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VOLTAMMETRIC STUDIES OF THE INTERACTION OF COPPER(II) WITH MELAMINE IN BRITTON-ROBINSON BUFFER SOLUTION

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Abstract

The redox behavior of Cu(II), and its interaction with melamine in Britton-Robinson (BR) buffer solution at different pH (0.63 - 4.06) has been studied using cyclic voltammetric method at a glassy carbon electrode (GCE). Cu(II) exhibits two cathodic peaks of different heights and an anodic peak at lower pH (0.63, 1.73 and 3.02). The weak cathodic peak is less prominent at higher pH and disappeared at pH $\geq$ 4.06. At all studied pH, Cu(II) interacts with melamine at different Cu(II) and melamine molar ratios. However, at pH 3.02 a strong interaction occurs at 1 : 2 molar ratio. This is perhaps the most favorable condition for Cu(II)-melamine interaction.

Key words: Britton-Robinson buffer, cyclic voltammetry, copper(II), melamine, glassy carbon electrode

Introduction

Melamine (2,4,6-triamino-1,3,5-triazine; Mel) (Scheme 1) is a highly symmetrical ligand with six potential N-donor atoms to coordinate to transition metals (Nockemann and Meyer 2004). Despite its apparent promise as a ligand, investigations of melamine in the area of coordination chemistry are remarkably few. The likely reasons are (i) the insolubility of melamine in all common solvents, except hot water, and (ii) the extensive hydrogen bonding tendency of melamine hinders the formation of coordination bond with the metal ions. The metal compounds of melamine that was reported till now are exclusively limited to group IB metals (Cu, Ag, etc.) and categorized as (i) melaminedi-cation (Scheme 2) salts associated with coordination anions (Colombo *et al.* 1985, Scott *et al.* 1988), (ii) inorganic salts co-crystallized with melamine (Zheng *et al.* 1999), and (iii) a few serendipitously formed coordination complexes (Zhu *et al.* 1999, Goodgame *et al.* 1999, Meyer *et al.* 2009, Wiles *et al.* 2006).

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Scheme : Structural representation of (1) melamine, and (2) melaminedi-cation

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There has been a report of a molecular zwitterionic complex $[MelH^+HgCl_3^-](Mel)$ (Nockemann 2002), in which Hg(II) contacts to one of the three ring N atoms of melamine. A manganese compound of melamine, $(H_5O_2)(MelH^+)_3$ $[Mn^{II/III}(pydc)_2]_2$ $(OH)(pydcH_2).5H_2O$ has been reported recently (Aghabozorg *et al.* 2009), in which charge is balanced by conversion of one of the water molecules to a hydroxide ion.

Melamine is unlikely to be digested or broken down in human body system although its many molecular characteristics have some similarities with protein molecules. If it is ingested in large amount, it may act as an important precursor of induced stones in the human kidney. Loosely bound metal ions, Cu(II), Co(II), Zn(II) etc. that are present in the blood serum in micromolar levels possibly interact with the melamine under *in vivo* condition and may cause serious renal problems. Thus the investigations of the interaction of melamine with different metal ions are believed to be implicative for better understanding of the melamine stone production mechanism in the human body.

Even though there are some reports on the preparation and characterization of metal-melamine complexes in the literature, the electrochemical investigations of the interaction of melamine with different metal ions are rare. It seems to be an unexplored field of research. Here the redox behavior of Cu(II) and the interaction of Cu(II) with melamine in aqueous BR buffer by cyclic voltammetric technique at various pH and molar ratios are reported. Because of its wide applications in electrocatalysis, sensors, batteries, microelectronics, electroplating and biochemical catalytic systems, copper(II) is targeted first for this study.

Experimental

Materials

Analar grade $CuCl_2.2H_2O$ was purchased from E. Merck, India and used without further purification. Analytical grade melamine (BDH, UK) was used in this study. Acetic acid (BDH, UK), phosphoric acid (Merck, Germany), and boric acid (Merck, Germany) were procured. Sodium hydroxide (Merck, Germany) and perchloric acid (BDH, UK) were used as it is available. All aqueous solutions were prepared in doubly distilled water obtained from a Milli-Q water purification system. Experiments were carried out at room temperature.

Equipments

A cylindrical electrochemical cell consisting of three electrodes system such as glassy carbon as the working electrode, Ag/AgCl (satd. KCl) as the reference electrode and a platinum wire as the counter electrode was used for cyclic voltammetric measurement. Voltammetry was performed using computerized electrochemical system, Model HQ-2040 developed by Advanced Analytics, USA. The pH of different solution was measured with a pH meter (Microprocessor pH meter, model pH 211, HANNA Instruments).

Methods

Preparation of Britton-Robinson (BR) buffer solution

Britton-Robinson buffer, a universal pH buffer is performed for the range pH 2.0 to 12.0. Although the present intention is to investigate the electrochemical behavior of Cu(II) in whole pH range it was not possible due to the precipitation of Cu(II) at higher pH. For the preparation of BR buffer solution, 0.04 M H_3BO_3, 0.04 M H_3PO_4 and 0.04 M CH_3COOH solutions were prepared, separately. The three solutions were then mixed together with same volume ratio. The desired pH values were adjusted by adding 0.2 M NaOH or $HClO_4$ solution. The pH of the buffer solution was measured using the pH meter.

Preparation of metal ion and melamine solution

Metal ion solution of 0.5 mM Cu(II) was prepared using Britton-Robinson (BR) buffer. For the complexation study, 0.5, 1.0, 1.5 and 2.0 mM melamine solutions were also prepared using BR buffer.

Preparation of glassy carbon electrode (GCE) surface

GCE was polished with fine alumina powder of 0.3 μ or lower size on a wet polishing cloth. For doing so a part of the cloth was made wet with deionized water and alumina powder was sprinkled over it. The GCE was then polished on this surface by pressing softly the electrode against the polishing surface for about 5 - 10 min. A shiny black mirror like electrode surface was then thoroughly washed with deionized water.

Preparation of cell for voltammetry

First of all, the cell was filled with desired volume of the experimental solution and the Teflon cap was placed on the cell. The purging glass tube together with electrodes was inserted through the holes. Under computer controlled stirring, experimental solution was deaerated by purging for at least 10 min with 99.997% pure nitrogen gas. Thus traces of dissolved oxygen were removed from the solution.

Results and Discussion

Cyclic voltammetric investigation of Cu(II) in BR buffer solution and its interaction with melamine of different concentrations in an identical voltammetric condition has been performed. The results are presented below.

Voltammetric response of Cu(II) in BR buffer solution

Cyclic voltammogram of 0.5 mM Cu(II) in BR buffer solution at different pH has been recorded at GCE within the potential window of +500 to - 500 mV. Figure 1 shows a series of cyclic voltammograms of 0.5 mM Cu(II) in BR buffer solution with scan rate of

100 mV/s at 0.63, 1.73, 3.02 and 4.06 pH. In the forward scan two cathodic peaks (Figure 1) at about - 37.0 and - 113.8 mV and in the reverse scan an intense anodic peak at about 41.0 mV is observed. The first cathodic peak is assigned for the reduction of Cu(II) to Cu(I) and the second peak is for the reduction of Cu(I) to Cu(0), while the anodic peak is due to the oxidation of Cu(0) to Cu (II) species.

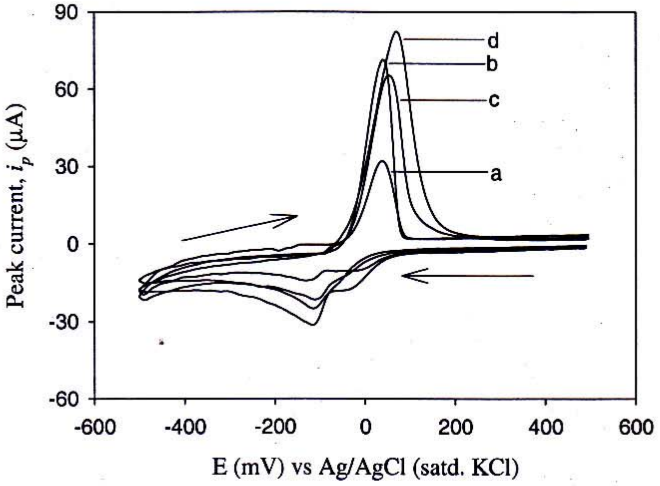

Figure 1. Cyclic voltammograms of 0.5 mM Cu(II) in BR buffer at different pH: (a) 0.63, (b) 1.73, (c) 3.02 and (d) 4.06 at GCE.

With the increase of pH, the current of first cathodic peak gradually decreases and finally disappears at pH ≥ 4.06. This fact probably owes much to be the presence of electroactive $[Cu(H_2O)_6]^{2+}$ and $[Cu(H_2O)_{6-x}]^+$ ions in significant amount at low pH limit while at high pH (~4.06), $[Cu(OH)(H_2O)_5]^+$ ion is considered to be the only electroactive species (Anderson and Shain 1976). It is also noticeable that the peak heights of the second cathodic peak and anodic peak increase with increasing pH. Moreover, both of the cathodic and anodic peak potentials are shifted randomly at different pH.

The effect of the scan rate on the electrochemical response of Cu(II) at pH 1.73 is also examined by recording the cyclic voltammograms of Cu(II) at scan rates of 25, 50, 75, 100 and 125 mVs^{-1} in identical condition. With the increasing of scan rate the cathodic and anodic peak current is increased which is shown in Figure 2.

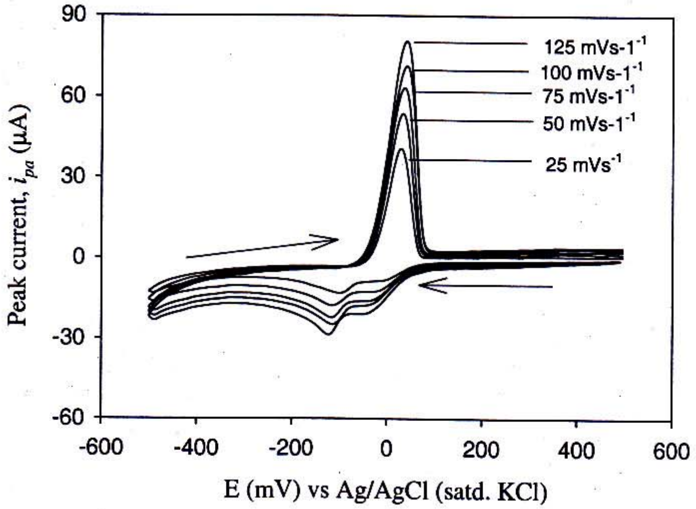

Figure 2. **Cyclic voltammograms of 0.5 mM Cu(II) in BR buffer solution at diferent scan rates of 25, 50, 75, 100 and 125 mV/s at pH 1.73.**

This observation suggests that the electrode process is diffusion controlled in BR buffer medium. Again the variations of anodic and cathodic peak currents with square root of scan rate are linear (Figure 3) that corroborate with Randless-Sevcik equation. Thus the electrode processes are diffusion controlled. The peak potential separation and peak current ratio reveal that the redox process of Cu(II)/Cu(0) is quasireversible, which is also characterized by the shape of the cathodic and anodic peaks (Quentel and Madec 1990).

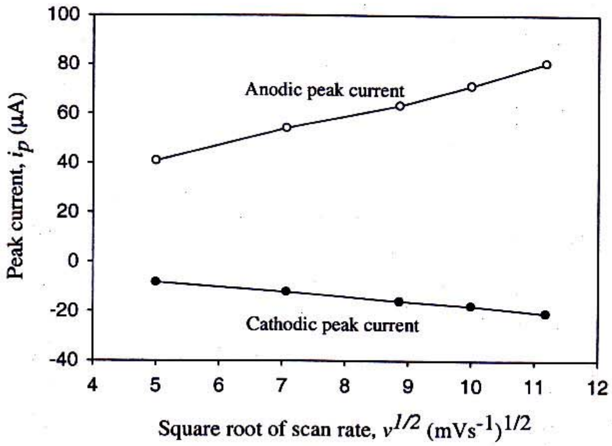

Figure 3. **A plot of peak current, i_p (μA) vs square root of scan rate, $v^{1/2}$ (mV/s)$^{1/2}$.**

Voltammetric response of Cu(II) in presence of melamine in BR buffer solution

The voltammograms of Cu(II) in presence of melamine in BR buffer at various Cu(II) and melamine molar ratio, 1 : 1, 1 : 2, 1 : 3 and 1 : 4 have been recorded at pH 3.02 with a glassy carbon electrode (GCE) within the same potential window as it recorded for Cu(II). Cyclic voltammograms of Cu(II) in presence of melamine with different molar concentrations of melamine have been recorded (Figure 4). A dramatic change of the voltammograms has been observed. The anodic peak currents in the voltammograms for each molar ratio of Cu(II) and melamine (Figure 4) are lower than that of solely Cu(II) while the cathodic peaks disappear completely. The anodic peak potentials are also slightly shifted. Furthermore, the heights of the peaks are apparently erratic with respect to melamine concentration. Since the lowest peak current (Table 1) is found for the voltammogram of 1 : 2 molar ratio of Cu(II) and melamine, the maximum interaction is indeed, occurred at this molar ratio in this pH medium.

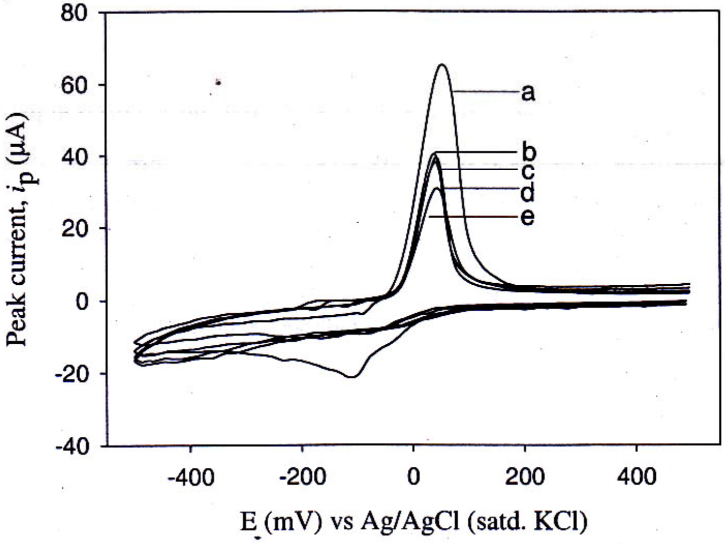

Figure 4. **Cyclic voltammograms of (a) Cu(II), and Cu(II) in presence of melamine at different ratio (b) 1 : 3, (c) 1 : 1, (d) 1: 4 and (e) 1 : 2 in BR buffer at pH 3.02.**

It may be noted that the voltammogram of melamine in identical condition has been recorded and it exhibits no anodic or cathodic peak at all pH range within the studied potential window. Figure 5, shows a comparative CVs of Cu(II) and melamine at identical scan rate (100 mV/s) and concentration (0.5 mM) at GCE.

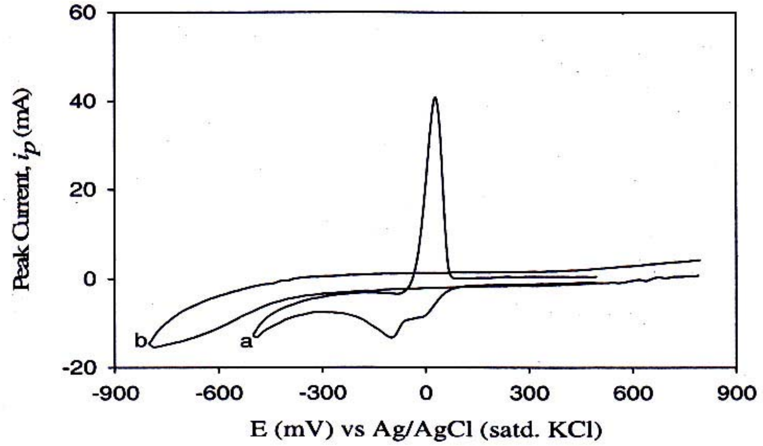

Figure 5. Cyclic voltammograms of (a) 0.5 mM Cu(II) and (b) 0.5 mM melamine in BR buffer with scan rate of 100 mV/s at GCE.

The voltammograms of Cu(II) at various Cu(II) and melamine molar ratio, 1 : 1, 1 : 2, 1 : 3 and 1 : 4 at pH 0.63 have also been examined (Figure 6). At this pH both the cathodic and anodic peaks are apparent in the voltammograms and their peak currents are relatively lower than that of Cu(II) alone. The peak potentials are also slightly shifted (Figure 6). Additionally, the heights of the peaks are apparently erratic with melamine concentration. The lowest peak current is again found at 1 : 2 molar ratio of Cu(II) and melamine and thus the interaction occurs at this molar ratio is maximum.

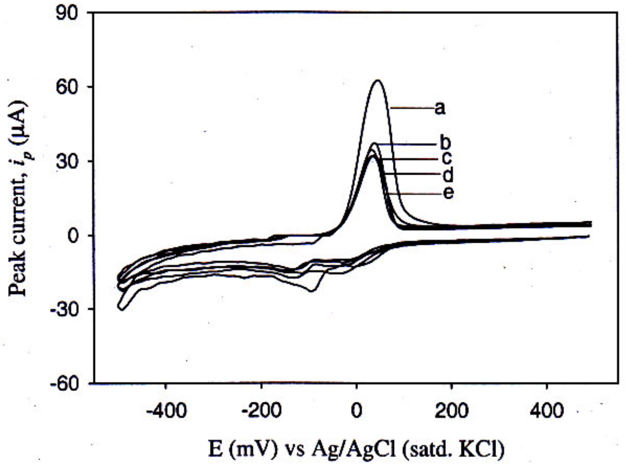

Figure 6. Cyclic voltammograms of (a) Cu(II), and Cu(II) in presence of melamine with different molar ratio (b) 1 : 3, (c) 1 : 4, (d) 1 : 2 and (e) 1 : 1 in BR buffer at pH 0.63.

In the presence of melamine, Cu(II) displays identical electrochemical behavior at pH 1.73 and 3.02. However, at pH 4.06 the complete disappearance of cathodic peak was observed. The common behaviors include (i) the significant decrease of the peak current of Cu(II), (ii) the slight shifting of peak potentials, (iii) the erratic response of peak current with respect to Cu(II)/melamine molar ratios, and (iii) the maximum interaction of Cu(II) with melamine at their 1 : 2 molar ratio. The voltammograms recorded at pH 1.73 and at 4.06 are shown in Figure 7 and Figure 8, respectively.

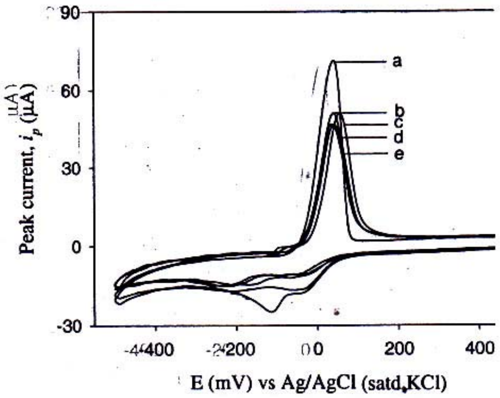

Figure 7. **Cyclic voltammograms of (a) Cu(II), and Cu(II) in presence of melamine with different ratio (b) 1 : 3, (c) 1 : 4, (d) 1 : 1 and (e) 1:2 in BR buffer at pH 1.73.**

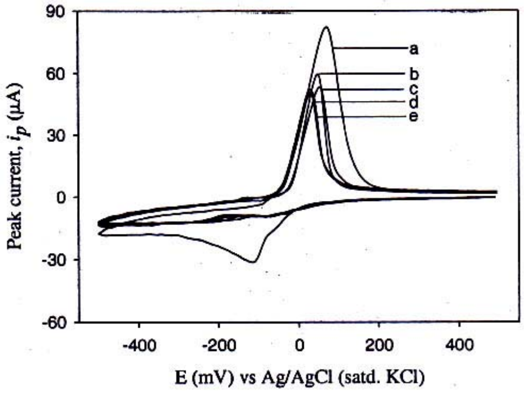

Figure 8. **Cyclic voltammograms of (a) Cu(II), and Cu(II) in presence of melamine with different ratio (b) 1: 4, (c) 1 : 3, (d) 1 : 1 and (e) 1 : 2 in BR buffer at pH 4.06.**

Table 1. The data for the voltammograms recorded for 1 : 2 molar ratio of Cu(II)/melamine at different pH at GCE with scan rate of 100 mV/s.

Solution pH	Peak current (μA)		Peak potential (mV)		Peak current ratio (i_{pa}/i_{pc})	Peak potential separation, ΔE_p
	$-i_{pc}$	i_{pa}	$-E_{pc}$	E_{pa}		
0.63	14.92	31.88	137.0	33.0	2.13	170.0
1.73	16.95	46.55	207.0	43.0	2.74	250.0
3.02	-	30.66	-	43.0	-	-
4.06	-	51.32	-	33.0	-	-

Epc = Cathodic peak potential, Epa = Anodic peak potential, i_{pa} = Anodic peak current, i_{pc} = Cathodic peak current.

From the above observation it can be concluded that copper(II) interacts with melamine at molar ratio of 1 : 2 in all pH under study in BR buffer, but the maximum interaction occurs at pH 3.02. The data for the different voltammograms recorded at various pH is tabulated in Table 1.

Conclusion

Voltammetric study of Cu(II) in BR buffer exhibits two cathodic peaks of different heights and an anodic peak at lower pH (pH 0.63, 1.73 and 3.02). The weaker cathodic peak gradually diminishes with increasing pH and completely disappears at pH 4.06. However, in the presence of melamine both the cathodic and anodic peak currents of Cu(II) are significantly reduced. This observation indicates that the interaction between Cu(II) and melamine occurs in BR buffer medium in acidic pH region. Among the studied pH region maximum interaction is found at pH 3.02, when the molar ratio of Cu(II)/melamine is 1 : 2.

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