

Electrochemical Studies of the pH Dependence of Cu(II) Reduction in Aqueous Britton-Robinson Buffer Solution

A. A. Shaikh*, J. Firdaws, Badrunnessa, S. Serajee, M. S. Rahman and Pradip K. Bakshi

Department of Chemistry, University of Dhaka, Dhaka 1000, Bangladesh

*E-mail: aftabshaikh@univdhaka.edu

Received: 28 April 2011 / Accepted: 31 May 2011 / Published: 1 July 2011

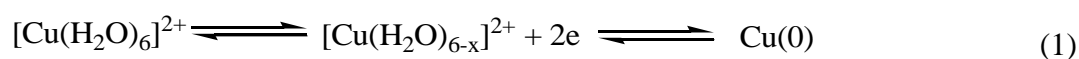
The electrochemical reduction of Cu(II) has been studied in aqueous Britton-Robinson (BR) buffer medium with glassy carbon electrode (GCE) at various pH values. It is observed that at low pH values Cu(II) follows two-step electrochemical reduction while at high pH it undergoes one-step reduction process. On the other hand the oxidation of Cu(0)/Cu(II) couple follows one-step oxidation reaction in the studied pH range. The intensities of both cathodic and anodic peak current are also increased with increasing scan rate consistent with Randles-Sevcik equation. A linear behavior of peak current versus square root of scan rate indicates that the electrochemical processes are diffusion controlled.

Keywords: Cyclic voltammetry, Cu(II)-reduction, Britton-Robinson buffer, quasi-reversible, diffusion-controlled.

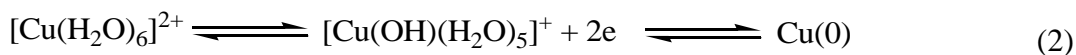
1. INTRODUCTION

Electrochemical studies of Cu(II) reduction in various supporting electrolytes in the acidic pH range [1-6] and basic medium [7,8] has been investigated. Reviews of Cu(II) electrochemistry and typical kinetic parameters for Cu(II) reduction have been presented elsewhere [9-11]. The mechanism and kinetic behavior of the reduction of hexaqua Cu(II) have been investigated using a number of techniques, such as dc polarography [2,6,12], ac polarography [6,12,13-15], hydrodynamic voltammetry [16-18], chronoamperometry at constant potential [4,19], and coulometry [20,21].

In the previous study [14], at low pH deaquation of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ prior to charge transfer was found. Whereas $[\text{Cu}(\text{OH})(\text{H}_2\text{O})_5]^+$ was assumed to be the only electroactive species at high pH. The electrode reactions could be schematically summarized by equations 1 and 2.



where, $[\text{Cu}(\text{H}_2\text{O})_{6-x}]^{2+}$ with $x = 1$ to 6.



However, Anderson and Shain [22] suggested that in nitrate and perchlorate media the Cu(II) reduction process was pH dependent and the proposed mechanism involved a chemical reaction interposed between two one-electron charge transfer steps - the ECE mechanism.

Conflicting results of previous electrochemical studies of Cu(II) reduction in various supporting electrolytes in the acidic pH range encourage us to make a contribution in this field. Aqueous BR buffer medium was chosen in our study. BR buffer is a universal pH buffer used for the range pH 2 to 12. It can also act as a nominally noncomplexing supporting electrolyte. As cyclic voltammetry is the most effective and versatile technique in the diagnosis of complex electrode mechanisms, in the present study this technique is employed to examine the electrochemical reduction of Cu(II) in aqueous BR buffer medium.

2. EXPERIMENTAL

2.1. Materials

Analar grade copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) was purchased from E. Merck, Germany. For the preparation of BR buffer, extra pure acetic acid (BDH, England), phosphoric acid (BDH, England), and boric acid (Merck, Germany) were procured. To adjust the pH of the solution perchloric acid (Merck, Germany) and sodium hydroxide (BDH, England) were used.

2.2. Methods

$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was dissolved in BR buffer to prepare 0.5-2.0 mM Cu(II) solutions with different pH values. BR buffer solution was prepared as follows: 0.4 M acetic acid, 0.4 M phosphoric acid and 0.4 M boric acid solutions were prepared separately in 100 mL volumetric flasks and then the solutions were mixed together with requisite volume for buffer solution. Milli-Q deionized water was used throughout the experiments.

Glassy carbon electrode (GCE) was polished with fine alumina powder of 0.3 micron or lower sized 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 minutes. A shiny black mirror like electrode surface was then thoroughly washed with deionized water.

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 reference electrode was inserted through the holes. Under computer controlled stirring, experimental solution was deaerated by purging for at least 10 minutes with 99.9977% pure nitrogen gas. By this way, traces of dissolved oxygen were

removed from the solution. Solution pH and the scan rate were varied from 0.63 to 5.01, and 20 to 300 mVs^{-1} respectively.

2.3. Equipments

Three electrodes system consists of GCE as a working electrode, Ag/AgCl (satd. KCl) as the reference electrode and platinum wire as the counter electrode were used. Cyclic voltammetric measurement was performed using Computerized Electrochemical System, Model HQ-2040 developed by Advanced Analytics, USA. Solution pH was measured with a pH meter (TOA Model HM-16S).

3. RESULTS AND DISCUSSION

Cyclic voltammetric study of 0.5 to 2 mM Cu(II) in BR buffer at different pH values (0.63 to 5.01) was investigated at GCE within the potential windows of 500 to -500 mV. At more positive or negative potential values only solvent decomposition current was observed. Fig. 1 shows a cyclic voltammogram of 1 mM Cu(II) in BR buffer solution with scan rate of 100 mVs^{-1} at pH 1.03. In the forward scan two cathodic peaks i_{pc1} and i_{pc2} at about -22.37 and -82.0 mV respectively and in the reverse scan an intense anodic peak i_{pa2} at about 53.0 mV were observed. The first cathodic peak (i_{pc1}) is due to the reduction of Cu(II) to Cu(I) and the second peak (i_{pc2}) is for the reduction of Cu(I) to Cu(0).

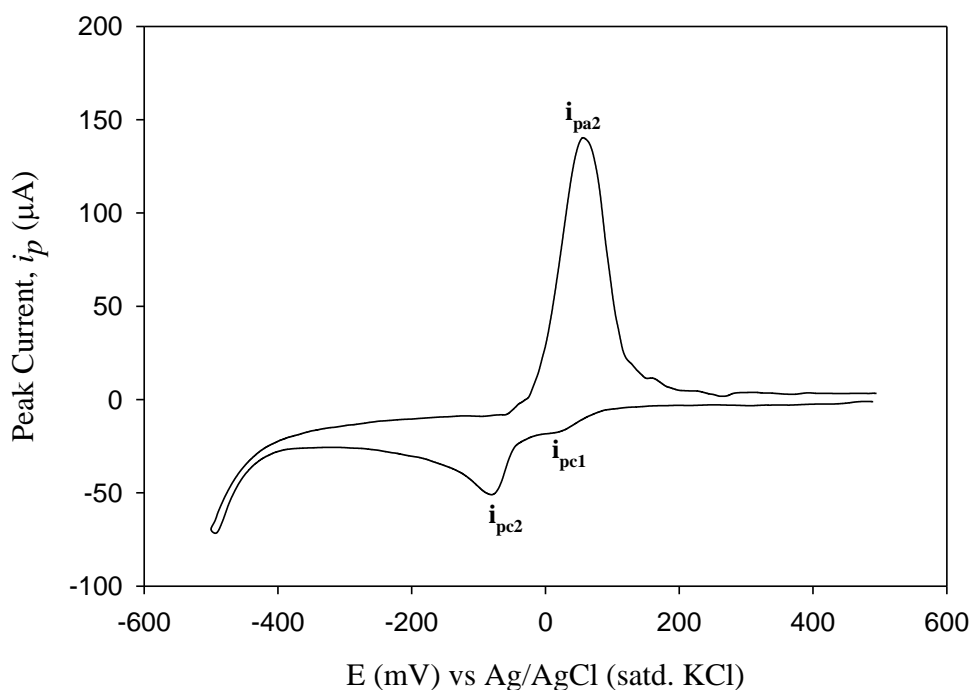


Figure 1. Cyclic voltammogram of 1 mM Cu(II) in Britton-Robinson (BR) buffer at pH 1.03, with scan rate of 100 mVs^{-1} at GCE.

This experimental observation is very much similar to the previous study involving electrochemical reduction of Cu(II) in acidic aqueous perchlorate solutions of varying pH [22]. Hydrated Cu(II) ion, $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ in aqueous BR buffer medium at low pH (pH 1.03) undergoes deaquation first $[\text{Cu}(\text{H}_2\text{O})_{6-x}]^{2+}$ at the electrode surface followed by charge transfer to $[\text{Cu}(\text{H}_2\text{O})_{6-x}]^+$. The value of x is unknown; however, it is generally believed that loss of the two axially distorted H_2O molecules from the Cu(II) coordination sphere is easier which may perhaps enhance the electron transfer rate.

It is established that Cu(II)/Cu(I) electron transfer couple is very distinctive. In polar solvents Cu(II) complexes exist predominantly as five or six coordinate species (tetragonal), however, Cu(I) complexes are expected to favor four (tetrahedral) or lower coordination numbers. Electron transfer between Cu(II) and Cu(I) would be therefore, accompanied by major structural and stereochemical changes.

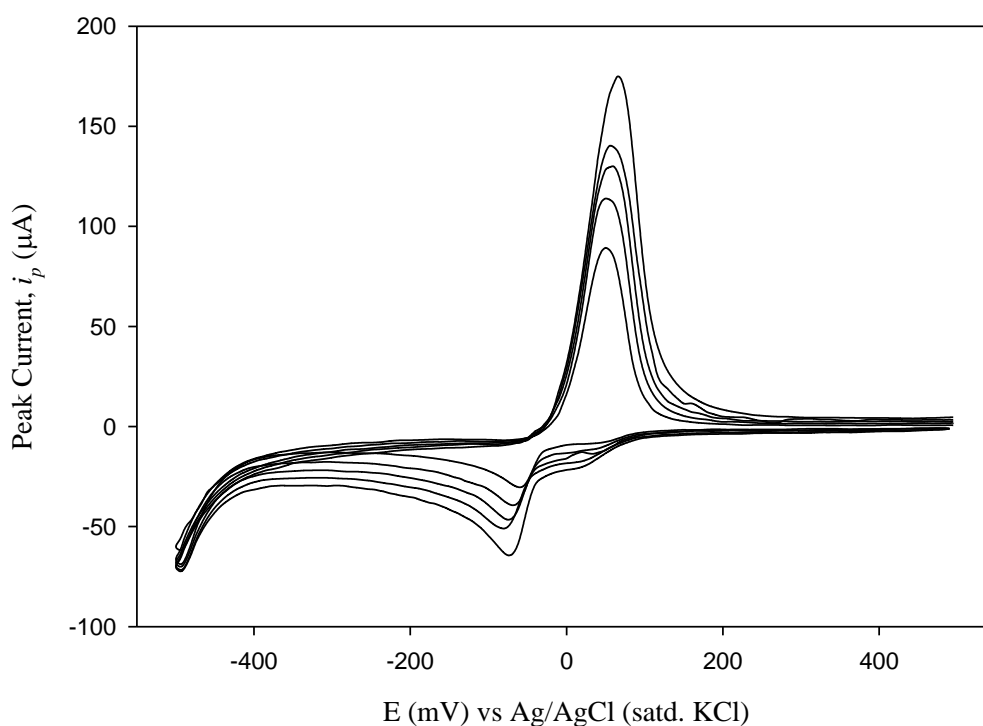
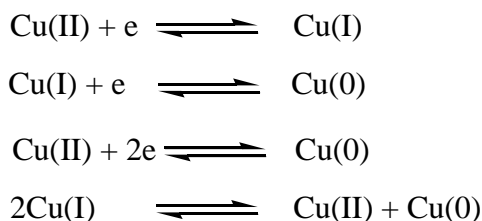


Figure 2. Cyclic voltammograms obtained on GCE in BR buffer containing 1 mM Cu(II) at different scan rates from 25, 50, 75, 100 and 125 mVs^{-1} .

While the second cathodic peak (i_{pc2}) is for the reduction of $[\text{Cu}(\text{H}_2\text{O})_{6-x}]^+$ to Cu(0). Since lower-charged species are more likely to be involved in water loss steps than higher-charged species, therefore deaquation of Cu(I) species is more rapid than for Cu(II) species. Reduction of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ to Cu(0) experiences loss of all the H_2O ligands. The feature of the aqueous chemistry of copper can be summarized by the following equilibrium reactions:



The peak (i_{pc1}) due to the Cu(II)/Cu(I) electron transfer couple is less intense than the peak (i_{pc2}) for the Cu(I)/Cu(0) reduction couple. This can be explained on the basis of the stability of Cu(II) and Cu(I) ions which depends highly on environment in solution. Stability in aqueous conditions depends on the hydration energy of the ions when they bonded to the water molecules. The Cu(II) ion has a greater charge density than the Cu(I) ion and therefore, forms much stronger bonds releasing more energy. On the other hand Cu(I) is significantly stable in presence of complexing ligand such as Cl⁻ [23]; and in nonaqueous media [24]. In nonaqueous solvents, the stability of Cu(I) is due to the fact that these solvents solvate Cu(II) less strongly than does water and they solvate Cu(I) more strongly than does water. Thus the $[\text{Cu}(\text{H}_2\text{O})_{6-x}]^+$ species is less stable in the presence of GCE in aqueous BR buffer medium and gives a less intense peak (i_{pc1}). In the reverse scan Cu(0) oxidized directly to Cu(II) resulting into a significantly intense anodic peak (i_{pa2}) with strong peak current. The effect of the scan rate (Fig. 2) on the electrochemical response of Cu(II) under the same condition (1 mM Cu(II), pH 1.03) was examined between 25 and 125 mVs⁻¹. Their anodic and cathodic peak potentials, peak current (i_p); peak current ratio (i_{pa2}/i_{pc2}) and peak potential separation (ΔE_p) are gathered in Table 1.

Table 1. Peak currents and peak potentials at different scan rate of 1 mM Cu(II) in BR buffer at pH 1.03.

Scan rate, ν (mVs ⁻¹)	Cathodic peak current, i_{pc} (μA)		Anodic peak current, i_{pa} (μA)	Cathodic peak potential, E_{pc} (mV)		Anodic peak potential, E_{pa} (mV)	Peak current ratio, i_{pa2}/i_{pc2}	$\Delta E = E_{pa2} - E_{pc2}$ (mV)
	i_{pc1} (-)	i_{pc2} (-)	i_{pa2}	E_{pc1}	E_{pc2} (-)	E_{pa2}		
25	7.71	30.38	89.27	47.94	62.00	48.00	2.93	110
50	10.71	39.32	113.94	38.35	72.00	48.00	2.90	120
75	13.59	46.61	130.01	33.00	77.00	58.00	2.79	135
100	16.06	50.99	140.24	22.37	82.00	53.00	2.75	135
125	20.07	64.40	174.88	15.98	77.00	63.00	2.71	140

With the increasing of scan rate both anodic and cathodic peak current increases and the cathodic peak potentials have shifted towards negative values, while anodic peak potential move towards more positive values. This observations suggest that the electrode process is diffusion controlled in BR buffer medium.

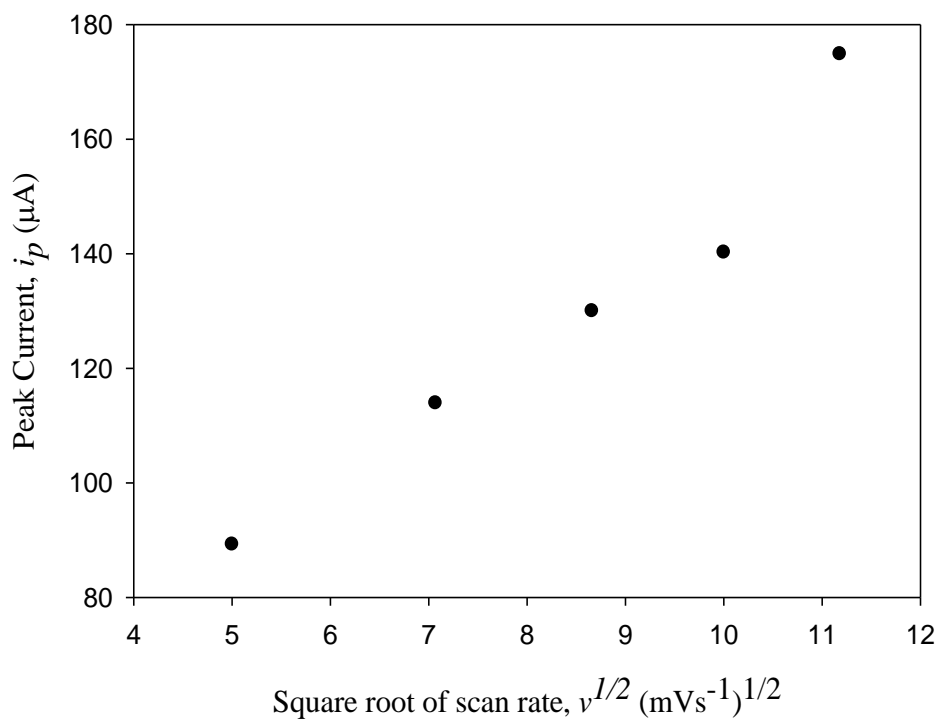


Figure 3. Dependence of peak current with square root of scan rate for copper system in BR buffer at pH 1.03.

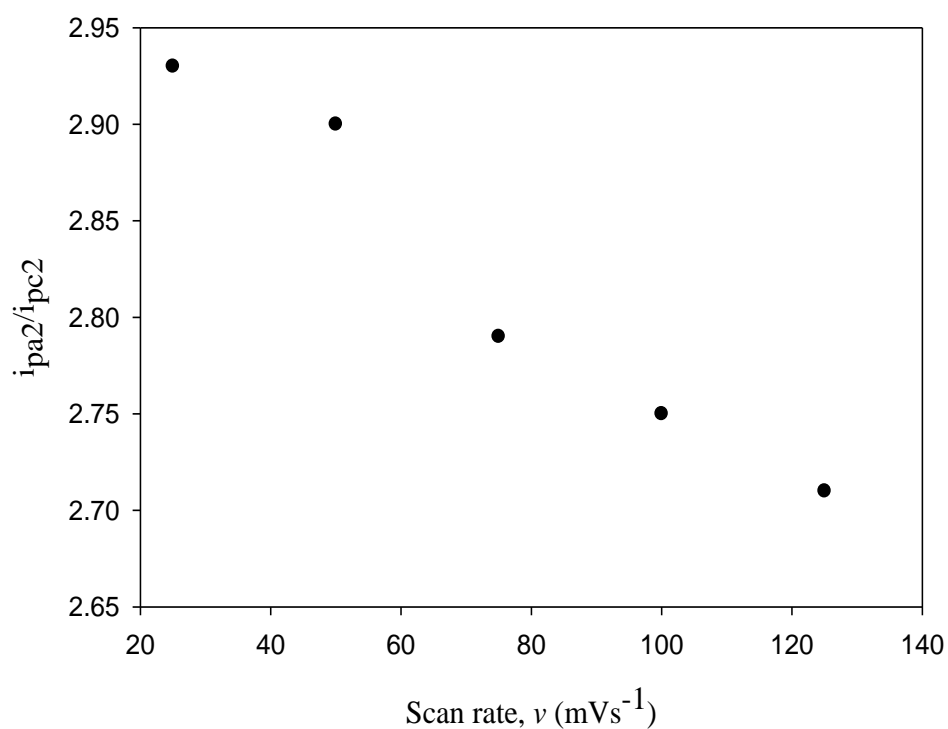


Figure 4. Peak current ratio (i_{pa2}/i_{pc2}) dependence on scan rate of 1 mM Cu(II) in BR buffer medium at pH 1.03.

In Fig. 3, it is apparent that the peak current for the electrochemical reduction of Cu(II) in BR buffer has linear relation with square root of scan rates and it passes through the origin. This observation is again in favor of the fact that the electrode process is diffusion controlled with no adsorption on the electrode surface. The result agrees well with the previous study.

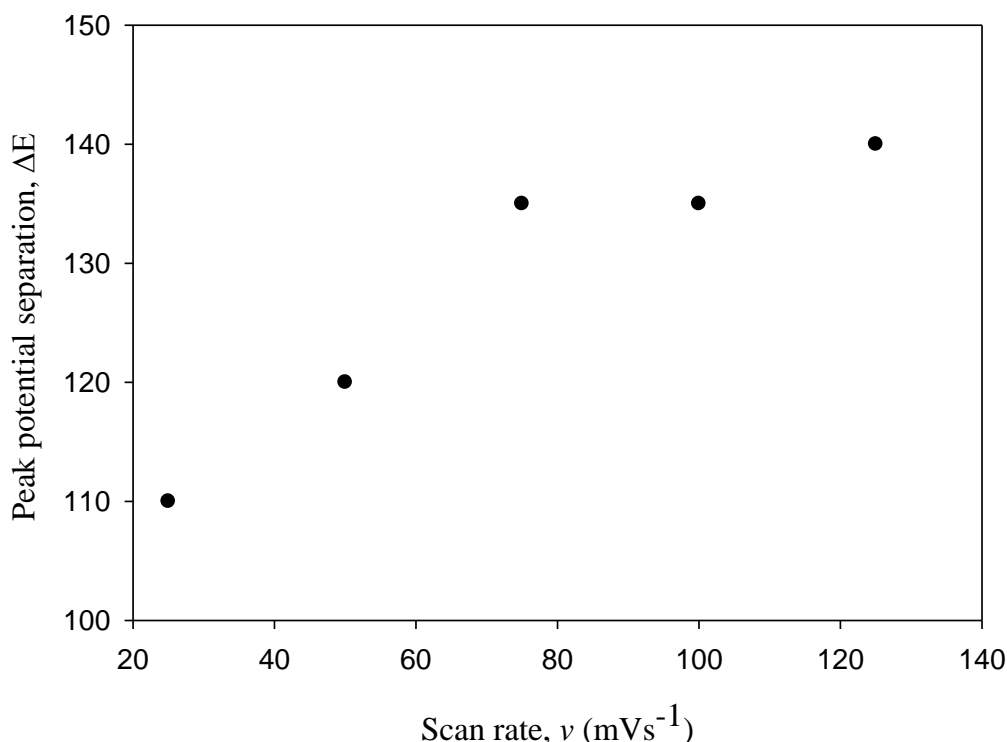


Figure 5. Variation of peak potential separation with scan rate of 1 mM Cu(II) in BR buffer at pH 1.03.

The ratio of the oxidation peak current to its corresponding reduction counterpart, i_{pa2}/i_{pc2} is about 2.93-2.71. The peak current ratio is decreased with the increasing of scan rate (Fig. 4). Also the peak potential separation, $\Delta E_p = E_{pa} - E_{pc}$ is between 110-140 mV. It is increased with the variation of scan rate (Fig. 5). These suggest that the redox process is quasi-reversible reaction rather than a reversible reaction.

The effect of pH on the cyclic voltammograms of the reduction of Cu(II) in BR buffer has been investigated at GCE. A series of recorded voltammograms at different pH are shown in Fig. 6. At low pH ranging from 0.63 to 3.53, two distinguish cathodic peaks and an intense anodic peak is appeared. With the increase of pH, the first cathodic peak current (indicated by an arrow) gradually decreases and finally disappears at pH 4.08. At low pH limit $[Cu(H_2O)_6]^{2+}$ and $[Cu(H_2O)_{6-x}]^+$ ions can be assumed to be present in significant amount while at high pH (~ 4.08), $[Cu(OH)(H_2O)_5]^+$ ion is understood to be the only electroactive species. No hydrolysis equilibrium appear to have been reported for Cu(I).

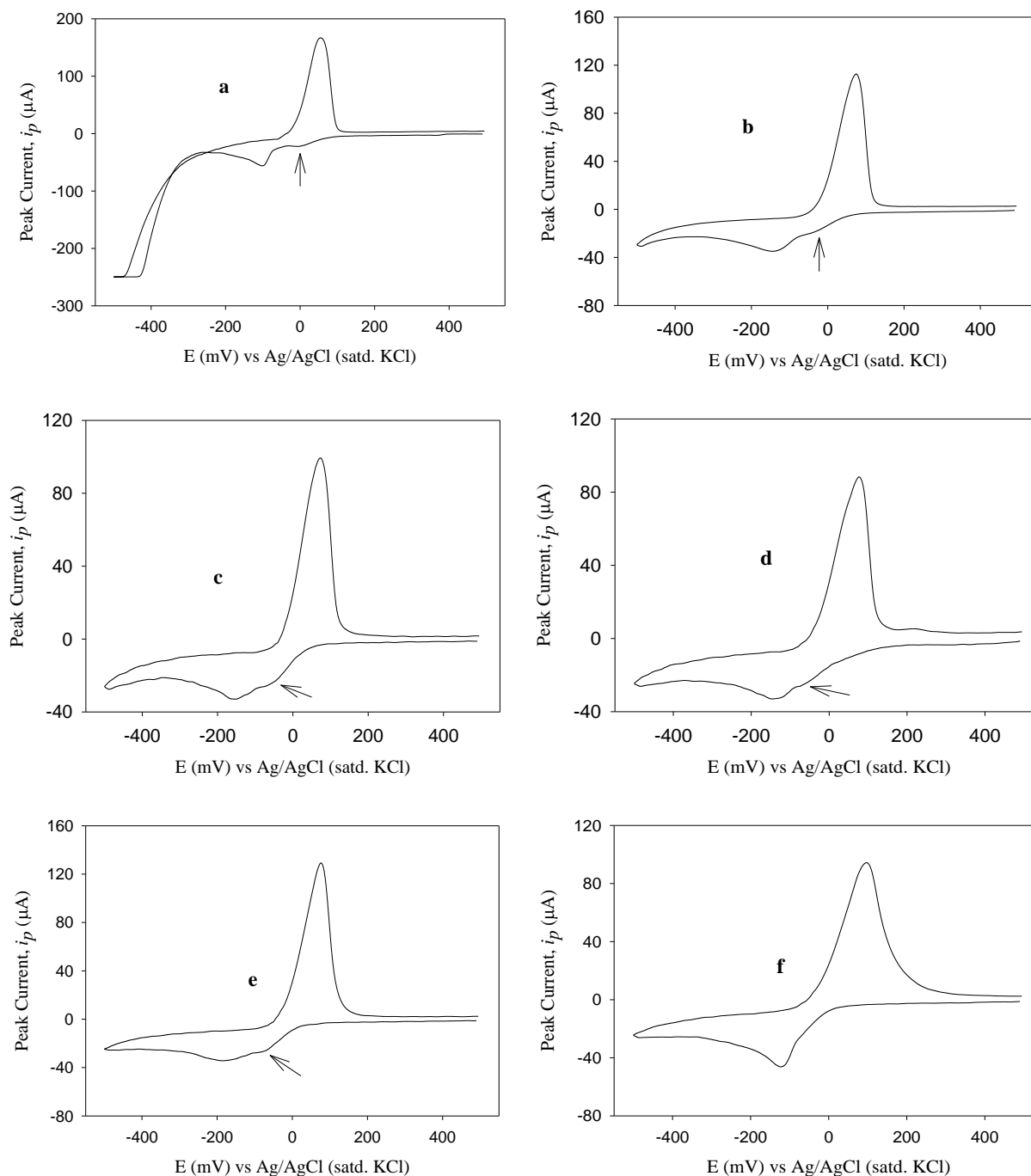
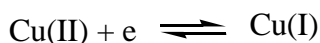


Figure 6. Cyclic voltammograms of 1 mM Cu(II) in BR buffer at different pH: (a) 0.63, (b) 1.64, (c) 2.50, (d) 3.00, (e) 3.53 and (f) 4.08.

Since NaOH was added to raise the pH of the analyte solution, the availability of the water molecules was gradually increased. At pH 4.08 or above, the solution becomes highly aqueous and therefore, in such a medium the monohydroxy copper(II) complex reduced directly to Cu(0) in the forward scan and in the reverse situation is assumed. Since the Cu(II) ion precipitated as the Cu(OH)₂ species above pH 5.75 [14], the monohydroxy complex would be present at values of pH just acidic of precipitation. Precipitation of Cu(II) ions as Cu(OH)₂, decrease the concentration of Cu(II) ions in the

bulk of solution significantly above this pH (= 5.75) decreases the peak current drastically, shown in Fig. 7. The mechanism of the reduction processes can be summarized as below:

At low pH values ($\text{pH} < 4.08$)



At high pH values ($\text{pH} \geq 4.08$)

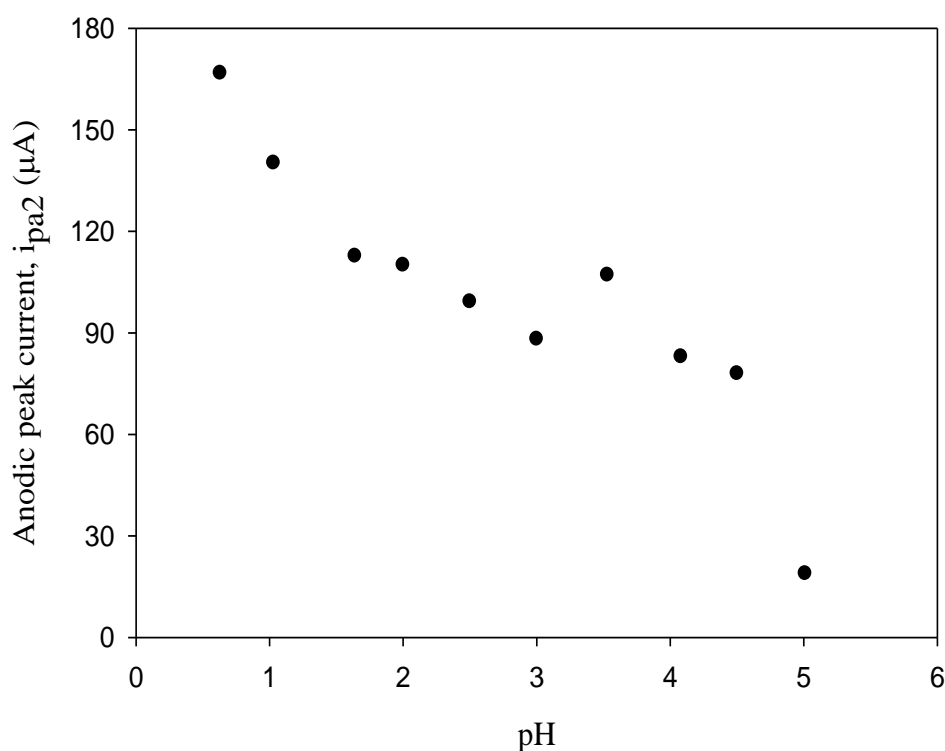
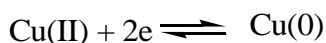


Figure 7. Effect of pH on peak current of 1 mM Cu(II) in BR buffer at GCE with scan rate of 100 mVs^{-1} .

Fig. 8 shows cyclic voltammograms at GCE for 1 mM solution of Cu(II) in BR buffer (pH 4.08) with the potential scan rate as variable. The larger peak separation, ΔE_p coupled with the systematic increase of ΔE_p with scan rate was observed. With the increase of scan rate positive shift in E_{pa} and a corresponding negative shift in E_{pc} were found. This behavior indicates that the severe kinetic limitations in charge transfer with this redox system were occurred.

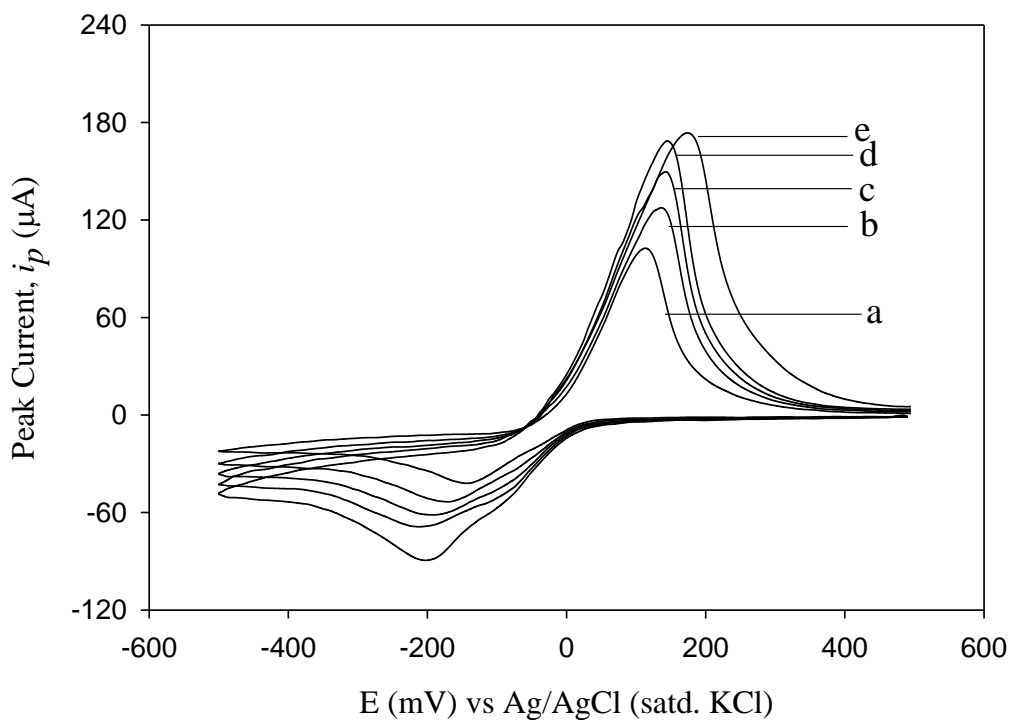


Figure 8. Cyclic voltammograms of 1 mM Cu(II) in BR buffer at pH 4.08 with various scan rates: (a) 25, (b) 50, (c) 75, (d) 100 and (e) 125 mVs^{-1} .

4. CONCLUSION

The electrochemical reduction of Cu(II) in aqueous BR buffer medium with different pH at GCE has been investigated. At low pH values ($\text{pH} < 4.08$), Cu(II) undergoes two-step electrochemical reduction process corroborate with two cathodic peaks in the voltammograms. Their mechanistic pathways are very similar to that reported earlier by Anderson and Shain [22]. While at high pH values ($\text{pH} \geq 4.08$), it follows one-step electrochemical reduction and shows one cathodic peak. It is also noticeable that in the studied pH range (0.63 – 5.01) the Cu(0)/Cu(II) couple follows one-step oxidation process resulting into an intense anodic peak in the voltammograms. However, both the electrochemical processes are diffusion controlled indicated by the linearity of peak current vs. square root of scan rate.

Acknowledgements: The authors are grateful to Higher Education Quality Enhancement Project (HEQEP) of the University Grants Commission of Bangladesh for the financial support.

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