CHAPTER 1

INTRODUCTION

1.1 Introduction

Thiourea and substituted thioureas are soft donor ligands, their structures are shown in Figure 1. The thioamide group (H_2NCSNH_2) is an important common characteristic.
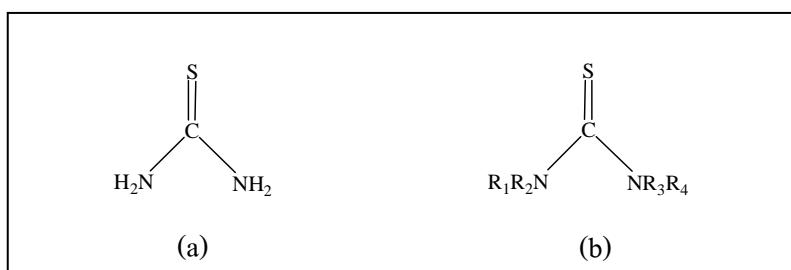

Figure 1 The structures of thiourea, TU (a) and substituted thioureas, TUs (b)

Ligands containing a thioamide structure have considerable coordination potential. The flexibility based on the tautomerism, thiol ⟷ thione can afford various coordination modes, as shown in Figure 2. They are potentially capable of forming coordinate bonds through both sulfur and nitrogen even though the extremely low basicity of the ligand militates against the formation of nitrogen-metal bond.
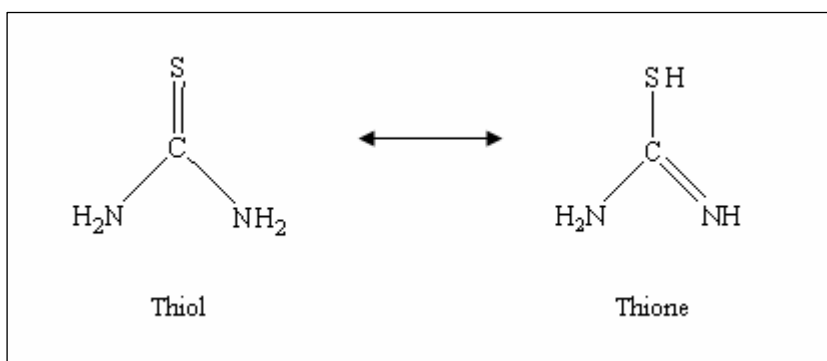

Figure 2 The tautomerism structure of thiourea

Thiourea and substituted thioureas are widely used as additives in various electrochemical processes; for example: electroplating, electrolytic refining and electrodepositing of metal such as iron (Fe) and copper (Cu) from acidic media in order to enhance the deposition process. The most important role of thiourea is its ability to act as a leveling and brightening agent apparently involving adsorption of thiourea on the surface. The adsorption of thiourea and substituted thioureas on solid electrodes such as gold (Garcia *et al*., 2003) and copper (Lukomaka *et al*., 2006) were studied by electrochemical, spectroscopic and radiochemical methods. As it was evidenced by SERS method, the process of thiourea and substituted thioureas adsorption depends on the applied electrode potential, bulk concentration of thiourea and substituted thioureas and kind of the supporting electrolyte. Moreover, the process of adsorption is accompanied by coadsorption of the active anions such as Cl^- , SO_4^{2-} which interact with the adsorbed species. It was also found that TU adsorbed on the metal surfaces via the sulfur atom and then desorbed at sufficiently negative potentials. Thiourea and substituted thioureas are used as catalysts for accelerating the electroreduction of cations such as Zn^{2+} (Sykut *et al*., 1984) and Cd^{2+} (Souto *et al*., 1985).

Furthermore, Thiourea and substituted thioureas such as N-thiophosphorylthiourea, N-diisopropoxythiophosphoryl-N'-phenylthiourea and their crown containing or open-chained derivatives are of great interest because of their ability to realize different complexation mechanism like chelate and guest-host complexes formation. Electrodes modified by these ligands can be used for voltammetric determination of metal ions (Larisa *et al*., 2001).

Thiourea and substituted thioureas can form complexes with metals such as Au, Ni, Cd and Cu. Thiourea and substituted thioureas are also known to form stable complexes with both cupric and cuprous ions (Alodan and Smyrl, 1998). Normally, additives modify the kinetics and mechanism of the electrochemical processes depend on the strength of metal-thiol interaction that are favored by the tautomeric form of thiourea and substituted thioureas, which, in turn depends on the solution composition and the strength of the electric field at the metal-solution interface (Widring *et al*., 1991).The polynuclear aggregates obtained in reaction of copper(I) with sulfur- containing ligand display a wide variety in composition and structure. Some copper(I) compounds in the species of metallothioneines (which have Cu=S bond in the

structures) are believed to play a role in the metabolism and detoxification of a number of essential and non-essential trace metal in animals and plants (Baumgartner *et al*., 1993).

Recently, the complexes of copper(I) with thiourea and substituted thioureas have been of growing interest due to not only the variety of their structures but also their similarity to metallothioneines, i.e. they contain coordinated Cu-S which plays an important role in animals and plants. The last research, the complexes of thiourea and substituted thioureas, were investigated by spectroscopic method (Joy and Srinivasan, 1999) and x-ray diffraction method (Yuan *et al*., 2001). However, there are only a few researches on electrochemical studies of these complexes. The properties of the complexes are more complicated and still not very well understood. Therefore, in this work, we study the properties of copper(I) complexes with substituted thioureas by cyclic voltammetry technique. The structures of substituted thioureas in this work are shown in Figure 3.
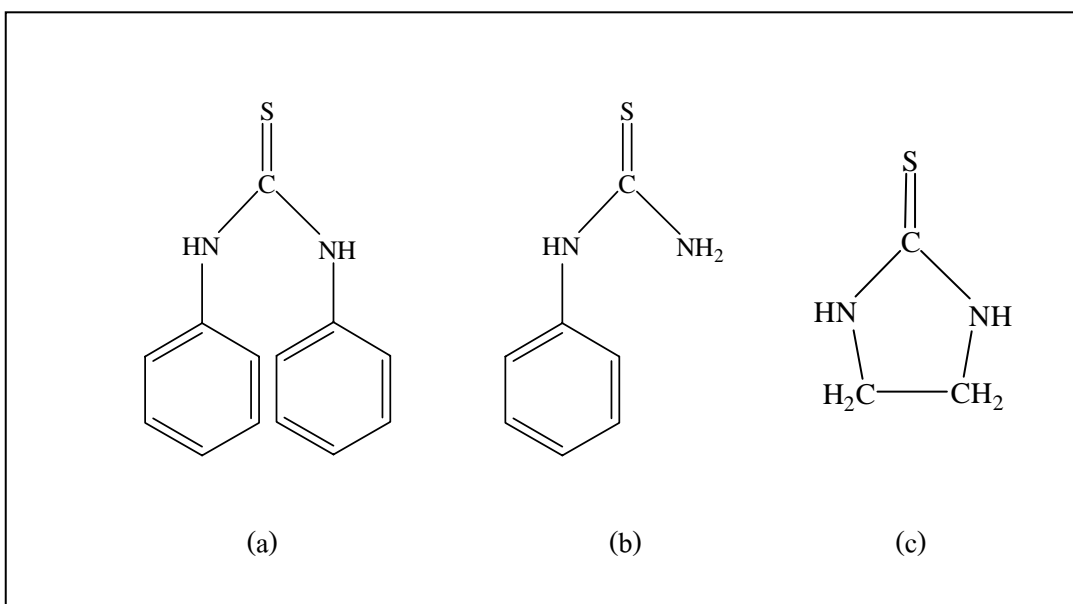

Figure 3 The structures of ligands (a) *N,N′*-diphenylthiourea (dptu) (b) *N*-phenylthiourea (ptu) and (c) *N,N′*-ethylenethiourea (etu).

1.2 Literature Review

1.2.1   The electrochemical of thiourea and substituted thioureas

The electrochemical behavior of thiourea has been studied in aqueous solutions and acetonitrile by cyclic voltammetry and potentiostatic coulometry at glassy carbon and platinum electrode. In acetonitrile, thiourea exhibits one oxidation peak and one reduction peak which is reversible couple (Kirchnerova *et al*., 1981). In aqueous solutions with the pH up to 6, there is a second oxidation peak at positive potential which is irreversible and its height is sensitive to acidity (Yan *et al*., 1996). From the first redox peak, c,c'-dithiodiformamidinium ion is formed as shown in Figure 4.
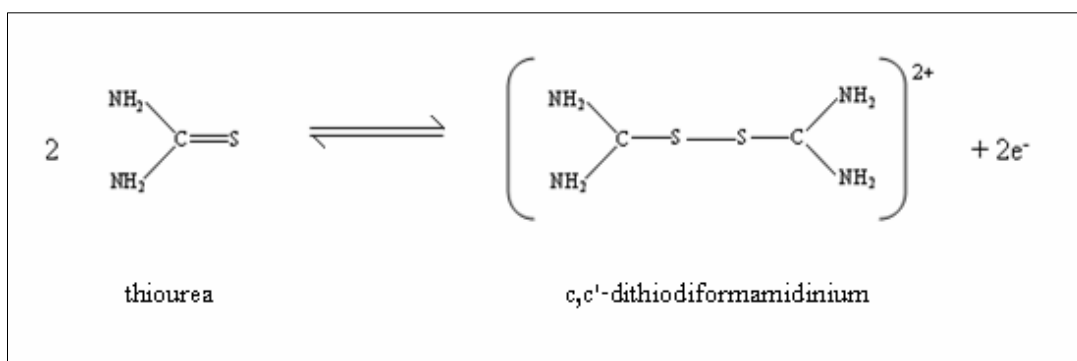

Figure 4 The redox reaction of thiourea

The electrochemical behavior of substituted thioureas (TUs) such as methylthiourea (MTU), 1,3-dimethylthiourea (DMTU) and tetramethylthiourea (TMTU) have been studied in aqueous solutions at platinum electrode. In all cases, substituted thioureas (TUs) exhibits the redox peak in the range of potential window form 0.05 V to 1.6 V (versus SHE). It related principally to the formation of the corresponding formamidine disulphide. The first oxidation peak shifts to negative potential in the order of TMTU > DMTU >MTU. The electrochemical behavior of all TUs can be described by common reaction. Slight discrepancies resulting from TMTU can be attributed to TMTU-platinum planar adsorption interactions instead of almost linear S-platinum interactions for the other TUs (Bolzan *et al*., 2004).

The voltammetric behaviors of *N*-benzoylthiourea (BTU) and some of its *N,N′*-disubstituted derivatives were studied using glassy carbon and carbon paste electrodes in ethanolic solution. Irreversible reductions of the compounds take place in a potential range of -0.5 V to -1.1 V, where carbon surface groups are reduced as well. The products formed by reductive cleavage of the C-N bond of the amide group are oxidized in the subsequent positive scan at +0.5 V. Irreversible oxidation of the thiocarbonyl group of BTU (or its derivatives) takes place at nearly +1.0 V, followed further by an oxidation of its *N,N′*-dialkyl and morpholine derivatives take place at more positive potentials. Oxidation current at +0.8 V is only observed in the case of the *N,N′*-diphenyl derivative (Lubert *et al*., 1999).

Pozdeeva and Novikov studied the electrochemical reduction of 2-formylpyridine thiosemicarbazone (PATS2) in Et_4NCl methanol solution at silver electrode. They have proposed two possible mechanisms for the reduction reaction of PATS2, one occurring in the pyridine ring, resulting in dihydropyridine and another one occurring at the C- S bond, forming a thiol. Those mechanisms for the reaction are shown in Figure 5(A) (Pozdeeva and Novikov, 1966). On the other hand, Kitaev and Lund described a mechanism involving four electrons: the cleavage of the N- N bond in PATS2, followed by the reduction of the imines formed. In this mechanism 2-picolylamine and thiourea are formed as final products. The mechanisms of the reaction are shown in Figure 5(B) (Kitaev *et al*., 1967 and Lund *et al*., 1997). Recently, Pessoa and co-worker studies the reduction products of 2-formylpyridine thiosemicarbazone (PATS2) using SERS and UV-vis techniques couple with cyclic voltammetry. The results have shown the reduction products of PATS2 are 2-picolylamine and thiourea, confirming the mechanism proposed by Kitaev and Lund (Pessoa *et al*., 2003).
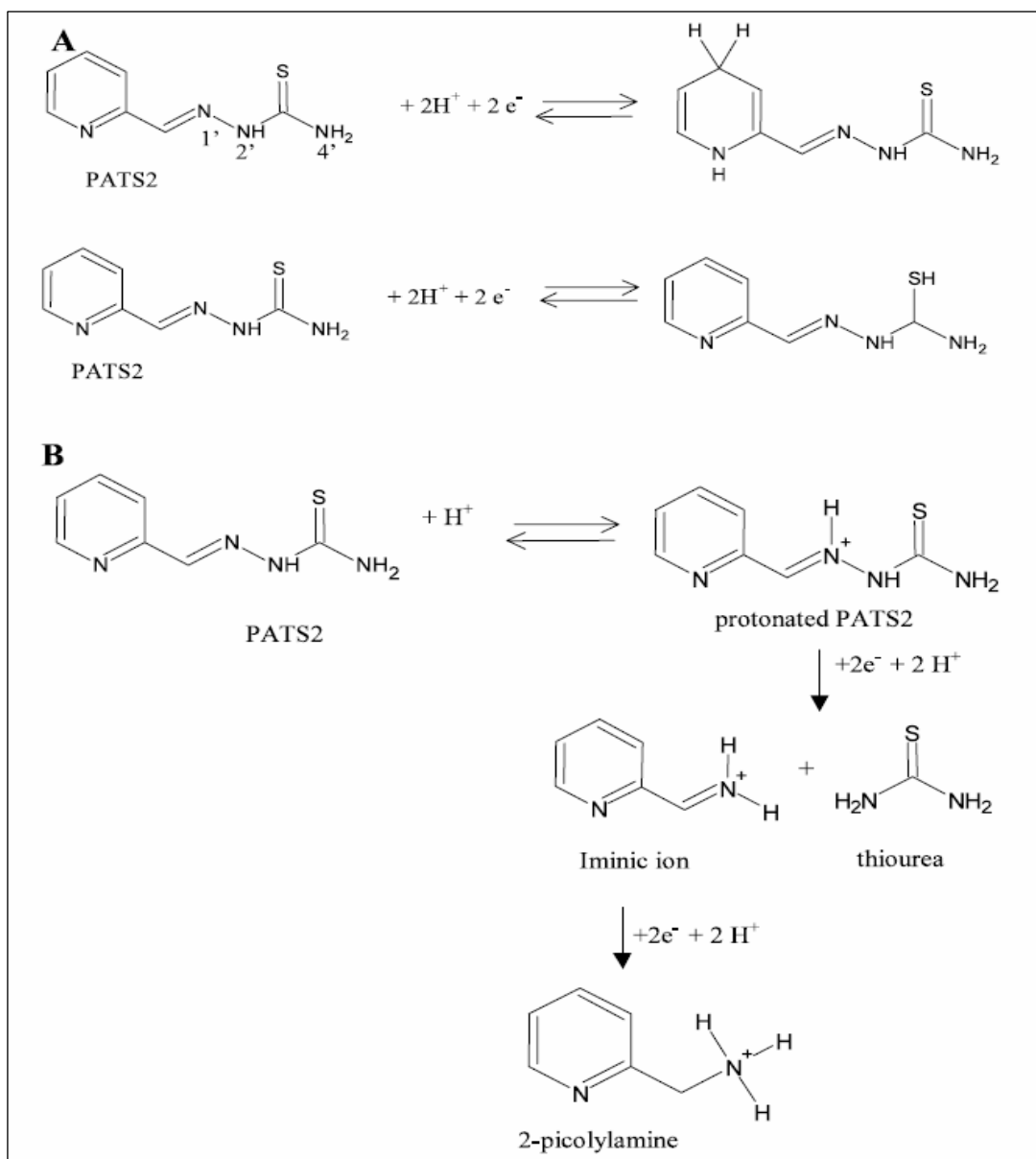
Figure 5 (A) The PATS2 reduction mechanisms proposed by Pozdeeva and Novikov, 1966.

(B) The PATS2 reduction mechanism proposed by Kitaev *et al*., 1967. Lund *et al*., 1959 and Monica *et al*., 2003.

1.2.2   The electrochemical of metals with thiourea and substituted thioureas

The electrochemical behaviors of the complexes of *N,N*-disubstituted-*N′*-benzoylthiourea with copper have been studied by cyclic voltammetry. The results obtained from cyclic voltammogram for the oxidation irreversible corresponds to copper(II)/copper(I) process. This slightly potential changed is due to the influence of the different substituents (Mohamadou *et al.*, 1994). Moreover, Losada and Peso studied the electrochemical behavior of copper (II) and nickel (II) complexes with *N′*-benzoylthiourea ligands by coulometry and cyclic voltammetry on platinum and glassy carbon electrode. Their experiment was carried out in acetonitrile. The copper and nickel complexes show two cathodic waves and three irreversible anodic waves. The cyclic voltammogram exhibits the oxidation corresponds to copper(II)/(I) and nickel(II)/(I) process. The difference of potential values is depended on the different substituents. The oxidation peak at 1.10-1.35 V and 1.48-1.74 V are observed at nearly the same potential values as ligand. Thus, it can be assigned to the irreversible oxidation of the pyrrole group and the benzoylthiourea groups (Losada and Isabel, 2000).

The heterocyclic thioureas are known to reduce copper(II) to yield copper(I) complexes. On the other hand, heterocyclic thioureas can form copper(II) complexes. The complex of N-(2-pyridyl)-*N′*-benzoylthiourea with copper(II) chloride led to a chloride bridged one-dimensional copper(II) polymer. This polymer involves monodentate coordination of a ligand, which have a thiadiazole ring with the sulfur bonding to the pyridine nitrogen. The present of thioureas react by sulfur, forming a bond with the aryl carbon ortho to the thiourea moiety. Thus, the use of a weakly coordinating oxidizing agent should be allowed to formation of metal complexes with a number of modified heterocyclic ligands from substituted thioureas and sulfur compounds. The ease of thiourea formation makes an attractive approach to study for the new metal complexes (West *et al.*, 2003).

The electrochemical behavior of *N,N*-disubstituted-*N′*-ferrocenoylthiourea with copper(II) complexes has been investigated by cyclic voltammetry. The complexes exhibit two redox couples. The first redox wave represents the electrochemical behavior to free ligand which corresponds to ferrocen (Fe(II)/Fe(III) process). The second redox wave corresponds to Cu(II)/Cu(I) process (Seidelmann and Beyer, 1997). Moreover, the cyclic voltammetric behavior of *N*-ferrocenoyl-*N′*-aryl-(alkyl)thiourea complexes with copper has been studied using CH_2Cl_2

as solvent. The coordination chemistry of *N*-ferrocenoyl-*N'*-aryl-(alkyl)thiourea ligands (H$_2$L) is dominated by a strong intramolecular hydrogen bond which locks the thiourea N-H moiety and amidic O-donor atom into a six membered ring, following the ligand coordinates to the Cu(I) ion through the S atom only. The Cu(II) was reduced to Cu(I) during the coordination process with oxidation of the ligand. The complexes exhibit one reversible wave. It is shown that the two ferrocenyl fragments within ferrocenoyl-thiourea-copper complexes are electro-chemically equivalent, simultaneously oxidized with no mutual interaction. However, one peak corresponding to the oxidation process of the Cu(I)/Cu(II) couple is observed for the complexes in the scan rate 100 mVs^{-1}. A plausible explanation is that the higher affinity of the sulfur atom to Cu(I) evidently plays a certain role. At the same time, intramolecular hydrogen bonds of the type NH⋯Cl contribute to the stabilization of the Cu(I) complexes (Yuan *et al*., 2001).

Lopez-Torres and Mendiola studied the electrochemical behavior of Cd(II) and Co(III) with 5-methoxy-5-6-diphenyl-4,5-dihydro-2H-[1,2,4] trazine-3-thion (LH$_2$OCH$_3$) complexes. Cd(II) complex exhibits three cathodic waves at -0.892, -1.482 and -1.847 V. and one anodic wave at -0.261 V related to the one at -0.892 V. This redox couple with E$_{1/2}$= -0.576 V corresponds to Cd(II)/Cd(I) process, although it is shifted to more negative potential. Co(III) complex shows three cathodic waves and one anodic wave. The redox couple is at E$_{1/2}$= -0.150 V which corresponds to Co(III)/Co(II) process and two irreversible cathodic peaks correspond to ligand reduction process (Lopez-Torres and Mendiola, 2005).

In the case of the electrochemical behavior of triazine-3-thione with mercury and methylmercury complexes, the mercury complex shows a reversible redox couple. In contrast, the cyclic voltammogram of methylmercury complex shows a redox couple which corresponds to a Hg(II)/Hg(I) process, and two irreversible cathodic peaks correspond to ligand reduction processes. The reduction process Hg(II)/Hg(I) is more difficult in mercury complex, where the mercury atom is bonded to two sulfur atoms. It is due to the fact that electronic density over the mercury atom is bigger than electronic density of mercury atom is bonded to a sulfur and one carbon atom, as in methyl mercury complex in the same condition (Lopez-Torres *et al*., 2006).

1.3 Principle of cyclic voltammetry

Cyclic voltammetry is the most widely used technique in acquiring qualitative information about electrochemical reactions. The power of cyclic voltammetry results from its ability to rapidly provide considerable information on the thermodynamics of redox processes and the kinetics of heterogeneous electron-transfer reactions, and on coupled chemical reactions or adsorption processes. Cyclic voltammetry is often the first experiment performed in an electroanalytical study. In particular, it offers a rapid location of redox potentials of the electroactive species, and convenient evaluation of the effect of media upon the redox process.

The most common experimental configuration for studying cyclic voltammetry consists of an electrochemical cell that has three electrodes (working electrode, auxiliary electrode and reference electrode, show in Figure 6), all immersed in a liquid and connected to a potentiostat. The potentiostat allows the potential difference between the reference and working electrode to be controlled with minimal interference from IR drop. In this configuration, the current flowing through the reference electrode also can be minimized thereby avoiding polarization of the reference electrode and hence keeping the applied potential distribution between the working and reference electrode stable (Scholz, F. 2002)
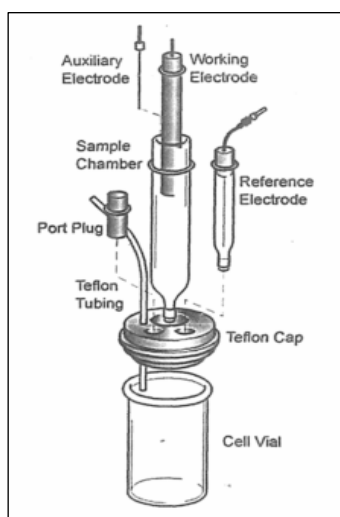

Figure 6 The three electrode system in the electrochemical cell of cyclic voltammetry.

Cyclic voltammetry make are of the scanning linearly the potential of a stationary working electrode, with a triangular potential waveform (Figure 7). Depending on the information sought, single or multiple cycles can be used.
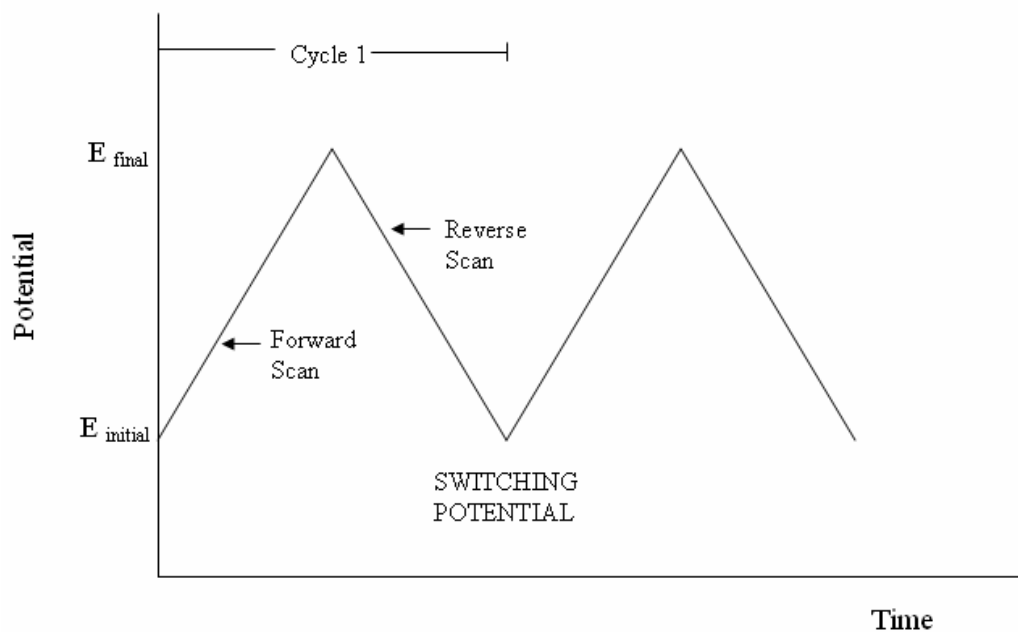

Figure 7 Typical excitation signal for cyclic voltammetry.

During the potential sweep, the potentiostat measures the current resulting from the applied potential. The resulting plot of current vs. potential is termed a cyclic voltammogram. The cyclic voltammogram is a complicated, time-dependent function of a large number of physical and chemical parameters.
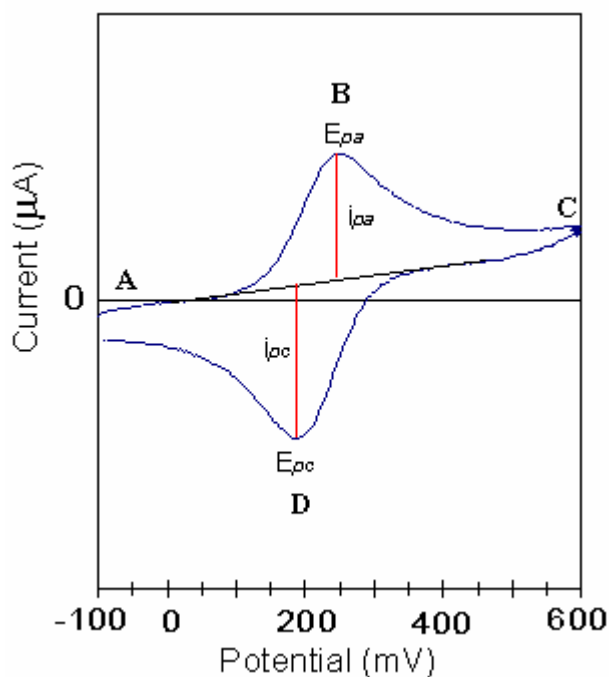
Figure 8 Cyclic voltammogram of a Nerntian redox couple (Wang, 2000).

Figure 8 illustrates the expected response of a reversible redox couple during a single potential cycle. Here, it is assumed that only the oxidized form O is present initially. Thus, a negative-going potential scan is chosen for the first half cycle, starting from a value where no reduction occurs. As the applied potential approaches the characteristic $E°$ for the redox process, a cathodic current begins to increase until a peak is reached. After traversing, the potential region in which the reduction process takes place, the direction of the potential sweep is reversed.

$$O + e^- --> R$$
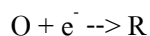
During the reverse scan, R molecules (generated in the forward half cycle, and accumulated near the surface) are reoxidized back to O and an anodic peak is resulted.

$$R --> O + e^-$$
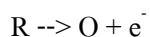
If a redox system remains in equilibrium throughout the potential scan, the redox process will be reversible (equilibrium requires that the surface concentration of O and R

are maintained at the values required by Nernst equation). The following parameters are used to specify the characteristic of the electrochemical process:

Electrochemically reversibility:

The peak potential separation $\Delta E_p = (E_{pc} - E_{pa}) = 59/n$ mV at all scan rates at 25 $^{\circ}$C. Thus, the peak separation can be used to determine the number of electrons transferred, and as a criterion for a Nerntian behavior. The positions of the peak on the potential axis (Epa) is related to the formal potential of the redox process. The formal potential for reversible couple is centered between Epa and Epc:

$$E^{o\prime} = (Epa+Epc) / 2$$

Chemically reversibility:

The peak current ratio $= I_{pa}/I_{pc} = 1$ at all scan rates

Criteria for diffusion controlled reaction:

The peak current function $i_p/\upsilon^{1/2}$ (υ = scan rate) is independent of υ.

The peak current is given by the Randles-Sevcik equation:

$$i_p = (2.69 \times 10^5) \, n^{3/2} ACD^{1/2} \upsilon^{1/2}$$

When: n = the number of electrons

A = the electrode area (cm^2)

C = the concentration (mol/cm^3)

D = the diffusion coefficient (cm^2/s)

υ = the scan rate (V/s)

Accordingly, the current is directly proportional to concentration and it increases with increasing the square root of the scan rate. The ratio of the reverse-to-forward

peak currents, i_{pr}/i_{pf}, is unity for a simple reversible couple. This peak ratio is strongly affected by chemical reactions coupled to the redox process. The current peaks are commonly measured by extrapolating the preceding baseline current. Thus, the peak separation can be used to determine the number of electrons transferred, and as a criterion for a Nernstian behavior.

Accordingly, a fast one-electron process exhibits an ΔE_p of about 59 mV. Both the cathodic and anodic peak potentials are independent of the scan rate. It is possible to relate the half-peak potential ($E_{p/2}$, where the current is half of the peak current) to the polarographic half-wave potential, $E_{1/2}$

$$E_{p/2} = E_{1/2} \pm 29 \text{ mV/n}$$

(The sign is positive for a reduction process.) For multielectron-transfer (reversible) processes, the cyclic voltammogram consists of several distinct peaks, if the E^o values for the individual steps are successively higher and are well separated.

The situation is very different when the redox reaction is slow or coupled with a chemical reaction. Indeed, it is these "nonideal" processes that are usually of the greatest chemical interested which the diagnostic power of cyclic voltammetry is most useful. Such information is usually obtained by comparing the experimental voltammograms with those derived from theoretical (simulated) ones. The cyclic voltammogram of reversible systems is shown in Figure 9.
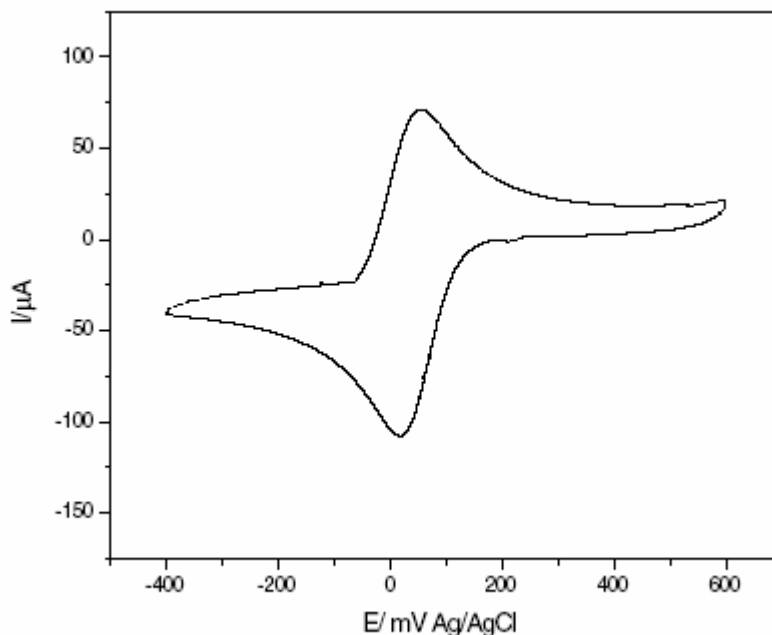
Figure 9 Cyclic voltammogram responses of 5.0 mmol/l $K_3[Fe(CN)_6]$ containing 1.0 mol/l KCl, at a glassy carbon electrode, scan rate 100 mV/s. (Wang *et. al*., 2006).

For irreversible processes (those with sluggish electron exchange), the individual peaks are reduced in size and widely separated. Totally irreversible systems are characterized by a shift of the peak potential with the scan rate:

$$E_p = E° - (RT/\alpha n_a F)[0.78 - \ln(k°/(D)^{1/2}) + \ln (\alpha n_a Fn/RT)^{1/2}]$$

When: α is the transfer coefficient

n_a is the number of electrons involved in the charge-transfer step.

Thus, E_p occurs at potentials higher than E° with the overpotential related to k° and α. Independent of the value k°, such peak displacement can be compensated by an appropriate change of the scan rate. The peak potential and the half-peak potential (at 25°C) will differ by $48/\alpha n$ mV. Hence, the voltammogram becomes more drawn-out as αn decreases.

The peak current which given by:

$$i_p = (2.99 \times 10^5)n(\alpha n_a)^{1/2} ACD^{1/2} \upsilon^{1/2}$$

,is still proportional to the bulk concentration, but will be lower in height (depending upon the value of α). Assuming $\alpha = 0.5$, the ratio of the reversible-to-irreversible current peaks is 1.27 (*i.e.* the peak current for the irreversible process is about 80% of the peak for a reversible one). For quasi-reversible systems (with $10^{-1} > k° > 10^{-5}$ cm/s) the current is controlled by both the charge transfer and mass transport. The shape of the cyclic voltammogram is a function of the ratio $k°/(\P \upsilon nFD/RT)^{1/2}$. As the ratio increases, the process approaches the reversible case. For small values of it, the system exhibits an irreversible behavior. Overall, the voltammograms of a quasi-reversible system are more drawn out and exhibit a larger separation in peak potentials compared to a reversible system.
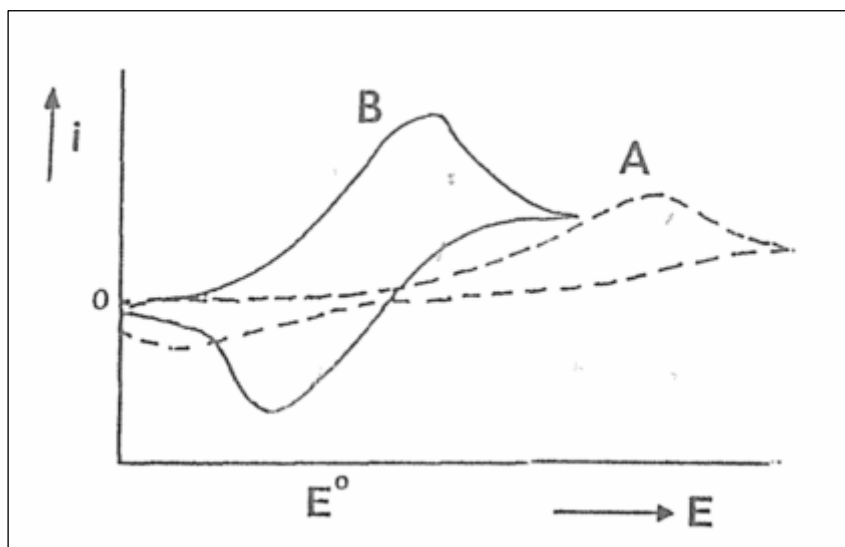

Figure 10 Cyclic voltammogram for irreversible (curve A) and quasi- reversible (curve B) redox processes.

1.4 The objectives

1. To study the electrochemical behavior of substituted thioureas by cyclic voltammetry technique.

2. To study the electrochemical behavior of copper(I) halides and substituted thiourea complexes by cyclic voltammetry technique.