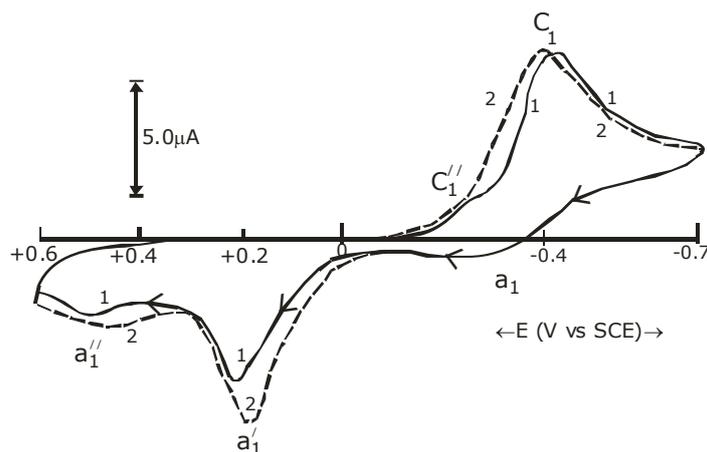


Figure 1: CV of 1:1 Cu (II) pmtdt system, 1mM Cu (ClO₄)₂ at pH 7.10 and 25mV/s

At pH 9.10, the CV features differ from that at pH 7.10 in that the peak current $I_{pa_1'}$ is smaller and its potential has shifted towards negative direction at pH 9.10. Also, a new cathodic peak c_1' at -210mV appeared in the second cycle which may be attributed to the reduction of electro-oxidised Cu(II) species to Cu(0) (figure 2).

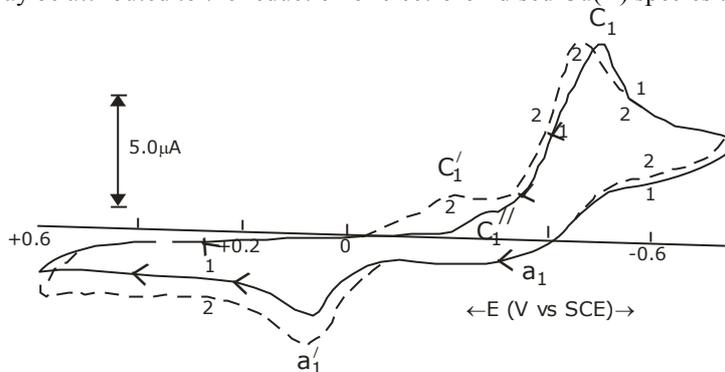


Figure 2: CV of 1:1 Cu (II) pmtdt system, 1mM Cu (ClO₄)₂ at pH 9.10 and 25mV/s

At pH 10.20, the CV features are similar to that at pH 9.10 except that a very small new oxidation peak a_2 at -250mV assigned to electro-oxidation of copper(0) into copper(I) species appeared. Also, the oxidation peak a_1'

further shifted cathodically. When the potential window was increased to -1.05V, an irreversible additional cathodic peak, c_2 corresponding to Cu^{+0} redox change appeared. However, in the reverse scan, the oxidation peak, a_1' appeared as stripping peak followed by another oxidation peak a_1'' at pH 7.10. At pH 9.10, a rather more complicated oxidation processes a_1 , a_1'' and a_1''' appeared. The CV features at 10.20 differ from that at pH 9.10 with respect to oxidation processes occurring at a_2 , a_1' and a_1'' . The broad oxidation peak a_2 is absent while a_1' is very large at pH 9.10.

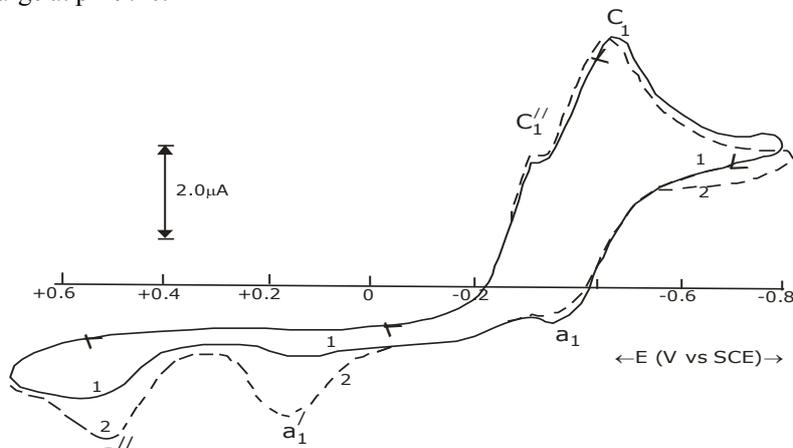


Figure 3: CV of 1:2 Cu (II) pmtdt system, 1mM Cu (ClO₄)₂ at pH 7.10 and 10mV/s

For 1:2mM Cu(II)-pmdt system ,at pH7.10, the CV (figure 3) features scanned at 10mV/s showed two reduction peaks c_1'' and c_1 and three anodic peaks a_1 , (small), a_1' (broad) and a_1'' (broad). The cathodic peak current $I_{pc_1'}$ is larger as compared to 1:1mM Cu(II)-pmdt system at pH 7.10. This indicates that both the species are prominent in 1:2 ratio at this pH. The oxidation peaks a_1' and a_1'' are absent at $v \geq 100\text{mV/s}$ (figure 4). This clearly demonstrates that EC mechanism(Nicholson & Shain,1964; Becker et al 1982; Harmalker et al 1983; Pandeya et al 1994), is involved in the electrode process. Furthermore, an increase in pH to 9.10 results into decrease in the peak current $I_{pc_1'}$.

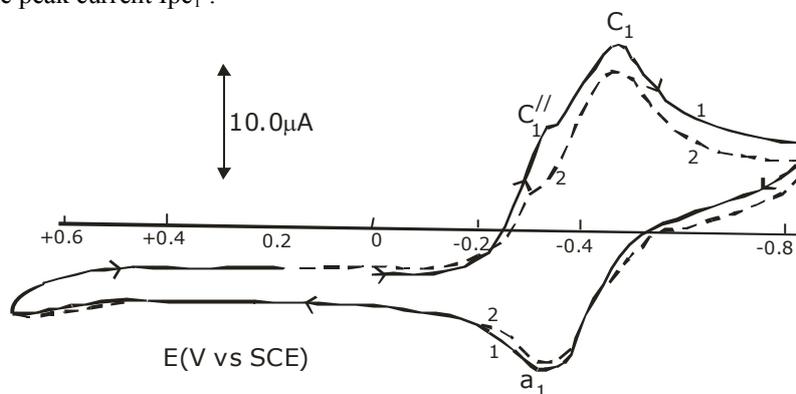


Figure 4: CV of 1:2 Cu (II) pmtdt system, 1mM Cu (ClO₄)₂ at pH 7.10 and 100mV/s

Figure 5 is the CV for 1:10 mM Cu(II)-pmdt system at pH 7.10. A comparison of figure 5 with figure 3 shows that the CV features for 1:10 and 1:2 Cu(II)-pmdt systems are similar at pH7.10 except that the second anodic peak a_1' is absent in the first cycle in the case of 1:10mM Cu(II)-pmdt system. However, the oxidation peak, a_1' appears and the magnitudes of the anodic peak currents I_{pa_1} , $I_{pa_1'}$ and $I_{pa_1''}$ are increased in the second cycle for 1:10 Cu(II)-pmdt system. The CV features for 1:10 Cu(II)-pmdt system at pH 9.10 and 11.04 are similar to that at pH 7.10. Similarly, the CV features for 1:100 Cu(II)-pmdt system are similar to that for 1:10 molar ratio at pH7.10 (figure 5), except that only a very small oxidation peak a_1'' appeared in the 1:100 molar ratio. At pH 11.04, a well defined quasi-reversible redox couple c_1/a_1 appeared in the case of 1:100 Cu(II)-pmdt system.

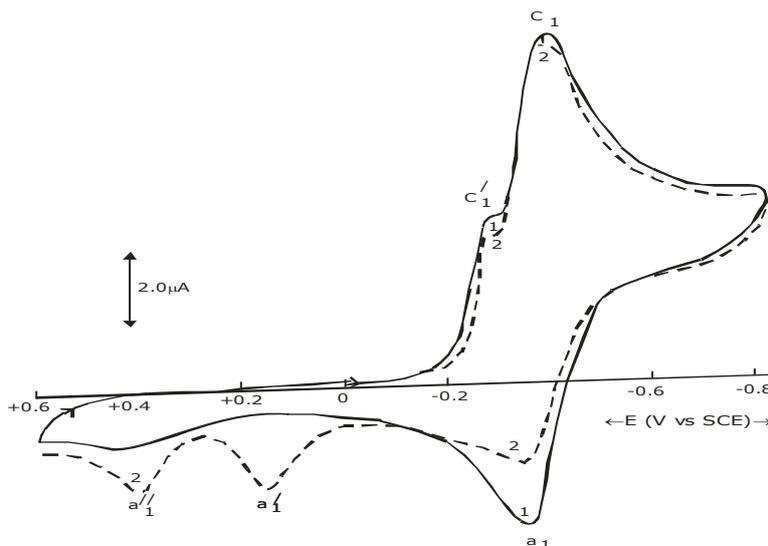


Figure 5: CV of 1:10 Cu (II) pmtd system, 1mM Cu (ClO₄)₂ at pH 7.10 and 25mV/s
 The effect of scan rate on the electrochemical response of Cu(II)-pmtd system for the first couple Cu⁺² was examined and the best fit was found for 1:100Cu(II)pmtd at pH7.10 between scan rate 25 to 250 mV/s.

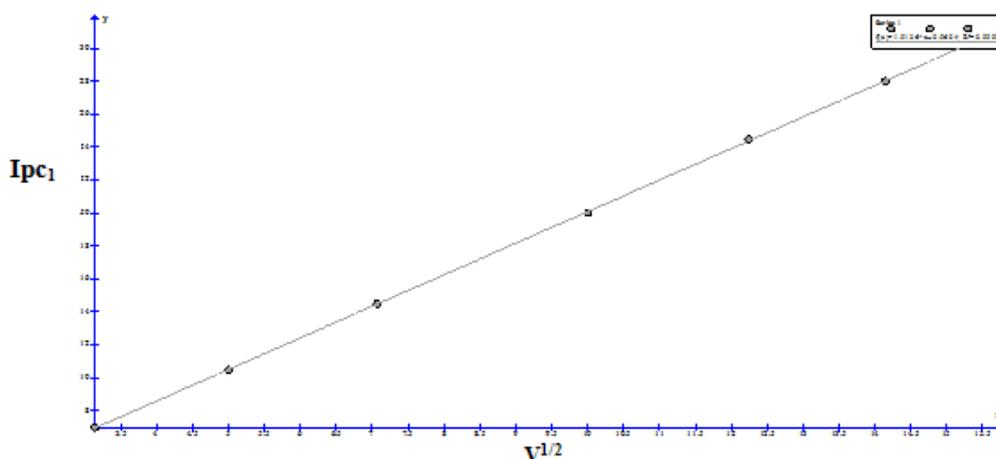


Figure 6: Dependence of Ipc₁ with V^{1/2} for 1:100 Copper (II) pmtd system in 0.2NaClO₄ at pH 7.10

The cathodic (Epc₁) and anodic (Epa₁) peak potentials, peak currents (Ip₁) and peak current ratio (Ipa₁/Ipc₁) and peak separation ΔEp are gathered in table 1. With increasing scan rate, both cathodic and anodic peak current increases and the cathodic peak potentials have shifted towards negative values while anodic peak potentials move towards more positive values. These observation suggest that the electrode process is diffusion controlled at GCE(Shaikh et al 2011; Nicholson and Shain 1964).In figure 6, it is apparent the peak current for 1:100mMCu(II)pmtd system has a linear relation with square root of scan rate with a correlation coefficient of 0.9999 and intercept of +0.9604. Also the Slope of log Ipc₁ vs log v (figure7) was 0.46 which is in good agreement with the theoretical expected value of 0.50 for purely diffusion controlled process (Shaikh et al 2011; Deepa, et al 2012). This indicate that diffusion controlled conditions dominate the mass transfer mechanisms of the monomer to the electrode surface(Shaikh et al 2011).

Table 1 Peak currents and peak potentials at different scan rate of 1:100 Cu(II)-pmtd system at pH 7.10

Scan rate mV/s	Epc ₁ /mV	Epa ₁ /mV	Ipc ₁ /μA	Ipa ₁ /μA	Ipa ₁ /Ipc ₁	ΔEp/mV
10	-415	-350	7.0	4.5	0.64	75
25	-415	-340	10.5	6.5	0.61	80
50	-420	-335	14.5	9.0	0.62	80
100	-430	-330	20.5	12.0	0.60	90
150	-435	-330	24.5	14.5	0.59	95
200	-440	-330	28.0	17.0	0.60	100
250	-440	-320	31.2	18.5	0.59	110

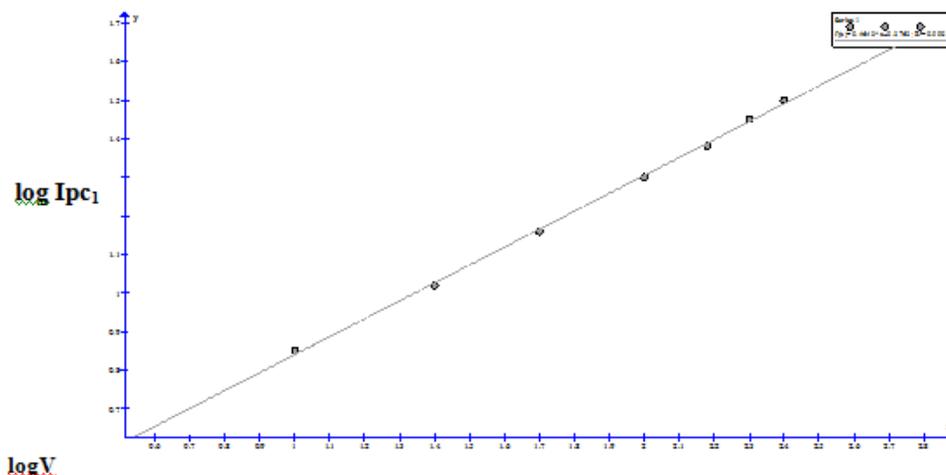


Figure 7: Dependence of log Ipc₁ with log V for 1:100 Copper (II) pmdt system in 0.2NaClO₄ at pH 7.10

The ratio of the oxidation peak current to its reduction counterpart I_{pa_1}/I_{pc_1} , is 0.64-0.59 which remains approximately constant with increasing scan rate. Also, the ΔE_p is between 75 to 110. It is increased with the variation of scan rate (table 1). These suggest that the redox process is quasi-reversible rather than reversible (Shaikh et al 2011). The analysis of the electrode process for 1: 10mM Cu(II)-pmdt system shows that at pH 7.10, a larger peak separation, ΔE_p coupled with a systematic increase of ΔE_p with scan rate (110-165) occurred. With the increase of scan rate, negative shift in E_{pc_1} and a corresponding positive shift in E_{pa_1} were found. These behaviours indicate kinetic limitations in charge transfer (Shaikh et al 2011) with the redox system at this pH and for 1:10 molar ratio.

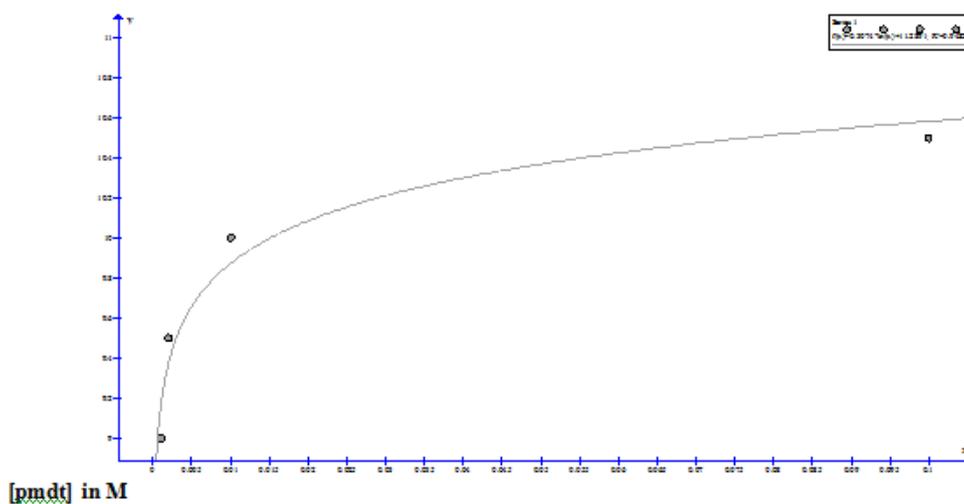


Figure 8: Dependence of log Ipc₁ with concentration of pmdt for Cu (II) pmdt system in at pH 7.10

The plot of I_{pc_1} versus concentration of pmdt in the range of $.001 \times 10^{-3}$ to $.1 \times 10^{-3} M$ showed that at pH 7.10 I_{pc_1} increases with increase in concentration of pmdt (figure 8) while the opposite was observed at pH 9.10 (figure 9). This indicates that probably, at pH 7.10, the complex species in solution are stabilized. However at pH 9.10, probably destabilization of complex species due to the steric effect of bulky pmdt is pronounced contrary to expectation since at high pH, OH^- ions are expected to participate in formation of stable Cu(II) complex species such as $[Cu(pmdt)(OH_2)]^{2+}$ or $[Cu(pmdt)(OH_2)](ClO_4)_2$ (Patel, et al 2004) in solution.

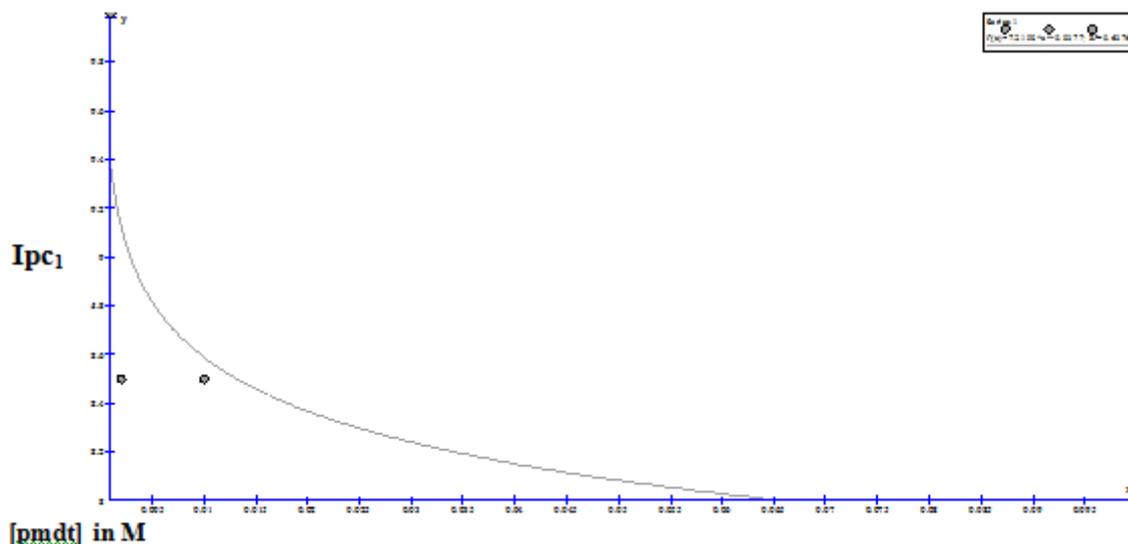


Figure 8: Dependence of $\log I_{pc1}$ with concentration of pmdt for Cu (II) pmdt system in at pH 7.10

IV. Conclusions

The results obtained from cyclic voltammetry indicate unambiguously that under the experimental conditions there are more than one Cu(II) complex species in solution except in 1: 100 Cu(II)-pmdt system at pH 11.04 where a well defined Cu^{II}/Cu^{I} redox couple is obtained. The appearance of complicated anodic peaks is an interesting observation which needs characterisation using additional technique. The result obtained confirms that the electrode process is best fit for 1:100mM Cu(II)pmdt at pH 7.10.

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