ELECTROCHEMICAL AND SPECTROSCOPIC CHARACTERISATION OF FERROCENE-THIOSEMICARBAZONE LIGAND AND COPPER COMPLEXES

By

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DECLARATION

This thesis is my original work and has not been examined or presented for examination in this or any other university

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I dedicate this work to the entire Kiratu’s family especially Mum and Dad and those who contributed towards the success of this work.
ACKNOWLEDGEMENT

First and foremost I would like to thank Almighty God for giving me life, good health and determination to finish my research work successfully and in time. I wish to sincerely extend my gratitude to my supervisors Prof. G.N Kamau, Prof. L. Njenga and Dr. Peter Guto for their guidance, patience, encouragement and academic and technical support during my research. I also wish to thank the entire chemistry department especially technical staff Mr Amani, Mr Njoroge and Ms Rose for their tireless effort and working closely with me during my research. I acknowledge the physics department for allowing me to use their potentiostat in my research. I also do thank Mr Muthoka and Mr Omuchemi of physics department for their time and tireless effort while I worked in their department.

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ABSTRACT

Electrochemical and spectral behavior of two thiosemicarbazone ligands, containing ferrocene as a substituent and their two copper complexes; as well as a ligand with no ferrocene substituent and its copper complex were studied using cyclic voltammetry, ultraviolet-visible (UV/Vis) spectroscopy and infrared (IR) spectroscopy.

The ligands included: acetylferrocenyl-4-phenylthiosemicarbazone (Dan 1), acetylpyridine-2-thiophenecarboxylsemicarbazone (Dan 5), acetylferrocenyl-2-thiosemicarboxyl-semicarbazone (Dan 11). Their respective copper complexes were Dan 2, Dan 6 and Dan 12.

Ferrocene and Potassium ferrocyanide were used as standards and they gave reversible voltamograms of one electron transfer due to Fe$^{+2}$/Fe$^{+3}$ redox couple and diffusion coefficient of $2.8 \times 10^{-5} \pm 0.08 \text{cm}^2\text{s}^{-1}$ and $7.0 \times 10^{-6} \pm 0.03 \text{cm}^2\text{s}^{-1}$, respectively, which was comparable to the literature value. Preliminary work also involved characterization of a Nitrosyl ligand 4-phenacetylidene-2,2,5,5-tetramethyl-3-imidazolidin-1-oxyl nitroxyl, which was done in order to ensure that the electrochemical procedure followed was appropriate for the current research work. It was possible to reproduce the voltammetric behavior of the nitrosyl ligand.

All the Thiosemicarbazone ligands gave well defined cyclic voltamograms. Dan 1 showed a reversible voltammogram at a scan rate of 0.030v/s, where the ratio of anodic current and cathodic current was approximately unity, thus confirming reversibility. Its cathodic to anodic peak potential difference ($\Delta$E) increased with scan rate which is characteristic of slow electron transfer. Dan 2 which was the copper complex of Dan 1
gave a reduction and oxidation peak at -0.494V and -0.21V Vs SCE reference electrode, respectively.

The peak ratio was greater than unity which is common in transition metal complex due to shift in the geometry of coordination sphere. The ratio decreased with the scan rate and came closer to unity at higher scan rates, which suggested a chemical reaction follow up, showing that the oxidation product was not stable. This phenomenon was observed in all other copper complexes, but their peak potentials differed depending on the side chains of the thiosemicarbazone ligand. Dan 5 exhibited a one electron transfer reversible voltamogram where the current ratio (ip_a/ip_c) was approximately unity and ΔE was 0.084±0.01 V. Dan 11 also gave a one electron electron transfer at a scan rate of 0.025 V/s. ΔE was 0.065±0.01 versus SCE.

For the three ligands and the three metal complexes UV/visible spectral gave a weak absorption peak at 450nm and this was attributed to weakly allowed asymmetrical d-d transition for the metal in the ligand and the two metals in the complex. Intense separate peaks of shorter wave lengths (λ_max) were observed for all compounds which are characteristics of charge transfer absorption peaks.

When the ligand (Dan 1) was complexed with copper to form Dan 2 UV-Vis exhibited blue shift, i.e., the absorption peak of the complex shifted to shorter wavelength, suggesting transfer of electron from the ligand into the d orbitals of the metal (ligand-metal charge transfer), which is predominant if complexes have ligands with relatively high energy lone pairs (example Sulphur) or if the metal has low lying empty d orbitals. When the ligand (Dan 5) was complexed with copper to form Dan 6 UV-Vis exhibited
red shift suggesting metal-ligand charge transfer, similar to what was observed for Dan 11 and 12.

IR spectrophotometry confirmed the bidentate character of Dan 1 and Dan 11 ligands for the copper complexes. C=N band of the thiosemicarbazone which appeared at 1601 cm\(^{-1}\) in Dan 1 shifted towards lower wave number in Dan 2, indicating coordination via nitrogen to the copper metal. The band at 818 cm\(^{-1}\), corresponding to C=S was shifted towards lower wave numbers when complexed with copper metal, which indicates presence of thione sulphur coordination. Other characteristic bands observed were 1650 cm\(^{-1}\) for C=O, 3367 cm\(^{-1}\) for N-H and 1041 cm\(^{-1}\) for N=N.

The above Thiosemicarbazone (Dan 1, Dan 2, Dan 5, Dan 11 and Dan 12) are known to exhibit bioactivity properties from previous research work hence the recommendation for further work to correlate the present research results to the bioactivity of the compound.
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List of abbreviations

CT-charge transfer
Cm- centimeters
IR-infrared spectroscopy
IR-infrared spectroscopy
Mol- moles
MM-millimoles
L-litres
MLCT-metal to ligand charge transfer
MO-molecular orbital
nm- nanometers
Sec-seconds
TBAP-tetrabutylammonium perchlorate
TEAB-Tetraethylammoniumbromide
UV/VIS-ultraviolet/visible spectroscopy
mV-millivolts
A-amperes
CHAPTER ONE

1.0 Introduction

1.1 Background of the study

The increasing interest in thiosemicarbazones (TSCs) that has arisen in the last decade is related to their wide range of biological properties which include: antitumor [French and Blanz, 1966; Moore et al., 1970], antiviral [Logan et al., 1975], antimalarial [(Klayman et al. 1979] and antileprotic [Hooper and Purohit, 1983]. Thiosemicarbazones compounds are known to block DNA synthesis through inhibition of ribonucleotide diphosphate reductase enzyme [Kumbhar et al. 1991]. The figure 1.1 shows general structure of a semicarbazone.

![General Chemical structure of a semicarbazones.](image)

**Figure 1.1**: General Chemical structure of a semicarbazones.

Semicarbazone is a derivative of an aldehyde or ketone formed by a condensation reaction between a ketone or aldehyde and semicarbazide.
For ketones:

\[ H_2NNHC(=O)NH_2 + RC(=O)R \rightarrow R_2C=NNHC(=O)NH_2 \]...........................1.1

For aldehydes:

\[ H_2NNHC(=O)NH_2 + RCHO \rightarrow RCH=NNHC(=O)NH_2 \]...........................1.2

A Thiosemicarbazone is an analog of a semicarbazone which contains a sulfur atom in place of the oxygen atom (figure 1.2)

![General chemical structure of thiosemicarbazones.](image)

**Figure 1.2:** General chemical structure of thiosemicarbazones.

Some semicarbazones, such as nitrofurazone and thiosemicarbazones are known to have anti-viral and anti-cancer activity, usually mediated through binding to copper or iron in cells. Many semicarbazones are crystalline solids [Williamson and Kenneth, 1999]. Studies have shown that their complexes especially those containing Copper II and Iron II are more active than uncoordinated thiosemicarbazone molecules [Scovii et al. 1982]. This enhanced biological activity of metal thiosemicarbazone has been under study for some time and studies on the antifugal properties were published a few years ago [Parwana et al. 1985]. Cyclic voltamograms of copper II complex of thiosemicarbazone were correlated with the antifugal properties.
According to Kumbhar et al. (1991), reduction potentials of these compounds not only gave a broad-spectrum antifungal activity for copper(II)-thiosemicarbazone complexes, but also ways in which reduction potentials of these compounds can be controlled for effective biological activities.

In the last decade, great attention has been focused to the area of multinuclear complexes with extended bridges mainly because of the need to gain insight into the electron transfer pathways in biological systems [Zhuang et al. 1991]. Several metal complexes have been synthesized which include: Copper complexes of acetylferrocenyl-4-phenylthiosemicarbazone, acetylpyridine-2-thiophenecarboxylsemicarbazone, acetylferrocenyl-2-thiosemicarboxyl-semicarbazone in order to obtain detailed information about the exchange mechanism in the systems. Since biomolecules are known to be involved in important biological processes such as catalysis.

The following are the compounds to be investigated in the current research work:

Acetylferrocenyl-4-phenylthiosemicarbazone (Dan 1) figure 1.3, acetylpyridine-2-thiophenecarboxylsemicarbazone (Dan 5) (figure 1.4), acetylferrocenyl-2-thiosemicarboxyl-semicarbazone (Dan 11) figure 1.5 and their copper complexes which will be referred as Dan 2, Dan 6 and Dan 12 where “Dan” is the name of the person who synthesized these compounds.
Figure 1.3: acetylferrocenyl-4-phenylthiosemicarbazone.

DAN 2- $[\text{Cu}(\text{LH})_2]\text{Cl}_2$

Copper (II) complex of acetylferrocenyl-4-phenylthiosemicarbazone.

Figure 1.4: Acetylpyridine-2-thiophenecarboxylesemicarbazone.
DAN 6- \([\text{Cu(LH}_2\text{)}]\text{Cl}_2\)

Copper complex of Acetylpyridine-2-thiophenecarboxylsemicarbazone

![Molecular structure of Dan 11](image)

**Figure 1.5:** Acetylferrocenyl-2-thiosemicarboxyl-semicarbazone.

DAN 12- \([\text{CuT}_2]\)

Copper complex of Acetylferrocenyl-2-thiosemicarboxyl-semicarbazone.

These ligands and metal complexes (Dan 1, Dan 2, Dan 5, Dan 6, Dan 11 and Dan 12) were synthesized and characterized by elemental analysis which agrees with the formulation as well as proton and C-13 NMR, FT-IR and mass spectroscopy at the University of Namibia. Their biological activities against chloroquine resistant strain of malaria parasite were done at the University of California, San Francisco [Daniel et al. 2008]. They were all found to be bioactive.

In 1991 it was proposed by kumbhar et al. that electrochemistry of thiosemicarbazone contributed to their biological activities, where the electrochemical potentials of copper(II)
complexes of 2-acetylpyridine N-dialkylthiosemicarbazones indicated to play a significant role in the antifungal properties against common subcutaneous fungi, viz. *Aspergillus niger* and *Paecilomyces variotti*.

The above compounds are also thiosemicarbazone compounds hence there is a need to obtain electrochemical and spectroscopic information of these newly synthesized Dan 1, Dan 5, Dan 11 ligands and their copper complexes.

### 1.2 problem statement

Thiosemicarbazone compounds have emerged as important sulphur containing ligands in the last two decades [Belicchi et al. 1999]. They contain wide range of biological properties depending on parent aldehyde or ketone which include: antitumor [Afrasiabi et al. 2004], Antibacterial and antifungal [Singh et al. 2001 and Agarwal et al. 2006]. Antimalarial activity has been exhibited by Dan 1, Dan 5 and Dan 12 and their respective copper complexes which are newly synthesized.

In 1991 Kumbhar et al. reported that electrochemistry of thiosemicarbazone copper complex was responsible for the biological properties of the thiosemicarbazone compounds. Electrochemistry of 2-acetylpyridine thiosemicarbazones was done and correlated with the spectral and antifungal properties and it was found that the redox couple of Cu II /Cu I correlate to their antifungal activity.

Although Dan 1, Dan 5, Dan 11 and their copper complexes have been synthesized and found to be bioactive, there is little or no electrochemistry work which has been done. There is scarce information to understand the bioactivity of this newly synthesized Dan 1, Dan 5 Dan 11
ligands and their copper complexes, hence the need to undertake chemical and spectroscopic studies in the present research work.

1.3 Justification and novelty of the work

Currently, there is an increase of different diseases and the study of effective drugs is going on. Hence, compounds found to be bioactive should be thoroughly screened to come up with appropriate effective drugs for these diseases.

Dan 1, Dan 5, Dan 11 and their copper complexes are newly synthesized and only the structural and biological characterization has been so far done. In 2008 Daniel et.al (2008) reported that the compound possess antimalarial properties.

In 1991 Kumbhar et al. work indicated that the electrochemistry of thiosemicarbazone compounds is responsible for their biological activity. Therefore, there is great need to investigate electron transfer behavior of these compounds using electrochemical and spectroscopic methods in order to avail information for understanding well the biological aspects. This backs the current research work.

The thiosemicarbazone compounds studied in the current research work are different from those studied earlier using electrochemical methods. This suggests the novelty of the current study, as it tackles a different type of thiosemicarbazones.
1.4 OBJECTIVES

The overall objective for current research work was to investigate the electron transfer behavior of the newly synthesized thiosemicarbazone Dan 1, Dan 2 and Dan 5 and their copper complexes.

The specific objectives for the current research work were to:

1) use appropriate standards to calibrate the cyclic voltammetry instrument used,

2) obtain cyclic voltamograms of the ligand and their copper complexes and their electron transfer properties,

3) calculate the number of electrons transferred during the electrochemical process for both the ligand and the metal complex,

4) obtain UV/visible spectrum of the ligands and their copper complexes in order to compare their light absorption characteristics,

5) find out if there is relationship between correlation the spectra from the UV/visible and the cyclic voltamogram,

6) obtain coordination on the metal complexes using infrared spectra,

7) investigate the stability of the complexes in acetonitrile-water solution.
CHAPTER TWO

2.0 LITERATURE REVIEW

2.1.0 Electrochemistry

It is a branch of chemistry that enables one to study chemical reactions which take place in a solution at the interface of an electron conductor or electrode (a metal or a semiconductor) and an ionic conductor (the electrolyte), and which involve electron transfer between the electrode and the electrolyte or chemical species of interest in solution.

If a chemical reaction is driven by an external applied voltage, as in electrolysis, or if a voltage is created by a chemical reaction as in a battery, it is an electrochemical reaction. Chemical reactions where electrons are transferred between molecules are called oxidation/reduction (redox) reactions. In general, electrochemistry deals with situations where oxidation and reduction reactions are separated in space or time, connected by an external electric circuit to understand each process [William et al. 2004].

The principle of electrochemistry is based on redox reactions where an electron is transferred to or from a molecule or ion and thus changing its oxidation state. This reaction can occur through the application of an external voltage (electrolytic cell) or through the release of chemical energy (galvanic cell).

The term redox comes from the two concepts of reduction and oxidation. It can be explained in simple terms [Brown et al. 2003]:

Oxidation describes the loss of electrons / hydrogen or gain of oxygen / increase in oxidation
state by a molecule, atom or ion.

Reduction describes the gain of electrons / hydrogen or a loss of oxygen / decrease in oxidation state by a molecule, atom or ion.

2.1.1 Electrochemistry of copper

The electrochemical characteristics of the Cu(II)/Cu(I) and the Cu(I)/Cu(0) couples in acetonitrile solutions have been studied [MacLeod et al. 1981] and it was found that a slow chemical step precedes oxidation of Cu(1) to Cu(11) on all electrodes in solutions of high acetonitrile content. The slow step may be partial removal of acetonitrile from the solvated Cu(I) ion prior to electron transfer. Electrode processes are faster in chloride ions than in sulfate ion solutions. Reduction of Cu(1) in acetonitrile-water was quite slow on glassy carbon. Adsorption of acetonitrile solvent on platinum and carbon influences the processes [Ahmed et al. 1982].

The electron transfer in copper can involve two electrons transfer or one electron transfer

\[
\begin{align*}
\text{Cu} (s) & \rightarrow \text{Cu}^{2+} + 2e & \text{..................2.1} \\
\text{Cu} (s) & \rightarrow \text{Cu}^{1+} + 1e & \text{..................2.2}
\end{align*}
\]

2.1.2 Electrochemistry of thiosemicarbazones

Electrochemistry of uncomplexed thiosemicarbazone depends on the substituent attached to them. Work done on electrochemical behavior of some substituted thiosemicarbazones and their reaction products with tetracyanoethylene showed that electrochemical reduction of 2-formylpyridine thiosemicarbazone was an irreversible process since no peak was observed in the
positive sweep [Refaey et al. 2007].

In 1992 Avinash et al. performed electrochemical studies of transition metal complexes of 2-acetylpyridine thiosemicarbazones and correlations with spectral and antifungal properties of copper(II) complexes of 2-acetylpyridine 3-azacyclothiosemicarbazones. It was found that the complexes undergo a quasireversible one electron reduction in the range - 0.400 to - 0.450 V versus Ag/AgCl, attributable to the copper(II)/- copper(I) redox couple [Avinash S. et al. (1992)].

The electrochemical, as well as spectral characteristics of these complexes, were correlated with their antifungal activity against Aspergillus niger, Paecilomyces variotti, Penicillum rubrum and Aspergillus terreus and was found to correlate.

2.2 Spectroscopy

Spectroscopy is the study of the interaction between radiation and matter as a function of wavelength (λ). In fact, historically, spectroscopy referred to the use of visible light dispersed according to its wavelength, e.g. by a prism. Later the concept was expanded greatly to comprise any measurement of a quantity as function of either wavelength or frequency. Thus it can also refer to a response to an alternating field or varying frequency (v). A further extension of the scope of the definition added energy (E) as a variable, once the very close relationship E = hv for photons was realized (h is the Planck constant). A plot of the response as a function of wavelength or more commonly frequency is referred to as a spectrum.

The method is often used in physical and analytical chemistry for the identification of substances
through the emitted from or absorbed light.

2.3 Transition metals

A transition metal is an element whose atom has an incomplete d sub-shell, or which can give rise to cations with an incomplete d sub-shell. The following is the table of transition metals (table 2.1):

Table 2.1 A section of periodic table showing the transition metals.

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Because of their structure and partially filled d-orbitals, transition metals form many different coloured ions and complexes which depend on:

- the nature of the metal ion, specifically the number of electrons in the d orbitals
- the arrangement of the ligands around the metal ion (for example geometric
isomers can display different colours) and

- the nature of the ligands surrounding the metal ion. The stronger the ligands then the greater the energy difference between the split high and low 3d groups. [Cotton et al. 1999]

2.4 Ligand

A ligand is either an atom, ion, or molecule that has a lone pair of electron which can be donated to the empty orbital of metal to give a coordination complex. The bonding between the metal and ligand generally involves formal donation of one or more of the ligand's electrons. The metal-ligand bonding ranges from covalent to ionic. Furthermore, the metal-ligand bond order can range from one to three. Ligands are viewed as Lewis bases, although rare cases involving Lewis acidic ligands are known [Cotton et al. (1999)].

Ligands in a complex dictate the reactivity of the central metal atom, including ligand substitution rates, the reactivity of the ligands themselves and their redox process. Ligand selectivity is a critical consideration in many practical areas, including bioinorganic and medicinal chemistry, homogeneous catalysis and environmental chemistry.
2.5 Electrochemical techniques

Electrochemical techniques refer to methods in which there is an interaction between electrical power and matter. Electroanalytical methods in particular are methods where electricity is used to analyze matter. Electrochemical measurements on chemical systems are used by chemists for different purpose. These include: to obtain thermodynamic data about a reaction, to generate unstable intermediates so as to study their rate of decay or spectroscopic properties, to analyze trace amounts of some species of interest, to synthesize new compounds or to decompose a given chemical species.

Electroanalytical techniques involve a great variety of methods each differing from one another by the phenomena occurring within the electrochemical cell [Sawyer et al. (1974)]. They include:

(i) potentiometry in which the potential energy (E) is measured as a function of the reactant at currents which are constant or approach zero, (ii) chronopotentiometry, where the potential (E) versus time (t) is measured at a constant current, (iii) electrogravimmetry in which the amount of metal or metal oxide deposited on an electrode by either reduction or oxidation is measured either the potential (E) or current (i) is controlled, (iv) conductometry whereby measurements of conductance versus volume of reagent are done at constant potential, (v) voltammetry where
the current is measured as a function of the potential at constant concentrations and makes use of micro-electrode, (vi) amperommetry whereby measurements of current versus volume of reagent is done at a fixed potential. It is an application of voltammetry; (vii) controlled potential coulometry and controlled current coulometry. Whereby the quantity of electricity (coulombs) is measured at controlled potential and current respectively and (viii) anodic stripping voltammetry is a method whereby metal is concentrated on micro-electrode by electrodeposition followed by anodic reoxidation to produce large current. Polarography is a voltammetric method where dropping mercury electrode (DME) is used as working electrode and includes d.c polarography and controlled potential coulometry using stationery electrodes.

Electrochemical methods can be grouped into two categories [Willard et al 1986]:

(i) Equilibrium methods (non-polarized). In this case the solution is stirred vigorously or the electrode rotated or both so that the concentration gradients at the electrode are completely or nearly eliminated. This assures equilibrium effectively,

(ii) transient or dynamic (polarized or diffusion controlled) method. In this case both the electrode and solution are static thus after electrolysis begins the concentration gradients at the electrode surface become time independent or diffusion controlled. They include methods such as voltammetry, chronopotentiometry and chronoamperometry. In a transient method the substrate or speci
es of interest is brought to the surface of electrode by the influence of concentration gradient unlike in equilibrium method where such movement is influenced by combination of gradient in electrical and chemical potential and both natural and forced convection (mass transport).

Mass transport is the process by which species of interest move from one location of the solution to another (from the bulk solution to the electrode surface or vice versa) [Bard and Faulkner, 1980].

Mass transfer processes include: (a) migration, which is the movement of charged species under influence of applied field; (b) convection which is brought about by agitation of electrode or stirring of the solution causing fluid to flow because of natural convection caused by density gradient and forced convection; and (c) diffusion which is the movement of the species of interest under the influence of gradient of chemical potential (concentration gradient). In voltammetry electrical migration is minimized by the use of highly concentrated of inert supporting electrolyte (at least 10 times concentrated) e.g. KNO₃ [Scoog et al. 1988]. When a current is applied the ions of the electrolyte migrate thus hindering the chemical species of interest from migrating. The high concentrated inert ions eliminate attraction or repulsion forces between the electrode and the analyte and instead the inert ions are attracted or repulsed but they are not electrolyzed. On the other
hand convection is minimized by using transient electrochemical method [Willard et. al. 1986].

Mass transfer to an electrode is governed by Nernst-Planck equation, which is written for one dimensional mass transfer along x-axis as:

\[
E_{cell} = E_{cell}^{\circ} - \frac{RT}{zF} \ln Q
\]

Where

- \( E_{cell} \) is the cell potential (electromotive force) or applied potential.
- \( E_{cell}^{\circ} \) is the standard cell potential.
- \( R \) is the universal gas constant: \( R = 8.314 \ 472(15) \ J \ K^{-1} \ mol^{-1} \).
- \( T \) is the absolute temperature (K).
- \( F \) is the Faraday constant, the number of coulombs per mole of electrons: \( F = 9.648 \ 533 \ 99(24) \times 10^4 \ C \ mol^{-1} \).
- \( z \) is the number of electrons transferred in the cell reaction or half-reaction.
- \( Q \) is the reaction quotient.

2.5.1 **linear sweep potential Voltammetry (LSPV)**

voltammetry technique uses a microelectrode for microanalysis to enhance polarization. It comprises electroanalytical methods in which analysis is achieved by the measurement of the current, i,
as a function of the applied potential, \( E_{\text{app}} \), during electrolysis performed under conditions that encourage polarization of the electrode [Bard and Faulkner, 1980]. A complete concentration polarization exist when the current in an electrochemical cell is limited by the rate of mass transfer of the reactant to the electrode surface [Bard and Faulkner, 1980]. As \( E_{\text{app}} \) is scanned, the dilute solution of the analyte produce a limiting current at a given potential which is independent of \( E_{\text{app}} \) but depends on the rate at which the reactant is brought to the electrode surface. Since the reactions are steady state, the only process involved in mass transport is diffusion and thus such a current is called diffusion-controlled limiting current or diffusion controlled, \( i_d \) [Willard et al 1986]. The decomposition by such a current does not alter the concentration of the reactant significantly when the voltammogram is being obtained [Pletcher, 1975].

LSPV includes:-

a) single -sweep voltammetry.

In this technique a rapidly changing ramp of potential (from \( E_i \) to \( E_f \)) is applied to the working electrode as a function of time and the resulting current is then measured as a function of the applied potential. The electrode reaction is carried out in un-stirred solution, hence mass transport is as a result of diffusion alone [Bard and Faulkner, 1980]. The rate of reaction increases as the pot
ential is increased towards the potential where reduction or oxidation occurs. However, since th
solution is un-stirred, the region in the vicinity of the working electrode is depleted off the spec
ies of interest. A potential is reached where the increase in the rate balances the depletion effect a
and thus a current plateau is recorded. This is the so called diffusion-controlled current, \( i_d \), at pote
ntial beyond this point the current decreases as the potential is increased and peak is recorded. Th
e \( i-E \) curve for a simple electrode process shows a marked current peak instead of the smooth s-s
haped for an equilibrium technique for reversible system [Sawyer et al.1974]. The following reac
tion occurs.

\[
\text{O} + \text{ne} \rightleftharpoons \text{R} \tag{2.4}
\]

The potential, \( E_p \) is given by:

\[
E_p = E_{1/2} - 1.109(RT/nF) \tag{2.5}
\]

At 25°C,

\[
E_p = E_{1/2} - 0.0285/n \text{ V} \tag{2.6}
\]

where \( E_p \) is the peak potential and \( E_{1/2} \) is the potential at which the current is half the diffusion lim
ited value \( (1/2i_d) \).
The peak current, $i_p$, in amperes is given by

$$i_p = 0.4463nfA C_o(nF/RT)^{1/2} V^{1/2} D_o^{1/2}$$

(2.7)

At 25°C

$$i_p = (2.69 \times 10^5)n^{3/2} AC_o(nF/RT)^{1/2} V^{1/2} D_o^{1/2}$$

(2.8)

where

- $A$ is the electrode area (cm$^2$),
- $n$ is the number of electrons transferred,
- $C_o$ is the concentration of oxidised species (O) at the bulk of the solution in mol/cm$^3$,
- $V$ is the scan rate in Vsec$^{-1}$,
- $D_o$ is the diffusion coefficient of the oxidised species O in cm$^2$sec$^{-1}$,
- $f$ is the faradaic constant,
- $R$ is the gas constant and
- $T(K)$ is absolute temperature.
Since the peak is slightly broad, causing difficulties in determining peak potential $E_p$ it is sometimes convenient to report the potential at half $i_p$ called half-peak potential, $E_{p/2}$. This however has no direct thermodynamic significance.

$$E_{p/2} = E_{1/2} + 1.09 \frac{RT}{nF}$$  

At 25°C

$$E_{p/2} = E_{1/2} + (0.0285/n)V$$

The potential $E_{1/2}$ occurs about midway between $E_p$ and $E_{p/2}$ thus for Nernstian wave

$$|E_p - E_{p/2}| = 2.2 \left(\frac{RT}{nF}\right)V$$  

At 25°C

$$|E_p - E_{p/2}| = (0.0565/n)V$$

This shows that for reversible wave $E_p$ is independent of the scan rate and of $i_p$ as well the current at any point on the wave but $i_p$ is proportional to square root of scan rate [Bard and Faulkner, 1980]. For irreversible systems the $i$-$E$ relationship is not simple and contains terms relating to the electron transfer characteristic of the reaction process [Bard and Faulkner, 1980].
Deviations from linearity in the plot of $i$ vs $v^{1/2}$ sometimes indicate that the redox event is associated with other processes, such as association of a ligand, dissociation of a ligand, or a change in geometry or related chemical reactions [Bard and Faulkner, 2001].

(b) Cyclic voltammetry

Cyclic voltammetry or CV is a type of potentiodynamic electrochemical measurement. In a cyclic voltammetry experiment the working electrode potential is ramped linearly versus time like linear sweep voltammetry. Cyclic voltammetry takes the experiment a step farther than linear sweep voltammetry which ends when it reaches a set potential. When cyclic voltammetry reaches the switching potential, the working electrode's potential ramp is inverted. This inversion can happen multiple times during a single experiment. The current at the working electrode is plotted versus the applied voltage to give the cyclic voltammogram trace. Cyclic voltammetry is generally used to study the electrochemical properties of an analyte in solution [Allen et al., 2000].

In cyclic voltammetry, the electrode potential ramps linearly versus time. This ramping is known as the experiment's scan rate (V/s). The potential is measured between the reference electrode and the working electrode and the current is measured between the working electrode and the counter electrode. This data is then plotted as current ($i$) vs. potential ($E$). As the waveform shows, the forward scan produces a current peak for any analytes that can be reduced (or oxidized depending on the initial scan direction) through the range of the potential scanned. The current will increase as the potential reaches the reduction potential of the analyte, but then drops
as the concentration of the analyte is depleted close to the electrode surface. If the redox couple is reversible then when the applied potential is reversed, it will reach the potential that will reoxidize the product formed in the first reduction reaction, and produce a current of reverse polarity from the forward scan. This oxidation peak will usually have a similar shape to the reduction peak. As a result, information about the redox potential and electrochemical reaction rates of the compounds is obtained.

For instance if the electronic transfer at the surface is fast and the current is limited by the diffusion of species to the electrode surface, then the current peak will be proportional to the square root of the scan rate. This relationship is described by the Cottrell equation [Bard, A. J. and Faulkner, 2001].

2.5.2 Characterization using cyclic voltammetry

The utility of cyclic voltammetry is highly dependent on the analyte being studied. The analyte has to be redox active within the experimental potential window. It is also highly desirable for the analyte to display a reversible wave. A reversible wave is when an analyte is reduced or oxidized on a forward scan and is then reoxidized or rereduced in a predictable way on the return scan as shown in figure 2.1.
Figure 2.1 cyclic voltamogram of reversible analyte [Christopher and Ana Maria, 1993].

The waveform of the voltage applied to the working electrode versus the reference electrode is triangular shaped. Since this voltage varies linearly with time, the slope is referred to as the scan rate (V/s). On the reverse scan, the ferricyanide, formed during the forward scan, is reduced back to ferrocyanide. The peak shape of the oxidative and reverse current-potential (I-E) curve in Figure 2.3 is typical for an electrode reaction in which the rate is governed by diffusion to a planar electrode surface. That is, the rate of the electron transfer step is relatively fast compared to that of diffusion. In such a case the peak current, $I_p$, is governed by the Randle-Sevcik relationship:

$$I_p = k n^{3/2} A D^{1/2} C V^{1/2} \quad \text{...........................................(2.13)} \quad \text{[Larry and Faulkner, 1983]}$$

Where $I_p$ is peak current,
constant, \( k \), has a value of \( 2.72 \times 10^5 \);

\( n \) is the mole of electrons transferred per mole of electro active species.

\( A \) is the area of the electrode in \( \text{cm}^2 \),

\( D \) is the diffusion coefficient in \( \text{cm}^2/\text{s} \),

\( C \) is concentration in \( \text{mole/cm}^3 \), and

\( V \) is the scan rate of the potential in volt/s.

The \( I_p \) is linearly proportional to the bulk concentration, \( C \), of the electroactive species and the square root of the scan rate, \( V^{1/2} \). Thus, an important diagnostic is a plot of the \( I_p \) vs \( V^{1/2} \). If the plot is linear, it is reasonably safe to say that the electrode reaction is controlled by diffusion, which is the mass transport of electroactive species to the surface of the electrode across a concentration gradient. The thickness, \( d \), of the "diffusion" layer can be approximated by: \( d \sim [Dt]^{1/2} \), where \( D \) is the diffusion coefficient and \( t \) is time in seconds. A "quiet" i.e. unstirred solution is required. The presence of supporting electrolyte, such as the KCl in the example, is required to eliminate movement of the charged electroactive species due to migration in the electric field gradient. Reversible peaks have a distinct absolute potential difference between the reduction (\( E_{pc} \)) and oxidation peak (\( E_{pa} \)). In an ideal system, \( \left| E_{pc} - E_{pa} \right| = \frac{57 \text{ mV}}{n} \) for one electron process [Nicholson and Irving, 1964]. In addition, the ratio of the currents passed at reduction (\( i_{pc} \)) and end oxidation (\( i_{pa} \)) is near unity (\( 1 = i_{pa}/i_{pc} \)) for a reversible peaks.

When such reversible peaks are observed thermodynamic information in the form of half cell potential \( E^0_{1/2} \) can be determined. When waves are semi-reversible such as when \( i_{pa}/i_{pc} \) is less than or greater than 1, it can be possible to determine even more information especially kinetic
processes like following chemical reaction.

When waves are non-reversible it is impossible to determine what their thermodynamic \( E^{0}_{1/2} \) is with cyclic voltammetry. However, \( E^{0}_{1/2} \) can be determined. It often requires equal quantities of the analyte in both oxidation states. When a wave is non-reversible cyclic voltammetry cannot determine if the wave is at its thermodynamic potential or shift to a more extreme potential by some form of over potential. The couple could be irreversible because of a following chemical process; a common example for transition metals is a shift in the geometry of the coordination sphere. If this is the case, then higher scan rates may show a reversible wave. It is also possible that the wave is irreversible due to a physical process most commonly some form of precipitation [Bosch et al. 2007].

2.6 Spectroscopic Techniques

An electromagnetic radiation possesses some amount of energy and can be considered to propagate as a transverse wave which can be described in terms of wavelength, \( \lambda \), frequency, \( v \), or wave number. The energy \( (E) \) of a radiation or photon is described by the equation:

\[
E = hv = \frac{hc}{\lambda} \tag{2.14}
\]

where

\( E \) is the energy of a unit radiation,
h is Planck's constant and
c is the velocity of the light.

The entire energy region of electromagnetic wave is called an electromagnetic spectrum. The electromagnetic spectrum is thus divided into different regions according to the energy possessed or the wavelength value [Scoog et al. 1985].

2.6.1 Ultraviolet-visible spectroscopy

Ultraviolet-visible spectroscopy or ultraviolet-visible spectrophotometry (UV/Vis) involves the spectroscopy of photons in the UV-visible region. It uses light in the visible and adjacent near ultraviolet (UV) and near infrared (NIR) ranges. In this region of the electromagnetic spectrum, molecules undergo electronic transitions. This technique is complementary to fluorescence spectroscopy, in that fluorescence deals with transitions from the excited state to the ground state, while absorption measures transitions from the ground state to the excited state as shown in fig 2.2.

UV/Vis spectroscopy is routinely used in the quantitative determination of solutions of transition metal ions and highly conjugated organic compounds.

The Ultraviolet (UV) region extend from about 10-380 nm. Most important region for analysis is 200-380 nm (the near Ultraviolet region). The region below 200nm is called the vacuum UV region simply because the instrument has to be operated under vacuum since air absorbs...
appreciably. The visible region extends from 380-780 nm in the electromagnetic spectrum [Kotz and Purcell, 1987].

All molecules contain electrons which can be excited to higher energy levels, thus they can absorb radiation in the entire UV-Visible region. Electronic transitions in this region are due to the absorption of radiation by specific types of groups, bonds and functional groups within the molecule. The absorption wavelength depends on the molecule. Four types of transition are possible for an organic compound (figure 2.2):

![Diagram of electron transition](image)

**Figure 2.2:** Electron transition for an organic compound following absorption of electromagnetic radiation.

From sigma bonding to sigma-anti bonding orbital $\sigma \rightarrow \sigma^*$

Non-bonding electrons excited to sigma-anti-bonding orbital $n \rightarrow \sigma^*$
Non-bonding electrons raised to pi-anti-bonding orbital \( n \rightarrow \pi^* \)

Pi bonding orbital electrons excited to a pi-anti-bonding orbital \( \pi \rightarrow \pi^* \)

In addition to \( n \rightarrow \pi^* \) transition exhibited by a number of inorganic anions, inorganic compounds show charge transfer transitions, (which is the movement of electrons from the metal orbitals to unoccupied orbitals of the ligand and vice versa). Most application of UV and visible spectrometry to organic compounds are based upon the \( n \rightarrow \pi^* \) or \( \pi \rightarrow \pi^* \) transition whose absorption peaks occur 200-700 nm region. These two types of transitions require the presence of unsaturated functional groups which provide the \( \pi \) orbitals. These unsaturated absorbing centers are called chromophores [Rodgers, 1994].

Solutions of transition metal ions can be coloured (i.e., absorb visible light) because d electrons within the metal atoms can be excited from one electronic state to another. The colour of metal ion solutions is strongly affected by the presence of other species, such as certain anions or ligands also charge transfer complexes also give rise to colours. For the latter, the colours are often too intense to be used for quantitative measurement.

2.6.1a Experimental principles of uv-visible

The Beer-Lambert law states that the absorbance of a radiation by a solution is directly proportional to the concentration of the absorbing species in the solution and the path length.

\[ A = \log_{10}(I/I_0) = \epsilon \cdot c \cdot L \] ..............................(2.15)

where
\( A \) is the measured absorbance, 

\( I_0 \) is the intensity of the incident light at a given wavelength. 

\( I \) is the transmitted intensity, 

\( L \) the path length through the sample in cm 

\( c \) the concentration of the absorbing species in \( \text{mol/cm}^3 \) for each species and wavelength.

\( \varepsilon \) is a constant known as the molar absorptivity or extinction coefficient. This constant is a fundamental molecular property in a given solvent, at a particular temperature and pressure its units are \( \text{L mol}^{-1} \text{ cm}^{-1} \)

Ultraviolet/visible spectroscopy involves the absorption of ultraviolet/visible light by a molecule thereby causing the promotion of an electron from a ground electronic state to an excited electronic state [Day et al. 1991].

2.6.1b Characterization of chemical species using UV-Visible spectrometry

Quantitative analysis

When a beam of light of intensity \( P_0 \) passes through a layer of solution containing appropriate chemical species, having a thickness of \( b \) cm and a concentration, \( C \), of the absorbing species. The power or the intensity is reduced from \( P_0 \) to \( P \). The transmittance, of the solution is given by:

\[
T = \frac{P}{P_0}
\]

(2.16)

And absorbance, \( A \), is
\[ A = -\log_{10} \frac{P_0}{P} \]  

(2.17)

The absorbance, \( A \), is directly proportional to the path length \( b \) and the concentration \( C \) (Beer’s-Lambert law). Thus,

\[ A = abC \]  

(2.18)

Where \( a \) is a proportionality constant called specific absorptivity.

When \( C \) is expressed in molesL\(^{-1}\) of the solution and \( b \) is in cm, then the absorptivity is called molar absorptivity, \( \varepsilon \), and has the units Lcm\(^{-1}\)mol\(^{-1}\)

\[ A = \varepsilon bc \]  

(2.19)

A plot of absorbance versus the concentration gives a straight line passing through the origin and of slope \( \varepsilon b \). From such a plot the unknown concentration of a given sample can be determined. Thus due to the direct relationship between absorbance and concentration quantitative analysis can be done from absorption at specific wavelength. UV/VIS spectroscopy can be used to determine the concentration of the absorber in a solution. Also one can get the \( \lambda_{\text{max}} \) and from this the molar absorptivity or extinction coefficient can be calculated. Deviations from Beer’s-Lambert law are encountered due to the variation of \( \varepsilon \) which depends upon the nature of the absorbing species in the solution and wavelength of the radiation. In addition chemically-based and instrument-based deviations are also encountered [Rodgers, 1994].
Qualitative analysis

The application of UV-Visible spectroscopy to qualitative identification is limited because of the few absorption maxima and minima observed. Even though it does not give unambiguous identification of organic compounds, the region of absorption by a given sample helps in detecting the presence of certain functional groups acting as chromophores. In addition, changing the solvent polarity can tell what kinds of transition are involved. Charge transfer, CT, in complexes can be identified from Intensity: CT absorptions bands are highly intense and often lie in the ultraviolet or visible portion of the spectrum. The typical molar absorptivities, $\varepsilon$, of charge transfer complexes are about 50000 L mol$^{-1}$ cm$^{-1}$, that are three orders of magnitude higher than typical $\varepsilon$ of 20 L mol$^{-1}$ cm$^{-1}$ or lower, for d-d transitions (transition from $t_{2g}$ to $e_{g}$). This is because the charge transfer, CT, transitions are not spin or Laporte forbidden as d-d transitions. Also the shift of the spectrum when a ligand is added can indicate an electron transfer [Rodgers, 1994].

2.6.2 Absorption by inorganic anions

A number of inorganic anions exhibit ultraviolet absorption peaks which are a consequence of $\pi \rightarrow \pi^*$ transitions. Examples include nitrate (313nm), carbonate (217nm), nitrite (360 and 280 nm), azido (230 nm) and trithiocarbonate (500 nm) ions.

2.6.2a Absorption by elements of the first and second transition-metal series

Most transition-metal ions absorb in the ultraviolet or visible region of the spectrum. For lanthanide and actinide series, the absorption process results from electronic transition of 4f and
5f electrons; for elements of the first and second transition–metal series, the 3d and 4d electrons are responsible. The ions and complexes of the 20 elements in the first two transition series tend to absorb visible radiation in one if not all of their oxidation states. In contrast to the lanthanide and actinide elements, however, the absorption bands are often broad and are strongly influenced by environmental factors. An example of the environmental effect is found in the pale blue color of the aquo copper (II) ion and the much darker blue of the copper complex with ammonia.

Metals of the transition series are characterized by having partially occupied d orbitals. Each capable of accommodating a pair of electrons. These orbitals do not generally participate in bond formation; nevertheless, it is clear that the spectra characteristics of transition metals involve electronic transition among the various energy levels of these d orbitals.

Two theories have been advanced to rationalize the colors of transition-metals ions; and the profound influence of chemical environment on these colors: the crystal-field theory and molecular-orbital theory. Both theories are based upon the premise that the energies of d orbitals of the transition-metal ions in solution are not identical and that absorption involves the transition of electrons from a d orbital of lower energy to the higher energy.

In general the electronic spectrum [lever, 1974] of a complex, such as ML₆ can be sub classified into three main divisions namely:

i) Transition between levels primarily located on the ligand i.e, \( \pi \rightarrow \pi^* \) transition in aromatic ligands.

ii) Transition between levels primarily located on metal (i.e, the well known d-d transitions)

iii) Transition in which there is an electron transferred from the metal to the ligand or vise
In a molecular orbital since electron transitions between electronic levels of different atoms necessary take place, through sometimes with very high energy the relative energy of the highest filled and lowest empty orbital on an atom of the ionization potential and electron affinity respectively of the atom. Thus atoms or ions which have low ionization potential (i.e., are readily oxidisable) have filled orbital of relatively high energy. Conversely, atoms or ions which have high electron affinity (i.e., are readily reducible have relatively low lying empty orbital).

If a complex is formed between a metal for example which is readily oxidisable and a ligand which is readily reducible, it can be expected that the separation between the highest filled level on the metal and the lowest empty level on the ligand will be relatively small if the separation between these levels is too small. Then there will be a total electron transferred between the species resulting in oxidation of the metal and the reduction of the ligand. Provided that the energy separation is great enough for the complex to be stable, a charge transfer absorption will be seen at relatively low energies, corresponding to a transition which may be written schematically as:

\[
\text{M}^{(n-1)+} \quad \text{L} \quad \rightarrow \quad \text{M}^{n+} \quad \text{L}^{-} \quad [\text{Lever, 1974}]
\]

Such transitions are called metal-to-ligand charge transfer (MLCT) and these complexes arise from transfer of electrons from MO with metal like character to those with ligand like character. This is most commonly observed in complexes with ligands having low-lying \( \pi^* \) orbitals especially aromatic ligands. The transition will occur at low energy if the metal ion has a low oxidation number for its d orbitals will relatively be high in energy conversely, if a readily
redisable metal is complexed with oxidisable ligand (usually an anion) a ligand-to metal charge transfer absorption occurs.

It is noteworthy that these transitions do not involve the complete transfer of one electron from one atom to another. In a molecular orbital, they represent the transition of an electron from a molecular orbital primarily located on another atom. The spectra are often (though not necessary) very intense and may make the weaker d-d transitions.

Ligand-to metal charge transfer transitions can be expected to be in or close to the visible region. If oxidisable ligands are complexed to reducible metals (i.e., metals in the higher oxidation states) the more readily oxidisable ligands, are those with low ionization potential and are therefore the more polarizable ligands, such as I⁻ and sulphides [lever 1974].

2.6.3 Infrared spectroscopy (IR)

Infrared (IR) spectroscopy is one of the most common spectroscopic techniques used by organic and inorganic chemists. Simply, it is the absorption measurement of different IR frequencies by a sample positioned in the path of an IR beam. The main goal of IR spectroscopic analysis is to determine the chemical functional groups in the sample. Different functional groups absorb characteristic frequencies of IR radiation. Using various sampling accessories, IR spectrophotometer can accept a wide range of sample types such as gases, liquids, and solids. Thus, IR spectroscopy is an important and popular tool for structural elucidation and compound identification.

Infrared radiation spans a section of the electromagnetic spectrum having wave numbers from
roughly 13,000 to 10 cm\(^{-1}\), or wavelengths from 0.78 to 1000 \(\mu\)m. It is bound by the red end of
the visible region at high frequencies and the microwave region at low frequencies.

IR absorption positions are generally presented as either wavenumbers (\(\bar{\nu}\)) or wavelengths (\(\lambda\)).

Wavenumber defines the number of waves per unit length. Thus, wavenumbers are directly pro-
portional to frequency, as well as the energy of the IR absorption [Jones and McClelland (1992)].

The wavenumber unit (cm\(^{-1}\), reciprocal centimeter) is more commonly used in modern IR instru-
ments that are linear in the cm\(^{-1}\) scale. In the contrast, wavelengths are inversely proportional to
frequencies and their associated energy. IR absorption information is generally presented in the
form of a spectrum with wavelength or wavenumber as the x-axis and absorption intensity or per
cent transmittance as the y-axis.

2.6.3a Experimental principles

At temperatures above absolute zero, all the atoms in molecules are in continuous vibration with
respect to each other. When the frequency of a specific vibration is equal to the frequency of the
IR radiation directed on the molecule, the molecule absorbs the radiation.

\[
A = \log_{10}(1/T) = -\log_{10}T = -\log_{10}I/I_0 \quad [\text{Katon et al.1992}]....................(2.20)
\]

Where

\(A\) is the Absorbance which is the logarithm to the base 10 of the reciprocal of the transmittance 
(\(T\)).
T (Transmittance) is the ratio of radiant power transmitted by the sample \( (I) \) to the radiant power incident on the sample \( (I_0) \).

Each atom has three degrees of freedom, corresponding to motions along any of the three Cartesian coordinate axes \((x, y, z)\). A polyatomic molecule of \( n \) atoms has \( 3n \) total degrees of freedom. However, 3 degrees of freedom are required to describe translation, the motion of the entire molecule through space. Additionally, 3 degrees of freedom correspond to rotation of the entire molecule. Therefore, the remaining \( 3n - 6 \) degrees of freedom are true, fundamental vibrations for nonlinear molecules. Linear molecules possess \( 3n - 5 \) fundamental vibrational modes because only 2 degrees of freedom are sufficient to describe rotation. Among the \( 3n - 6 \) or \( 3n - 5 \) fundamental vibrations (also known as normal modes of vibration), those that produce a net change in the dipole moment may result in an IR activity and those that give polarizability changes may give rise to Raman activity. Naturally, some vibrations can be both IR- and Raman-active. The total number of observed absorption bands is generally different from the total number of fundamental vibrations. It is reduced because some modes are not IR active and a single frequency can cause more than one mode of motion to occur. Conversely, additional bands are generated by the appearance of overtones (integral multiples of the fundamental absorption frequencies), combinations of fundamental frequencies, differences of fundamental frequencies, coupling interactions of two fundamental absorption frequencies, and coupling interactions between fundamental vibrations and overtones or combination bands (Fermi resonance). The intensities of overtone combination and difference bands are less than those of the fundamental bands. The combination and blending of all the factors thus create a unique IR spectrum for each compound. The major types of molecular vibrations are stretching and bending. The various
types of vibrations are illustrated in Figure 2.3. Infrared radiation is absorbed and the associated energy is converted into these types of motions. The absorption involves discrete, quantized energy levels. However, the individual vibrational motion is usually accompanied by other rotational motions. These combinations lead to the absorption bands, not the discrete lines, commonly observed in the mid IR region [Smith, 1979].
Asymmetrical stretching (ν₁, CH₂)

Symmetrical stretching (ν₂, CH₂)

Stretching vibrations

In-plane bending or scissoring (δ, CH₂)

Out-of-plane bending or wagging (ω, CH₂)

Out-of-plane bending or twisting (τ, CH₂)

In-plane bending or rocking (ρ, CH₂)

Bending vibrations

Figure 2.3: Major vibrational modes for a nonlinear group, CH₂.
The IR region is commonly divided into three smaller areas: near IR, mid IR, and far IR.

The far IR requires the use of specialized optical materials and sources. It is used for analysis of organic, inorganic, and organometallic compounds involving heavy atoms (mass number over 19). It provides useful information to structural studies such as conformation and lattice dynamics of samples.

Near IR spectroscopy offers high-speed quantitative analysis without consumption or destruction of the sample it needs minimal or no sample preparation. Its instruments can often be combined with UV-visible spectrometer and coupled with fiber optic devices for remote analysis.

2.6.3b Characterization using infrared spectroscopy

The combination of the fundamental vibrations or rotations of various functional groups and the subtle interactions of these functional groups with other atoms of the molecule results in the unique, generally complex IR spectrum for each individual compound. IR spectroscopy is mainly used in two ways: structural elucidation and compound identification
structural elucidation

Because of complex interactions of atoms within the molecule, IR absorption of the functional groups may vary over a wide range. However, it has been found that many functional groups give characteristic IR absorption at specific, narrow frequency ranges regardless of their relationship with the rest of the molecule. Generalized tables of the positions and relative intensities of absorption bands have been established and used to determine the functional groups present or absent in a molecule [Luypaert et al. 2003].
CHAPTER THREE

3.0.0 Methodology and instrumentation

3.1.0 Cyclic voltammetry instrumentation

The method uses a reference electrode, working electrode, and counter electrode which in combination are sometimes referred to as a three-electrode setup. An electrolyte is usually added to the test solution to ensure sufficient conductivity and minimal electrolytic migration. The combination of the solvent, electrolyte, specific working electrode material and reference electrode determines the range of the potential or potential window.

Electrodes are static and sit in unstirred solutions during cyclic voltammetry. This "still" solution method results in cyclic voltammetry's characteristic diffusion controlled peaks. This method also allows a portion of the analyte to remain after reduction or oxidation where it may display further redox activity. Stirring the solution between cyclic voltammetry traces is important as to supply the electrode surface with fresh analyte for each new experiment. The solubility of an analyte can change drastically with its overall charge. Since cyclic voltammetry usually alters the charge of the analyte it is common for reduced or oxidized analyte to precipitate out onto the electrode. This layering of analyte can insulate the electrode surface, display its own redox activity in subsequent scans, or at the very least alter the electrode surface. For this and other reasons it is often necessary to clean electrodes between scans.
3.1.1 Working electrode

Common materials for working electrodes include glassy carbon, platinum, and gold. These electrodes are generally encased in a rod of inert insulator with a disk exposed at one end. A regular working electrode has a radius within an order of magnitude of 1 mm. Having a controlled surface area with a defined shape is important for interpreting cyclic voltammetry results. In the present research work, glassy carbon and pyrolytic carbon working electrode were used [Kissinger et al. 1996].

3.1.1a Glassy carbon

Glassy carbon, also called vitreous carbon, is a non-graphitizing carbon which combines glassy and ceramic properties with those of graphite. The most important properties are high temperature resistance, extreme resistance to chemical attack and impermeability to gases and liquids. Glassy carbon is widely used as an electrode material in electrochemistry, as well as for high temperature crucibles and as a component of some prosthetic devices. The structure of glassy carbon has long been a subject of debate. Early structural models assumed that both sp$^2$ and sp$^3$-bonded atoms were present, but it is now known that glassy carbon is 100% sp$^2$. However, more recent research has suggested that glassy carbon has a fullerene-related structure [Harris, 2003].

Glassy carbon should not be confused with amorphous carbon. Glass-like carbon cannot be described as amorphous carbon because it consists of two-dimensional structural elements and does not exhibit ‘dangling’ bonds. It exhibits a conchoidal fracture [Cowlard and Lewis 1967].
Glassy carbon electrode (GCE) in aqueous solutions is considered to be an inert electrode for hydronium ion reduction: [Sawyer D.T. et al (1995)]

\[
\text{H}_3\text{O}^+_{(aq)} + e^- \text{ GCE} \rightleftharpoons \text{H}^+_{(aq)} + \text{H}_2\text{O}, \quad E^\circ = -2.10 \text{ V versus NHE at 25°C}\ldots(3.1)
\]

Comparable reaction on platinum:

\[
\text{H}_3\text{O}^+_{(aq)} + e^- \text{ Pt} \rightarrow \text{H}^+_{(aq)} + \text{H}_2\text{O}, \quad E^\circ = 0.000 \text{ V versus NHE at 25°C}\ldots(3.2)
\]

The difference of 2.1 V is attributed to the properties of platinum which stabilizes a covalent Pt-H bond.

To run cyclic voltammetry experiments at a regular working electrode is insufficient. High scan rates create peaks with large currents and increased resistances which result in distortions of voltammograms. Ultra microelectrodes can be used to minimize the current and resistance.

3.1.1b Pyrolytic carbon

Pyrolytic carbon is a material similar to graphite, but with some covalent bonding between its graphene sheets as a result of imperfections in its production (figure 3.1).
Generally it is produced by heating a hydrocarbon nearly to its decomposition temperature and permitting the graphite to crystallize (pyrolysis). One method is to heat synthetic fibers in a vacuum. Another method is to place seeds or a plate in the very hot gas to collect the graphite coating [Cook, et al. 1999].

Pyrolytic carbon samples usually have a single cleavage plane, similar to mica, because the graphene sheets crystallize in a planar order, as opposed to graphite, which forms microscopic randomly-oriented zones. Because of this, pyrolytic carbon exhibits several unusual anisotropic properties. It is more thermally conductive along the cleavage plane than graphite, making it one of the best planar thermal conductors available. It is also more diamagnetic against the cleavage plane, exhibiting the greatest diamagnetism of any room temperature (by weight) diamagnet. It is even possible to levitate reasonably pure and sufficiently ordered samples over rare earth permanent magnets [Cook et al. 1999].
3.1.2 Counter electrode

The counter electrode, also known as the auxiliary or second electrode, can be any material which conducts easily and won't react with the bulk solution (inert materials such as gold, platinum, or carbon). Reactions occurring at the counter electrode surface are unimportant as long as it continues to conduct current well. To maintain the observed current the counter electrode will often oxidize or reduce the solvent or bulk electrolyte. The auxiliary electrode's potential is opposite in sign to that of the working electrode, but its current and potential are not measured. Rather, it is used to ensure that current does not run through the reference electrode (three electrode system), which would disturb the reference electrode's potential. The auxiliary electrode often has a surface area much larger than that of the working electrode to ensure that the reactions occurring on the working electrode are not surface area limited by the auxiliary electrode.

When using a three electrode cell system to perform electro-analytical chemistry, the auxiliary electrode is often isolated from the working electrode using a glass frit. Such isolation prevents any by-products generated at the auxiliary electrode from contaminating the main test solution and interfering with the analytical measurement being made at the working electrode [Zoski and Cynthia, 2007].

3.1.3 Reference electrode

A Reference electrode is an electrode which has a stable and well-known electrode potential. The high stability of the electrode potential is usually reached by employing a redox system with
constant (buffered or saturated) concentrations of each participants of the redox reaction [Allen J et al. (2000)]. The ideal reference electrode should posses the following properties;

- It should be reversible and obey the Nernst equation with respect to some species in the electrolyte.
- Its potential should be stable with time.
- Its potential should return to the equilibrium potential after small currents are passed through the electrode.
- If it is an electrode like the Ag/AgCl reference electrode, the solid phase must not be appreciably soluble in the electrolyte.
- It should show low hysteresis with temperature cycling.

There are many ways reference electrodes are used. The simplest is when the reference electrode is used as a half cell to build an electrochemical cell. This allows the potential of the other half cell to be determined. An accurate and practical method to measure an electrode’s potential in isolation (absolute electrode potential) has yet to be developed. There are four kind of reference electrode: Aqueous Reference Electrodes, nonaqueous Reference Electrodes, Quasi-Reference Electrode (QRE), Pseudo-reference electrodes.
3.1.3a **Aqueous Reference Electrodes** [Gritzner and Kuta 1984].

Common reference electrodes and potential with respect to the standard hydrogen electrode:

- Standard hydrogen electrode (SHE) \((E=0.000 \text{ V})\) also known as "normal hydrogen electrode" (NHE)
- Reversible hydrogen electrode (RHE) \((E=0.000 \text{ V} + 0.0591*pH)\)
- Saturated calomel electrode (SCE) \((E=+0.242 \text{ V saturated})\)
- Copper-copper(II) sulfate electrode \((E=+0.314 \text{ V})\)
- Silver chloride electrode \((E=+0.197 \text{ V saturated})\)
- pH-electrode (in case of pH buffered solutions, see buffer solution)
- Palladium-hydrogen electrode
3.1.3b Silver chloride electrode

Figure 3.2 Ag-AgCl reference electrode

A silver chloride electrode is a type of reference electrode, commonly used in electrochemical measurements. For example, it is usually the internal reference electrode in pH meters. As another example, the silver chloride electrode is the most commonly used reference electrode for testing cathodic protection and corrosion control systems in sea water environments. The above reference electrodes consist of a plastic tube electrode body. The electrode is a silver wire that is coated with a thin layer of silver chloride, either physically by dipping the wire in molten silver chloride, or chemically by electroplating the wire in concentrated hydrochloric acid. A porous plug on one end allows contact between the field environments with the silver chloride electrolyte. An insulated lead wire connects the silver rod with measuring instruments. A voltmeter negative lead is connected to the test wire. The reference electrode contains potassium
to stabilize the silver chloride concentration.

The electrode functions as a redox electrode and the reaction is between the silver metal (Ag) and its salt — silver chloride (AgCl, also called silver(I) chloride).

The corresponding equations can be presented as follows:

\[ \text{Ag}^+ + \text{e}^- \leftrightarrow \text{Ag}(s) \] (3.3)

\[ \text{Ag}^+ + \text{Cl}^- \leftrightarrow \text{AgCl}(s) \] (3.4)

or an overall reaction can be written:

\[ 2\text{Ag}^+ + \text{Cl}^- + \text{e}^- \leftrightarrow \text{Ag}(s) + \text{AgCl}(s) \] (3.5)

This reaction characterized by fast electrode kinetics, meaning that a sufficiently high current can be passed through the electrode with the 100% efficiency of the redox reaction (dissolution of the metal or cathodic deposition of the silver-ions). The reaction has been proved to obey these equations in solutions with pH's of between 0 and 13.5.

Dependence of potential on the electrolyte is shown in table 3.1
Table 3.1: The potential of a silver:silver chloride reference electrode with respect to the standard hydrogen electrode depends on the electrolyte composition [Greeley, R.S. (1960)].

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Potential $E^0 + E_1$</th>
<th>Temperature Coef. (mV/°C) at around 25 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>SHE</td>
<td>0.000</td>
<td>+0.87</td>
</tr>
<tr>
<td>Ag/AgCl/Sat. KCL</td>
<td>+0.197</td>
<td>-1.01</td>
</tr>
<tr>
<td>Ag/AgCl mol/kg KCL</td>
<td>+0.205</td>
<td>-0.73</td>
</tr>
<tr>
<td>Ag/AgCl/1.0 mol/kg KCL</td>
<td>+0.235</td>
<td>+0.25</td>
</tr>
<tr>
<td>Ag/AgCl/0.6 mol/kg KCL</td>
<td>+0.25</td>
<td></td>
</tr>
<tr>
<td>Ag/AgCl (Seawater)</td>
<td>+0.266</td>
<td></td>
</tr>
</tbody>
</table>

The electrode has many features and advantages making it suitable for use in the field:

- Simple to construct
- Inexpensive to manufacture
- Stable potential
• Non-toxic components

It is usually manufactured with saturated potassium chloride electrolyte, but can be used with lower concentrations such as 1 mol/kg potassium chloride. As noted above, changing the electrolyte concentration changes the electrode potential. Silver chloride is slightly soluble in strong potassium chloride solutions, so it is sometimes recommended that the potassium chloride be saturated with silver chloride to avoid stripping the silver chloride off the silver wire.

3.1.3c Nonaqueous Reference Electrodes

While it is convenient to compare solvents to qualitatively systems it is not quantitatively meaningful. Much as pK\textsubscript{a} are related between solvents, but not the same, so is the case with E\textdegree. While the SHE might seem to be a reasonable reference for nonaqueous work as it turns out the platinum is rapidly poisoned by many solvents including acetonitrile causing uncontrolled drifts in potential. Both the SCE and saturated Ag/AgCl are aqueous electrodes based around saturated aqueous solution. While for short periods it may be possible to use such aqueous electrodes as references with nonaqueous solutions the long-term results are not trustworthy. Using aqueous electrodes introduces undefined, variable, and unmeasurable junction potentials to the cell in the form of a liquid-liquid junction as well as different ionic composition between the reference compartment and the rest of the cell [Pavlishchuk et al. 2000]. The best argument against using aqueous reference electrodes with nonaqueous systems, as mentioned earlier, is that potentials measured in different solvents are not directly comparable.[Geiger and William, 2007]
3.1.3d Quasi-Reference Electrode (QRE)

A Quasi-Reference Electrode (QRE) avoids the issues mentioned above. A QRE with Ferrocene or similar internal standard (Cobaltocene) is ideal for nonaqueous work. Since the early 1960s ferrocene has been gaining acceptance as the standard reference for nonaqueous work for a number of reasons. In 1984 IUPAC recommend ferrocene (II/III) as a standard redox couple [Gritzner and Kuta, 1984] The preparation of the QRE electrode is simple allowing a fresh reference to be prepared with each set of experiments. Since QREs are made fresh there is also no concern of improper storage or maintenance of the electrode. QREs are also more affordable than other reference electrodes.

3.1.3e Pseudo-reference electrodes

A pseudo-reference electrode is a term that is not well defined and boarders on having multiple meanings since pseudo and quasi are often used interchangeably. There are a class of electrodes named pseudo-reference electrodes because they do not maintain a constant potential but vary predictably with conditions. If the conditions are known, the potential can be calculated and the electrode can be used as a reference. Most electrode work over a limited range of conditions, such as pH or temperature, outside of this range the electrodes behavior becomes unpredictable. The advantage of a pseudo-reference electrode is that the resulting variation is factored into the system allowing researchers to accurately study systems over a wide range of conditions. [Bosch. et al. 2007].
3.2 Ultraviolet-visible (UV-Vis) spectrophotometry instrumentation

The instrument used in ultraviolet-visible spectroscopy is called a UV/vis spectrophotometer. It measures the intensity of light passing through a sample \( I \) and compares it to the intensity of light before it passes through the sample \( I_0 \). The ratio \( I / I_0 \) is called the *transmittance*, and is usually expressed as a percentage \((\% T)\). The absorbance, \( A \), is based on the transmittance:

\[
A = - \log(\% T / 100\%) \tag{3.6}
\]

Spectrophotometers are classified as either manual or recording, or as single or double beam depending on the operating mode or the design, respectively. Another classification can be based upon the spectral region used e.g. infrared and UV-Visible spectrophotometer.

The basic parts of a spectrophotometer are: a radiation source, wavelength selectors, sample container, radiation detectors and amplifiers and readout devices (figure 3.3).
3.2.1 Radiation source

The radiation source must provide sufficient radiant energy that is continuous at the region where absorption is measured. Secondly the radiation should be of constant intensity during the entire period of measurement. The radiation source is often a Tungsten filament (300-2500 nm), a deuterium arc lamp which is continuous over the ultraviolet region (190-400 nm), and more recently light emitting diodes (LED) and Xenon Arc Lamps[8] for the visible wavelengths.

3.2.2 Wavelength selector

In most spectroscopic analyses a single band of radiation is required. This is necessary so as to obtain a linear relationship between absorbance or emission and concentration (Beer's law). Thus an optical device is required to isolate a beam of high spectral purity of the desired
wavelength from a continuous source. The two types of wavelength selectors employed are monochromators and filters. Monochromator basically consists of an entrance slit to resist unwanted radiation, a lens or mirror to produce parallel beam of radiation, a prism or grating for dispersing the incident radiation (polychromatic beam), a mirror or lens (collimator) to reform images of the entrance slit and an exit slit for isolating the desired spectral band. The exit slit blocks all the dispersed radiation except those which fall within a given range on the focal plane. The difference between prism and grating monochromators is that in prism monochromator refraction at the two faces of a prism results in angular dispersal of the radiation while in the latter angular dispersal is as a result of diffraction that occurs at the reflective surfaces [Demirdöven et al 2004].

3.2.3 Detectors

Detectors should be highly sensitive in the spectral region of interest with linear response to radiant power and high signal-to noise ratio. In addition they should have a fast response time and minimal output signal in the absence of radiation. Photoelectric detectors are commonly employed for UV- VIS and their principle of operating is based upon the photoelectric effect. They include : (i) the photovoltaic cells in which a photocurrent is generated at the interface of a semiconductor layer e.g. (Selenium) and metallic plate (e.g. Iron) when the radiant energy falls on the interface. A thin semi-transparent layer of silver or gold is coated on the outer surface of the semiconductor to serve as a second collector electrode. The magnitude of the resulting current is proportional to the number of photons striking the semiconductor surface; (ii) photoemission tubes, in which electrons are emitted from the surface of photosensitive
negative electrons (cathode) when irradiated with photons of sufficient energy. Phototubes consist of an evacuated envelope containing a pair of electrodes across which a potential is maintained. The electrons are accelerated towards the positive electrode (anode) which results to a current flow in the circuit. The number of electrons ejected from the cathode is directly proportional to the intensity of the radiation striking the surface. However, the current produced is depended upon the potential applied across the two electrodes and is directly proportional to the radiation power; (iii) photomultiplier tubes: in these, electrons emitted from photo emissive cathode are multiplied by a series of photo-emissive electrodes (dynodes) each at a more positive potential (50-90V) than the one before it. The electrons eventually fall on anode and current is generated. (iv) Silicon photodiodes: they consist of a reverse-biased pn junction formed on a silicon chip. For a current flow to be produced in the external circuit, a photon must reach the active (intrinsic silicon material) area. When photons interact with the diode, electrons are promoted. Current is generated which is proportional to the radiant power [Demirdöven et al. (2004)].

3.2.4 Sample containers

Cuvette holds the sample. It is normally rectangular in shape, commonly with an internal width of 1 cm (This width becomes the path length, $L$, in the Beer-Lambert law.

There are three different types of cuvettes commonly used, with different usable wavelengths:

(i) Glass, with a wavelength from 380 to 780 nm (visible spectrum); (ii) Plastic, with a wavelength from 380 to 780 nm (visible spectrum) and (iii) Quartz, with a wavelength below
380 nm (ultraviolet spectrum).

The requirements of the cuvettes for holding sample are that: they must be made up of material that is transparent to the light radiation in the spectral region of interest and which does not react with the sample or solvent. In addition the cells must be well matched, used to and maintained as quality of absorbance data depend on these factors [Demirdöven et al. (2004)].

3.2.5 Amplification and readout

The electrical signal (current) from the detector is amplified by a signal processor which in addition can change the signal from dc to ac (or vice versa), alter the signal phase and filter to remove any unwanted components. The signal is finally displayed on a meter, recorder or digital voltmeter.

A spectrophotometer can be either single beam or double beam. In a single beam instrument (such as the Spectronic 20), all of the light passes through the sample cell. \( I_0 \) must be measured by removing the sample. This was the earliest design, but is still in common use in both teaching and industrial labs.

In a double-beam instrument, the light is split into two beams before it reaches the sample. One beam is used as the reference; the other beam passes through the sample. Some double-beam instruments have two detectors (photodiodes), and the sample and reference beam are measured at the same time. In other instruments, the two beams pass through a beam chopper, which
blocks one beam at a time. The detector alternates between measuring the sample beam and the reference beam.

### 3.3 Infrared (IR) spectroscopy instrumentation

An IR spectrometer consists of three basic components: radiation source, monochromator, and detector (figure 3.4).

![Infrared Spectrometer Diagram](image)

**Figure 3.4:** IR spectrometer set up [S. Mukamel (2000)].

#### 3.3.1 Radiation source

The common radiation source for the IR spectrometer is an inert solid heated electrically to 1000 to 1800 °C. Three popular types of sources are Nernst glower (constructed of rare-earth oxides), Globar (constructed of silicon carbide), and Nichrome coil. They all produce continuous radiations, but with different radiation energy profiles [Day et al. 1991].
3.3.2 monochromator

The monochromator is a device used to disperse a broad spectrum of radiation and provide a continuous calibrated series of electromagnetic energy bands of determinable wavelength or frequency range. Prisms or gratings are the dispersive components used in conjunction with variable-slit mechanisms, mirrors, and filters. For example, a grating rotates to focus a narrow band of frequencies on a mechanical slit. Narrower slits enable the instrument to better distinguish more closely spaced frequencies of radiation, resulting in better resolution. Wider slits allow more light to reach the detector and provide better system sensitivity. Thus, certain compromise is exercised in setting the desired slit width [Day et al. 1991].

3.3.3 Detectors

Detectors used in dispersive IR spectrometers can be categorized into two classes: thermal detectors and photon detectors. Thermal detectors include thermocouples, thermistors, and pneumatic devices (Golay detectors). They measure the heating effect produced by infrared radiation [Hobart et al. 1988].
3.4.0 Methodology:

3.4.1 Chemicals and solutions

Ferrocene (98%), tetraethylammoniumbromide [TEAB](98%), Lithium chloride were from Aldrich Chemical Co. perchlorate was from Eastman Kodak. Acetonitrile, Dichloromethane (DCM) were supplied by Kobian chemical Co. All the chemicals were analytical reagent grade and were used as received. Water was de-ionized by an Elga water purification apparatus.

Thiosemicarbazone ligands and their complexes samples were obtained from the University of Namibia and used as received.

Solution of the free ligand and metal complexes containing the ligand (0.3-0.7mM) and 0.1M tetraethylammoniumbromide in (1:1) acetonitrile-water was prepared freshly for each procedure.

3.4.2 Apparatus and procedure for cyclic voltametry.

Autolab Princeton applied research (PAR) analyzer, a three electrode potentiostat was used to control the potential for all the electrochemical experiments and all potential were referred to saturated calomel electrode (SCE). Platinum wire was employed as the counter electrode and glassy carbon (0.071cm²) and pyrolytic carbon was used as working electrode. The glassy carbon electrode was polished for about 2 min. with alumina slurry before each potential scan. All the electrolytic solutions were de-aerated for at least 25 min by passing Nitrogen gas through them before taking the measurements. All experiments were done at room temperature (20-25°C).
(i) the electrochemical cell was washed with deionised water and rinsed thoroughly.

(ii) the working electrode surface was polished using alumina slurry and for the pyrolytic graphite a razor blade was used to cut the surface to have a new working surface.

(iii) solution of 0.1 M electrolyte in acetonitrile water was first run to establish the working window.

(iv) Cyclic voltammetry studies of 10ml of 0.4mM ferrocene in a homogeneous acetonitrile-water (1:1) solvent were done. 0.1 tetraethylammoniumbromide was used as supporting electrolyte. The potential was swept from -0.250V to 0.750V and back to -0.250V at varying scan rate of 0.01, 0.015, 0.02, 0.025, 0.03 and 0.04 VSec^{-1}

(v) The procedure (iv) was repeated for potassium ferrocyanide.

Sample solution of thiosemicarbazone ligand and their complexes were prepared freshly and 10ml of the solution in 0.1M TEAB in (1:1) Acetonitrile:water was used for the study. Potential was swept from -1 to +1 then back at varying scan rate of 0.01 to 0.04 VSec^{-1}. The window was reduced according to the observed peaks.

3.4.3 Apparatus and procedure for UV-Visible spectrophotometer

The UV-Visible spectra for the different samples were done using SP8-37000DUV spectrophotometer and the samples (0.3-0.7mM) were prepared in Acetonitrile solution and were diluted five times before the study. The solution was put in the Quartz cuvettes and the instrument was run at wavelength range of 280 to 700nm:
(i) the instrument was switched on and left to initialize for about two hours,

(ii) baseline correction was done using acetonitrile as the blank and instrument was set to run between the wavelength of 700 to 280nm.

(iii) cuvettes were cleaned using deionised water and rinsed with acetonitrile.

(iv) One of the two cuvettes was filled with acetonitrile and the other with the sample solution containing the thiosemicarbazone complexes.

(v) The instrument was run and the spectra recorded and saved in the computer,

(vi) The procedure was repeated for all the compounds and this was also repeated during the stability studies.

3.4.4 Apparatus and procedure for IR spectrophotometer

Infrared (IR) spectrophotometry studies were done using IR -297 Infrared spectrophotometer:

(i) The instrument was switched on and left to initialize for about thirty minutes.

(ii) The sample was first ground with a mulling agent (kerosene) in a marble mortar with a pestle.

(iii) A thin film of the mull was applied onto the salt plate (NaCl) then the plates were placed into the instrument and run.

(iv) their spectra was recorded and saved. This was repeated for all the ligands and their metal complexes.
4.0: Results and discussion

4.1 Voltammetric study of 4.0mM ferrocene in 0.1M TEAB in acetonitrile/water (1:1) as a standard

Ferrocene is popularly used as standard for the study of electrode processes [Hinman et al. 1985]. Ferrocene (bis-cyclopentadienyl iron), [(C₅H₅)₂Fe] has the iron atom symmetrically placed between two cyclopentadienyl rings. Each of the anion forms a covalent bond to the ferrous ion symmetrically; it is readily oxidized to Ferrocenium ion [Wilkinson et al. 1952]. Ferrocene has been studied as a standard in previous work and in this work the some of the compounds being studied have ferrocene as their substituent. Therefore, it was considered appropriate to use ferrocene as the standard for present research work. The results of the voltammetric studies of ferrocene in 0.1 M TEAB in acetonitrile/water (1:1) are given in table 4.1:
### Table 4.1: Scan rate studies of ferrocene in 0.1 M TEAB, acetonitrile/water (1:1)

<table>
<thead>
<tr>
<th>Scan rate volts/sec</th>
<th>Epa Volts v/s SCE</th>
<th>Ipa, A</th>
<th>Epc, Volts v/s SCE</th>
<th>Ipc, A</th>
<th>ΔEp Volts v/s SCE</th>
<th>Ipc/Ipa</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.010</td>
<td>0.389</td>
<td>5x10^5</td>
<td>0.317</td>
<td>5x10^5</td>
<td>0.072</td>
<td>1</td>
</tr>
<tr>
<td>0.015</td>
<td>0.389</td>
<td>5.9x10^5</td>
<td>0.317</td>
<td>5.9x10^5</td>
<td>0.072</td>
<td>1</td>
</tr>
<tr>
<td>0.020</td>
<td>0.384</td>
<td>6.9x10^5</td>
<td>0.317</td>
<td>6.9x10^5</td>
<td>0.067</td>
<td>1</td>
</tr>
<tr>
<td>0.030</td>
<td>0.400</td>
<td>9.6x10^5</td>
<td>0.320</td>
<td>9.6x10^5</td>
<td>0.080</td>
<td>1</td>
</tr>
<tr>
<td>0.040</td>
<td>0.390</td>
<td>10.4x10^5</td>
<td>0.310</td>
<td>10.4x10^5</td>
<td>0.080</td>
<td>1</td>
</tr>
</tbody>
</table>

Cyclic voltammetry studies on 0.4mM ferrocene in 0.1M Tetraethylammoniumbromide (TEAB) gave one peak for each of the anodic and cathodic potential scans. Both peaks were of similar

- 65 -
shape as shown in figure 4.1 below:

![Cyclic voltammogram of 4mM ferrocene in 0.1 M TEAB in acetonitrile/water (1:1) at a scan rate of 0.030 VS⁻¹.](image)

**Figure 4.1**: Cyclic voltammogram of 4mM ferrocene in 0.1 M TEAB in acetonitrile/water (1:1) at a scan rate of 0.030 VS⁻¹.

A plot of the anodic peak current against square root of scan rate gave a straight line (figure 4.2).
**Figure 4.2:** A plot of peak anodic current versus square root of scan rate for ferrocene.

While that of the same current against the scan rate gave a curve (figure 4.3)

![Graph showing peak current versus square root of scan rate](image)

**Figure 4.3:** A plot of peak current versus scan rate for ferrocene

The above plots (figure 4.2, 4.3) were expected for a reversible system [Christopher and Ana Maria, 1993]. The fact that $i_{pa}$ is proportional to the square root of scan rate indicates diffusion controlled electrode process [Bard et al. 2001].

The ratio of anodic peak current and cathodic peak current (table 4.1) was unity ($i_{pa}/i_{pc} = 1$) which implied a diffusion-controlled electrode process [Nicholson and Irving 1964].

The anodic peak potential, $E_{pa}$, was $0.390 \pm 0.006 \text{V vs SCE}$ for five different scan rate while the cathodic peak potential, $E_{pc}$, was $0.316 \pm 0.003 \text{V vs SCE}$ for five different scan rate. The values
of Epa (0.390 ± 0.006) were within experimental error compared to 0.354 ± 0.09 V in tetrabutylammonium tetrafluoroborate (TBABF₄) reported by Mirriam. (1998) and also 0.34 V in 21% DDAB microemulsion reported by Iwunze et al. (1990), 0.304±0.002 v/s SCE in 0.2 LiCl₄/CH₃CN/H₂O, at highly polished glassy carbon electrode reported by Kamau et al (1994).

This was also the case for cathodic peak current which was comparable to the reported value 0.297 ± 0.002 v/s SCE by Mirriam (1996).

The increase in anodic peak potential with increase of the scan rate (table 4.1) agrees with the result observed by Mirriam (1996) and by Iwunze et al. (1990) for ferrocene in 21% DDAB microemulsion.

The anodic to cathodic peak potential separation observed for the five scan rate was 65 ±0.006 mV vs.SCE as expected for nearly reversible one electron transfer system [Nicholson and Irving, 1964]. The increase of peak separation with increase in scan rate observed at higher scan rates (table 4.1) is consistent with what has been reported for 1.0 mM ferrocene in 21% DDAB microemulsion [Iwunze et al.1999], 0.4mM ferrocene in 0.1M tetrabutylammonium perchlorate [Kadish et al 1984] and 0.1 mM ferrocene in 0.1 M TBAP/CH₃CN using platinum electrode [Hinman et al.1985]. Such an increase may be attributed to uncompensated resistance (IR) or the quasi-reversible behavior (non-linear diffusion) of oxidation of ferrocene at higher scan rate as reported by Haque et al. The effect of solution resistance and uneven potential distribution (resistivity and electrode radius or shift in reference electrode potential) on linear sweep voltammetry was shown experimentally to cause a displacement of the anodic peak potential towards a positive potential while the reverse is observed for the cathodic peak [Hinman et al. 1985], even under optimum conditions for the reduction. uncompensated resistance (IR) remains
[Kadish et al 1984]. Such uncompensated resistance shifts the peak such that $\Delta E_p$ obtained increases with the scan rate [Brown et al 1966]. Similar increase in $\Delta E_p$ is observed for slow or quasi-reversible electron transfer kinetics. Haque et al. (1996) found out that ferrocene oxidized conventionally shows quasi-reversibility behaviour by cyclic voltammetry similar to what was reported by Kamau and Rusling, 1985. Therefore, in this work the observed increase in $\Delta E_p$ is due to uncompensated iR and quasi-reversibility of ferrocene.

Diffusion coefficient ($D_0$) for the electroactive species in anodic scan was $2.8 \times 10^{-5} \pm 0.08$ cm$^2$sec$^{-1}$ in TEAB and $2.6 \times 10^{-5} \pm 0.09$ cm$^2$sec$^{-1}$ in LiCL. Comparing this value with the reported values, it was higher than one reported by Iwuenze $6.3 \times 10^{-6}$ cm$^2$sec$^{-1}$ in 21% DDAB microemulsion [Iwunze et al. 1999], $2.4 \times 10^{-5}$ cm$^2$sec$^{-1}$ for 0.4 ferrocene in 0.1M TBAP/CH$_3$CN and $1.4 \times 10^{-5}$ cm$^2$sec$^{-1}$ in 0.1M TBPA/CH$_2$Cl$_2$ [Kadish et al. 1984]. However, the value calculated is within the range and the low diffusion coefficient in microemulsion is associated with the fact that ferrocene being oil soluble diffuses with slow rates characteristic of dodecane [Iwunze et al. 1999]. Thus the $D_0$ obtained in present research compares favorably with what has been reported before. Difference in diffusion coefficients in different solvent are expected [Nicholas et al. 1965]. This is due to the difference in specific resistance of the media [Kadish et al 1984]. The type of supporting electrolyte affects the specific resistance of the solvent-supporting electrolyte solution, the electron transfer rate constant, the mass transfer phenomena, characteristic electron transfer and charge transfer coefficient [Nicholas et al 1965]. These parameters contribute directly or indirectly to the diffusion coefficient which was observed for LiCL and TEAB.

However, scatter of data in this work is attributed to normal variance in electrode polishing as
reported by [Kamau et al 1985]. The variation in ferrocene diffusion coefficient reported by several researchers is due to the formation of aggregate by the oxidation product i.e. ferrocenium ion.

4.2 Voltammetric study of 4.0Mm 4-phenacetylidene-2,2,5,5-tetramethyl-3-imidazolidin-1-oxyl nitroxyl free radical ligand in 0.1M TEAB in acetonitrile/water (1:1) and potassium ferrocynide in 0.1M KNO₃ in water

Electrode reaction performed here was aimed at reproducing voltammetric data reported previously by Kamau et al. (1998). This was done to confirm if the procedure followed to characterize the compounds of interest in the current research was appropriate. The Nitrosyl ligand voltammetric studies gave one anodic peak and one cathodic peak (figure 4.4) as expected.

Figure 4.4: Cyclic voltammogram for 4.0mM 4-phenacetylidene-2,2,5,5-tetramethyl-3-imidazolidin-1-
oxyl nitroxy free radical ligand in acetonitrile/water (1:1) solution containing TEAB at 23± 2°C and scan rate of 0.025V/S versus SCE

The plot of Ep versus [i/id-i] exhibited a straight line Figure 4.5, suggesting presence of a reversible system.

![Plot of applied potential against log [i/id-i] for nitrosyl.](image)

**Figure 4.5:** Plot of applied potential against log [i/id-i] for nitrosyl.

The value of n calculated using equation \( E = E_{1/2} - 0.0591/n \log [i/i_d-i] \) was found to range from a value of 0.7 to 1.3 which compares favorably with that reported by Kamau et al (1998) which was 0.6 to 1.2. The peaks in previous work appeared at -0.06V and -0.241V [Kamau et. al (1998)]. This compares to figure 4.4 where the peaks appeared at -0.053±0.001 V and -
0.246±0.002V.

The potassium ferrocyanide gave a well defined voltammogram (figure 4.6) as expected from the literature [Bard et al. 2001].

![Voltammogram Graph](image)

**Figure 4.6:** cyclic voltammogram for potassium ferrocyanide in 0.1M KNO3 in water at scan rate of 0.025V/S.

The plot of anodic peak current versus square root scan rate gave a straight line and the diffusion coefficient calculated using Randle-Sevcik relationship yielded $4.4 \times 10^{-6} \text{cm}^2 \text{sec}^{-1}$, which compares with the literature value of $7.0 \times 10^{-6} \text{cm}^2 \text{sec}^{-1}$ [Bard et al.2001].

Considering the above preliminary studies, it was concluded that the procedure followed was
appropriate for the current research.

4.3.0 Cyclic voltammetry studies of acetylferroceny1-4-phenylthiosemicarbazone (Dan1) and its copper complex (Dan 2)

Dan 1 (figure 1.3) is a thiosemicarbazone which contained ferrocene as its side chain:

\[
\text{Dan 1} = \begin{array}{c}
\text{Fe} \\
\text{Me} \\
\text{N} \\
\text{N} \\
\text{C} \\
\text{H} \\
\text{H} \\
\text{Cl} \\
\text{S} \\
\text{Ph}
\end{array}
\]

= LH, L = ligand, H = ionizable hydrogen

The electrochemical studies using cyclic voltammeter were done at different scan rates and the result was as follows (Table 4.2):
Table 4.2 Scan rate studies of acetylferrocenyl-4-phenylthiosemicarbazone (Dan1) in 0.1 M TEAB, acetonitrile/water (1:1)

<table>
<thead>
<tr>
<th>Scanrate (V/S)</th>
<th>Epa (Volts)</th>
<th>Ipa (A) $10^6$</th>
<th>Epc (Volts)</th>
<th>Ipc (A) $10^6$</th>
<th>Ipa/Ipc</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.010</td>
<td>-0.215</td>
<td>1.3</td>
<td>-0.465</td>
<td>1.5</td>
<td>1.08</td>
</tr>
<tr>
<td>0.015</td>
<td>-0.167</td>
<td>2.7</td>
<td>-0.456</td>
<td>2.5</td>
<td>1.08</td>
</tr>
<tr>
<td>0.020</td>
<td>-0.138</td>
<td>3.0</td>
<td>-0.500</td>
<td>2.7</td>
<td>1.10</td>
</tr>
<tr>
<td>0.030</td>
<td>-0.171</td>
<td>2.5</td>
<td>-0.539</td>
<td>2.5</td>
<td>1.00</td>
</tr>
<tr>
<td>0.035</td>
<td>-0.154</td>
<td>3.3</td>
<td>-0.547</td>
<td>2.9</td>
<td>1.13</td>
</tr>
<tr>
<td>0.040</td>
<td>-0.150</td>
<td>8.3 $\sim$</td>
<td>-0.575</td>
<td>7.5</td>
<td>1.10</td>
</tr>
</tbody>
</table>
The resultant cyclic voltamogram for Dan 1 is shown in figure 4.7. One anodic peak at -0.165 ± 0.02V and cathodic peak at -0.513 ± 0.04V was observed.

**Figure 4.7** cyclic voltammogram for acetylferrocenyl-4-phenylthiosemicarbazone (Dan1) in acetonitrile/water (1:1) solution containing TEAB at 23 ± 2°C and scan rate of 0.010VS versus SCE.

The voltamogram was due to Fe^{II}/Fe^{III} redox reaction, since the reversible oxidation processes of the ferrocene derivatives always occur on the metal atom [Braz, 2000]. From table 4.2 the ratio of anodic peak current and cathodic peak current was approximately one and this indicates reversibility [Bard and Faulkner 1980]. The potential observed was at higher potential due to the presence of sulphur which due to its higher electron negativity which cause Fe to be electron poorer,he
nce its greater difficulty to be oxidised. This has been confirmed by previous work done on ferrocene derivatives where oxygen was replaced with sulphur and it was easier to oxidise iron since there is less electron density available to ferrocene, making it easier to be oxidised [Braz, 2000].

4.3.1 Cyclic voltammetry study of copper complex acetylferrrocenyl-4-phenylthiosemicarbazone (Dan2)

Dan 2 which was the copper complex of Dan 1 (figure 1.3) cyclic voltametry study gave the voltamogram below (figure 4.8):

![cyclic voltammogram](image)

**Figure 4.8** cyclic voltammogram for copper complex of acetylferrrocenyl-4-phenylthiosemicarbazone (Dan 2) in acetonitrile/water (1:1) solution containing TEAB at 23± 2°C and scan rate of 0.010V/S.

Oxidation peak was larger than reduction peak such that the current peak ratio of ipa/ipc was not equal to unity. This implies that much of the Oxidation product (O) made electrochemically is
destroyed by a chemical step. This shows the instability of O and there is little reconversion of O back to (R) and thus little reductive current flowing.

The reduction peak increased with the increase of the scan rate (table 4.3):

**Table 4.3: scan rate studies of Dan 2.**

<table>
<thead>
<tr>
<th>Scan rate (V/S)</th>
<th>Reduction peak current(A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.020</td>
<td>3.1x10^-6</td>
</tr>
<tr>
<td>0.030</td>
<td>3.8x10^-6</td>
</tr>
<tr>
<td>0.035</td>
<td>5.0x10^-6</td>
</tr>
<tr>
<td>0.040</td>
<td>6.3x10^-6</td>
</tr>
</tbody>
</table>

This was due to the time taken to record the voltamogram. when the scan rate is much faster it is possible that there is no much time for chemical reaction to take place hence bigger signal as compared to the slow scan rate where there is ample time for reaction to take place, hence smaller signal is observed.

The irreversibility may have been caused by the shift in the geometry of the coordination sphere which is characteristic of transition metal complexes [Bard et al. 2000].

From this, where the ipa/ipc was not equal to unity it is possible to determine more information
especially kinetics process like chemical reaction which is being proposed for continuity of this work.

Dan 2 being copper complex of dan1, it was expected that the oxidation and reduction peak observed in Dan 1 to appear in Dan 2 but this was not the case. This may be due to the presence of Sulphur which has higher electron negativity and readily coordinate with the copper metal, making the iron to be poorer electron donor, hence the observed signals are due to Cu^{II}/Cu^{I} redox reaction [Kumbhar et al. 1991].

4.4 Cyclic voltammetry studies of acetylferrocenyl-2-thiosemicarboxyl-semicolonbazone(dan11) and its copper complex (dan 12)

Dan 11 also contain ferrocene as its side chain (figure 1.5) and the sulphur present in Dan 1 is replaced by oxygen.

![Figure 1.5](image)

The resultant voltamogram of Dan 11 was as shown below (figure 4.9):
Figure 4.9: cyclic voltammogram for acetylferrocenyl-2-thiosemicarboxyl-semicarbazone (Dan11) in acetoniitrile/water (1:1) solution containing TEAB at 23± 2°C and scan rate of 0.020V/S versus SCE

The resultant voltammogram of dan 11 gave the current peak ratio, ipa/ipc, being greater than unity (table 4.4). The anodic peak was higher than cathodic peak and this suggest that not all the oxidation product is converted back during the reduction. Hence, irreversibility which can be explained by the trend taken by the cathodic peak current whereby it increases with the increase of the scan rate table 4.4:
Table 4.4: Scan rate studies of acetylferrocenyl-2-thiosemicarboxyl-semicarbazone (Dan 11) in 0.1 M TEAB, acetonitrile/water (1:1).

<table>
<thead>
<tr>
<th>Scan rate V/s</th>
<th>Epa (V)</th>
<th>Ipa (A) $10^{-6}$</th>
<th>Epc (V)</th>
<th>Ipc (A) $10^{-6}$</th>
<th>ΔE</th>
<th>Ipa/Ipc</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.010</td>
<td>0.551</td>
<td>7.5</td>
<td>0.517</td>
<td>4.1</td>
<td>34</td>
<td>1.8</td>
</tr>
<tr>
<td>0.015</td>
<td>0.555</td>
<td>13</td>
<td>0.513</td>
<td>5.8</td>
<td>42</td>
<td>2.2</td>
</tr>
<tr>
<td>0.020</td>
<td>0.562</td>
<td>17</td>
<td>0.513</td>
<td>8.8</td>
<td>49</td>
<td>1.9</td>
</tr>
<tr>
<td>0.025</td>
<td>0.565</td>
<td>19</td>
<td>0.510</td>
<td>11</td>
<td>55</td>
<td>1.7</td>
</tr>
<tr>
<td>0.030</td>
<td>0.568</td>
<td>22</td>
<td>0.506</td>
<td>14</td>
<td>62</td>
<td>1.5</td>
</tr>
<tr>
<td>0.035</td>
<td>0.568</td>
<td>26</td>
<td>0.510</td>
<td>17</td>
<td>58</td>
<td>1.5</td>
</tr>
</tbody>
</table>

This suggests that the oxidation product is not stable and there may be a chemical process following up the oxidation process [Bard et al 2000].

Equation 2.14 was used to estimate the number of electrons transferred,

$$|E_{pc} - E_{pa}| = \frac{57 \text{ mV}}{n} \quad \text{(2.14)}$$
The number of electron (n) was calculated and found to be one. Therefore, the number electrons involved in this process was one. Although there is reverse peak not all the oxidized species is reduced [Bard et al. 2000].

The reaction involved is the redox reaction of Fe$^{II}$/Fe$^{III}$ since oxidation processes of the ferrocene derivatives always occur on the metal atom (iron) in the absence of another metal [Braz, 2000].

The fact that the redox peak is far removed from that of ferrocene suggest that the side chains have a significant effect on the energy states of the iron.

From table 4.4, $\Delta E$ increases with the scan rate and is much higher at higher scan rates. This was due to uncompensated solution resistance and non-linear diffusion which is characteristic of slow electron transfer kinetics [Bard et al. 2000].

4.4.1 Cyclic voltammetry study of copper complex acetylferrocenyl-2-thiosemicarboxyl-semicarbazone (Dan 12)

Dan 12 which was the copper complex of Dan 11 (figure 1.5) was studied using cyclic voltammetry. It gave the voltamogram shown below (figure 5.0).
**Figure 5.0:** Cyclic voltammogram for copper complex of acetylferrocenyl-2-thiosemicarboxyl-semicarbazone (Dan 12) in acetonitrile/water (1:1) solution containing TEAB at 23± 2°C and scan rate of 0.010V/S.

Oxidation peak was larger than the reduction peak such that current peak ratio of ipa/ipc was not equal to unity. This implies that much of the Oxidation product (O) made electrochemically is destroyed by a chemical step. This shows that oxidation product (O) is not stable. Hence there is little reconversion of O back to (R) and thus little reductive current flowing.

The reduction peak increased with the increase of the scan rate (table 4.5) also by looking at the trend of the ratio of peak current, IpA/Ipc, it reduces with the increase in scan rate suggesting that at higher scan rate the reaction may be reversible since there is no ample time for the chemical reaction to take place. This is also the same trend observed in Dan 11 (tables 4.4). This suggest a follow up chemical which may have been caused by the shift in the geometry of the coordination...
sphere which is characteristic of transition metal complexes [Bard et al. 2000], or may be also due to the physical process which entails the formation of aggregate by oxidation product [Kamau et al. 1994].

Table 4.5: Scan rate studies of acetylferrocenyl-2-thiosemicarboxyl-semicarbazone copper complex (dan 12) in 0.1 M TEAB, acetonitrile/water (1:1).

<table>
<thead>
<tr>
<th>Scan rate V/s</th>
<th>Epa (V) v/s SCE</th>
<th>Ipa(A) 10^-5</th>
<th>Epc (V) v/s SCE</th>
<th>Ipc (A) 10^-5</th>
<th>Ipa/Ipc</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.010</td>
<td>-0.172</td>
<td>1.8</td>
<td>-0.383</td>
<td>0.6</td>
<td>3</td>
</tr>
<tr>
<td>0.015</td>
<td>-0.177</td>
<td>2.0</td>
<td>-0.400</td>
<td>1.2</td>
<td>1.6</td>
</tr>
<tr>
<td>0.020</td>
<td>-0.177</td>
<td>2.5</td>
<td>-0.400</td>
<td>1.6</td>
<td>1.5</td>
</tr>
<tr>
<td>0.025</td>
<td>-0.177</td>
<td>2.6</td>
<td>-0.400</td>
<td>1.7</td>
<td>1.5</td>
</tr>
<tr>
<td>0.030</td>
<td>-0.166</td>
<td>3.3</td>
<td>-0.3833</td>
<td>2.3</td>
<td>1.4</td>
</tr>
</tbody>
</table>

4.5: Cyclic voltammetry study of acetylpyridine-2-thiophenecarboxylsemicarbazone (dan5) and its copper complex (dan 6)

Acetylpyridine-2-thiophenecarboxylsemicarbazone (Dan5) had pyridine instead of ferrocene as it side chain as shown in figure 1.4. It also contained oxygen in place of sulphur in Dan 1.
Dan 5 =

= JH, J = ligand, H = ionizable hydrogen

Figure 1.4:

Dan 5 gave a well defined voltamogram with one anodic peak at 0.338 ± 0.003 V and cathodic peak at 0.250 ± 0.002 V (figure 5.1).

Figure 5.1: cyclic voltammogram for acetylpyridine-2-thiophencarboxylsemicarbazone (dan5) in acetonitrile/water (1:1) solution containing TEAB at 23 ± 2°C and scan rate of 0.020 V/s
The plot of potential, $E$, versus $\log[i/i_d-i]$, figure 5.2, gave a straight line and using

\[ E = E_{1/2} - 0.0591/n \log \frac{i}{i_d - i} \]

The slope the number of electrons ($n$) was calculated using equation

The number of electron involved in the process was found to be one. Therefore, acetylpyridine-2-thiophenecarboxylsemicarbazone (Dan5) in acetonitrile/water (1:1) solution containing TEAB at $23\pm 2^\circ C$ undergo a reversible one electron reduction. This occurs in the range of 0.338V to 0.250V versus SCE. These results compare favorably with those of Avinash where in 1992 the
author did cyclic voltametry study of 2-acetylpyridine 3-azacyclothiosemicarbazone and found similar results [Avinash et al (1992)].

The peak current ratio, \( \text{ipa}/\text{ipc} \), was approximately unity which implied possible reversibility.

4.5.1 Cyclic voltammetry study of copper complex of acetylpyridine-2-thiophenecarboxylsemicarbazone (Dan 6)

Dan 6 which was the copper complex of dan 5 gave the following voltamogram (figure 5.3):

\[ \text{Oxidation peak was larger than reduction peak such that current peak ratio of ipa/ipc was not equal to unity. This implies that much of the Oxidation product (O) made electrochemically is destroyed by a chemical step showing the instability of O. Hence, there is little reconversion of O} \]
back to (R) and thus little reductive current flowing.

The reduction peak increased with the increase of the scan rate (table 4.6):

**Table 4.6:** Scan rate studies of acetylpyridine-2-thiophenecarboxylsemicarbazone copper complex (Dan 6) in 0.1 M TEAB, acetonitrile/water (1:1).

<table>
<thead>
<tr>
<th>Scan rate(V/S)</th>
<th>Epa</th>
<th>ipa</th>
<th>Epc</th>
<th>ipc</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.010</td>
<td>-0.171</td>
<td>5.8 x 10^{-5}</td>
<td>-0.385</td>
<td>2.5 x 10^{-5}</td>
</tr>
<tr>
<td>0.015</td>
<td>-0.171</td>
<td>6.9 x 10^{-5}</td>
<td>-0.392</td>
<td>2.8 x 10^{-5}</td>
</tr>
<tr>
<td>0.020</td>
<td>-0.175</td>
<td>7.5 x 10^{-5}</td>
<td>-0.431</td>
<td>3.1 x 10^{-5}</td>
</tr>
<tr>
<td>0.025</td>
<td>-0.170</td>
<td>9.2 x 10^{-5}</td>
<td>-0.400</td>
<td>3.3 x 10^{-5}</td>
</tr>
<tr>
<td>0.030</td>
<td>-0.170</td>
<td>10 x 10^{-5}</td>
<td>-0.400</td>
<td>4.2 x 10^{-5}</td>
</tr>
<tr>
<td>0.035</td>
<td>-0.174</td>
<td>11 x 10^{-5}</td>
<td>-0.413</td>
<td>4.3 x 10^{-5}</td>
</tr>
</tbody>
</table>

This is also the same trend observed in Dan 11 and Dan 2. Which were all copper complexes of thiosemicarbazone. This suggest a possible follow up chemical which may have been caused by the shift in the geometry of the coordination sphere which is characteristic of transition metal complexes [Bard et al. 2000].

Comparing the voltamogram of Dan 5 to that of Dan 6, it is clear that for the Copper complex it
is the Cu metal, which is oxidised but not the ligand (Dan 5). One notes with interest that there is change in electrochemical behavior when the ligand forms a complex with the copper metal. This variation in electrochemical characteristics may further explain the bioactivity behavior of the complex, which requires further investigation.

4.6.0: Ultraviolet/Visible spectrophotometry study

4.6.1 ultraviolet/visible spectrophotometry study for acetylferrocenyl-4-phenylthiosemicarbazone (Dan 1) and its copper complex (Dan 2).

For the UV/visible spectral of Dan 1 there was a weak absorption peak at 450nm (figure 5.4):

Figure 5.4: UV/visible spectrum of acetylferrocenyl-4-phenylthiosemicarbazone (dan1)
This was possibly attributed to weakly allowed asymmetrical d-d transition (transition from t_{2g} to e_{g}) in metal. The visible light of the correct wavelength was absorbed, promoting a lower d-electron to a higher excited state. This absorption of light causes color as the excited electrons revert to ground state. These colors are usually quite faint. This is because of two selection rules:

The spin rule: $\Delta S = 0$

On promotion, the electron should not experience a change in spin. Electronic transitions which experience a change in spin are said to be spin forbidden. d-d transition are spin forbidden.

Laporte's rule: $\Delta l = \pm 1$

d-d transition are laporte forbidden since $\Delta l = 0$ but spectral of lower absorption is observed because of slight relaxation in laporte rule when transition metal ion forms a complex. The metal is surrounded by ligands and some mixing of d and p orbitals may occur, in this case transition is no longer pure d-d in nature [Lee, (1996)].

Intense peak of 0.8176 absorbance at shorter wave length of 310 nm was also observed, figure 5.4. This peak is characteristic of charge transfer absorption peak [Lee, (1996)].

Charge-transfer complexes exist in many types of molecules, inorganic as well as organic, and in all phases of matter, i.e. in solids, liquids, and even gases. Most charge-transfer complexes involve electron transfer between metal atoms and ligands. The charge-transfer bands in transition metal complexes result from movement of electrons between molecular orbitals (MO) that are predominantly metal in character and those that are predominantly ligand in character.
Charge transfer absorption band can be identified by their intensity. They are highly intense and often lie in the ultraviolet or visible portion of the spectrum. This is because the charge transfer transitions are not spin or Laporte forbidden as d-d transitions. The electron moves through a considerable distance, which means that the transition dipole may be large and the corresponding absorption is large [Atkins et. Al. 1999].

The above observation of the spectra of Dan 1 was also made in copper complex of Dan 2 (figure 5.5):

![Graph](image)

**Figure 5.5:** UV/visible spectrum of copper complex of acetylferrocenyl-4-phenylthiosemicarbazone (dan2)

Comparing acetylferrocenyl-4-phenylthiosemicarbazone ligand (Dan 1) and its copper complex (Dan 2) the following was observed. (figure 5.6):
Dan 1 and Dan 2 exhibited blue shift of 22nm (table 4.7) i.e. Dan 2 absorbed at shorter wavelength suggesting transfer of electron from the ligand into the d orbital of the metal, ligand-metal charge transfer [Kuhn Karl F and Theo Koupelis (2004)]. This is contrary to the expected result for first row transition metals which are known to exhibit metal-ligand charge transfer. This can be explained by the fact that, complexes having ligands with relatively high energy lone pairs (example S or Se) or if the metal has low lying empty orbitals give ligand-metal charge transfer. Dan 1 contains sulphur in its main chain (figure 1.3), hence the justification of the above results.
4.6.2 ultraviolet/visible spectrophotometry study for acetylferrocenyl-2-thiosemicarboxyl-
semicarbazone(dan11) and its copper complex (dan12)

The resultant absorbance peak of Dan 11 gave two peaks at 450nm and 317nm (figure 5.7). The weak peak at 450nm wavelength, as discussed previously, was attributed to possible d-d transition.

![uv/vis spectrum of acetylferrocenyl-2-thiosemicarboxyl-semicarbazone (dan11)](figure)

**Figure 5.7** uv/visible spectrum of acetylferrocenyl-2-thiosemicarboxyl-semicarbazone (dan11) in acetonitrile solution.

The second observed peak was intense and appeared at shorter wavelength of 317nm. This is characteristic of charge transfer absorption peak as discussed previously which is due to movement of electron from the ligand to the metal or vise versa.
On the other hand, Dan 12 gave an intense, well pronounced absorption peak (figure 5.8)

Figure 5.8: UV/Visible spectrum of acetylferrocenyl-2-thiosemicarboxyl-semicarbazone copper complex (Dan12) in acetonitrile solution.

The intense peak of Dan 12 had an absorbance of 0.722 which showed a significant shift towards longer wave lengths compared to Dan 11 (figure 5.9):
**Figure 5.9:** UV/visible spectrum of acetylferrocenyl-2-thiosemicarboxyl-semicarbazone (Dan11) and its copper complex (Dan 12) in acetonitrile solution.

The red shift exhibited in figure 5.9 is possibly due to metal-ligand charge transfer, that is the electron is moving from the metal to the ligand in the complex. This mainly occurs in divalent ions of 1st row transition elements (Sc to Cu) together with ligands that have low lying pi antibonding orbitals. The electrons are excited from sigma bonding orbitals of the metal to pi antibonding of the ligand.

**4.6.3 ultraviolet/visible spectrophotometry study for acetylpypyridine-2-thiophenecarboxylsemicarbazone (Dan 5) and its copper complex (Dan 6)**

Dan 5 which had a very faint pink color gave the following absorption spectra (figure 6.0):
Figure 6.0: UV/visible spectrum of acetylpyridine-2-thiophenecarboxylsemicarbazone (Dan 5) acetonitrile solution.

The intense peak of absorbance 2.011 is characteristic of charge transfer and the faint absorption peak for d-d transition at around 450nm was also observed. The faint absorption peak explains the faint pink color of this ligand.

The intense peak was also observed in the copper complex of the above ligand (Dan 5) and the resultant absorption peak is shown in figure 6.1:
**Figure 6.1:** UV/visible spectrum of acetylpyridine-2-thiophenecarboxylsemicarbazone copper complex (Dan 6) acetonitrile solution.

The peak shifted towards longer wave length, red shift, compared to the absorption peak of the ligand, as shown in figure 6.2.
The red shift exhibited suggests metal-ligand charge transfer upon complexation and this is also the case for Dan 11 and Dan 12. Dan 11 and Dan 5 contain oxygen in place of sulphur which is present in the main chain of Dan 1 which exhibited a blue shift.

The charge transfer transitions are generally intense. Their molar absorption coefficient is of order of $10^3$ to $10^4$ mol$^{-1}$ Cm$^{-1}$. According to the table 4.7 below the observed peaks in this study correspond to charge transfer bands.
Table 4.7 UV/Visible study results.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \lambda_{\text{max}} ) (nm)</th>
<th>absorbance</th>
<th>Molar absorptivity ( \text{Mol}^{-1}\text{Cm}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dan 1</td>
<td>310</td>
<td>0.8176</td>
<td>2.7 ( \times ) 10^3</td>
</tr>
<tr>
<td>Dan 2</td>
<td>288</td>
<td>0.1181</td>
<td>3.1 ( \times ) 10^3</td>
</tr>
<tr>
<td>Dan 5</td>
<td>307</td>
<td>2.0116</td>
<td>2.5 ( \times ) 10^3</td>
</tr>
<tr>
<td>Dan 6</td>
<td>380</td>
<td>1.0071</td>
<td>3.5 ( \times ) 10^3</td>
</tr>
<tr>
<td>Dan 11</td>
<td>317</td>
<td>0.6341</td>
<td>2.1 ( \times ) 10^3</td>
</tr>
<tr>
<td>Dan 12</td>
<td>380</td>
<td>0.7221</td>
<td>2.5 ( \times ) 10^3</td>
</tr>
</tbody>
</table>

According to the table 4.7 the metal complexes had high molar absorptivities than the ligands. Furthermore, this work demonstrated that including copper in the ligand containing iron, enhances charge transfer intensities.
4.7.0 Stability studies using ultraviolet/visible spectrophotometer

Based on the principle behind UV/visible spectrophotometry, where absorbance is directly proportional to the concentration:

\[ A = \varepsilon \cdot C \cdot L \]

Where,

\( A \) is the absorbance

\( L \) is the path length of light and \( C \) is the concentration.

\( \varepsilon \) is the molar absorption coefficient.

It is possible to determine the stability of absorbing chemical species by monitoring the absorbance of a particular chemical species at a specific \( \lambda_{\text{max}} \) over time. The change corresponds to concentration change of absorbing chemical species. The change in \( \lambda_{\text{max}} \) may correspond to formation of new product. The following were the results observed over a period of 45 days at an interval of seven days for each reading:
4.7.1: Stability studies for acetylferrocenyl-4-phenylthiosemicarbazone (Dan 1)

Dan 1 was monitored over a period of 45 days and exhibited a gradual decrease in absorbance (A) figure 6.3.

![Figure 6.3: UV/Visible spectra for acetylferrocenyl-4-phenylthiosemicarbazone (Dan 1) in acetonitrile/water solution over a period of 45 days](image)

For the first 3 days Dan 1 was stable and similar spectral was observed in each day (figure 6.3). Beyond the third day, the concentration started to decrease with time as shown in figure 6.3. The absorbance decreases with time as observed in figure 6.3, suggesting decrease in concentration with time.

4.7.1a Stability studies for acetylferrocenyl-4-phenylthiosemicarbazone copper complex (Dan 2)

Dan 2 is the copper complex of Dan 1. The UV/visible spectral observed over a period of time...
Figure 6.4: UV/visible spectra for copper complex of acetylferrocenyl-4-phenylthiosemicarbazone (Dan 2) in acetonitrile/water solution over a period of 45 days.

Similar spectra behavior was observed. For the complex, it was stable for two days but after the second day to the fifteenth day the concentration reduced a bit as shown in figure 6.4 above.

From 15-45 days, the absorbance reduced to 0.08.

From the above it can be concluded that the ligand is just stable for three days and the complex is stable for two days in the solution of acetonitrile.
4.7.2: Stability studies of acetylpyridine-2-thiophenecarboxylsemicarbazone (Dan 5) and its copper complex

The spectral obtained for a period of 45 days for the ligand acetylpyridine-2-thiophenecarboxylsemicarbazone (Dan 5) and its copper complex (Dan 6) was as shown below (figure 6.5 and 6.6).

**Figure 6.5:** UV/visible spectra for acetylpyridine-2-thiophenecarboxylsemicarbazone (Dan 5) in acetonitrile/water solution over a period of 45 days.

Similar spectral with same absorbance value was obtained over the period of 45 days as shown in figure 6.5 above. This indicates that the ligand was stable over that period of time. The same was observed in case of copper complex as shown below in figure 6.6.
Figure 6.6: UV/visible spectra for copper complex of acetylpyridine-2-thiophenecarboxylsemicarbazone (Dan 6) in acetonitrile/water solution over a period of 45 days.

4.7.3: Stability studies of acetylferrocenyl-2-thiosemicarboxyl-semicarbazone (Dan 11) and its copper complex (Dan 12)

For the first three days, Dan 11 gave similar uv/visible spectrum (figure 6.7), but beyond the third day, it gave a different absorption peak. The resultant spectrum for a period of 45 days is shown in figure 6.7:
Figure 6.7: UV/visible spectra for acetylferrocenyl-2-thiosemicarboxyl-semicarbazone (dan11) in acetonitrile/water solution over a period of 45 days.

The above observation indicates that beyond the third day there is a chemical change. Since, there is a change at the point of absorption $\lambda_{\text{max}}$ indicating possible formation of new absorbing species. This suggests possible formation of aggregate, giving red shifts, which requires further investigation.

This was not the case for the copper complex. For the 25 days, the complex was stable. Beyond the twenty-fifth day the concentration decreased with time as indicated by decrease in absorbance, which is directly proportional to concentration as shown in figure 6.8 below:
4.8: Infrared spectroscopy study

Interpretation of an infrared spectrum help to reveal the structure of a new compound by giving the groups present and also it can be used to predict coordination of a particular compound. Interpretation is not simple matter since band may appear obscured by overlapping of other bands, the bands may be shifted by various structural features e.g conjugation, electron withdrawal by neighboring substituent, angle strain or van der walls strain. In table 4.8. The chief IR bands of the ligands were identified by correlations of data for similar compounds. The IR spectra of the ligands is almost identical in the region of 1002-1550 cm\(^{-1}\) to those of their corresponding copper complexes whose proposed structures have already been reported.

The following is the table of important bands (cm\(^{-1}\)) of infrared spectra and their assignments.
Table 4.8 Important infrared spectral bands and their assignment (cm$^{-1}$).

<table>
<thead>
<tr>
<th></th>
<th>N-H</th>
<th>N-N</th>
<th>C=N</th>
<th>C=S</th>
<th>C=O</th>
<th>C-H</th>
</tr>
</thead>
<tbody>
<tr>
<td>DAN 1</td>
<td>3367 cm$^{-1}$</td>
<td>1041 cm$^{-1}$</td>
<td>1601 cm$^{-1}$</td>
<td>818 cm$^{-1}$</td>
<td>-</td>
<td>2871 cm$^{-1}$</td>
</tr>
<tr>
<td>DAN 2</td>
<td>3274 cm$^{-1}$</td>
<td>1148 cm$^{-1}$</td>
<td>1518 cm$^{-1}$</td>
<td>-</td>
<td>-</td>
<td>2856 cm$^{-1}$</td>
</tr>
<tr>
<td>DAN 5</td>
<td>3182 cm$^{-1}$</td>
<td>1158 cm$^{-1}$</td>
<td>1650 cm$^{-1}$</td>
<td>-</td>
<td>1601 cm$^{-1}$</td>
<td>2876 cm$^{-1}$</td>
</tr>
<tr>
<td>DAN 6</td>
<td>3241 cm$^{-1}$</td>
<td>-</td>
<td>1669 cm$^{-1}$</td>
<td>-</td>
<td>1601 cm$^{-1}$</td>
<td>2860 cm$^{-1}$</td>
</tr>
<tr>
<td>DAN 11</td>
<td>3192 cm$^{-1}$</td>
<td>1299 cm$^{-1}$</td>
<td>1635 cm$^{-1}$</td>
<td>-</td>
<td>1604 cm$^{-1}$</td>
<td>3041 cm$^{-1}$</td>
</tr>
<tr>
<td>DAN 12</td>
<td>3237 cm$^{-1}$</td>
<td>1153 cm$^{-1}$</td>
<td>1635 cm$^{-1}$</td>
<td>-</td>
<td>1608 cm$^{-1}$</td>
<td>3036 cm$^{-1}$</td>
</tr>
</tbody>
</table>
IR spectrophotometry confirmed the bidentate character of Dan 1 and Dan 11 for the copper complexes. C=N band of the thiosemicarbazone which appeared at 1601 cm\(^{-1}\) in Dan 1 shifted towards lower wave number and the intensity has increased in comparison with that of corresponding thiosemicarbazone, Dan 2, this was due to the loss of N-H proton in the thiosemicarbazone moiety in the complex and additional C=N absorption which was found at higher energy than C=N of the uncomplexed thiosemicarbazone, indicating coordination via nitrogen (figure 6.9) which is in agreement with work done by Joseph et. al. (2006).

The band at 818 cm\(^{-1}\) for C=S was shifted towards lower wave number which indicates thiole sulphur coordination which was in agreement with previous thiosemicarbazone studies shown in figure 6.9 [West et al. (1999)].

![Figure 6.9: proposed metal ligand coordination.](image-url)
CHAPTER FIVE

5.1 CONCLUSION

5.1.1 Cyclic voltammetry

The results from cyclic voltammetry demonstrated that voltammograms obtained depend on the electrolyte and the solvent used. The solvent of choice must dissolve the chemical species of interest fully. For the present research work the best electrolyte was found to be Tetraethyl ammonium bromide (TEAB) and the best solvent was found to be acetonitrile/water in the ratio of 1:1.

All of the semicarbazone ligand and their copper complexes in the present research work gave well defined cyclic voltamogram. For the ligand having ferrocene in their structures, that is, Dan 1 and Dan 5, the voltamogram was due to the redox reaction of iron (Fe^{II}/Fe^{III}). From the graphs drawn from the result, it was found that the number of electrons involved in the electrochemistry was one. Their copper complex that is Dan 2 and Dan 12 voltamograms were due to the redox reaction of copper. The expected peak for ferrocene was not observed and this confirms the earlier research work on [Kumbhar et al. 1992]. Thiosemicarbarzone compounds containing ferrocene and Sulphur. It has been reported that sulphur affects the electrochemistry of iron making it to occur at higher potentials.

It was observed that for copper complex the current peak ratio was not equal to unity. The ratio approached unity at higher scan rates. This observation suggests a possible chemical reaction follow up.
5.1.2 Correlation of the spectral from UV/Visible and cyclic voltamogram

From spectroscopic studies using UV/Visible spectroscopy, it was observed that the absorption peak were due to charge transfer and d-d transition. There was a shift in the absorption peak for the copper complexes relative to ligand. This confirms the exchange electron which is correlated to the voltamogram obtained since they are as result of exchange of electron.

5.1.3 Stability of the compounds

Table 5.1 stability study of the six thiosemicarbazone compounds.

<table>
<thead>
<tr>
<th>Thiosemicarbazone compound</th>
<th>Stability in acetonitrile/water solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dan 1</td>
<td>First three days</td>
</tr>
<tr>
<td>Dan 2</td>
<td>First two days</td>
</tr>
<tr>
<td>Dan 5</td>
<td>Stable over 45 days</td>
</tr>
<tr>
<td>Dan 6</td>
<td>Stable over 45 days</td>
</tr>
<tr>
<td>Dan 11</td>
<td>Stable for the first three days</td>
</tr>
<tr>
<td>Dan 12</td>
<td>Stable over 25 days</td>
</tr>
</tbody>
</table>

For Dan 1 and Dan 2 the concentration decreased with time and the absorption peaks were observed at the same wavelength. It can be concluded that though there is decrease in the concentration of the chemical species of interest there was no new compound formed, indicating
absence of chemical reaction.

For Dan 11 the absorption peak observed after the first three days, occurred at different wavelength. This indicates the formation of a new compound suggesting presence of a chemical reaction. Which absorbs within the wavelength range considered.

5.1.4 Coordination of the ligand

The results from the infrared studies indicated that the semicarbazone ligand have a bidentate character where it coordinate via nitrogen and sulphur as found previously and shown in figure 6.9. This suggest square planar copper complexes, which requires further experiments for confirmation.
5.2 Recommendations

Based on the conclusions made from the results of the current research work the following are the recommendations for further work:

1) Tetraethyl ammonium bromide as electrolyte and acetonitrile/water solution as solvent give good results and can be recommended for preparation of the compound solution for further electrochemistry studies.

2) The voltamogram of the copper complexes gave current peak ratio not equal to unity. This suggests a chemical follow up reactions which should be subject for further work to establish the kinetics of the possible reaction.

3) The study did not cover the effect of the different side chain to the electrochemistry of the compound. Further study should be carried out to establish if the electrochemistry depend on this side chains.

4) More research work to be done on correlating biological activities of these compounds with the electrochemistry results obtained.

5) The cause of decrease and shift of absorption bands in UV/Visible spectrophotometry requires further investigation.
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