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ELECTROCHEMICAL SYNTHESIS AND CHARACTERIZATION OF A SCHIFF BASE LIGAND AND SCHIFF BASE-NICKEL COMPLEX

BY: BOGALE ANBESU

July 2008

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Abstract

The electropolymerizations of the Schiff base ligand and the Ni-Schiff base complex were carried out in aqueous H_2SO_4 solution. The film coated glassy carbon electrode showed an electrochemical response. The factors that affect the electroactivity of the film, such as number of cycles used for the film formation and pH were studied for both Schiff bases. The effect of sulphuric acid concentrations in which the Schiff base complex is dissolved was studied. Also, the stability of the polymer film in 1 M H_2SO_4, 1 M NaOH and methanol-water mixture (1:1) was investigated for the case of the Ni-metal Schiff base complex. The poly-film got the least stability in methanol-water (1:1) mixture.

Keywords: Schiff bases, Schiff base- Ni metal complex, 6-(2-hydroxyphenylamino)-1,10-phenanthrolin-5-ol, Electropolymerization.

1. Introduction

Polymers serve as the basis of life in the form of nucleic acids, proteins and polysaccharides. They permit replication energy transformation, transmission of foods with in plants and animals, act as essential natural building materials, etc. They are present in a variety of forms- as fibers and clothes, paper, lumber, plastics, coatings, adhesives, ceramics, enzymes, DNA, concretes and are major ingredients in soils and plant life[1].

Polymers have got a number of applications in modern technology. In recent years, the development of modified electrodes using conducting polymers has been a very active area of research, triggered by their potential theoretical and technological applications. Among the numerous methods, one proven method of preparing modified electrodes consists in coating a metallic or semiconductor electrode with a thin film of electroactive polymer [2]. An enormous number of polymers have been used to prepare chemically modified electrodes. These polymers can be divided into three general categories- redox polymers, ion-exchange and coordination polymers, and electronically conductive polymers. Redox polymers are polymers that contain electroactive functionalities either within the main polymer chain or in side groups pendant to this chain. Ion-exchange and coordination polymers are not electroactive themselves, but can incorporate electroactive guest molecules. For example, ion-exchange polymers incorporate electroactive counter ions via an ion-exchange reaction. The third class of polymers used to prepare chemically modified electrodes is the electronically conductive polymers. The polymer chains in this family of materials are themselves electroactive [3]. This class includes polymers such as polypyrrole and polyaniline, which can also be considered as ion-exchange materials, since the polymer redox processes are usually accompanied by incorporation of ions into the polymer network. These conducting electroactive polymers are also referred to as synthetic metals. The first report of electrical conductivity in a conducting polymer was observed for polyacetylene in 1977 by Shirakawa, Heeger and MacDiarmid. Since then, the field of conducting polymers has attracted the interest of thousands of academic and industrial researchers [4,5]. In this study, some Schiff bases which exhibit electrical conductivity are examined.

2. Electronically conducting polymers

Most polymers are insulators, with desired properties such as light weight, processability, durability, and low cost. By designing the molecular structure of polymers, chemists have developed new materials that exhibit electrical conductivities comparable to metals while retaining the advantage of polymers. Electronically conducting polymers are composed of conjugated polymer chains with π-electrons delocalized along the backbone. In the neutral or undoped form, the polymers are either insulating or semi conducting. The polymers are converted to the electrically conductive or doped form via oxidation or reduction reactions that create delocalized charge carriers [1]. This can be explained by the schematic band diagram shown in figure 1. Polymerization causes the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the monomer to split into π and π* bands. In solid-state terminology, these are the valence and conduction bands, respectively. In the neutral forms, the valence band is filled, the conduction band is empty, and the band gap (Eg) is typically 2-3 eV. There is therefore little intrinsic conductivity [6].

There are two types of doping to convert polymers to electrically conducting form: p-doping and n-doping. Simplistically, p-doping (oxidation) can be viewed as the creation of mobile holes in the valence band, and n-doping as the addition of mobile electrons to the conduction band. However, these modifications actually change the band structure, creating various mid gap states (figure 1). For p-doping, removal of one electron from a segment of the chain creates a mobile polaron (radical cation). Removal of a second electron, or the combination of two polarons, creates a mobile bipolaron (dication). These charge carriers cause local distortions in the geometry of the chain, and create states above the top of the valence band, as shown in figure 1. Similar states are created just below the conduction band when the polymer is n-doped [6].

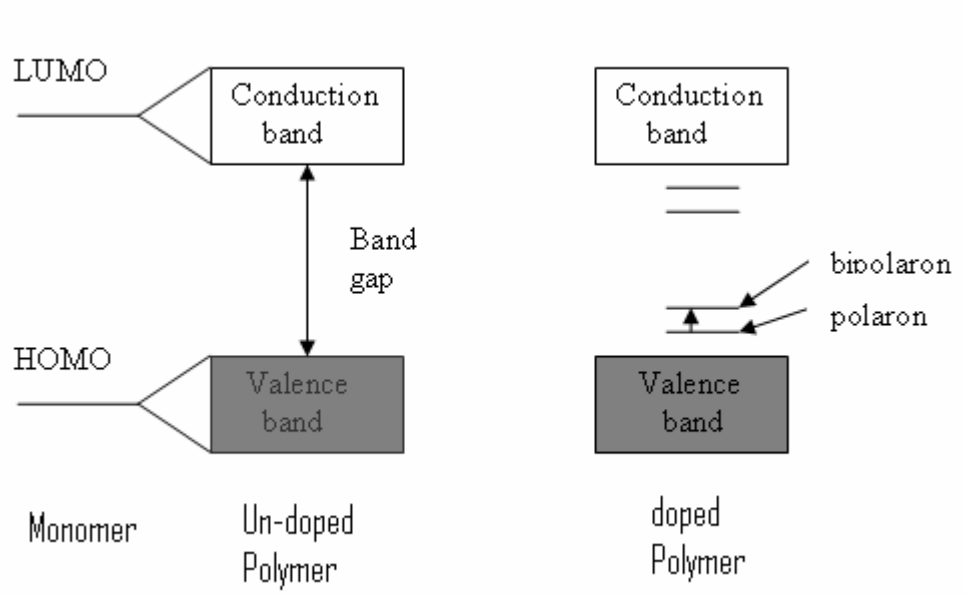


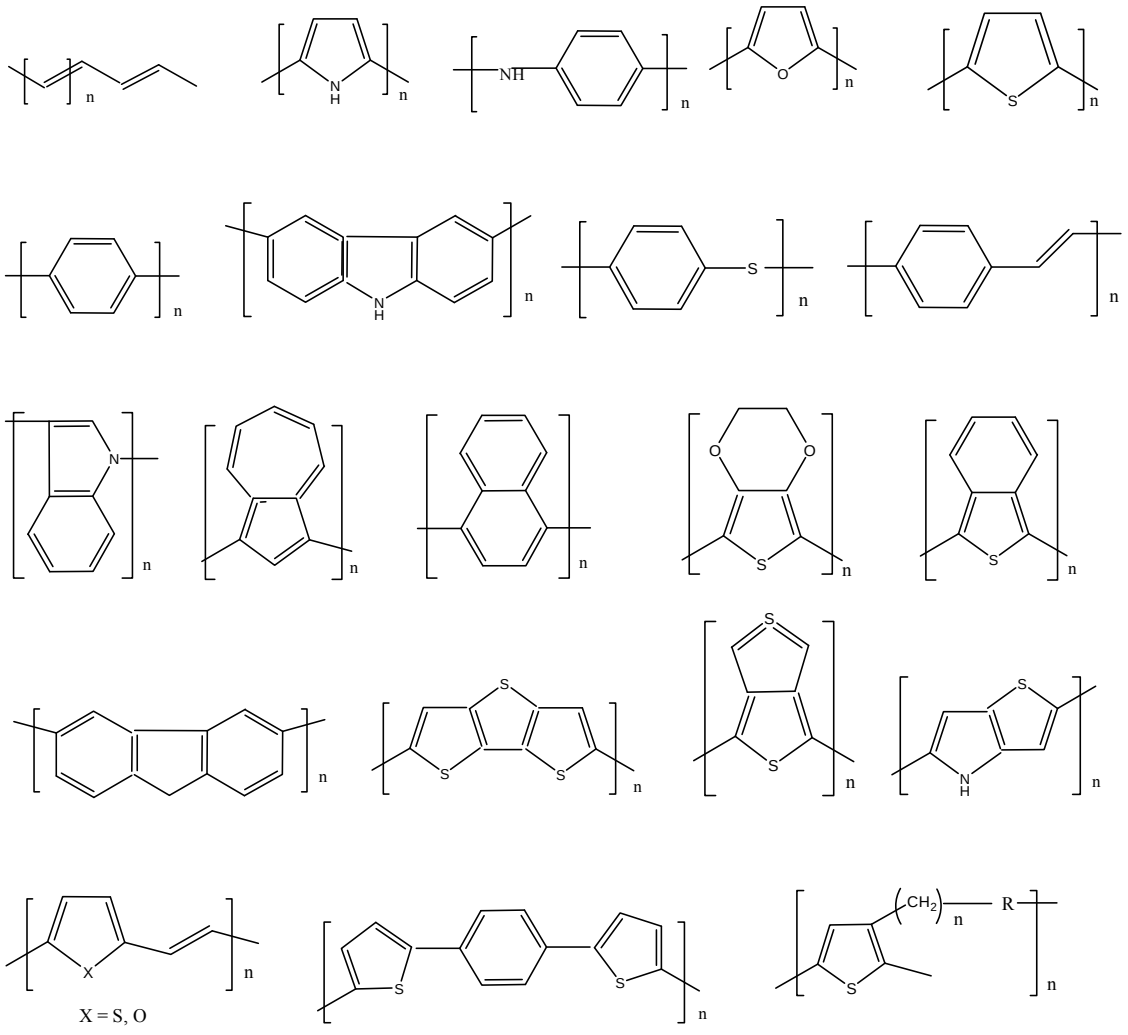
Figure 1 Schematic diagram of the evolution of the band structure of a conducting polymer.

Due to the double bond alteration in the conjugated polymer backbone, the charged species formed upon doping are able to move along the carbon chain allowing electron transport and thus giving an electronically conductive material. The extensive delocalization of π-electrons is well known to be responsible for the array of remarkable characteristics that these polymers tend to exhibit [4,5]. Charge balance is accomplished by incorporating an oppositely charged counter ion into the polymer matrix.

To place conducting polymers in context, copper has a conductivity of about $5x10^5$ S/cm, and polystyrene has a value of $1x10^{-18}$ S/cm. Nylon has a value of 10^{-14} S/cm, Hg has a conductivity of 10^4 S/cm. Typically, undoped conducting polymers have values comparable to those of other insulating polymers (10^{-12} S/cm), which on doping are increased to 10^2 S/cm [1].

2.1 Synthesis of Electronically Conducting Polymers

Conducting polymers are prepared either directly, by electro- or oxidative- polymerization, or are polymerized and then oxidized chemically or electrochemically. Among the well known conducting polymers, polyacetylene and poly(phenylene vinylene) are synthesized almost exclusively by chemical polymerization or from precursor route. Polyheterocycles such as polythiophene or polypyrrole are synthesized by both chemical and electrochemical polymerization [1]. Nowadays, a great number of different monomers are known that form conducting polymers upon chemical and electrochemical preparation techniques. Such starting materials include heterocycles and other hydrocarbons as given below in scheme 1 [7].

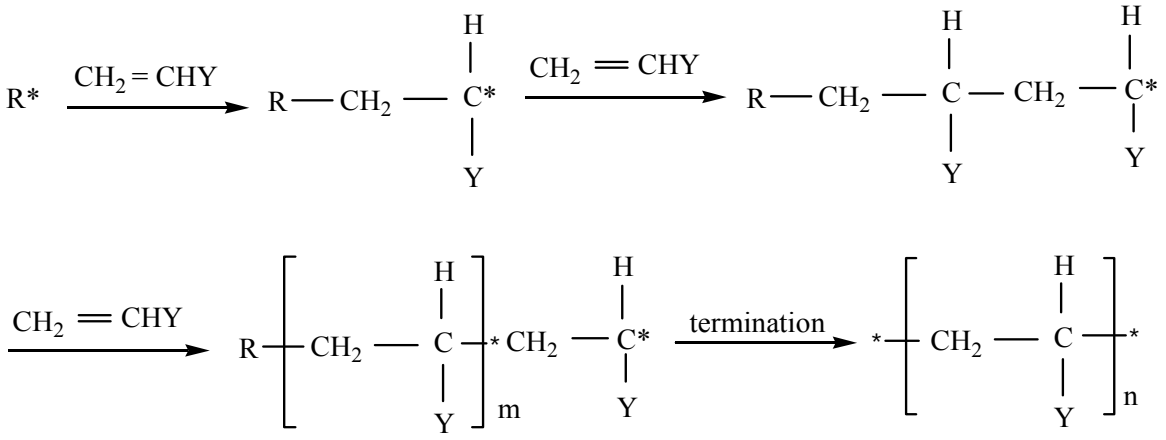


Scheme 1 Monomeric building units of conducting polymers.

2.1.1 Chemical Synthesis of conducting Polymers

One method of formation of conducting polymers is the chemical synthesis. The formation of these synthetic polymers is a process which occurs via chemical connection of many hundreds up to many thousands of monomer molecules. As a result, macromolecular chains are formed. They are, in general, linear, but can be branched, or cross linked as well. However, depending on the number of different monomers and how they are connected, homo-or one of the various kinds of copolymers can result. The chemical process of chain formation may be subdivided roughly into two classes, depending on whether it proceeds as a chain-growth or as a step-growth reaction [8].

Step polymerizations proceed by the stepwise reaction between the functional groups of reactants. The size of the polymer molecules increases at a relatively slow rate in such polymerizations. One proceeds slowly from monomer to dimmer, trimmer, tetramer, pentamer, and so on until eventually large polymer molecules have been formed. Chain polymerizations require an initiator from which it is produced an initiator R* with a reactive center. The reactive center may be a free radical, cation, or anion. Polymerization occurs by the propagation of the reactive center by the successive addition of large numbers of monomer molecules in a chain reaction happening in very shot times. Monomer can react only with the propagating reactive center, not with monomer. By far the most common example of chain polymerization is that of vinyl monomers scheme 2. The growth of the polymer chain ceases when the reactive center is destroyed by one of the possible termination reactions [9].



Scheme 2 Chain polymerization of vinyl monomers

2.1.2 Electrochemical Synthesis of Conducting Polymers

In electrochemical synthesis, also known as electropolymerization, a solution of monomer is oxidized, or reduced to intermediates which polymerize sufficiently rapidly to form a polymer film directly on the electrode [10]. Films of electronically conducting polymers are generally deposited onto a working electrode surface by anodic oxidation of the corresponding monomer in the presence of an electrolyte solution. The oxidation of the monomer to a cation radical is followed by the attack on another molecule of the monomer to form a dimmer. Subsequent formations of monomeric or dimeric radicals lengthen the polymeric chain, and repeated formations produce the final polymer [4,5].

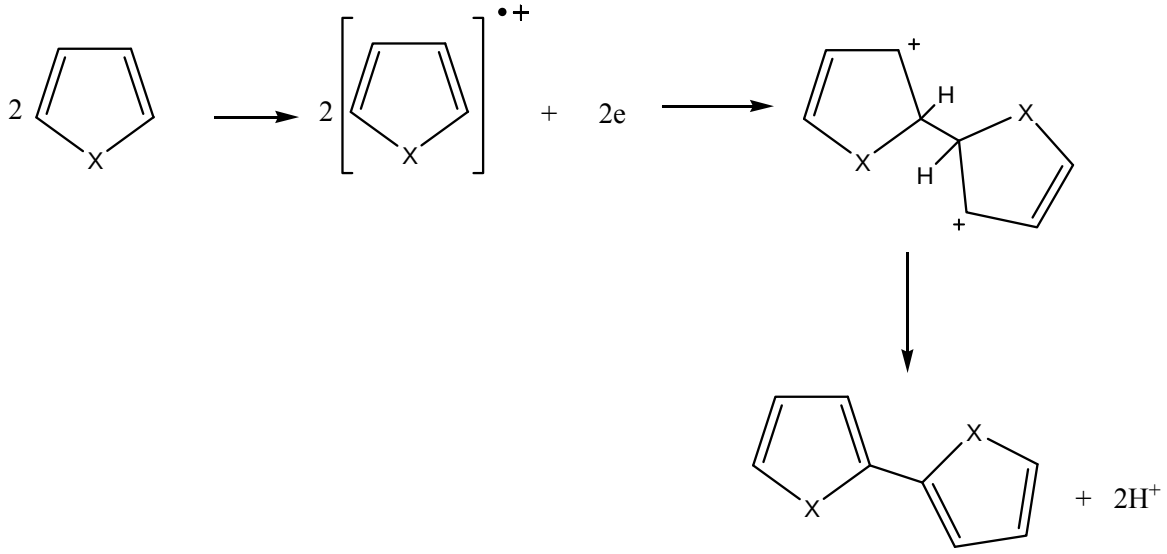
A number of electrically conducting polymers have been synthesized electrochemically. There are certain requirements while synthesizing polymers electrochemically. First, the monomer has to have an oxidation potential which is accessible via a suitable solvent. It should also produce a radical cation which reacts more quickly with other monomers to form the polymer than it does with other nucleophiles in the electrolyte solution. The polymer produced should be with a lower oxidation potential than that of the monomer. During the synthesis, the monomer is dissolved in a suitable solvent and a simple cell is used to polymerize the materials on an electrode under either potentiostatic or galvano- static conditions. Electropolymerization provides a better control of film thickness and morphology, and cleaner polymer when compared to chemical oxidation [4,5]. Electrochemical synthesis has also the advantage of producing the material (polymer) in situ on an electrode already located in a cell, on which further experiments may be performed without necessity for any intermediate treatments such as heating. Electrochemical synthesis is used to produce a large number of materials, as it is simple to perform.

2.1.3 Mechanism of Electropolymerization

The most widely accepted mechanism for the anodic polymerization involves the coupling of the radical cations produced at the electrode. The polymerization mechanisms of monomers like pyrroles and thiophenes are given in scheme 3. The oligomers so produced, which are more easily oxidized than the monomer, are rapidly oxidized and couple with each other and with monomer radical cations. In the case of pyrroles and thiophenes,

coupling occurs predominantly at the α-positions (i.e., 2- and 5-positions), and so pyrroles and thiophenes with substituents in either of these positions do not undergo anodic polymerization. Two electrons are required for each monomer unit to be incorporated into a chain [6].

1.



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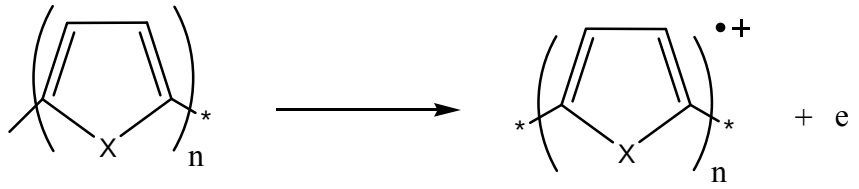

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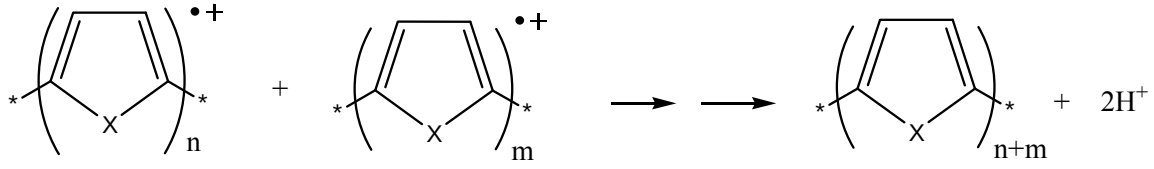


X: N, S

Scheme 3 Electropolymerization Mechanism of pyrroles and thiophenes.

2.2 Applications of conducting polymers

The starting point for the applications of conducting polymers was the discovery that polyacetylene can function as an active electrode in a rechargeable polymer battery. Since then, the prospects of technical applications have grown considerably. Apart from the battery electrode, conducting polymers are used as potential electrochromic displays, antistatic materials, anticorrosives, electrocatalysts, and light emitting materials [7].

One of the most promising near-future applications of conductive polymers is their use in rechargeable batteries. These batteries will use the polymers as active electrodes, because they are light weight, flexible and have a large capacity to reversibly accept and donate electrical charge. Rechargeable batteries are among the first commercial products based on conducting polymers [2]. The more successful batteries have been constructed using polypyrrole, polythiophene, polyaniline, or their derivatives as cathodes, and Li metal or Li-Al alloy as anodes. Batteries that compare well with the Ni-Cd battery in terms of long life, low power, and reliability have been fabricated and are used as backup batteries for static random access memories, cellular phones, hand-held calculators, and so on [11].

Light-emitting diodes (LED) prototypes that use a conductive polymer have received much attention after the first report by Burroughes and co-workers in 1990. A LED consists of a positive hole-injecting electrode (with a high work function, such as In-SnO_2 (ITO) or an electro active polymer), a negative electron injecting electrode with a low work function such as Al, In, Mg, or Ca, and the light-emitting conductive polymer sandwiched between these two electrodes. The conductive polymer films are solution cast, vacuum deposited or generated directly by the polymerization reaction. In these layered structure the injection of holes and electrons migrate across the polymer layer, combine to form excitons, which then decay with photon emission. The use of conductive polymers in light-emitting diodes offers several important advantages over inorganic and molecular organic materials. The polymers can be processed into flexible films with good mechanical properties and large surface areas. Their spectral response can be adjusted and they are less expensive to produce [11].

Conductive polymers are electrochromic and undergo color change when they are switched between the neutral and oxidized states. They are particularly suited for use in electrochromic display devices (ECDs) where the color displayed is controlled by the applied voltage. The basic structure of ECD device is a layered structure containing three different films, a transparent conductive layer (In-SnO_2 or SnO_2) on a glass or plastic which is also an electrode, the electrochromic layer supported on the second electrode, and an ion-conducting electrolyte which separates these two electrochromic layers (electrodes) physically. Polyaniline, polythiophene, polypyrrole, and their derivatives have been tested in prototype ECDs and shown to be quite stable to the switching process in the absence of impurities in the electrolyte. These polymers can function well as the complementary electrode in the electrochromic display device. These polymers can be prepared as thin films by less expensive procedures such as solution casting or electrodeposition.

Conductive polymers have been used successfully in the development of enzyme biosensors for the detection of glucose, penicillin, and other biologically important substances in biomedical analysis. Polypyrrole and polyaniline films are particularly appropriate for this application because they are environmentally stable and enzymes can be immobilized on them by electrodeposition. In general, enzyme biosensors measure a current or resistance change in the conductive polymer film in response to the products of the enzymatic reaction. Conductive polymers have been used for development of gas sensors. The operation of conductive polymer gas sensors is based on the decrease in the film resistance when the polymer is oxidized. Such sensors are used to detect oxidant gases such as SO_2, NO_2 and I_2. Gas sensors using polypyrrole in the oxidized form were used to detect reducing gases such as NH_3, and H_2S.

Conductive polymers have also been considered for use in many other applications. This includes a variety of unrelated unique applications such as electromagnetic (EMF) shields, conductive adhesives, electrostatic dissipators, antistatic films, paints, and fibers [11].

2.3 Electron Transport across the Electrode/Electrolyte Interface

Electron transfer processes lie at the heart of many chemical, biological and technological processes. For example, the microscopic steps in photosynthesis, redox reactions in batteries and corrosion, hinge on the underlying electron transfer dynamics [12]. Electron transfer across the electrode/electrolyte interface represents a class of processes that is important to investigate from both the theoretical (charge transfer theory development) as well as technological (e.g. solar energy utilization) point of view [13]. Attention has been directed recently at the acceleration of the rates of electrode processes by means of simple, organic, outer-sphere redox catalysts attached to the surface of electrodes. Polymeric ligands, polyelectrolytes, and various forms of polymerized transition metal complexes have proved to be particularly useful in confining large quantities of potential catalysts with in polymeric domains at electrode surfaces [14]. Redox polymer coated electrodes show promise in electrochromic, electrocatalytic and antiphotocorrosion experiments. Key to success in such applications, ultimately, is the rate at which electrochemical charge can be made to propagate through the redox polymer film. Quantitative measurements of charge transport rates are therefore of interest [15].

The kinetics of electrochemical reactions mediated by polymer films has been considered in a number of studies in recent years. Initially, attention was focused on the electron-exchange reaction between the substrate dissolved in solution and the active form of the mediator incorporated in the polymer film as the current-limiting factor (after mass transport of the substrate from the bulk of the solution to the film-solution interface had been accounted for). The other consideration is the diffusion of the substrate from the film-solution interface to the electrode surface as a possible rate-limiting factor. An expression for the thickness of the reaction layer for the exchange reaction in this context was also derived. Somewhat later, the diffusion like transport of charge between the electrode-film and film-solution interfaces was taken into account as a possible current-controlling factor. It is now well recognized that these three factors (i.e., the kinetics of electron-exchange reactions, substrate diffusion, and charge transport) may act simultaneously to determine the currents observed at the electrodes coated with polymers [16]. A schematic picture of the typical situation is given in the figure 2 below, wherein a primary reactant, A, in the external solution is converted to a

product, B. This can occur by mass transport of A moving through the film to the underlying electrode or by cross-reaction with a catalyst, Q, contained in the film and renewed electrochemically. Species A might react with Q either within the film or at the film/solution interface [17].

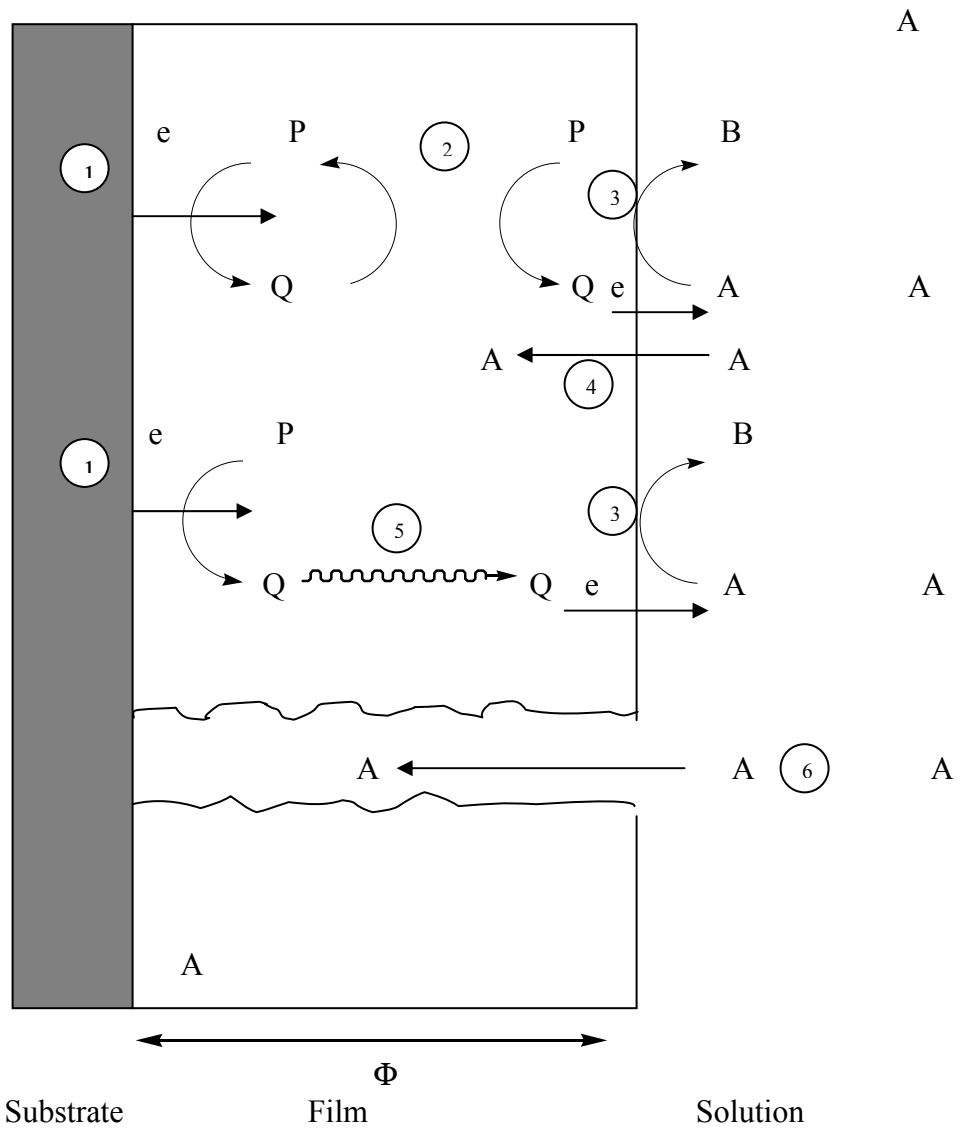


Figure 2 Schematic diagram of processes that occur at a modified electrode. P represents a reducible substance in a film on the electrode surface and A, a species in solution. Processes shown are: 1) heterogeneous electron transfer to P to produce the reduced form, Q; 2) electron transfer from Q to an other P in the film (electron diffusion or electron hopping in the film); 3) electron transfer from Q to A at the film/solution interface; 4) Penetration of A into the film; 5) movement (mass transfer) of Q within the film; 6) movement of A through a pinhole or channel in the film to the substrate, where it can be reduced [17].

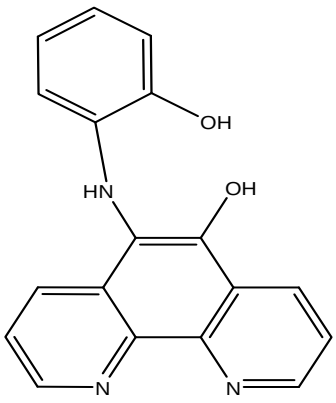
3. Schiff bases (imines)

Schiff bases, named after the German scientist Hugo Schiff, constitute one of the most widely used families of organic compounds as synthetic intermediates [18]. Schiff bases are compounds having a formula RR'C=NR'' where R is an aryl group, R' is a hydrogen atom and R'' is either an alkyl or aryl group. However, usually compounds where R'' is an alkyl or aryl group and R' is an alkyl or aromatic group are also counted as Schiff bases. The Schiff base class is very versatile as compounds can have a variety of different substituents [19].

3.1 Schiff base Ligands

3.1.1 Structure and properties of Schiff base Ligands

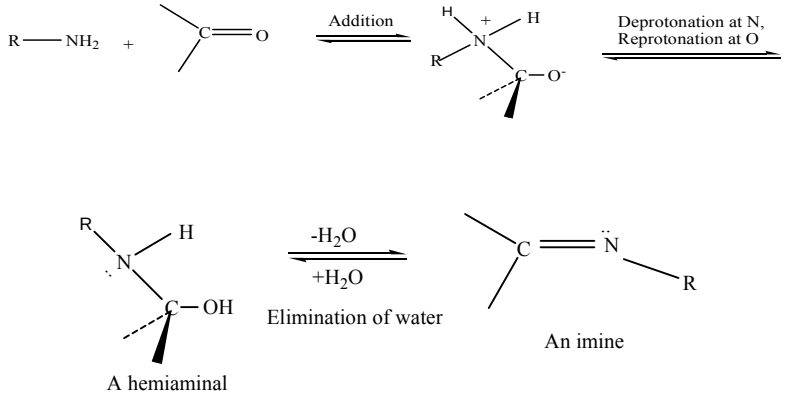
Schiff bases have a chelating structure and are in demand because they are straightforward to prepare and are moderate electron donors with easily-tunable electronic and steric effects thus being versatile. Substituents of Schiff bases affect their stability and reactivity and as an indication of this, Schiff bases are stabilised and made applicable for polymerisation reactions by introducing bulky groups into the phenoxy ring near the oxygen [19]. Most Schiff bases are chemically unstable and show a tendency to be involved in various equilibria, like tautomeric interconversions, hydrolysis, or formation of ionized species. Therefore, successful application of Schiff bases requires a careful study of their characteristics [20]. For this project the structure of the Schiff base ligand is given in scheme 4.



Scheme 4 Structure of the ligand (6-(2-hydroxyphenylamino)-1,10-phenan throlin-5-ol).

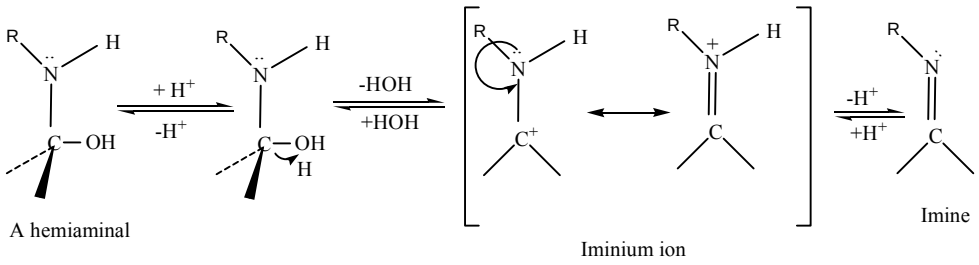
3.1.2 Synthesis of Schiff base Ligands

There are several reaction pathways to synthesize Schiff bases. The most common one is an acid catalysed condensation reaction of amine and aldehyde or ketone under refluxing conditions. On exposure to an amine, aldehydes and ketones form hemiaminals, the nitrogen analogs of hemiacetals. Hemiaminals of primary amines readily lose water to form a carbon-nitrogen double bond. This functional group is known as an imine (an older name is Schiff base) and is the nitrogen analog of a carbonyl group. The mechanism of this reaction is shown in scheme 5 [21].



Scheme 5 Imine formation from Amines and Aldehydes or Ketones

The mechanism of the elimination of water from the hemiaminal is the same as that for the decomposition of a hemiacetal to the carbonyl compound and alcohol. It begins with protonation of the hydroxyl group. Dehydration follows, and then deprotonation of the intermediate iminium ion, as shown in scheme 6 below.



Scheme 6 Mechanism of Hemiaminal Dehydration

Processes such as imine formation from a primary amine and an aldehyde or ketone, in which two molecules are joined with the elimination of water, are called condensation

reactions. Imine formation is reversible, and the usual measures have to be employed to shift the equilibrium in the desired direction [21].

Many factors affect the condensation reaction, for example the pH of the solution as well as the steric and electronic effects of the carbonyl compound and amine. As amine is basic, it is mostly protonated in acidic conditions and thus cannot function as a nucleophile and the reaction cannot proceed. Furthermore, in very basic reaction conditions the reaction is hindered as sufficiently protons are not available to catalyse the elimination of the hemiaminal hydroxyl group. In general, aldehydes react faster than ketones in Schiff base condensation reactions as the reaction centre of aldehyde is sterically less hindered than that of ketone. Furthermore, the extra carbon of ketone donates electron density and thus makes the ketone less electrophilic compared to aldehyde [19].

3.1.3 Applications of Schiff base Ligands

Schiff bases derived from aromatic amines and aromatic aldehydes have a wide variety of applications in many fields. For instance, they are largely used in biological, inorganic and analytical chemistry. Application of many new analytical devices requires the presence of organic reagents as essential compounds of the measuring system. They are used in optical and electrochemical sensors, as well as in various chromatographic methods, to enable detection of enhanced selectivity and sensitivity. Among the organic reagents actually used, Schiff bases possess excellent characteristics, structural similarities with natural biological substances, relatively simple preparation procedures and the synthetic flexibility that enables design of suitable structural properties. Schiff bases are widely applicable in analytical determination, using reactions of condensation of primary amines and carbonyl compounds in which the azomethine bond is formed (i.e., for determination of compounds with an amino or carbonyl group); using complex formation reactions (determination of amines, carbonyl compounds and metal ions); or utilizing the variation in their spectroscopic characteristics following changes in pH and solvent (pH of solvent polarity indicators) [20].

An interesting application of Schiff bases is their use as an effective corrosion inhibitor, which is based on their ability to spontaneously form a monolayer on the surface to be

protected. Some Schiff bases have been studied in acidic or basic solutions aiming at corrosion protection of Al, Cu, and stainless steel. Many commercial inhibitors include aldehydes or amines, but presumably due to the C=N bond the Schiff bases function more efficiently in many cases. The principal interaction between the inhibitor and the metal surface is chemisorption. The inhibitor molecule should have centres capable of forming bonds with the metal surface by electron transfer. In such cases the metal acts as an electrophile and the inhibitor acts as a Lewis base. Nucleophilic centres, such as oxygen and nitrogen atoms, of the protective compound have free electron pairs which are readily available for sharing. Together with the atoms of the benzene rings they create multiple absorption sites for the inhibitor thus enabling stable monolayer formation [19].

A large number of different Schiff base ligands have been used as cation carriers in potentiometric sensors as they have shown excellent selectivity, sensitivity, and stability for specific metal ions such as Ag(II), Al(III), Co(II), Cu(II), Hg(II), Ni(II), Pb(II), Y(III), and Zn(II) [19]. Schiff bases of isatin were reported to possess antibacterial, antifungal, antiviral, anti-HIV, antiprotozoal, and anthelmintic activities. They also exhibit significant anti convulsant activity, apart from other pharmacological properties [22].

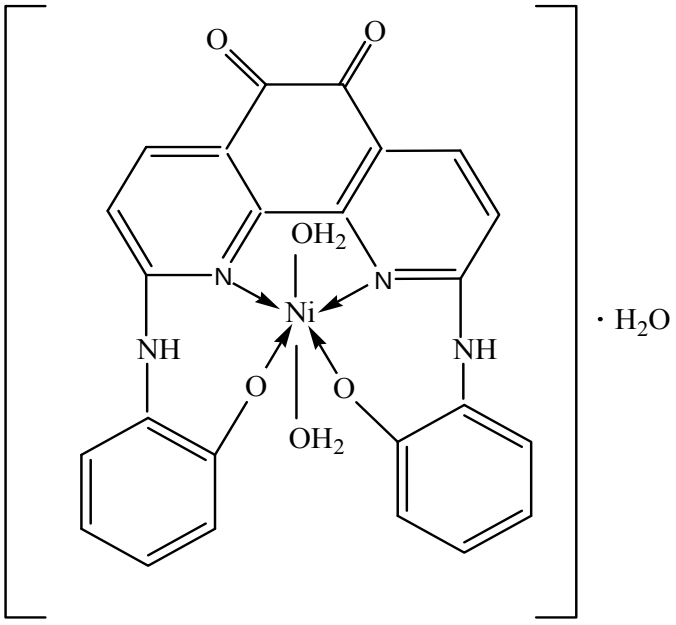
3.2 Schiff base-Metal Complexes

During the past two decades, considerable attention has been paid to the chemistry of the metal complexes of Schiff bases containing nitrogen and other donors. This may be attributed to their stability, biological activity and other potential applications in many fields such as oxidation catalysis, electrochemistry etc. Co and Cu Schiff base complexes were the first complexes whose crystallographic structure was determined using ancient methods[23,24].

Metal complexes with Schiff base ligands have played an important role since the early days of coordination chemistry, not only from an inorganic point of view but also because of possible biological interest in such compounds. A great deal of work has been performed in the synthesis and characterization of transition metal complexes of Schiff base ligands.

3.2.1 Structure and properties of Schiff base-metal Complexes

Schiff bases with multidentate coordination sites or groups are known to form complexes with transition-metal ions readily. Schiff base polymers have been researched because of their high thermal stability, complex-forming ability, and semiconducting properties. The incorporation of transition-metal ions into polymeric Schiff bases not only affects the physical characteristics, such as the strength, but also the chemical activity. The catalytic activities of Schiff base complexes of transition-metal ions in a variety of organic reactions have been known for a long time. However, when the metal ions are complexed with functional polymeric Schiff bases, the activity of the metal complexes changes because of a polymeric effect. Transition-metal/polymer complexes of polymeric Schiff base ligands are always of interest as they lead to novel structural types and display a wide variety of magnetic properties [25]. It has been reported that the structure of the R-group bonded to the imine nitrogen severely affects the coordination for complexes formed between ON type Schiff bases and transition metals [23]. The chemical structure of the Schiff base Nickel complex is shown in the scheme 7.



Scheme 7 Proposed structure of the Schiff base-Ni metal complex (mono hydrated Ni (II)-2,9-bis(2-hydroxyphenylamino)-1,10-phenanthroline-5,6-dione) complex.

3.2.2 Synthesis of Schiff base-metal Complexes

Schiff base ligands can form adducts or chelates with metals depending on the reaction conditions used. There are basically several synthetic pathways for the preparation of Schiff base-metal complexes and the method preferred depends on the metal. In some of the methods, the starting material is metal alkoxide, metal amide, metal alkyl or aryl compound, or metal acetate or halide. In other methods, a sodium or potassium salt of the ligand is prepared first which is then reacted with metal halide. The ligand precursor could also be deprotonated by lithium bases but it is advisable to form sodium or potassium salt of the ligand. Metal acetates are considered the most convenient starting materials for complexation with Schiff bases because they are soluble in alcohols and are salts of a weak acid [19].

3.2.3 Applications of Schiff base-metal Complexes

Recently, Schiff base complexes have been widely investigated for their properties and applications in different fields, such as catalysis and materials chemistry. Schiff base complexes have also a variety of applications in biological, clinical, analytical and pharmacological areas. Studies of a new kind of chemotherapeutic Schiff bases are now attracting the attention of biochemists. Earlier work reported that some drugs showed increased activity, when administered as metal complexes rather than as organic compounds. Deoxyribonucleic acid (DNA) is the primary target molecule for most anticancer and antiviral therapies according to cell biologists. Investigations on the interaction of DNA with small molecules are important in the design of new types of pharmaceutical molecules. Since the chemical nuclease activity of transition metal complexes was discovered in the 1980s, studying the interaction model and the mechanism of transition metal complexes with DNA, and exploring the application of metal complexes in antineoplastic medication, molecular biology and bioengineering have become hotspots in recent years. Some kind of metal complexes interacted with DNA could induce the breakage of DNA strands by appropriate methods. In the case of cancer genes, after DNA strands are cleaved, the DNA double strands break. The replication ability of cancer gene is destroyed. Copper complex could cleave DNA in the presence of ascorbate or hydroquinone [26].

3.3 Biological Transformations Involving Schiff bases (Imines)

The mechanism used by enzymes to catalyze reactions between organic molecules occurs through the formation of Schiff bases (imines) [27]. For instance, the related molecules pyridoxal and pyridoxamine assist in the interconversion of carbonyl groups and primary amine functions in biology. Pyridoxamine undergoes enzyme-catalyzed condensation with the carbonyl group of 2-oxocarboxylic acids to produce an imine. Rearrangement furnishes a new imine, which hydrolyzes to pyridoxal and a 2-aminocarboxylic acid (an amino acid). In the forward direction this process synthesizes several of the naturally occurring amino acids; in the reverse mode it aids in their metabolism [21].

A key step in the chemistry of vision is binding of an aldehyde to an enzyme via an imine formation. It starts with β-carotene, which undergoes oxidative cleavage in the liver to give an alcohol retinol or vitamin A. Oxidation of vitamin A gives 11-cis-retinol. In the eye, this combines with an amino group of the protein opsin to form an imine, rhodopsin. When rhodopsin absorbs a photon of visible light, the cis double bond of the retinol unit undergoes a photochemical cis-to-trans isomerization, which is attended by a dramatic change in its shape and a change in the conformation of rhodopsin. This conformational change is translated into a nerve impulse perceived by the brain as a visual image [27].

3.4 Objectives of the Study

The main objective of this project is to study the electroactivity of Schiff base ligand (6-(2-hydroxyphenylamino)-1,10-phenanthrolin-5-ol) and a Schiff base-Nickel complex (Ni (II)-2,9-bis(2-hydroxyphenylamino)-1,10-phenanthroline-5,6-dione).

The study also involves the electrochemical characterizations of the resulting polymer films. The factors that affect the electroactivity of the polymer film such as number of cycles (film thickness) and pH were investigated for both the Schiff base ligand (6-(2-hydroxyphenylamino)-1,10-phenan throlin-5-ol) and Schiff base Nickel complex (Ni (II)-2,9-bis(2-hydroxyphenylamino)-1,10-phenanthroline-5,6-dione).

Moreover, the stability of the poly-Schiff base complex was studied in 1.0 M H_2SO_4, 1M NaOH and methanol-water mixture (1:1) by soaking the modified electrodes in each of them for two hours.

4. Cyclic Voltammetry

4.1 Basic Principles of Cyclic Voltammetry

Cyclic voltammetry is the most versatile electroanalytical technique for the study of electroactive species, and it is widely used in industrial applications and academic research laboratories. Cyclic voltammetry involves the measurement of current-voltage curves under diffusion-controlled, mass transfer conditions at a stationary electrode, utilizing symmetrical triangular scan rates ranging from a few millivolts per second to hundreds of volts per second [28].

In cyclic voltammetry, the triangular wave form shown in figure 3 is applied to the working electrode.

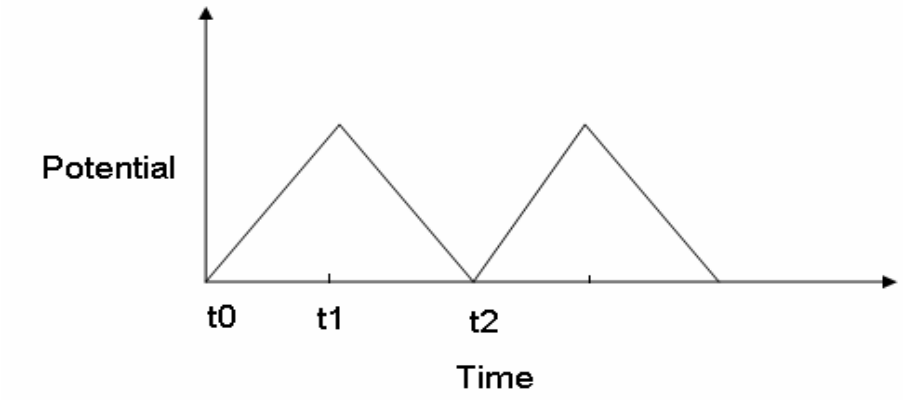


Figure 3 Waveform used in cyclic voltammetry

After applying a linear voltage ramp between times t_0 and t_1, the ramp is reversed to bring the potential back to its initial value at time t_2. The cycle may be repeated many more times [29]. The triangle returns at the same speed and permits the display of a complete voltammogramme with cathodic (reduction) and anodic (oxidation) wave forms one above the other.

In CV the typical concentration gradient prevails at potentials more positive than the reduction potential. Once this point has been passed, however, the rate of variation of the potential is too rapid for diffusional processes to maintain equilibrium with the bulk of the

solution. As more and more material is consumed, the diffusion layer extends further and further into the solution. Unlike the case with dropping electrodes, this process is not periodically reversed by the stirring associated with the drop fall, so that the signal decay continues and a peak-shaped curve is obtained. Further more, in the course of the cathodic variation in potential; the reduced form of the reactant is produced in the vicinity of the electrode while a depletion of the oxidized form occurs. Given sufficient time, the reduced form would diffuse into the bulk of the solution, but the potential is taken back to the initial value at a rate such that some of the reduced form is still present at the electrode surface and undergoes a process of oxidation back to the form of the couple initially present in the solution [28].

To obtain a cyclic voltammogram, the current at the working electrode is measured during the potential scan. The important parameters of a cyclic voltammogram are the magnitudes of the peak currents, i_{pa} and i_{pc}, and the potentials at which the peaks occur, E_{pa} and E_{pc}. A redox couple in which both species rapidly exchange electrons with the working electrode is termed an electrochemically reversible couple. Such a couple can be identified from the measurement of the potential difference between the two peak potentials. The following equation applies to a system that is both electrochemically and chemically reversible.

$$\Delta E = E_{pa} - E_{pc} \approx 0.058/n \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 1$$

Where E_{pa} and E_{pc} are the potentials at which the peak anodic and peak cathodic currents are observed and n is the number of electrons in the half-reaction. The half-wave potential, $E_{1/2}$, lie mid way between the two peak potentials [3]. Figure 4 illustrates the behavior of a reversible reaction that is fast enough to maintain equilibrium concentration of reactant and product at the electrode surface. The peak anodic and peak cathodic currents have equal magnitudes in a reversible process. That is the ratio of the anodic current to that of the cathodic current is nearly equal to unity [17,29].

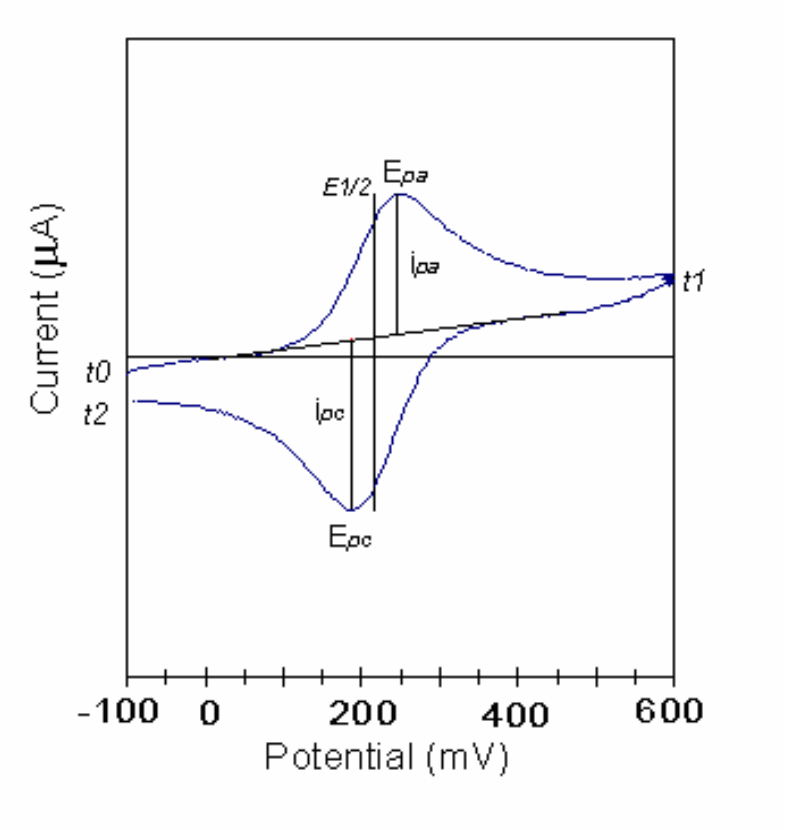


Figure 4 The basic shape of the current response for a cyclic voltammetry experiment.

Electrochemical irreversibility is caused by slow electron exchange of the redox species with the working electrode. For an irreversible reaction, the cathodic and anodic peaks are drawn out and more separated. At the limit of irreversibility, where the oxidation is very low, no anodic peak is seen. For a reversible reaction, the peak current (i_p, amperes) for the forward sweep of the first cycle is proportional to the concentration of analyte and the square root of sweep rate. The peak current is defined by the Randles-Sevcik equation,

$$\boldsymbol{i}_p = (2.69\text{x}10^5)\, n^{3/2} A C D^{1/2} v^{1/2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 2$$

where n is the number of electrons in the half-reaction, A is the area of the electrode (cm^2), C is the concentration of (mol/cm^3), D is the diffusion coefficient of electroactive species (cm^2/s), v is scan rate (V/s). The faster the sweep rate, the greater the peak current, as long as the reaction remains reversible. If the electroactive species is confined close to the surface of the electrode and cannot diffuse freely into solution, the peak current is directly proportional to scan rate instead of to the square root of scan rate. In the case of an

irreversible system, the equation for i_p is,

$$\boldsymbol{i}_p = (2.99\text{x}10^5)\, n(\alpha n_a)^{1/2} A D^{1/2} C v^{1/2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 3$$

where α is the transfer coefficient and n_a is the number of electrons in the rate-determining step of the electrode process[3,29].

Cyclic voltammetry yields information about reaction reversibilities and also offers a very rapid means of analysis for suitable systems. The method is particularly valuable for the investigation of step wise reactions, and in many cases direct investigation of reactive intermediates is possible. By varying the scan rate, systems exhibiting a wide range of rate constants can be studied, and transient species with half-lives of the order of milliseconds are readily detected [28]. Cyclic voltammetry has become a standard technique in all fields of chemistry as a means of studying redox states. The method enables a wide potential range to be rapidly scanned for the reducible or oxidizable species. This capability, together with its variable time scale and good sensitivity, makes cyclic voltammetry the most versatile electroanalytical technique thus far developed. However, quantitative measurements (of rates or concentration) are best obtained via other means (e.g., step, pulse, or hydrodynamic techniques).

4.2 Electrodes and Electrolytes used in Cyclic Voltammetry

For techniques like potentiometry, wherein only a negligible current is drawn across the cell, two electrodes suffice to complete the electrochemical cell. The second electrode is chosen to be an ideal non-polarizable electrode of known potential called a reference electrode. For the dynamic techniques such as voltammetry, especially when rather large currents flow in response to the potential perturbation, a three-electrode cell arrangement is needed. In this arrangement, the current is passed between the working electrode and an auxiliary (counter) electrode. That is, the auxiliary electrode is the current-supporting partner of the working electrode. The working electrode is the electrode at which the reaction of interest occurs. The auxiliary electrode should have a large area relative to the working electrode. In three-electrode arrangement, the reference electrode is the electrode against which the potential of the working electrode can be measured. Negligible current flows at the reference electrode,

so its potential is unaffected by ohmic potential, concentration polarization, and over potential. It truly maintains a constant reference potential [29].

i. Working Electrodes

A number of solid electrodes have been used as working electrodes in electrochemistry. These include heavy metals electrodes like platinum and gold, carbon and so on. Carbon materials in the form of graphite, glassy carbon, carbon fibers, etc. have been important players in solid electrode development for several reasons. First, they are available in a variety of forms and are generally inexpensive. Second, the slow kinetics of carbon oxidation leads to a wide useful potential range, particularly in the positive direction. This characteristic is an important advantage over platinum and mercury, which exhibit significant or overwhelming background oxidation currents. Third, carbon has a reach surface chemistry, which can be exploited to influence reactivity. In particular a wide variety of chemical derivatizations is possible on graphite or glassy carbon surfaces. Fourth, controlled variation of electron transfer kinetics and adsorption on carbon surfaces can be used to enhance analytical utility [3]. Overall, these properties of carbon made it preferred in this project work and glassy carbon was used as the working electrode for the entire experiment.

ii. Reference Electrodes

A ideal reference electrode should show 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 its initial value after some currents are passed through the electrode; if it is the electrode of the second kind (e.g., Ag/AgCl), the solid phase must not be appreciably soluble in the electrolyte and the likes. A variety of reference electrodes are commercially available. These include: hydrogen electrode, palladium-hydrogen electrode, silver-silver chloride electrode, calomel electrode and many others. Next to the hydrogen electrode, the silver-silver chloride electrode is probably the most reproducible and reliable reference electrode, and it is certainly one of the most convenient electrodes to construct and use.

The solubility of AgCl in water is about 10^{-5} M at 25^0C, which sets a lower limit on the use of the electrode as an ion-specific electrode for chloride ion. The solubility in saturated KCl solution increases to about $6x10^{-3}$ M, due to the formation of soluble complexes of the type $AgCl_2^-$. For this reason the saturated KCl electrolyte must be pre saturated with silver chloride; otherwise the electrode becomes stripped of its AgCl coating [30].

iii. Auxiliary (Counter) Electrodes

As already mentioned above, in a three-electrode cell, the current is passed between the working and a counter (or auxiliary) electrode. The auxiliary electrode can be any convenient one, because its electrochemical properties do not affect the behavior of the electrode of interest. It is usually chosen to be an electrode that does not produce substances by electrolysis that will reach the working electrode surface and cause interfering reactions there. Frequently, it is placed in a compartment separated from the working electrode by a sintered-glass disk or other separator [17].

iv. Electrolytes and Solvents

Almost every electrochemical experiment is carried out in a medium consisting of a solvent and supporting electrolyte. There is no universal solvent, and even for a given application one rarely finds an ideal system. The influence of migration is avoided by adding a supporting electrolyte, ions of which do not discharge themselves at the electrode in the experimental conditions. This supporting electrolyte is added at high concentrations to the sample and could be a simple salt, acid, base or a buffer solution or a chelating reagent. A good solvent system (i.e., medium consisting of solvent and supporting electrolyte) for one type of experiment may be wholly unsuitable for other applications. The most important properties that the ideal solvent system ought to possess are electrochemical inertness (stability over a wide range of potentials), high electrical conductivity, good solvent power, chemical inertness, availability in pure form or ease of purification and low cost.

5. Experimental Part

5.1 Materials and Reagents

The experiments were carried out in acidic aqueous solutions consisting of different molar concentrations of sulfuric acid (H_2SO_4) supplied from Riedel-deHaën and used without further purification. Freshly distilled water was used for preparing the aqueous solutions and washing. Sodium sulphate (Na_2SO_4) (Nice), Sodium hydroxide (NaOH) (Labmerk) and Methanol, (BDH) were also used in the study. The Schiff bases were prepared in inorganic chemistry laboratory of Addis Ababa University and supplied to us by Professor V.J.T Raju.

5.2 Apparatus and Instruments

Cyclic Voltammetry (Cv)

Cyclic voltammograms were recorded using the BAS CV-50W voltammetric analyzer. Electropolymerization of the monomers was conducted using a standard three-electrode cell. The electrodes consisted of a glassy carbon electrode (diameter = 3 mm) as working electrode, Ag/AgCl/(sat'd KCl) as the reference electrode, and a platinum wire as counter electrode. Before each use, the working electrode was mechanically polished using Alumina powder, (Al_2O_3) to a mirror finish, rinsed with distilled water, and then treated for several cycles in 0.1 M H_2SO_4 solution in potential range between -0.5 and 1.6 V until a constant response is obtained.

pH meter

A 4330 (Jenway) model conductivity and pH meter was used for the measurement of the pH values of solutions.

Analytical Balance

Analytical balance (Denver, model XE-50) was used to measure mass of solid chemicals.

6. Results and Discussion

6.1 Schiff base Ligand (6-(2-hydroxyphenylamino)-1,10-phenanthrolin-5-ol)

6.1.1 Electropolymerization of Schiff base ligand

The electrochemical characterization of the ligand was started by studying if the monomer can undergo electrochemical oxidation or not. Cyclic voltammetry is used for this study. A $5x10^{-4}$ M Schiff base monomer solution was prepared by dissolving in aqueous solution consisting 0.1 M H_2SO_4. Figure 5 shows a typical cyclic voltammogram recorded during the electro-chemical growth of poly-Schiff base ligand film at glassy carbon electrode for 15 cycles.

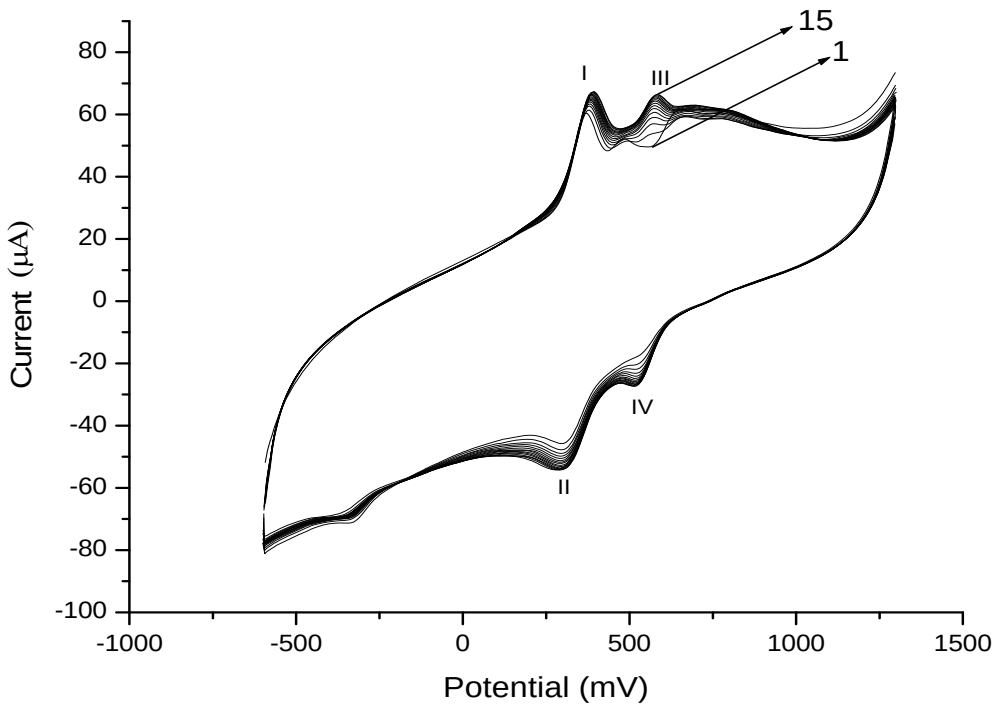


Figure 5 Cyclic voltammogram of $5x10^{-4}$ M of Schiff base ligand at glassy carbon electrode in an aqueous solution containing 0.1 M H_2SO_4. Scan rate (v) = 100 mV/s. The numbers show the number of polymerization cycles.

The monomer electrooxidizes in a reversible manner producing two redox couple systems, (*I-II* and *III-IV*). On the first positive potential sweep, the monomer shows an anodic oxidation peak at E_{pa1} = 531 mV and E_{pa2} = 331 mV. The complementary reduction peaks on

the negative potential sweep appear at E_{pc1} = 568 mV and E_{pc2} = 370 mV. On increasing the number of cycles for the polymer film formation, an increase in peak currents is observed for both redox couples. This shows the accumulation of an electroactive polymer film on the electrode [2,31]. The ratio of the anodic to the cathodic peak currents gave a value of 0.95. This value is fairly close to unity which indicates reaction reversibility. The number of electrons calculated as per equation 1 gives value of n of 1.4. Chemical reactions coupled to the electrode processes might have affected this value.

6.1.2 Electroactivity of poly-Schiff base ligand film

After deposition, the electrode was transferred with careful rinsing to a fresh monomer free electrolyte (0.1 M H_2SO_4) solution. Figure 6 shows the cyclic voltammograms of a bare glassy carbon in acidic aqueous solution consisting of 0.1M H_2SO_4 (dashed line) and a glassy carbon electrode covered with the poly-Schiff base ligand film in acidic aqueous solution consisting of 0.1M H_2SO_4 in the absence of the monomer (solid line). The appearance of the redox peaks confirms the electroactivity of poly-schiff base ligand in acidic aqueous solution [32].

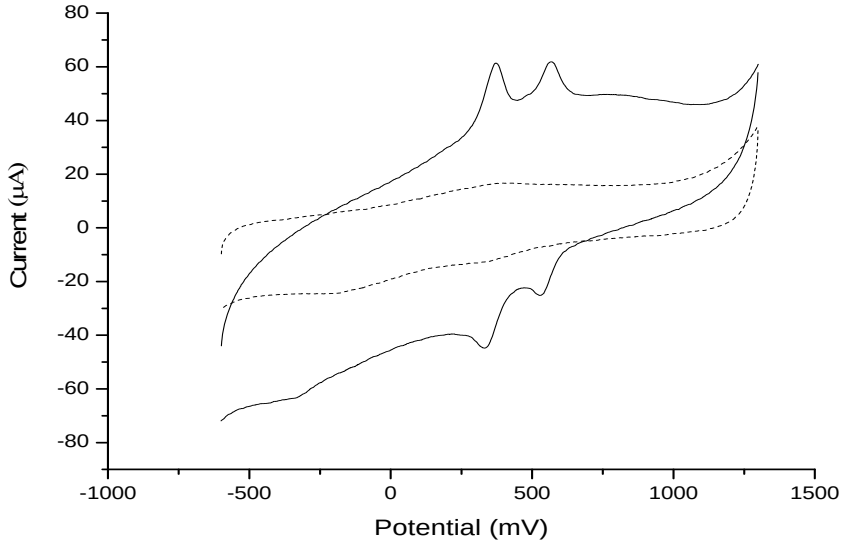


Figure 6 Cyclic voltammograms of bare glassy carbon in acidic aqueous solution consisting of 0.1M H_2SO_4 (----) and a glassy carbon electrode covered with the poly-schiff base ligand film in the absence of the monomer in 0.1 M H_2SO_4 (___).

The factors that affect the electroactivity of the film such as number of cycles and pH were tested in the coming sections [33].

6.1.3 Effect of Scan rate

To see the effect of scan rate (v) on the electroactivity of poly-schiff base ligand film, the schiff base ligand was electrochemically deposited on the glassy carbon electrode by 15 polymerization cycles by sweeping the electrode potential between -1000 and 1500 mV at scan rate of 100 mV/s. Then, the scan rate is varied in the range from 20 to160 mV/s and the response was recorded as shown in figure 7 (A).

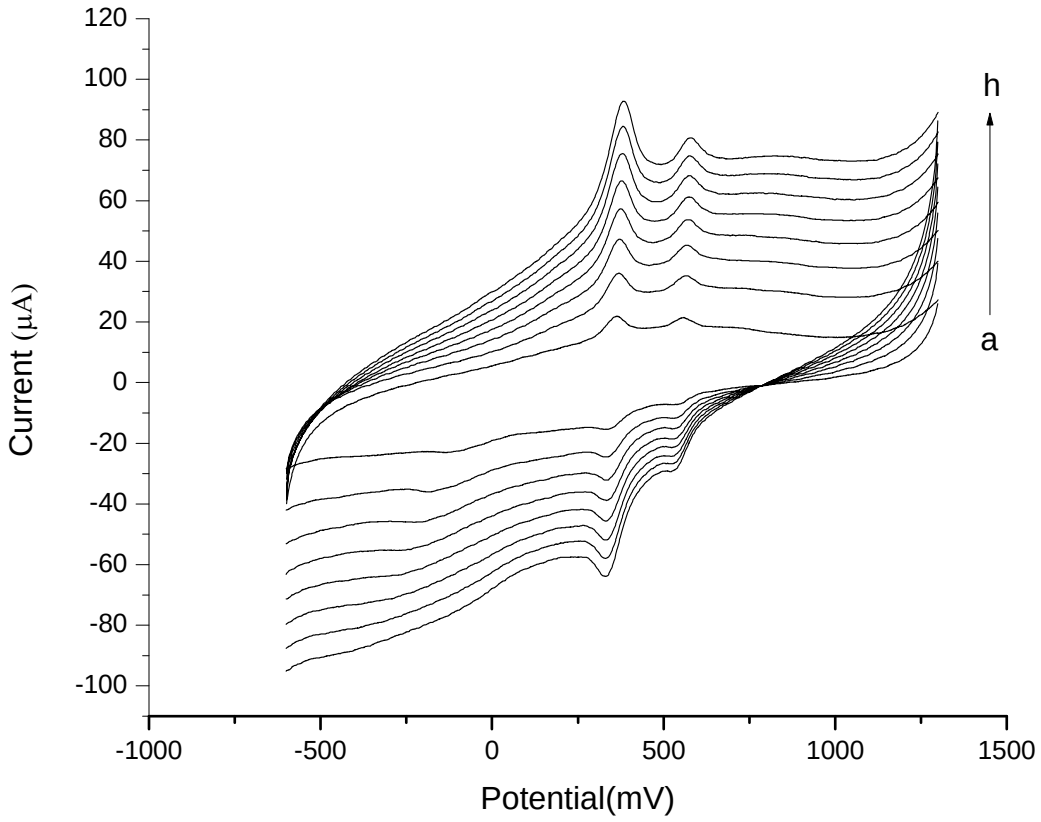


Figure 7 (A) Cyclic voltammograms of glassy carbon/schiff base ligand modified electrodes in 0.1 M H_2SO_4 aqueous solution at different scan rates (mV/s): a) 20, b)40, c) 60, d) 80, e) 100, f) 120, g) 140, h) 160.

Moreover, plots of the anodic peak currents (I_{pa1} and I_{pa2}) of the two redox couples *I-II* and *III-IV* against the scan rates show a linear variation as can be inferred from figures 7 (B) and (C). These facts indicate the typical behavior of a thin layer of strongly adsorbed electrochemically active species on the electrode surface [2,31].

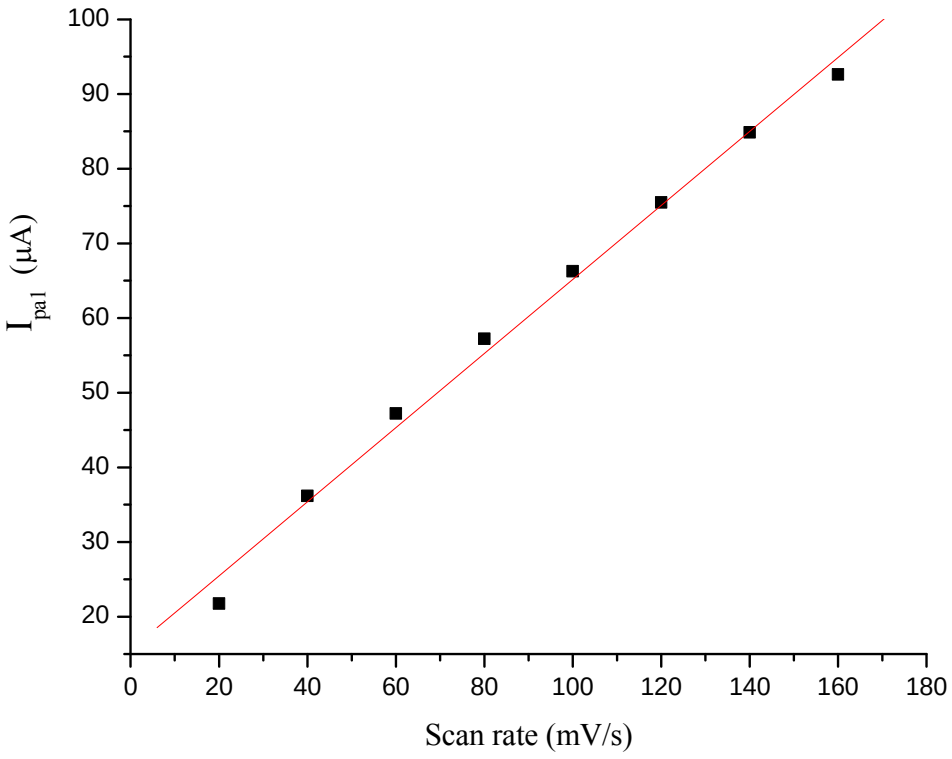


Figure 7 (B) Anodic peak currents (I_{pa1}) of the redox couple *I-II* as a function of the scan rate (v). The film was produced for $5x10^{-4}$ M of Schiff base ligand at glassy carbon electrode in an aqueous solution containing 0.1 M H_2SO_4. Scan rate (v) = 100 mV/s. The number of polymerization cycles is 15. Slope = (0.50 ± 0.1) μAs/mV and R= 0.99657.

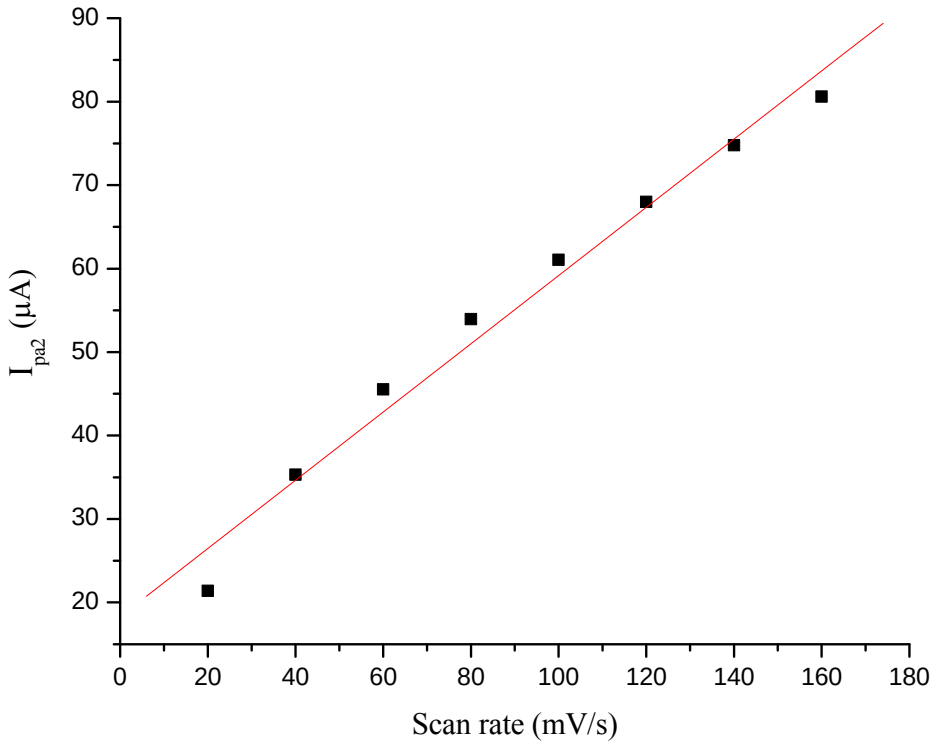


Figure 7 (C) Anodic peak currents (Ipa_2) of the redox couple *III-IV* as a function of the potential scan rate (v). The film was produced for $5x10^{-4}$ M of Schiff base ligand at glassy carbon electrode in an aqueous solution containing 0.1M H_2SO_4. Scan rate (v) = 100 mV/s. The number of polymerization cycles is 15. Slope = (0.41 ± 0.1) μAs/mV and R = 0.99013.

6.1.4 Effect of pH

Figure 8 shows the cyclic voltammograms of poly-schiff base ligand film, deposited on a glassy carbon electrode, in aqueous solutions of various pHs. As the pH increases: the waves shift to the negative direction of potential and the potential separation between the anodic and cathodic peak potentials (ΔEp) increases. This behavior is due to the increase of the film resistance [2,31]. The plots of the cathodic and anodic peak potentials with pH gives slopes of -35 ± 5 and -19 ± 5 respectively. These values indicate that both reduction and oxidation processes are a 2 e^-/1 H^+ reactions [34,35].

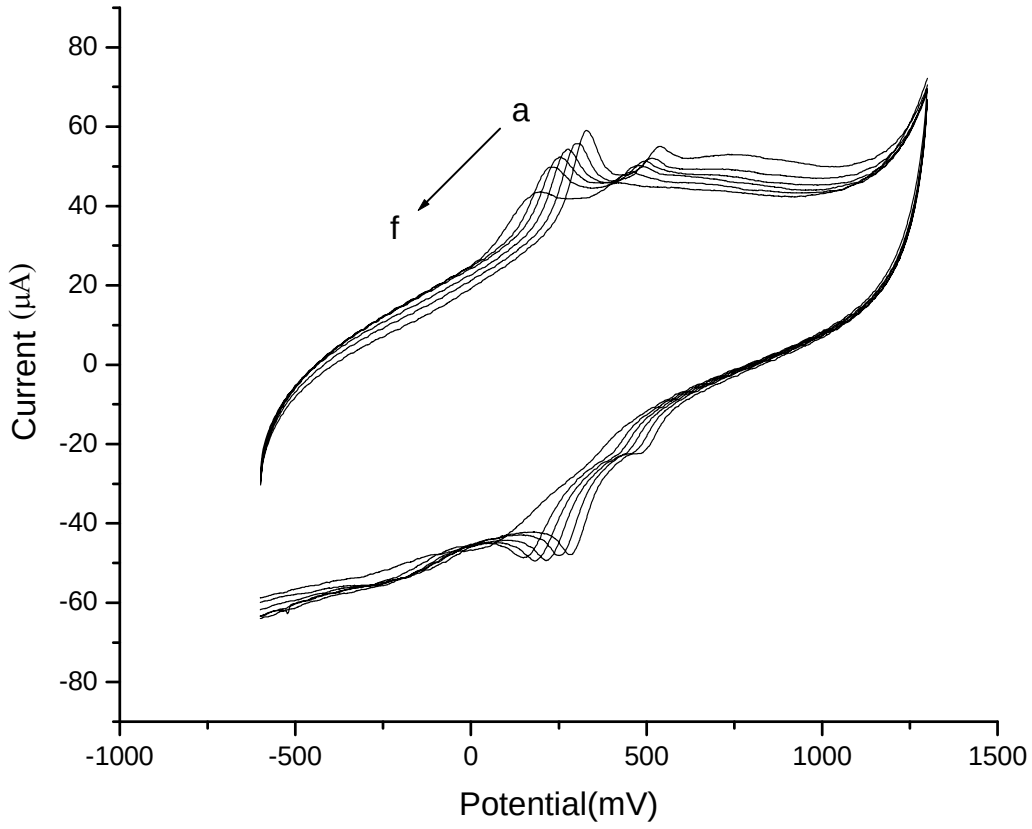


Figure 8 Cyclic voltammograms of poly-schiff base ligand films in aqueous solutions of different pHs: a) 0.5, b) 1.0, c) 1.2, d) 1.75, e) 2.1, f) 7.3. The films were produced for $5x10^{-4}$ M of Schiff base ligand at glassy carbon electrodes in an aqueous solution containing 0.1 M H_2SO_4. Scan rate (v) = 100 mV/s.

6.1.5 Effect of the film thickness

Poly-schiff base ligand films were prepared using different number of cycles in the range from 5 to 30. The anodic peak currents (I_{pa1} and I_{pa2}) were recorded after each number of cycles used for the polymer film formation. Figure 9 shows plots of I_{pa1} and I_{pa2} of the two redox systems against the number of cycles. The variation of the two peak currents with the number of cycles is slightly different. Overall, better peak current are noticed for the number of cycles between 10 and 20. Hence, the optimum number of cycles for polymer film formation for both redox systems was taken as 20 since the two peak currents have better values at this point. On increasing the number of cycles further, the peak currents of both redox couples decrease. This behavior implies the diminishing of the polymerization process as the film thickness increases. This might be due to the retardation of the electron transfer through the thicker polymer film. Also, the peak separation potential, ΔEp, increases with increasing the number of cycles which suggests that thicker films are more insulating than thinner ones for the poly-schiff base ligand (figure 10) [2,31,33].

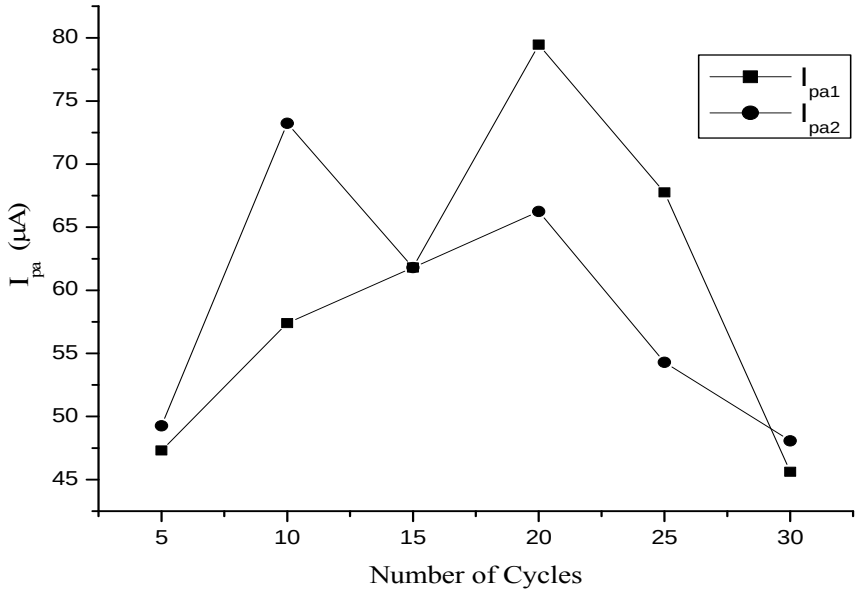


Figure 9 Dependence of the anodic peak currents (I_{pa1} and I_{pa2}) of the two redox systems on the number of cycles of the film formation. The films were produced for $5x10^{-4}$ M of Schiff base ligand at glassy carbon electrodes in an aqueous solution containing 0.1 M H_2SO_4. Scan rate (ν) = 100 mV/s.

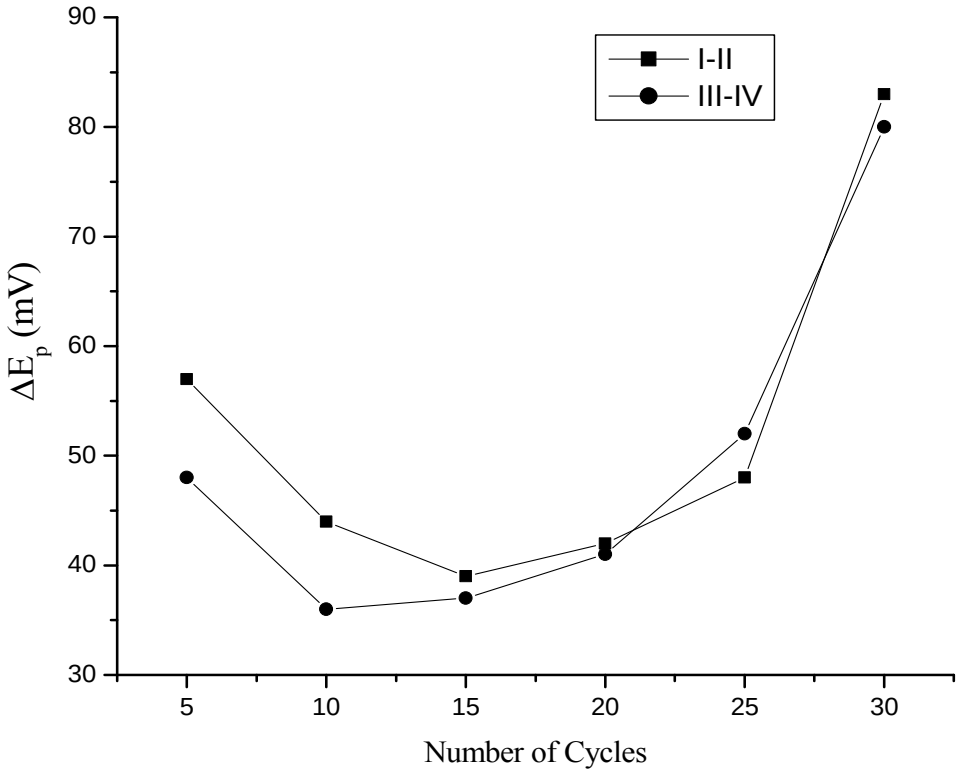


Figure 10 Dependence of the peak separation, ΔEp, of poly-schiff base ligand film on the number of cycles of the film formation. The films were produced for $5x10^{-4}$ M of Schiff base ligand at glassy carbon electrodes in an aqueous solution containing 0.1M H_2SO_4. Scan rate (ν) = 100 mV/s.

6.2 Schiff base-Ni complex (Ni (II)-2,9-bis(2-hydroxyphenylamino)-1,10-phenanthroline-5,6-dione)

6.2.1 Electropolymerization of the Schiff base -Nickel complex

A $1x10^{-3}$ M Schiff base complex monomer solution was prepared by dissolving a known amount in aqueous solution consisting 0.05 M H_2SO_4. A cyclic voltammogram was recorded for this solution between -1000 mV and 1500 mV. Figure 11 shows a typical cyclic voltammogram recorded during the electrochemical growth of poly-Schiff base complex film at glassy carbon electrode for ten cycles.

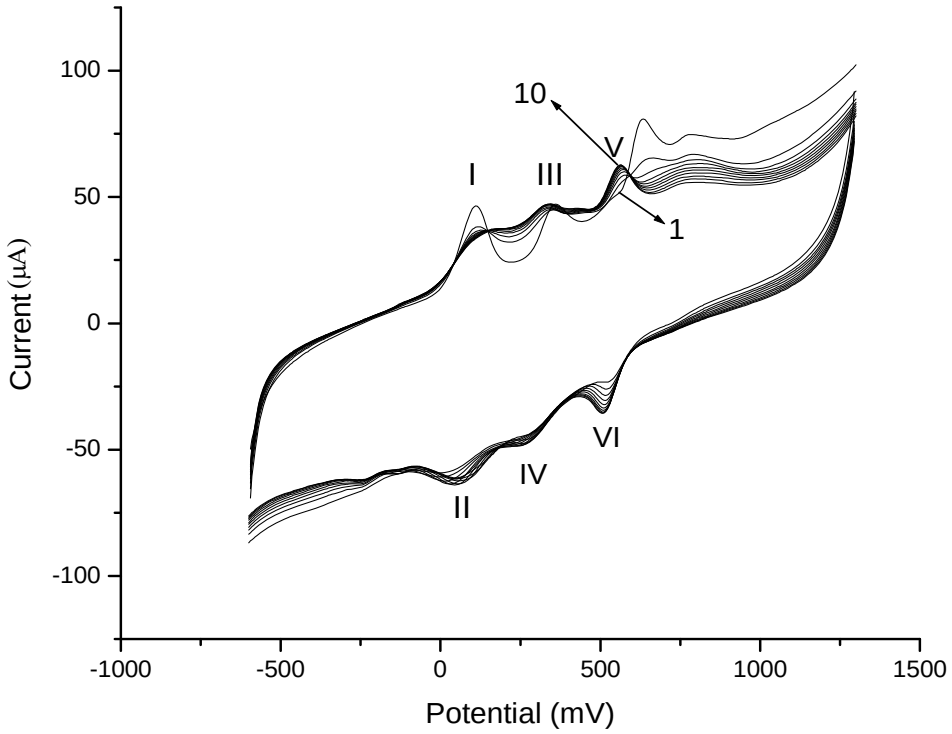


Figure 11 Cyclic voltammogram of $1x10^{-3}$ M of Schiff base complex at glassy carbon electrode in an aqueous solution containing 0.05 M H_2SO_4. Scan rate (v) = 100 mV/s. The numbers show the number of polymerization cycles.

On the first positive potential sweep, the monomer electrooxidizes giving three reversible peaks. The oxidation products appear as a complex system composed of three redox peaks. The redox system *I-II* appears at E_{pa} = 109 mV and E_{pc} = 25 mV, the redox system *III-IV* appears at E_{pa} = 347 mV and E_{pc} = 263 mV and a third redox system *V-VI* appears at E_{pa} =

632 mV and E_{pc} = 515 mV. However, an increase in peak currents is observed only for the redox peak system *V-VI* by continuous cycling. This shows the characteristic behavior of a deposited electroactive substance [2,31,33]. The ratio of the anodic to the cathodic peak current gives a value of 0.86, which is not far from unity. The number of electrons transferred in the half reaction is calculated to be about 1.45. The background current and the precision of the potential measurements might have caused the deviations.

6.2.2 Electroactivity of poly-schiff base complex film

Once the Schiff base complex monomer is deposited, the electrode was transferred with careful rinsing to a fresh monomer free electrolyte (0.05 M H_2SO_4) solution. In the absence of the monomer, the glassy carbon electrode covered with the poly-schiff base complex film shows the redox peaks in acidic aqueous solution same as observed during the film formation (figure 12). The cyclic voltammogram of the bare glassy carbon in the same electrolyte solution was also obtained as shown in figure 12. The appearance of the redox peaks confirms the electro activity of poly-Schiff base complex in acidic solution [32].

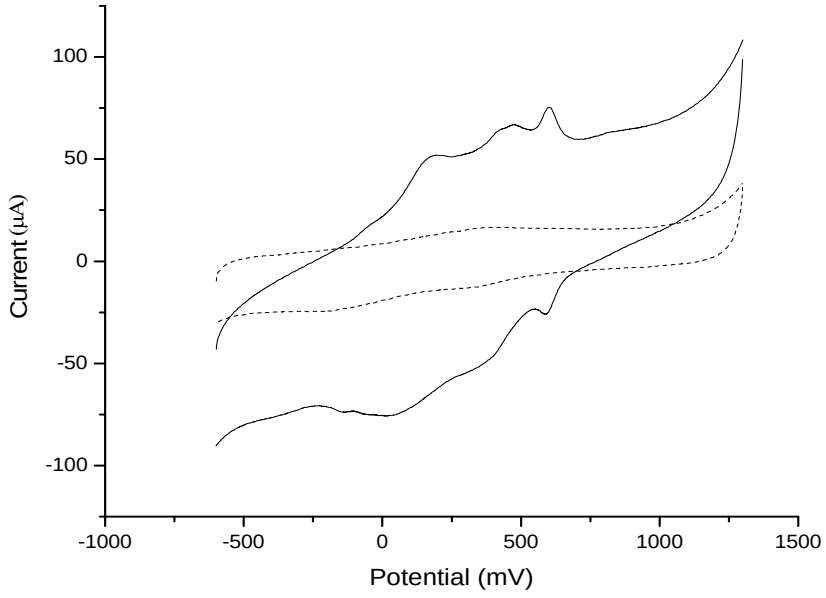


Figure12 Cyclic voltammograms of bare glassy carbon in acidic aqueous solution consisting of 0.05 M H_2SO_4 (----) and glassy carbon electrode covered with the poly-schiff base complex film in the absence of the monomer in 0.05 M H_2SO_4 (___). The film is prepared by sweeping the potential for 10 cycles at scan rate of 100 mV/s.

6.2.3 Effect of sulphuric acid concentration in the polymerization medium

The effect of H_2SO_4 concentration in the polymerization medium on the electroactivity of the poly-schiff base complex film was investigated for various [H_2SO_4] in the range from 0.05 to 2 M. Several $1x10^{-3}$ M Schiff base complex aqueous solutions were prepared in different sulphuric acid concentrations. Then, using each of these solutions, glassy carbon/poly-schiff base complex modified electrodes were prepared by sweeping the electrode potential between -1000 and 1500 mV at scan rate of 100 mV/s for 10 cycles. Figure 13 shows that the anodic peak currents (I_{pa}) of the redox system (*VI-V*) increases as the acid concentration in the preparation medium decreases up to 0.05 M H_2SO_4. In H_2SO_4 concentration less than 0.05 M, the solubility of the Schiff base complex is very less. Thus, 0.05 M H_2SO_4 was taken as the optimum H_2SO_4 concentration for the preparation medium. As the acid concentration in the preparation medium increases, there is a marked drop in the film electroactivity. This may be due to the partial distortion of the film active sites in the presence of high acid concentration [2].

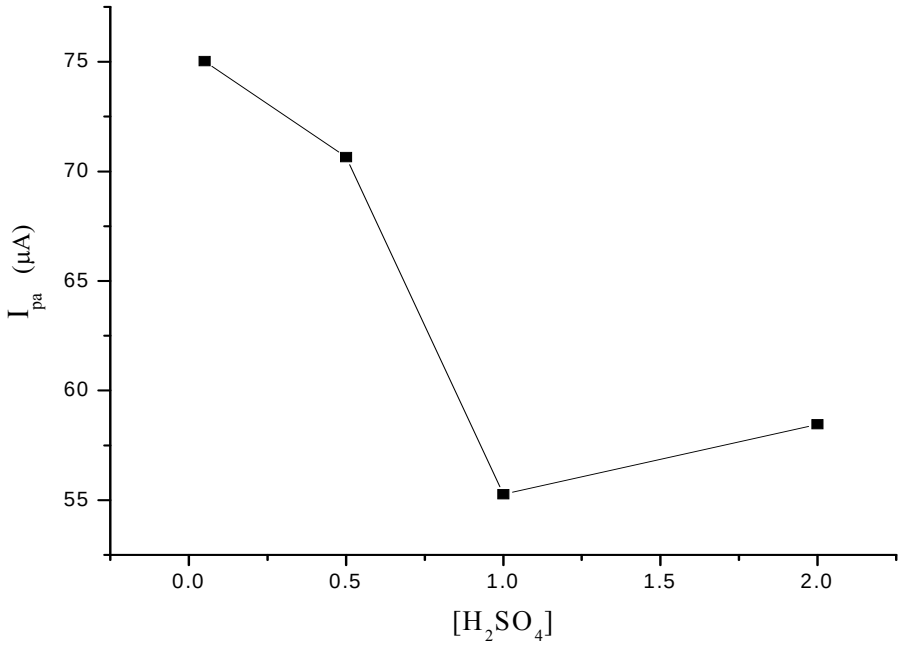


Figure 13 Effect of sulphuric acid concentration in the preparation medium on the electroactivity of the poly-schiff base complex film. The anodic peak currents were recorded for the redox peak system (*VI-V*) in monomer free solution after the electrode is modified by sweeping the potential for 10 cycles.

6.2.4 Effect of Scan rate

The effect of scan rate (*v*) on the electroactivity of poly-schiff base complex films deposited on the glassy carbon electrodes by ten polymerization cycles by sweeping the electrode potential between -1000 and 1500 mV was examined in the range from 40 to160 mV/s as shown in figure 14 (A).

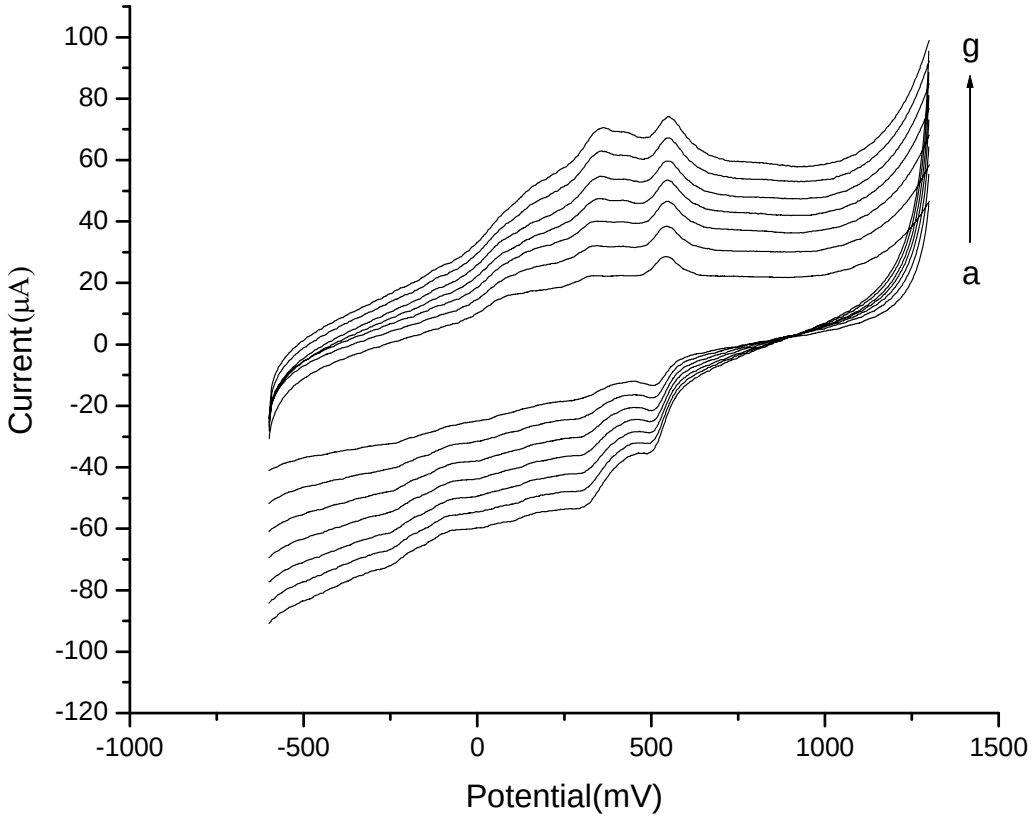


Figure 14 (A) Cyclic voltammograms of glassy carbon/film electrodes in 0.05 M H_2SO_4 aqueous solution at different scan rates (mV/s): a) 40, b) 60, c) 80, d) 100, e) 120, f) 140, g) 160. The film was produced for $1x10^{-3}$ M of Schiff base complex at glassy carbon electrode in an aqueous solution containing 0.05 M H_2SO_4 for 10 cycles. Scan rate (*v*) = 100 mV/s.

There is a linear relationship between the scan rate and the peak current (I_{pa}) of the redox system (*VI*-*V*). This can be observed by plotting I_{pa} with the scan rate as shown in the figure 14 (B). This is a typical behavior of a strongly adsorbed electrochemically active species and was intensively reported for film modified electrodes with thin layer behavior [2,31].

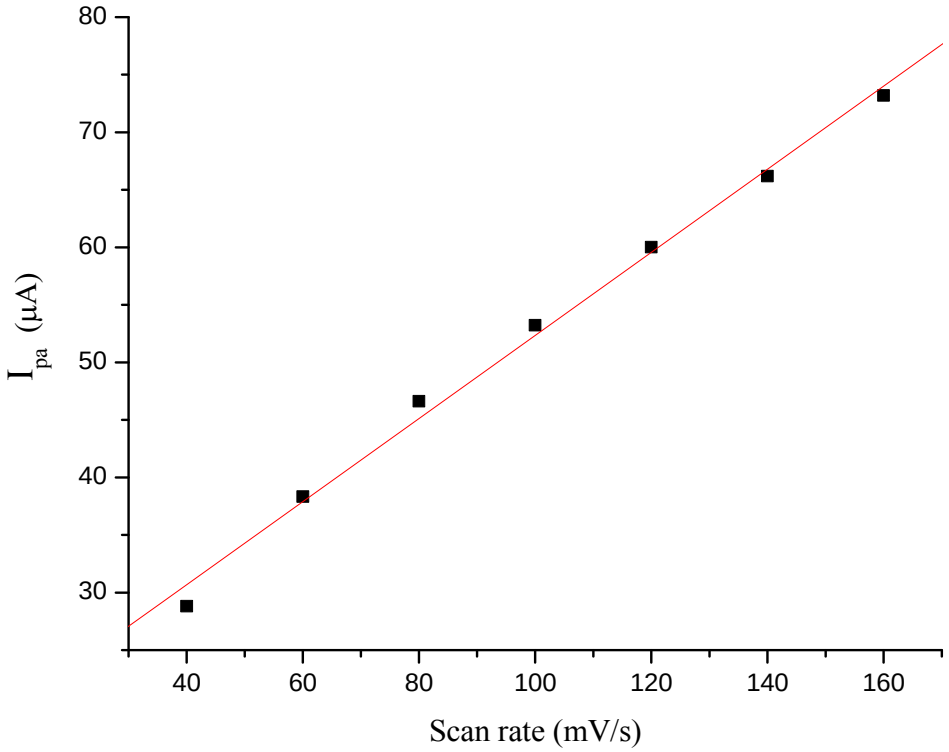


Figure 14 (B) Anodic peak currents (I_{pa}) of the redox system (*VI*-*V*) as a function of the potential scan rate (v). The films were produced for $1x10^{-3}$ M of Schiff base complex at glassy carbon electrode in an aqueous solution containing 0.05 M H_2SO_4 for 10 cycles. Scan rate (v) = 100 mV/s. Slope = (0.36 ± 0.1) μAs/mV and R = 0.9973.

6.2.5 Effect of pH

Figure 15 (A) shows the cyclic voltammograms of poly-schiff base complex film, deposited on a glassy carbon electrode, in aqueous solutions of various pHs between 1 and 5. As the pH increases: the waves shift to the negative direction of potential, the anodic and cathodic peak currents decreases slightly, and the potential separation between the anodic and cathodic peak potentials (ΔE_p) increases (figure 15 B). This behavior is due to the increase of the film resistance and the kinetics of the heterogenous electron transfer process at the electrode/polymer film interface and the homogenous charge transport process within the film [2,31]. The electroactivity of the film decreases continuously as the pH is increased and no appreciable charge transfer reaction across the film/solution interface takes place for pH

greater than 7. The plots of the cathodic and anodic peak potentials against pH gives slopes of -43 ± 5 and -31 ± 5 respectively. These values indicate that both reduction and oxidation processes are a 2 e^-/1 H^+ reactions [34,35]

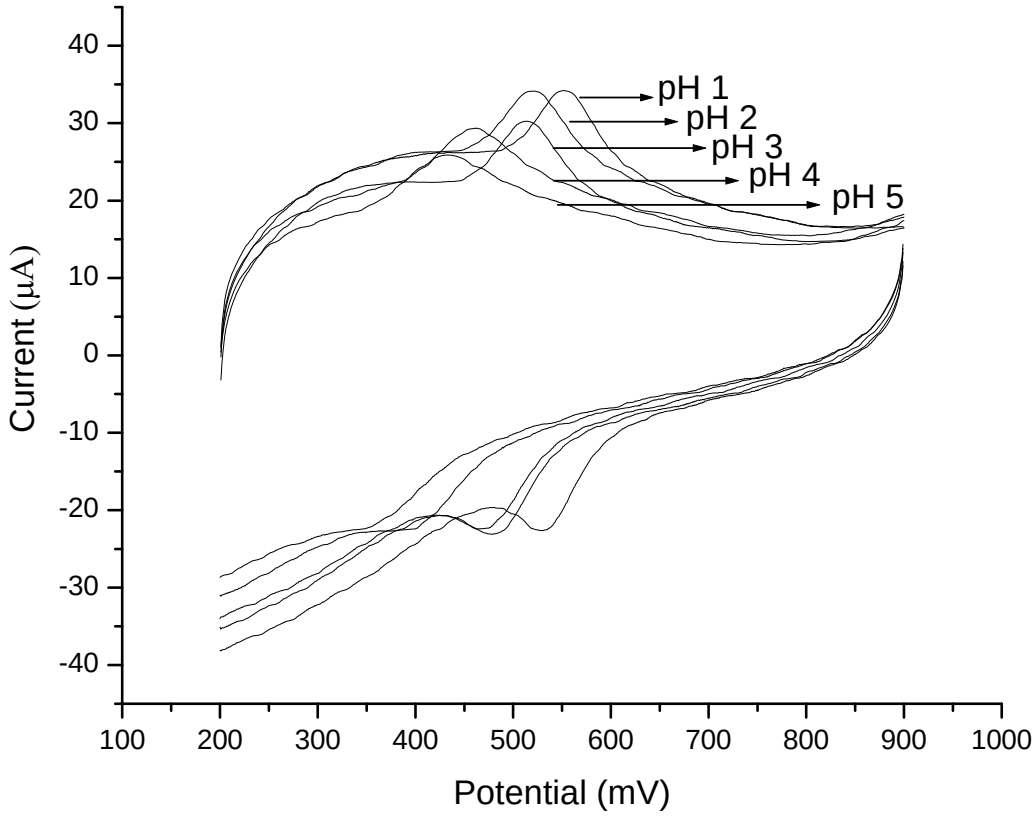


Figure15 (A) Cyclic voltammograms of poly-schiff base complex films of the redox system (*VI-V*) in aqueous solutions of different pHs (1 to 5). The films were produced for $1x10^{-3}$ M of Schiff base complex at glassy carbon electrode in an aqueous solution containing 0.05 M H_2SO_4. Scan rate (*v*) = 100 mV/s.

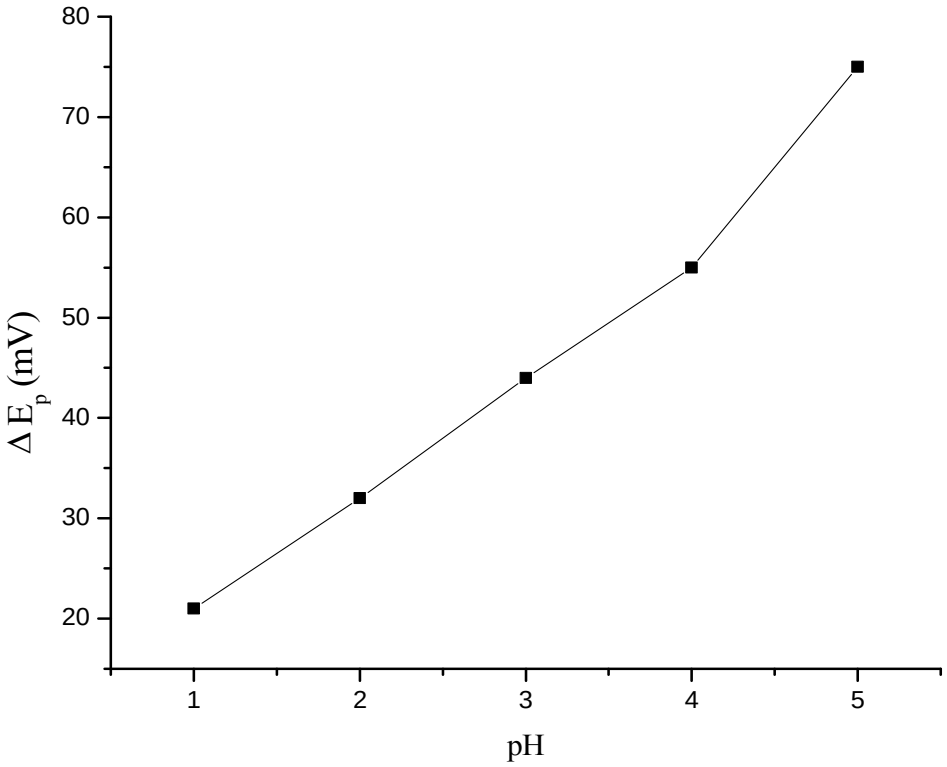


Figure 15 (B) Dependence of the peak separation, ΔE_p, of the poly-schiff base complex films on pH of the aqueous solution. The films were produced for $1x10^{-3}$ M of Schiff base complex at glassy carbon electrode in an aqueous solution containing 0.05 M H_2SO_4. Scan rate (v) = 100 mV/s.

6.2.6 Effect of the film thickness

The thickness of the poly-schiff base complex film is estimated or controlled by the number of cycles during polymerization. The film thickness affects the electroactivity and the stability of polymer film. Hence, investigating the number of cycles where the polymer has the best electroactivity is necessary. To do so, poly-schiff base complex films were prepared using different number of cycles in the range from 5 to 25. The anodic currents (I_{pa}) were taken as an index to follow the increase in thickness of the polymer film with increasing the number of cycles used for the polymer film formation. As figure 16 indicates, I_{pa} of the redox system increases with increasing the number of cycles to reach a limiting value of 10 cycles. After this value, the peak currents decrease with increasing number of cycles. This behavior implies the diminishing of the polymerization process as the film thickness

increases. This might be due to the retardation of the electron transfer through the polymer film. The increase in peak separation potential, ΔE_p, with increasing the number of cycles illustrates the fact that thicker films are more insulating than thinner ones for the poly-schiff base complex (figure 17) [2,31,33].

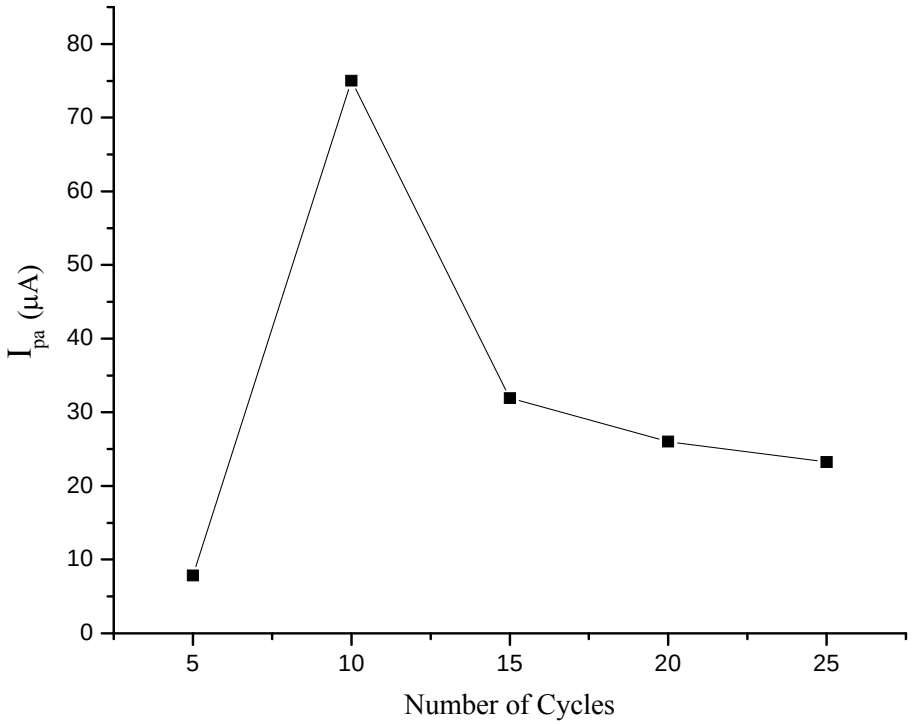


Figure 16 Dependence of the anodic currents (I_{pa}) of the film redox systems on the number of cycles of the film formation. The films were produced for $1x10^{-3}$ M of Schiff base complex at glassy carbon electrode in an aqueous solution containing 0.05 M H_2SO_4 for different cycles in the range from 5 to 25. Scan rate (v) = 100 mV/s.

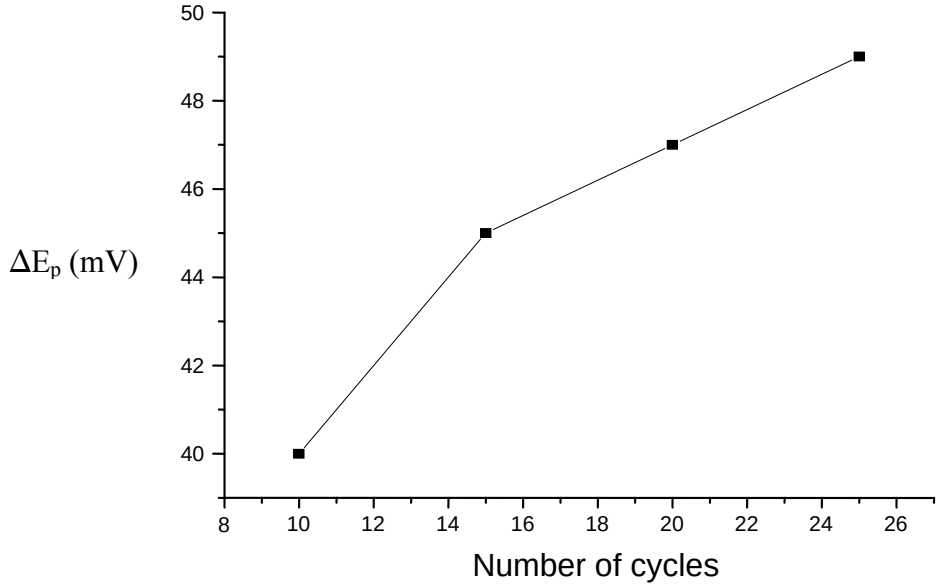


Figure 17 Dependence of the peak separation, ΔEp, of poly-schiff base complex film on the number of cycles of the film formation. The films were produced for $1x10^{-3}$ M of Schiff base complex at glassy carbon electrode in an aqueous solution containing 0.05 M H_2SO_4 for different cycles in the range from 10 to 25. Scan rate (v) = 100 mV/s.

6.2.7 Stability of the Schiff base complex film

Cyclic voltammetric response can also be used as a tool to examine the stability of the Schiff base complex film. The poly-schiff base complex modified electrode was prepared by sweeping the potential between -0.1 and 1.5 V at scan rate of 100mV/s for 10 cycles. Just after polymerization, the response of the modified electrode is more or less stable (after the first cycle) in 0.05 M H_2SO_4 (figure 18).

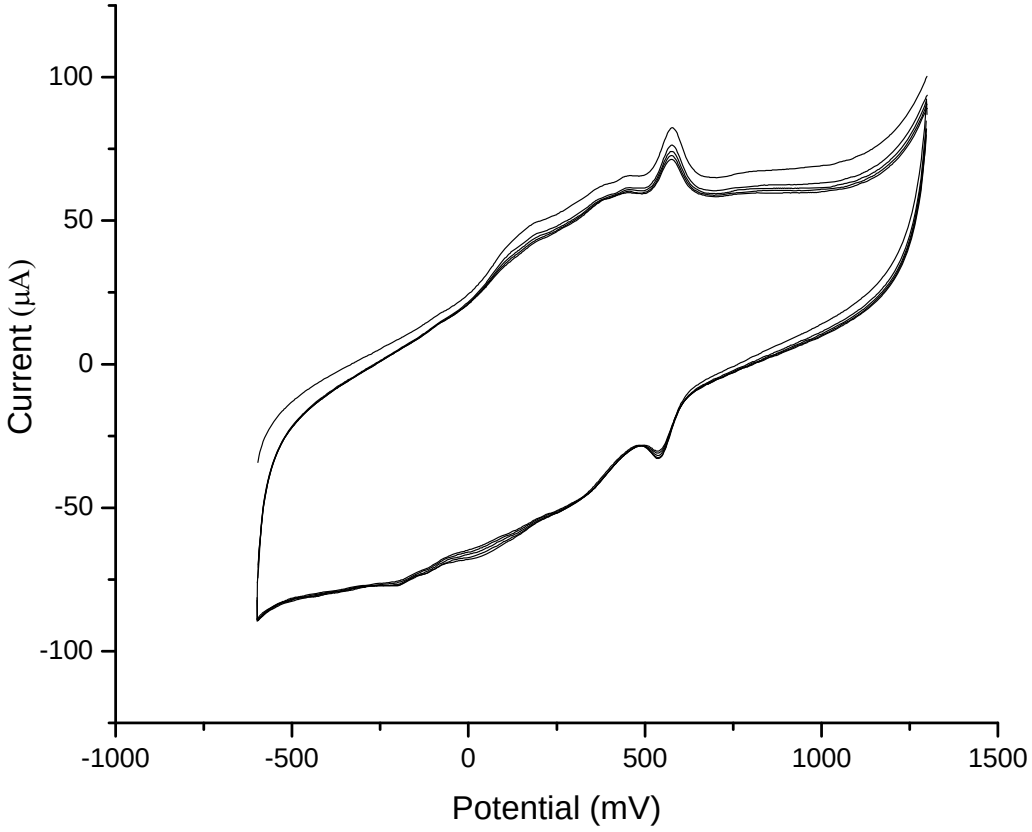


Figure 18 Cyclic voltammogram of poly-Schiff base complex modified electrode in 0.05 M H_2SO_4 aqueous solution just after polymer deposition for 5 cycles. The glassy carbon electrode is modified using $1x10^{-3}$ M of Schiff base complex in an aqueous solution containing 0.05 M H_2SO_4 for 10 cycles. Scan rate (v) = 100 mV/s.

Then, cyclic voltammogram was recorded for the modified electrode in 0.05 M H_2SO_4 solution just after the polymer deposition for one cycle. The stability of this modified electrode was checked by soaking it in 1 M H_2SO_4 for 2 hrs. When the cyclic voltammogram is recorded for this electrode in 0.05 M H_2SO_4 again, no appreciable change in the voltammogram was seen (figure 19 (A)). This shows the stability of the poly-schiff base modified electrode in acidic medium [33].

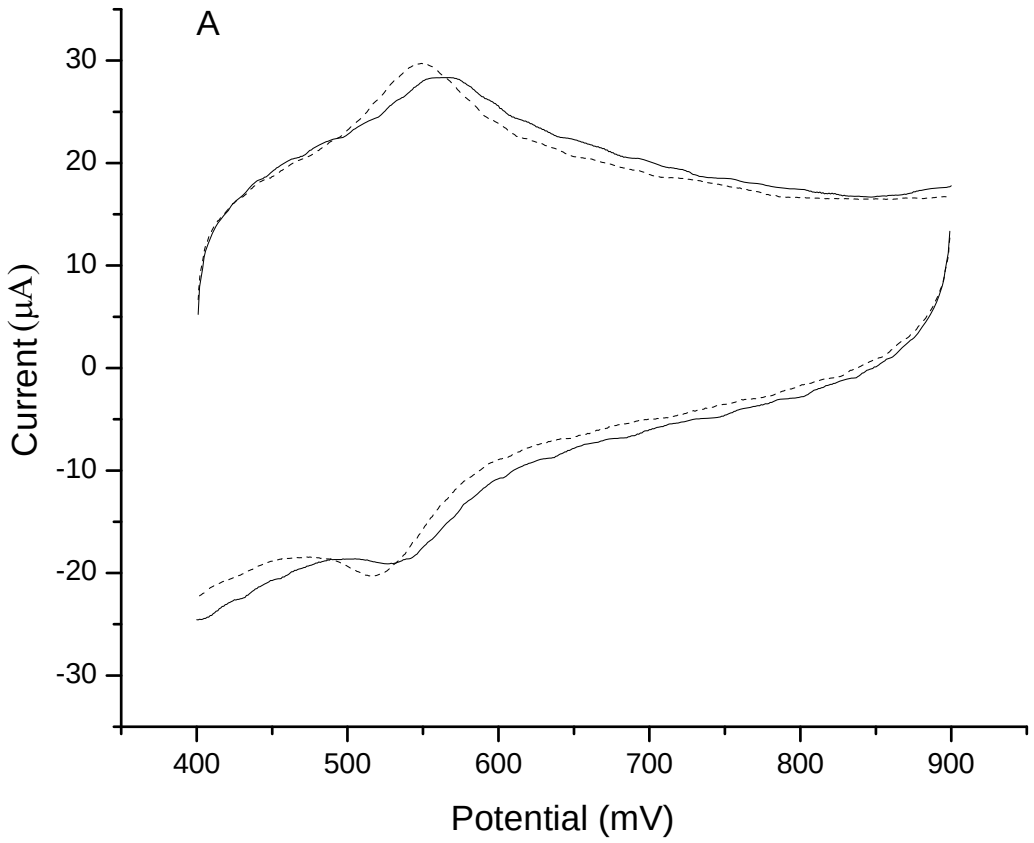


Figure 19 (A) Cyclic voltammograms of poly-Schiff base complex modified electrode in 0.05 M H_2SO_4 aqueous solution: just after polymer deposition(----), and after soaking in 1 M H_2SO_4 solution for 2 hrs (___). The glassy carbon electrode is modified using $1x10^{-3}$ M of Schiff base complex in an aqueous solution containing 0.05 M H_2SO_4 for 10 cycles. Scan rate (v) = 100 mV/s.

This same experiment was done for 1 M NaOH and the cyclic voltammograms for the polymer just after deposition and after soaking for 2 hrs in 1 M NaOH are shown in figure 19 (B). As can be seen from the figure, the I_{pa} drops by 74% and the I_{pc} decrease by 58%, and hence, the electroactivity of the polymer film reduces to a greater extent. This implies that the poly-Schiff base complex is unstable in basic medium. Furthermore, the stability of the polymer film was observed in methanol-water mixture (ratio 1:1 by volume). Figure 19 (C) indicates the cyclic voltammograms of the poly-schiff base complex film before and after soaking the modified electrode in methanol-water mixture. A very significant drop in

electroactivity (i.e., 90 % drop in I_{pa} and 87% drop in I_{pc}) was noticed in this case and thus the polymer film is unstable in solvents like methanol [32].

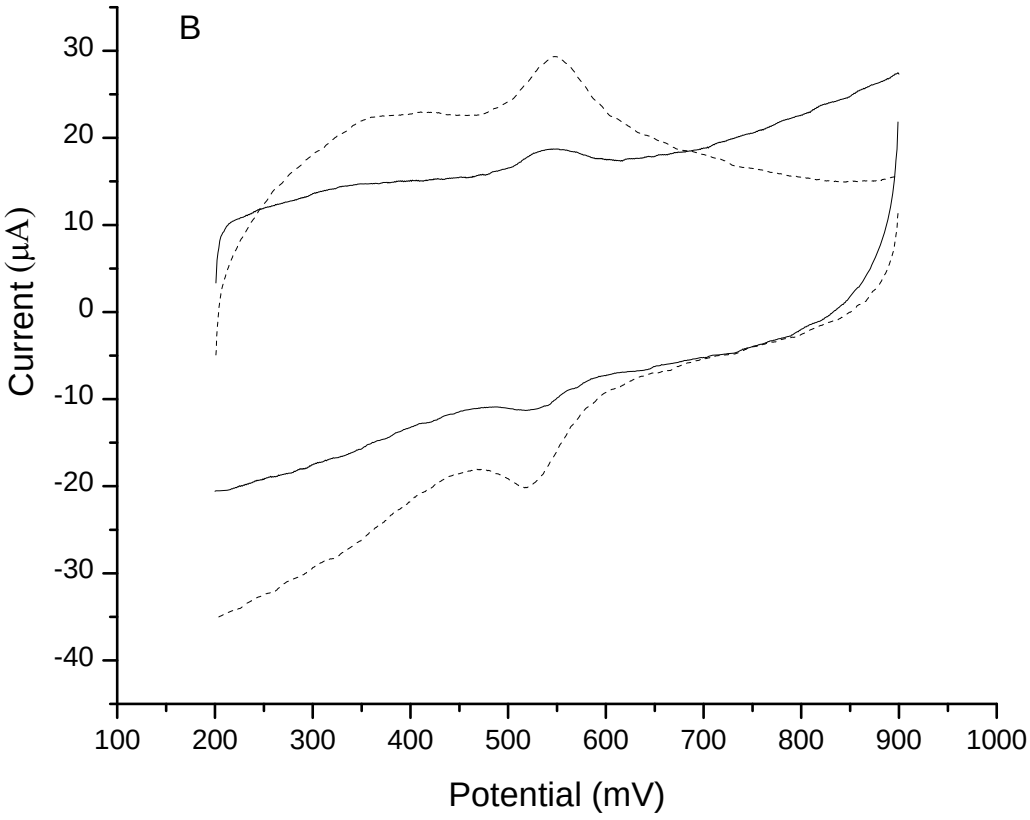


Figure 19 (B) Cyclic voltammograms of poly-Schiff base complex modified electrode in 0.05 M H_2SO_4 aqueous solution: just after polymer deposition (----), and after soaking in 1 M NaOH solution for 2 hrs (___). The glassy carbon electrode is modified using $1x10^{-3}$ M of Schiff base complex in an aqueous solution containing 0.05 M H_2SO_4 for 10 cycles. Scan rate (v) = 100 mV/s.

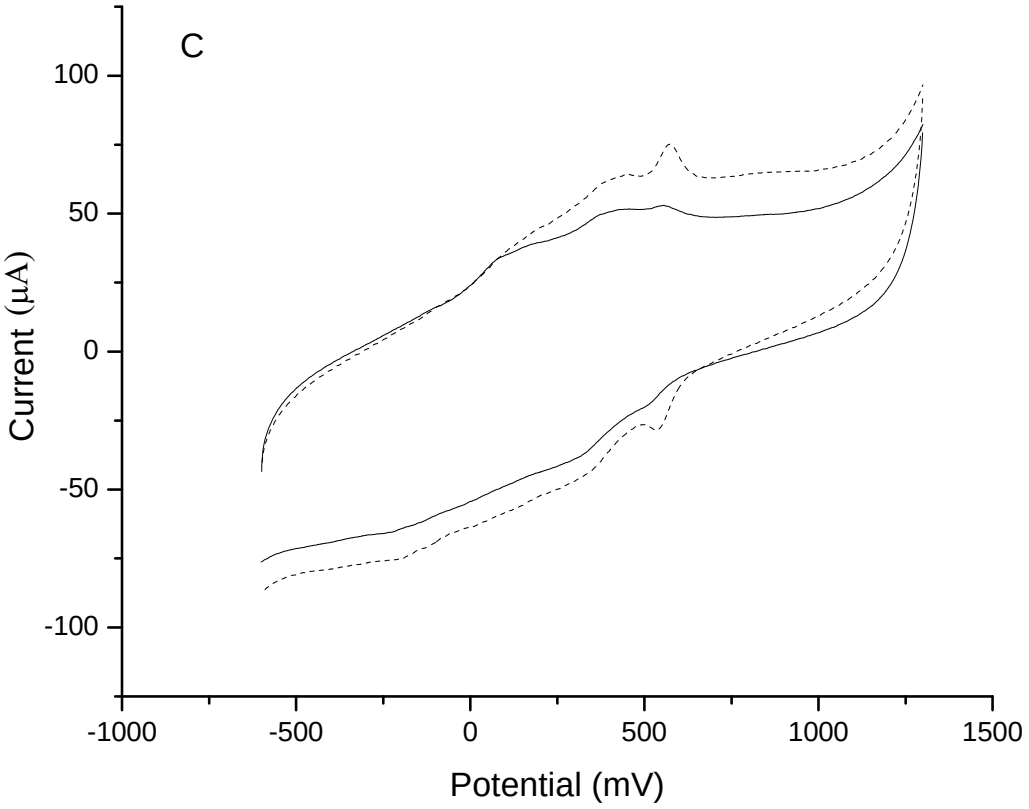


Figure 19 (C) Cyclic voltammograms of poly-Schiff base complex modified electrode in 0.05 M H_2SO_4 aqueous solution: just after polymer deposition (----), and after soaking in methanol-water mixture (ratio 1:1 by volume) for 2 hrs (___). The glassy carbon electrode is modified using $1x10^{-3}$ M of Schiff base complex in an aqueous solution containing 0.05 M H_2SO_4 for 10 cycles. Scan rate (v) = 100 mV/s.

7. Conclusions

Based on the above-mentioned results it can be concluded that both poly-ligand and the poly-Ni complex could be electrochemically prepared on glassy carbon electrode in aqueous dilute H_2SO_4 solutions. Some of the factors that affect the electroactivity of the produced films such as pH and number of cycles were studied. For the case of the Schiff base ligand (6-(2-hydroxyphenylamino)-1,10-phenan throlin-5-ol), the best electroactive redox response was obtained when the polymer is prepared by sweeping the potential for 20 cycles at scan rate 100 mV/s. The linear relationships between the scan rate and the anodic peak currents indicate that a thin electroactive layer of both Schiff bases was adsorbed on the electrode surface. Also, the film resistance of both poly-ligand and poly-complex was found to increase with increasing the pH of the solution. The best electroactive response of the films of the Schiff base-Ni complex is obtained if the film is prepared by 10 polymerization cycles at scan rate of 100 mV/s. The electroactivity of the Schiff base-Ni metal complex was also found to depend greatly on the concentration of sulphuric acid in which it is dissolved. It is found out that using acid concentration more than 0.5 M is accompanied by a marked decrease in the anodic peak currents of the redox couple (*V-VI*), and hence in the electroactivity. Finally, the poly-schiff base-Ni complex was found to be unstable in methanol-water (1:1) mixture and highly stable in 1 M H_2SO_4 solution after soaking the modified electrode for two hrs.

8. References

1. Craver, C. D.; Carraher, C. E. *Applied Polymers Science 21st Century*, 1st ed.; Elsevier Science Ltd: London, **2000**, pp 325-337.

2. Yousef, U. S. *Eur. Polym. J* **2000**, 36, 1629-1644.

3. Peter, T.K.; William, R.H. *Laboratory Techniques in Electroanalytical Chemistry*, 2nd ed.; Marcel Dekker, Inc: New York, **1996**, pp 76-91.

4. Juan-Carlos, V.; Esperanza, G. R.; Juan-Ramon, C. *Microchim. Acta* **2003**, 143, 93-111.

5. Sadki, S.; Schottland, P.; Brodiec, N.; Sabouraud, G. *Chem. Soc. Rev.* **2000**, 29, 283-293.

6. White, R. E.; Bockris, J. O.; Conway, B. E. *Modern aspects of Electrochemistry*, No. 33; Kluwer Academic/Plenum Publishers: New York, **1999**, pp 549-597.

7. Lund, H.; Hammerich, O. *Organic Electrochemistry*, 4th ed.; Marcel Dekker, Inc: New York, **2001**, pp 1309-1333.

8. Braun, D.; Cherdron, H.; Rehahn, M.; Ritter, H.; Voit, B. *Polymer Synthesis: Theory and Practice,* 4th ed.; Springer: Berlin, **2005**, pp 39-41.

9. Odian, G. *Principles of Polymerization*, 3rd ed.; John Wiley and Sons, Inc: New York, **1991**, pp 1-8.

10. Bard, A. J. *Electroanalytical Chemistry*, Vol. 13, 1st ed.; Marcel Dekker, Inc: New York, **1984**, pp 297-300.

11. Rubinstein, I. *Physical Electrochemistry*; *Principles, Methods and Applications*, 1st ed.; Marcel Dekker, Inc: New York, **1995**, pp 555-583.

12. Calhoun, A.; Voth, G. A. *J. Phys. Chem.* **1996**, 100, 10746-10753.

13. Boroda, Y. G.; Calhoun, A.; Voth, G. A. *J. Phys. Chem*. **1997**, 107, 8940-8954.

14. Anson, F. C. *J. Phys. Chem.* **1980**, 84, 3336-3338.

15. Daum, P.; Lenhard, J. R.; Rolison, D.; Murray, R.W. *J. Am. Chem. Soc*. **1980**, 102, 4649-4653.

16. Anson, F. C.; Saveant, J.; Shigehara, K. *J. Phys. Chem*. **1983**, 87, 214-219.

17. Bard, A. J.; Faulkner, L. R. *Electrochemical Methods, Fundamentals and Applications*, 2nd ed.; John Wiley and Sons, Inc: New York, **2001**, pp 24-27.

18. Tidwell, T.T *Angew. Chem. Int. Ed*. **2007**, 46, 2-7.

19. Räisänen, M. *Schiff Base Complexes and their Assemblies on Surfaces*, Ph. D thesis, University of Helsinki, Finland, **2007**, pp 1-30.

20. Mohamed, N. I.; Salah E. A. S. *E-J. Chem.* **2007**, 4, 531-535.

21. Vollhardt, K. P. C.; Schore, N. E. *Organic Chemistry*, 2nd ed.; W. H. Freeman and Company: New York, **1995**, pp 650-652.

22. Ayse, E.; Sema, O. Y.; Mehmet, A. *Chin. Chem. Lett*. **2006,** 17, 243-246.

23. Yildirim, L. T.; Emregul, K. C.; Kurtaran, R.; Atakol, O. *Cryst. Res. Technol.* **2002**, 37, 1344–1351.

24. Xishi, T.; Xianhong, Y.; Qiang, C.; Minyu, T. *Molecules* **2003**, 8, 439-443.

25. Kaliyappan,T.; Rajagopan, S.; Kannan, P. *J. App. Poly. Sci.* **2004**, 91, 494–500.

26. Raman, N.; Raja, J. D.; Sakthivel, A. *J. Chem. Sci*. **2007**, 119, 303–310.

27. Carey, F. A. *Organic Chemistry*, 3rd ed.; McGraw-Hill, Inc: New York, **1996**, pp 700-703.

28. Willard, H. H.; Merrit, L. L.; Dean, J. A.; Settle, F. A. *Instrumental Methods of Analysis*, 6th ed.; Litton Educational Publishing, Inc: Taiwan, **1981**, pp 712-713.

29. Harris, D. A. *Quantitative Chemical Analysis*, 4th ed.; W. H. Freeman and Company: New York, **1995**, pp 503-505.

30. Sawyer, D. T.; Sobkowiak, A.; Roberts, J. L. *Electrochemistry for Chemists*, 2nd ed.; John Wiley and Sons, Inc: New York, **1995**, pp 184-206.

31. Yousef, U. S.; Hathoot, A. A.; Abdel-Azzem, M. *Eur. Polym. J* **2001**, 37,1267-1276.

32. Losada, J.; Peso, I.; Beyer, L. *J. Electroanal.Chem.* **1998**, 447, 147-154.

33. Diab, A. S.; Hathoot, A. A.; Abdel-Azzem, M.; Merz, A. *Eur. Polym. J* **2000**, 36, 1959-1965.

34. Huang, W.; Humphrey, B. D.; MacDiarmid, A. G. *J. Chem. Soc., Faraday Trans.* **1986**, 82, 2385-2400.

35. Chen, C.; Gao, Y. *Electrochim. Acta* **2006**, 52, 3143-3148.

Declaration

I, the undersigned, confirm that the results reported in this work were obtained by research carried out by me under the supervision of my Advisor at the Faculty of Science, Department of Chemistry, Addis Ababa University in the academic year 2007 - 2008.

Name: _____ Signature: _____

This project work has been submitted for examination with my approval as university advisor.

Advisor: Dr. Shimelis Admassie

Signature: _____

Date: _____

Place and date of submission: School of Graduate Studies
Addis Ababa University
July 2008