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Electrochemical investigation of copper–DTPI interactions

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Abstract

The electrochemical behavior of copper in the absence and presence of a dithiophosphinate type collector, sodium diisobuthyldithiophosphinate (NaDTPI), was determined to investigate the interactions between a copper surface and NaDTPI as a function of pulp potential (Eh) and pH. The electrochemical studies were performed by Cyclic Voltammetry (CV) in the −355 to +1550 mV (SHE) potential range and at different pHs from slightly acidic to strongly alkaline conditions. The electrochemical studies were carried out for copper and DTPI alone as well as with DTPI added copper system. DTPI addition had considerable effects on the electrochemical behavior of copper. CuDTPI formation was the main reaction at all pHs through a mixed mechanism and oxidation of the copper surface was followed by a chemical reaction between copper and DTPI ions. Formation of a cupric metal-collector complex, $Cu(DTPI)_2$, was observed only in acidic conditions in the form of an unstable surface compound.

1. Introduction

Flotation has been the most common method for the concentration of valuable metallic sulphides over the last three decades. Obtaining higher recoveries with lower costs, applicability to very low grade ores and adaptability to different deposits makes flotation the most important technique for sulphide minerals processing. However, selectivity is a critical issue for the concentration of complex sulphide ores.

Xanthate is an important collector group for easy-to-process sulphide ores. With their relatively high collecting power, Xanthates provided high recoveries. The behavior of Xanthate in flotation pulps and its interaction with sulphide minerals has attracted considerable interest. Pang and Chander [1] studied the effect of Xanthate on the wetting and oxidation behavior of chalcopyrite. Pang and Chander proposed mechanisms for the interactions between Xanthate and the chalcopyrite surface in nitrogenated and oxygen saturated solutions. Leppinen [2] used FTIR and microflotation to investigate the adsorption mechanisms of Ethyl Xanthate on pyrite, pyrrhotite, chalcopyrite and sphalarite. Leppinen also discussed results in activated and non-activated conditions concluding that acidic pH favored the adsorption of Xanthate on non-activated minerals and neutral pH was the optimum condition for Xanthate adsorption on activated minerals. Woods et al. [3] investigated Ethyl Xanthate-copper systems through voltammetry experiments and derived Eh-pH diagrams. Allison et al. [4] and Persson [5] reported that Xanthate made chalcopyrite and pyrrohotite surfaces hydrophobic by adsorbing on these minerals in the form of dixanthogen (X_2). However, the strong collecting ability of Xanthates resulted in deficiencies in selectivity. When a number of different metallic sulphide minerals with similar surface behavior are concerned, as in the case of chalcopyrite-pyrite, Xanthates were ineffective in selectivity. Studies focused on the investigation of new reactives that had the collecting power of Xanthates and the selectivity towards certain metallic sulphides [6, 7]. As a result, different collectors such as Mercaptans and Dithiophosphates were studied and found application in the processing of complex sulphides.

Sodium diisobuthyldithiophosphinate (NaDTPI), produced by Cytec Co., was suggested as an important substitute in the flotation of metallic sulphide ores [8]. NaDTPI was developed to provide excellent selectivity in the treatment of some complex ores with which Xanthate gave poor grade results [9]. NaDTPI was most advantageous in the flotation of chalcopyrite-pyrite. DTPI offers specific selectivity towards chalcopyrite [9]. The problem in the flotation of chalcopyrite from pyritic gangue is the similar physicochemical surface behaviors of chalcopyrite and pyrite. The responses given by chalcopyrite and pyrite would be interfering for most of the reactives, resulting in the undesired flotation of pyritic gangue with the chalcopyrite concentrate [10]. The only difference in the chemical composition of chalcopyrite from pyrite is Cu atoms. Copper may be found in different ionic forms depending on the pulp conditions. Therefore, the role of Cu ions in the flotation of complex sulphide ores is an important aspect [10]. Copper ions may adsorb on the mineral surfaces and change their flotation characteristics. It was reported that selectivity during the flotation of sphalerite ores with low grade galena associates, could be improved by the activation of sphalerite with an exchange of Zn^{2+} ions with cupric (Cu^{2+}) ions [11, 12]. Some sulphides would become selectively hydrophobic and float without a collector as a result of the activation by the copper ions [13, 14]. Conversely, the hydrolysis of copper ions would lead to accidental activation of an undesired sulphide mineral [15]. Activation of pyrite by the replacement of Fe^{2+} with Cu^{2+} ions and galvanic interaction between chalcopyrite and pyrite are two common cases for accidental activation [15, 16]. The probable interactions between Cu and NaDTPI also have critical importance from the standpoint of the affinity of NaDTPI towards chalcopyrite.

In this study the interactions between NaDTPI and the copper surface were investigated with respect to pulp conditions. The investigation of copper–NaDTPI interactions was carried out using metallic copper through detailed electrochemical studies in different potential ranges and pH conditions. Firstly the redox behavior of the copper surface was studied with changes in the pulp potential and pH. Next the redox behavior of the copper surface in NaDTPI added conditions and the interactions between the ionic states of Cu with NaDTPI were determined.

2. Experimental

2.1. *Materials*

The working electrode for the cyclic voltammetry (CV) studies was prepared using a thick, high purity (99%) copper rod. For the investigation of the pH effect buffer solutions from slightly acidic to strongly alkaline pHs (4.67, 6.97, 9.2 and 11.0) were used. Table 1 shows the composition of the buffer solutions [16, 17]. Prior to the CV experiments, the buffer solution in the electrochemical cell was deoxygenated with high purity N_2 (99.9%) through an immersed nozzle for 15 min. Then the cell was tightly sealed and the experiment was started.

The interactions between copper and the dithiophosphinate type collector were investigated using DTPI in its commercial form, Aerophine 3418. Aerophine 3418, produced by Cytec. Co., has a molecular weight of 223.26 g. NMR spectroscopy showed that DTPI was in the sodium diisobuthyl dithiophosphinate form and its molecular formula was $C_8H_{18}PS_2Na$ [18]. The chemical structure of Aerophine 3418 is given in Figure 1.

Table 1. The compositions of the buffer solutions used in the study

pH	Composition
4.67	0.5 M CH_3COOH + 0.5 M CH_3COONa
6.97	0.025 M KH_2PO_4 + 0.025 M Na_2HPO_4
9.20	0.05 M $Na_2B_4O_7$
11.0	0.025 M $NaHCO_3$ + 0.023 M NaOH

2.2. *Method*

Cyclic voltammetry (CV) was used to investigate the interactions between copper and DTPI. The setup for the CV experiments consisted of a potentiostat device connected to an isolated three-electrode cell. The three-electrode cell involved a calomel electrode, a platinum electrode and a copper electrode as reference, counter and working electrodes, respectively. The surface of the working (copper) electrode was cleaned by abrading with 800 and 1000 grit silicon carbide papers and 1 μm Struers diamond paste. Then the fresh surface was rinsed several times with distilled water and immediately placed in the electrochemical cell. The calomel electrode was rinsed with distilled water and the platinum electrode was kept in dilute chromic acid and rinsed with distilled water before each experiment. The pulp potential was controlled with a Bank Elektronik Wenking PGS95 model potensiostat and its computer program, Zyklo. The potential values, recorded against the standard calomel electrode (SCE), were converted to the standard hydrogen (SHE) scale according to the formula [19]:

$$E_{\mathrm{SHE}} = E_{\mathrm{SCE}} + 0.245 \text{ V} \tag{1}$$

Investigation of the copper–DTPI interactions involved two successive parts. In the first part the redox reactions related to DTPI were studied. Cyclic voltammetry experiments with a platinum electrode were carried out in collectorless and DTPI added systems at the given pHs. This allowed characterizing the platinum surface as a function of pulp potential first, and to distinguish the specific oxidation–reduction reactions caused by DTPI. Collectorless and DTPI added experiments were run from positive to negative potential values in the −355 to 1550 mV range at 50 mV s^{-1}. The amount of DTPI addition was 3.80×10^{-4} M in the collector added experiments.

In the second part, the interactions between copper and DTPI and the nature of these interactions as a function of pulp potential and pH were determined. The

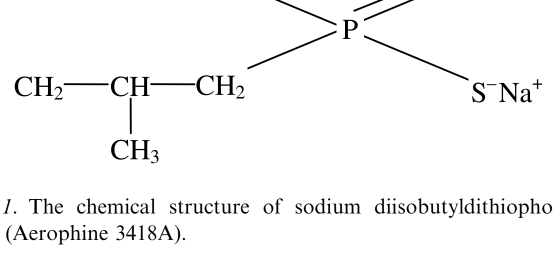

Fig. 1. The chemical structure of sodium diisobutyldithiophosphinate (Aerophine 3418A).

electrochemical behavior of the copper surface was characterized through CV experiments. The mutual interactions between copper and DTPI were investigated using the same electrochemical procedure and in the same conditions.

3. Results and discussion

3.1. *Electrochemical behavior of platinum electrode*

The experiment in acidic conditions (pH = 4.67) provided two cathodic and anodic reactions (Figure 2a). The intensities of these reactions were in the form of one shoulder and one peak in both anodic and cathodic scans. In the anodic scan one broad shoulder with low intensity and a higher intensity peak initiated around 1045 and 1445 mV, respectively (Figure 2a). The anodic shoulder is due to oxidation of the platinum surface. Oxidation of platinum occurs as a result of two successive processes. In the first one the platinum surface takes the platinum-hydroxide form with the hydroxide ions coming from the oxidative decomposition of water. Next platinum-hydroxide oxidizes into platinum-oxide with the removal of one hydrogen ion [20]. The related reactions are as follows:

$$\mathrm{Pt} + \mathrm{H_2O} = (\mathrm{Pt{-}OH}) + \mathrm{H^+} + \mathrm{e} \qquad (2)$$

$$(\mathrm{Pt{-}OH}) = (\mathrm{Pt{-}O}) + \mathrm{H^+} + \mathrm{e} \qquad (3)$$

The anodic peak around 1445 mV corresponds to the decomposition of water. This results in O_2 evolution and formation of free hydrogen ions in the solution based on the reaction:

$$2\mathrm{H_2O} = \mathrm{O_2} + 4\mathrm{H^+} + 4\mathrm{e} \qquad (4)$$

In the cathodic scan the cathodic shoulder around 495 mV was followed by a higher intensity peak around −305 mV. The cathodic shoulder corresponds to reduction of oxygen, which is adsorbed chemically on the platinum surface at highly positive potentials, to hydroxide form. The cathodic peak is due to reduction of the previously formed platinum hydroxide and the successive evolution of H_2 [20]. The mechanisms of these reactions are as follows:

$$(\mathrm{Pt{-}O}) + \mathrm{H^+} + \mathrm{e} = (\mathrm{Pt{-}OH}) \qquad (5)$$

$$(\mathrm{Pt{-}OH}) + \mathrm{H^+} + \mathrm{e} = \mathrm{Pt} + \mathrm{H_2O} \qquad (6)$$

$$\mathrm{H^+} + \mathrm{e} = \mathrm{H}$$

$$\mathrm{H} + \mathrm{H} = \mathrm{H_2} \qquad (7)$$

It should be noted that the oxidation reactions 5 and 6 are the reverse forms of cathodic reactions 3 and 2, respectively. That is, oxidation of the platinum surface was a reversible process.

In the voltammogram at pH = 6.97, two broad oxidation regions in the anodic scan at 695 and 1045 mV shows oxidation of the platinum surface according to Reactions 2 and 3. The peak after 1445 mV shows decomposition of water according to Reaction 4. In the cathodic scan two peaks were seen (Figure 2b). The first peak around +195 mV had higher intensity and is due to reduction of the platinum surface from Pt–O to Pt–OH form, as in Reaction 5. The second peak around −155 mV had lower intensity and shows reduction of Pt–OH according to Reaction 6. The important difference between acidic and neutral conditions is the variation of the peak potentials although they occurred due to the same reactions. It was reported that an increase in pH resulted in a shift of the oxidation/reduction potential of a reaction to a more negative value [21]. Thus, the evolution of hydrogen gas was not observed in neutral conditions since this reaction shifted to a more negative potential which was not within the scanned potential range.

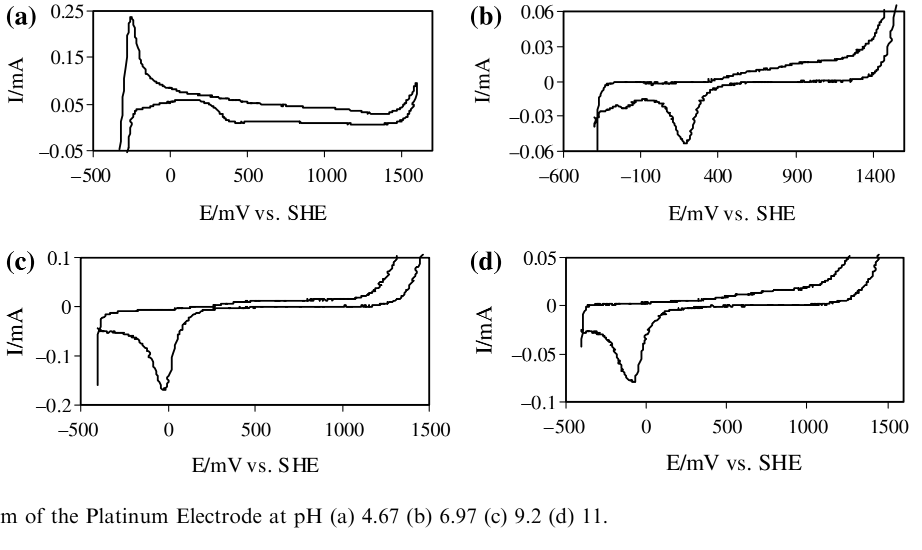

Fig. 2. Voltammogram of the Platinum Electrode at pH (a) 4.67 (b) 6.97 (c) 9.2 (d) 11.

Unlike acidic and neutral conditions, one anodic and one cathodic peak were observed in slightly and strongly alkaline conditions ($pH = 9.2$ and 11). The anodic peak, after 1000 mV, at $pH = 9.2$ and 11.0 corresponds to O_2 evolution at highly positive potentials. The cathodic peak corresponds to reduction of platinum-oxide to hydroxide form. This peak was observed at −35 and −85 mV at $pH = 9.2$ and 11, respectively (Figures 2c and d). Since the reactions shifted to more negative potentials with the increase in pH, the cathodic Pt–OH reduction and H_2 evolution reactions were not observed at $pH = 9.2$ and 11.0.

These observations show that oxidation of platinum into oxide and hydroxide forms in the anodic scan and reverse reduction into the platinum state in the cathodic scan are the characteristic electrochemical behaviors of platinum. The potentials of these reactions depend on pH, shifting to more negative potentials as pH increases.

3.2. *Experiments with the platinum electrode in the presence of DTPI*

The end potentials were increased by 200 mV at each cycle in order to investigate the starting potentials of the anodic and cathodic reactions and to determine whether the reactions are reversible or not.

In slightly acidic conditions ($pH = 4.67$), the anodic shoulder, starting from 1045 mV in the absence of DTPI (Figure 2a), was also observed in the presence of DTPI (Figure 3a), but with a higher intensity. This shows oxidation of the platinum surface and dimer formation on the electrode according to the reaction:

$$2DTPI^- = (DTPI)_2 + 2e \qquad (8)$$

The increase in the intensity of this shoulder is due to dimer formation. The cathodic peak starting around 445 mV in the absence of DTPI (Figure 2a) was also observed in the DTPI added conditions (Figure 3a). The intensity of this peak decreased and the peak was completely lost after the second cycle. This peak corresponds to reduction of Pt. The decrease in the intensity is due to coverage of the platinum surface by DTPI.

The same anodic shoulder occurred in neutral pH with a high intensity (Figure 3b). This shoulder corresponds to oxidation of Pt and successive dimer fomation. The cathodic peak shifted to a more negative potential (around 195 mV), as in the absence of DTPI. The intensity of the cathodic peak decreased gradually and finally the peak was lost due to coverage of the platinum surface by DTPI, as in $pH = 4.67$.

In alkaline conditions, dimer formation was observed at $pH = 9.2$, but with a lower intensity compared with slightly acidic and neutral pHs. Dimer formation in slightly alkaline conditions occurred at a lower potential, after 750 mV. Dimer formation was not seen at $pH = 11$. The cathodic behavior of platinum was the same for collectorless and DTPI added conditions at both $pH = 9.2$ and 11.0. The cathodic peak showing reduction of Pt–O to Pt–OH was the only reduction reaction in DTPI added conditions and occurred at almost the same potential as those in collectorless conditions (Figures 2c, d and 3c, d).

The only effect of DTPI addition was the increase in the intensity of the anodic shoulder around 1045 mV in slightly acidic and neutral conditions. DTPI addition did not result in any new anodic and cathodic reactions, however, the platinum surface gradually became passivated and the peak intensities decreased due to DTPI adsorption.

3.3. *Electrochemical behavior of copper electrode*

In the voltammogram of the copper electrode at $pH = 4.67$, two anodic peaks were seen (Figure 4a). The first anodic peak with a high intensity occurred around 460 mV. Another peak with a broader form and a lower intensity was seen around 645 mV. It is known that Cu^0 first oxidizes into a metal-oxide form in an anodic process. If oxidation continues, higher oxidation states would be achieved in the form of oxides and hydroxides [19, 20]. The oxidation peaks in the anodic scan are due to successive oxidation of Cu^0 to the metal-oxide and metal-hydroxide states. The first anodic peak shows oxidation of Cu^0 to Cu_2O according to the reaction:

$$Cu + H_2O \rightarrow Cu_2O + 2H^+ + 2e^-$$

$$Eh = 0.471 - 0.059\ pH \qquad (9)$$

Using the above equation, the Eh value was found as 195 mV. This value corresponds to the potential of the first anodic peak.

The broad form of the second anodic peak shows that formation of a higher metal-oxide state of copper and oxidation of Cu_2O into copper hydroxide occurred successively (Figure 4a) according to the mechanisms:

$$Cu_2O + H_2O \rightarrow 2CuO + 2H^+ + 2e^-$$

$$Eh = 0.669 - 0.059\ pH \qquad (10)$$

$$Cu_2O + 3H_2O \rightarrow 2Cu(OH)_2 + 2H^+ + 2e^-$$

$$Eh = 0.747 - 0.059\ pH \qquad (11)$$

The theoretical Eh values for the above reactions were 393.5 and 471.5 mV, respectively, showing that these reactions occur at close potentials. However, the second anodic peak started at a higher potential than the theoretical Eh value (Figure 4a). It has been

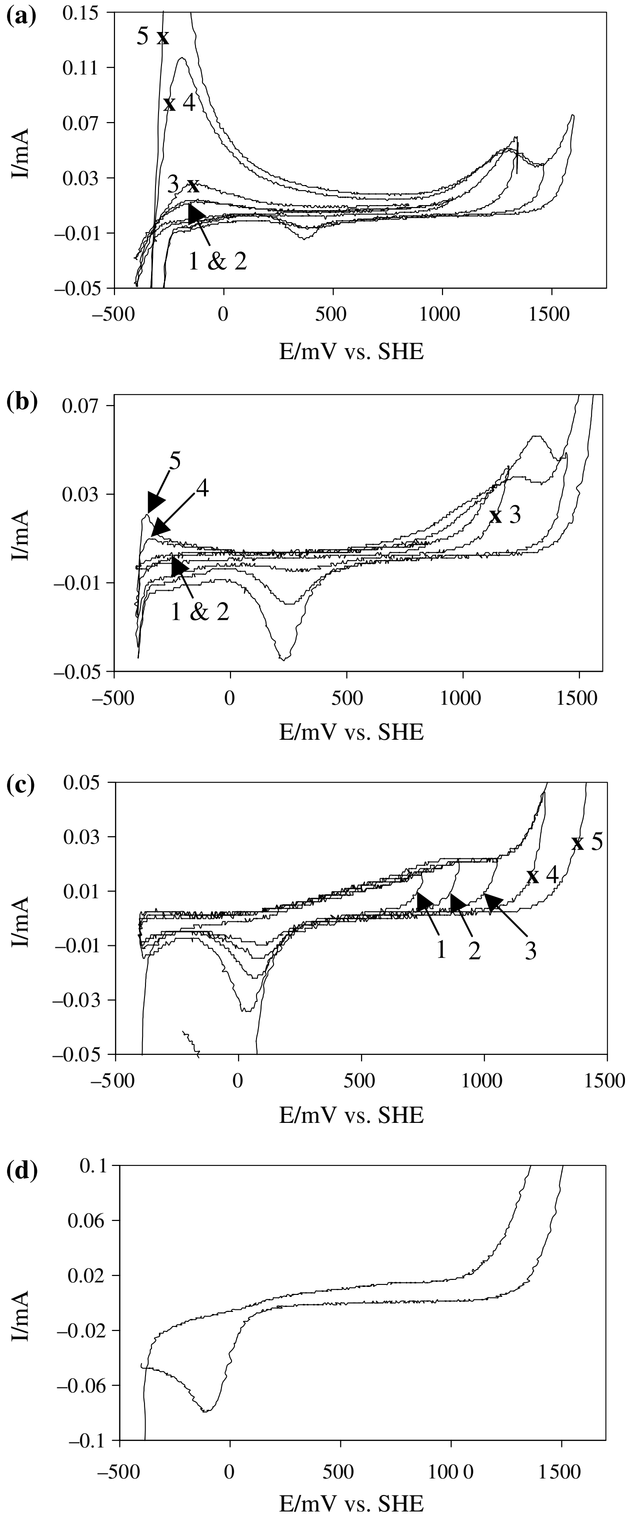

Fig. 3. Voltammogram of the Platinum Electrode in the Presence of NaDTPI at pH (a) 4.67 (b) 6.97 (c) 9.2 (d) 11.

reported that when more than one oxidation/reduction reactions occur successively, the first reaction may shift the following reactions to higher potentials (during an anodic scan) or to lower potentials (during a cathodic scan) than the theoretical Eh values [22, 23]. The first reaction may even offset the second reaction [22, 23].

In the cathodic scan two peaks were observed, starting around 245 and 80 mV respectively (Figure 4a). These peaks show reduction of $Cu(OH)_2$ and/or CuO into Cu_2O and successive reduction of Cu_2O into Cu^0 state. The mechanisms of these reactions are the reversed forms of Reactions 11 and 10, respectively. The intensities of both peaks were lower

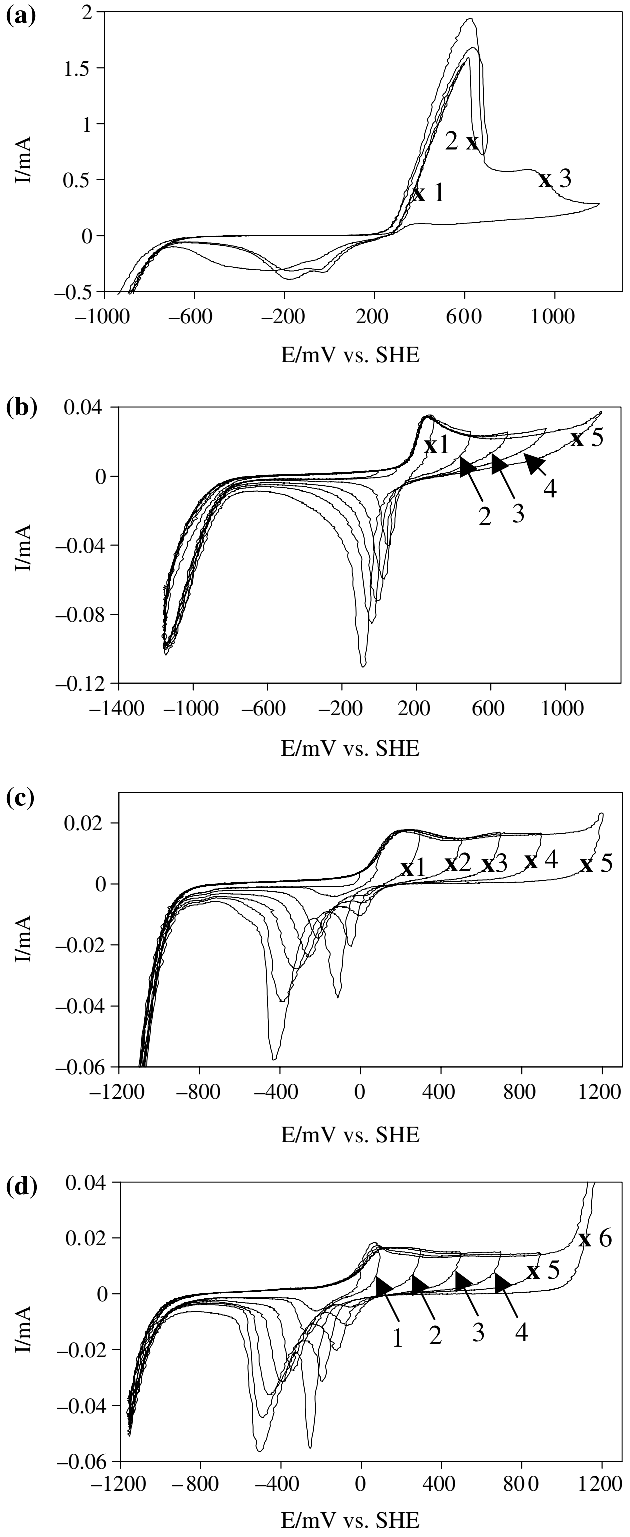

Fig. 4. Voltammogram of the Copper Electrode at pH (a) 4.67 (b) 6.97 (c) 9.2 (d) 11.

than their anodic peak couples. This indicates that the extent of oxidation and reduction reactions were not the same. In other words, the oxidation reactions were not completely reversible. The limited reversibility of the oxidation processes at pH = 4.67 shows that the copper oxide/hydroxide compounds were stable, and copper was in an oxidized form rather than its elemental form, Cu^0.

In the voltammogram of the copper electrode at pH = 6.97 one anodic and one cathodic peak were seen (Figure 4b). The anodic peak at around 245 mV corresponds to oxidation of Cu^0 to Cu_2O according to Reaction 9. In neutral conditions, the anodic peak of Cu^0 oxidation occurred at a lower potential compared with pH = 4.67. Further oxidation of Cu_2O did not occur, as shown by the narrow and sharp form of the anodic peak.

In the cathodic scan the reduction peak occurred at lower potentials as the anodic end potential was increased in each scan (Figure 4b). The decrease in the potential of the reduction peak with an increasing amount of oxidation (or an increased oxidation range) is typical of a process in which the oxidation products inhibit the cathodic process [20]. The cathodic peak corresponds to reduction of Cu_2O back into Cu^0 according to the reversed form of Reaction 9. Observation of a single reduction peak confirmed that further oxidation of Cu_2O did not occur during the anodic scan.

The electrochemical behavior of the copper electrode was similar in slightly alkaline (pH = 9.2) and strongly alkaline (pH = 11.0) conditions (Figures 4c and d). At both pHs one anodic and two cathodic peaks were observed. In both alkaline conditions, the anodic peaks were broad. The starting potential of the anodic peak was around 0 and −150 mV at pH = 9.2 and pH = 11.0, respectively. In the cathodic scan the first reduction peak occurred below 100 mV at pH = 9.2 and below 50 mV at pH = 11.0. The second cathodic peak was observed below −100 mV at pH = 9.2 and below −150 mV at pH = 11.0. The cathodic peaks started at lower potentials in the successive scans due to increased oxidation, as the anodic end potential was increased.

The observation of two successive peaks in the cathodic scan indicates a two-step reduction process. Oxidation of the copper surface from Cu^0 to Cu_2O and oxidation of Cu_2O to CuO and/or $Cu(OH)_2$ occurred as successive processes during the anodic scan. The broad form of the anodic peak indicates this situation. Therefore, the cathodic peaks show reduction of copper oxide/hydroxide compounds back into Cu^0 through a two-step cathodic process according to the reversed forms of Reactions 11, 10 and 9. Alkaline conditions allowed significant electrochemical activity on the copper surface, involving both oxidation of Cu^0 up to Cu^{2+} and reversible reduction of the oxidation products. The extent of the reduction peak intensities shows that the stability of the oxidation products decreased as pH became alkaline.

3.4. *Experiments with the copper electrode in the presence of DTPI*

In DTPI added conditions, the voltammogram changed significantly at pH = 4.67 (Figures 4a and 5a). One anodic peak was seen which started at 245 mV. In the

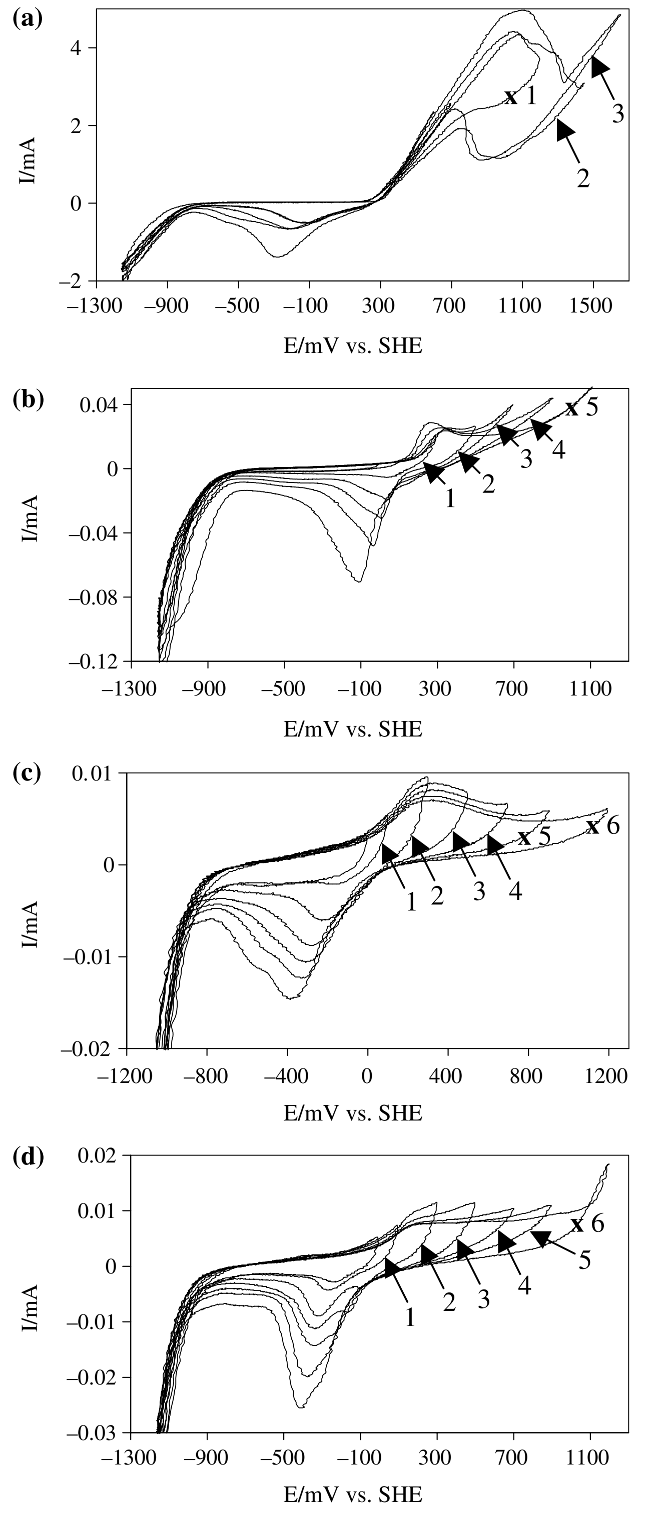

Fig. 5. Voltammogram of the Copper Electrode in the Presence of NaDTPI at pH (a) 4.67 (b) 6.97 (c) 9.2 (d) 11.

cathodic scan two cathodic peaks at 945 and −250 mV were observed. The anodic peak corresponds to oxidation of Cu^0 to Cu^+ and successive formation of CuDTPI compounds. The mechanisms for these reactions are:

$$Cu^0 \rightarrow Cu^+ + e^- \tag{12}$$

$$Cu^+ + DTPI^- \rightarrow CuDTPI \tag{13}$$

Formation of a copper–DTPI complex is a two-step process in which the initial electrochemical reaction (Reaction 12) is followed by a chemical reaction between the oxidized Cu^+ and $DTPI^-$ ions. The overall reaction is:

$$Cu^0 + DTPI^- \rightarrow CuDTPI + e^- \tag{14}$$

The presence of a high intensity reduction peak at around 945 mV in the cathodic scan indicates additional oxidation processes during the anodic scan. In the previous part of the study, dimer formation of $DTPI^-$ was determined at highly oxidizing potentials. It is thought that remaining Cu^+ ions oxidized into a cupric state and reacted with the dimer form of DTPI to create $Cu(DTPI)_2$ complexes. Oxidation of copper from cuprous to cupric state and the dimer formation were involved in a single oxidation peak. The occurrence of these anodic processes in succession explains the broad form of the anodic peak from 245 to1300 mV and its apparently higher intensity compared with neutral and alkaline pHs (Figures 4a–d).

Similar findings were reported about the formation of $Cu(X)_2$ and $Cu(DTP)_2$ in copper-Xanthate and copper-Dithiophosphate systems [20, 24, 25]. However, Chander and Fuerstenau [20] noted that $Cu(DTP)_2$ was a thermodynamically unstable compound which decomposed after formation, leaving Cu(DTP) as the stable metal-collector complexes. The reduction peak around 945 mV shows that Chander and Fuerstenau's finding applies for the Cu–DTPI system. The cupric collector complex decomposed into a more stable cuprous form, resulting in a high intensity reduction peak around 945 mV. The mechanism for this reaction is:

$$Cu(DTPI)_2 + e^- \rightarrow Cu(DTPI) \tag{15}$$

The reduction peak at −250 mV corresponds to the second cathodic region in collectorless conditions (Figures 4a and 5a). This peak shows reduction of non-reacted copper oxide sites back into a Cu^0 state. Owing to the decrease in the amount of non-reacted copper oxide sites and the passivation of the surface due to formation of CuDTPI layers, the intensity of this peak decreased after the first scan. Passivation of the electrode surface shows that adsorption of CuDTPI was stable and irreversible.

Copper electrode had a similar behavior in neutral pH ($pH = 6.97$) with the collectorless conditions (Figure 5b). One anodic and one cathodic peak were observed in the DTPI added experiment, as in the collectorless conditions. However, these peaks had broader forms and lower intensities (Figure 5b). These observations suggest that DTPI was adsorbed on the copper electrode and formed a passive layer by an electrochemical mechanism. The cathodic peak indicates reduction of the remaining non-reacted copper oxides (Figure 5b). No cathodic peak showing a $Cu(DTPI)_2$ reduction was observed in neutral conditions, and the intensity of the anodic peak was lower unlike the acidic conditions (Figures 5a and b). This shows that oxidation of Cu^0 to a cupric state was inhibited in neutral pH due to surface passivation as a result of DTPI adsorption.

In alkaline conditions (pH = 9.2 and pH = 11.0) the voltammograms obtained after DTPI addition were different from the collectorless conditions (Figures 5c and d). In the anodic scan the oxidation peaks started above −50 and −150 mV at pH = 9.2 and pH = 11.0, respectively. For both pHs, the anodic reactions occurred as broad shoulders with decreased intensities (Figures 4c, d and 5c, d). In the cathodic scan one cathodic peak was seen at both pHs. In general, the electrochemical behaviors in alkaline conditions had similar natures with that of neutral pH. The anodic shoulder at pH = 9.2 and pH = 11.0 corresponds to the CuDTPI formation. The decrease in the intensity of the anodic shoulder during successive scans indicates surface passivation of copper due to DTPI adsorption. The stable CuDTPI compounds on the copper surface decreased the exposed surface area to the solution in successive scans. This results in a decrease in the amount of free Cu^0 ions available for oxidation, as indicated by the reduced intensities of the anodic peaks. It should also be noted that the decrease in the intensity was higher at pH = 11.0, showing higher passivation as the solution became more alkaline.

In the cathodic scan one cathodic peak was seen below 0 and 50 mV at pHs 9.2 and pH = 11.0 respectively (Figures 5c and d). This peak corresponds to reduction of the copper oxide sites which did not react with DTPI. Observation of a reduction peak in the cathodic scan suggests a single-step oxidation–reduction activity on the copper surface in alkaline conditions. No indication of a $Cu(DTPI)_2$ formation was observed and DTPI prevented further oxidation of the copper surface in alkaline conditions, as in neutral pH.

4. Conclusion

Cyclic voltammetry experiments with platinum and copper with and without DTPI show that the main interaction between copper and DTPI is the formation of CuDTPI compounds. This is through a mixed mechanism (oxidation of Cu^0 to Cu^+ followed by chemical reaction between Cu^+ and $DTPI^-$). The formation of CuDTPI was observed at all pHs, and the occurrence of a cuprous metal-collector complex resulted in increasing passivation of the copper surface as the pulp became more alkaline. Formation of higher state copper compounds, such as CuO, was observed in collectorless conditions. However, DTPI addition and the successive CuDTPI formation prevented further oxidation of copper than the Cu^+ state in both neutral and alkaline conditions. Only in acidic pH was an additional electrochemical interaction between the copper surface and DTPI observed, resulting in the formation of cupric $Cu(DTPI)_2$ complexes. On the other hand, $Cu(DTPI)_2$ was unstable and decomposed into a more stable Cu(DTPI) form during the cathodic scan. The interaction between copper and DTPI relied on chemical adsorption, forming irreversible Cu(DTPI) complexes on the copper surface at all pHs.

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