CHAPTER 1

INTRODUCTION

1.1 Quinones and their roles

Quinones have two carbonyl groups in the structure with widespread importance in biology and chemistry. Quinones, for example, function in cellular respiration, photosynthesis, and blood coagulation. Their biological action is often linked to their electron transfer rates and redox potentials (Janell *et al.*, 1998).

Quinones participate as electron carriers in the oxidative phosphorylation process that occurs in the mitochondrial membrane, where ATP formation is thermodynamically favoured as a consequence of the electrons transferred by the quinines; from the NADH or $FADH_2$ to molecular oxygen. Depending on the molecular structure, some quinones can be used as vitamins or drugs (Magali *et al.*, 2003).

Several naturally occurring quinones have a hydroxyl function (represented as Q-OH) in their structure. The presence of this type of hydroxyl functionality seems to be related to the biological activity of this kind of compound and the position of this functional group can alter the typical redox behavior such as 1,2-Dihydroxyanthraquinone, 1,4-Dihydroxyanthraquinone and 1,8-Dihydroxyanthraquinone.

Anthraquinone derivatives constitutes an important class of antitumour drugs which mainly act by intercalating the DNA of the cell of tumour tissues (Danuta *et al.*, 1997). Quinones (anthraquinone, naphthoquinone and heteronaphthoquinone) are important naturally occurring pigments that are widely distributed in nature and are known to demonstrate various physiological activities as antibiotics and anti-cancer

agents. Junko and Izumi studied about correlation of redox potentials and inhibitory effects on Epstein-Barr virus activation of 2-azaanthraquinones (Junko *et al.*, 2004).

The anthracycline drugs daunorubicin (R = H) and doxorubicin (R = OH) (Scheme 1) have been in clinical use for nearly 2 decades in the treatment of various human cancers (Janell *et al.*, 1998).

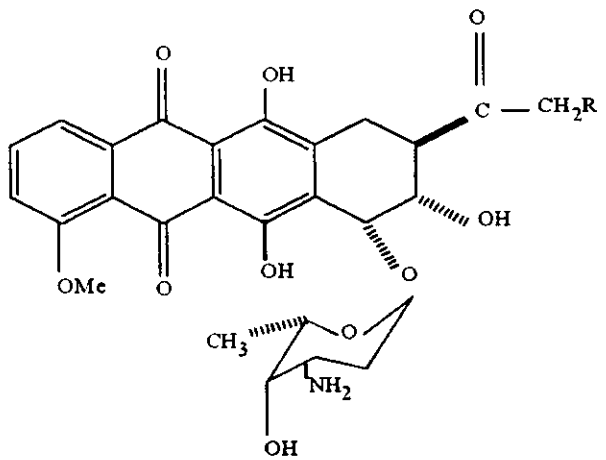

Figure 1 The structure of anthracycline drug

Recently these drugs have also been found to inhibit the infectivity and replication of human immunodeficiency virus (HIV) in vitro and may find applicability as antiviral agents in the treatment of acquired immune deficiency syndrome (AIDS) and AIDS-related complex (ARC) (Lindun *et al.*, 1988).

Three phenyl substituted para-quinones are widespread in biological system such as [2,3-dimethoxy-5-methyl-6-polyprenyl-1,4-benzoquinones] is found in all mitochondria and in many bacteria, [2-methyl-3-polyprenyl-1,4-naphthoquinones] occur in many bacteria and plastoquinones, [2,3-dimethyl-5-pollyprenyl-1,4-benzoquinones] are present in chloroplasts. One of their main functions is redox electron transfer, addition of one electron giving the semiquinone ($Q^{\cdot-}$) and of two electrons giving the dianion (Q^{2-}) (Roger *et al.*, 1983).

Several naturally occurring quinones have a hydroxyl function (represented as Q-OH) in their structure. The presence of this type of hydroxyl functionality seems to be related to the biological activity of this kind of compound and the position of this functional group can alter the typical redox behavior.

1.2 Review of Literatures

1.2.1 Cyclic voltammetry of some ketones and quinones

Quinones and ketones have been studied over many decades. The electro-chemical behaviour of ketone compounds such as benzophenone in aprotic solvents such as dimethylformamide (DMF) acetonitrile (CH_3CN) is well documented in the literature (Grimshaw and Hamilton, 1980). Simple quinone derivatives undergo two successive and distinct reduction/oxidation process such as benzoquinone (Mark and Dennis, 2001) and anthraquinone (Wightman *et al.*, 1976), 9,10-anthraquinone-2-sulfonic acid Na-salt, 9,10-anthraquinone-1,5-disulfonic Na-salt and 1,4-Dihydroxy-9,10-anthraquinone were investigated as to their ability to act as mediator for indirect electrochemical reduction of dispersed organic dyestuffs (Bechtold *et al.*, 1999).

Kim and Chung study about determination of biologically active acids based on the electrochemically reduction of quinone in acetonitrile and water mixed solvent (Kim *et al.*, 2001).

In an attempt to understand such phenomena, the electrochemical behavior of a variety of ketones and quinones have been servey in this research.

Tadeurz Ossowski studied the interaction of semiquinone anion radicals derived from hydroxyl derivatives of anthraquinone with molecular oxygen and anthraquinone with superoxide anion radical by means of electrochemical methods and UV-spectroscopy (Tadeurz *et al.*, 2000).

1,4-benzoquinone is one of the most important and fundamental π-electron systems because of its high electron affinity and photoreactivity (Shinobu *et al.*, 2005).

The electrochemical analysis by cyclic voltammetry and double potential step chronoamperometry of two α-hydroxyquinones (2-hydroxy-1,4-naphthoquinone and perezone) in acetonitrile, reveals that in the first electron transfer process, self-potonation reaction are present. One of the products of this reduction is the deprotonated original quinone. This last intermediate is reduced by a monoelectronic process in the second reduction step, generating a radical dianion. The radical dianions formed can be detected by EC-ESR coupled experiments and the spectra characteristics were explained in terms of the electron delocalization properties of the analyzed compounds (Carlos *et al.*, 2004).

1.2.2 Interaction of quinones and metals ion

Quinone, as a class of ligand, constitutes important family of biologically relevant molecules in many biological processes such as electron transfer and redox reactions. Eventhough, the coordination chemistry of transition metal-quinone complexes has been the subject of exploration for variety of purposes, it is rather surprising that there are relatively few reports on the structural propensities of lanthanides-quinone chelates (Prasad *et al.*, 2004).

There is considerable interest in metal complexes containing quinone and quinone-derived ligands such as 2,3-dimethoxy-1,4-naphthoquinone with zinc (II) (Simpson and JRT, 1990), 1,4-bis-(prop-2′-enyloxy)-9,10-anthraquinone with lead (II) (Mousavi *et al.*, 2001). These ligands can potentially bind to metal ions in three different forms, namely quinone, semiquinone or dianion.

The interaction of quinones and their reduced species with metal ions such as manganese (II), manganese (III), iron (II), iron (III) and copper (II) has been used as a

model for some biological systems, for example Photosystem II of green plant photosynthesis (Veronica *et al.*, 1993).

Alizarin red S (dihydroxyanthraquinonesulfonate, ARS) has strong chelating abilities and has been widely used for the preconcentration and analysis of metal ions. Recently researchers have incorporated ARS into polypyrrole-modified electrodes to electroanalyze Cu^{+} and Cu^{2+} species (Hong-Ping Dai and Kwok-Keung Shiu, 1998).

Of course these interesting compounds have been investigated a lot. Those worth mentioning here includes benzophenone, benzoquinone, anthraquinone and 1,4-dihydroxyanthraquinone. However, there have been only an investigation to study the relationship between the structure and electrochemical behavior of the compounds. The knowledge is crucial for the understanding of the role in biochemical processes and industrial applications.

In this work the results of spectroscopic of complex of ketones and quinones to silver ion by using UV-Visible spectroscopy only will be shown. Finally, the interaction of ketones and quinones to silver ion were investigated by making use of the chemically modified carbon paste electrode to determine the best modifier for silver ion analysis.

1.2.3 Principle of cyclic voltammetry

In cyclic voltammetry, the current response of a small stationary electrode in an unstirred solution is excited by a triangular potential wave form, such as that shown in Figure 2.

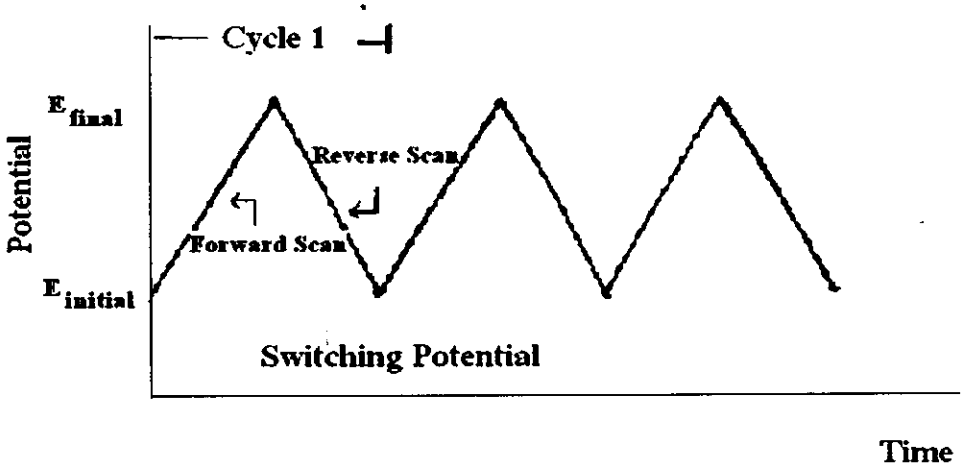

Figure 2 Cycilc voltammetric excitation signal used to obtain voltammogram.

Cyclic voltammetry is the most widely used technique for acquiring qualitative information about electrochemical reactions. Cyclic voltammetry consists of scanning linearly the potential of a stationary working electrode (in an unstirred solution) using a triangular potential waveform (Figure 2) . The resulting plot of current versus potential is termed a cyclic voltammogram.

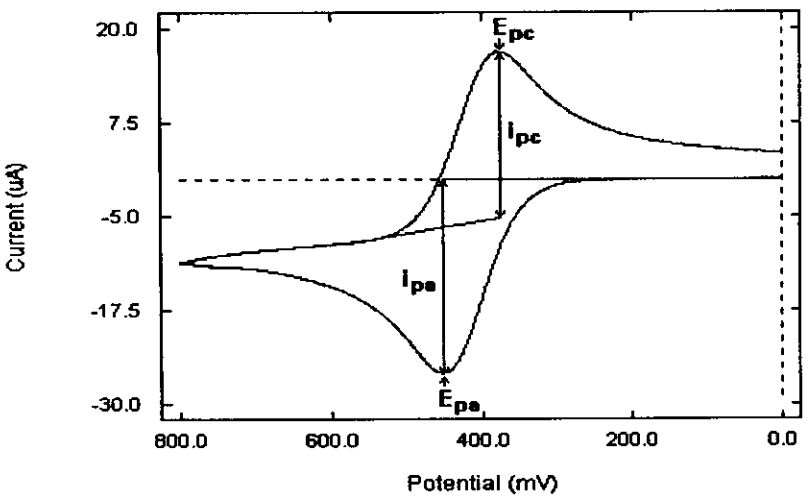

Figure 3 Cyclic voltammogram of a Nerntian redox couple showing various parameter the relationship between current and potential (Wang, 2000).

Figure 3 illustrates the expected response of a reversible redox couple during a single potential cycle. It is assumed that only the oxidized form 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^{O} 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 (at leat 90/n mV beyond the peak), the direction of the potential sweep is reversed. During the reverse scan, reduced molecules (generated in the forward half cycle, and accumulated near the surface) are reoxidized back to oxidize and an anodic peak results (Joseph, 2000).

If a redox system remains in equilibrium throughout the potential scan, the redox process is said to be reversible (equilibrium requires that the surface concentrations of O and R are maintained at the values required by the Nernst equation). The following parameters are used to characterize the cyclic voltammogram of a reversible process:

1. The peak potential separation $\Delta E_p = (E_{pc} - E_{pa}) = 59/n$ mV at all scan rates at 25 °C. Thus, the peak separation can be used to determine the number of electrons transferred, and as a criterion for a Nerntian behavior.

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

3. The position of the peaks on the potential axis (Ep) is related to the formal potential of the redox process. The formal potential for a reversible couple is centered between Epa and Epc which $E^{o'} = (Epa + Epc) / 2$

4. The peak current function $i_p/n^{1/2}$ (n = scan rate) is independent of n (see equation for peak current).

The peak current is given by the Randle Sevcik equation: $I_p = 2.69x10^5 n^{3/2} ACD^{1/2} \upsilon^{1/2}$.

Where: n = number of electrons transferred/molecule

$\upsilon^{1/2}$ = Square root of scan rate

A = electrode surface area (cm^2)

C = concentration (mol cm^{-3})

D = diffusion coefficient ($cm^2\ s^{-1}$)

For a reversible process, $E^{o'}$ is given by the mean of the peak potentials. Departures from reversible behavior for a redox process are shown by variations of the above parameters from the values observed for reversible processes. There are two major causes for irreversible behavior and these are discussed below (Joseph, 2000).

Example of Nernstian (reversible) behaviour

- Family of cyclic voltammograms for ferrocene carboxylic acid in an aqueous pH 7.0 phosphate buffer electrolyte showing typical Nernstian (reversible) behaviour. In this instance, a plot of peak height (anodic or cathodic) against the square root of the scan rate will result in a straight line passing through the origin (Figure 4).

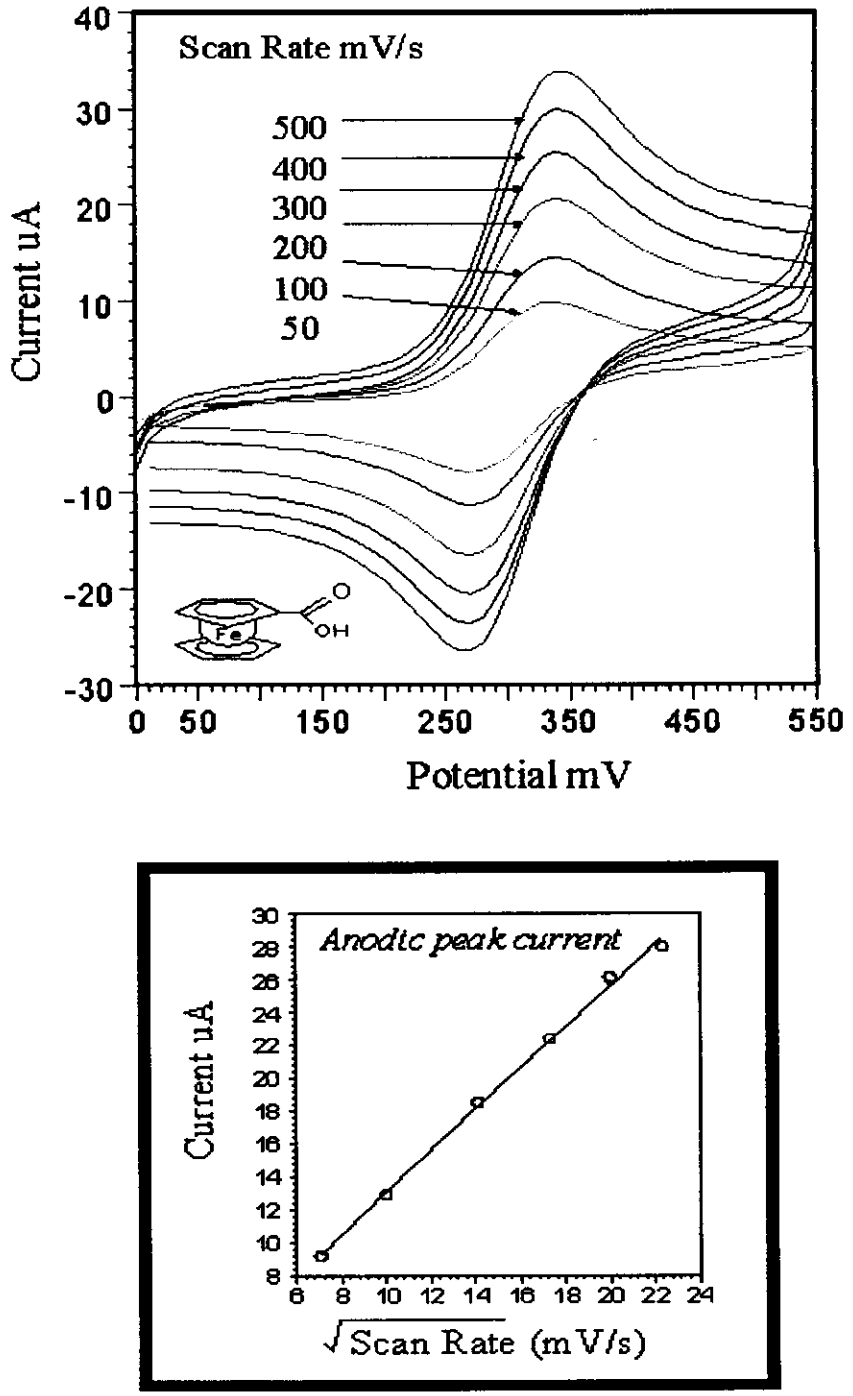

Figure 4 The relationship between current and square root of scan rate which follow Randles sevcik equation at scan rate 50, 100, 200, 300, 400 and 500 mV/s respectively

In figure 5, the potential is first varied linearly from +0.8 V to -0.2 V versus a saturated calomel electrode, whereupon the scan direction is reversed and the potential is returned to its original value of +0.8 V. This exitation cycle is often repeated several times. The potentials at which reversal takes place (in this case, -0.2 and +0.8 V) are called switching potentials. The range of switching potentials chosen for a given experiment is one in which a diffusion controlled oxidation or reduction of one or more analytes occurs. Depending upon the composition of the sample, the direction of the initial scan may be either negative as shown or positive (a scan in the direction of more negative potentials is termed a forward scan, while one in the opposite direction is called a reverse scan). Generally, cycle times range from 1 ms or less to 100 s or more. In this example, the cycle time is 40 s.

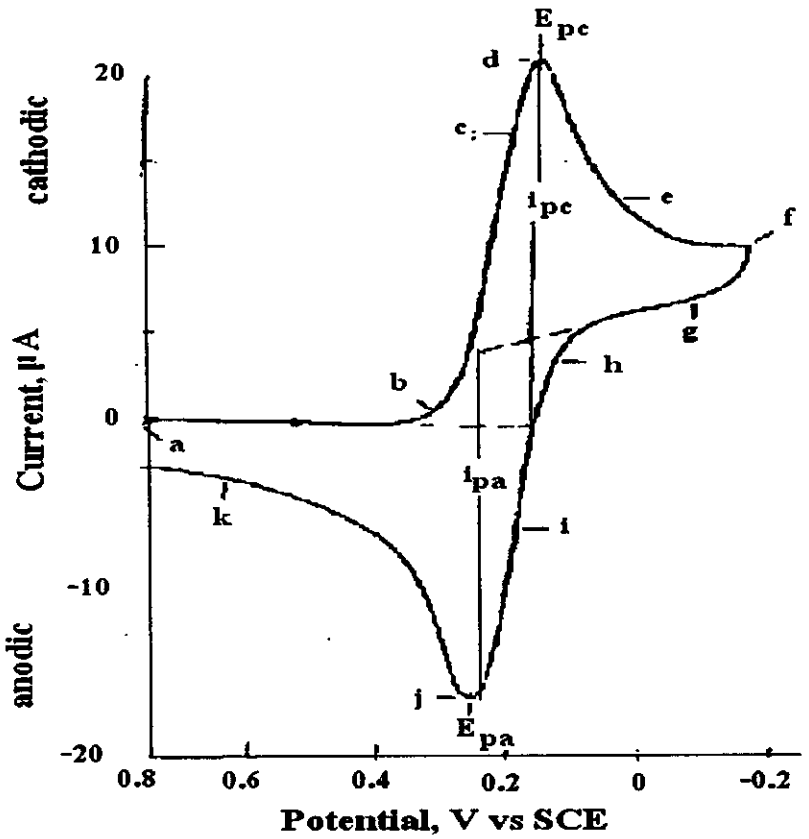

Figure 5 Cyclic voltammogram for a solution that is 6.0 mM in $K_3Fe(CN)_6$ and 1.0 M in KNO_3, (Douglas *et al.*, 1996)

Figure 5 shows the current response when a solution that is 6 mM in $K_3Fe(CN)_6$ and 1 M in KNO_3 is subjected to the cyclic excitation signal shown in Figure 2. The working electrode was a stationary platinum microelectrode and the reference electrode was a saturated calomel electrode.

At the initial potential of +0.8 V, a tiny anodic current is observed, which immediately decreases to zero as the scan is initiated. This initial current arises from the oxidation of water to give oxygen (at more positive potentials, this current rapidly increases and becomes quite large at about +0.9 V). No current is observed between a potential of +0.7 and +0.4 V, because no reducible or oxidizable species is present in this potential range. When the potential becomes somewhat less positive than +0.4 V, a cathodic current develops (point b) due to the reduction of the ferricyanide ion to ferrocyanide ion. The reaction at the cathode is then

$$[Fe^{III}(CN)_6]^{3-} + e- \longleftrightarrow [Fe^{II}(CN)_6]^{4-}$$

A rapid increase in the current occurs in the region of b to d as the surface concentration of $[Fe^{III}(CN)_6]^{3-}$ becomes smaller and smaller. The current at the peak is made up of two components. One is the initial current surge required to adjust the surface concentration of the reactant to its equilibrium concentration as given by the Nernst equation. The second is the normal diffusion controlled current. The first current then decays rapidly (points d to g) as the diffusion layer is extended farther and farther away from the electrode surface. At point f, the scan direction is switched. The current, however, continues to be cathodic even though the scan is toward more positive potentials, because the potentials are still negative enough to cause reduction of $[Fe^{III}(CN)_6]^{3-}$. Once the potential becomes positive enough so that reduction of $[Fe^{III}(CN)_6]^{3-}$ can no longer occur, the current goes to zero and then becomes anodic. The anodic current results from the reoxidation of $[Fe^{II}(CN)_6]^{4-}$ that has accumulated

near the surface during the forward scan. This anodic current peaks and then decreases as the accumulated $[Fe^{II}(CN)_6]^{4-}$ is used up by the anodic reaction.

Important parameters in acyclic voltammogram are the cathodic peak potential Epc, the anodic peak potential Epa, the cathodic peak current ipc, and the anodic peak current ipa. How these parameters are established is illustrated in Figure 5. For a reversible electrode reaction, anodic and cathodic peak currents are approximately equal and the difference in peak potentials is 0.0592/n, where n is the number of electrons involved in the half-reaction.

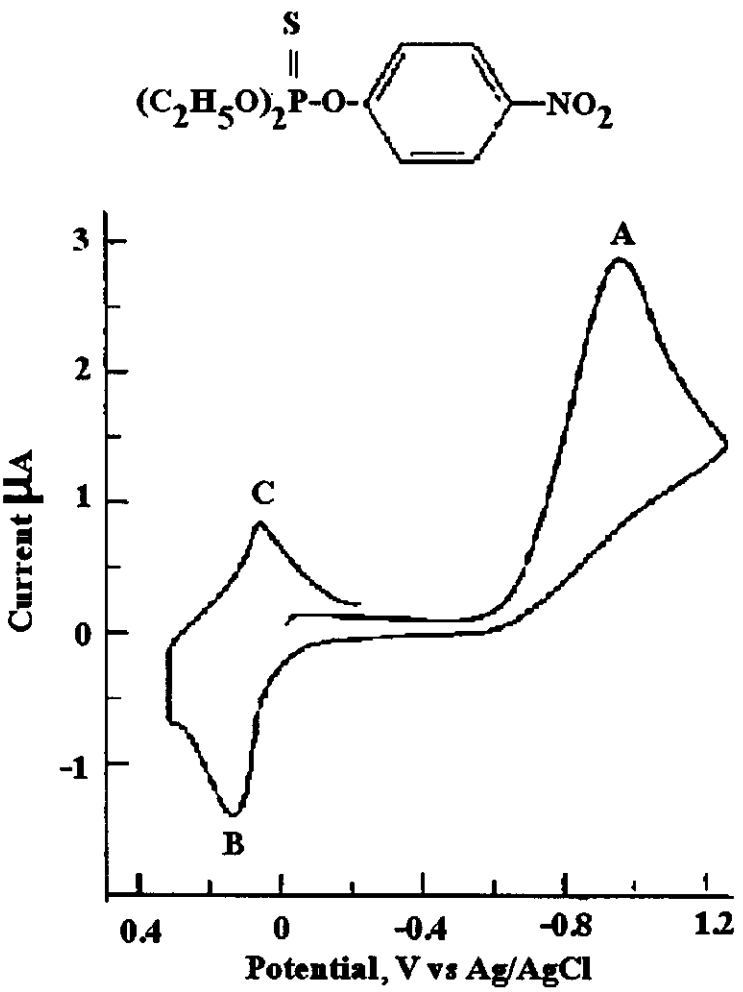

Figure 6. CV of the insecticide parathion in 0.5 M pH 5 sodium acetate buffer in 50% ethanol. Hanging mercury drop electrode. Scan rate: 200 mV/s (Douglas *et al.*, 1996).

The primary use of cyclic voltammetry is as a diagnostic tool that provides qualitative information about electrochemical processes under various conditions. As an example, consider the cyclic voltammogram for the agricultural insecticide parathion that is shown in Figure 6.

Here, the switching potentials were about -0.8 V and +0.3 V. The initial forward scan was, however, started at 0.0 V and not +0.3 V. Three peaks were observed. The first cathodic peak (A) results from a four-electron reduction of the parathion to give a hydroxylamine derivative (Φ is aromatic ring).

$$\Phi NO_2 + 4e^- + 4H^+ \longrightarrow \Phi NHOH + H_2O$$

The anodic peak at B arises from the oxidation of the hydroxylamine to a nitrso derivative during the reverse scan. The electrode reaction is

$$\Phi NHOH \longrightarrow \Phi NO + 2H^+ + 2e^-$$

The cathodic peak at C results from the reduction of the nitroso compound to the hydroxylamine as shown by the equation

$$\Phi NO + 2e^- + 2H^+ \longrightarrow \Phi NHOH$$

Cyclic voltammograms for authentic samples of the two intermediates confirmed the identities of the compounds responsible for peaks B and C.

Cyclic voltammetry, while not used for routine quantitative analyses, has become an important tool for the study of mechanisms and rates of oxidation/reduction processes, particularly in organic and metal-organic systems. Often, cyclic voltammograms will reveal the presence of intermediates in oxidation/reduction reactions (Figure 6, for example). Usually, platinum is used to fabricate micro-electrodes used with this technique.

1.3 The objectives

The objectives of this research work can be summarized as follows:

1. To investigate the trend of redox properties of quinones according to their structures and functional groups.
2. To investigate the ratio of silver (I) ion with ketones and quinones in the complexes by using UV-Visible spectroscopy.
3. To investigate the potentiality of ketones and quinones to silver ion by modified carbon paste electrode.

1.4 Scope of the research

1.4.1 Ketones and Quinones

Due to the fact that there are a lot of ketone compounds, the compounds were investigated according to the increasing complexity as follows:

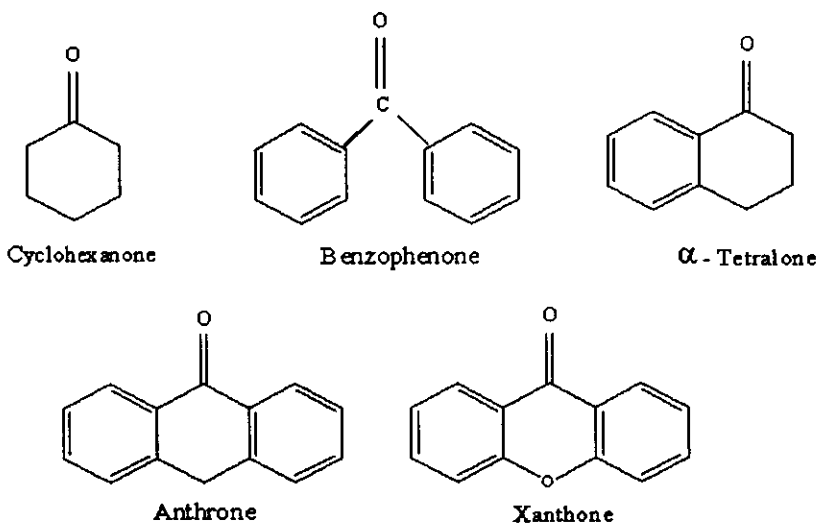

Figure 7 The structure of ketone compounds under investigation.

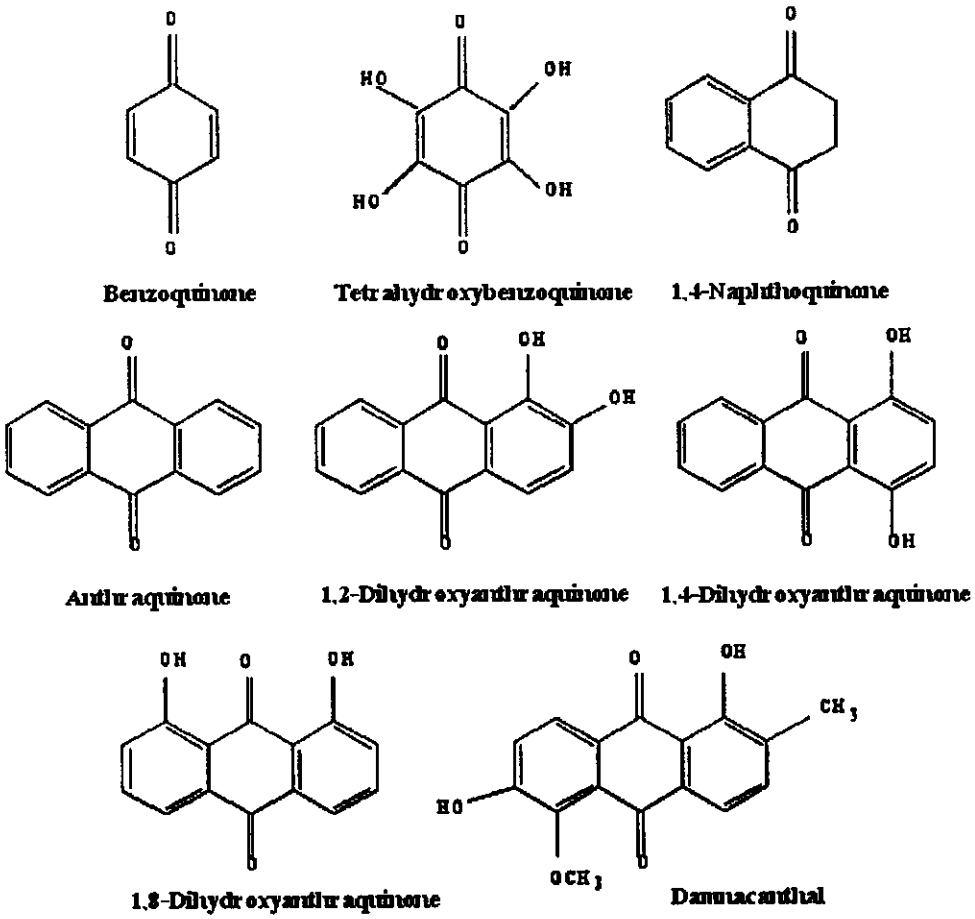

Figure 8 The structure of quinone compounds under investigation.

1.4.2 Metal

Serveral metals show strong reactivity towards quinones, especially those with hydroxy groups (Runurak *et.al.* 2004). However, there are many quinones and metals that have not been investigated. Silver ion was selected to be a model due to the fact that there have been some significant preliminary studies.

1.4.3 Electrochemical conditions

To make this study applicable, the electrochemical experiments are performed in the following conditions.

1.4.3.1 Glassy carbon electrode was polished by alumina powder 0.05 micron diameter before using all experiments (Alumina powder was prepared by dissolving in distill water).

1.4.3.2 CH_3CN and DMSO were solvents.

1.4.3.3 Tetraetylammonium perchlorate (TEAP) or Tetrabutylammonium hexafluorophosphate (TBAP) as an electrolyte.

1.4.3.4 Pt wire as a counter electrode.

1.4.3.5 Ag/AgCl as a reference electrode which had saturated KCl is internal solution.

1.4.3.6 Scan rate were run at 100, 200, 300, 400, 500, 600 mV/s respectively for prediction of electrochemical reversible and phenomena of adsorption of test solution on working electrode.

1.4.3.7 The purging the test solutions for at least 3 min with nitrogen gas (99.99%).

1.4.3.8 The CVs were run starting from positive potential to negative potential with the potential window from +0.000 V to -3.000 V vs Ag/AgCl electrode.

1.4.3.9 The cyclic voltammogram was performed by scanning two cycle.

1.4.4 Determination of the ratio of complex by UV-Visible

In the mole-ratio method, a series of solutions is prepared in which the analytical concentration of one reactant (usually the cation) is held constant while that of the other is varied. A plot of absorbance versus mole ratio of the reactants is then prepared. If the formation constant is reasonably favorable, two straight lines with different slopes are obtained. The two intersect at a mole ratio that corresponds to the combining ratio in the complex. Typical mole ratio plots are shown in Figure 1.
Note that the ligand of the 1:2 complex absorbs at the wavelength selected so that the slope beyond the equivalence point is greater than zero. We deduce that the

uncomplexed cation involved in the 1:1 complex absorbs because the initial point has an absorbance greater than zero.

Formation constants can be evaluated from the data in the curved portion of mole-ratio plots. A mole-ratio plot may reveal the stepwise formation of two or more complexes as successive slope changes, provided the complexes have different molar absorptivities and provided the formation constants are sufficiently different from each other (Douglas *et al.*, 1996). The relationship of absorbance and mole ligand per mole cation is shown in Figure 9.

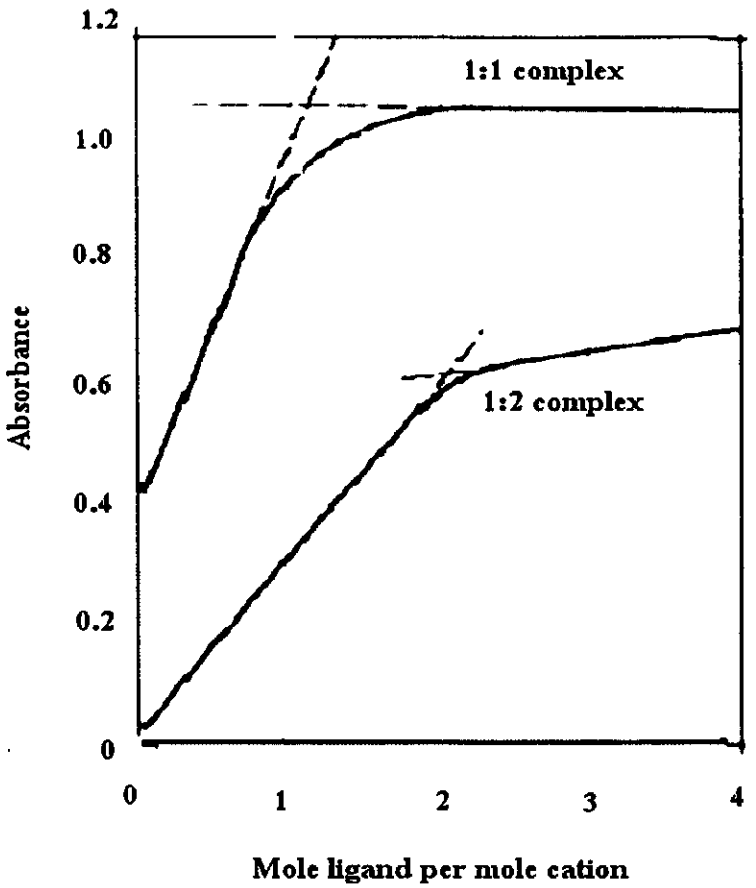

Figure 9 Mole ratio plots for a 1:1 and a 1:2 complex. The 1:2 complex is the more stable, as indicated by less curvature near the stoichiometric ratio (Douglas *et al.*, 1996).

1.4.5 The investigation potential of ketones and quinones to silver ion by using modified carbon paste electrode

Electrochemical conditions

To make this study applicable, the electrochemical experiments are performed in the following condition.

1. Unmodified carbon paste electrode (UME) and modified carbon paste electrode were used in this experiment.
2. CH_3CN was solvent.
3. Scan rate was performed at 180 mV/s.
4. The CVs were run with the potential window starting from 0.000 to +0.500 V vs Ag/AgCl reference electrode.
5. Ag/AgCl reference electrode was contained in a Pyrex tube with a softened glass cracked tip, filled with aqueous Tetramethylammonium chloride at a concentration to give a potential of 0.00 V vs SCE and placed inside a Luggin capillary.
6. The platinum-wire auxiliary electrode was placed inside a glass frit.
7. The test solution was nitric acid 0.2 M containing 1 x 10^{-3} M of $AgNO_3$.
8. The solution was stirred for 30 s.