CHAPTER 3

RESULTS AND DISCUSSION

3.1 The preparation of the complexes

The suitable conditions of synthesis complexes have been figured and they are summarized in Table 2. Some of their physical properties together with reacting ligand are compiled in Table 3.

Table 2 The suitable conditions of complexes synthesis.

Reactants	Mole ratio	Solvent	Temperature(^{o}C)	Complexes
CuCl : dptu	1 : 2	Acetonitrile	60	$[Cu(dptu)_2Cl]H_2O$
CuBr : dptu	1 : 2	Acetonitrile	60	$[Cu(dptu)_2Br]H_2O$
CuI : dptu	1 : 2	Acetonitrile	60	$[Cu(dptu)_2I]H_2O$
CuCl : ptu	1 : 3	Acetonitrile	50	$[Cu(ptu)_4]Cl$
CuBr : ptu	1 : 2.5	Acetonitrile	60	$[Cu_4(ptu)_6Br_4]_2$
CuI : ptu	1 : 3	Acetonitrile	60	$[Cu_4(ptu)_6I_4]_2$
CuCl : etu	1 : 2	Water	50	$[Cu_2(etu)_4Cl_2]$
CuBr : etu	1 : 3	Water	25	$[Cu(etu)_3Br]$
CuI : etu	1 : 2	Water	25	$[Cu_2(etu)_4I_2]$

Table 3 The physical properties of ligands and complexes

Compounds	Physical properties		
	Appearance	Colors	Melting point (^{o}C)
dptu	Powder	White	150-153
$[Cu(dptu)_2Cl]H_2O$	Crystal	Colorless	170
$[Cu(dptu)_2Br]\ H_2O$	Crystal	Colorless	190
$[Cu(dptu)_2I]\ H_2O$	Crystal	Colorless	195
ptu	Powder	White	145-150
$[Cu(ptu)_4]Cl$	Needle	Colorless	161
$[Cu_4(ptu)_6Br_4]_2$	Plate	Colorless	205-207
$[Cu_4(ptu)_6I_4]_2$	Plate	Colorless	190-192
etu	Powder	White	203-204
$[Cu_2(etu)_4Cl_2]$	Plate	Colorless	168
$[Cu(etu)_3Br]$	Plate	Colorless	146-148
$[Cu_2(etu)_4I_2]$	Plate	Colorless	173-175

3.2 The electrochemical behavior of blank solution

Cyclic voltammogram of all blank solutions were recorded with the potential range of -2.50 V to 2.50 V vs Ag/AgCl. No significant peak was obtained, indicating that there were no significant impurities as shown in Figure 13.

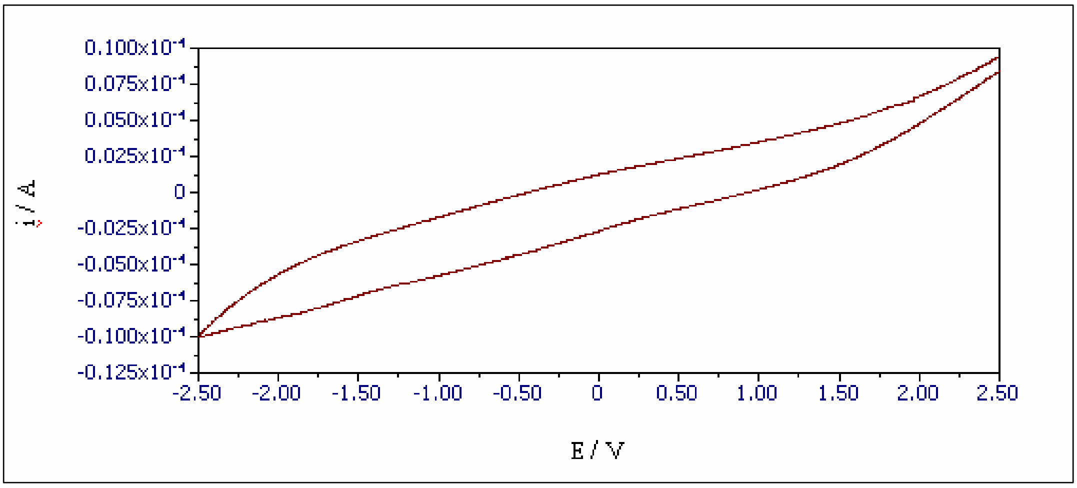

Figure 13 Cyclic voltammogram of blank solution at glassy carbon electrode in 25 ml CH_3CN solution which 0.1 M TBAP as supporting electrolyte within the range of -2.50 V to 2.50 V with scan rate of 0.1 V/s.

3.3 The electrochemical behavior of copper ion

Cyclic voltammogram of blank solution was performed with the potential range of 2.50 V to -2.50 V vs Ag/AgCl. It was found that there were no significant impurities.

Cyclic voltammogram of Cu(II) in CH_3CN at glassy carbon electrode is shown in Figure 14. Starting from the resting potential, the first reduction peak appears at 0.734 V. The second reduction peak appears at -0.667 V. When the scan is reversed, the first oxidation peak occurs at –0.259 V and the second oxidation peak occurs at 0.812 V.

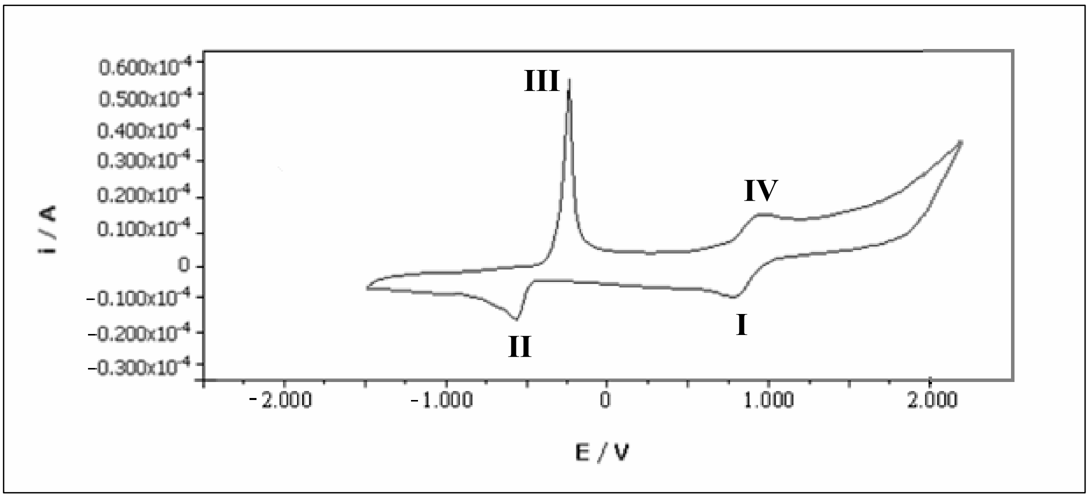

Figure 14 Cyclic voltammogram of 1.0 x 10^{-3} M Cu(II) nitrate at glassy carbon electrode in 25 ml CH_3CN solution with 0.1M TBAP as supporting electrolyte within the range of -1.75 V to 2.00 V with scan rate of 0.1 V/s and the resting potential of 0.3 V.

The scan is started at resting potential, the reduction peak at Epc = 0.734 V and the oxidation peak at Epa = 0.812 V corresponds to the redox reaction of copper(II)/(I). The reduction peak at Epc = -0.667 V and the oxidation peak at Epa = -0.259 V corresponds to the redox reaction of copper(I)/(0). The reactions and corresponding potentials are shown in Figure 15.

$Cu^{2+}(aq) + e^- \rightleftharpoons Cu^{+}(aq)$ $E^{o\prime}_1 =$ 0.773 V (I, IV)

$Cu^{+}(aq) + e^- \rightleftharpoons Cu^{0}(s)$ $E^{o\prime}_2 =$ -0.463 V (II, III)

Figure 15 The redox reactions of copper(II)/copper(I) and copper(I)/copper(0)

3.4 The electrochemical behavior of halide ions

3.4.1 The electrochemical behavior of chloride ion

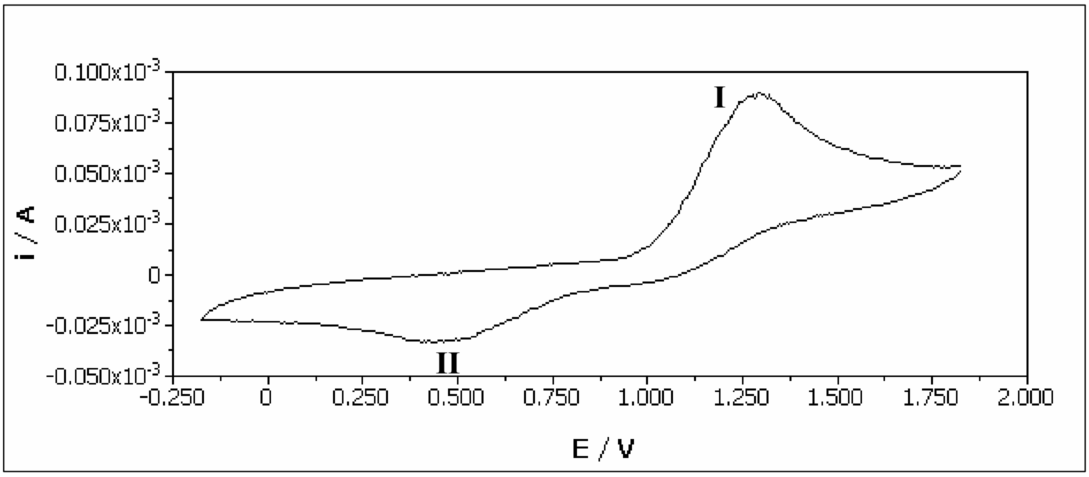

Figure 16 Cyclic voltammogram of 1x10^{-2} M tetrabutylammonium chloride at glassy carbon electrode in 25 ml CH_3CN solutions with 0.1 M TBAP as supporting electrolyte. The scan rate of 0.1 V/s and the resting potential of 0.64 V.

Cyclic voltammogram of blank solution was performed with the potential range of -2.50 V to 2.50 V vs Ag/AgCl. It was found that there were no significant impurities.

The cyclic voltammogram of chloride ion exhibits a redox couple in acetonitrile as shown in Figure 16. The oxidation peak occurs at 1.256 V with Ipa = 6.2365 x 10^{-5} A and the reduction peak occurs at 0.435 V with Ipc = -1.047 x 10^{-5} A. The behavior of a redox couple is quasi-reversible and not completely chemically reversible (Ipa/Ipc = 5.965). That is, the oxidation of chloride ion to its chlorine and chlorine can be reduced to form chloride. The corresponding mechanism is shown in Figure 17.

$$2Cl^- \rightleftharpoons Cl_2 + 2e- \qquad E^{o\prime} = 0.8455\ V \qquad (I, II)$$

Figure 17 The redox reactions of chloride ions

3.4.2 The electrochemical behavior of bromide ion

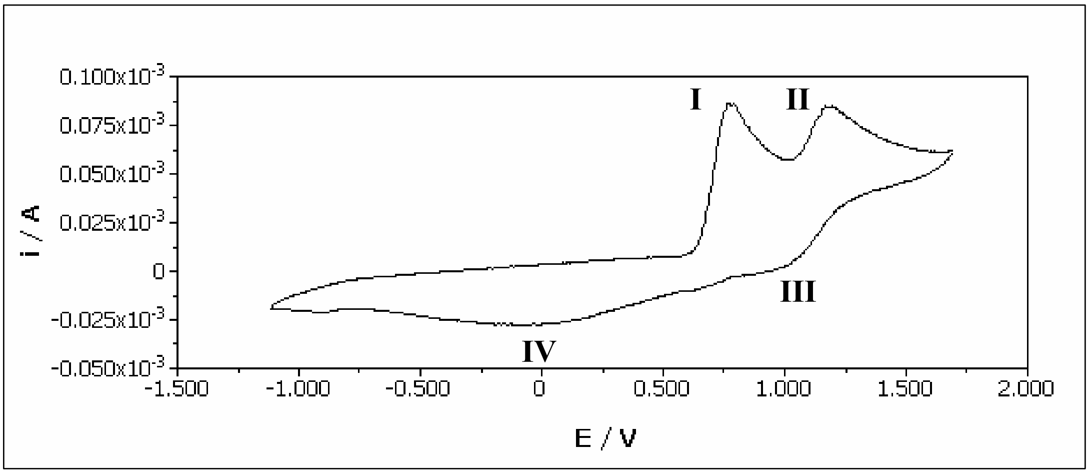

Figure 18 Cyclic voltammogram of 1x10^{-2} M tetrabutylammonium bromide at glassy carbon electrode in 25 ml CH_3CN solution which 0.1 M TBAP as supporting electrolyte with scan rate of 0.1 V/s and the resting potential of 0.34 V.

Cyclic voltammogram of blank solution was performed with the potential range of -2.50 V to 2.50 V vs Ag/AgCl. It was found that there were no significant impurities.

The cyclic voltammogram of bromide ion reveals two redox reactions in acetonitrile as shown in Figure 18. The first oxidation peak occurs at 0.764 V with Ipa_1 = 5.9269 x 10^{-5} A and the corresponding reduction peak occurs at -0.089 V with Ipc_1 = 9.7384 x 10^{-6} A (Ipa_1/Ipc_1 = 6.0861). This couple is electrochemical quasi-reversible reflecting slow electron transfer under the experimental condition. There is another independent oxidation peak which occurs at 1.169 V with Ipa_2 = 2.6512 x 10^{-5} A and the reduction peak occurs at 1.050 V with Ipc_2 = 7.7907 x 10^{-6} A (Ipa_2/Ipc_2 = 3.4030). This couple is electrochemical quasi-reversible. Both two redox are not completely chemically reversible.

The first electrochemical quasi-reversible couple is due to the oxidation of bromide ion to its tribromide which can be oxidized to form bromine (Monvemay *et al.*, 1987). The reactions are shown in Figure 19.

$$3Br^- \rightleftharpoons Br_3^- + 2e^- \qquad E^{o\prime}_1 = 0.3375\ V \qquad (I, IV)$$

$$2Br_3^- \rightleftharpoons 3Br_2 + 2e^- \qquad E^{o\prime}_2 = 1.1095\ V \qquad (II, III)$$

Figure 19 The redox reactions of bromide ions

3.4.3 The electrochemical behavior of iodide ion

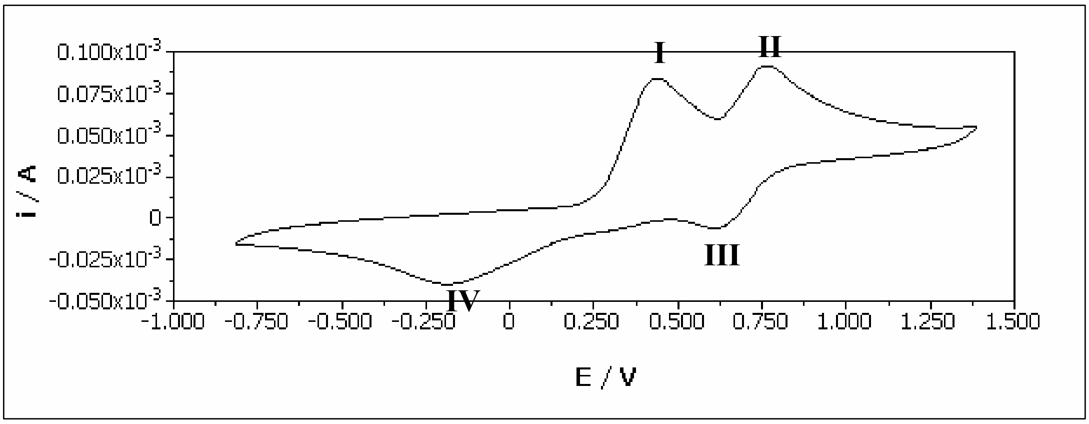

Figure 20 Cyclic voltammogram of 1x10^{-2} M tetrabutylammonium iodide at glassy carbon electrode in 25 ml CH_3CN solution with 0.1 M TBAP as supporting electrolyte with scan rate of 0.1 V/s and the resting potential of 0.28 V.

Cyclic voltammogram of blank solution was performed with the potential range of -2.50 V to 2.50 V vs Ag/AgCl. It was found that there were no significant impurities.

Iodide ions exhibit two redox couples in acetonitrile as shown in Figure 20. The first redox couple occurs at Epa_1 = 0.424 V with Ipa_1 = 4.86 x 10^{-5} A and Epc_1 = -0.177 V with Ipc_1 = -2.81 x 10^{-5} A. The second redox couple occurs at Epa_2 = 0.765 V with Ipa_2 = 3.31 x 10^{-5} A and Epc_2 = 0.634 V with Ipc_2 = -2.08 x 10^{-5} A. The two redox couples are quasi-reversible and not completely chemically reversible with Ipa/Ipc = 1.7295 and 1.5913 respectively.

The electrochemical quasi-reversible couples are due to the oxidation of iodide ion to its triiodide which can be oxidized to form iodine (Yaraliyev., 1984). The reactions are shown in Figure 21.

$$3I^- \rightleftharpoons I_3^- + 2e^- \qquad E^{o\prime}_1 = 0.1235\ \text{V} \qquad \text{(I, IV)}$$

$$2I_3^- \rightleftharpoons 3I_2 + 2e^- \qquad E^{o\prime}_2 = 0.6995\ \text{V} \qquad \text{(II, III)}$$

Figure 21 The redox reactions of iodide ions

3.5 The electrochemical behavior of substituted thioureas

3.5.1 The electrochemical behavior of *N,N′*-diphenylthiourea (dptu)

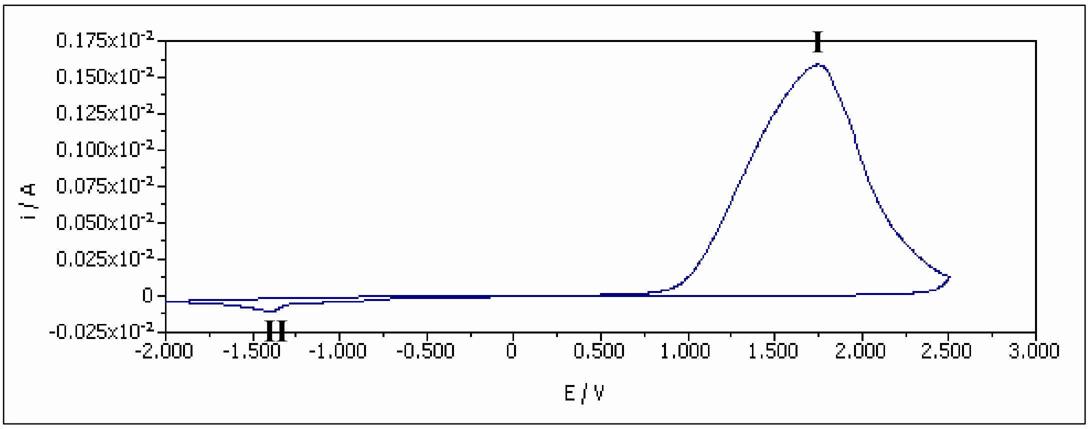

Figure 22 Cyclic voltammogram of 0.1 M *N,N′*-diphenylthiourea (dptu) at glassy carbon electrode in 25 ml CH_3CN solution with 0.1 M TBAP as supporting electrolyte, within the range of -2.00 V to 2.50 V with scan rate of 0.2 V/s and the resting potential of 0.296 V.

Cyclic voltammogram of blank solution was performed with the potential range of -2.50 V to 2.50 V vs Ag/AgCl. It was found that there were no significant impurities.

The cyclic voltammogram of *N,N′*-diphenylthiourea (dptu) solution was performed with the potential range of -2.00 to 2.50 V vs Ag/AgCl. Diphenylthiourea exhibits a redox reaction in acetonitrile as shown in Figure 22. The oxidation peak occurs at Epa = 1.745 V with Ipa = 1.5 x 10^{-3} A and the reduction peak occurs at Epc = -1.385 V with Ipc = 5.84 x 10^{-5} A. This redox peak is electrochemically quasi-reversible and not completely chemically reversible with Ipa/Ipc = 25.684.

The oxidation of *N,N′*-diphenylthiourea is purely diffusion controlled due to the fact that it exhibits a linear relationship between peak currents and the square root of scan rates as shown in Figure 23. However, the reduction of *N,N′*-diphenylthiourea is not diffusion controlled. The non linear relationship between peak currents and square root of scan rates is shown in Figure 24. The oxidation peak has high current which is possibly due to the fact that there is a peak overlap between the oxidation peak of sulfur and amine group.

Table 4 The relationship of the square roots of scan rates and current peaks of *N,N′*-diphenylthiourea.

Scan rate ($mV\ s^{-1}$)	Square root of scan rate ($(mV^{-1})^{1/2}$)	Ipa (A)	Ipc (A)
100	10.00	9.82 x 10^{-4}	-2.67 x10^{-6}
200	14.14	1.16 x10^{-3}	-3.48 x10^{-6}
300	17.32	1.35 x10^{-3}	-3.68 x10^{-7}
400	20.00	1.50 x10^{-3}	-5.84 x10^{-5}
500	22.36	1.61 x10^{-3}	-8.57 x 10^{-5}

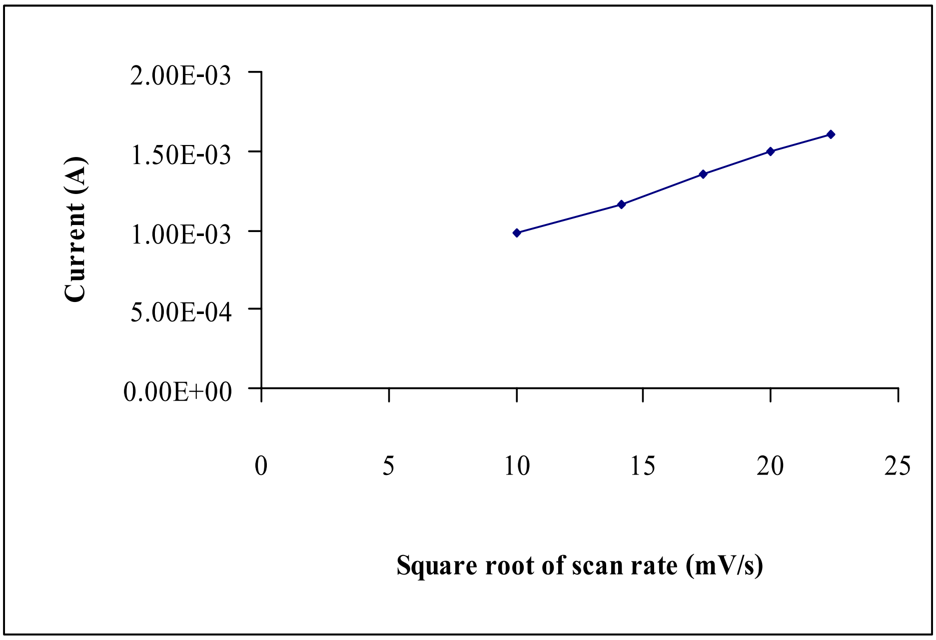

Figure 23 The relationship between square roots of scan rates and oxidation currents (Ipa) of *N,N'*-diphenylthiourea.

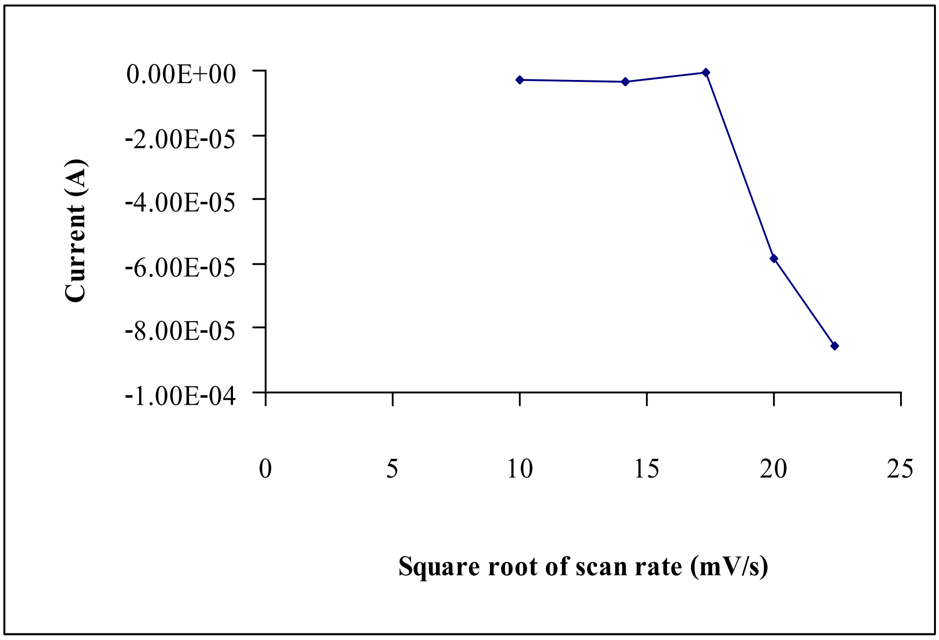

Figure 24 The relationship between the square roots of scan rates and reduction currents (Ipc) of *N,N'*-diphenylthiourea.

3.5.2 The electrochemical behavior of *N*-phenylthiourea (ptu)

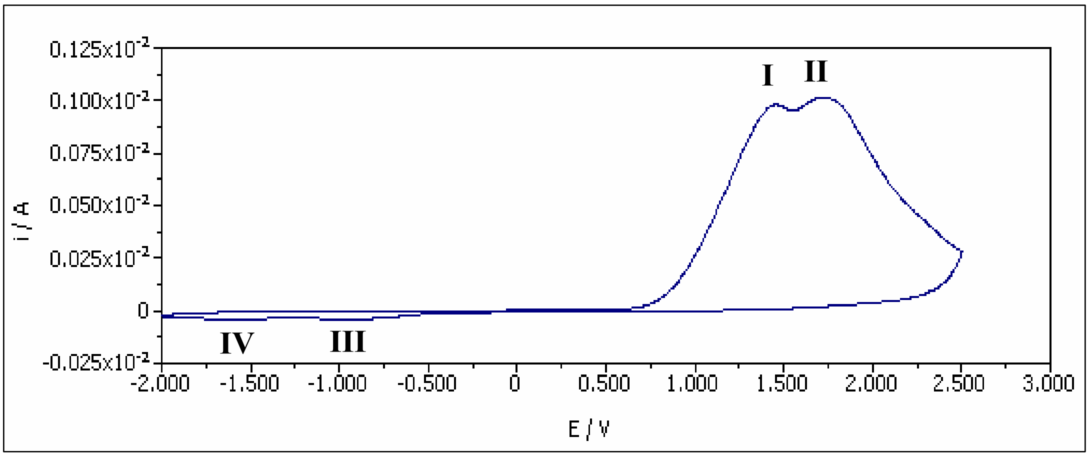

Figure 25 Cyclic voltammogram of 0.1 M phenylthiourea (ptu) at glassy carbon electrode in 25 ml CH_3CN solution with 0.1 M TBAP as supporting electrolyte, within the range of -2.00 V to 2.50 V with scan rate of 0.2 V/s and the resting potential of 0.227 V.

Cyclic voltammogram of blank solution was performed with the potential range of -2.50 V to 2.50 V vs Ag/AgCl. It was found that there were no significant impurities.

The cyclic voltammogram of *N*-phenylthiourea (ptu) solution was performed with the potential range of -2.00 to 2.50 V vs Ag/AgCl. *N*-Phenylthiourea exhibits two redox couples in acetonitrile as shown in Figure 25.

The first redox couple occurs at Epa_1 = 1.462 V and Epc_1 = -0.945 V vs Ag/AgCl. The second redox couple occurs at Epa_2 = 1.711 V and Epc_2 = -1.595 V vs Ag/AgCl. The behavior of two redox couples is electrochemical quasi-reversible. Both redox reactions of *N*-phenylthiourea are not diffusion controlled, it exhibits a non linear relationship between peak currents and square root of scan rate as shown in Figure 26 and 27. The first redox couple of *N*-phenylthiourea can be assigned to be due to the oxidation and reduction of sulfur group [Kirchnerova *et al.*, 1981] and the second redox couple of *N*-phenylthiourea is due to the oxidation and reduction of aromatic amine group [Mabbott G. A., 1983].

Table 5 The relationship of the square roots of scan rates and current peaks of *N*- phenylthiourea.

Scan rate (mV s^{-1})	Square root of scan rate (mV $^{-1}$)$^{1/2}$	Ipa1 (A)	Ipa2 (A)	Ipc1 (A)	Ipc2 (A)
100	10.00	2.34 x 10^{-4}	4.45 x 10^{-4}	-2.65 x10^{-6}	-2.54 x10^{-7}
200	14.14	3.60 x10^{-5}	1.98 x10^{-4}	-2.11 x10^{-6}	-2.86 x10^{-6}
300	17.32	2.00 x10^{-5}	5.51 x10^{-5}	-2.82 x10^{-6}	-6.85 x10^{-6}
400	20.00	1.14 x10^{-5}	5.16 x10^{-5}	-4.53 x10^{-6}	-1.23 x10^{-5}
500	22.36	1.73 x10^{-5}	4.39x10^{-5}	-1.18 x 10^{-5}	-1.57 x 10^{-5}

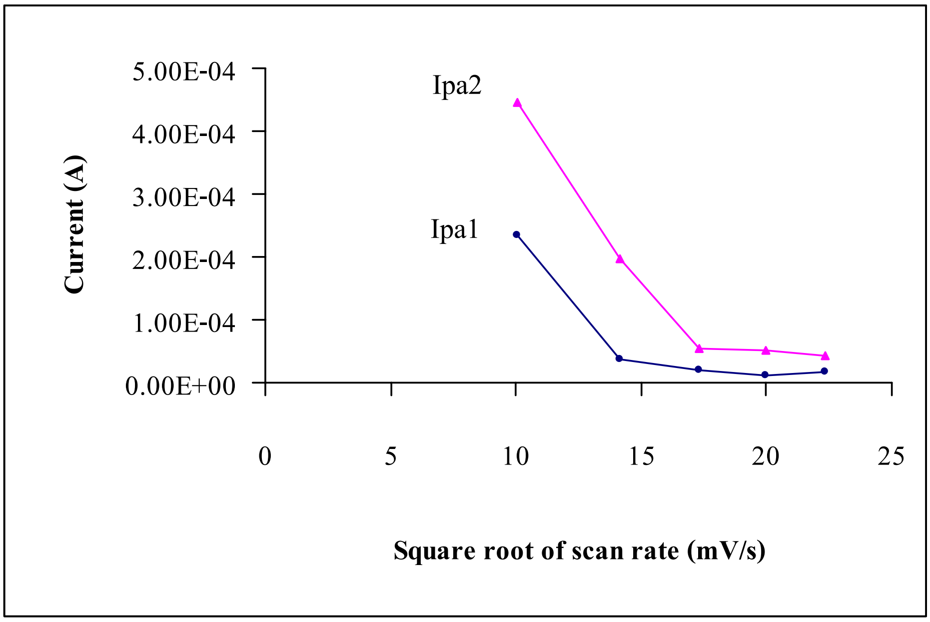

Figure 26 The relationship between the square roots of scan rates and oxidation currents (Ipa) of *N*-phenylthiourea.

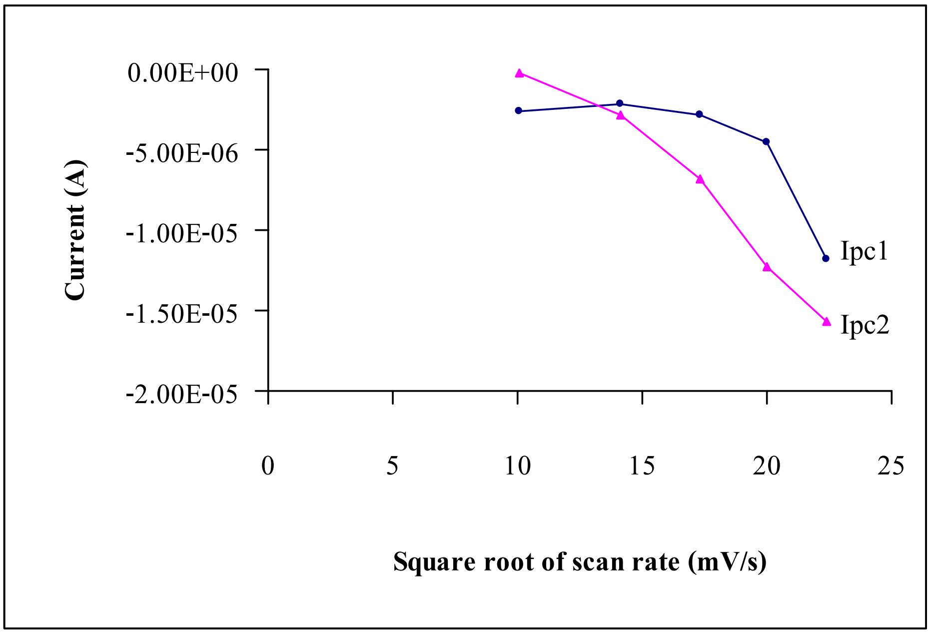

Figure 27 The relationship between the square roots of scan rates and reduction currents (Ipc) of *N*-phenylthiourea.

3.5.3 The electrochemical behavior of *N,N′*-ethylenethiourea (etu)

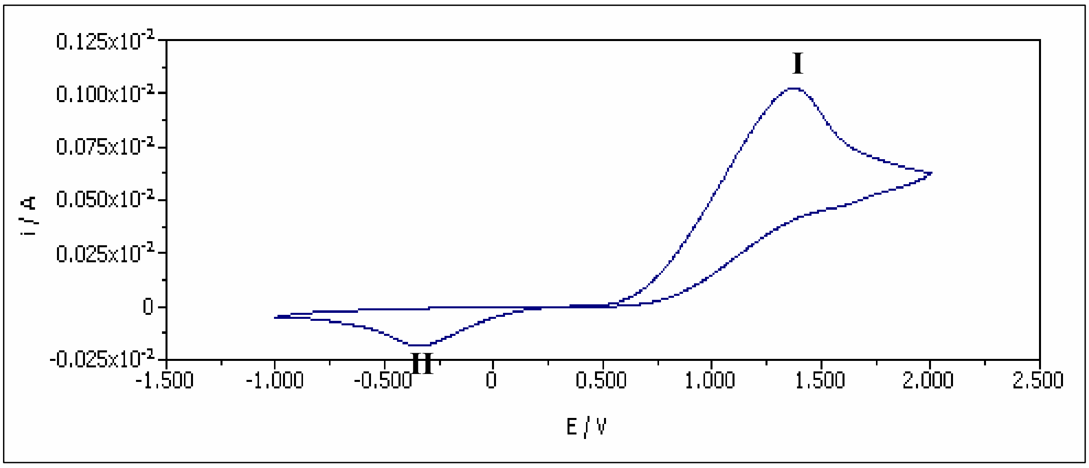

Figure 28 Cyclic voltammogram of 0.1 M *N,N′*-ethylenethiourea (etu) at glassy carbon electrode in 25 ml CH_3CN solution with 0.1 M TBAP as supporting electrolyte, within the range of -1.00 V to 2.00 V with scan rate of 0.1 V/s and the resting potential of 0.323 V.

Cyclic voltammogram of blank solution was performed with the potential range of -2.50 V to 2.50 V vs Ag/AgCl. It was found that there were no significant impurities.

The cyclic voltammogram of *N,N′*-ethylenethiourea (etu) solution was performed with the potential range of -1.00 V to 2.00 V vs Ag/AgCl. It was found that *N,N′*-ethylenethiourea exhibits a redox couple in acetonitrile as shown in Figure 28.

The oxidation peak appears at Epa = 1.349 V with Ipa = 6.64 x 10^{-4} A when the scan was reversed, the reduction peak appears at Epc = -0.341 V with Ipc = -1.57 x 10^{-4} A. The redox couples therefore have the behavior of electrochemically quasi-reversible and not completely chemically reversible with Ipa/Ipc = 4.2293. Both the oxidation and reduction reactions of *N,N′*-ethylenethiourea are purely diffusion controlled due to the fact that it exhibits a linear relationship between peak currents and square root of scan rate as shown in Figure 29 and 30. The redox couple of *N,N′*-ethylenethiourea is due to the oxidation and reduction of sulfur group (Kirchnerova *et al.*, 1981).

Table 6 The relationship of the square roots of scan rates and current peaks of *N,N′*-ethylenethiourea.

Scan rate ($mV\ s^{-1}$)	Square root of scan rate ($(mV^{-1})^{1/2}$)	Ipa (A)	Ipc (A)
100	10.00	2.81 x 10^{-4}	-3.35 x 10^{-5}
200	14.14	5.56 x 10^{-4}	-1.05 x 10^{-4}
300	17.32	6.64 x 10^{-4}	-1.57 x 10^{-4}
400	20.00	7.82 x 10^{-4}	-2.22 x 10^{-4}
500	22.36	8.54 x 10^{-4}	-2.79 x 10^{-4}

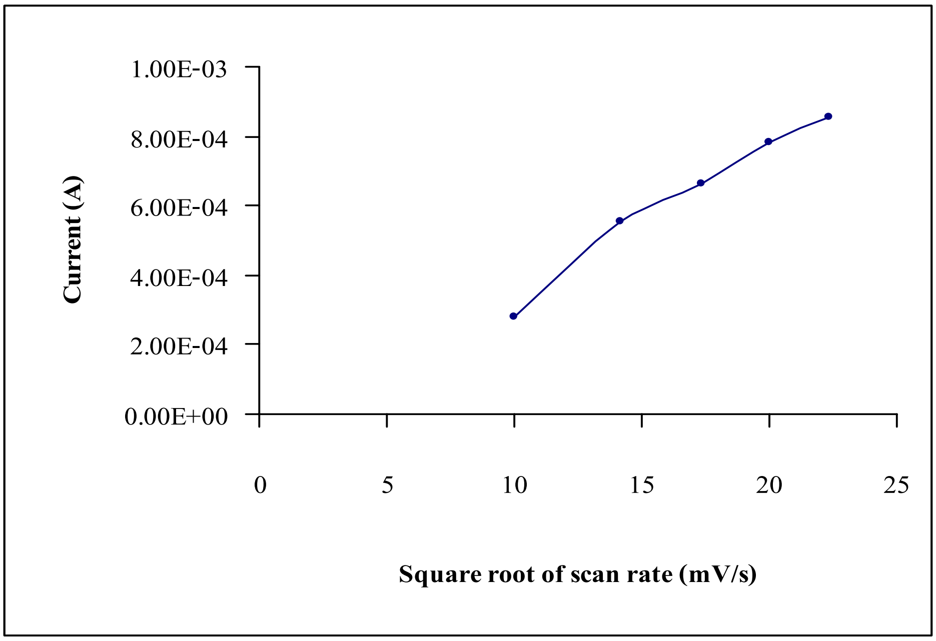

Figure 29 The relationship between square roots of scan rates and oxidation currents (Ipa) of *N,N′*-ethylenethiourea.

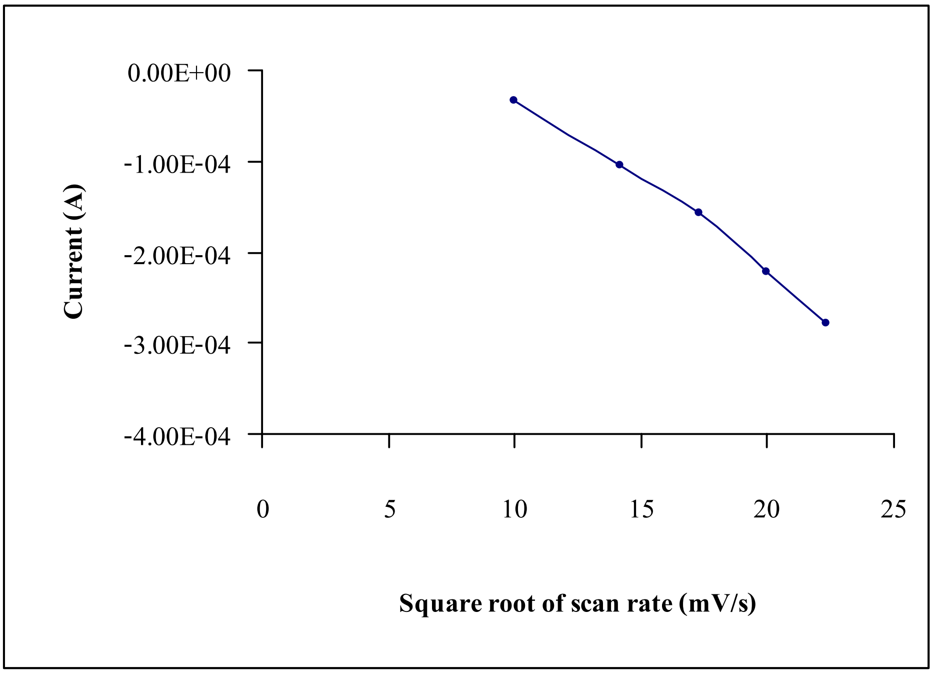

Figure 30 The relationship between square roots of scan rates and reduction currents (Ipc) of *N,N′*-ethylenethiourea.

3.5.4 Discussion on the electrochemical behavior of substituted thiourea compounds

The electrochemical behaviors of substituted thioureas including *N,N′*-diphenylthiourea, *N*-phenylthiourea and *N,N′*-ethylenethiourea are found to be different. The presence of phenyl group makes the oxidation potential shift to more positive value and the reduction potential shift to more negative value. The resonance effect in their structure reasonable makes the oxidation reaction and the reduction reaction occurs more difficult.

In the case of *N,N′*-diphenylthiourea (dptu), it exhibits an oxidation peak and a reduction peak due to the fact that *N,N′*-diphenylthiourea contributes steric effect by its structure (two phenyl groups). But *N*-phenylthiourea (ptu) has only one phenyl group yet exhibits two redox couples. The first redox reaction of this compound is due to the reaction of sulfur group. The second redox reaction is due to the reaction of amine group which similar to the redox reaction of *N,N′*-diphenylthiourea. The electrochemical behavior of *N,N′*-diphenylthiourea gives a result similar to the compound of 2-formylpyridine thiosemicarbazone (PATS2) which the redox reaction occurs at amine group (Monica *et al.*, 2003).

N-ethylenethiourea (etu) has the CH_2-CH_2 group as a substituent. This compound exhibits a redox couple, occurring at Epa = 1.349 V and Epc = -0.341 V vs Ag/AgCl. *N*-ethylenethiourea has the redox potentials close to those of thiourea (Epa = 0.809 V and Epc = -0.145 V vs Ag/AgCl) under the same conditions. The oxidation potential of *N*-ethylenethiourea shifts to more positive value. The reduction potential shifts to more negative value due to the steric effect from its structure. The electrochemical behavior of *N*-ethylenethiourea is similar to the electrochemical behavior of thiourea. Therefore it may be assumed to contribute to the redox reaction of *N*-ethylenethiourea which occurs at sulfur group similar to thiourea (Kirchnerova *et al.*, 1981). Both compounds have a purely diffusion controlled redox reaction.

The redox reaction of *N,N′*-ethylenethiourea occurs at different group compared with *N,N′*-diphenylthiourea and *N*-phenylthiourea due to the fact that *N,N′*-ethylenethiourea does not have a phenyl group in structure. Therefore there is no resonance effect. This causes sulfur to give away the electron much easier. The redox reaction of aliphatic amine in *N,N′*-ethylenethiourea is more difficult because it does not have the delocalized radical.

3.6 The electrochemical behavior of Cu(I) halide with *N,N′*-diphenylthiourea complexes

3.6.1 The electrochemical behavior of [Cu(dptu)$_2$Cl]H$_2$O complex

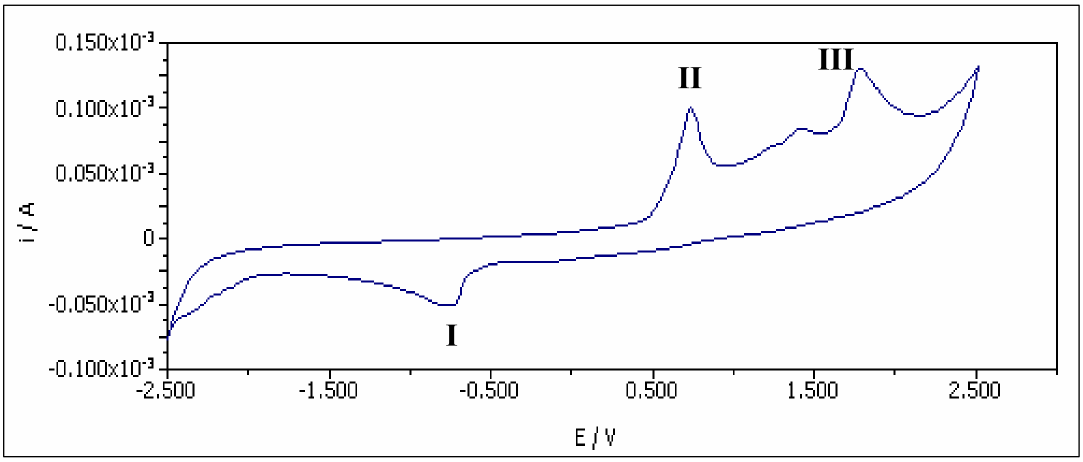

Figure 31 Cyclic voltammogram of 1x10^{-3} M [Cu(dptu)$_2$Cl]H$_2$O complex at glassy carbon electrode in 25 ml CH$_3$CN solution with 0.1 M TBAP as supporting electrolyte, within the range of -2.50 V to 2.50 V with scan rate of 0.2 V/s.

Cyclic voltammogram of blank solution was performed with the potential range of -2.50 V to 2.50 V vs Ag/AgCl. It was found that there were no significant impurities.

The cyclic voltammogram of [Cu(dptu)$_2$Cl]H$_2$O complex in acetonitrile at glassy carbon electrode was performed with the potential range of -2.50 V to 2.50 V vs Ag/AgCl. The cyclic voltammogram of [Cu(dptu)$_2$Cl]H$_2$O complex exhibits a reduction peak occurs at Epc = -0.761 V, and two oxidation peaks occurs at Epa = 0.778 V and 1.718 V as shown in Figure 31.

The reduction peak at Epc = -0.761 V (peak I) and the oxidation peak at Epa = 0.778 V (peak II) corresponds to the redox reaction of copper(I)/(0). The reduction peak shifts to negative potential and the oxidation peak shifts to more positive potential, indicating more difficult redox reaction of copper(I)/(0) in the complex.

The oxidation peak at Epa = 1.718 V (peak III) is similar to the oxidation peak of diphenylthiourea ligand (1.745 V). From the cyclic voltammogram of this complex, the redox peak of chloride disappears due to the strong bond with copper.

3.6.2 The electrochemical behavior of [Cu(dptu)$_2$Br]H$_2$O complex

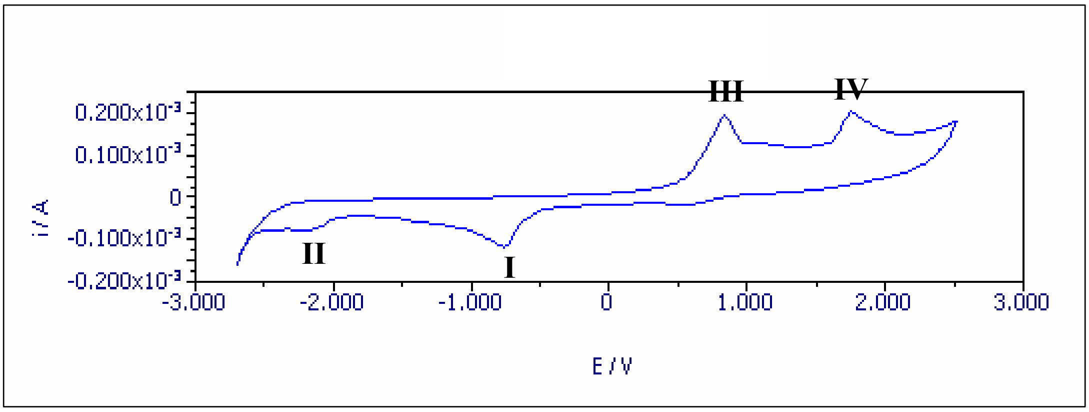

Figure 32 Cyclic voltammogram of 1x10^{-3} M [Cu(dptu)$_2$Br]H$_2$O complex at glassy carbon electrode in 25 ml CH$_3$CN solution with 0.1 M TBAP as supporting electrolyte, within the range of -2.80 V to 2.50 V with scan rate of 0.2 V/s.

Cyclic voltammogram of blank solution was performed with the potential range of -3.00 V to 2.50 V vs Ag/AgCl. It was found that there were no significant impurities**.**

The cyclic voltammogram of [Cu(dptu)$_2$Br]H$_2$O complex in acetonitrile at glassy carbon electrode was performed with the potential range of -2.80 V to 2.50 V vs Ag/AgCl. The cyclic voltammogram of [Cu(dptu)$_2$Br]H$_2$O complex exhibits two reduction peaks which are at Epc = -0.761 V and -2.160 V and two oxidation peaks which are at Epa = 0.718 V and 1.758 V as shown in Figure 32.

The reduction peak at Epc = -0.761 V (peak I) and the oxidation peak at Epa = 0.718 V (peak III) corresponds to the redox reaction of copper(I)/(0). The reduction peak shifts to negative potential and the oxidation peak shifts to more positive potential, indicating more difficult redox reaction of copper(I)/(0) in the complex.

Additional reduction peak at Epc = -2.160 V (peak II) and the oxidation peak at Epa = 1.758 V (peak IV) are similar to those of *N,N'*-diphenylthiourea ligand. From the cyclic voltammogram of this complex, the redox peak of bromide disappears due to the strong bond with copper.

3.6.3 The electrochemical behavior of [Cu(dptu)$_2$I]H$_2$O complex

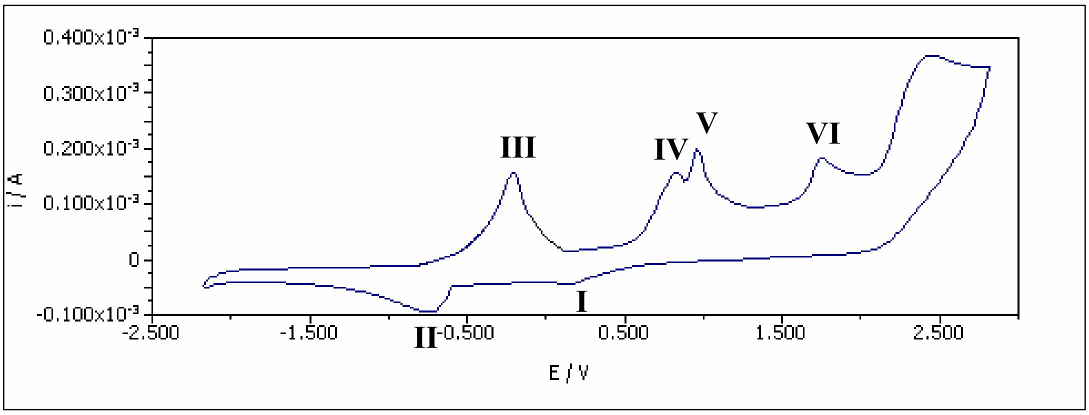

Figure 33 Cyclic voltammogram of 1x10^{-3} M [Cu(dptu)$_2$I]H$_2$O complex at glassy carbon electrode in 25 ml CH$_3$CN solution with 0.1 M TBAP as supporting electrolyte, within the range of -2.30 V to -2.80 V with scan rate of 0.2 V/s.

Cyclic voltammogram of blank solution was performed with the potential range of -2.50 V to 3.00 V vs Ag/AgCl. It was found that there were no significant impurities.

The cyclic voltammogram of [Cu(dptu)$_2$I]H$_2$O complex in acetonitrile at glassy carbon electrode was performed with the potential range of -2.50 V to 2.80 V vs Ag/AgCl. The cyclic voltammogram of [Cu(dptu)$_2$I]H$_2$O complex exhibits two reduction peaks at Epc = 0.159 V and -0.741 V and four oxidation peaks at Epa = -0.321 V, 0.790 V, 0.958 V and 1.738 V vs Ag/AgCl as shown in Figure 33.

The reduction peak at Epc = -0.741 V (peak II) and the oxidation peak at Epa = –0.321 V (peak III) correspond to copper(I)/(0). The reduction peak shifts to negative potential, and the oxidation peak shifts to positive potential, indicating difficult redox reaction of copper(I)/(0) in the complex.

The oxidation peak at Epa = 1.738 V (peak VI) is similar to the oxidation peak of *N,N'*-diphenylthiourea ligand (1.745 V). The oxidation peaks at Epa = 0.790 V (peak IV), 0.958 V (peak V) and the reduction peak at Epc = 0.159 V (peak I) are similar to those of iodide but the reduction peaks are not complete due to the fact that iodide in this complex forms a weak bond with copper.

3.6.4 Discussion on the electrochemical behavior of Cu(I) halide with *N,N'*-diphenylthiourea complexes

The electrochemical behaviors of all there complexes of $[Cu(dptu)_2Cl]H_2O$ $[Cu(dptu)_2Br]H_2O$ and $[Cu(dptu)_2I]H_2O$ are different.

The *N,N'*-diphenylthiourea complexes exhibits the redox peak corresponding to copper(I)/(0) process. But the redox reactions of copper in these complexes are difficult to occur due to the bonding as shown by the value of ΔEp or ΔEpa of copper in the Table 7. Moreover, the values of ΔEp of copper have more negative value in the order of $[Cu(dptu)_2Cl]H_2O$ > $[Cu(dptu)_2Br]H_2O$ > $[Cu(dptu)_2I]H_2O$. It can be to summarize the strong bond with copper when halides are small.

In the case of $[Cu(dptu)_2Cl]H_2O$ and $[Cu(dptu)_2Br]H_2O$ complexes, the redox peaks of chloride and bromide disappear. A plausible explanation is that higher affinity of chloride atom to Cu(I) and benefits of intramolecular hydrogen bonds of the type NH--Cl contribute to the stabilization of the Cu(I) complex (Yuan *et al.*, 2001). In the case of $[Cu(dptu)_2I]H_2O$ complex, it shows the reaction peak corresponding to iodide but the reduction peaks do not completely occur. A plausible explanation is that lower affinity of Cu(I) to iodide. The bond distances of copper with iodide were found to be longer than those of that chloride and bromide respectively (Singhagomol, 1999). The results of intramolecular hydrogen bonds distance the NH--I is longer than that of chloride and bromide, revealing that the stabilization of the copper(I) complexes decreases in the order of chloride, bromide and iodide respectively (Singhagomol, 1999). The results are in good agreement with those from electrochemistry. In addition, from cyclic voltammogram, the oxidation peak of *N,N'*-diphenylthiourea ligand appears in all cases but shifts to positive potential with a change in the peak shape. The oxidation reaction of this ligand is more difficult to occur in the complexes.

Table 7 The difference in peak potentials ΔEp, ΔEpa and ΔEpc of copper in various *N,N'*-diphenylthiourea complexes

Complexes	Δ Epa of Cu(I)		Δ Epc of Cu(I)		Δ Ep of Cu(I)
	Epa	ΔEpa	Epc	ΔEpc	Epc - Epa
[Cu(dptu)$_2$Cl]	0.778	1.037	-0.761	-0.094	-1.539
[Cu(dptu)$_2$Br]	0.718	0.977	-0.761	-0.094	-1.479
[Cu(dptu)$_2$I]	-0.321	0.589	-0.741	-0.074	-0.420
Copper(I)	-0.259	-	-0.667	-	-0.408

Remarks: ΔEpa of copper = Epa of copper in complexes - Epa of free copper

ΔEpc of copper = Epc of copper in complexes - Epc of free copper

3.7 The electrochemical behavior of Cu(I) halide with *N*-phenylthiourea complexes

3.7.1 The electrochemical behavior of [Cu(ptu)$_4$]Cl complex

Cyclic voltammogram of blank solution was performed with the potential range of -2.50 V to 3.00 V vs Ag/AgCl. It was found that there were no significant impurities.

The cyclic voltammogram of [Cu(ptu)$_4$]Cl complex in acetonitrile at glassy carbon electrode was performed with the potential range of -2.00 V to 2.00 V vs Ag/AgCl. The cyclic voltammogram of [Cu(ptu)$_4$]Cl complex exhibits two reduction peaks at Epc = 0.419 V and -0.461 V and two oxidation peaks at Epa = 1.158 V and 2.138 V. Both of the oxidation and reduction peaks are shown in Figure 34.

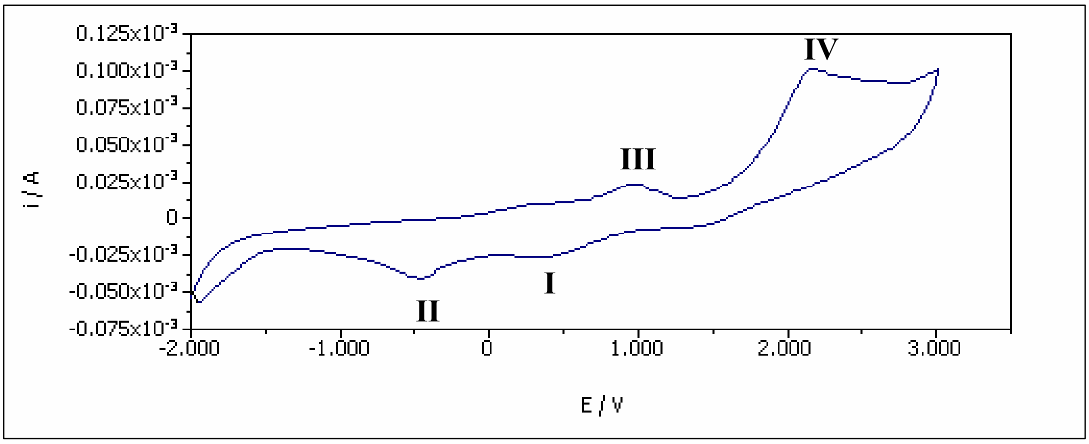

Figure 34 Cyclic voltammogram of 1x10^{-3} M $[Cu(ptu)_4]Cl$ complex at glassy carbon electrode in 25 ml CH_3CN solution with 0.1 M TBAP as supporting electrolyte, within the range of -2.00 V to 3.00 V. with scan rate of 0.2 V/s.

The reduction peak at Epc = -0.461 V (peak II) corresponds to the reduction of copper(I)/(0). The reduction peak shift to less negative value so the reduction reaction of copper(I) in the complex is easier.

The oxidation peak of chloride ion occurs at Epa = 1.158 V (peak III) and the reduction peak occurs at Epc = 0.419 V (peak I). The redox potential value of chloride ion does not change and the electrochemical behavior similar to free halide. Therefore, it may be due to the free form of chloride in this complex.

The oxidation peak at Epa = 2.138 V (peak IV) corresponds to the second oxidation reaction of *N*-phenylthiourea ligand. The first oxidation peak of *N*-phenylthiourea ligand disappears because sulfur can form stronger bond with copper in the complex.

3.7.2 The electrochemical behavior of $[Cu_4(ptu)_6Br_4]_2$ complex

Cyclic voltammogram of blank solution was performed with the potential range of -2.50 V to 2.50 V vs Ag/AgCl. It was found that there were no significant impurities.

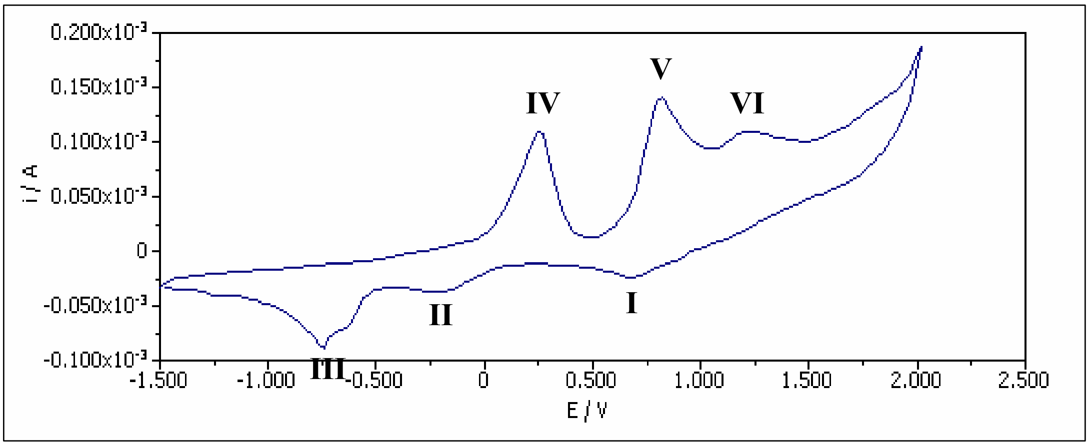

Figure 35 Cyclic voltammogram of 1x10^{-3} M $[Cu_4(ptu)_6Br_4]_2$ complex at glassy carbon electrode in 25 ml CH_3CN solution with 0.1 M TBAP as supporting electrolyte, within the range of -1.50 V to 2.00 V with scan rate of 0.2 V/s.

The cyclic voltammogram of $[Cu_4(ptu)_6Br_4]_2$ complex in acetonitrile at glassy carbon electrode was performed with the potential range of -2.00 to 2.00 V vs Ag/AgCl. The cyclic voltammogram of $[Cu_4(ptu)_6Br_4]_2$ complex exhibits three reduction peaks at Epc = 0.619 V, -0.181 V and -0.740 V and three oxidation peaks at Epa = 0.339 V, 0.819 V and 1.219 V vs Ag/AgCl. Both oxidation and reduction peaks are shown in Figure 35.

The reduction peak at Epc = -0.740 V (peak III) and the oxidation peak at Epa = -0.339 V (peak IV) correspond to copper(I)/(0). The reduction peak shifts to more negative potential and the oxidation peak shifts to more positive potential, indicating that copper(I)/(0) process is more difficult in the complex.

The oxidation peaks at 0.819 V (peak V) and 1.219 V (peak VI) as well as the reduction peaks at 0.619 V (peak I) and -0.181 V (peak II) are similar to those of bromide ion but the reactions are more difficult in the complex. The redox peaks of *N*-phenylthiourea ligand disappear.

3.7.3 The electrochemical behavior of $[Cu_4(ptu)_6I_4]_2$ complex

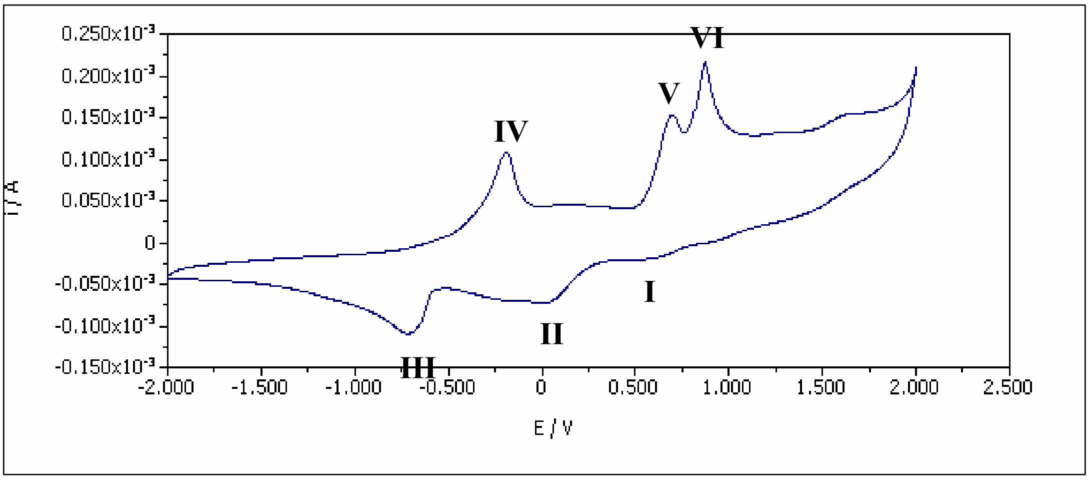

Figure 36 Cyclic voltammogram of $1x10^{-3}$ M $[Cu_4(ptu)_6I_4]_2$ complex at glassy carbon electrode in 25 ml CH_3CN solution with 0.1 M TBAP as supporting electrolyte, within the range of -2.00 V to 2.00 V. with scan rate of 0.2 V/s.

Cyclic voltammogram of blank solution was performed with the potential range of -2.50 V to 2.50 V vs Ag/AgCl. It was found that there were no significant impurities.

The cyclic voltammogram of $[Cu_4(ptu)_6I_4]_2$ complex in acetonitrile at glassy carbon electrode was performed with the potential range of -2.00 V to 2.00 V vs Ag/AgCl. The cyclic voltammogram of $[Cu_4(ptu)_6I_4]_2$ complex exhibits three reduction peaks at Epc = 0.620 V, 0.022 V and -0.716 V and three oxidation peaks at Epa = -0.125 V, 0.686 V and 0.871 V vs Ag/AgCl. Both oxidation and reduction peaks are shown in Figure 36.

The reduction peak at Epc = -0.716 V (peak III) and the oxidation peak at Epa = -0.125 V (peak IV) correspond to copper(I)/(0) process. The reduction peak shifts to more negative potential and the oxidation peak shifts to more positive potential, indicating that copper(I)/(0) process is difficult in the complex.

The oxidation peaks at 0.686 V (peak V) and 0.871 V (peak VI) as well as the reduction peaks at 0.620 V (peak I) and 0.022 V (peak II) are similar to the redox reaction peak of iodide ion but the reactions are more difficult in the complex. The redox peaks of *N*-phenylthiourea ligand disappear.

3.7.4 Discussion on the electrochemical behavior of Cu(I) halide with phenylthiourea complexes

The electrochemical behavior of all complexes ($[Cu(ptu)_4]Cl$, $[Cu_4(ptu)_6Br_4]_2$ and $[Cu_4(ptu)_6I_4]_2$) are different.

The $[Cu(ptu)_4]Cl$ complex exhibits the reduction peak of copper(I)/(0) shift to less negative potential. Indicating that copper(I)/(0) process is difficult in the complex. The second oxidation peak of *N*-phenylthiourea also appears but shifts to more positive potential. The first oxidation peak of *N*-phenylthiourea disappear, a plausible explanation is that higher affinity of sulfur atom to Cu(I) evidently plays a certain role because sulfur can form stronger bond with copper in this complex. The redox peaks of chloride appear similar to free halide, suggests to free chloride in the complex. This behavior is in good agreement with X-ray results which show that the complex consists of a $[Cu(ptu)_4]^+$ cation and a Cl^- anion in molecule (Tanchatchawal S., 2004).

In the case of $[Cu_4(ptu)_6Br_4]_2$ and $[Cu_4(ptu)_6I_4]_2$ complexes, the redox couple corresponding to copper(I)/copper(0) process appear. But the redox reactions of copper in these complexes are difficult to occur due to the bonding as shown by the value of ΔEp or ΔEpa of copper in the Table 8. The redox peaks of bromide and iodide are similar to free halide but these reactions are more difficult in the complex. Bromide and iodide can be interpreted to contribute to the weak bond with copper but the bromide complex has lower value of ΔEp of copper than iodide, suggesting that the bromide has the strong bond with copper more than iodide. The confirming evidence is bond distances of copper with bromide and iodide which are longer than that with sulfur (Tanchatchawal S., 2004). Another reason is that the complexes of *N,N'*-phenylthiourea with copper(I) does not have influence of intramolecular hydrogen bond of the type NH--X (X=Br and I) which contributes to the unstable behavior of the Cu(I) complexes.

Table 8 The difference in peak potentials ΔEp, ΔEpa and ΔEpc of copper in various *N*-phenylthiourea complexes.

Complexes	ΔEpa of Cu(I)		ΔEpc of Cu(I)		ΔEp of Cu(I)
	Epa	ΔEpa	Epc	ΔEpc	Epc - Epa
$[Cu(ptu)_4Cl]$	-	-	-0.461	0.206	-
$[Cu_4(ptu)_6Br_4]_2$	0.339	0.598	-0.740	-0.073	-1.079
$[Cu_4(ptu)_6I_4]_2$	-0.125	0.134	-0.716	-0.049	-0.591
Copper(I)	-0.259	-	-0.667	-	-0.408

Remarks: ΔEpa of copper = Epa of copper in complexes - Epa of free copper

ΔEpc of copper = Epc of copper in complexes - Epc of free copper

3.8 The electrochemical behavior of Cu(I) halide with *N,N'*-ethylenethiourea complexes

3.8.1 The electrochemical behavior of $[Cu_2(etu)_4Cl_2]$ complex

Cyclic voltammogram of blank solution was performed with the potential range of -2.50 V to 2.50 V vs Ag/AgCl. It was found that there were no significant impurities.

The cyclic voltammogram of $[Cu_2(etu)_4Cl_2]$ complex in acetonitrile at glassy carbon electrode was performed with the potential range of -2.00 V to 2.00 V vs Ag/AgCl. The cyclic voltammogram of $[Cu_2(etu)_4Cl_2]$ complex exhibits three reduction peaks at Epc = 0.539 V, 0.059 V and -0.741 V and three oxidation peaks at Epa = -0.121 V, 0.199 V and 0.759 V vs Ag/AgCl. Both oxidation and reduction peaks are shown in Figure 37.

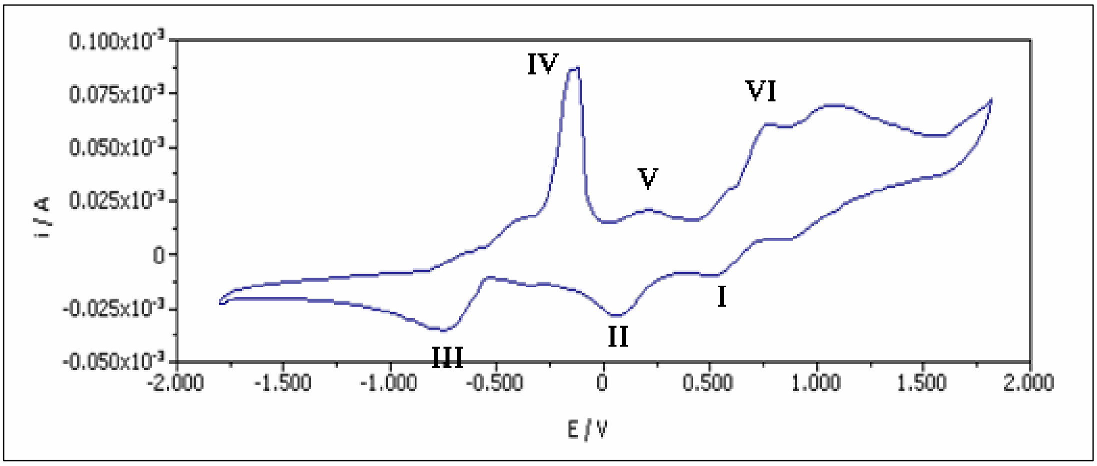

Figure 37 Cyclic voltammogram of 1x10^{-3} M [$Cu_2(etu)_4Cl_2$] complex at glassy carbon electrode in 25 ml CH_3CN solution with 0.1 M TBAP as supporting electrolyte, within the range of -2.00 V to 2.00 V with scan rate of 0.1 V/s.

The reduction peak at Epc = -0.741 V (peak III) and the oxidation peak at Epa = -0.121 V (peak IV) corresponds to copper(I)/copper(0) process. The shape of the redox peak is similar to that of the copper(I)/copper(0) process. The reduction peak shifts to less negative potential and the oxidation peak shifts to more positive potential, indicating that copper(I)/(0) process is more difficult in the complex.

The oxidation peak at 0.759 V (peak VI) and the reduction peak at 0.539 V (peak I) are similar to those of chloride ion. In the cyclic voltammogram of complex, the redox peaks of *N,N'*-ethylenethiourea ligand disappear.

3.8.2 The electrochemical behavior of [$Cu(etu)_3Br$] complex

Cyclic voltammogram of blank solution was performed with the potential range of -2.50 V to 2.50 V vs Ag/AgCl. It was found that there were no significant impurities.

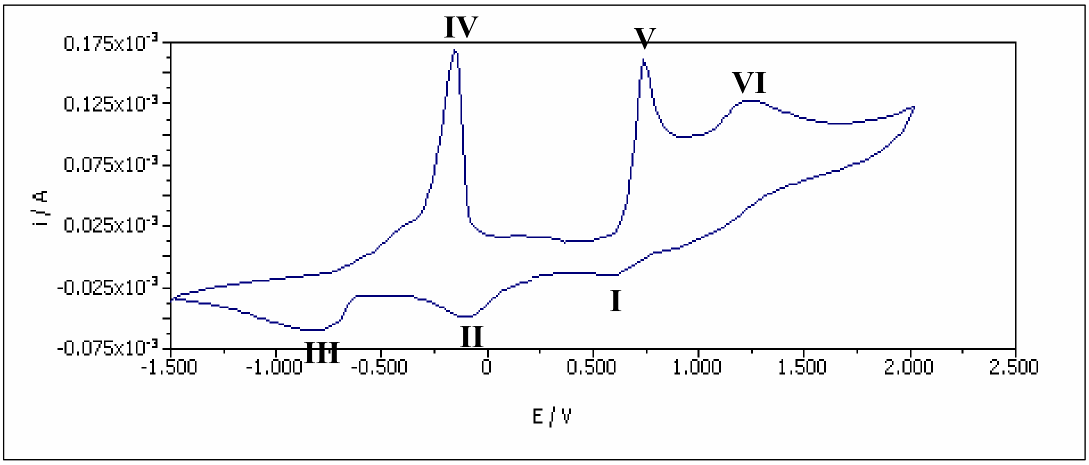

Figure 38 Cyclic voltammogram of 1x10^{-3} M [Cu(etu)$_3$Br] complex at glassy carbon electrode in 25 ml CH_3CN solution with 0.1M TBAP as supporting electrolyte, within the range of -1.50 V to 2.00 V with scan rate of 0.1 V/s.

The cyclic voltammogram of [Cu(etu)$_3$Br] complex in acetonitrile at glassy carbon electrode was performed with the potential range of -1.50 V to 2.50 V vs Ag/AgCl. The cyclic voltammogram of [Cu(etu)$_3$Br] complex exhibits three reduction peaks at Epc = 0.652 V, 0.021 V and -0.720 V and three oxidation peaks at Epa = -0.141 V, 0.719 V and 1.219 V vs Ag/AgCl as shown in Figure 38.

The reduction peak at Epc = -0.720 V (peak III) and the oxidation peak at Epa = -0.141 V (peak VI) corresponds to copper(I)/copper(0) process. The shape of the redox peak is similar to that of the copper(I)/copper(0) process. The reduction peak shifts to less negative potential and the oxidation peak shifts to more positive potential, indicating that copper(I)/(0) process is more difficult in the complex.

The oxidation peaks at 0.719 V (peak V) and 1.219 V (peak VI) as well as the reduction peaks at 0.652 V (peak I) and 0.021 V (peak II) are similar to those of bromide ion. In the cyclic voltammogram of complex, the redox peaks of *N,N'*-ethylenethiourea ligand disappear.

3.8.3 The electrochemical behavior of [$Cu_2(etu)_4I_2$] complex

Cyclic voltammogram of blank solution was performed with the potential range of -2.50 V to 2.50 V vs Ag/AgCl. It was found that there were no significant impurities.

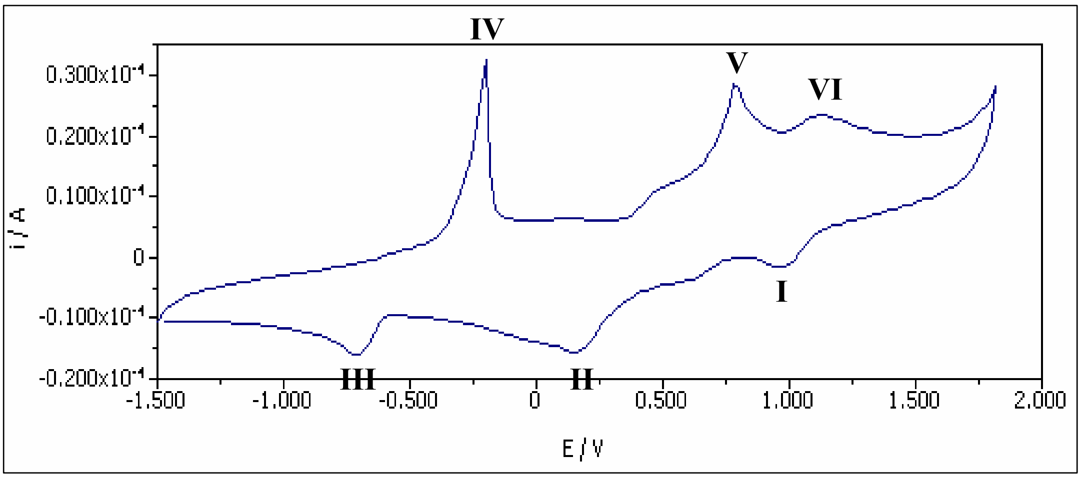

Figure 39 Cyclic voltammogram of $1\text{x}10^{-3}$ M [$Cu_2(etu)_4I_2$] complex at glassy carbon electrode in 25 ml CH_3CN solution with 0.1 M TBAP as supporting electrolyte, within the range of -1.50 V to 2.00 V with scan rate of 0.1 V/s.

The cyclic voltammogram of [$Cu_2(etu)_4I_2$] complex in acetonitrile at glassy carbon electrode was performed with the potential range of -1.50 V to 2.00 V vs Ag/AgCl. The cyclic voltammogram of [$Cu_2(etu)_4I_2$] complex exhibits three reduction peaks at Epc = 0.979 V, 0.159 V and -0.700 V and three oxidation peaks at Epa = -0.201 V, 0.779 V and 1.119 V vs Ag/AgCl as shown in Figure 39.

The reduction peak at Epc = -0.700 V (peak III) and the oxidation peak at Epa = -0.201 V (peak IV) corresponds to copper(I)/copper(0) process. The shape of the redox peaks are similar to that of the copper(I)/copper(0) process. The reduction peak shifts to less negative potential and the oxidation peak shifts to positive potential, indicating that copper(I)/(0) process is more difficult in the complex.

For the two redox couples, the first redox couple occurs at Epa_1 = 0.779 V (peak V) and Epc_1 = 0.159 V (peak II) vs Ag/AgCl. The second redox couple occurs at Epa_2 = 1.119 V (peak VI) and Epc_2 = 0.979 V (peak I) vs Ag/AgCl. The behavior of two redox couples is quasi-reversible. The electrochemical quasi-reversible couples are due to the oxidation of iodide ion to its triiodide and then triiodide can be oxidized to form iodine. In the cyclic voltammogram of complex, the redox peaks of *N,N′*-ethylenethiourea ligand disappear.

3.8.4 Discussion on the electrochemical behavior of Cu(I) halide with *N,N′*-ethylenethiourea complexes

The cyclic voltammogram of ethylenethiourea complexes including $[Cu_2(etu)_4Cl_2]$, $[Cu(etu)_3Br]$ and $[Cu_2(etu)_4I_2]$ in acetonitrile solution suggesting that the electrochemical behaviors are similar.

The redox peaks of *N,N′*-ethylenethiourea ligand disappear in all complexes due to sulfur in this ligand form strong bond with copper.

The redox couple corresponding to copper(I)/copper(0) process appears in all complex. The shape of this redox peak is similar to that of the copper(I)/copper(0) process in acetonitrile. The redox reactions of copper in all complexes are difficult to occur in the order of chloride, bromide and iodide respectively, as shown by the value of ΔEp or ΔEpa of copper in the Table 9. The electrochemical behavior of these complexes give a results which similar to the complex of triazine-3-thione with Cd which shows the redox couple of Cd(II)/Cd(I) process (Lopez and Mendiola, 2005). The redox peaks of halide ions in all complexes are similar to the free form. A plausible explanation is that the bonds of copper-halides are weak so halides can be reduced and oxidized as in free halide. Another reason is that the complexes of *N,N′*-ethylenethiourea with copper(I) does not have an influence of intramolecular hydrogen bond of the NH--X (X = Cl, Br and I) type which contributes to the unstable behavior of the Cu(I) complexes.

Table 9 The difference in peak potentials ΔEp, ΔEpa and ΔEpc of copper in various ethylenethiourea complexes.

Complexes	ΔEpa of Cu(I)		ΔEpc of Cu(I)		ΔEp of Cu(I)
	Epa	ΔEpa	Epc	ΔEpc	Epc - Epa
$[Cu_2(etu)_4Cl_2]$	-0.121	0.138	-0.741	-0.074	-0.620
$[Cu(etu)_3Br]$	-0.141	0.118	-0.720	-0.053	-0.579
$[Cu_2(etu)_4I_2]$	-0.201	0.058	-0.700	-0.033	-0.499
Copper(I)	-0.259	-	-0.667	-	-0.408

Remarks: ΔEpa of copper = Epa of copper in complexes - Epa of free copper

ΔEpc of copper = Epc of copper in complexes - Epc of free copper