

## CONTENTS

	<b>Page</b>
CONTENTS	vi
LIST OF TABLES	ix
LIST OF FIGURES	x
LIST OF ABBREVIATIONS AND SYMBOLS	xii
CHAPTER	
1. INTRODUCTION	
1.1 Introduction	1
1.2 Literatures Review	4
1.3 Principle of cyclic voltammetry	9
1.4 The objectives	16
2. EXPERIMENTS	
2.1 Chemicals and reagents	17
2.2 Instruments	19
2.3 Procedure	21
2.3.1 Preparation of complexes	21
2.3.2 Electrochemical procedures	23
2.3.2.1 Cyclic voltammetry of the blank solution	23
2.3.2.2 Cyclic voltammetry of copper ions	24
2.3.2.3 Cyclic voltammetry of halide ions	24
2.3.2.4 Cyclic voltammetry of substituted thioureas	25
2.3.2.5 Cyclic voltammetry of Cu(I) halide with <i>N,N'</i> -diphenylthiourea complexes	25
2.3.2.6 Cyclic voltammetry of Cu(I) halide with <i>N</i> -phenylthiourea complexes	26
2.3.2.7 Cyclic voltammetry of Cu(I) halide with <i>N,N'</i> -ethylenethiourea complexes	27

## CONTENTS (Continued)

	Page
3. RESULTS AND DISCUSSION	
3.1. The preparation of the complexes	28
3.2. The electrochemical behavior of blank solution	30
3.3. The electrochemical behavior of copper ion	30
3.4. The electrochemical behavior of halide ions	32
3.4.1 The electrochemical behavior of chloride ion	32
3.4.2 The electrochemical behavior of bromide ion	33
3.4.3 The electrochemical behavior of iodide ion	34
3.5. The electrochemical behavior of substituted thioureas	35
3.5.1 The electrochemical behavior of <i>N,N'</i> -diphenylthiourea (dptu)	35
3.5.2 The electrochemical behavior of <i>N</i> -phenylthiourea (ptu)	38
3.5.3 The electrochemical behavior of <i>N,N'</i> -ethylenethiourea (etu)	40
3.5.4 Discussion on the electrochemical behavior of substituted thiourea compounds	43
3.6. The electrochemical behavior of Cu(I) halide with <i>N,N'</i> -diphenylthiourea complexes	44
3.6.1 The electrochemical behavior of [Cu(dptu) <sub>2</sub> Cl]H <sub>2</sub> O complex	44
3.6.2 The electrochemical behavior of [Cu(dptu) <sub>2</sub> Br]H <sub>2</sub> O complex	45
3.6.3 The electrochemical behavior of [Cu(dptu) <sub>2</sub> I]H <sub>2</sub> O complex	46
3.6.4 Discussion on the electrochemical behavior of Cu(I) halide with <i>N,N'</i> -diphenylthiourea complexes	47
3.7. The electrochemical behavior of Cu(I) halide with <i>N</i> -phenylthiourea complexes	48
3.7.1 The electrochemical behavior of [Cu(ptu) <sub>4</sub> ]Cl complex	48
3.7.2 The electrochemical behavior of [Cu <sub>4</sub> (ptu) <sub>6</sub> Br <sub>4</sub> ] <sub>2</sub> complex	49
3.7.3 The electrochemical behavior of [Cu <sub>4</sub> (ptu) <sub>6</sub> I <sub>4</sub> ] <sub>2</sub> complex	51
3.7.4 Discussion on the electrochemical behavior of Cu(I) halide with <i>N</i> -phenylthiourea complexes	52

## CONTENTS (Continued)

	<b>Page</b>
3.8. The electrochemical behavior of Cu(I) halide with <i>N,N'</i> -ethylenethiourea complexes	53
3.8.1 The electrochemical behavior of [Cu <sub>2</sub> (etu) <sub>4</sub> Cl <sub>2</sub> ] complex	53
3.8.2 The electrochemical behavior of [Cu(etu) <sub>3</sub> Br] complex	54
3.8.3 The electrochemical behavior of [Cu <sub>2</sub> (etu) <sub>4</sub> I <sub>2</sub> ] complex	56
3.8.4 Discussion on the electrochemical behavior of Cu(I) halide with <i>N,N'</i> -ethylenethiourea complexes	57
4. CONCLUSION	59
REFERENCES	61
APPENDIX	66
A	67
B	69
C	79
VITAE	80

## LIST OF TABLES

Table	Page
1. Chemicals and reagents	17
2. The suitable conditions of complexes synthesis	28
3. The physical properties of ligands and complexes	29
4. The relationship of the square roots of scan rates and current peaks of <i>N,N'</i> -diphenylthiourea	36
5. The relationship of the square roots of scan rates and current peaks of <i>N</i> -phenylthiourea	39
6. The relationship of the square roots of scan rates and current peaks of <i>N,N'</i> -ethylenethiourea	41
7. The difference in peak potentials $\Delta E_p$ , $\Delta E_{pa}$ and $\Delta E_{pc}$ of copper in various <i>N,N'</i> -diphenylthiourea complexes	48
8. The difference in peak potentials $\Delta E_p$ , $\Delta E_{pa}$ and $\Delta E_{pc}$ of copper in various <i>N</i> -phenylthiourea complexes	53
9. The difference in peak potentials $\Delta E_p$ , $\Delta E_{pa}$ and $\Delta E_{pc}$ of copper in various <i>N,N'</i> -ethylenethiourea complexes	58

## LIST OF FIGURES

Figure	Page
1. The structures of thiourea, TU and substituted thioureas, TUs	1
2. The tautomerism structure of thiourea	1
3. The structures of <i>N,N'</i> -diphenylthiourea, <i>N</i> -phenylthiourea and <i>N,N'</i> -ethylenethiourea ligands	3
4. The redox reaction of thiourea	4
5. The reduction mechanisms of PATS2	6
6. The three electrode system in the electrochemical cell of cyclic voltammetry	9
7. Typical excitation signal for cyclic voltammetry	10
8. Cyclic voltammogram of a Nerntian redox couple	11
9. Cyclic voltammogram responses of 5.0 mmol/l $K_3[Fe(CN)_6]$ containing 1.0 mol/l KCl, at a glassy carbon electrode, scan rate 100 mV/s	14
10. Cyclic voltammogram for irreversible and quasi- reversible redox processes	15
11. The electrochemical apparatus, AUTOLAB PGSTAT 100 (Metrohm)	20
12. The three electrode system in the electrochemical cell	20
13. Cyclic voltammogram of blank solution at GCE	30
14. Cyclic voltammogram of $1 \times 10^{-3}$ M copper (II) nitrate at GCE	31
15. The redox reactions of copper(II)/copper(I) and copper(I)/copper(0)	31
16. Cyclic voltammogram of $1 \times 10^{-2}$ M tetrabutylammonium chloride at GCE	32
17. The redox reactions of chloride ions	32
18. Cyclic voltammogram of $1 \times 10^{-2}$ M tetrabutylammonium bromide at GCE	33
19. The redox reactions of bromide ions	34
20. Cyclic voltammogram of $1 \times 10^{-2}$ M tetrabutylammonium iodide at GCE	34
21. The redox reactions of iodide ions	35
22. Cyclic voltammogram of 0.1 M <i>N,N'</i> -diphenylthiourea (dptu) at GCE	35
23. The relationship between square roots of scan rates and oxidation currents ( $I_{pa}$ ) of <i>N,N'</i> -diphenylthiourea	37

## LIST OF FIGURES (Continued)

Figure	Page
24. The relationship between square roots of scan rates and reduction currents ( $I_{pc}$ ) of <i>N,N'</i> -diphenylthiourea	37
25. Cyclic voltammogram of 0.1 M <i>N</i> -phenylthiourea (ptu) at GCE	38
26. The relationship between square roots of scan rates and oxidation currents ( $I_{pa}$ ) of <i>N</i> -phenylthiourea	39
27. The relationship between square roots of scan rates and reduction currents ( $I_{pc}$ ) of <i>N</i> -phenylthiourea	40
28. Cyclic voltammogram of 0.1 M <i>N,N'</i> -ethylenethiourea (etu) at GCE	40
29. The relationship between square roots of scan rates and oxidation currents ( $I_{pa}$ ) of <i>N,N'</i> -ethylenethiourea	42
30. The relationship between square roots of scan rates and reduction currents ( $I_{pc}$ ) of <i>N,N'</i> -ethylenethiourea	42
31. Cyclic voltammogram of $1 \times 10^{-3}$ M $[\text{Cu}(\text{dptu})_2\text{Cl}]\text{H}_2\text{O}$ complex at GCE	44
32. Cyclic voltammogram of $1 \times 10^{-3}$ M $[\text{Cu}(\text{dptu})_2\text{Br}]\text{H}_2\text{O}$ complex at GCE	45
33. Cyclic voltammogram of $1 \times 10^{-3}$ M $[\text{Cu}(\text{dptu})_2\text{I}]\text{H}_2\text{O}$ complex at GCE	46
34. Cyclic voltammogram of $1 \times 10^{-3}$ M $[\text{Cu}(\text{ptu})_4]\text{Cl}$ complex at GCE	49
35. Cyclic voltammogram of $1 \times 10^{-3}$ M $[\text{Cu}_4(\text{ptu})_6\text{Br}_4]_2$ complex at GCE	50
36. Cyclic voltammogram of $1 \times 10^{-3}$ M $[\text{Cu}_4(\text{ptu})_6\text{I}_4]_2$ complex at GCE	51
37. Cyclic voltammogram of $1 \times 10^{-3}$ M $[\text{Cu}_2(\text{etu})_4\text{Cl}_2]$ complex at GCE	54
38. Cyclic voltammogram of $1 \times 10^{-3}$ M $[\text{Cu}(\text{etu})_3\text{Br}]$ complex at GCE	55
39. Cyclic voltammogram of $1 \times 10^{-3}$ M $[\text{Cu}_2(\text{etu})_4\text{I}_2]$ complex at GCE	56

## LIST OF ABBREVIATIONS AND SYMBOLS

A = Ampere

Ag/AgCl = Silver/Silver chloride

Au = Gold

Br = Bromide

BTU = *N*-benzoylthiourea

C = Concentration

Cd = Cadmium

CH<sub>3</sub>CN = Acetonitrile

Cl = Chloride

Co = Cobalt

Cu = Copper

CuBr = Copper bromide

CuCl = Copper chloride

CuI = Copper iodide

Cu(NO<sub>3</sub>)<sub>2</sub> = Copper(II) nitrate

CV = Cyclic voltammogram

CVs = Cyclic voltammograms

D = Diffusion coefficient

DMTU = 1,3-dimethylthiourea

dptu = *N,N'*-diphenylthiourea

E = Potential

E<sup>o'</sup> = Formal potential

E<sub>pa</sub> = Oxidation peak potential

E<sub>pc</sub> = Reduction peak potential

E<sub>p/2</sub> = Half-peak potential

E<sub>1/2</sub> = Half-wave potential

ΔE<sub>p</sub> = Separation potential

## LIST OF ABBREVIATIONS AND SYMBOLS (Continued)

$\Delta E_{pa}$  = Oxidation separation potential

$\Delta E_{pc}$  = Reduction separation potential

etu = *N,N'*-ethylenethiourea

Fe = Iron

g = Gram

GCE = Glassy carbon electrode

Hg = Mercury

hrs = Hours

i = Current

I = Iodide

$I_{pa}$  = Anodic peak current

$I_{pc}$  = Cathodic peak current

$LH_2OCH_3$  = 5- methoxy-5-6-diphenyl-4,5-dihydro-2H-[1,2,4] triazine-3-thion

M = Molar

$\mu$  = Micron

mA = Milliampere

MTU = Methylthiourea

mg = Milligram

$mg L^{-1}$  = Milligram per litre

mL = Millilitre

mV = Millivolt

$mV s^{-1}$  = Millivolt per second

n = Number of electron

$NH_2$  = Amine

Ni = Nickel

PATS2 = 2-formylpyridine thiosemicarbazone

ptu = *N*-phenylthiourea



## LIST OF ABBREVIATIONS AND SYMBOLS (Continued)

s = Second

S = Sulfur

SERS = Surface Enhanced Raman Spectroscopy

SHE = Standard Hydrogen Electrode

$\text{SO}_4^{2-}$  = Sulfate

t = Time

TBAP = Tetrabutylammonium hexafluorophosphate

TMTU = Tetramethylthiourea

TU = Thiourea

TUs = Substituted thiourea

UV-vis = Ultraviolet-Visible

V = Volt

U = Scan rate

Zn = Zinc