RUTHENIUM-CONTAINING POLYMERS

-- SYNTHESIS, CHARACTERISATION AND ELECTROCHEMICAL PROPERTIES.

by

SUZANNE M. GERATY

A Thesis presented to Dublin City University for the degree of Doctor in Philosophy.

Chemistry Department,

Dublin City University.   July 1989

This thesis has not been submitted as an exercise for a degree at this or any other University. Except as otherwise indicated, the work herein has been carried out by the author alone.

SUZANNE M. GERATY.

TO MY PARENTS

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

Page

ABSTRACT

RUTHENIUM-CONTAINING POLYMERS
- SYNTHESIS, CHARACTERISATION AND ELECTROCHEMICAL PROPERTIES.

Author:- Suzanne M. Geraty, B.Sc., GRSC.

In this work, the synthesis and characterisation of a series of ruthenium-containing metallopolymers based on poly-N-vinylimidazole are reported, with a view to subsequently investigating their electrochemical properties and potential applications of electrodes modified with these polymers. The prepared complexes were characterised using spectroscopic and electrochemical techniques. It was found that the products, or ratios of products, obtained depended on the reaction conditions, i.e. polymer:metal ratios, reflux time and reaction solvent. The two main products obtained were of the from $[Ru(bipy)_2(PNVI)Cl]^+$ and $[Ru(bipy)_2(PNVI)_2]^{2+}$. The electrochemical properties of these materials were examined as films on the surface of glassy-carbon electrodes. Sweep-rate dependence, electrolyte dependence and film stability were subsequently studied. The electrochemical response was found to depend strongly on the nature of the supporting electrolyte. Glassy-carbon electrodes coated with methanolic solutions of $[Ru(bipy)_2(PNVICl]^+$ and $[Ru(bipy)_2(PNVI)_2]^{2+}$ were used to study the photochemical properties of these materials. Electrolyte dependence was again found to be very significant, both as a function of the reaction product and as a function of film stability. $[Ru(bipy)_2(PNVI)Cl]^+$ was found to exhibit interesting photochemical properties, particularly in sulphate-based electrolytes where a photostable sulphate intermediate complex was found to form. This lends possibilities to potential applications in switching devices. The photoresponsive properties of $[Ru(bipy)_2(PNVI)_2]^{2+}$ have also been investigated in the presence of suitable external quenchers. The diffusion co-efficient of the electron in the film was investigated using the technique of chronoamperometry. The charge-transport diffusion co-efficient was determined to be of the order of 10^{-10} $cm^2 s^{-1}$. The mediating properties of the monosubstituted complex were studied. This complex was found to catalyse the oxidation of Fe(II) to Fe (III) is aqueous solution. Two substrates, $(NH_4)_2Fe(SO)_2$ and $K_4Fe(CN)_6$ were studied for this purpose. Electrolyte and film thickness were found to be important features in the results obtained for these studies. All results obtained were compared to similar results previously obtained for polyvinylpyridine based analogues.

CHAPTER I

Properties and Applications of Modified Electrodes

I.1 Concept and Characteristics of Modified Electrodes

Twenty years ago the concept of controlling the surface structure of electrodes in a general way at the chemical level was unknown. Today, the electrode surface is seen to be the ground on which the electrochemistry of the next decade will be built [1].

The use of molecular reagents to manipulate the properties of electrode surfaces has attracted considerable attention recently due to the wealth of potential applications in areas such as electrocatalysis, electrochromic devices, the fabrication of molecular electronic devices and solar energy conversion [2 - 22].

In the 1960's electrochemists were directing their attention chiefly toward development of a selection of techniques for characterisation purposes. These new techniques included cyclic voltammetry and differential pulse voltammetry which were really developed around this time. Around 1970 some new techniques were emerging including Auger electron spectrometry and low-energy electron diffraction. These provided the ability to obtain information about surface structures. It was at this point realised among chemists that these surface structures could be

3

tailored or adapted for specific purposes. Thus the restriction to carbon and a few metals for electrode surfaces could be removed. It was thus realized that the surface of an electrode is a convenient place to build microstructures and putting adept ones there can prove to be very useful.

The development of modified electrodes only really started in 1975 as a result of the systematic work carried out by Murray's group in the United States [23]. Prior to this development, systems were investigated whereby molecules, such as alkynes or alkenes, where chemisorbed onto a platinum electrode surface [24]. This tendency for olefins to chemisorb irreversibly on platinum electrodes was thus exploited to attach a variety of reactive entities to the electrode surface and the electrochemical properties of these systems could then be investigated. Other work in this area investigated, for example, is the anchoring of a dinitrogen complex to the electrode surface [25]. Here Leigh and co-workers, adopting methods developed by Murray and his co-workers [26], anchored an organonitrile compound to a tin oxide electrode via the organic moiety and employed the free CN group to bind molybdenum and tungsten also bearing dinitrogen. These surface species were then characterised. In the early years of modified electrodes the main intention was to develop methods for making modified electrodes

and establishing the presence of the film on the host electrode surface. The properties of these films were also characterised. However, with significant progress in these areas the emphasis of interest has shifted and lies in the understanding of electron transfer processes etc. within the film.

Murray, being responsible for the earliest developments in modified electrodes, was also involved in a lot of the earliest examples of these modified electrode systems. In 1976, he reported electrochemical and ESCA evidence for the irreversible electrochemical reduction of methyl-pyridinium ions covalently bound to SnO_2 and TiO_2 electrodes [27]. With further work the same group reported the first example of a reversible electrochemical reaction for a redox centre covalently bound to an electrode surface [28].

One can divide the study of modified electrodes into three main areas:

1. the preparation and characterization of the films
2. the investigation of the applications of these systems
3. the kinetics of the electron transfer processes involved.

I will deal firstly with the former of these areas.

It has been shown that in a solvent in which both the oxidized and reduced forms of a polymer are insoluble or strongly adsorbed on the electrode, the electrode should closely resemble a chemically modified electrode [24, 25, 29 - 32]. A typical example of this type of system involves the preparation of a polyvinyl-ferrocene-coated platinum electrodes [33]. Other materials have also been used for the purpose of electrode modification, including $[Ru(NH_3)_5L]^{2+}$ (L is a large aromatic ligand) attached to a graphite electrode [34], or 2,2' bipyridyl complexes of ruthenium attached to platinum oxide electrodes [35], to name but a few. There are various described procedures for the attachment of a variety of molecules, such as pyridine-pentamineruthenium (II) complexes, to electrode surfaces [24, 27, 34, 36, 37]. Once on the surface these materials can then be characterised and their electrochemical properties as films rather than in solution can be studied.

Of all the materials used for electrode modification, polymeric molecules have advanced as one of the most potent agents in this regard. One of the most attractive aspects of polymeric coatings is the relative ease with which they can be applied -- simple dip coating by immersion of the electrode in a solution of the polymer often suffices to produce sufficient quantities of anchored ligand sites [33, 38]

6

- 40. Several examples of this have been presented in the literature [27, 29, 31, 39]. In 1979 work by Oyama and Anson [40] involved the attachment of polyvinylpyridine and polyacrylonitrile moieties to graphite electrode surfaces with the subsequent incorporation of ruthenium based ligands. In this manner, the behaviour of $[Ru(edta)]^{3+}$, $[Ru(NH_3)_5L]^{3+}$ and Cu(II) complexes was studied by electrochemical techniques i.e. cyclic voltammetry. Different properties of the system were investigated including the influence of supporting electrolyte concentration and ligand substitution reactions which were found to occur [40]. Still on the theme of polymeric coating, Nafion, an ion exchange polymer, has been studied in this regard [41]. $[Ru(bipy)_3]^{2+}$ was incorporated into the polymer film and the resulting electrode was studied electrochemically. Unusually large peak-to-peak separations were observed and explained by limitations in the overall rate of the redox process by mass transfer within the film, charge transfer at the substrate/film interface and associated chemical reactions of the electroactive forms. Peak currents were found to be proportional to (scan rate)$^{1/2}$ indicating that the current was controlled by electron diffusion in these thick polymer layers of Nafion - containing $[Ru(bipy)_3]^{2+}$.

There are several important characteristics of films

on electrode surfaces which have been investigated. One of the most prominent of these is the electrolyte effect which can influence various aspects including the voltammetric response, photoprocesses observed for various systems and electrocatalytic processes. It has been observed in several cases that the shape and nature of cyclic voltammograms obtained depend on the electrolyte used [32, 42 - 46]. This effect can be two-fold i.e. there can be a pH effect or the influence of the nature of the counter-ion which effects its penetration into a given polymer layer.

In 1976 work carried out by Brown and co-workers [32], relied upon the tendency of certain classes of reactants, phenanthrenequinones to adsorb very strongly on graphite electrodes to produce electroactive surface species which could subsequently be examined. Studies indicated the possibility of influencing the electrochemistry of these adsorbed reactants by altering the composition (pH, ligand concentration) of the electrolytes used for the electrochemical investigations. It was found that the peak potential shifted with each change in pH. Variations were also found when the electrolyte composition was altered e.g. with addition of imidazole or pyridine anodic shifts in peak potentials were observed.

Systems using poly(4-vinylpyridine) (PVP) or polyacrylonitrile, with incorporated $[Ru(edta)]^{3+}$ $[Ru(NH_3)_5L]^{3+}$ have been studied [40]. Differences between anodic and cathodic peak potentials were found to vary with electrolyte concentration. Decreasing the electrolyte concentration was found to increase the difference in the peak potentials. Overall, results showed that changes in ionic strength of supporting electrolytes composed of small unhindered ions can have profound effects of voltammograms obtained for reactants anchored to electrode surfaces - this is attributed to the double layer effects on charge transfer kinetics. Ewing and co-workers [47] have studied the permeability of polycationic complexes, anchored to electrode surfaces, to ferrocene, ferrocenium, tetracyanoquinodimethane (TCNQ) and $TCNQ^-$. Permeabilities were found to vary with electrolyte concentration. Permeability is independent of, decreases and increases, with decreasing electrolyte concentration, for the neutral compounds ferrocene and TCNQ, cationic ferrocenium and anionic $TCNQ^-$, respectively. The main factor governing the changing permeability with electrolyte concentration is the permeant partition coefficient into the polymer. The effect of the counter ion concentration on the cyclic voltammetric behaviour of TCNQ polymer film electrodes was studied in different aqueous electrolytes [48].

The variations of the peak currents and peak potentials as a function of the counter ion concentration is explained in terms of salt or ion-pair formation between the reduced redox sites in the film and the counter ions, as well as the polyelectrolyte behaviour of the surface layer. With increasing concentration of the supporting electrolyte, the reduced polymer film adopts a more compact structure and the diffusion of the counter ions becomes hindered.

There can also be situations where no dependence on the kind of supporting electrolyte is found [2]. Itaya and co-workers have shown that the structure of the polymer poly(N-methylethyleneimine), is not strongly affected by pH or the kinds of electrolyte used. On the other hand, Oyama and Anson [49] observed differences in the response of Ru(III)(edta) attached PVP modified electrodes with various supporting electrolytes. The difference was explained by the facilitation of electron transfer because of protonation of the pyridine groups. The comparison of the above two systems indicates that the electrochemical behaviour is dependent on the properties of the film materials.

In 1986, Doblhofer and co-workers [50] studied the role of ionic transport in polymer-modified electrodes with

10

poly-4-vinylpyridine based films. A combined diffusion/migration mechanism for $[Fe(CN)_6]^{3-}$ transport across the film is demonstrated. The overall observed effect is dependent on the electrolyte concentration.

The pH effect of the supporting electrolyte is also an important consideration and has been the subject of some study. In 1981, Samuels and Meyer devoted an entire paper to this theme where they employed an oxidation catalyst based on Ru(IV) bound to the electrode surface and studied pH "encapsulation" in a polymer film [45]. It was found that at pH values less than 4, the potentials of the couples in question varied with pH, whereas at pH values greater than 4, the redox couples were no longer found to respond to pH changes in the bulk solution. This was attributed to the deprotonation of the unbound pyridyl groups in the polymer at higher pH. Electron transfer in a surface coating polymer bound dopamine has also been found to depend on the pH of the supporting electrolyte [42]. Cheek and co-workers have studied at the potential-pH response of platinum surfaces modified by electropolymerised phenol (PhOH) films [51]. This response was studied over a pH range from 3 to 11. The pH response of the coated electrode indicated that protons could reach the electrode surface through the polymer film. It was also found that the film had

only a small effect on the pH response of the electrodes studied implying efficient electron transfer through the modified electrodes. The pK_a values of the surface bound anthraquinone polymers were determined [46]. One other point to note is the stability of the coating, which can often be largely dependent on the pH of the bulk solution [43]. It is also important to point out the influence of electrolyte composition/electrolyte pH on processes associated with the film e.g. photoprocesses. Other important parameters which have been investigated include scan rate effect and electron transport but these will be discussed in later chapters.

Apart from studies of films on electrodes one must also consider the modes of preparation of the modified electrode. Most of the work mentioned has involved the application of pre-prepared materials to the electrode surface. However another important means of film preparation is electrochemical polymerization. A solution of monomer can be oxidized (as with phenols) [51, 52] or reduced (as with activated olfins [53 - 56] under dry conditions) to intermediates which polymerize sufficiently rapidly as to form a polymer film directly on the electrode. This method tends to yield few gross pin-holes in the films since exposed surface reacts rapidly with monomer to accentuate polymer growth at the pin-holes. To grow films of

significant thickness, the polymer film must itself be redox active and capable of electrocatalytically oxidizing or reducing fresh monomer, or the polymer film must be rather permeable to fresh monomer. Otherwise electrode passivation soon occurs and film growth is halted.

I.2   **Applications of Modified Electrodes.**

Having discussed the preparation/studies of properties, of modified electrodes one must consider the impetus behind their development, which is largely due to their potential applications.

Surface confined redox-polymers can undergo large optical spectral changes upon oxidation and reduction. This may be useful in the development of new kinds of display devices. Molecule-based materials offer the ability to develop systems having a wide range of colours that depend on potential. Molecules sometimes have several accessible redox states, each with a characteristic spectrum. Studies of these type systems have lead to the development of several types of electrochromic devices [14, 22, 57 - 59]. Electrochromic polymers that are good electronic conductors in one redox level such as poly-3-methylthiophene [60], polypyrrole [61] or polyaniline [62] have been studied. Voltammetric and spectral studies

on thin films of Prussian Blue have shown interesting electrochromic properties [22, 63].

It has been shown that an electrode modified using bathophenanthrolinedisulfonate and polycations such as poly(N-methylpyridinium iodide), poly(N-methylethyleneimine) with an incorporated Fe complex can be used for the purpose of electrochromic applications [14]. A monomeric metal complex, tris (5,5'-dicarbo(3-acrylatoprop-1-oxy)-2,2'-bipyridine) ruthenium(II) was spin coated onto optically transparent SnO_2 and thermally polymerised to yield a polymer-modified electrode with multicolour electrochromic properties [64]. It has further been shown by Elliot et al. that electrodes modified with tris (5,5' - dicarboxyester -2, 2'-bipyridine) ruthenium(II) show electrochromic properties, with the advantage that these films are stable [64]. Normally redox chromophores have rather limited colour ranges. Discrete molecular species usually exist in a relatively small number of oxidation states, thus only a small selection of colours is possible. Mixtures of chromophores can cause complications with overlapping transitions so a single chromophore with a large number of oxidation states is advantageous. Spectroelectrochemical studies of a variety of tris complexes of ruthenium, with ring substituted bipyridine have shown properties which make several of

14

these complexes potentially interesting as redox adjustable chromophores.

Electrocatalysis, being one of the most important applications of modified electrodes, has been the subject of extensive and rapidly growing research. In some cases an application may be the result of the joint effect of photochemical and electrocatalytic properties. In biological systems e.g. the visible light-driven oxidation of cytochrome C indicates that it may be possible to exploit redox enzymes as catalysts for multielectron transfer, fuel-forming reactions [65]. Photocathodes or p-type semi-conductors have also been modified with molecule-based material to improve photoelectrochemical performance. A noteworthy example, with respect to optical energy conversion, concerns catalysis of hydrogen evolution [66]. One elegant and potentially useful example of electrocatalysis by means of molecular derivatization of a surface is the catalysis of the reduction of molecular oxygen in acid solution [67, 68].

Catalytic activity has been reported in the case of superficially oxidized graphite electrodes for the oxidation of ascorbic acid [1] and of a poly-p-nitrostyrene coated platinum electrode for the reduction of oxygen [39]. Other examples include the use of a poly (1,2 diaminobenzene) film electrode as a

15

potentiometric sensor for the determination of Co(II) in solution [69]. The catalysis of electrode processes, such as Fe(II) oxidation by multiply-charged metal complexes, such as $[IrCl_6]^{2-}$ electrostatically bound to polyelectrolyte coatings (PVP) on graphite electrodes and the use of polymer-coated rotating disc electrodes in diagnosing kinetic and conduction mechanisms for $[Fe(CN)_6]^{4-}$ oxidation by films of PVP with incorporated $Ru(II)(edta)^{3+}$ have been investigated [5]. In general, experiments in which electroactive, molecular species, bound to the surface of conductors are charged and in turn perform redox reactions on solution species have been the subject of a considerable amount of research [1 - 4, 39, 42, 70 - 72]. This effect is illustrated in Figure 1.1.

FIGURE 1.1 Schematic diagram of a modified electrode system .
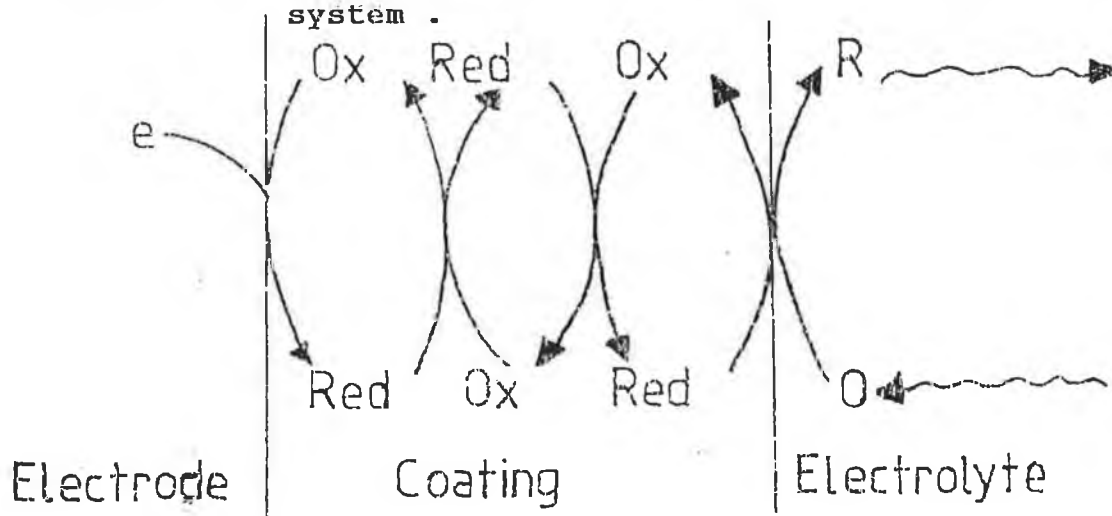
A most important aspect of electrocatalysis is the study of the kinetics and electron-transfer mechanisms, much of which has been carried out by .Andrieux, Saveant and co-workers [8, 18, 73 - 77]. A

detailed analysis of this area will be presented in Chapter 5.

Electrodes modified by electrochemically reversible compounds e.g. quinones and transition metal complexes, are widely used to catalyse the electrode reaction of organic compounds, e.g. NADH [78], ascorbic acid oxidation [9], oxygen [7] and carbonyl compounds reduction [79]. The use of redox enzymes and other biocatalyzers increase the possibilities of oxidative-reductive electrocatalysis considerably e.g. redox polymers for electrocatalytic oxidation or reduction of NAD and NADH containing redox enzymes. It has been shown that a benzidine modified pyrolytic graphite electrode can be used to catalyze an electrode reaction where ascorbic acid is the substrate in question [1]. The design of this system was greatly influenced by experience with mediators used to couple electron transfer between electrodes and biological redox components [80]. Dautaras and co-workers also investigated ascorbic acid oxidation using plasma polymerised vinylferrocence film electrodes [81]. Iron based substances also constitute quite a large proportion of the area of electrocatalysis [82 - 84]. Oxidation of Fe(II) [82, 83], mediation of the Fe(III)/Fe(II) oxido reduction [85], reduction/oxidation of ferrocene, ferrocenium, and tetracyanoquinodimethane [47], have been studied using

17

electrodes modified by films of polyvinylpyridyl bound ruthenium complexes. This type of catalysis has also been investigated using films of polyvinylpyridine with incorporated $[IrCl_6]^{-2}$ [86]. Still considering the iron containing substrates, the oxidation of Fe(II) to Fe(III) by multiply-charged metal complexes electrostatically bound to polyelectrolyte coatings on graphite electrodes has been investigated [2]. So poly-styrenesulfonate has been studied as a possible matrix for the mediated oxidation of [ferrocene-1,1'-disulfonate $[Fe(CpS)_2]^{2-}$ by electrostatically bound tris (2,2'bipyridine) osmium (III) [87].

The catalytic reduction of O_2 to H_2O_2 has been investigated using electrodes modified with polymeric attached metalloporphyrins [88] and adsorbed anthraquinone polymers [89]. Substrates of a more 'biological' nature have also been the subject of some research. This includes the oxidation of NADH by films of polymer-bound dopamine [42], mediation of the reduction of dissolved 1-aminophenazine, Ce(IV), Fe(III) and O_2 at electrodes coated with 1-aminophenazine [90] and the electrocatalytic oxidation of cytochrome-C at a quaternized poly-4-vinylchloride/ferricyanide modified gold surface [91].

The electrochemical response towards various other substrates has been investigated such as, organic

dihalide reduction by poly-p-nitrostyrene coated electrodes [92, 93], dibromoalkyl reductions using electrodes with covalently immobilized metallotetraphenylporphyrins [94], reduction of Fe(III) (edta)⁻ at electrodes coated with poly-l-lysine films [8], oxidation of $[Co(tpy)_2]^{2+}$, where tpy = 2,2',2"-terpyridine, at electrodes coated with poly-l-lysine copolymer with incorporated electroactive anions [95], and finally the oxidation of carboxylate anions at electrodes coated with poly(4,4'-dibromo-4"-vinyl triphenylamine) [96].

It has been shown that semi-conductor photoelectrodes provide a way of efficiently converting optical energy directly to electricity, or stored chemical energy in the form of high-energy redox products [97]. An approach to suppressing photocorrosion is to modify the semiconductor surface with a redox polymer that can recapture photogenerated oxidizing equivalents and transfer them to appropriate solution species [98]. One example of such is the suppression of silicon photoanode corrosion with anodically grown polypyrrole [99].

Basic research in the area of electrode modification has led to opportunities for the development of new kinds of microelectronic devices involving molecular materials as the active elements. Murray and co-

workers have demonstrated the possibility of fabrication microelectrochemical diodes having characteristics (turn-on voltage and switching speed) that depend on the combination of molecular materials used [55]. Polymer-polymer bilayer assemblies that could function as diodes, when immersed in an electrolytic solution, have been demonstrated [55]. Another important "device" demonstrated with a macroscopic system, is the ion-gate electrode which is an electroactive membrane [100]. Work involving surface modification to improve the rate of heterogeneous redox reaction of biological redox reagents (enzymes and their substrates) should prove especially fruitful in combination with microfabrication techniques.

The examples given have illustrated some of the potential applications of modified electrodes. More detailed descriptions of the applications which have been studied for this project will be given in the relevant chapters.

I.3   Modifying Materials

Having discussed the concept/characteristics and applications of modified electrodes one must now consider the materials which can and have been used for this purpose.

There has been a natural progression in the changes in materials used for electrode modification. Much of the early work in this area was carried out using chemically modified electrodes [24, 28, 35, 101, - 103]. Starting in 1973, the work of Lane and Hubbard involved the study of the electrochemistry of chemisorbed substituted olefins - alkynes and alkenes react with platinum surfaces to form irreversibly chemisorbed species which can be used to bind other reactants e.g. metal ions [24]. The prepared systems were studied by cyclic voltammetry. In 1977 Lenhard and Murray succeeded in binding organosilanes to a platinum electrode surface and 3,5 dinitrobenzamide to a platinum oxide surface, thereby achieving reversible electrochemically active systems [30]. In the same year, Moses and Murray achieved covalent binding of nitrobenzamides to the surface of SnO_2 electrodes again preparing chemically modified electrodes [28]. These systems were then studied by cyclic voltammetry and ESCA. Results showed that it was possible to obtain reversible electron transfer reactions for redox centres covalently bound to and separated from, an electrode by a saturated molecular chain.

Leigh and Pickett have described the anchoring to an electrode surface of a metal complex (organonitrile dinitrogen complexes of molybdenum and tungsten)

capable of binding dinitrogen - this is a first step in the development of an electron capable of mediating the protonation of alkylation of dinitrogen [25].

The ease with which complexes of edta (ethylenediaminetetraacetate) binds to the surface of a graphite electrode which is coated with polyvinylpyridine (PVP), or polyacrylonitrile (PAN) has been exploited [104]. This process is based on the fact that one of the carboxyl groups of the EDTA is not co-ordinated to the metal centre (Ru(III) in this case) and is, therefore available for coupling with amine groups on the electrode surface. Once attached to the electrode surface the ligand substitution chemistry of the metal complex can be studied as well as their functioning as redox catalysts. Procedures have been presented for attaching pyridine - pentamineruthenium (II) complexes to graphite electrodes by covalent binding and irreversible adsorption [34]. The electrochemical behaviour of the attached complexes was studied using differential pulse voltammetry and cyclic voltammetry.

Of all the materials used in electrode surface modification, ruthenium based metallopolymers represent a class of materials which have received a great deal of interest. Interest in the area of metallopolymers stems largely from the idea of

combining the potential advantages offered by polymeric materials with the extensive ground - and excited - state chemistry which has been established for poly(pyridyl) complexes of ruthenium. Monomeric and dimeric ruthenium complexes have proven to be of value in the development of redox catalysts [105, 106], for the existence of exploitable excited states [107] and as model compounds for the study of electon transfer processes [108]. Metallopolymers in which ruthenium-bipyridyl complexes are chemically bound to poly(4-vinylpyridine) [20, 91, 109 - 112] whose preparations are largely based on the substitutional chemistry of $Ru(bipy)_2Cl_2$ [20], have been extensively reported. There are numerous examples of the above mentioned polymers being used for the purpose of electrode modification. This facility of polymeric ligands to act as anchoring groups for the attachment of metal complexes to electrode surfaces has been studied [109]. In work by Oyama and Anson poly(4-vinylpyridine) was applied to a graphite electrode surface. The resulting coating had the ability to extract metal complexes, $[Ru(edta)]^{3+}$, $[Ru(NH_3)_5]^{3+}$ and Cu(II) complexes, from solution thus allowing their electrochemical behaviour when incorporated into a polymeric film, rather than in solution, to be investigated. This polymeric moiety has been employed for several such applications, [5, 20, 47, 49, 100 - 118]. Once on the electrode surface these

23

metallopolymeric materials can be characterised electrochemically and their electrochemical properties can be investigated with a view to developing potential applications already discussed.

The materials used for electrode modification are usually characterised largely by the potential of the redox couples exhibited in various electrolytes. Thus, by comparison with analogous materials it is possible to determine the nature of the materials in question. It is possible to determine the type of co-ordination of the metal-containing ligand to the polymer-coated electrodes [109, 113] and the quantity of the metal incorporated into the coating (by integration of peak area of a cyclic voltammogram) [111, 113, 117, 119]. With respect to electrochemical properties much effort has been directed towards electrolyte effect, charge transfer through the layer and sweep-rate dependency by these factors will be discussed in more detail at a later stage. The potential applications of these systems are very much dictated by the electrochemical properties mentioned above. For example, Oyama and Anson [5], employing electrodes coated with PVP containing $[IrCl_6]^{2-}$, were able to catalyse the oxidation of Fe^{2+} to Fe^{3+} (in solution). With detailed studies it was found in this case, possible to distinguish currents, limited by the rate of a redox reaction between a dissolved substrate

and a catalyst anchored to an electrode coating, from those limited by electron transfer through the coating.

Ruthenium based materials constitute a large percentage of the electroactive components incorporated into polymeric films. Many ruthenium complexes are electrochemically and substitutionally robust. A rich background of their synthetic, excited state and catalytic chemistry exists in homogeneous studies, their electron transfer rates are normally very fast and possibilities of multielectron transfer rates exist. Considerable attention has consequently been given to forming polymeric films containing ruthenium centres. Many of the films are based on co-ordination to performed polymers [49, 111] notably poly(vinylpyridine), either as polymer films already on electrodes, or in more conventional synthetic circumstances with later film forming steps. As is typical of such co-ordination chemistry, because of steric or electrostatic limitation, not all the polyvinylpyridine ligands in these films become bound to ruthenium centres. Other polymer containing ruthenium complexes have been based on electrochemical or organosilane polymerization of monomers of ruthenium complexes, which produces full metallated films and the most dense concentration of redox centres.

The earliest ruthenium-containing polymeric films are those reported by Oyama and Anson [49, 120]. These were derived from poly(vinylpyridine) and polyacrylonitrile films on basal plane graphite. These films were subsequently reacted with Ru(III)(edta), Ru(II)(edta), Cu^{2+} and $[Ru(NH_3)_5OH_2]^{3+}$ solutions. The resulting co-ordination reaction produced electrochemical waves at potentials appropriate for the pyridine co-ordinated forms of these complexes. The extent and stability of polymer adsorbed on carbon is best at high PVP molecular weight [49].

In similar work, Meyer and co-workers [111] and Haas and colleagues [114] have synthesized the polymer complexes $[PVP-Ru(II)(bipy)_2OH_2]^{2+}$ and $[PVP-Ru(II)(bipy)_2Cl]^+$ respectively. These films were found to exhibit well-developed, generally symmetrical waves at the expected Ru(III)/(II) potential. The preformed $[PVP-Ru(bpy)(trpy)]^{2+}$ polymers prepared by Calvert and Meyer [111] have been especially well characterised. The ratio of co-ordinated ruthenium redox sites to the total number of pyridine sites in the polymer was determined by elemental analysis, U.V./vis spectrophotometry, X-ray photoelectron spectrometry (XPS). Detailed electrochemical characterisation was also carried out. The reductive electrochemical polymerization of ruthenium complexes with vinyl-substituted ligands has been reported. Numerous

complexes of ruthenium have been electropolymerized to form electroactive films on electrodes and have been used successfully for many purposes [53 - 55, 121].

Of particular relevance to this project are ruthenium based metallopolymers or polyvinylpyridyl based materials. In 1980 Haas and Vos prepared and characterised electrodes coated with poly 4-vinylpyridine bound ruthenium complexes [110]. The ruthenium was incorporated in a bipyridyl complex. The metallopolymers [Ru(bipy)$_2$ClPVP]Cl and [Ru(bipy)$_2$py(PVP)]Cl$_2$ were prepared as described previously [20]. The fact that the redox potential of the ruthenium complexes is readily changed by the choice of the ligands and the possible catalytic activity of these compounds make this system attractive. The metallopolymeric complexes were attached to carbon, platinum, gold, rhodium and iridium electrodes. The peak intensity obtained from cyclic voltammograms was found to depend on the polymer: metal ratio in the product and also on the way the electrode was prepared. Better results were obtained using longer curing times for the electrodes. The linear dependence of the peak current on scan rate and the symmetrical voltammograms indicated fast electron exchanging species. The materials were characterised using U.V./vis spectroscopy and electrochemical studies.

The properties of poly(pyridyl) Ru(II) complexes of PVP were also studied by Calvert and Meyer [111]. These materials were prepared by reacting PVP with Ru(II) (2, 2', 2"-terpyridine) (2,2'-bypridine) $OH_2]^{2+}$. The preformed PVP-Ru(bpy)trpy polymers prepared here were especially well characterised. The ratio of co-ordinated ruthenium redox sites to the total number of pyridine sites in the polymer was determined by elemental analysis, U.V./vis spectrophotometry, NMR and X-ray photoelectron spectroscopy. Redox properties were also investigated. Overall, the data presented here suggested that a great deal of the chemistry of monomeric complexes can be extended to polymer-attached groups and that chemical composition of the resulting materials with regard to the extent of metallation can be established in detail. It has also been shown that the metallopolymers are not merely synthetic novelties but have the potential to elucidate fundamental questions regarding such diverse phenomena as the mechanism of charge transfer through polymeric matrices, intra-molecular energy and electron transfer and the effects of multiple excitation within polymer strands.

Work carried out by Kelly and co-workers using bipyridyl complexes of ruthenium follows largely as a result of their use as intermediates in the dissociation of water by visible light [112, 122]. They

have prepared and characterised hydride complexes $(Ru(bipy)_2(CO)H]^+$ and a series of polymeric materials reacting poly(2-vinylpyridine) or poly(4-vinylpyridine) with ruthenium (III) chloride in methanol. Reaction times and polymer to metal ratios were varied in order to give rise to the formation of different products which were determined by elemental analysis and infra red spectroscopy. Electronic spectra were considered, as had previously been used for bis(bipyridyl)ruthenium(II) complexes of poly(4-vinylpyridine) [20], in order to determine the co-ordination sphere of the complexes. As already mentioned, bipyridyl complexes of ruthenium (II) have been proposed as a photocatalyst for the decomposition of water by solar irradiation. For an efficient photochemical conversion system, the use of a heterogeneous reaction is desirable because a photochemical reaction in a homogeneous solution usually accompanies the backward reaction which consumes photochemically acquired energy. Thus, the backward reaction could be hindered if the reaction products could be separated from each other using a heterogeneous system. To achieve this, tris(bipyridyl)ruthenium (II) $[Ru(bipy)_3]^{2+}$ has been incorporated into monolayer assemblies, but the immobilization of this complex onto a polymer support must be also useful for this purpose. The first example of polymer-supported $[Ru(bipy)_3]^{2+}$ was

reported by Kaneko and co-workers [123]. They reacted low molecular weight polystyrene (PSt) with $[Ru(bipy)_3]^{2+}$. The formation of $(PSt-bpy)_3Ru$ complexes was confirmed by elemental analysis and U.V./vis and infra-red spectroscopy. They studied the photochemical reduction of methylviologen (MV^{2+}) and found that Pst pendant $[Ru(bipy)_3]^{2+}$ groups showed catalytic activity of the photoreduction of this species.

Mixed phosphine 2,2'-bipyridine complexes of ruthenium have also been prepared [124]. These were of the type $[(bpy)_2Ru(PPH_3)Cl]^+$ and $[(bpy)_2Ru(Ph_2PCH_2PPh_2)]^{2+}$ and were prepared from the reaction of the appropriate group 5 ligand and $Ru(bpy)_2Cl_2$. Spectral and electrochemical studies were used to find information about the nature of the Ru-group 5 ligand bond. It was also desired to develop a synthetic chemistry which would provide the basis for a series of di (tertiary phosphine)-bridged Ru-Ru dimers. The synthesised products were characterised using electronic spectra, NMR and redox properties as is the normal procedure.

Lindholm and Sharp have prepared polyelectrolyte coatings directly on glassy carbon electrodes by reacting PVP with alkyldihalides in the solid phase [86]. Hexachloroiridate and hexacyanoferrate were then

incorporated into these films. This was done for the purpose of catalysing or mediating the transfer of charge between the electrodes and a dissolved substrate. The stability and other properties of the films were studied electrochemically.

Redox couples that contain unbound amine, hydroxy or carboxylate groups can be incorporated at room temperature into p-chlorosulfonated polystyrene films via sulfonamide, sulfonester or sulfonanhydride linkages respectively [125]. This polymeric moiety has been used in a wide variety of applications including co-incorporation of more than one redox site, fabrication of bilayers in which different redox couples are held in separate films, selectivity and directed charge transfer for redox couples in the external solution and incorporation of emitting chromophores into the polymeric films. Polystyrene also offers the advantage of ease of preparation and control of molecular weight over a wide molecular weight range. Also an extensive background chemistry exists toward its functionalization. The p-chlorosulfonated polystyrene films can be cast onto virtually any surface including platinum and glassy carbon electrodes [125]. The redox couples incorporated in these films include polypyridyl complexes of ruthenium, osmium and iron. Before and after

incorporation, the films were characterised. Electrochemical studies included film stability, redox potentials of the incorporated electroactive species and also environmental dependence. As shown by electrochemical, spectral and excited state measurements, the bound redox sites retain many of the properties of their solution analogues.

Other types of polymeric materials have also been prepared and studied as films on electrode surfaces. Polyester has been prepared and deposited on platinum electrodes [126]. The films were analysed using X-ray photoelectron spectroscopy and high resolution scanning electron microscopy. Information concerning the extent to which the polymer layer inhibited electrochemical events was obtained by studying the electrochemical response of the ferrocene/ferrocenium couple in solution. The cyclic voltammograms obtained using a bare electrode and a polyester coated electrode indicated that the film impedes normal electron transport. It was also found that, using a coated electrode, a reversible ferrocene couple was obtained but no peak was observed for ferrous chloride. This thus illustrates a system of selective inhibition.

Yasuda and co-workers have prepared and studied novel semi-conducting organometallic polymers containing

((CO)$_3$M(3-diene)) groups where M is ruthenium or iron [127]. They have described the unique electrochemical properties of the complex poly [Fe(CO$_3$)(3-((vinyloxy)ethyl)-[4]-1,3-pentadiene)] and the analogous ruthenium complex.

More recently distyryl bipyridine and methyldistyryl bipyridine complexes of iron, ruthenium, osmium and cobalt have been prepared by electropolymerisation [128]. The metal complexes are firstly synthesised and subsequently electropolymerised - the ligands undergo coupling reactions when the complexes are reduced electrochemically, resulting in the formation of smooth and adherent electroactive polymeric films on platinum electrodes. The electrochemical properties of these films could then be studied in detail.

Systems consisting of polycationic coatings of protonated poly(L-lysine) with incorporated electroactive anions have been prepared and studied by Anson and co-workers [8, 95] and have been used to study the kinetics of electron transfer cross reactions within redox polymers.

Poly(vinylferrocene) (PVF) has been widely used to modify electrodes. PVF has been deposited photochemically [129] and electrochemically in its oxidized form [33, 130] as poly(vinylferrocinium)

perchlorate. Vinylferrocene has been polymerized at the electrode surface by radiofrequency plasma discharge [81], [131], or by electrochemical reduction in acetonitrile solution. These films have been studied by cyclic voltammetry and have found application in, for example, electrocatalysis [132].

There are numerous other examples of materials which have been used to prepare modified electrodes, including oxidized 1,2 diaminobenzene [69] metallophenylporphyrins [94], anthroquinone polymers [89], poly-4-vinyl chloride/ferricyanide [91] p-chlorosulfonated polystyrene [132], and polymerized complexes of 4,4'distyryl-2,2'bipyridine (with metal containing ligands incorporated) [126]. Examples of other such systems are too numerous to mention but a most comprehensive list is available in the RSC Annual Report, 1981 [23].

The subject of this research has involved the preparation of some poly-N-vinylimidazole based metallopolymers, results of which have been reported [133], [134]. The interest in imidazole is largely due to its analogues present in biological systems. Transfer of an electron from one site to another in a molecule or between molecules is one of the most fundamental and ubiquitous processes in chemistry. As such it has been the focus of experimental and theoretical studies

34

for decades. In many relatively simple systems, the process is well-understood. That is not true in biological systems where electron transfer is an essential component of oxidation-reduction reactions. In an investigation of such systems ruthenium has been found to play an important role in studying the electron transfer process within protein molecules. Much of this work has been carried out by H. B. Gray at the California Institute of Technology and S. S. Isied at Rutgers University. Many proteins contain imidazole rings in the form of L-histidine and these groups are thought to be responsible for most of the buffering capacity of proteins in the physiological pH range and appear to be the principal sites of several hydrolytic enzymes - this has stimulated a study of the catalytic properties of polyvinylimidazole. The ability of imidazoles to complex with metals and bind dyes, the hydrophilicity of monomers and polymers and the latter's polyelectrolyte behaviour have stimulated interest in imidazole containing polymers for potential industrial users. Much of the polymer synthetic work involving the imidazole unit has been carried out by Bamford and Schofield [135].

The aim of this research project has been to synthesise, characterise and also to investigate the electrochemical, photochemical and mediating properties of a series of ruthenium-containing poly-N-

vinlyimidazole based metallopolymers. Results obtained from these studies could be compared to those obtained previously for poly-4-vinylpyridine analogues. Experimental details are given in Chapter II followed by the synthesis and characterisation which is contained in Chapter III. Details of the electrochemical studies will be given in Chapter IV. The photochemical properties and mediating properties of these metallopolymers are given in Chapters V and VI respectively. Conclusions drawn from this research are given in Chapter VII.

REFERENCES

1. J. F Evans, T. Kuwana, M. T. Henne and G. P.
    Royer,
    J. Electroanal. Chem., Interfacial Electro-
    chemistry, 80, 1977, 409.

2. L. L. Miller and M. R. Van de Mark,
    J. Am. Chem. Soc., 100, 1978, 3223.

3. D. C. Tse and T. Kuwana,
    Anal. Chem., 50, 1978, 1315.

4. J. B. Kerr and L. L. Miller,
    J. Electroanal. Chem., Interfacial Electro-
    chemistry, 101, 1978, 263.

5. N. Oyama and F. C. Anson,
    Anal. Chem., 52, 1980, 1192.

6. K. Shigehara and F. C. Anson,
    J. Electroanal. Chem., Interfacial Electro-
    chemistry, 139, 1982, 383.

7. P. Martigny and F. C. Anson,
    J. Electroanal. Chem., Interfacial Electro-
    chemistry 139, 1982, 383.

8.   F. C. Anson, J. M. Saveant and K. Shigehara,
     J. Am. Chem. Soc., 105, 1983, 1096.

9.   K. Kuo and R. W. Murray,
     J. Electroanal. Chem., Interfacial Electro-
     chemistry, 131, 1982, 37.

10. R. H. Schmehl and R. W. Murray,
     J. Electroanal. Chem., Interfacial Electro-
     chemistry, 152, 1983, 97.

11. F. C. Anson, J. M. Saveant and Y. M. Tsou,
     J. Electroanal. Chem., Interfacial Electro-
     chemistry, 178, 1984, 113.

12. M. S. Wrighton,
     Am. Chem. Soc. Symp. Ser., 192, 1982, 99.

13. F. B. Kaufman, A. H. Schroeder, E. M. Patel and V.
     Patel,
     Appl. Phys. Lett., 36, 1980, 422.

14. K. Itaya, H. Akohoshi and S. J. Toshima,
     J. Electrochem. Soc., 129, 1982, 762.

15. W. J. Albery and A. R. Hillman,
     Ann. Rep. Prog. Chem., Sect. C, 78, 1981, 377.

16. P. G. Pickup and R. W. Murray,
    J. Am. Chem. Soc., 105, 1983, 4510.

17. C. Amatone, J. M. Saveant and D. J. Tessier,
    J. Electroanal. Chem., Interfacial Electro-
    chemistry, 147, 1983, 39.

18. F. C. Anson, T. Ohsaka and J. M. Saveant,
    J. Phys. Chem., 87, 1983, 6210.

19. G. P. Kittlesen, S. H. White and M. S. Wrighton,
    J. Am. Chem. Soc., 107, 1985, 7373.

20. J. M. Clear, J. M. Kelly, D. C. Pepper and J. G.
    Vos,
    Inorg. Chim. Acta, 33, 1979, L139.

21. O. Haas, H. R. Zumbrunnen and J. G. Vos,
    Electrochim. Acta, 30, 1985, 1151.

22. C. D. Ellis, M. Eckhoff and V. D. Neff,
    J. Phys. Chem., 85, 1981, 1225.

23. W. J. Albery and A. R. Hillman,
    Royal Soc. Chem. Annual Report, 78, 1981, 377.

24. R. F. Lane and A. T. Hubbard,
    J. Phys. Chem., 77, 1973, 1401.

25. G. J. Leigh and C. Pickett,

    J. Chem. Soc. Dalton Trans., 1977, 1797.

26. P. R. Moses, L. Wier and R. W. Murray,

    Anal. Chem., 47, 1975, 1882.

27. P. R. Moses and R. W. Murray,

    J. Am. Chem. Soc., 98, 1976, 8272.

28. P. R. Moses and R. W. Murray,

    J. Electroanal. Chem., Interfacial Electro-
    chemistry, 77, 1977, 393.

29. B. F. Watkins, J. R. Behling, E. Kariv and L. L. Miller,

    J. Am. Chem. Soc., 97, 1975, 3549.

30. J. C. Lennox and R. W. Murray,

    J. Electroanal. Chem., Interfacial Electro-
    chemistry, 78, 1977, 395.

31. A. Diaz,

    J. Am. Chem. Soc., 99, 1977, 5838.

32. A. P. Brown, c. Koval and F. C. Anson,

    J. Electroanal. Chem., Interfacial Electro-
    chemistry, 72, 1976, 379.

33. A. Merz and A. J. Bard,
    J. Am. Chem. Soc., 100, 1978, 3222.

34. C. A. Koval and F. C. Anson,
    Anal. Chem., 50, 1978, 1223.

35. H. D. Abruna, T. J. Meyer and R. W. Murray,
    Inorg. Chem., 18, 1979, 3233.

36. J. R. Lenhard and R. W. Murray,
    J. Electroanal. Chem., Interfacial Electro-
    chemistry, 78, 1977, 195.

37. A. P. Brown and F. C. Anson,
    Anal. Chem., 49, 1977, 1589.

38. L. L. Miller and M. R. Van de Mark,
    J. Am. Chem. Soc., 100, 1978, 639.

39. M. R. Van de Mark and L. L. Miller,
    J. Am. Chem. Soc., 100, 1978, 3225.

40. N. Oyama and F. C. Anson,
    J. Am. Chem. Soc., 101, 1979, 739.

41. I. Rubinstein and A. J. Bard,
    J. Am. Chem. Soc., 102, 1980, 6641.

42. C. Degrand and L. L. Miller,

    J. Am. Chem. Soc., 102, 1980, 5728.

43. N. K. Cenas, A. K. Pocius and J. J. Kulys,

    Bioelectrochem. Bioenerg., 12, 1984, 583.

44. A. H. Schroeder and F. B. Kaufman,

    J. Electroanal. Chem., Interfacial Electro-
    chemistry, 113, 1980, 209.

45. G. J. Samuels and T. J. Meyer,

    J. Am. Chem. Soc., 103, 1981, 307.

46. C. Degrand and L. L. Miller,

    J. Electroanal. Chem., Interfacial Electro-
    chemistry, 117, 1981, 261.

47. A. G. Ewing, B. F. Feldman and R. W. Murray,

    J. Phys. Chem., 89, 1985, 1263.

48. G. Inzelt, J. Bacskai, J. Q. Chambers and R. W.
    Day,

    J. Electroanal. Chem., Interfacial Electro-
    chemistry, 201, 1976, 301.

49. N. Oyama and F. C. Anson,

    J. Electrochem. Soc., 127, 1980, 640.

50. K. Doblhofer, H. Braun and R. Lange,
    J. Electroanal. Chem., Interfacial Electro-
    chemistry, 206, 1986, 93.

51. G. Cheek, c. P. Wales and R. J. Nowak,
    Anal. Chem., 55, 1983, 380.

52. M. C. Pham, P. C. Lacaze and J. E. Dubois,
    J. Electroanal. Chem., Interfacial Electro-
    chemistry, 99, 1979, 331.

53. H. D. Abruna, P. Denisevich, M. Umana, T. J. Meyer
    and R. W. Murray,
    J. Am. Chem. Soc., 103, 1981, 4727.

54. P. Denisevich, K. W. Willman and R. W. Murray,
    J. Am. Chem. Soc., 103, 1981, 4727.

55. P. Denisevich, H. D. Abruna, C. R. Leidner, T. J.
    Meyer and R. W. Murray,
    Inorg. Chem., 21, 1982, 2153.

56. K. W. Willman and R. W. Murray,
    J. Electroanal. Chem., Interfacial Electro-
    chemistry, 133, 1982, 211.

57. M. Ito and T. Kuwana,

   J. Electroanal. Chem., Interfacial Electro-
   chemistry, 32, 1971, 415.

58. A. Desbene - Monvernay, P. C. Lacaze, J. e. Dubois
   and P. L. Desbene,

   J. Electroanal. Chem., Interfacial Electro-
   chemistry, 152, 1982, 87.

59. D. C. Bookbinder and M. S. Wrighton,

   J. Electrochem. Soc., 130, 1983, 1080.

60. J. W. Thackeray, H. S. White and M. S. Wrighton,

   J. Phys. Chem., 89, 1985, 5133.

61. K. S. Kanazawa,

   J. Chem. Soc., Chem. Commun., 1979, 854.

62. T. Kobayashi, H. Yoneama and H. Tamura,

   J. Electroanal. Chem., Interfacial Electro-
   chemistry, 161, 1984, 419.

63. V. D. Neff,

   J. Electrochem. Soc., 125, 1978, 887.

64. C. M. Elliot and J. G. Redepenning,

   J. Electroanal. Chem., Interfacial Electro-
   chemistry, 197, 1986, 219.

65. B. A. Parkinson and P. F. Weaver,
    Nature (London), 309, 1984, 148.

66. J. A. Bruce, T. Murahashi and M. S. Wrighton,
    J. Phys. Chem., 87, 1982, 1552.

67. R. R. Durand Jr., C. S. Bencosme, J. P. Collman
    and F. C. Anson,
    J. Am. Chem. Soc., 105, 1983, 2710.

68. J. P. Collman, M. Marrocco, P. Denisevich, C.
    Koval and F. C. Anson,
    J. Electroanal. Chem., Interfacial Electro-
    chemistry, 101, 1979, 117.

69. W. R. Heineman, J. J. Wieck and A. M. Yacynych,
    Anal. Chem., 52, 1980, 345.

70. J. M. Bolts and M. S. Wrighton,
    J. Am. Chem. Soc., 101, 1979, 6176.

71. N. Kobayashi, T. Matsue, M. Fujihira and T. Osa,
    J. Electroanal Chem., Interfacial Electro-
    chemistry, 103, 1979, 427.

72. J. B. Kerr, L. L. Miller and M. R. Van de Mark,
    J. Am. Chem. Soc., 102, 1980, 3383.

73. C. P. Andrieux and J. M. Saveant,

    J. Electroanal. Chem., Interfacial Electro-
    chemistry, 93, 1978, 163.

74. C. P. Andrieux, J. M. Dumas Bouchiat and J. M.
    Saveant,

    J. Electroanal. Chem., Interfacial Electro-
    chemistry, 114, 1980, 159.

75. C. P. Andrieux, J. M. Dumas Bouchiat and J. M.
    Saveant,

    J. Electroanal. Chem., Interfacial Electro-
    chemistry, 131, 1982, 1.

76. C. P. Andrieux and J. M. Saveant,

    J. Electroanal. Chem., Interfacial Electro-
    chemistry, 171, 1984, 65.

77. C. P. Andrieux, J. M. Dumas Bouchiat and J. M.
    Saveant,

    J. Electroanal. Chem., Interfacial Electro-
    chemistry, 169, 1984, 9.

78. O. Chi-Sing Tse and T. Kuwana,
    Anal. Chem., 50, 1978, 1315.

79. L. Roullier, E. Waldner and E. Laviron,
    J. Electroanal. Chem., Interfacial Electro-
    chemistry, 139, 1982, 199.

80. T. Kuwana and W. R. Heinemann,
    Bioelectrochem. Bioenerg, 1, 1974, 389.

81. M. F. Dautaras and J. F. Evans,
    J. Electroanal. Chem., Interfacial Electro-
    chemistry, 109, 1980, 301.

82. O. Haas and J. G. Vos,
    J. Electroanal. Chem., Interfacial Electro-
    chemistry, 113, 1980, 139.

83. S. M. Geraty, D. W. Arrigan and J. G. Vos,
    "Electrochemistry Sensors and Analysis",
    M. R. Smyth and J. G. Vos, Editors,
    P. 303, Elsevier Pub. Co., Amsterdam (1986).

84. J. F. Cassidy and J. G. Vos,
    J. Electrochem. Soc., 135, 1988, 863.

85. K. Niwa and K. Doblhofer,
    Electrochim. Acta., 31, 1986, 549.

86. B. Lindholm and M. Sharp,

   J. Electroanal. Chem., Interfacial Electro-
   chemistry, 198, 1986, 37.

87. E. Tracy Turner Jones,

   J. Electrochem. Soc., 132, 1985.

88. A. Bettelheim, R. J. H. Chan and T. Kuwana,

   J. Electroanal. Chem., Interfacial Electro-
   chemistry, 110, 1980, 93.

89. C. Degrand,

   J. Electroanal. Chem., Interfacial Electro-
   chemistry, 169, 1984, 259.

90. J. M. Bauldreay and M. D. Archer,

   Electrochim. Acta., 30, 1985, 1355.

91. B. Lindholm and M. Sharp,

   J. Electroanal. Chem., Interfacial Electro-
   chemistry, 215, 1986, 385.

92. J. B. Kerr and L. L. Miller,

   J. Electroanal. Chem., Interfacial Electro-
   chemistry, 101, 1979, 263.

93. J. B. Kerr, L. L. Miller and M. R. Van de Mark,

   J. Am. Chem. Soc., 102, 1980, 3383.

94. R. D. Rocklin and R. W. Murray,
    J. Phys. Chem., 85, 1981, 2104.

95. F. C. Anson, T. Ohsaka and J. M. Saveant,
    J. Am. Chem. Soc., 105, 1983, 4883.

96. J. C. Moutet,
    J. Electroanal. Chem., Interfacial Electro-
    chemistry, 161, 1984, 181.

97. A. Heller,
    Science, 223, 1984, 1141.

98. J. M. Bolts, A. b. Bocarsly, M. C. Palazzatto, E.
    G. Walton, N. S. Lewis and M. s. Wrighton,
    J. Am. Chem. Soc., 101, 1979, 1378.

99. R. Noufi, A. J. Frank and A. J. Nozic,
    J. Am. Chem. Soc., 103, 1981, 1849.

100. P. Burgmayer and R. W. Murray,
     J. Electroanal. Chem., Interfacial Electro-
     chemistry, 147, 1983, 339.

101. H. A. Laithinen and T. M. H. Seu,
     Anal. Chem., 51, 1979, 1550.

102. K. Itaya and A. J. Bard,
      Anal. Chem., 50, 1978, 1487.

103. P. R. Moses and R. W. Murray,
      J. Am. Chem. Soc., 98, 1976, 7435.

104. N. Oyama and F. C. Anson,
      J. Electroanal. Chem., Interfacial Electro-
      chemistry, 88, 1978, 289.

105. F. R. Keene, D. J. Salmon and T. J. Meyer,
      J. Am. Chem. Soc., 99, 1977, 4821.

106. B. A. Moyer, M. S. Thompson and T. J. Meyer,
      J. Am. Chem. Soc., 102, 1980, 2310.

107. N. J. Sutin,
      J. Photochem., 10. 1979, 19.

108. J. K. Nagle, W. J. Dressick and T. J. Meyer,
      J. Am. Chem. Soc., 101, 1979, 3993.

109. N. Oyama and F. C. Anson,
      J. Am. Chem. Soc., 101, 1979, 3450.

110. O. Haas and J. G. Vos.,
      J. Electroanal. Chem., Interfacial Electro-
      chemistry, 113, 1980, 139.

111. J. M. Calvert and T. J. Meyer,
      Inorg. Chem., 20, 1981, 27.

112. J. M. Kelly and J. G. Vos,
      Angew. Chemie, 21, 1982, 628.

113. K. Shigehara, N. Oyama and F. C. Anson,
      J. Am. Chem. Soc., 103, 1981, 2552.

114. O. Haas, M. Kriens and J. G. Vos,
      J. Am. Chem., Soc., 103, 1981, 1318.

115. T. Ikeda, P. Schmehl, P. Denisevich, K. Willman
      and R. W. Murray,
      J. Am. Chem. Soc., 104, 1982, 2683.

116. J. M. Calvert, J. V. Caspar, R. A. Binstead, T. D.
      Westmoreland and T. J. Meyer,
      J. Am. Chem. Soc., 104, 1982, 6620.

117. P. G. Pickup, K. N. Kuo and R. W. Murray,
      J. Electrochem. Soc., 130, 1983, 2205.

118. H. R. Zumbrunnen and F. C. Anson,
      J. Electroanal. Chem., Interfacial Electro-
      chemistry, 152, 1983, 111.

119. B. Lindholm and M. Sharp,
      J. Electroanal. Chem., Interfacial Electro-
      chemistry, 198, 1983, 37.

120. J. M. Clear, J. M. Kelly and J. G. Vos,
      Mackromol. Chem., 184, 1983, 613.

121. M. Kaneko, S. Nemoto, A. Yamada and Y. Kurimura,
      Inorg. Chim. Acta., 44, 1980, L289.

122. B. P. Sullivan, D. J. Salmon and T. J. Meyer,
      Inorg. Chem., 17, 1978, 3334.

123. C. D. Ellis and T. J. Meyer,
      Inorg. Chem., 23, 1984, 1748.

124. L. L. Miller and M. R. Van de Mark,
      J. Electroanal. Chem., Interfacial Electro-
      chemistry, 88, 1978, 437.

125. H. Yasuda, I. Noda, S. Miganaga and A. Nakamura,
      Makromolecules, 17, 1984, 2453.

126. C. R. Leidner, B. P. Sullivan, R. A. Reed, B. A.
      White, M. T. Crimmins, R. W. Murray and T. J.
      Meyer,
      Inorg. Chem., 26, 1987, 882.

127. D. R. Rolison, M. Umana, P. Burgmayer and R. W. Murray,

Inorg. Chem., 20, 1981, 2996.

128. P. J. Peerce and A. J. Bard,

J. Electroanal. Chem., Interfacial Electro-chemistry, 112, 1980, 97.

129. R. J. Nowak, F. A. Schultz, M. Umana, H. Abruna and R. W. Murray,

J. Electroanal. Chem., Interfacial Electro-chemistry, 94, 1978, 219.

130. C. D. Ellis, J. A. Gilbert, W. R. Murphy Jr. and T. J. Meyer,

J. Am. Chem. Soc., 105, 1983, 4843.

131. N. S. Scott, N. Oyama and F. C. Anson,

J. Electroanal. Chem., Interfacial Electro-chemistry, 110, 1980, 303.

132. P. K. Ghosh and T. G. Spiro,

J. Electrochem. Soc., 128, 1981, 1281.

133. S. M. Geraty and J. G. Vos,

J. Electroanal. Chem., Interfacial Electro-chemistry, 179, 1984, 389.

134. S. M. Geraty and J. G. Vos,

    J. Chem. Soc. Dalton Trans., 1987, 3073.

135. L. H. Bamford and E. Schofield,

    Polymer, 22, 1981, 1227.

CHAPTER II

Experimental Section

EXPERIMENTAL SECTION

Instrumentation

UV-vis spectra were recorded on a Pye-Unicam SP8-200 or a Shimadzu UV 240 - spectrophotometer. Emission spectra were recorded using a Perkin Elmer LS-5 Luminescence spectrometer. Spectra were recorded using an emission slit width of 10 nm at room temperature and of 2.5 nm at 77K and are not corrected for photomultiplier response. Electrochemical measurements were carried out using and E.G. and G. Par Model 174 a polarographic analyser with and E.G. and G. Par 175 Universal Programmer. An E.G. and G. Princeton Applied Research potentiostat/galvanostat Model 273 was also used.

A slide projector was included as a light source for photochemical investigations involving modified electrodes and a Pine Instrument, Model ASRE, analytical rotator was used for rotating disc measurements. Glassy carbon or pyrolytic graphite electrodes were coated with a known amount of a 10^{-3} mol/dm^3 solution (based on Ru) of the polymer in methanol. The electrodes were then left to dry for several days. A saturated potassium electrode (S.C.E.) was used as a reference electrode. This was replaced by a saturated sodium chloride electrode when

56

perchlorate based electrolytes were used due to the fact that potassium perchlorate precipitates out. Redox potentials reported for modified electrodes are average values obtained for different coatings. Variations of both peak potentials and peak to peak separations of up to 24mV are observed for different electrodes coated with the same sample.

H.P.L.C. studies were carried out using a Shimadzu SPD-6A system in conjunction with a ACS pump model 353, a 201 injector loop, a Partisil SCX radial PAK cartridge and a Commodore 8032-5K computer. The detection wavelength used was 280 nm. The chromatography was carried out using acetonitrile/water (80/20) containing 0.08M LiClO$_4$ as mobile phase. A flow rate of 2.0 ml/min was used.

Photochemical studies of solution species were carried out using a high pressure mercury lamp and a glass filter to cut out ultraviolet radiation.

Chronoamperometric experiments were carried out at the Universite de Paris VII. Cyclic voltammograms and potential step current-time curves were obtained using a PAR (175) function generator and a home-built potentiostat equipped with positive feedback compensation. An Ifelec 2502, XY chart recorder was employed. A Nicolet (3091) storage oscilloscope and

57

an Apple computer were included for potential step experiments. Elemental analyses were carried out at the Microanalytical Laboratory at University College Dublin.

Materials

Ru(bipy)$_2$Cl$_2$.2H$_2$O and Ru(bipy)$_2$CO$_3$ were prepared according to literature procedures [1]. N-vinylimidazole was obtained from Aldrich and distilled before used. Reagent grade solvents were used without further purification.

Poly-N-Vinylimidazole (PNVI)

Freshly distilled N-vinylimidazole was polymerized with 2,2'-azoisobutyronitrile (AIBN) as an initiator in a 20:1 ratio. The bulk polymerisation was carried out in vacuo at 70°C for two hours. After reprecipitation from acetone, the filtered product was then dried under vacuum at room temperature. Molecular weight was estimated to be 46,000 as determined by gel permeation chromatography. (Found: C, 59.0; H, 7.0; N, 27.2. (C$_5$H$_6$N$_2$O.H$_2$O)$_n$ requires C, 58.3; H, 6.8; N, 27.2%).

Reaction Of PNVI With Ru(bipy)$_2$Cl$_2$

Methanolic solutions of PNVI and the ruthenium complex were heated at reflux for up to three days. The reaction conditions have been given in Table 3.1. The materials were isolated by precipitation in diethylether or acetone and the solids obtained dried in vacuo. In some cases only half of the product was isolated; the remaining half was used to investigate the changes that occur in solution with time. PNVI was reacted with Ru(bipy)$_2$CO$_3$ as described in the literature for the corresponding poly-4-vinylpyridine complex [2].

[Ru(bipy)$_2$(MeIm)$_2$](PF$_6$)$_2$

Ru(bipy)$_2$Cl$_2$.2H$_2$O (255mg, 0.5 mmol) and 1-methylimidazole (MeIm) (246mg, 3 mmol) were heated at reflux in 150 cm^3 ethanol/water (75:25) for three hours. The product was then isolated as the PF$_6$-salt by addition of an excess of NH$_4$PF$_6$ in water. The solid obtained was recrystallised from acetone/water mixtures and dried in vacuo. Yield 332mg, 75%. (Found: C, 38.9; H, 3.0; N, 12.5. C$_{28}$H$_{28}$F$_{12}$N$_8$P$_2$Ru requires C, 38.7; H, 3.2; N, 12.91%), UV-vis (methanol), (log $\in$) 492 (3.99); 340 (3.89).

[Ru(bipy)$_2$(MeIm)Cl]PF$_6$

Ru(bipy)$_2$Cl$_2$2H$_2$O (255mg, 0.5 mmol) and MeIm (4mg, 0.5mmol) were heated at reflux in 150 cm^3 ethanol for seven hours. The product was isolated by the addition of aqueous NH$_4$PF$_6$. The solid obtained was recrystallised from acetone/water mixtures and dried in vacuo. Yield 240mg. 70% (Found: C, 52.4; H, 3.3; N, 12.0; Cl, 5.7. C$_{24}$H$_{22}$ClF$_6$N$_6$PRu requires C 52.6; H, 3.3; N, 12.41; Cl, 5.3%). UV-vis, (methanol), (log ϵ) 512 (3.84); 352 (3.83).

[Ru(bipy)$_2$(MeIm)H$_2$O](PF$_6$)$_2$.H$_2$O

69.9mg (0.103 mmoles) of [Ru(bipy)$_2$(MeIm)Cl]PF$_6$ were heated at reflux in 10 cm^3 water until dissolved, which took about five minutes. The product was then precipitated by addition of NH$_4$PF$_6$ in water. The filtered product (78mg, 94%) was dried under vacuum over night. (Found: C, 35.4; H, 3.0; N, 10.0 C$_{24}$H$_{26}$F$_6$N$_6$OPRu requires C, 35.1; H, 3.2; N, 10.2%). UV-vis, (methanol) (log ϵ) 487 (3.94); 338 (3.98).

REFERENCES

1. B. P. Sullivan, D. J. Salmon and T. J. Meyer,
    Inorg. Chem., 17, 1978, 3334.

2. J. M. Calvert and T. J. Meyer,
    Inorg. Chem., 21, 1982, 3978.

CHAPTER III

Synthesis and Characterisation of a Series of
Ruthenium – Containing Metallopolymers Based on Poly-
N-Vinylimidazole

III.1   INTRODUCTION

For reasons already outlined in Chapter 1, it was our aim to synthesise a series of ruthenium containing metallopolymers based on Poly-N-Vinylimidazole(PNVI). It was also our desire to compare and contrast the properties of these materials with previously prepared Poly-4-Vinylpyridine analogues [1 - 10].

There have been reports on the preparation of transition metal complexes based on polyvinylpyridine [11, 12]. These complexes have been formed by reaction of transition metal halides, $RuCl_3$, or transition metal chelates, $Ru(bipy)_2Cl_2$ with poly(4-vinylpyridine) PVP or indeed poly (2-vinylpyridine) P(2-VP) in ethanol. PVP has proved to be a useful material for the attachment of electroactive groups to electrode surface [7, 13 - 16]. In an investigation by Clear et al. [9], the spectroscopic properties (IR and UV-vis) of monomeric methylpyridine derivatives were used to elucidate the nature of the species formed by the reaction of P(2-VP) and PVP with $RuCl_3$. The solubility of the metallopolymers was found to depend on the mole ratio of reactants, their concentration and reaction conditions. By reaction of the chelate complexes $Ru(bipy)_2Cl_2$ with PVP, Kelly and co-workers have prepared soluble complexes of the type $[Ru(bipy)_2(PVP)Cl]^+$ and $[Ru(bipy)_2(PVP)_2]^{2+}$ which were

63

identified by comparison of spectroscopic properties with monomeric pyridine analogues [5]. The decision to study 2,2-bipyridyl complexes of ruthenium was prompted by the growing interest in complexes, such as $[Ru(bipy)_3]^{2+}$ and its analogues as sensitizer catalysts for the photodissociation of water by visible light [17, 18]. PVP is largely chosen as the polymeric reagent because it is hoped that the co-ordination chemistry of the $Ru(bipy)_2$ analogues might approximate to that of $[Ru(bipy_3)]^{2+}$ and also because there exists a substantial literature on the preparation and properties of PVP, its co-polymers and metal complexes.

In recent years, many investigations of ruthenium (II) bis(bipyridyl) complexes of PVP have concentrated on their behaviour in electrode coatings [4, 5, 7, 19 - 16]. In a study of the behaviour of $[Ru(bipy)_2(PVP)Cl]Cl$ films on electrodes, Haas et al. investigated the possibility of information storage based on the change in redox potential induced on photsubstitution of such coatings [22]. In general the photochemical properties of these systems have provided a large impetus for their extensive investigation but this factor will be discussed in more detail in a later chapter.

Metallopolymer films on electrode surfaces may also be

prepared be electropolymerisation [20, 23 - 25]. By this method, film thickness may be systematically varied. Bilayer films of complexes having different Ru^{III}/Ru^{II} redox potentials constitute rectifying interfaces and directed charge transfer from the outside film to the electrode has been observed. Metallopolymers of the type $[(Ru(bipy)(trpy)(PVP)]^{2+}$ have been prepared by reaction of $[Ru(bipy)(trpy)H_2O]^{2+}$ with PVP and characterised by ^1H - NMR, UV-vis spectroscopy, elemental analysis and electrochemical analysis both in homogeneous solution and as films on electrode surfaces, were examined. Certain complexes $[Ru(bipy)_2(PVP)X]^{n+}$ (where X = PVP, CN^-, MeCN, NO_2^-, NO_3^-, NO^+, N_3^-, OH_2, OH^-; n = 1, 2, 3) were prepared and found to retain the chemical and physical properties inherent in the respective monomer complexes [7]. Modifications in chemical and redox properties of these species as films were found to be due to (a) spatial separation affecting bimolecular processes and (b) pH dependent changes in local environment due to protonated and unprotonated pyridine groups on the main chain. Photophysical and photochemical properties of $[Ru(bipy)_2(PVP)_2]^{2+}$ in solution [8] and as films [10] have been investigated in some detail.

It has been our aim to carry out similar studies on ruthenium containing metallopolymers based on a poly-
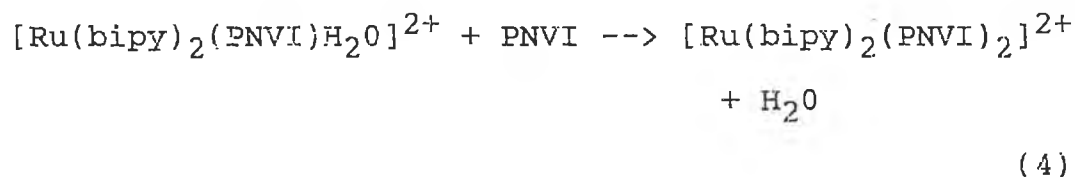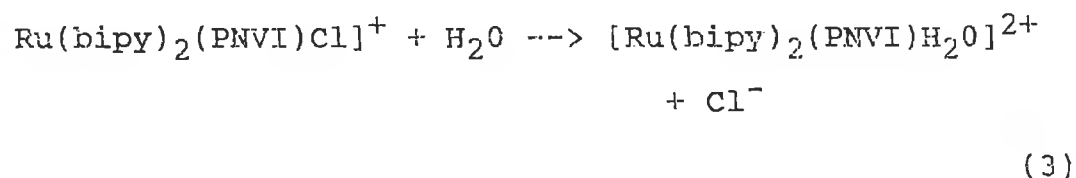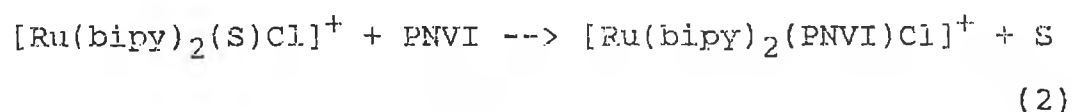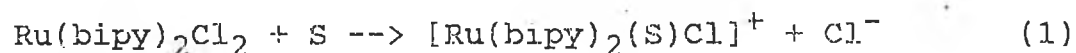
65

N-vinylimidazole backbone in the hope of developing some potentially useful applications, for example in electrocatalysis or photochemical processes.

III.2   RESULTS AND DISCUSSION

General

In a series of experiments hydrated bis(2,2'-bipyridyl) ruthenium (II) dichloride was treated with PNVI using different reaction solvents and reaction times. The stoichiometric ration of PNVI to ruthenium was varied from 5:1 to 50:1. The metallopolymers were either left in solution or isolated by evaporation of most of the solvent and subsequent precipitation in diethylether. The solids obtained were then dried in vacuo at room temperature. The metallopolymers isolated were found to be soluble immediately after their isolation but in most cases on storing for longer periods, would only partly redissolve. The characterisation of the series of polymer-bound complexes was accomplished by applying several techniques to each sample. The data obtained were compared with those for the mononuclear model compounds $[Ru(bipy)_2(MeIm)_2](PF_6)_2$, $[Ru(bipy)_2(MeIm)Cl]PF_6$ and $[Ru(bipy)_2(MeIm)H_2O](PF_6)_2$, where MeIm = N-methylimidazole, chosen as model compounds for the expected polymer-bound complexes $[Ru(bipy)_2(PNVI)Cl]^+$, and $[Ru(bipy)_2(PNVI)_2]^{2+}$ respectively. Spectroscopic and electrochemical data suggest that the species $[Ru(bipy)_2(PNVI)Cl]^+$ and $[Ru(bipy)_2(PNVI)_2]^{2+}$ are both present in most polymers

prepared from $Ru(bipy)_2Cl_2 \cdot 2H_2O$, their ratios depending on the reaction conditions. Reaction of $[Ru(bipy)_2(CO_3)]$ with PNVI yields, as expected, only the disubstituted product [7]. The formation of the different species from $Ru(bipy)_2Cl_2 \cdot 2H_2O$ probably occurs as shown in equations (1) - (4).

$$Ru(bipy)_2Cl_2 + S \longrightarrow [Ru(bipy)_2(S)Cl]^+ + Cl^- \qquad (1)$$

$$[Ru(bipy)_2(S)Cl]^+ + PNVI \longrightarrow [Ru(bipy)_2(PNVI)Cl]^+ + S$$
$$(2)$$

$$Ru(bipy)_2(PNVI)Cl]^+ + H_2O \longrightarrow [Ru(bipy)_2(PNVI)H_2O]^{2+}$$
$$+ Cl^-$$
$$(3)$$

$$[Ru(bipy)_2(PNVI)H_2O]^{2+} + PNVI \longrightarrow [Ru(bipy)_2(PNVI)_2]^{2+}$$
$$+ H_2O$$
$$(4)$$

In these reactions S is either methanol or water. The extent to which these reactions occur depends on the reaction conditions, which, along with the elemental analyses of the materials obtained, are given in Table 3.1. The elemental analysis of metallopolymers are known to be rather inconsistent. It should therefore be pointed out that the PNVI:Ru ratios calculated can only be taken as an indication of the composition of the products obtained.

Table 3.1 - Reaction conditions and elemental analyses for ruthenium containing Poly-N-vinyimidazole metallopolymers.

Code	PNVI (mg)	Ru[a] (mg)	mol ratio	Solvent	Reaction time (h)	Elemental Analysis				PNVI : Ru Ratio obtained
A	470	478	5 : 1	methanol	72	51.4	4.9	18.2	7.7	4.4
B	470	486	5 : 1	ethanol	24	50.9	5.0	18.0	7.7	4.2
C	470	484	5 : 1	methanol	24	50.6	4.9	17.7	8.1	4.0
D	470	486	5 : 1	methanol	48	50.4	4.8	18.0	8.4	4.0
E	235	243	5 : 1	meth/H_2O (1:1)	72					
F	470	97	25 : 1	methanol	72	55.4	5.8	23.7	3.4	14
G	470	28	10 : 1	methanol	72					
H	471	48	50 : 1	methanol	72					
I[b]	48	48	5 : 1	meth/H_2O (1:1)	72					

[a] metallopolymers prepared using Ru(bipy)$_2$Cl$_2$.2 H_2O; [b] prepared using Ru(bipy)$_2$CO$_3$.

One major problem encountered with these materials was their limited solubility. Metallopolymer solubility is determined principally by the loading of Ru centres along the polymer backbone and by cross linking of the polymer chains. This however only applied to certain of the samples in that the disubstituted complex could not be successfully isolated since if any solid was obtained it could not be dissolved completely, if at all, in any solvent. For this reason the disubstituted samples were left in solution. In the case of [Ru(bipy)$_2$(PNVI)Cl]Cl the product could be isolated and retained solubility, but only up to about three months after synthesis. This loss of solubility was thought to be due to some cross linking occurring in the sample with time. Samples were then refrigerated and it was found that they did retain solubility for any time up to one year or more after preparation.

III.3   CHARACTERISATION STUDIES

III.3.1 Electronic Spectra

The absorption and emission (at room temperature and liquid nitrogen temperature, 77K) spectra of the prepared materials were recorded.   Spectra of some representative materials have been given in Figure 3.1 - 3.3.   The absorption and emission maxima for the metallopolymers, together with the values obtained for the model compounds are given in Table 3.2.

In the absorption spectra two bands are observed in the visible region of the spectrum.   As mentioned in the introduction, bands in this region are attributed to metal-to-ligand charge transfer transitions (MLCT) of the type π^*(bipy) <---- dπ (Ru) [8]. Because of the strong similarities of the electronic spectra of the metallopolymers with those reported for similar compounds in the literature, these transitions are also thought to originate from bipy based MLCT states [7, 8].

The absorption maxima in the visible region do vary with the ligand composition of the complexes and therefore are generally used for identification purposes. To determine the co-ordination around the central metal ion in the polymer bound materials their

Table 3.2 - Spectroscopic and electrochemical data for metallopolymers and mononuclear model compounds.

| Sample	λ_{max}(abs.) (nm)[a]	λ_{max}(em. R.T.) (nm)[a]	λ_{max}(em. 77K) (nm)[b]	$E_{1/2}$ mV[c]	Product ratio
$[Ru(bipy)_2(MeIm)_2](PF_6)_2$	492,340	640	626	965*	
$[Ru(bipy)_2(MeIm)Cl]PF_6$	512,352	-	682	660*	
$[Ru(bipy)_2(MeIm)H_2O](PF_6)_2$	487,338	-	-	995*	
A	502,347	638	630(685)	570(805)	5.7
B	507,352	643	686	545(835)	7.5
C	502,348	633	689	570(805)	>8
C				677*	
D	500,348	630	682	535(810)	6.5
E	485,345	637	628	825(610)	>0.15
F	485,345	626	617	590(835)	2.0
G	487,343	637	619	860	-
H	481,340	636	618	840	-
I	482,340	640	618	855(1025*)	-
$[Ru(bipy)_2(PNVI)H_2O]^{2+}$				730(1020*)	

Table 3.2

a   :   solvent methanol;

b   :   measured in ethanol glass at 77K;

c   :   electrolyte 1M H_2SO_4.

Minor redox couples present are given in brackets; scan rate 50 mV/sec.

Reference electrode sce.

*   :   electrolyte is acetonitrile/0.1M
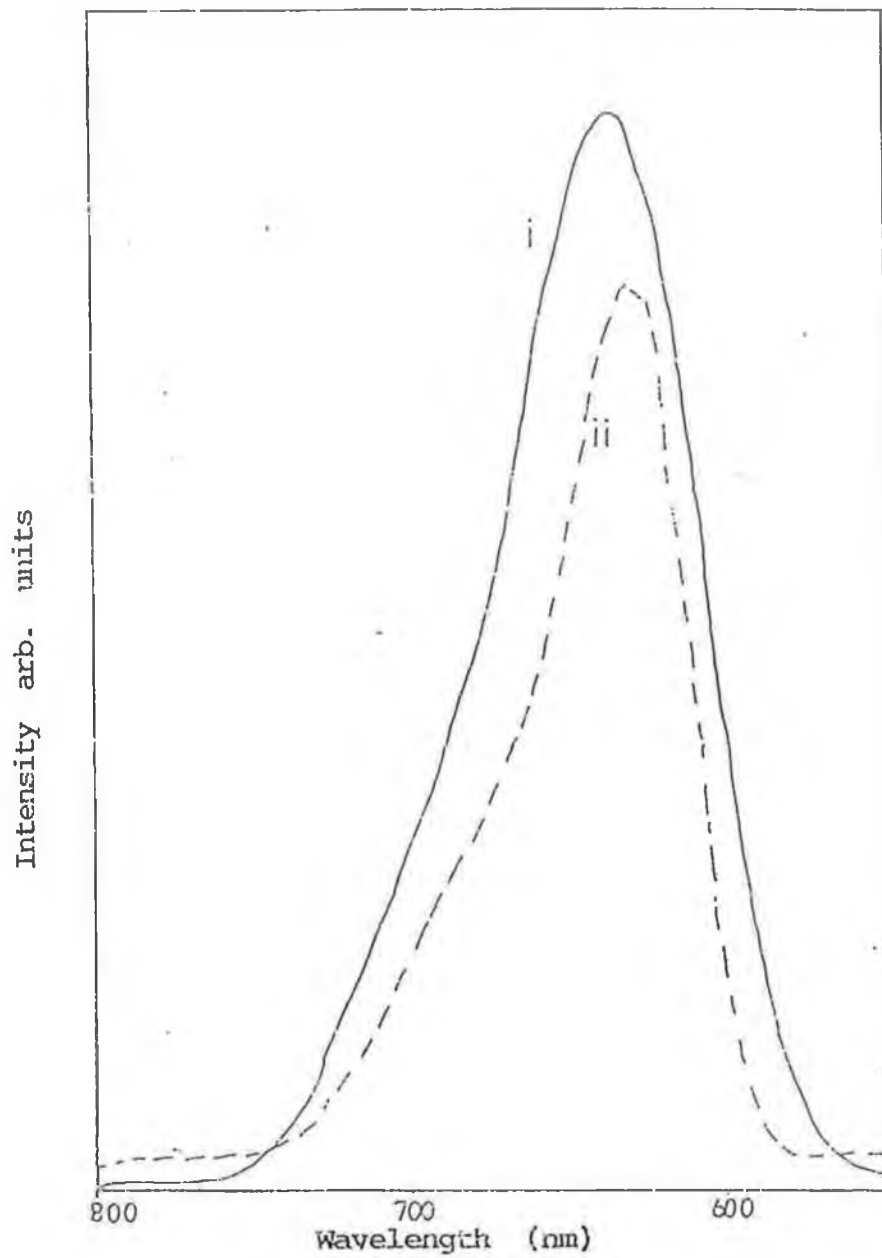   Tetraethylammoniumperchlorate.

FIGURE 3.1.
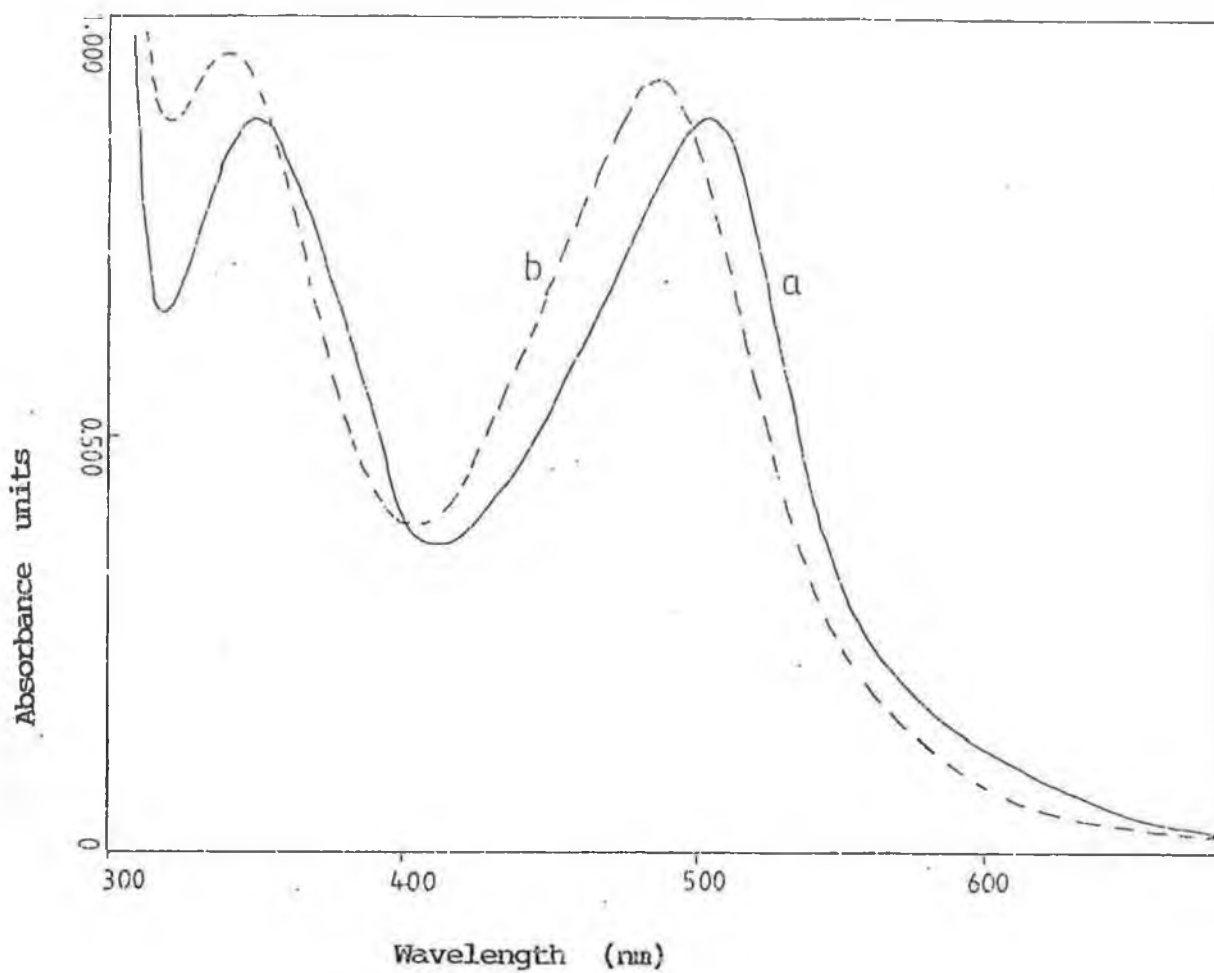
(a) U.V./Vis spectrum of sample C in methanol.

(b) U.V./Vis spectrum of sample E in methanol.

Sample concentration 10^{-4} mol/dm^3.
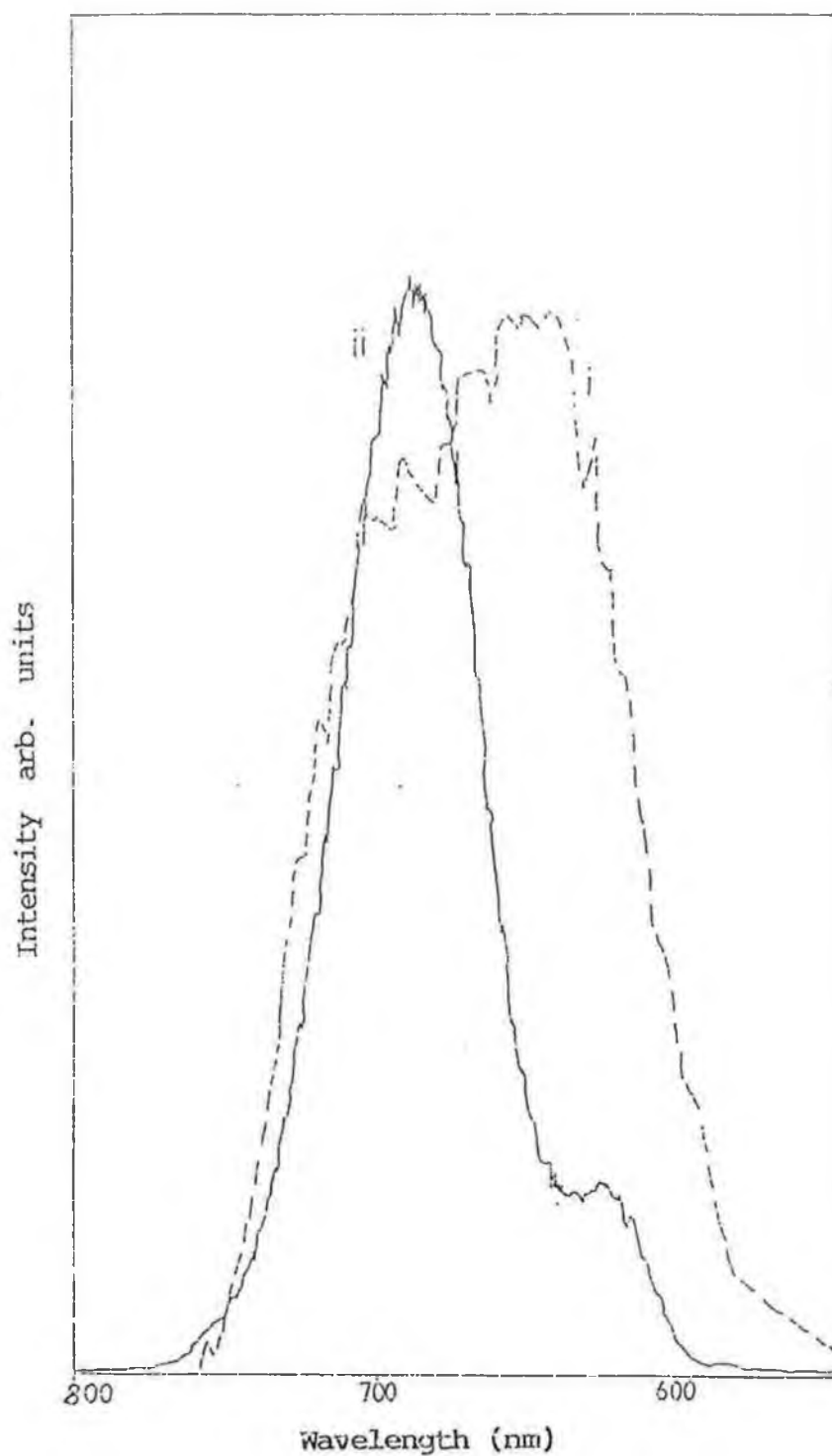
FIGURE 3.2.

(i) Room temperature emission spectrum
     of sample E in methanol.

(ii) 77 K emission spectrum of sample E
     in ethanol.

Sample concentration 10^{-4} mol/dm^3.

FIGURE 3.3.

(i) Room temperature emission spectrum
     of sample C in methanol.

(ii) 77 K emission spectrum of sample C
     in ethanol.

Sample concentration 10^{-4} mol/dm^3.

absorption spectra were compared with those of mononuclear model compounds, as has been done previously with poly-4-vinylpyridine analogues [9]. However, as evident from the data given, in our case the absorption maxima obtained for the different compounds are very close together and from these data alone no conclusions can be drawn as to the composition of the synthesised materials. However, the data do suggest certain probabilities. For samples A-D the presence of $[Ru(bipy)_2(PNVI)Cl]Cl$ is suggested as the predominant species whereas $[Ru(bipy)_2(PNVI)_2]Cl_2$ seems to be the main product for samples E-I. The absorption maxima for the polymeric complexes are observed at slightly higher energy than those of the corresponding mononuclear compounds but the overall trend is the same.

The results obtained suggest that increasing the polymer:metal ratio and the reaction time leads to a corresponding increase in the relative amounts of $[Ru(bipy)_2(PNVI)_2]Cl_2$ formed. Addition of water to the reaction solvent leads to the exclusive formation of $[Ru(bipy)_2(PNVI)_2]Cl_2$. As these results are not conclusive it was necessary to substantiate these suggestions by other techniques.

Emission spectra were obtained both in fluid solution at room temperature and in methanol glasses at 77K.

Polymer bound Ru(bipy)$_2$ complexes, like their pyridine or methylpyridine analogues, are weak emitters at room temperature. In the case of imidazole metallopolymers, the disubstituted complex is a relatively strong emitter at room temperature but because the monosubstituted complexes luminesce weakly at room temperature it was necessary to employ low temperature emission spectroscopy to distinguish between the two products. The materials synthesised were excited at their absorption maxima of their lowest energy MLCT band (500nm) and their luminescent responses were recorded.

As illustrated from the results recorded at room temperature all samples were found to emit at approximately the same wavelength (640nm). Their behaviour could be explained by the fact that as the monosubstituted complex is, at room temperature, such a weak emitter relative to the disubstituted complex, small traces of the latter in a predominantly monosubstituted sample, would emit strongly enough to mask any weak emission from [Ru(bipy)$_2$(PNVI)Cl]Cl. This was substantiated by examination of the individual spectra where two important factors are of note. The spectra obtained for a sample expected to contain mainly [Ru(bipy)$_2$(PNVI)Cl]Cl exhibit a much noisier signal and also evidence of a shoulder around 700nm as illustrated in Figure 3.2. These features

were absent for expected disubstituted samples. At 77K the model compounds $[Ru(bipy)_2(MeIm)_2](PF_6)_2$ and $[Ru(bipy)_2(MeIm)Cl]PF_6$ emitted at 626nm and 682nm respectively while for the species $[Ru(bipy)_2(MeIm)H_2O](PF_6)_2$ no emission was observed. At the same temperature the spectra obtained showed marked differences between given polymeric samples. For predominantly $\{Ru(bipy)_2(PNVI)Cl]Cl$ samples emission maxima were observed at approximately 700nm as opposed to the 640nm emission at room temperature, see Figure 3.3. For a pure sample it is expected that at low temperature the emission should shift to higher energy, lower wavelength and not to lower energy as was observed here. This indicates that the room temperature emission at 640nm was not due to the monosubstituted complex but to traces of the disubstituted complex present in the sample as was previously proposed. The expected disubstituted samples exhibited emission at 625nm at low temperature. Here we find that the transition has shifted to higher energy as expected. By comparison with the emissions of the model compounds at 77K mentioned above, one can clearly distinguish between $[Ru(bipy)_2(PNVI)_2]^{2+}$ which emits at 620nm. The same conclusions are reached here as from the electronic spectra concerning the nature of the products obtained and the effect of the synthetic conditions used. The absorption and emission data do not yield conclusive

information about the presence of the aquo species $[Ru(bipy)_2(PNVI)H_2O]^{2+}$.

III.3.2 Electrochemical Characterisation

Electrochemical studies were used both for characterisation purposes and for the investigation of the electrochemical/photochemical properties of the polymer film. In this section I will just address the former. Synthesised Poly-N-vinylimidazole bound $Ru(bipy)_2$ - complexes were attached to glassy carbon and pyrolytic graphite electrodes and the modified electrodes produced were studied by cyclic voltammetry.

Data obtained for model compounds and polymeric are given in Table 3.2. Typical examples of cyclic voltammograms are given in Figure 3.4. The cyclic voltammograms obtained in each case were found to show a decrease in peak-to-peak separation with decreasing scan rate and for scan rates up to 200mV/s, a linear dependence of the peak current on the scan rate was found as illustrated later in Figure 4.4. In general the polymer films showed the electrochemical behaviour that would be expected for surface bound, fast electron exchanging species [1, 26].

As indicated by the results given in Table 3.2 the position of the Ru(II)/Ru(III) redox couple was found to depend on the nature of the ligands bound to the ruthenium centre. From the results obtained for the

FIGURE 3.4.
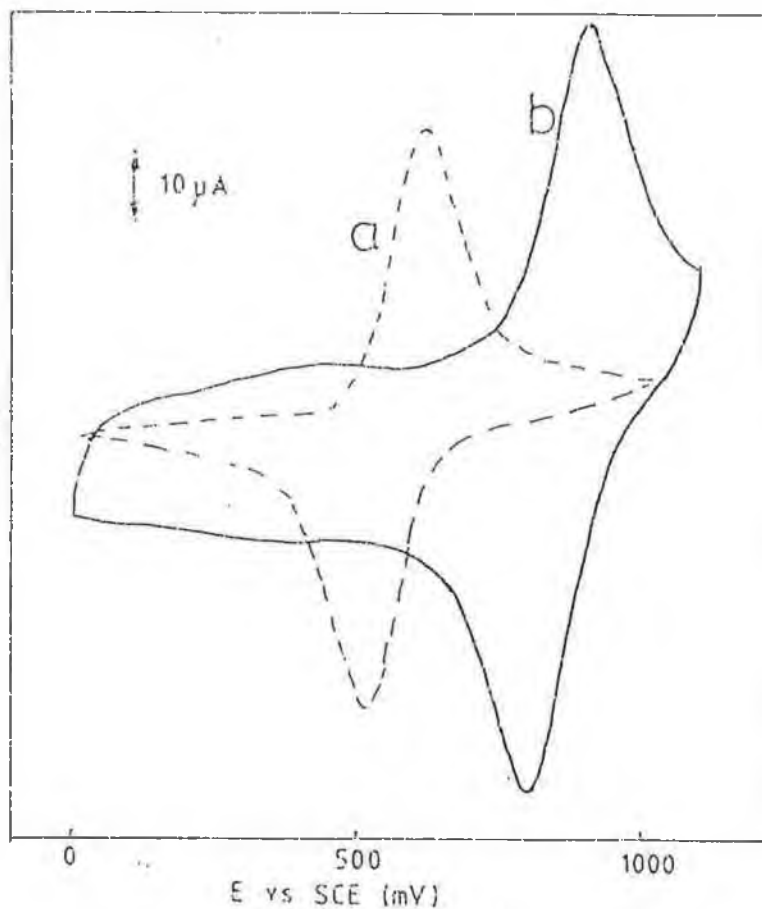
(a) cyclic voltammogram of a glassy carbon
    electrode coated with sample C.
    Scan rate 50 mV/sec,electrolyte 1M $HClO_4$.

(b) cyclic voltammogram of a glassy carbon
    electrode coated with sample I.
    Scan rate 50 mV/sec,electrolyte 1M $HClO_4$.

modified electrodes it could be concluded that depending on the reaction conditions used, two different polymeric ruthenium species were obtained. The influence of the reaction conditions on the products obtained could be judged from the ratio of the peak currents of the two redox couples (Table 3.2). These results illustrate that for a synthesis using methanol as solvent, short reflux times i.e. twelve hours and low PNVI:Ru ratio i.e. 5:1 a product with a redox potential of approximately 550mV was obtained which is attributed to a monosubstituted complex by comparison with those for model compounds, (see Table 3.2) and other similar metallopolymers [5, 6]. Longer reflux times, addition of water to the reaction, and higher PNVI:Ru ratio lead to the formation of a product with a redox couple of about 850mV. This redox couple has been assigned to the complex $[Ru(bipy)_2(PNVI)_2]^{2+}$ again by comparison with analogous compounds. As is evident, these results are found to be in agreement with those obtained using spectroscopic techniques. Again no trace of any aquo species was observed.

Using cyclic voltammetry one can also clearly monitor any changes which occur in the metallopolymers with time, particularly when in solution. Over a period of several months electrodes were periodically modified with an ageing polymer solution. With time a redox

couple was found to develop at a potential of 730mV at the cost of the original signal at 570mV. This indicated a change in the co-ordination chemistry of the polymer bound metal complex. In conjunction with photochemical studies, (see Chapter V), this new redox couple has been assigned to the formation of the aquo species, $[Ru(bipy)_2(PNVI)H_2O]^{2+}$. This process is irreversible and suggests that the $[Ru(bipy)_2(PNVI)Cl]^+$ species is not stable in solution. Increased concentration of $[Ru(bipy)_2(PNVI)Cl]^+$ relative to $[Ru(bipy)_2(PNVI)_2]^{2+}$ in any sample leads to formation of increased amounts of $[Ru(bipy)_2(PNVI)H_2O]^{2+}$. The disubstituted complex, $[Ru(bipy)_2(PNVI)_2]^{2+}$ was not found to undergo ligand substitution under similar conditions.

III.4   CONCLUSIONS

The results reported here indicate that it is possible to control the products or ratios of products obtained by controlling the synthetic conditions.   This is quite contrary to results obtained with Poly-4-vinylpyridine where $[Ru(bipy)_2(PVP)Cl]^+$ was the only product obtained up to PVP:Ru ratios of 100:1 [5].   It is also important to note that the nature of the polymer-bound metal complex changes with time both in solution and in the solid state.

It is clear that the materials prepared here cannot be characterised sufficiently using the techniques employed because of the fact that isolated materials become insoluble with time.   It was observed that the disubstituted complex could not be successfully isolated which is a disadvantage in the sense that one could not prepare accurate concentrations of the material and as a result of this, extinction co-efficients could not be calculated; nor could emission intensities for different samples be compared.   As a general comment the solubility of these materials did prove to be a problem in that even the monosubstituted complex only retained its solubility when refrigerated.   This suggested that cross-linking is most likely to be the determining factor with regard to the solubility of these materials.   It was also

observed that the corresponding aqua complex, $[Ru(bipy)_2(PNVI)H_2O]^{2+}$ could not be prepared using any of the preparative procedures described but only appeared as a result of a thermal reaction in solution, over a long time period, of the monosubstituted complex or by photochemical means.

The strong luminescent property of the disubstituted complex does suggest its potential for use in photochemical processes, which will be discussed in Chapter 5.

REFERENCES

1. N. Oyama and F.C. Anson,

    J. Am. Chem. Soc., 101, 1979, 3450.

2. J. M. Clear, J. M. Kelly, D. C. Pepper and J. G.
    Vos,

    Inorg. Chim. Acta, 33, 1979, L.139.

3. O. Haas and J. G. Vos,

    J. Electroanal. Chem., Interfacial Electro-
    chemistry, 113, 1980, 139.

4. J. M. Calvert and T. J. Meyer,

    Inorg. Chem., 20, 1981, 27.

5. J. M. Clear, J. M. Kelly, C. M. O'Connell and J.
    G. Vos,

    J. Chem. Research, (M), 1981, 3039.

6. O. Haas, M. Kriens and J. G. Vos,

    J. Am. Chem. Soc., 103, 1981, 1318.

7. J. M. Calvert and T. J. Meyer,

    Inorg. Chem. 21, 1982, 3978.

8. J. M. Calvert, J. V. Caspar, R. A. Binstead, T. D. Westmoreland, and T. J. Meyer,
    J. Am. Chem. Soc., 104, 1982, 6620.

9. J. M. Clear, J. M. Kelly and J. G. Vos,
    Makromol. Chem., 184, 1983, 613.

10. O. Haas, H. R. Zumbrunnen and J. G. Vos,
    Electrochim. Acta, 30, 1985, 1551.

11. M. Kaneko and E. Tsuchida,
    J. Polym. Sci. Macromolecular Reviews, 16, 1981, 397.

12. E. Tsuchida and H. Nishide,
    Adv. Polym. Sci., 24, 1977, 1.

13. N. Oyama and F. C. Anson,
    Anal. Chem., 52, 1980, 1192.

14. N. Oyama, T. Shimomura, K. Shigehara and F. C. Anson,
    J. Electroanal. Chem., Interfacial Electro-chemistry, 112, 1980, 271.

15. H. R. Zumbrunnen and F. C. Anson,
    J. Electroanal. Chem., Interfacial Electro-chemistry, 152, 1983, 111.

16. N. Oyama and F. C. Anson,

    J. Electrochem. Soc., 127, 1980, 247.

17. G. Sprintschnik, H. W. Sprintschnik, P. P. Kirwsch

    and D. G. Whitten,

    J. Am. Chem. Soc., 98, 1976, 2337.

18. S. J. Valenty and G. L. Gaines,

    J. Am. Chem. Soc., 99, 1977, 1285.

19. G. J. Samuels and T. J. Meyer,

    J. Am. Chem. Soc., 103, 1981, 307.

20. C. D. Ellis, W. R. Murphy Jr. and T. J. Meyer,

    J. Am. Chem. Soc., 103, 1981, 307.

21. T. D. Westmoreland, J. M. Calvert, R. W. Murray

    and T. J. Meyer,

    J. Chem. Soc., Chem. Commun., 1983, 65.

22. O. Haas, N. Muller and H. Gerischer,

    Electrochim. Acta, 27, 1982, 991.

23. J. M. Calvert, R. H. Schmehl, B. P. Sullivan, J.

    S. Facci, T. J. Meyer and R. W. Murray,

    Inorg. Chem., 22, 1983, 2151.

24. P. Denisevich, H. D. Abruna, C. R. Leidner, T. J. Meyer and R. W. Murray,
    Inorg. Chem., 21, 1983, 2153.

25. H. D. Abruna, P. Denisevich, M. Umana, T. J. Meyer and R. W. Murray,
    J. Am. Chem. Soc., 103, 1981, 1.

26. F. C. Anson, J. M. Saveant and K. Shigehara,
    J. Am. Chem. Soc., 105, 1983, 1096.

Electrochemical Properties of Ruthenium Containing
Poly-N-Vinylimidazole Based Metallopolymers

IV.1   INTRODUCTION

Our interest in poly-n-vinylimidazole metallopolymers has been elucidated in preceding chapters. In this section the electrochemical properties of the synthesised materials are discussed.

The effect of electrolyte and pH on the electrochemical response of redox systems has been the subject of extensive studies in relation to different types of system [1-6]. In 1976, Brown and co-workers, using pyrolytic graphite electrodes modified with 9, 10-phenanthrenequinone and iron protoporphyrin, studied how the electrochemistry of the system could be altered by changing the pH of the supporting electrolyte [3]. For the latter of these two systems the shift in potential as a function of pH was found to resemble its behaviour in homogeneous solution. The behaviour of other anthraquinones where a slope of 60 mV is obtained from a pH versus potential plot, and the pH dependence of anthraquinone polymers absorbed onto vitreous carbon or mercury electrodes has been studied [6]. Redox peaks were found to be narrower in acidic or slightly alkaline electrolyte. Their pH/potential relationship was studied over a pH range of 2 to 12. At pH values greater than 12 the surface coverages (Γ) [7] and values obtained for the peak current (i_p) were found to decrease slowly with

sequential scanning indicating instability at higher pH. In the pH range, 2 to 12, Σ was found to remain constant although peak shapes were found to change with pH indicating different limitations on charging of the layer at different pH values. Polymer-bound dopamine has been adsorbed onto electrode surfaces and the cyclic voltammetric behaviour was monitored as a function of pH [1]. For the pH range studies, pH 1 --> pH 10, values of ΔE_p were approximately constant over this range. The electrochemical charging rate is dependent on the amount of polymer adsorbed. For larger values of surface coverage larger values of ΔE_p were obtained indicating slower charging of the layer.

These type of phenomena have been investigated for different types of systems. Of particular interest for this research are polypyridyl ruthenium (II) complexes of poly-(4-vinylpyridine) and other similar materials. Koval and Anson have attached polyvinyl pyridine pentamineruthenium (II) complexes to graphite electrodes [8]. A study of the cyclic voltammetric behaviour indicated a symmetrical shape ($\Delta E_p = 0$ which led to the conclusion that surface behaviour was involved, i.e. this shape is common to thin layers, whereas thicker films exhibit diffusional behaviour. This effect was also observed for platinum oxide electrodes with covalently bound 2,2'-bipyridyl complexes of ruthenium (II) [9]. Again symmetrical

voltammograms were observed indicating 'surface' behaviour. It was also found here that the redox potentials of the $(bipy)_2Ru(II)/(III)$ couples varies with the nature of the ligands bound. This effect was also observed by Haas, Zumbrunnen and Vos for electrodes coated with $[Ru(bipy)_2(PVP)Cl]Cl$, $[Ru(bipy)_2(PVP)_2]^{2+}$ and $[Ru(bipy)_2(PVP)H_2O]^{2+}$ [10]. It was found that the electrochemical response of the coated electrode surface was dependent not only on the nature of the polymer, as was previously found by Calvert and Meyer [11], but also on the nature of the attached ruthenium complex.

Oyama and Anson have prepared electrodes coated with PVP (poly4-vinylpyridine) or PAN (polyacrylonitrile) with incorporated metal complexes based on; $[Ru(edta)]^{3+}$, $[Ru(NH_3)_5H_2O]^{3+}$ and Cu (II) [12]. At pH values less that 2, it was found that a large amount of immobile anionic charge was generated within the polymer coating. The creation of such large charge densities is expected to be sensitive to changes in the nature and concentration of the supporting electrolyte that supplies the counter-ions needed to balance the electrogenerated charge in the polymer layer. It was found that decreasing the concentration of the electrolyte lead to a large increase in ΔE_p which is attributed to ohmic drops in the more dilute electrolyte. Effects on shapes of cyclic

voltammograms resulting from changes in size of supporting electrolyte ions have been reported previously [13]. Changes in ionic strength of supporting electrolytes composed of small sterically unhindered ions can also have profound effects on voltammograms of reactants anchored to electrode surfaces, as reported by Oyama and Anson [12]. Haas and Vos [14] and Calvert and Meyer [11] have also been interested in the electrolyte dependence of the electrochemistry of electrodes coated with poly(4-vinylpyridine) bound ruthenium bipyridyl complexes. Shifts in the potential of the redox couples were also observed with variation in ionic strengths, achieved by addition of KCl to the electrolyte. Calvert and Meyer also attribute the change in redox potential observed upon a change of electrolyte to the probability of an alteration in anion absorption within the polymer film [11]. An unusual pH effect was observed in the polymer films composed of $[Ru(II)(bipy)_2H_2O]^{2+}$ groups bound to poly(4-vinylpyridine) [5]. At pH values less than 4, the redox couples of these systems were found to vary with pH as expected. At pH values greater than 4 where the unbound pyridyl groups in the polymer film become deprotonated, the redox couples no longer change as a function of pH of the bulk solution. The reason for this is supplied in the fact that protonation gives rise to an open structure so the electrolyte, upon

easy penetration into the layer, can dictate the properties of the redox sites. Deprotonation at high pH leads to the opposite effect. These effects were specific for the aquo complex. This behaviour is explained by the involvement of protons in the $Ru^{3+/2+}$ redox couple, because of the formation of $[(bipy)_2Ru^{IV}PVP]$ species. Electrodes coated with films composed of PVP with incorporated $[Fe(CN)_5OH_2]^{3+}$ have also been investigated [5]. No electrochemical response was detected in the presence of non-acidic electrolytes. At low pH values however, a more open polymer structure facilitates counterion entry into the film. Different electrochemical responses were obtained using quaternized PVP ($\overset{+}{Q}$PVP), because of swelling of the less hydrophobic QPVP films, whose high density of fixed and pH independent charges produce intrapolymer interactions, that facilitate both the counterion migration and segmental motion of polymer strands essential for rapid oxidation and reduction of the metal complexes within the coating.

The permeation of polycationic films of poly[tris(4-methyl-4'-vinyl-2,2'-bipyridine)ruthenium(II)] $^{2+}$ to various substrates e.g. ferrocene, has been found to vary with electrolyte concentration [15]. The results obtained allowed separation of the contributions of partition and diffusion of the electroactive permeant into and within the polymer. The permeability

dependence of electrolyte concentration varied with the nature of the permeant i.e. whether cationic, anionic or neutral. The electrolyte concentration also caused variation in half-wave potential values for the reduction/oxidation of the permeants. Doblhoffer and co-workers have studies the diffusion or migration of the substrate $[Fe(CN)_6]^{4-}$ across a poly-(4-vinylpyridinium) film [16]. It was found that increasing the electrolyte concentration causes the Donnan exclusion to break down. Anions and cations from the electrolyte enter the polymer matrix. Depending on their concentration and mobility, they can transport charge across the film and can determine the redox processes.

Similar studies were carried out by Elliot and Redpenning using electrodes modified with [tris(5,5'-dicarboxyester-2,2'bipyridine)ruthenium(II)]$^{2+}$ [17]. They studied the stabilities of the polymer films - the complex in the polymer changes from 2+ to 4- species. In the course of transversing the entire oxidation state range, the solvent and supporting electrolytes ions would be expected to influence the stability and response of the polymer, and indeed the degree of polymer swelling and thus the nature of the solvent found to effect the electrochemical response.

Studies of sweep rate dependence on the

electrochemical response have also been the subject of much work as they provide information about the kinetics of the electron transfer in a given polymer system [6, 14, 18, 19]. One such example is illustrated by Degrand and Miller [6], where the peak shapes and separations are found to depend on sweep rate. The shape and characteristics of waves in cyclic voltammograms depend on the thickness of the resulting films. As a general comment, thin films exhibit a linear dependence of i_p on sweep rate and ΔE_p approaches the diffusion free theoretical values of zero at slow sweep-rates. Large ΔE_p values and diffusional tailing is explained by slow electron transfer. If ΔE_p decreases with decreasing sweep rate then the electrochemical behaviour is kinetically controlled. With most systems which have been studied, tailing of the redox wave and larger ΔE_p values appear with increasing sweep rate. By monitoring the sweep rate dependence one can thus detect the transition between surface (thin layer) and diffusional behaviour [20 - 21].

In this section the electrochemical properties of electrodes coated with the synthesised materials are investigated. The dependence of the electrochemical response on the electrolyte, pH and sweep rate was investigated. The permeability of the films to a substrate material is also studied. Chrono-

amperometric experiments were carried out to allow
determination of the charge transport in the film.

IV.2   RESULTS AND DISCUSSION

IV.2.1   Electrolyte Effect

The significance of the choice of supporting electrolyte on the electrochemical response has been discussed in the introduction to this chapter. The electrochemical behaviour of representative samples of the synthesised materials was studied in a series of electrolytes. (Table 4.1). These results were obtained from cyclic voltammetric studies, examples of which have been illustrated in Figure 4.1.

As indicated from the tabulated results, the electrochemical response depends strongly on the nature of the supporting electrolyte. Considering the results for Sample C, as a representative sample of $[Ru(bipy)_2(PNVI)Cl]Cl$, it is evident from the redox potential and the peak shape that the least amount of diffusional behaviour occurs, i.e. ΔE_p is lowest, when $1M$ H_2SO_4 is used as the supporting electrolyte. The slowest electron transfer occurs when $HClO_4$ or $CH_3CN/TEAP$ are used. The same results are obtained for the disubstituted complex. In general, the influence of the electrolytes used is reflected in the shape of the cyclic voltammogram, where much broader bands with larger peak-to-peak separations are obtained in high pH or perchlorate media than in low
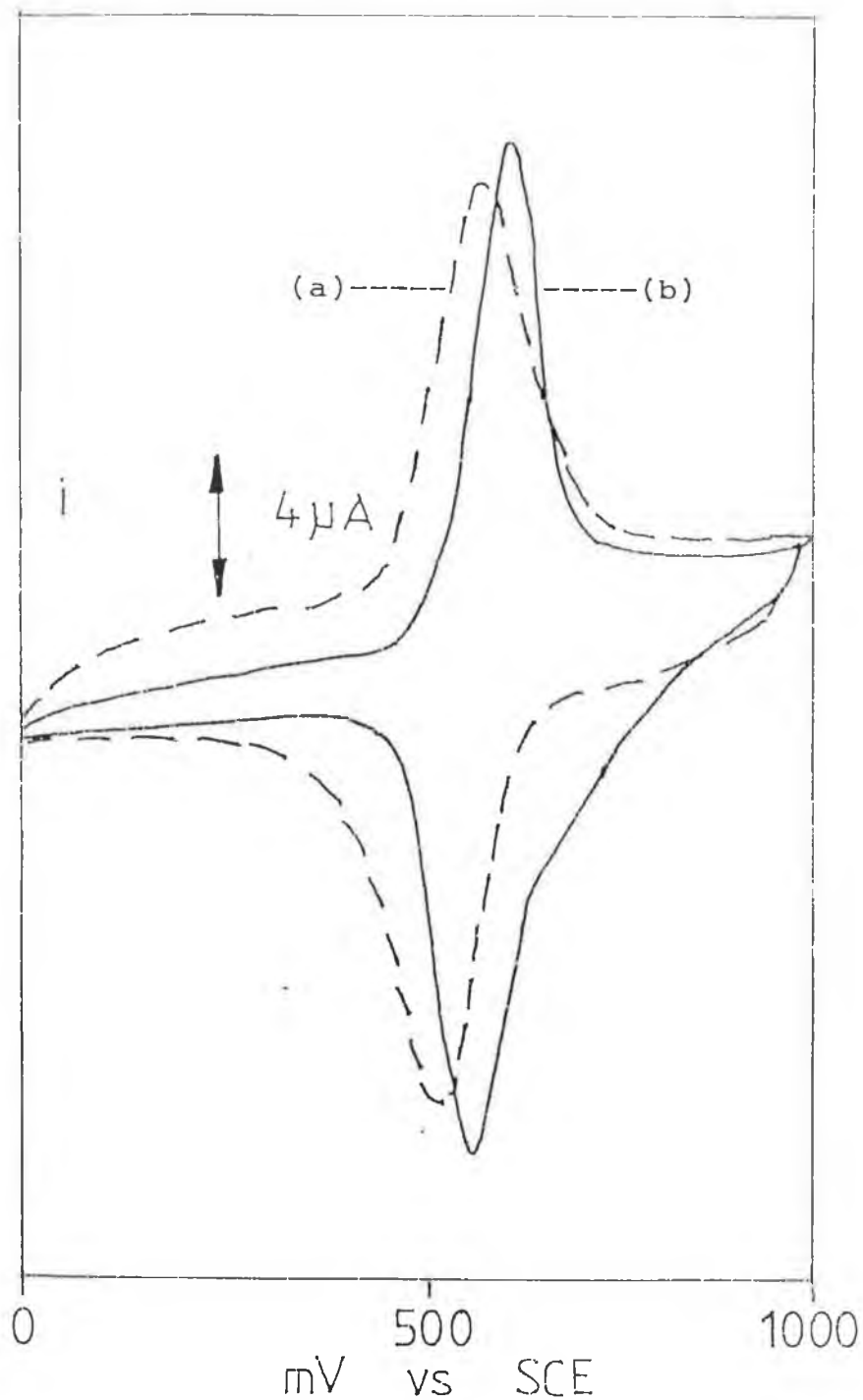
FIGURE 4.1.

(a) Cyclic voltammetric response of a $[Ru(bipy)_2(PNVI)Cl]^+$ coated electrode. Electrolyte : $0.9M$ $NaClO_4$ + $0.1M$ $HClO_4$. Coverage : 1×10^{-8} moles/cm^2.

(b) Cyclic voltammetric response of a $[Ru(bipy)_2(PNVI)Cl]^+$ coated electrode. Electrolyte : $0.9M$ $NaCl$ + $0.1M$ HCl. Coverage : 1×10^{-8} moles/cm^2.

Scan rate = 50mV/sec.

101

TABLE 4.1. Effect of different electrolytes on the $E_{1/2}$ values of the species $[Ru(bipy)_2(PNVI)Cl]^+$ (sample C) and $[Ru(bipy)_2(PNVI)_2]^{2+}$ (sample I).

	$E_{1/2}$	
Electrolyte	$[Ru(bipy)_2(PNVI)Cl]^+$	$[Ru(bipy)_2(PNVI)_2]^{2+}$
1M H_2SO_4	585(30)	860(60)
1M HCl	605(50)	925(50)
1M NaCl	660(55)	920(60)
1M $HClO_4$	550(100)	825(110)
* CH_3CN/ TEAP	665(125)	1025(90)

Measurements were taken using polymer modified glassy carbon electrodes. Surface coverage 3×10^{-8} moles/cm^2; scan rate 50 mV/sec. All potentials are mV vs SCE. Values in brackets are peak-to-peak separations.

* Electrolyte concentration 1M TEAP in CH_3CN.

pH sulphate or chloride media. This is most likely explained by the nature of the metallopolymer electrolyte interface.

Because of protonation of the polymer backbone the metallopolymer is more easily penetrated by an acidic electrolyte, 1M H_2SO_4, and this may lead to a lower redox potential in acidic media. The lower redox potential in the acidic perchlorate medium is not understood. The polymer is not soluble in this electrolyte and probably presents a closed structure not facilitating penetration of perchlorate ions. This would be expected to hinder electron transfer and lead to a redox couple at higher potential but this is not the case. It is possible that, with a closed structure the ruthenium centres are closer together, resulting in a faster charge transport process.

The electrochemical behaviour of the aquo species $[Ru(bipy)_2(PNVI)_2H_2O)]Cl_2$, which was prepared photochemically, was also studied in a series of electrolytes. On placement in 1M HCl, the system immediately reverses back to the monosubstituted species indicating how labile the aquo ligand is in chloride electrolyte. This effect is illustrated in Figure 4.2. The system could be reconverted to the aquo complex by photolysing again in 1M $HClO_4$. On integration of the area under the cyclic voltammogram
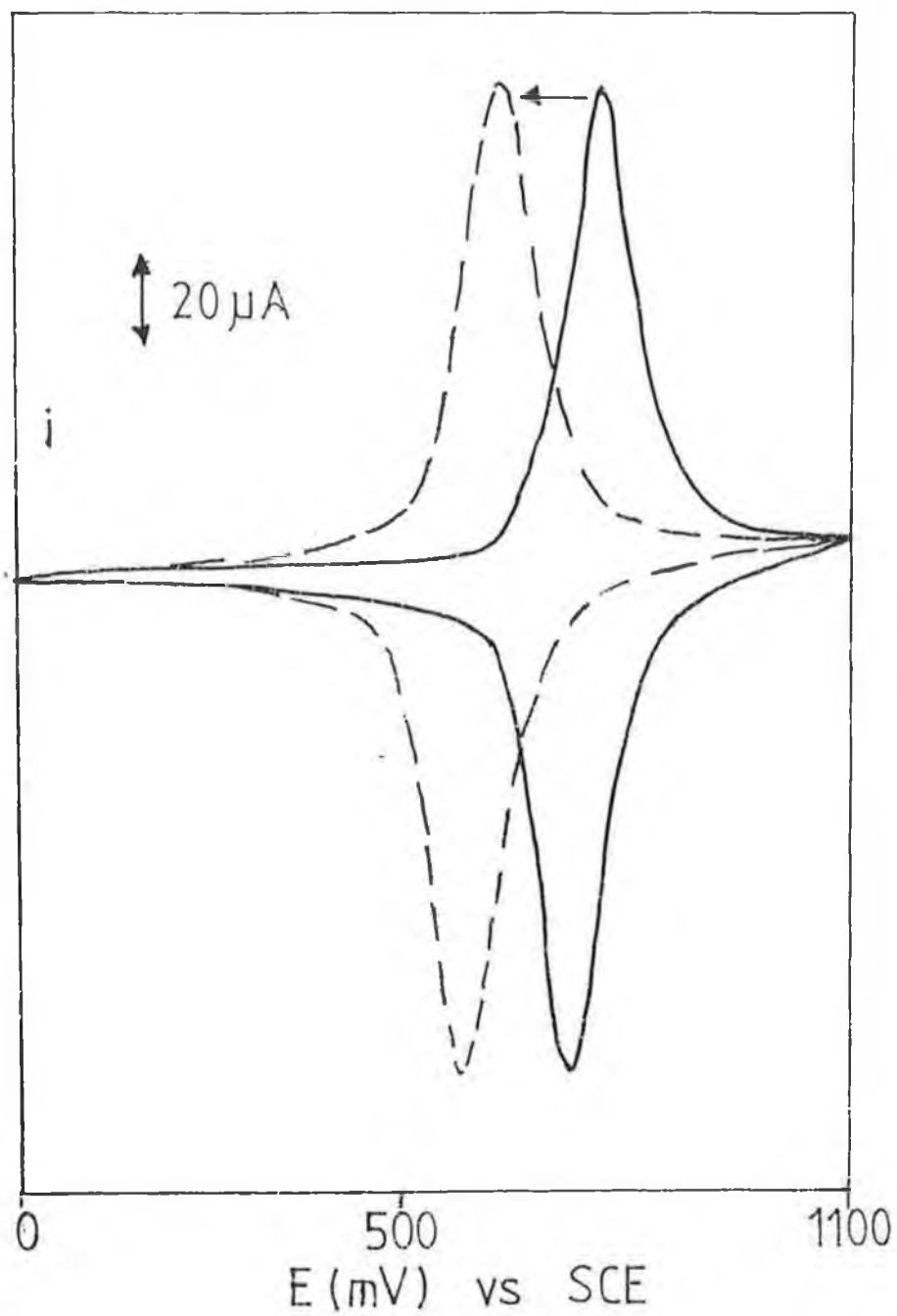
Figure 4.2. Cyclic voltammogram of $[Ru(bipy)_2(PNVI)H_2O]^{2+}$ in 1M HCl.

Sweep rate = 50mV/sec.

it was found that there was little or no loss of product from the electrode surface.

This study indicated that the aquo complex is photostable (not degraded) but very labile showing immediate response to experimental variations i.e. of electrolyte. This dependence of the electrochemical response on the electrolyte, concentration or nature of counterion, is a property common to many systems [1 - 6, 16, 17]. Overall it can be said that the change in electrochemical behaviour (redox potential) observed upon a change of electrolyte is probably due to an alteration in anion absorption within the polymer film as has been previously found with similar systems [16, 17].

IV.2.2 Sweep Rate Dependence

In order to examine the sweep rate dependence of these poly-N-vinylimidazole based systems, the peak current was measured as a function of sweep rate for sample C, which contains predominantly $[Ru(bipy)_2(PNVI)Cl]Cl$. Other samples were also studied and similar results were obtained. This relationship was investigated in two different electrolytes, 0.2 M $NaClO_4$ and 0.1 M H_2SO_4. The cyclic voltammograms obtained were found to show a decrease in peak-to-peak separation with decreasing scan rate. These features are illustrated

in Figure 4.3 and the results are given in Table 4.2. A linear dependence of the peak current on the scan rate was found to exist up to a certain limit. This limit was found to be dependent on the electrolyte used. In 0.2 M $NaClO_4$ the limit of the linear range was found to be 140 mV/s; in 0.1 M H_2SO_4 the limit of the linear range was found to extend to 200 mV/s. Above these limits the peak current was linearly proportional to (scan rate)$^{1/2}$. (See Figures 4.4 (a) and (b)). The difference in the two responses can be explained quite easily in terms of the ability of the electrolyte to permeate the layer. The polymer layer is protonated in the acidic sulphate medium and thus presents a more open structure for permeation by the electrolyte, facilitating the electron transport process. This deduction is supported by the fact that at any sweep rate the peak-to-peak separation is smaller in the acidic electrolyte than at neutral pH. Overall it can be concluded that the polymer films showed the electrochemical behaviour characteristic of surface-bound, fast electron exchanging species [22].

IV.2.3   Stability of Coated Electrode Surfaces

The stability of the films for all samples was found to depend on the electrolyte used. As a general observation, the monosubstituted complex was found to be more stable in the variety of electrolytes used,

Table 4.2 - Sweep-rate Dependence of ΔE_p.

Sweep Rate	ΔE_p
mV/s	mV
2	75
4	80
6	95
8	100
10	110
20	115
30	120
40	125
50	130

Measurements taken using polymer modified glassy carbon electrodes. Surface coverage 1.4 X 10^{-8} moles/cm^2, of [Ru(bipy)$_2$(PNVI)Cl]$^+$. Electrolyte 0.2M NaClO$_4$.
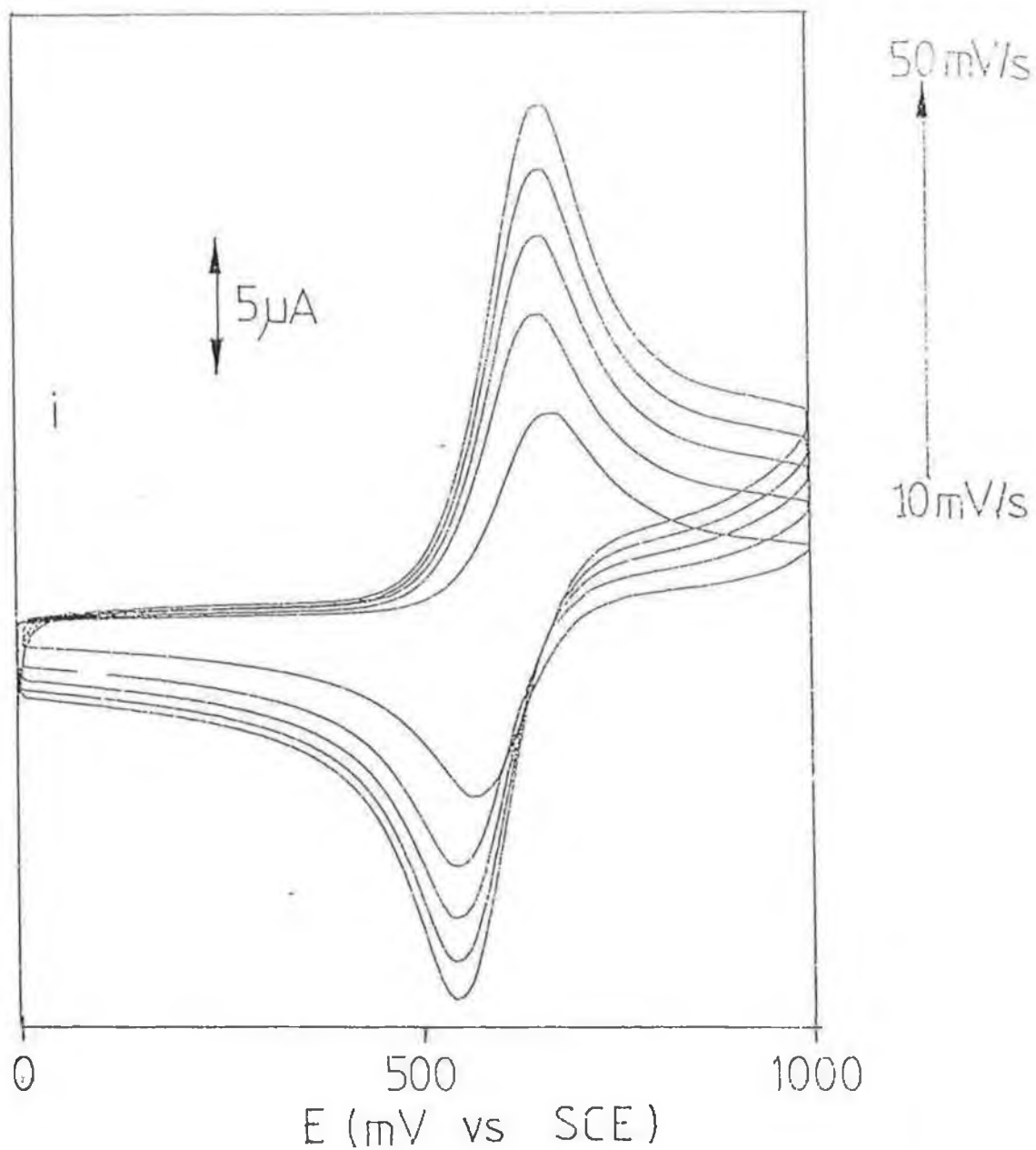
FIGURE 4.3.

Scan rate effect for an electrode coated
with 2.7×10^{-8} moles/cm^2 [Ru(bipy)$_2$(PNVI)Cl]$^+$.
Electrolyte : 0.2M NaClO$_4$.
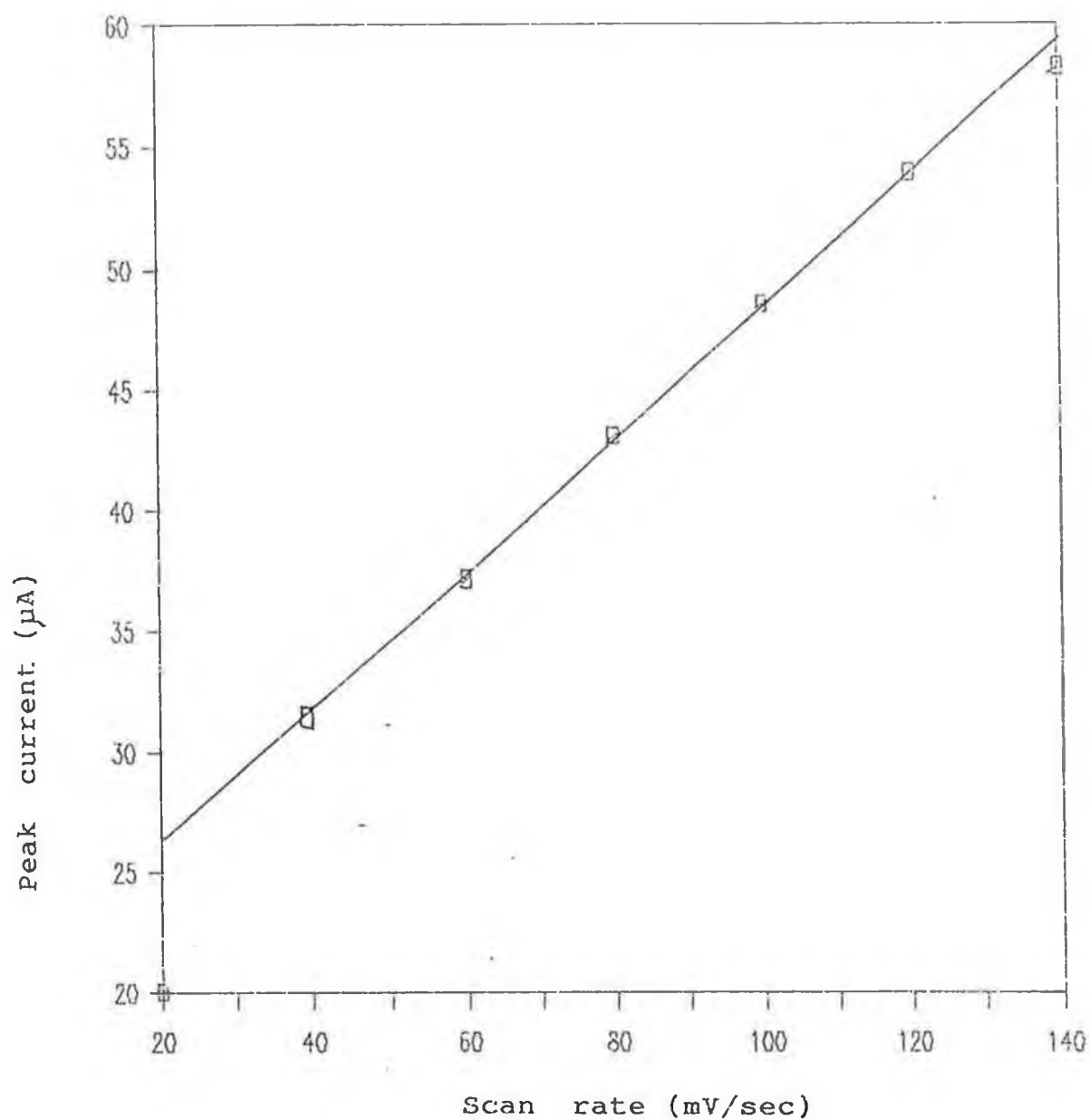
FIGURE 4.4 (a) Plot of peak current versus scan rate.

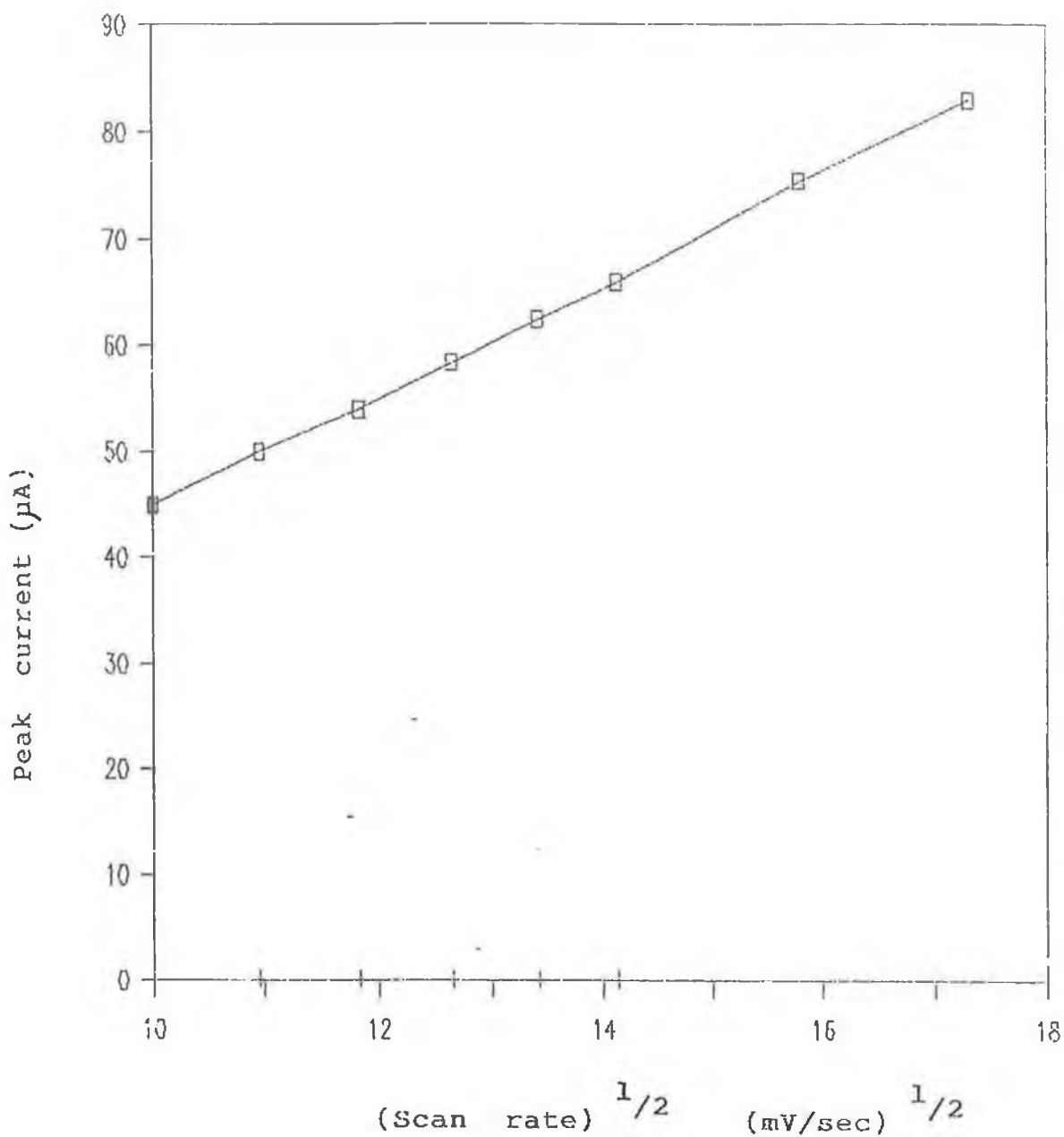Surface coverage : 2.7×10^{-8} moles/cm^2 of $[Ru(bipy)_2(PNVI)Cl]^+$.

Electrolyte : 0.2M $NaClO_4$.

FIGURE 4.4 (b). Plot of peak current versus (scan rate)$^{1/2}$.

Surface coverage : 2.7 x 10^{-8} moles/cm^2 of $[Ru(bipy)_2(PNVI)Cl]^+$.

Electrolyte : 0.2M $NaClO_4$.

than the disubstituted complex. The film stabilities could be monitored by sequential cyclic voltammetric scanning. In the case of the complex [Ru(bipy)$_2$(PNVI)Cl]Cl, the films were found to be initially a little unstable in 1M H$_2$SO$_4$ or other strong acids in which the polymer films are soluble. However, they do reach an "equilibrium" situation where no more material is leached off the electrode surface. The stability was found to improve somewhat by use of the cross-linking agent, 1,10-dibromodecane as has been employed by Lindholm and Sharp [23]. It should be noted that the materials were very sensitive to light with the occurrence of some photochemical reactions. These processes will be discussed in detail in the next chapter. With respect to the disubstituted complex instability in most electrolytes used was found to be a particular problem. In low pH sulphate based electrolytes, it was found that films of the complex, [Ru(bipy)$_2$(PNVI)$_2$]$^{2+}$, were completely degraded or leached off the electrode surface as observed by sequential cyclic voltammetric scanning. Indeed, for this complex the process was complete with the final scan being equivalent to that for a bare electrode.

IV.2.4   Effect   of   Addition   of   the   Substrate,
         $K_4[Fe(CN)_6]$,   to   Electrolyte   on   Cyclic
         Voltammetric   Response   of
         $[Ru(bipy)_2(PNVI)Cl]Cl$ Coated Electrodes

The permeation of iron-containing substrates through
the polymer film will be discussed in a subsequent
chapter in relation to mediated electrocatalysis.
Here the effect of such a substrate on the
electrochemical response of the film-coated electrodes
is investigated and also the role of the supporting
electrolyte itself is studied in this regard.

In the absence of any substrate, cyclic voltammograms
were recorded, at varying sweep rates, for a
$[Ru(bipy)_2(PNVI)Cl]Cl$ coated glassy carbon electrode.
As expected the peak current was found to increase
with increasing scan rate.

In the presence of $K_4[Fe(CN)_6]$ in 0.2 M $NaClO_4$, cyclic
voltammograms were recorded for varying sweep rates in
the range 2 mV/s to 100 mV/s.   In the range from 10
mV/s to 100 mV/s it was found that the peak current
for the Ru(II)/Ru(III) redox couple increased with
increasing sweep rate.   In this range it was found
that with decreasing sweep rate a new band was
starting to develop around 400 mV, as illustrated in
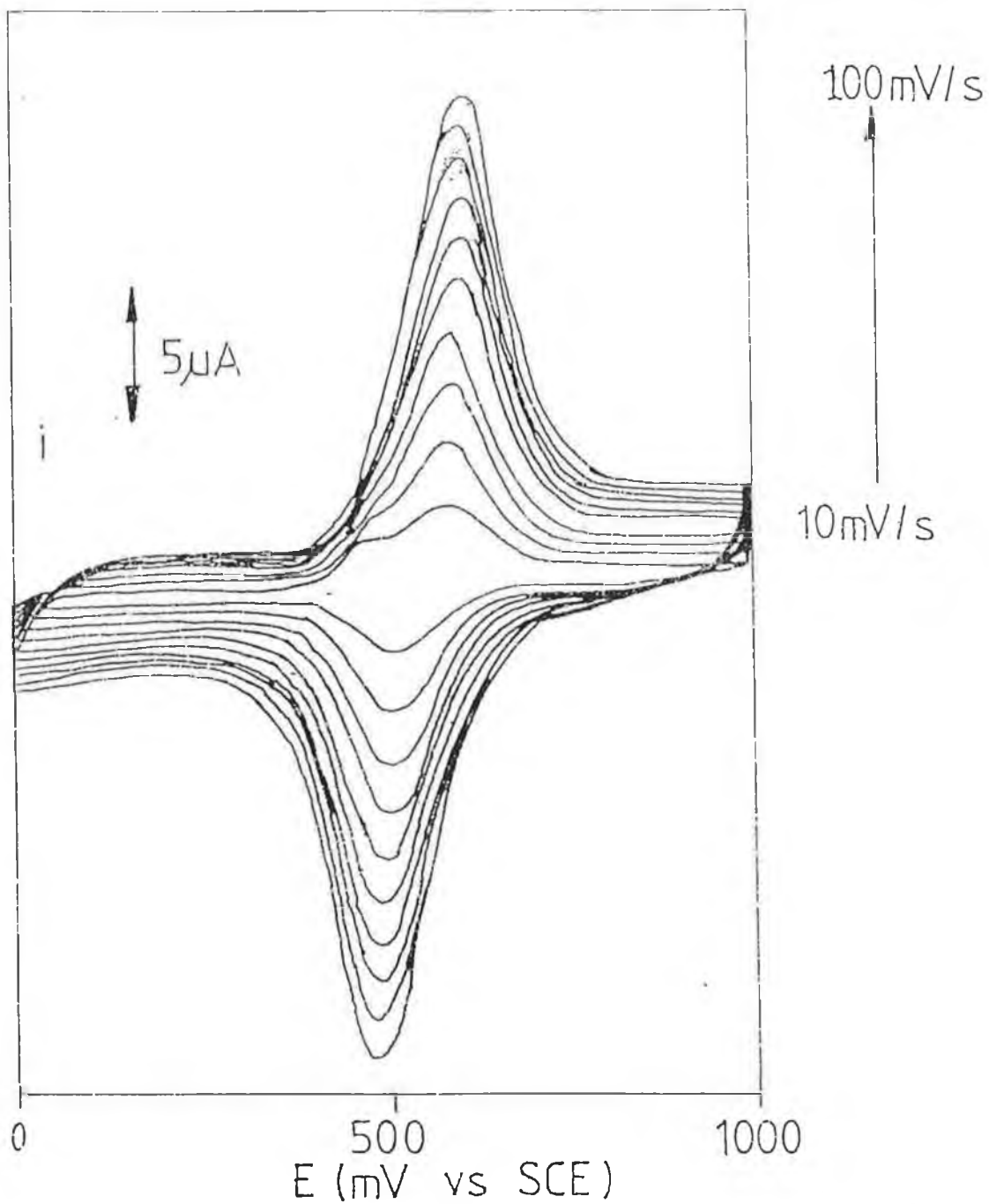Figure 4.5.   This effect became much more obvious at

FIGURE 4.5. Effect of scan rate on substrate penetration.
Surface coverage : 1.2×10^{-8} moles/cm^2 [Ru(bipy)$_2$(PNVI)Cl]$^+$
Electrolyte : 0.2M NaClO$_4$.
Substrate : 1mM K$_4$[Fe(CN)$_6$]

the lower sweep rates as shown in Figure 4.6. It was in fact found that the intensity of the band due to the iron redox couple increased with decreasing sweep rate. This suggests that we were not just looking at the reaction of Fe(II) with the bare electrode. If this were the case an increase in peak current with increasing sweep rate would be observed. Instead we are looking at a process which is dependent on migration or diffusion of the iron complex through the polymer layer. At slower sweep rates the substrate has more time to migrate through the film and so the signal becomes stronger. However, we could also be looking at some mediated oxidation of the Fe(II) by the Ru(II) present in the layer. At a bare electrode, the Fe(II)/Fe(III) redox couple occurs at 260 mV as opposed to 400 mV using the coated electrode. One other point to note here is that the Fe(II) oxidation is irreversible.

Increasing the amount of material bound to the electrode surface approximately two-fold caused an alteration of response for similar experiments. As indicated in Figure 4.7, even at the lowest sweep rate, 2 mV/s, no definite peak for the Fe(II)Fe(III) redox couple was observed. The oxidation wave of this couple appeared as a shoulder of the Ru(II)/Ru(III) oxidation wave. This would imply that the layer is too "thick" to penetrate through and does substantiate
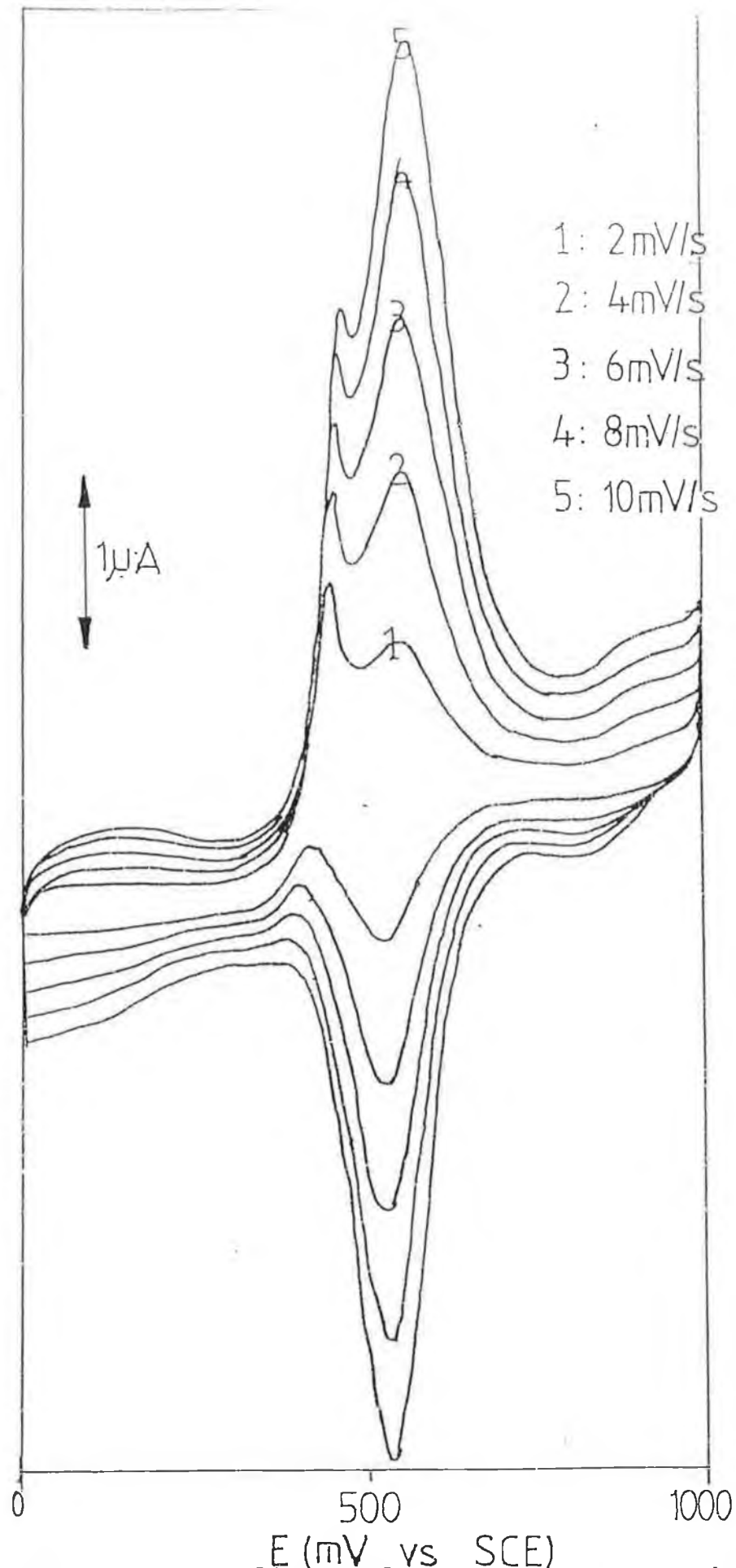
114

FIGURE 4.6. Effect of scan rate on substrate penetration.

Surface coverage : 1.2×10^{-8} moles/cm^2 [Ru(bipy)$_2$(PNVI)Cl]$^+$
Electrolyte : 0.2M NaClO$_4$.
Substrate : 1mM K$_4$[Fe(CN)$_6$]

the idea that we are looking at a migration process of the iron complex through the polymer film to the electrode surface. Increasing the $K_4[Fe(CN)_6]$ concentration to 2 mM does allow detection of the Fe(II)/Fe(III) redox couple which however only becomes visible at 2mV/s. At higher sweep rates it appears that the iron just serves to enhance the intensity of the Ru(II)/Ru(III) couple. This is attributed to the fact that the Fe(II)/Fe(III) couple is not distinguishable as a separate band; also the intensity of the oxidation band is somewhat stronger than that of the reduction signal which fits in with the result that the Fe(II) oxidation is irreversible. This compares with studies carried out by Cassidy and co-workers [29, 30].

This type of work is quite similar to some carried out by Doblhoffer, Braun and Lange [16], where they investigated the effect of increasing the concentration of background electrolyte to prevent other ions diffusing into the layer. By comparison to their results, it would appear that the negatively charged iron complex $[Fe(CN)_6]^{4-}$ is drawn into the layer in order to balance out the positive charge resulting from the oxidation of Ru(II). Using only 0.2M $NaClO_4$ must not supply sufficient anions (ClO_4^-) for this purpose so the $[Fe(CN)_6]^{4-}$ migrates into the layer.

Similar experiments were carried out using other electrolytes. Using a perchlorate electrolyte at pH of 2.0 the electrochemical response of the coated electrodes was measured as a function of sweep rate in the presence of $K_4[Fe(CN)_6]$. In this case the peak current was found to increase with increasing sweep rate for both the Ru(II)/Ru(III) and Fe(II)/Fe(III) redox couples indicating the penetration of the substrate to the electrode surface, see Figure 4.8. Another point of note is that the Fe(II)/ Fe(III) redox couples occurs at 300 mV indicating that it does not depend on migration through the film or any mediation by the ruthenium present in the film. It should also be noted that at this lower pH, the Fe(II) oxidation is reversible. This suggests a direct reaction at the bare electrode.

Experiments were also carried out in chloride media at pH 2.0 and pH 6.0. Considering first pH 2.0, the peak current of both redox couples increased with increasing sweep rate as expected. In an acidic, chloride based electrolyte one achieves a very open structure so anions and substrate can diffuse freely through the film thus allowing reaction of the substrate Fe(II) to react at the bare electrode. Results are illustrated in Figure 4.9. Similar results were obtained for a pH 6.0 chloride electrolyte, (Figure 4.10), indicating that it was not
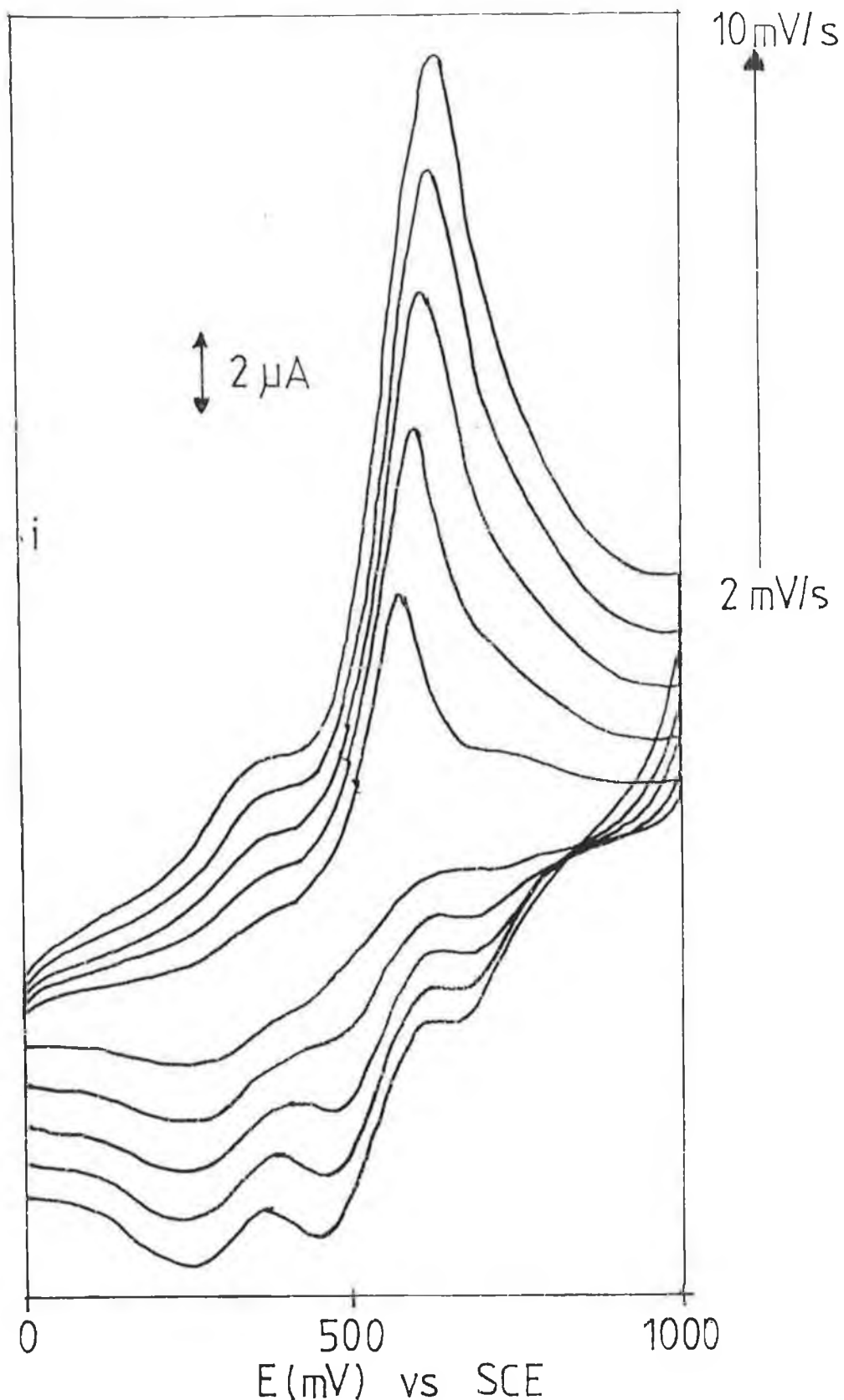
117

FIGURE 4.8. Effect of scan rate on substrate penetration.

Surface coverage : 0.9×10^{-9} moles/cm^2.

Electrolyte : 0.9M NaClO$_4$ + 0.1M HClO$_4$.
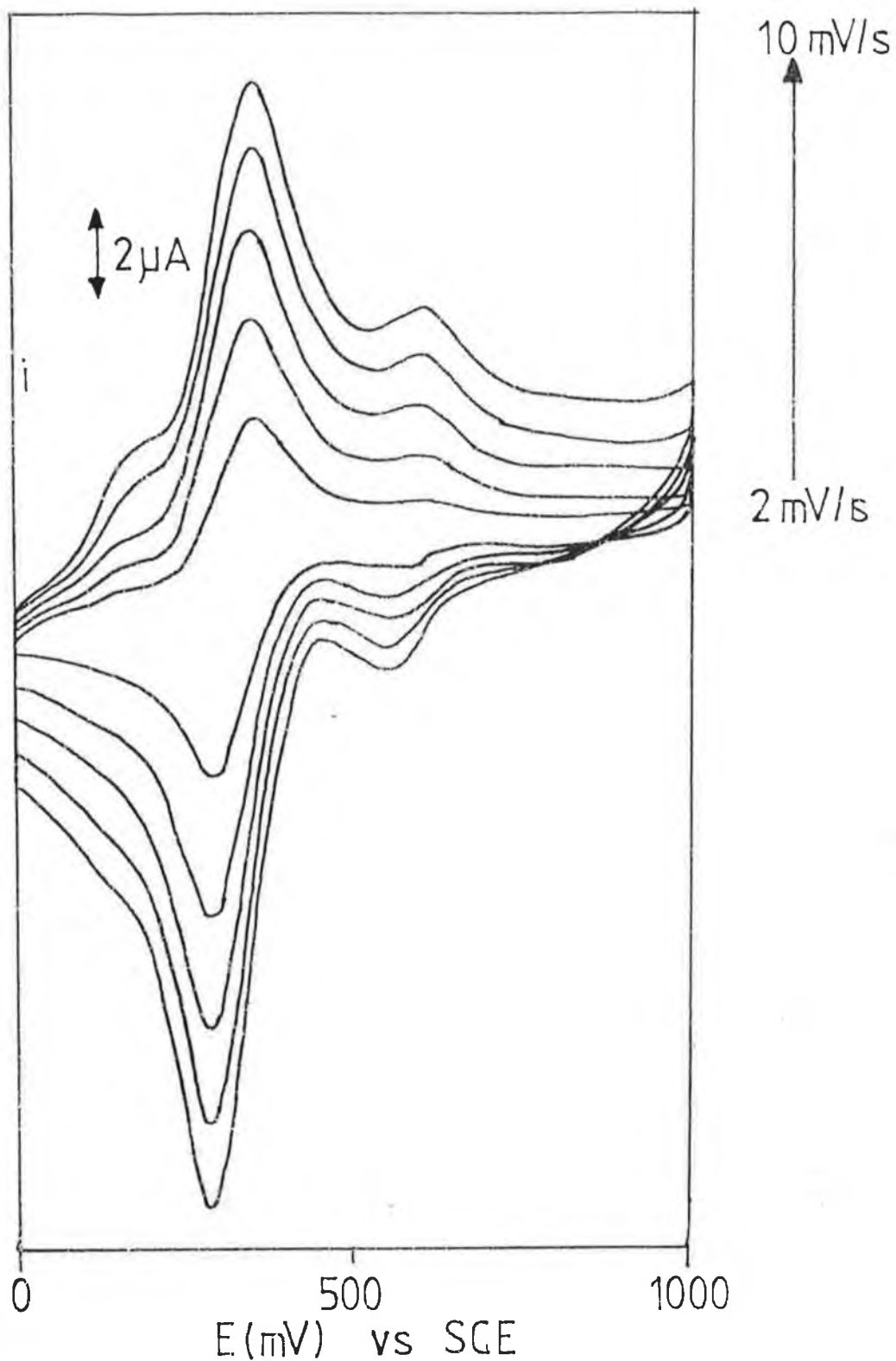
Substrate : 1mM K$_4$[Fe(CN)$_6$]

FIGURE 4.9. Effect of scan rate on substrate penetration.

Surface coverage : 1.1×10^{-8} moles/cm^2.

Electrolyte : 1M HCl.
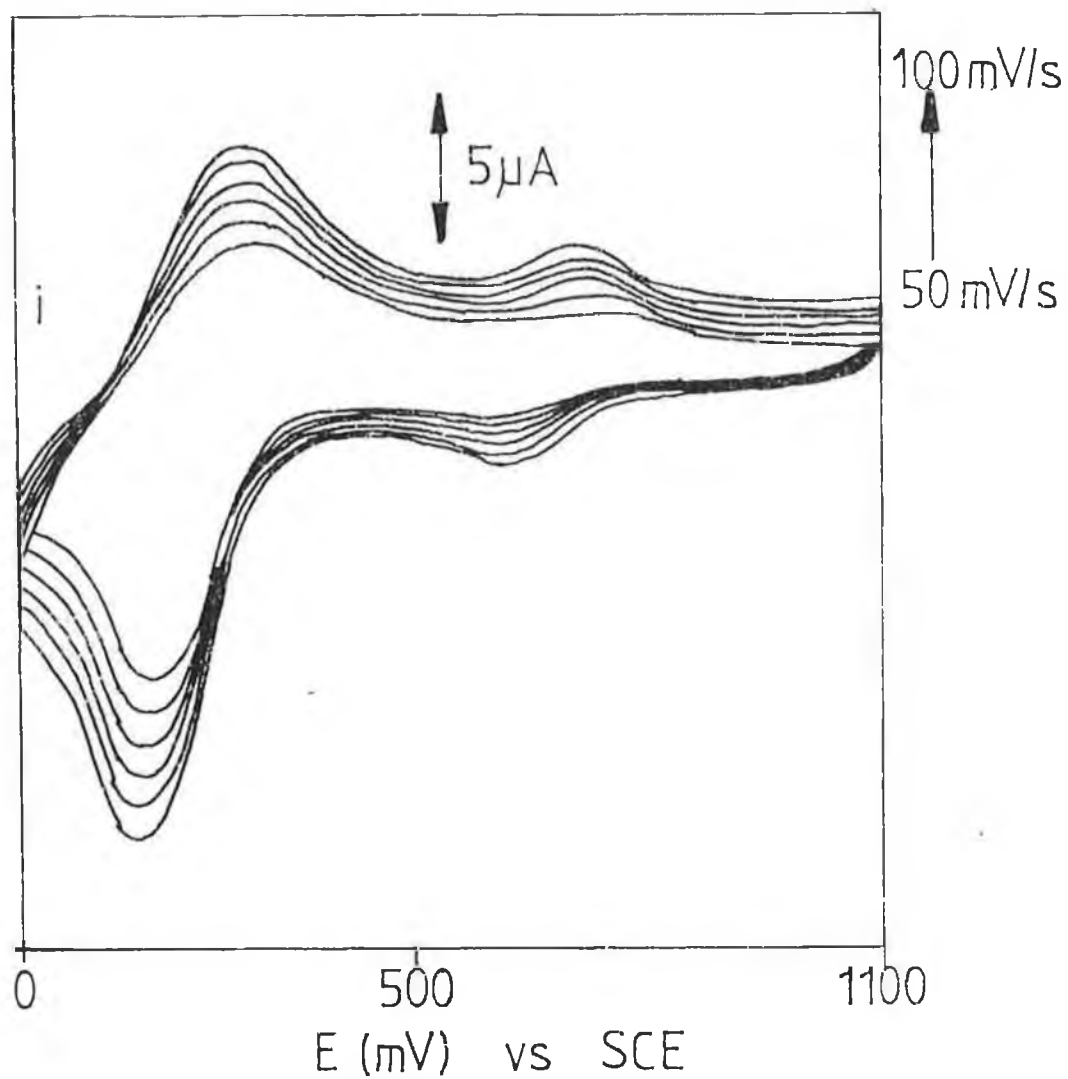
Substrate : 1mM $K_4[Fe(CN)_6]$

Figure 4.10. Effect of scan rate on substrate penetration.
Surface coverage : 1.2×10^{-8} moles/cm^2.

Electrolyte : 0.2M NaCl.

Substrate : 1mM $K_4[Fe(CN)_6]$.

just a pH effect which was observed but one dependent on the nature of electrolyte used. In this way the permeability of the metallopolymeric film is seen to be dependent on the nature of the supporting electrolyte ions. This thus determines whether a mediated redox reaction or a reaction at the bare electrode is observed.

IV.2.5   Chronoamperometric Experiments

The determination of the electron diffusion rate in the film has been studied. This parameter was investigated for this system in the presence of a supporting electrolyte and in the absence of any substrate material. The techniques commonly used for this purpose are chronocoulometry (charge-time plots) or chronoamperometry (current-time plots) [23 - 28]. The latter, also known as potential jump, has been employed here. This technique has been widely used to determine the charge transport rate, defined by the apparent diffusion co-efficient, D_{CT}, in polymer coatings. The charge transport can be controlled by 1) hopping of the electrons between neighbouring oxidized and reduced species, 2) diffusion of the counter-ion in the layer or 3) movements of polymeric chains. Values of D_{CT} (or more precisely those of $D_{CT}^{1/2}c$, c being the concentration of electroactive sites in the coating) are obtained by stepping the

121

potential between two limits which are dependent on the redox couple involved. The resulting i-t responses are transformed according to the Cottrell equation [27],

$$i = n \, FA \, D_{CT}^{1/2} \, c \, \pi^{-1/2} \, t^{-1/2} \qquad (1)$$

to give, ideally, a straight line or a large straight line component.

RESULTS AND DISCUSSION

The chronoamperometric response was recorded for both the anodic and cathodic processes in two different electrolytes with different pH values. The potential was stepped from 0.3 V to 0.9 V for the oxidative process and from 0.9 V to 0.3 V for the corresponding reductive process. The current was recorded as a function of time on a digital oscilloscope. The use of short-time data is limited by the rise-time of the potentiostat-cell system and uncertainties in correcting the total measured current for the non-faradaic current attributable to double-layer charging was carried out by repeating the potential step experiment in a region where the electroactive species contained in the polymeric film was unaffected i.e. from - 0.2 V to + 0.4 V and + 0.4 V to - 0.2 V for oxidation and reduction respectively. The currents

observed for these last experiments were then subtracted from those observed for experiments involving the actual redox couple to give a value only for the faradaic current.

Experiments were carried out using glassy carbon electrodes coated with different amounts of the electroactive species, [Ru(bipy)$_2$(PNVI)Cl]Cl. The surface coverages were calculated by running cyclic voltammograms before the potential jump experiments. Integration of the area under the peaks allows calculation of these coverages [7], results of which are indicated in Table 4.3. Surface concentrations can also be calculated from the potential jump experiments from he values of total charge passed. However, large discrepancies were found using the two methods, as illustrated in Table 4.3. Values were consistently found to be smaller using the latter method indicating that only part of the layer was active during the potential jump experiments. Differences were found to be greater where higher surface coverages were involved which would be expected as thinner layers would facilitate electron transport in the film.

Values for the diffusion co-efficients studied under different experimental conditions and calculated from the slopes of the i-t plots for anodic and cathodic reactions have been given in Table 4.3.

Typical chronoamperometric responses obtained have been illustrated in Figure 4.11 (a), (b), (c), and (d). It is evident from the examples given that there is more deviation from the "linear" Cottrell plots when 0.2 M $NaClO_4$ at pH 6, is used as the supporting electrolyte. This can be explained by the fact that in a more acidic (pH 2) electrolyte the polymer film presents a more open, swollen structure thus facilitating electron transport. The chrono-amperometric results tend to support the contention that ion transport within the polymer layer is the rate determining process, at least for a significant fraction of the reduction or oxidation time. The degree of polymer swelling and thus the nature of the solvent should therefore impact significantly on the electrochemical response time. Here, by realising the variation in response with different electrolyte, important information is gained with respect to film permeability which is of particular interest in relation to the evolving theory of mediated electrocatalysis, examples of which will be illustrated in a later chapter.

Comparison of the responses for different film thicknesses studied showed significant variations. Decreased film thickness resulted in more linear Cottrell plots, the linearity being a desirable feature of the system as the slopes of the plots would

be more accurate with less deviation from linearity. This has important consequences in the determination of the diffusion co-efficients of the electrons in the film; more accurate slopes will give more representative values for D_e. As illustrated in Table 4.5 values of D_e, calculated using equation (1) were found to be of the order of magnitude of $10^{-10} cm^2 s^{-1}$. In the pH 2 electrolyte the average values of D_e were found to be 1.98 X 10^{-10} cm^2 s^{-1} and 2.39 X $10^{-10} cm^2$ s^{-1} for the oxidation and reduction processes respectively. In the pH 6 electrolyte the average values of D_e were found to be 1.84 X 10^{-10} cm^2 s^{-1} and 0,91 X 10^{-10} cm^2 s^{-1} for the oxidation and reduction processes respectively. These values parallel in magnitude those found previously for poly-4(vinylpyridine) analogues as was expected [16].

It should be noted that each of these experiments was carried out in duplicate and very good agreement was found between similar experiments. With this in mind the values calculated can be considered representative for the system under investigation.

FIGURE 4.11(a).
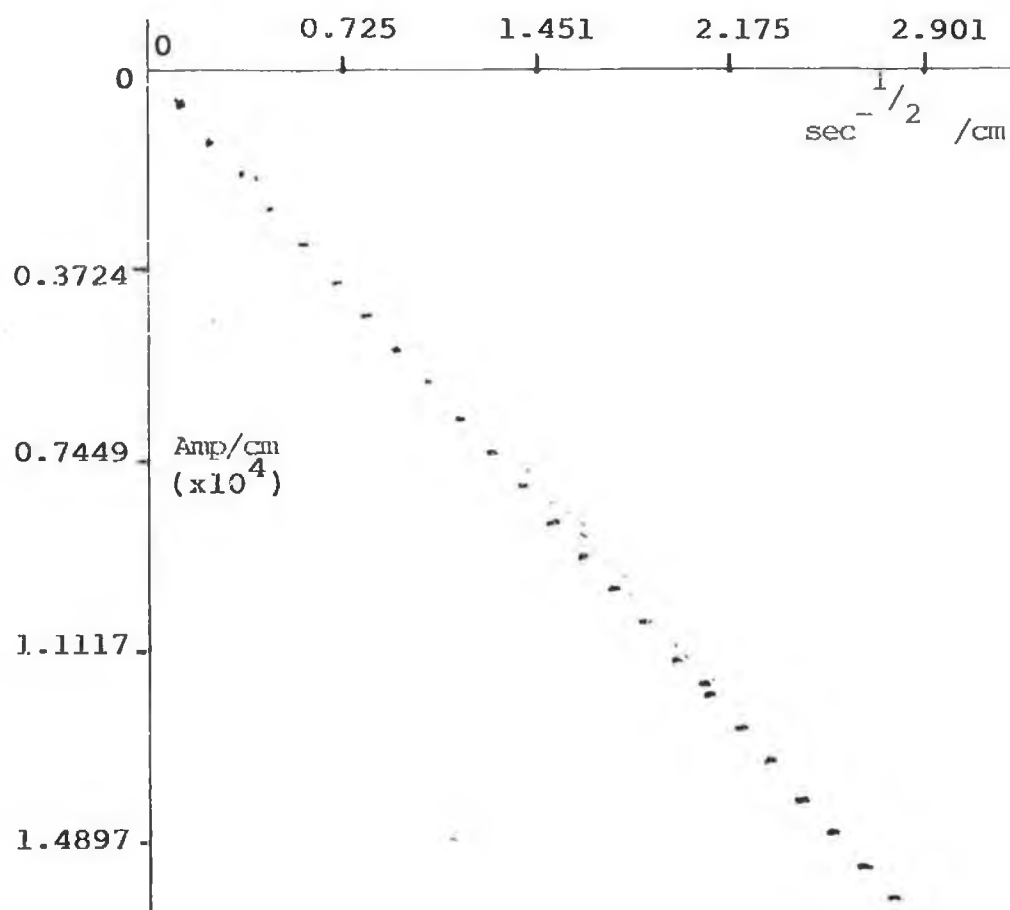
Cottrell plot for oxidation of $[Ru(bipy)_2(PNVI)Cl]^+$ in $0.9M\ NaClO_4 + 0.1M\ HClO_4$.

Vertical : 1.48972973 E-04 Ampere/cm.
Horizontal : 2.90125844 $sec^{-1/2}$/cm.
M = -6.29906176 E-05 $A.s^{1/2}$

FIGURE 4.11(b).
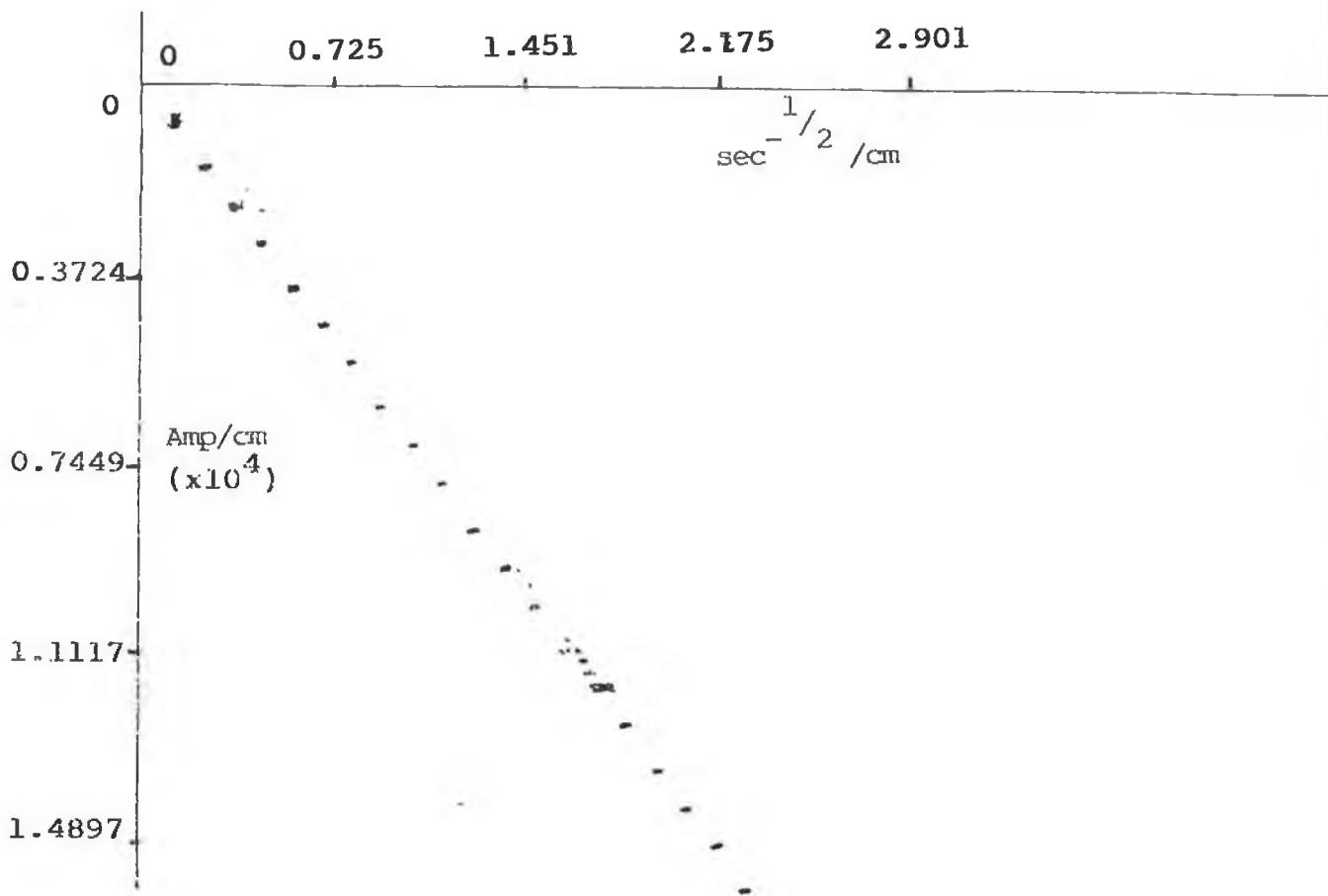
Cottrell plot for oxidation of $[Ru(bipy)_2(PMVI)Cl]^+$ in 0.2M $NaClO_4$.

Vertical : 1.48972973 E-04 Ampere/cm.

Horizontal : 2.90125764 $sec^{-1/2}$/cm.

M = -7.36847669 E-05As$^{1/2}$.

FIGURE 4.11(c).
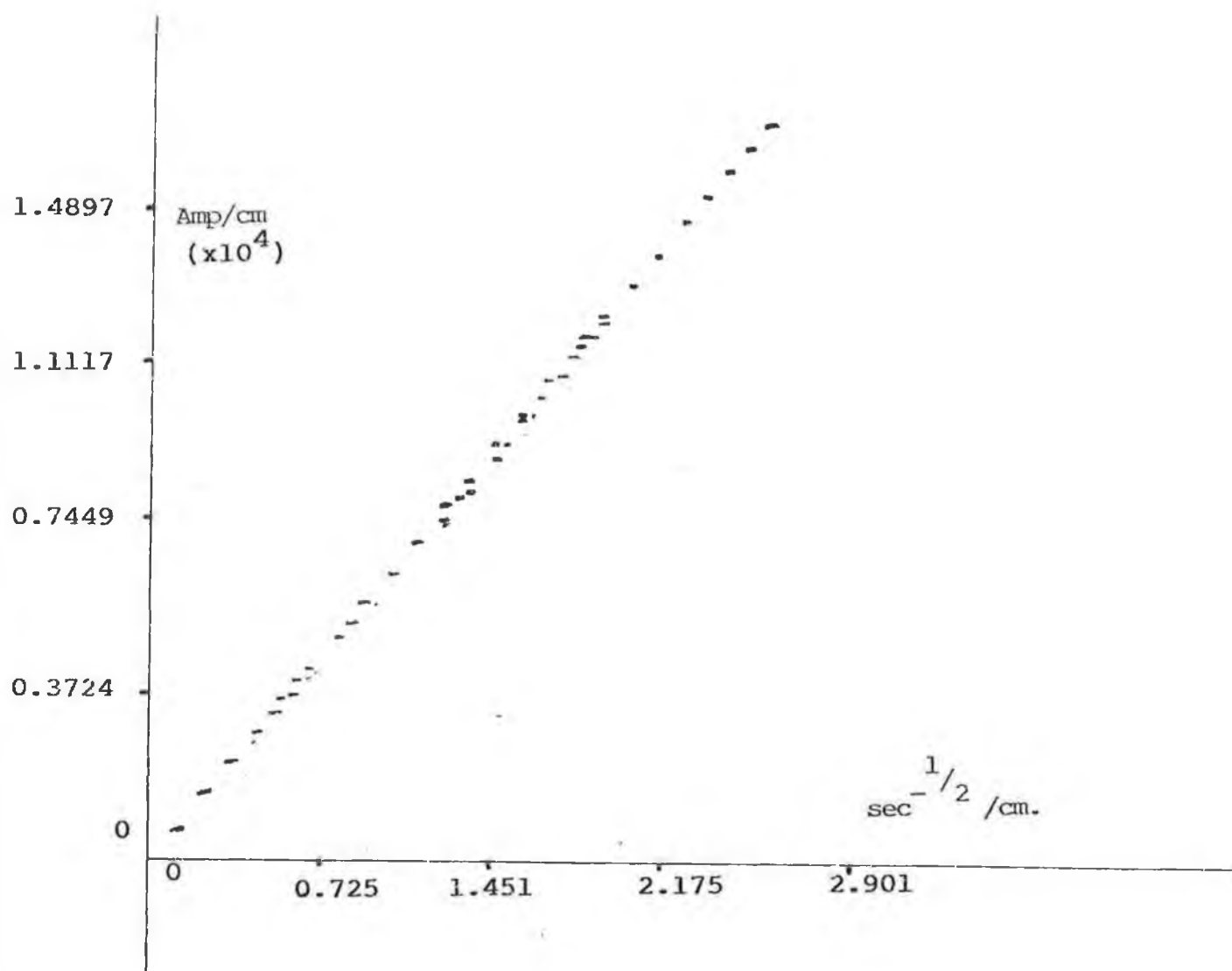
Cottrell plot for reduction of $[Ru(bipy)_2(PNVI)Cl]^+$ in 0.9 M $NaClO_4$ + 0.1M $HClO_4$.

Vertical : 1.48972973 E-04 Ampere/cm.

Horizontal : 2.90125764 $sec^{-1/2}$/cm.

M = 6.63829114 E-05 $A.s^{1/2}$.

FIGURE4.11(d)
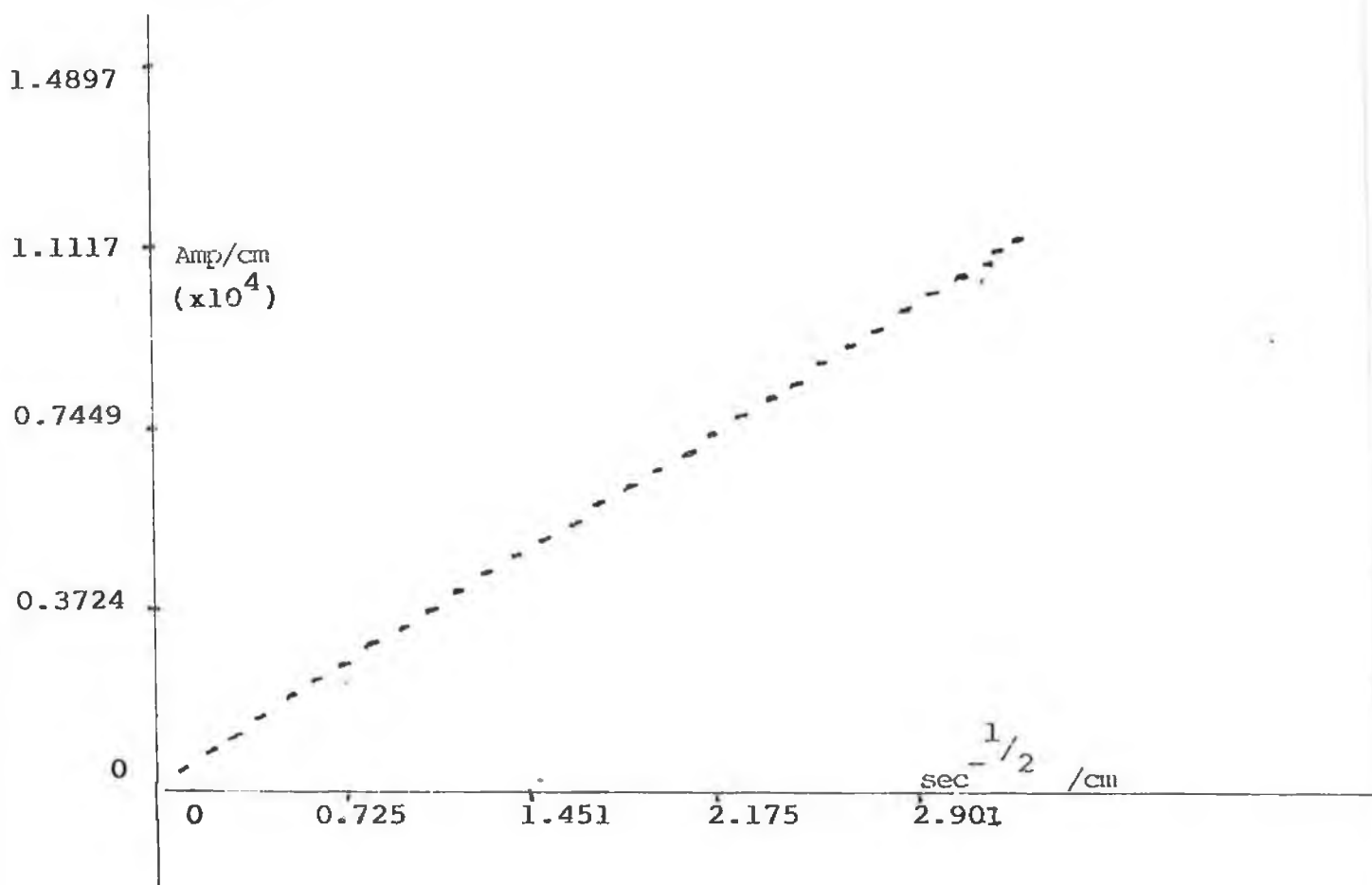
Cottrell plot for reduction of $[Ru(bipy)_2(PNVI)Cl]^+$ in $0.2M\ NaClO_4$.

Vertical : 1.49872973 E-04 Ampere/cm.

Horizontal : 2.90125764 $sec^{-1/2}$/cm.

M = 3.28096003 E-05 $A.s^{1/2}$.

129

Table 4.3 - Results of Chromoamperometric Experiments

EXPERIMENT NUMBER	(1) Γ_{Ru} (X 10^8) mol cm^{-2}	(2) Γ_{Ru} (X 10^9) mol cm^{-2}	$D_{CT}^{1/2}C$ (X 10^8) s$^{-1/2}$mol cm^{-2}	D_e^{a} (X 10^{10}) cm^{2}s^{-1}
1.	4.13	4.32	1.79	1.79
2.	3.38	4.8	2.03	2.03
3.	2.1	4.6	1.86	1.86
4.	1.27	4.85	1.685	2.225
5.	2.77	6.0	2.225	2.62
6.	0.87	7.45	2.62	2.62
7.	3.07	7.71	2.445	2.445
8.	1.8	4.59	1.88	1.88
9.	2.19	5.3	2.29	2.29
10.	2.7	3.49	1.42	1.42
11.	0.69	3.35	1.215	1.215
12.	1.08	4.24	2.423	2.423
13.	1.63	2.4	0.86	0.86
14.	1.77	3.69	1.32	1.32
15.	0.7	2.51	0.73	0.73
16.	0.68	1.37	0.73	0.73

(1) Represents the calculated film thickness from the area under the cyclic voltammogram.

(2) Represents the film concentration determined from applied charge passed (indicated from potential

jump experiment).

(3) Experiment 1 -> 4 oxidation process at pH2.
(0.9M Na ClO_4 + 0.1M $HClO_4$).

5 -> 8 reduction process at pH2.

9 -> 12 oxidation process at pH6.
(0.2M Na ClO_4).

13 -> 16 reduction process at pH6.

a: D_e is equivalent to D_{CT} and was calculated according to equation (1).

IV.3   CONCLUDING REMARKS

It has been illustrated here that the prepared ruthenium based poly-N-vinylimidazole polymers exhibit electrochemical properties common to other systems, including electrolyte, pH and sweep rate dependence. It has also been shown that these materials are somewhat less adherent under certain conditions than their polyvinylpyridine based analogues. This property could therefore limit their applicability to, for example, mediated electrocatalysis. This will be discussed in detail in Chapter 6. In relation to this, the addition of $K_4[Fe(CN)_6]$ did provide some interesting results. Of particular interest is the observation of a mediated oxidation of Fe(II) in an electrolyte which provides a closed polymeric structure. This implies that, for this case, the iron (II) was oxidized in the layer and not at the bare electrode. The irreversible nature of this mediated oxidation is also an important feature to note. The problems associated with choice of electrolyte for these systems i.e. in relation to layer stability, are a most important consideration as has been illustrated. The chronoamperometric experiments served to illustrate different features. One important result was the difference in values of Γ_{Ru} obtained using different methods, indicating that the whole film is not oxidized or reduced in the process

132

as would be expected for short times.

As previously mentioned values of D_e obtained are similar to those obtained for poly(4-vinylpyridinium) analogues [16]. Here, Doblhoffer and co-workers estimated the electronic diffusion co-efficient to be 10^{-12} to 10^{-11} cm^2 s^{-1}.

REFERENCES

1. C. Degrand and L. L. Miller,

    J. Am. Chem. Soc., 102, 1980, 5728.

2. N. K. Cenas, A. K. Pocius and J. J. Kulys,

    Bioelectrochem. Bioenerg, 12, 1984, 583.

3. A. P. Brown, C. Koval and F. C. Anson,

    J. Electroanal. Chem. Interfacial Electro-
    chem., 72, 1976, 379.

4. A. H. Schroeder and F. B. Kaufman,

    J. Electroanal. Chem. Interfacial Electro-
    chemistry, 113, 1980, 209.

5. G. J. Samuels and T. J. Meyer,

    J. Am. Chem. Soc., 103, 1981, 307.

6. C. Degrand and L. L. Miller,

    J. Electroanal. Chem. Interfacial Electro-
    chemistry, 117, 1981, 261.

7. P. R. Moses and R. W. Murray,

    J. Electroanal. Chem. Interfacial Electro-
    chemistry, 77, 1977, 393.

8. C. A. Koval and F. C. Anson,
    Anal. Chem., 50, 1978, 223.

9. H. D. Abruna, T. J. Meyer and R. W. Murray,
    Inorg. Chem., 18, 1979, 3233.

10. O. Haas, H. R. Zumbrunnen and J. G. Vos,
    Electrochim. Acta, 30, 1985, 1551.

11. J. M. Calvert and T. J. Meyer,
    Inorg. Chem., 20, 1981, 27.

12. N. Oyama and F. C. Anson,
    J. Am. Chem. Soc., 101, 1979, 3450.

13. M. S. Wrighton, M. C. Palazzotto, A. B. Bocarsly,
    J. M. Bolts, A. B. Fischer and L. Nadjo,
    J. Am. Chem. Soc., 101, 1978, 7264.

14. O. Haas and J. G. Vos,
    J. Electroanal. Chem. Interfacial Electro-
    chemistry, 113, 1980, 139.

15. A. G. Ewing, B. J. Feldman and R. W. Murray,
    J. Phys. Chem., 89, 1985, 1263.

16. K. Doblhoffer, H. Braun and R. Lange,
    J. Electroanal. Chem. Interfacial Electro-
    chemistry, 206, 1986, 93.

17. C. M. Elliot and J. G. Redepenning,
    J. Electroanal. Chem. Interfacial Electro-
    chemistry, 197, 1986, 219.

18. R. J. Lenhard and R. W. Murray,
    J. Electroanal. Chem. Interfacial Electro-
    chemistry, 78, 1977, 195.

19. L. L. Miller and M. R. Van de Mark,
    J. Electroanal. Chem. Interfacial Electro-
    chemistry, 88, 1978, 437.

20. E. Laviron, L. Roullier and C. Degrand,
    J. Electroanal. Chem. Interfacial Electro-
    chemistry, 112, 1980, 11.

21. C. D. Ellis and T. J. Meyer,
    Inorg. Chem., 23, 1984, 1751.

22. P. M. Hoang, S. Holdcroft and B. L. Funt,
    J. Electrochem. Soc., 132, 1985, 2129.

23. B. Lindholm and M. Sharp,

    J. Electroanal. Chem. Interfacial Electro-
    chemistry, 198, 1986, 37.

24. P. J. Peerce and A. J. Bard,

    J. Electroanal. Chem. Interfacial Electro-
    chemistry, 112, 1980, 97.

25. F. C. Anson, T. Ohsaka and J. M. Saveant,

    J. Am. Chem. Soc., 105, 1983, 4883.

26. Y. M. Tsou and F. C. Anson,

    J. Phys. Chem., 89, 1985, 3818.

27. L. Roullier and E. Waldner,

    J. Electroanal. Chem. Interfacial Electro-
    chemistry, 187, 1985, 97.

28. B. Lindholm and M. Sharp,

    J. Electroanal. Chem. Interfacial Electro-
    chemistry, 215, 1986, 385.

29. J. F. Cassidy and J. G. Vos,

    J. Electroanal. Chem. Interfacial Electro-
    chemistry, 235, 1987, 41.

30. J. F. Cassidy and J. G. Vos,

    J. Electrochem. Soc., 135, 1988, 863.

CHAPTER V

Photochemical Properties of Synthesised Ruthenium
Containing Poly-N-Vinylimidazole Polymers

V.1 INTRODUCTION

The intensity of interest in the chemistry of bipyridyl complexes of ruthenium has been largely generated by the use of these complexes as photocatalysts in the photodissociation of water by visible light [1 - 6]. Because of this and other potential applications, for example, in electrochromic devices [7 - 10], the photochemical properties of these metallopolymeric systems have been the subject of a great deal of research.

In order to construct an efficient photochemical conversion system, the use of a heterogeneous reaction is desirable, since photochemical reaction in a homogeneous solution usually accompanies the backward reaction which consumes the photochemically acquired energy. Thus the backward reaction could be hindered if the reaction products could be separated from each other by using a heterogeneous system. With this in mind, the incorporation of the photochemically active component, such as, $[Ru(bipy)_3]^{2+}$, onto a polymer support must be considered to be a useful way to immobilize the complex as an alternative approach to other methods including monolayer assemblies [3] and micelles [11].

Polymeric complexes of ruthenium (II) and their

monomeric analogues represent a class of such materials which have undergone a lot of study in this regard [5], [12 - 20]. Ru(II)bis(bipyridyl) complexes have been bound to polymeric backbones [6], [13 - 16], [18], including poly-4-vinylpyridine and the photochemical properties of these systems have been investigated both in solution and as films on the electrode surface. Kelly and co-workers [6] prepared a series of bis(bipyridyl) poly-4-vinylpyridine ruthenium (II) complexes and studied the photoreactions of these materials in methanol solutions. It was concluded from UV/vis spectroscopic studies that these complexes underwent photosubstitution reactions [13]. This feature did unfortunately indicate the unsuitability of these materials as solar energy converters. The photosubstitution reactions observed by Vos and co-workers, have been studied in solution [13] and as coatings on an electrode surface [14], [18].

In the latter case, photochemical ligand exchange can be detected as the redox potential changes markedly with photosubstitution. This is important where the coating is to be used to protect photoanodes or to catalyze a redox couple. The photoprocesses, as illustrated in equation 1, were found to be irreversible. This offers the possibility of information storage.
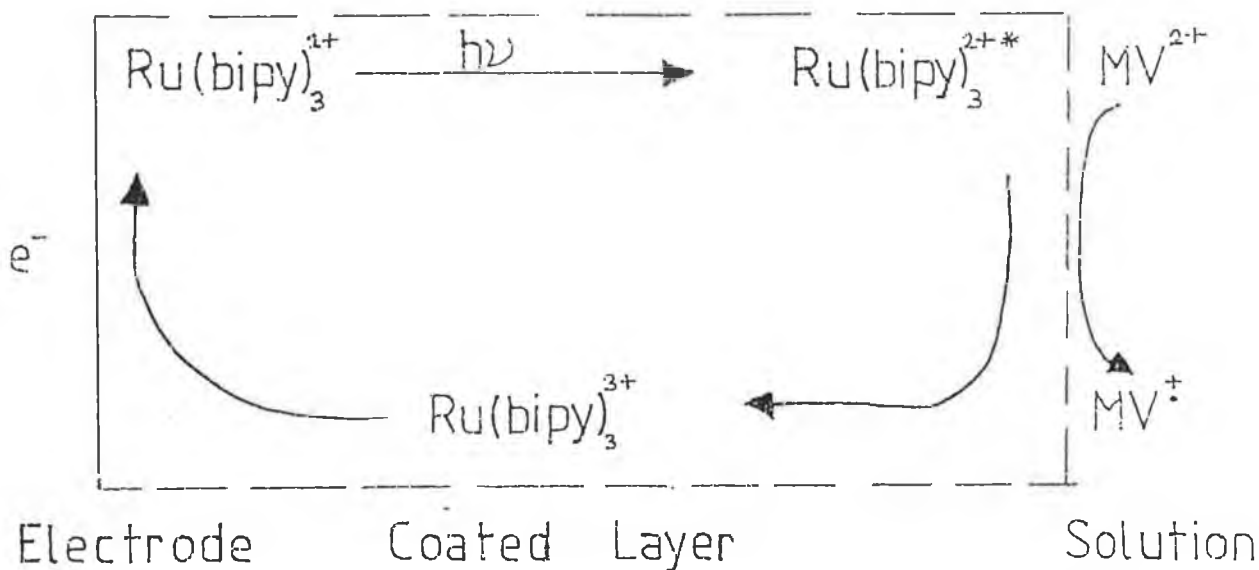
Equation 1

$$[Ru(bipy)_2Cl(PVP)] \xrightarrow[\text{electrolyte}]{h\nu +L} [Ru(bipy)_2L(PVP)]^{2+} \qquad (1)$$
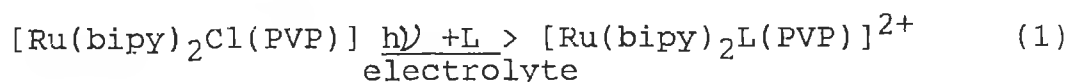
Such photosubstitution processes can be rationalized by assuming that under irradiation [3]MLCT to an empty ligand based π^* orbital takes place, and that via intersystem crossing a [3]MLCT becomes occupied. Since this state is in thermal equilibrium with an antibonding ligand field state, the Ru-ligand bond is weakened and the photosubstitution is facilitated [20]. Also it has been observed, for experiments carried out with modified electrodes, that the nature of the photoproduct depends strongly on the electrolyte [14, 18]. This allows the synthesis of a range of new materials, that can not be prepared by thermal means.

The preparation and photochemical behaviour of polystyrene pendant tris(bipyridyl) ruthenium (II) complex, $[Ru(bipy)_3]^{2+}$, has also been studied [21]. Analysis was carried out using U.V./visible spectroscopy. The authors also examined the catalytic activity of the ruthenium (II) polymeric complex towards the photoreduction of methyl viologen (MV^{2+}) where the photochemical formation of MV^+ was followed spectroscopically. The study of photoelectrochemical cells in relation to photoresponses has also been the subject of interest. A photoresponse, as a

photocurrent, is obtained as a consequence of the electron transfer between the excited state of the photosensitzer, for example $[Ru(bipy)_3]^{2+}$, in the film and redox quenchers either in solution or incorporated in the film. A typical example of the type of process involved is illustrated in Figure 5.1

FIGURE 5.1. Schematic diagram illustrating the photocatalytic properties of a modified electrode.

$$Ru(bipy)_3^{1+} \xrightarrow{\quad h\nu \quad} Ru(bipy)_3^{2+*} \quad MV^{2+}$$

e^-

$$Ru(bipy)_3^{3+} \qquad \qquad MV^{\cdot +}$$

Electrode   Coated Layer   Solution

When the electrode is coated with the Ru complex however, the $[Ru(bipy)_3]^{3+}$ formed by the photoreaction can react at the electrode. Meyer and co-workers have illustrated a photoelectrochemical cell based on electron transfer quenching of the excited state $[Ru(bipy)_3]^{2+}$ in which visible photolysis gave O_2 and an appreciable photocurrent was obtained [22]. They also described [23] the design of a photoelectrochemical cell based on the irreversible oxidative quenching of the excited state $[Ru(bipy)_3]^{2+}$ by $[Co(C_2O_4)_3]^{3-}$. In

the former of these two systems, the photochemical production of $[Ru(bipy)_3]^{3+}$ was coupled with oxidation of $Fe^{2+}(aq)$ to $Fe^{3+}(aq)$ in a second compartment which occurs with the production of appreciable photocurrents. With regard to the photochemical splitting of water, the experiment indicated that such photoelectrochemical cells have the distinct advantage of the component half reactions,
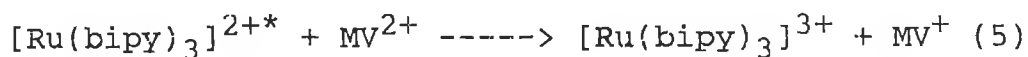
$$2H^+ + 2e^- \longrightarrow H_2 \qquad (2)$$

and $\qquad H_2O \qquad \longrightarrow 2H^+ + 2e^- + 1/2O_2 \qquad (3)$
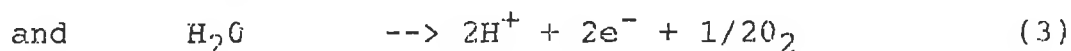
to be studied separately.

A photoelectrochemical cell which accomplished the reduction step, $2H^+ + 2e^- \longrightarrow H_2$ (2) had previously been reported [24]. Here the authors describe the operation of a cell in which the oxidation, $H_2O \longrightarrow 2e^- + 2H^+ + 1/2 O_2$ (3) is driven with quite high efficiency following visible photolysis. There are several examples reported in the literature where photoresponses have been obtained from Ru(II)-2,2'-bipyridine chromophores bound in thin films. One application is based on the known quenching of the metal to ligand charge transfer (MLCT) excited state of $[Ru(bipy)_3]^{2+*}$ by methyl viologen (MV^{2+}). In solution the overall quenching scheme involves excitation,

143

$$[Ru(bipy)_3]^{2+} \xrightarrow{h\nu} [Ru(bipy)_3]^{2+*} \qquad (4)$$
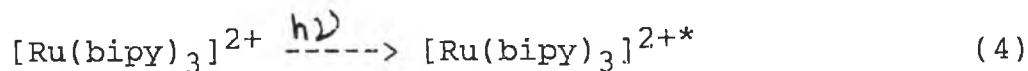
and bimolecular quenching,

$$[Ru(bipy)_3]^{2+*} + MV^{2+} \longrightarrow [Ru(bipy)_3]^{3+} + MV^+ \quad (5)$$

The recombination step limits such schemes to transient energy conversion and storage. In an electrode-bound film, electron capture reactions inhibit the backward process, in this way preventing the infusion of the photochemically acquired energy into the backward reaction.

Meyer and co-workers [1, 25] have reported the photophysical and photochemical properties of Ru(II)-bipy chromophores attached to a relatively short chain poly-4-vinylpyridine polymer. Photoeffects were also observed with this polymer adsorbed on electrodes in the presence of the irreversible oxidative quencher $[Co(C_2O_4)_3]^{3-}$. Oyama and co-workers [26] have studied photocurrent generation of graphite electrodes coated with polymer films confining tris(2,2'bipyridyl)ruthenium(II) and viologen. It was found that under illumination, the electrodes exhibited photocurrent responses in contact with aqueous solutions containing only supporting

electrolyte. In this situation Nafion was used as the supporting film for incorporation of $[Ru(bipy)_3]^{2+}$ and methylviologen chloride on the basal plane graphite.

The polymer complex, $[Ru\ P(St-Vbipy)(bipy)_3]^{2+}$, where P(St-Vbipy) is polymerised styrene vinyl bipyridyl, has also been used in the production of a photoresponse in the presence of MV^{2+} [18]. Results indicated that excitation of the ruthenium complex was responsible for the photoelectrochemical process as is to be expected. Kaneko and co-workers [28] have also carried out a preliminary study on the photocurrent produced by a carbon electrode modified with a polyanion layer containing the $[Ru(bipy)_3]^{2+}$ complex. Irradiation of a bare electrode in a mixed solution of $[Ru(bipy)_3]^{2+}$ and MV^{2+} yielded no photoresponse. However, with electrode modification a photoresponse was observed. It was considered here that the photoactive electrochemical system can be applied in solar energy conversion systems as a kind of photodiode. The fact that photochemical processes between two compounds can be utilized to obtain photoresponsive electrodes if the reaction components are coated on the electrode as a membrane has prompted further work by Kaneko's team [28]. Graphite electrodes were made photoresponsive by coating with bilayer membranes of Prussian Blue and polymer pendant $[Ru(bipy)_3]^{2+}$. The photocurrent, which was induced by

irradiating the coated electrode, was found to be proportional to the applied potential and also the light intensity. Major processes for the photocurrent generation in this system concern the excitation of the ruthenium complex, and the role of Prussian Blue as an electron mediator has been suggested. Murray and co-workers have carried out similar studies [29]. With platinum electrodes coated with $[(bipy)_2Ru(PVP)_2]^{2+}$, in the presence of MV^{2+}, a cathodic photocurrent was generated [30]. It was however small in magnitude, but it was enhanced by the presence of O_2. Although a photocurrent was generated, the photochemical cells used were not considered as energy conversion devices but rather as booster cells where H_2O_2 is produced by electrolysis.

Krishnan and co-workers [31] have described a voltammetric study of irradiation of n-type tin(IV) oxide modified with Nafion films containing $[Ru(bipy)_3]^{2+}$. The spectral response of the sensitized photocurrent was found to be the same as the absorption spectrum of the ruthenium complex. The anodic photocurrent at the absorption maximum was found to be higher for thin films than for thicker films. They also examined the quenching of the luminescence of incorporated $[Ru(bipy)_3]^{2+}$ by solution species with different permeability and at different oxidation states of the ruthenium complex.

The effect of film thickness and the magnitude of the photoresponse has been investigated by Cosnier [32]. They used platinum electrodes coated by electropolymerized polypyridyl complexes of Ru(II)-containing pyrrole groups and as an external quencher, 4 methylbenzendiazonium tetrafluoroborate. It was found that after a limiting value of photocurrent was reached.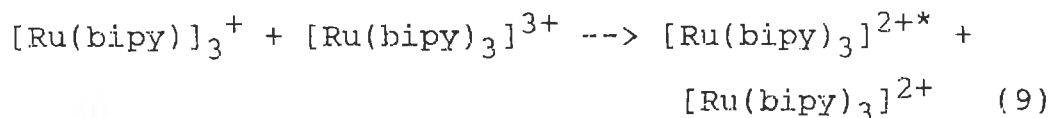 This situation compares well with the effect of film thickness with redox polymer electrodes in electrochemical catalysis [33].

The direct electrochemistry of cytochrome C at a surface-modified gold electrode was used as the source of reducing equivalents for a membrane enriched in photosystem 1 [34]. These researchers have suggested that faradaic electrochemistry is well-suited to the investigation of heterogeneous electron transfer in complex biological systems. Upon illumination of the coated electrode, a photochemically generated reduction current was observed. This work demonstrates how it is possible to unite photosynthetic and electrochemical electron transfer systems.

Another important photochemical property of some of these modified electrode systems is electrogenerated chemiluminescence (ECL). Rubinstein and Bard [35] have studied Nafion-coated electrodes and electrogenerated

chemiluminescence of surface attached tris(2,2'-bipyridine) ruthenium (II). Upon applying a positive potential to the electrode in an aqueous solution containing oxalate ions, a very intense, constant light emission identified as the luminescence of $[Ru(bipy)_3]^{2+*}$, was generated. Similar studies, were carried out by Abruna and Bard [36], where they prepared a chemiluminescent polymer based on a tris(4-vinyl-4'methyl-2,2'-bipyridyl) ruthenium (II) system. ECL was observed in MeCN from a platinum electrode coated with a polymer film of the above-mentioned system. Pulsing between +1.5V and -1.45V ECL was found to decay in this example and this was attributed to generation of some electroinactive products in the polymer film - as determined by running cyclic voltammograms before and after the ECL experiment. $[Ru(bipy)_3]^{2+}$ has been incorporated into polymerised 2,2'-bipyrazine and ECL studies were carried out in the presence of oxalate ions, pH6 [37]. The reaction sequence involved is illustrated in equations 6 - 9.

$$[Ru(bipy)_3]^{2+} \longrightarrow [Ru(bipy)_3]^{3+} + e^- \qquad (6)$$

$$[Ru(bipy)_3]^{3+} + [C_2O_4]^{2-} \longrightarrow [Ru(bipy)_3]^{2+} + CO_2 \\ + CO_2^- \qquad (7)$$

$$CO_2^- + [Ru(bipy)_3]^{2+} \longrightarrow [Ru(bipy)]_3^+ + CO_2 \qquad (8)$$

$$[Ru(bipy)]_3^+ + [Ru(bipy)_3]^{3+} \longrightarrow [Ru(bipy)_3]^{2+*} +$$
$$[Ru(bipy)_3]^{2+} \qquad (9)$$
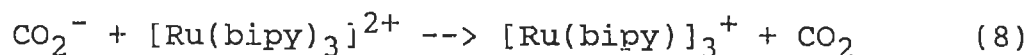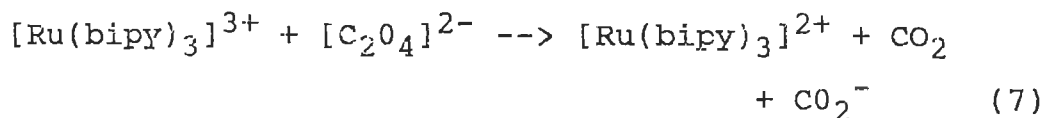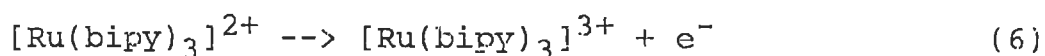
The oxalate ions appeared to have rapid access into the film and ECL was observed. A luminescence probe has been used for measurements of electron-exchange rates in polymer films on electrodes [38]. Photoluminescence experiments in which the electron exchange rate is related to the rate of quenching of an exciton in a bimolecular encounter, were carried out using $[Ru(bipy)_3]^{2+}$ immobilized in a layer of sulfonated polystyrene.

Ellis and Meyer [39] have prepared polystyrene-coated platinum electrodes with incorporated $[(bipy)_2 Ru(5\text{-}phen\ NH_2)]^{2+}$. For these modified electrodes emission was observed but was quenched when the redox sites were oxidized electrochemically or chemically to Ru(II). Complete quenching was also obtained in the presence of excess Ce(IV). Partial regeneration of emission does occur by re-reduction of redox sites in the film to Ru(II) by electrochemical means. Rajeshwar and co-workers [41] have studied the photoelectrochemical oxidation of halide ions at naked, catalytically modified and polymer-coated n-cadmium sulfide electrode in aqueous media. Photoanodes were prepared from n-cadmium sulfide stabilized in Cl^- or Br^- containing aqueous media

through the use of catalytically modified polymer coating. RuO_2 was used as the catalyst in a polymer matrix comprising a polystyrene backbone with pendant $[Ru(bipy)_3]^{2+}$ moieties.

Ferrocenophanes have been suggested as effective catalysts in the photoelectrochemical hydrogen evolution from acidic aqueous media [40]. Ferrocenophane does catalyse the evolution of hydrogen from acidic media where this reaction would otherwise be inhibited by overvoltages. This can also be effected by illuminated p-type silicon cathodes and continuous hydrogen evolution can be observed. Deposition of the polymer p-type silicon produces a permanently modified and photoelectroactive cathode. It was found that when connected to a platinum anode the illumination of this photocathode lead to liberation of hydrogen at a more positive potential than for its evolution on shiny platinum under the same conditions. No loss in activity was obtained on continuous irradiation.

The design of electrochromic materials represents another important area with respect to the photochemical properties of some of these redox systems. The crucial properties of electrochromic materials are, the colour (colours) involved, the change in absorptivity per unit charge passed to

effect the colour change, the speed of switching from one colour to another and the durability of the electrochromic material. There are several reported examples in the literature of systems which can and have been applied to the design of electrochromic devices. Lacaze and co-workers [42] have prepared poly-N-vinylcarbazole modified electrodes and it was found that the colour can be bleached by electrochemical reduction.

This bleaching process was found to be more pronounced in the presence of tetrafluoroborate ions $(BF_4)^-$ than in that of hexafluorophosphate ions $(PF_6)^-$ or in tetrabutylammoniumperchlorate. Bathophenanthrolinedisulfonate and other polycations [9], for example, poly(N-methylpyridinium iodide) have been used for electrode modification. These electrodes could be used for an electrochromic device, the colour change being from red to transparent and the system exhibited excellent stability. The same research group has prepared polyviologens-poly(styrenesulfonate) modified electrodes [43]. The change of the colour of the polymer film on electrodes was from red to purple. Kaufman and co-workers have prepared thin-film electrochromic materials which were found to change colour reversible with good switching speed and with no degradation of materials [44]. Elliot and Redpenning [45] studied the stability and response

of multicolour electrochromic polymer modified electrodes prepared from tris(5,5'- dicarboxyester-2,2'bipyridine) ruthenium (II). This system yielded polymer modified electrodes with multicolour (7 colour) electrochromic properties. The system exhibited rapid electrochemical responses through the seven oxidation states. From these examples it can be seen that these redox systems have several different potential applications which will be further exploited in the future.

In this laboratory the synthesis and analysis of the photochemical properties of some poly-4-vinylpyridine complexes of ruthenium (II) [6, 13 - 16, 18]. My main interest has been in poly-N-vinylimidazole complexes of ruthenium (II). In this chapter, it will be shown that these synthesised materials exhibit interesting photosubstitution properties. They can however, under the right conditions, also be used for the generation of appreciable photoresponses in the presence of suitable external quenchers.

V.2 RESULTS AND DISCUSSION

V.2.1 Photoelectrochemical Properties of Poly-N-Vinylimidazole Based Metallopolymers

The photochemical properties of the synthesised polymeric complexes were investigated by electrochemical means. Photolysis was carried out on thin films of the PNVI based metallopolymers in different electrolytes. It was hoped that results obtained would indicate a potential application of these systems in solar energy conversion or information storage devices.

Photolysis in 1 M H_2SO_4

$[Ru(bipy)_2(PNVI)Cl]^+$ (sample C) was photolysed in
1M H_2SO_4. The half-wave potential of the starting
redox couple was found to occur at 570mV (Table 3.2).
On photolysis, the intensity of this band was found to
decrease with the development of two new bands
indicating the presence of two new materials. These
bands are found at 730mV and 540mV as shown in Figure
5.2. It was found that within a few minutes an
equilibrium situation was reached with the peak
heights of the newly-formed bands remaining the same.
The photosubstitution process was slower when the
electrode was continuously cycled through the
oxidation potential during the photolysis. If the
electrode, still in solution, is subsequently placed
in darkness total conversion to a single species at
730 mV, with no loss of product from the electrode
surface, was observed, as illustrated in Figure 5.3.
On re-irradiation of the coated electrode the system
was found to revert back to the equilibrium situation
with two redox couples. The conversions from one
state to another were found to be fast and reversible.
Clearly the species at 730 mV is more stable in the
dark while the species with a redox couple at 540 mV
is stabilized by photolysis. By comparison with redox
potentials obtained for similar metallopolymers and
with model compounds the species having a redox couple

FIGURE 5.2
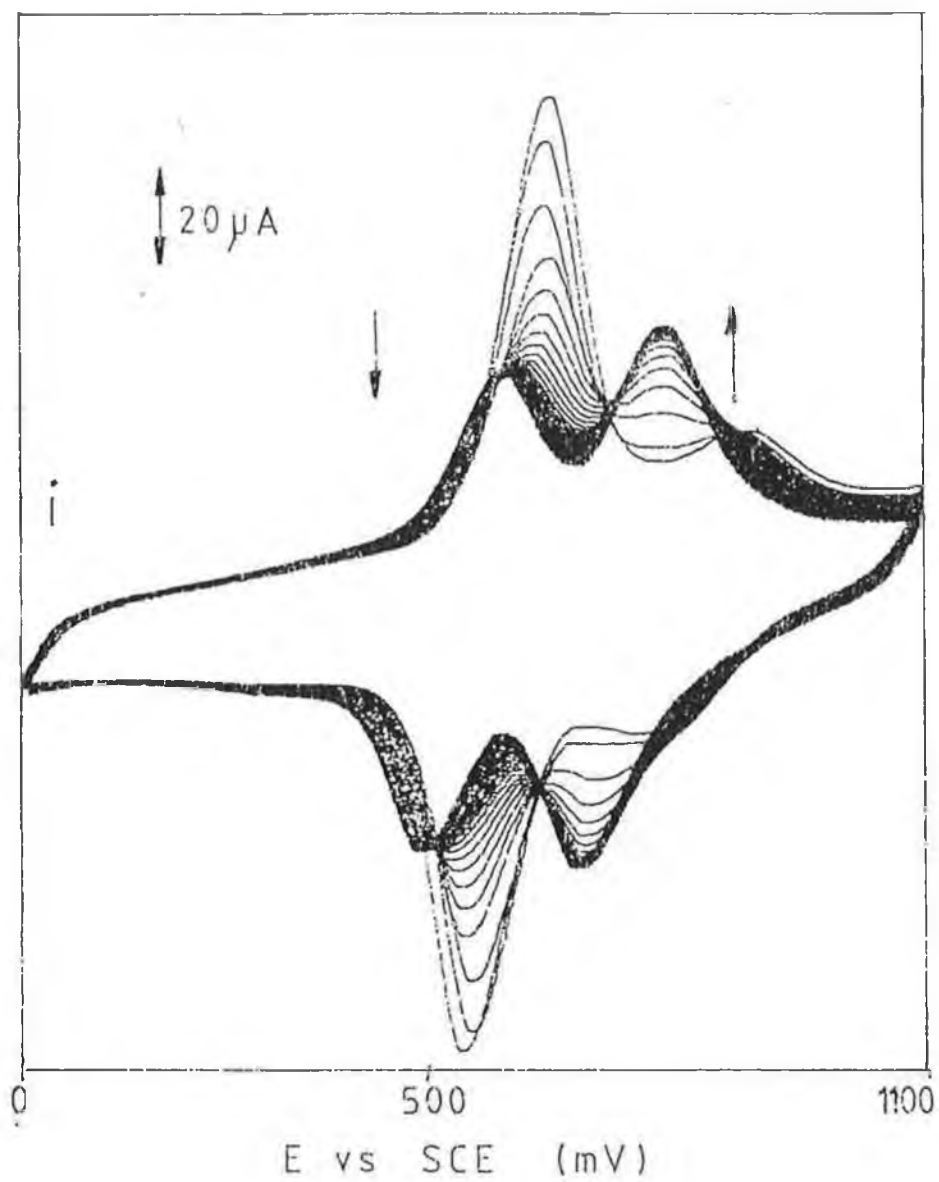
Photochemical reaction of sample C in 1M H$_2$SO$_4$.

FIGURE 5.3.
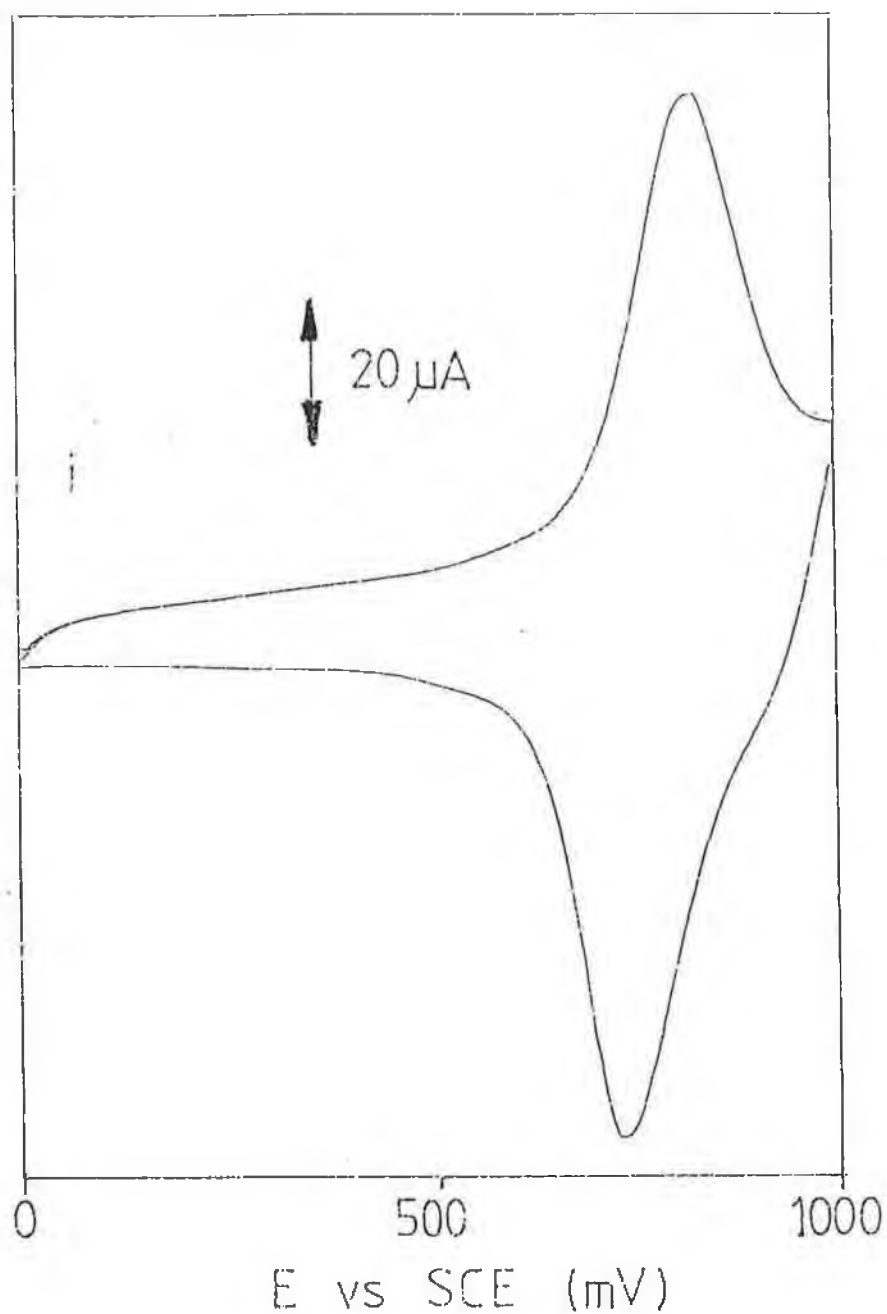
Cyclic voltammogram obtained after leaving the irradiated the electrode of Figure 5.2. in the dark for several minutes.

at 730 mV was identified as $[Ru(bipy)_2(PNVI)H_2O]^{2+}$. The development of a second redox couple at 540 mV is possibly explained by the formation of a photostabilized sulphate complex $[Ru(bipy)_2(PNVI)SO_4]$ by comparison with results obtained previously by Haas, Zumbrunnen and Vos [18].

Results obtained here indicated that this system could be used for information storage or switching devices. In the former case the electrode remembers whether it has been irradiated or not, as determined by cyclic voltammetry. In the latter case the fast interconversion process implies the possibility of being able to "switch" from one situation to another without any difficulty. $[Ru(bipy)_2(PNVI)_2]^{2+}$ (sample E) was photolysed in 1M H_2SO_4. This leads to the loss of the electroactive centre from the electrode surface. This could suggest that both the polymeric units are substituted thus causing the loss of the ruthenium based ligand from the electrode surface - i.e. the material breaks up completely. The photochemical behaviour of the aquo complex $[Ru(bipy)_2(PNVI)H_2O]^{2+}$, as prepared by photolysis of the chloro complex in 1M $HClO_4$, was also investigated in 1M H_2SO_4. As was expected the equilibrium situation already mentioned and illustrated in Figure 5.2, developed immediately.
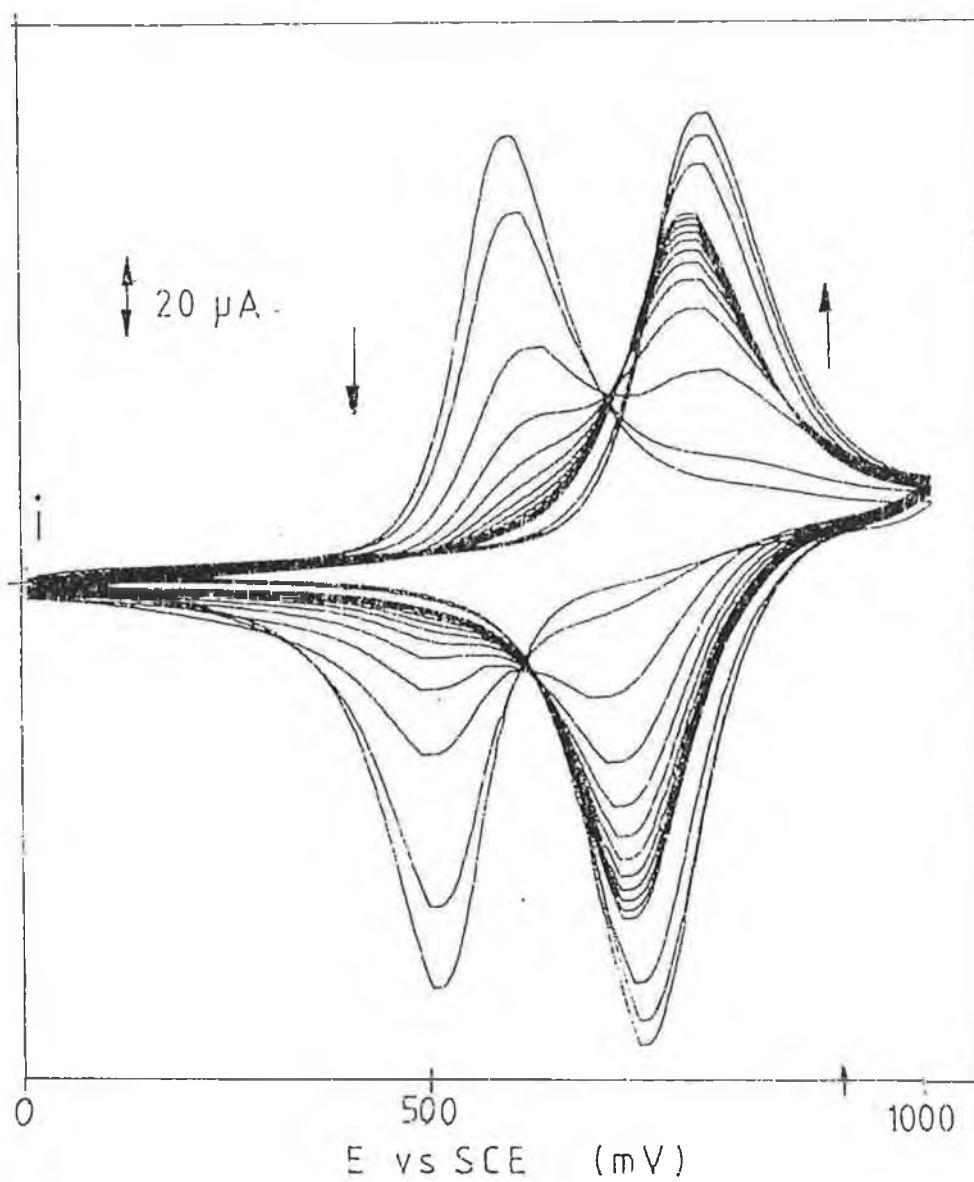
Photolysis in 1M HClO$_4$

[Ru(bipy)$_2$(PNVI)Cl]$^+$, sample C, was photolysed in 1M HClO$_4$. It was found that this material does undergo a quantitative conversion to the aqua species with a redox potential at 750 mV as illustrated in Figure 5.4. This provides a very useful method for the preparation of the aqua complex and allows the study of [Ru(bipy)$_2$(PNVI)H$_2$O]$^{2+}$, a material which cannot be prepared easily by other means. When [Ru(bipy)$_2$(PNVI)$_2$]$^{2+}$, sample E was photolysed in 1M HClO$_4$, the film was found to be photostable with no formation of any new products and no loss of product from the electrode surface. As no photosubstitution was observed here the complex might have interesting properties as a photosensitzer under these conditions. This will be discussed in a later section. The photostability of the PNVI based material, in this electrolyte, seems to be greater than observed for the analogous PVP based metallopolymer [Ru(bipy)$_2$(PVP)]$^{2+}$ [18].

Photolysis in CH$_3$CN/0.1 M TEAP

Photolysis of [Ru(bipy)$_2$(PNVI)Cl]$^+$ in CH$_3$CN/.1M TEAP leads to loss of the electroactive centre from the electrode surface. This was an unexpected result and was contrary to other similar experiments using this
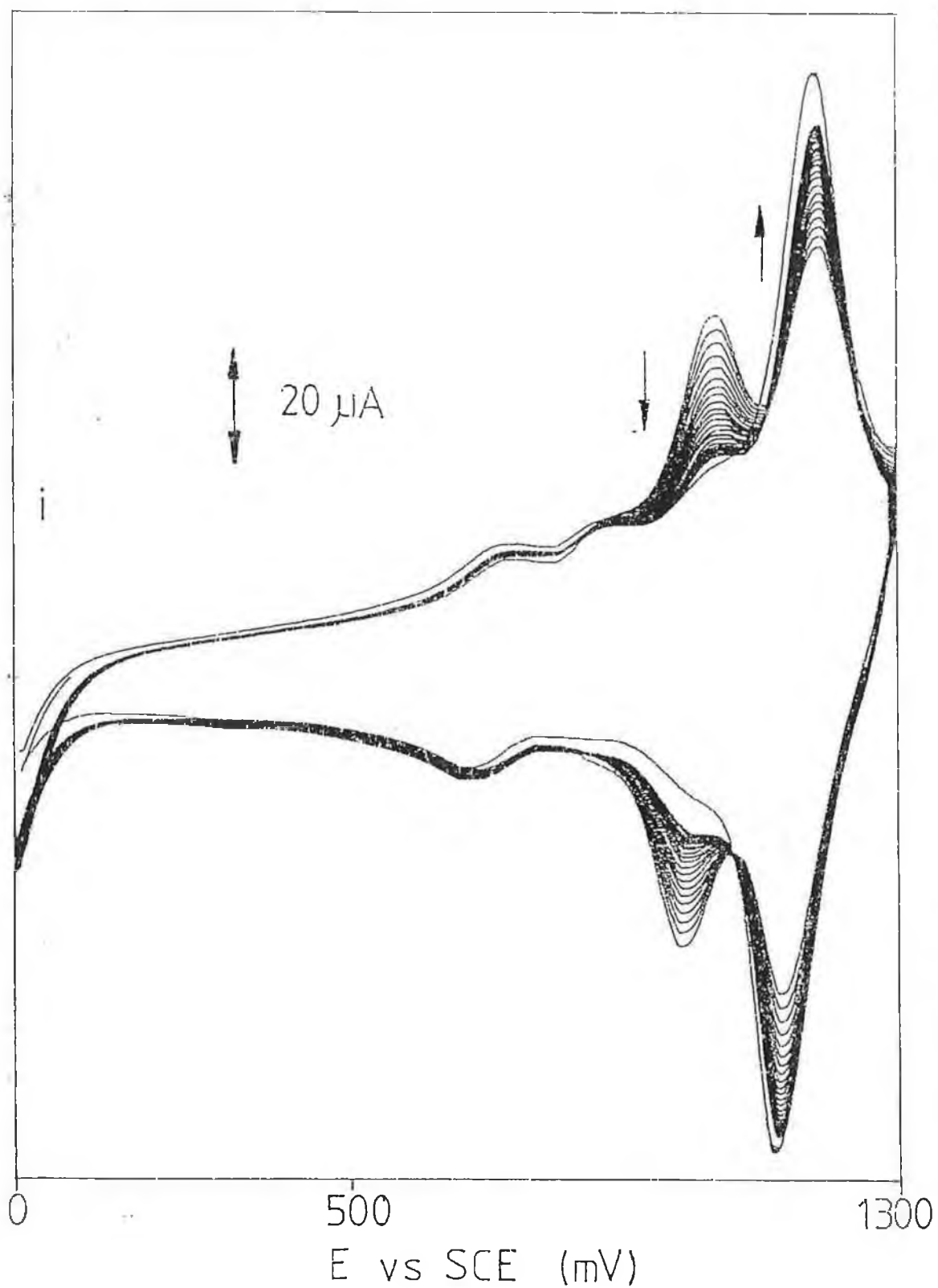
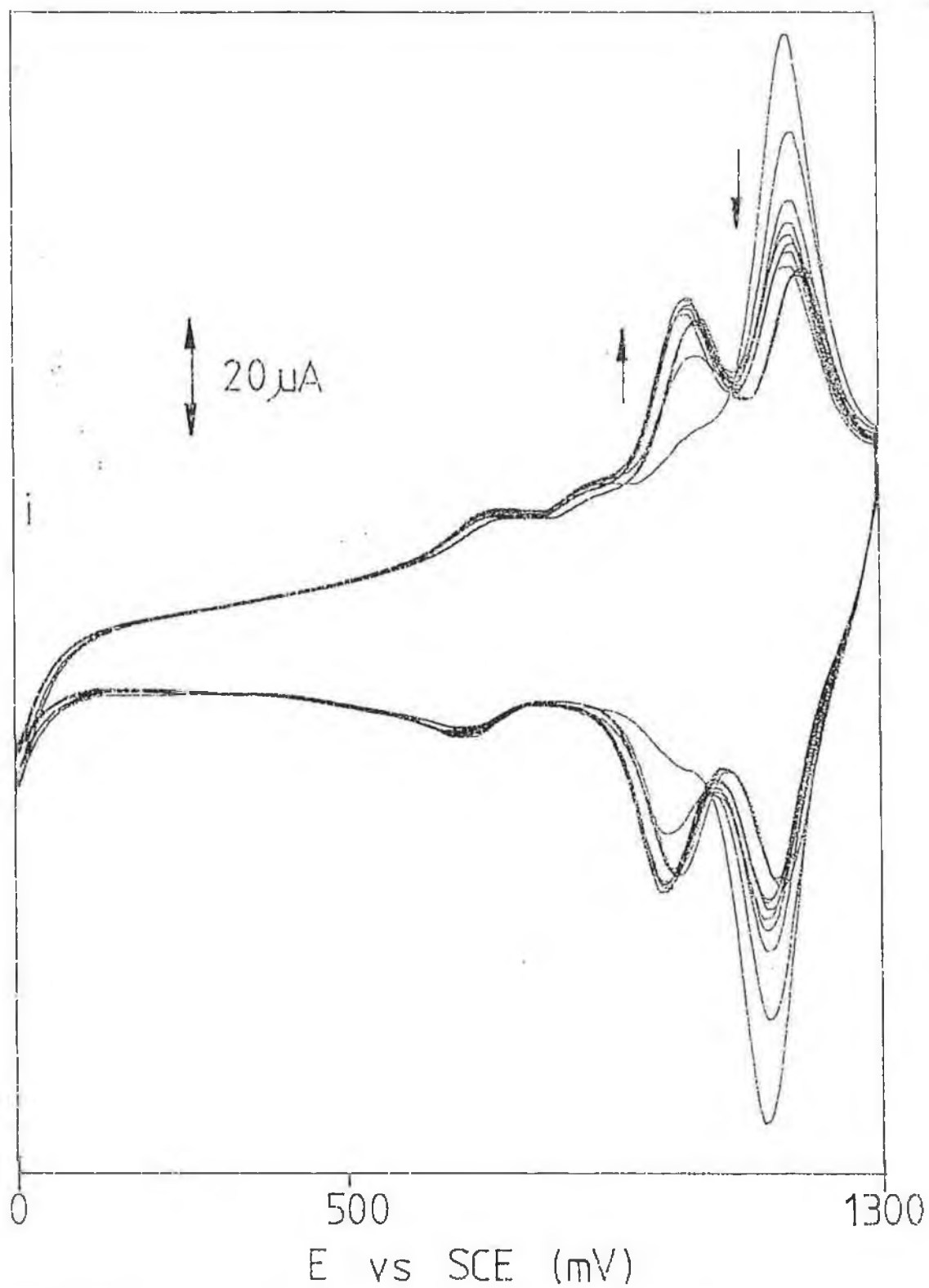FIGURE 5.4.

Photochemical reaction of sample C in 1M $HClO_4$.

electrolyte using polyvinylpyridine based analogues. Photolysis of $[Ru(bipy)_2(PNVI)_2]^{2+}$ in the above electrolyte also lead to the loss of the electroactive centre from the electrode surface. This rules out the use of these materials in solar energy conversion systems under these conditions. The photoproduct $[Ru(bipy)_2(PNVI)H_2O]^{2+}$ was also investigated. On immersion into CH_3CN two redox couples were observed immediately. The first which occurred at 1010 mV was attributed to the aqua species; the second couple occurred at 1155 mV was attributed to the formation of the CH_3CN complex $[Ru(bipy)_2(PNVI)(CH_3CN)]^{2+}$ [14] and the intensity of this band was found to increase with continuous scanning. The peak height of the first couple experienced a corresponding decrease. However, on irradiation, the CH_3CN species was found to be unstable and the peak height was found to decrease. The aqua species was photostable and the peak intensity was found to increase correspondingly. It was also observed that there was a loss of product from the electrode surface on continuous scanning in this electrolyte as determined by integration of the area under a cyclic voltammogram. The above features are illustrated in Figures (5.5) to (5.6).

FIGURE 5.5.

20 μA

i

0   500   1300

E vs SCE (mV)

Cyclic voltammetric response of Sample C in

CH$_3$CN / 0.1M TEAP .

161

FIGURE 5.6.

20 μA

i

0   500   1300

E vs SCE (mV)

Photolysis of Sample C in CH$_3$CN / 0.1 M TEAP .

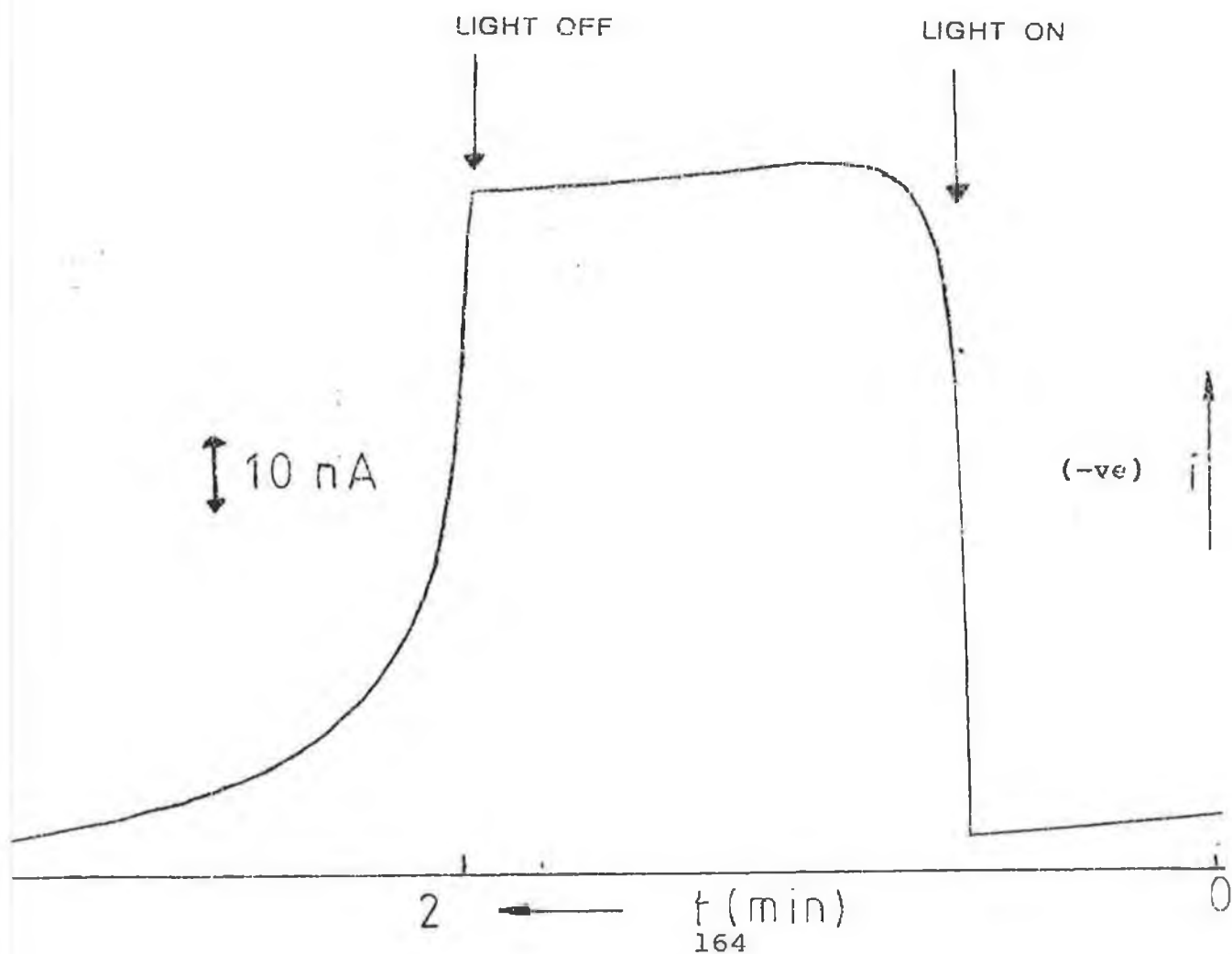## V.2.2 Photosensitizing Properties of Poly-N-Vinylimidazole Based Complexes

The initial experiments in this section were carried out using the external quencher, paraquat (or methyl viologen MV^{2+}). The material used to coat the electrode surface was $[Ru(bipy)_2(PNVI)_2]^{2+}$. The supporting electrolyte must satisfy certain criteria; the metallopolymer must be stable in it, particularly under irradiation, the quencher must be soluble in it and the electrolyte must penetrate the layer well. Overall a perchlorate based electrolyte would be most suitable but for methyl viologen a sulphate based electrolyte was used to facilitate the second of the above conditions. By using this electrolyte the stability of the layer had to be compromised. The electrode potential was set at 0.3V - here the ruthenium was maintained in an oxidation state of 2+. Under irradiation a photoresponse, in the form of a photocurrent, was obtained as illustrated in Figure 5.7. The magnitude of the photocurrent was found to be $10\mu A/cm^2$. This was found to decrease with time; and from cyclic voltammograms run before and after the experiment this decrease was attributed to the loss of the electroactive centre from the electrode surface. Typical magnitudes of the photo currents obtained in the literature are of the order of 10-100 $\mu A/cm^2$ as

Figure 5.7

Photoresponse of an electrode coated with 2.8×10^{-8} moles/cm^2 of $[Ru(bipy)_2(PNVI)_2]^{2+}$.
Electrolyte : 0.9M Na_2SO_4 + 0.1M H_2SO_4.
Substrate : 2mM MV^{2+}.

$$[Ru(BPY)_2(PNVI)_2]^{2+} \xrightarrow{\quad h\nu \quad} [Ru(BPY)_2(PNVI)_2]^{2+*}$$

$$[Ru(BPY)_2(PNVI)_2]^{2+*} + MV^{2+} \longrightarrow [Ru(BPY)_2(PNVI)_2]^{3+} + MV^+$$

$$[Ru(BPY)_2(PNVI)_2]^{3+} \xrightarrow{\quad e^- \quad} [Ru(BPY)_2(PNVI)_2]^{2+}$$

LIGHT OFF   LIGHT ON

10 nA

(−ve) i

2 ⟵ t (min)   0
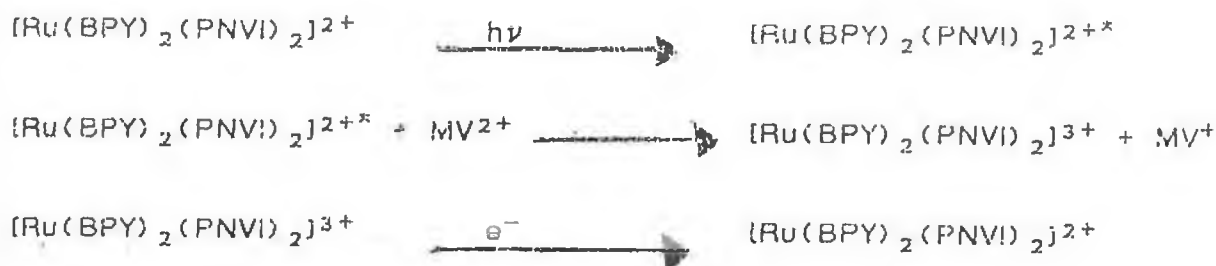
has been found here. However the instability of the film in this sulphate electrolyte does limit the viability of potential applications of this system. For this reason, other electrolytes were used.

By comparison with work carried out by Murray and co-workers it was decided to investigate the use of oxalates as external quenchers [29]. Using these materials allowed the use of perchlorate based electrolytes which are more amenable to the stability of the metallopolymeric coating. The system was investigated as a function of film thickness and quencher concentration.

The photoresponse was first studied using $[Fe(C_2O_4)_3]^{3-}$. It was found that the photocurrent rose and reached a steady-state value quickly. The high current level could be maintained for a few minutes but was found to decrease with time as illustrated in Figure 5.8. This decrease was attributed to the irreversible loss of Fe^{3+} from oxalate or possibly the reduction of $[Ru(bipy)]^{3+}$ by released oxalate which is in competition with diffusion of substrate to the electrode as was previously found by Murray et al [29].

This typical type of response obtained has been illustrated in Figure 5.8. Equation 10 --> 13 explain

Light on   Light off

(-ve) 100nA

166

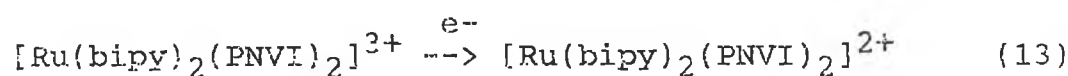1Minute
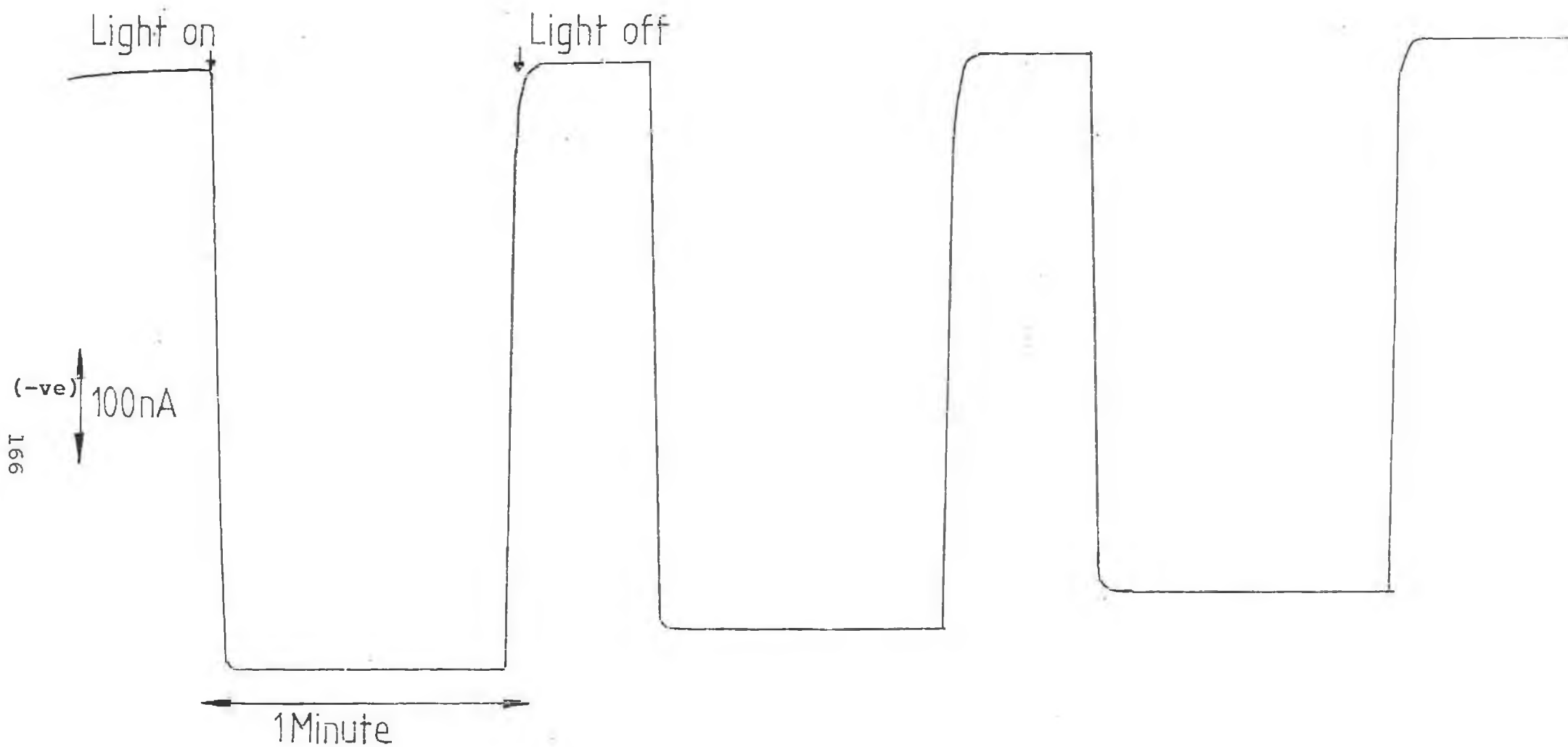
Figure 5.8

Photoresponse of a glassy carbon electrode coated with 2.4×10^{-8} moles/cm^2 [Ru(bipy)$_2$(PNVI)]$^{2+}$

Substrate : 0.01M [Fe(C$_2$O$_4$)$_3$]$^{3-}$ in 0.9M NaClO$_4$ + 0.1M HClO$_4$

Electrode potential = 0.3V

the series of reactions involved in this photoresponsive system.

$$[Ru(bipy)_2(PNVI)_2]^{2+}, \xrightarrow{h\nu} [Ru(bipy)_2(PNVI)_2]^{2+*} \quad (10)$$

$$[Ru(bipy)_2(PNVI)_2]^{2+*}, [Fe(C_2O_4)_3]^{3-} \longrightarrow$$
$$[Ru(bipy)_2(PNVI)_2]^{3+}$$
$$[Fe(C_2O_4)_3]^{4-} \quad (11)$$

$$6H_2O + 6H^+ + [Fe(C_2O_4)_3]^{4-} \longrightarrow$$
$$[Fe(H_2O)_6]^{2+} + 3H_2C_2O_4 \quad (12)$$

$$[Ru(bipy)_2(PNVI)_2]^{3+} \xrightarrow{e^-} [Ru(bipy)_2(PNVI)_2]^{2+} \quad (13)$$
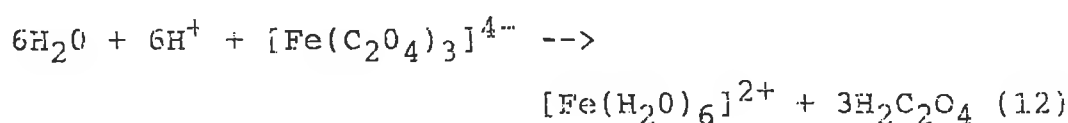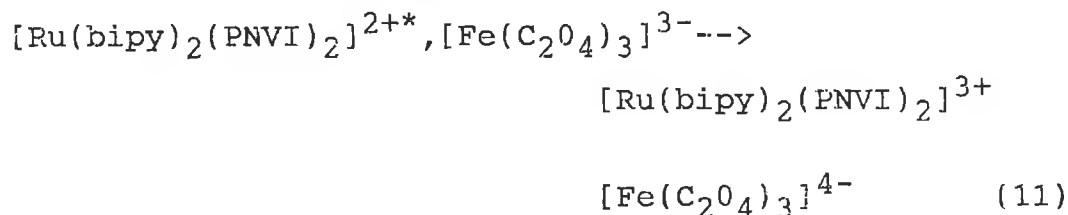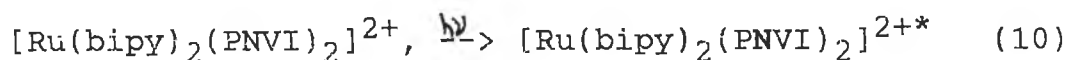
For this system, different experimental parameters were varied including the film and quencher concentration. This work is similar to studies carries out by Cosnier and co-workers who investigated electrodes coated with polypyridyl complexes of ruthenium(II)-containing pyrrole groups in the presence of 4-methylbenzenediazonium tetrafluoroborate as external quencher [32]. Results obtained from our studies are given in Table 5.1. The data show that up to a limit, an increase in film thickness and an increase in quencher concentration result in an increase in the photocurrent. It must however be

Table 5.1   Photoresponse as a function of film thickness and substrate concentration.

[Ru] moles/cm^2	[Fe(C$_2$O$_4$)$_3$$^{3-}$] moles/L	i$_{photo}$ μA/cm^2
	1×10^{-3}	0.21
2.8×10^{-9}	5×10^{-3}	0.32
	1×10^{-2}	0.32
	1×10^{-3}	0.22
5.6×10^{-9}	5×10^{-3}	0.27
	1×10^{-2}	0.286
	1×10^{-3}	0.47
1.3×10^{-8}	5×10^{-3}	0.5
	1×10^{-2}	0.57
	1×10^{-3}	0.39
2.8×10^{-8}	5×10^{-3}	0.42
	1×10^{-2}	0.40
	1×10^{-3}	0.57
5.2×10^{-8}	5×10^{-3}	0.494
	1×10^{-2}	0.41
	1×10^{-3}	0.76
8.4×10^{-8}	5×10^{-3}	0.704
	1×10^{-2}	0.565

noted that the results cannot be treated quantitatively. This is due to the fact that the light source is not consistent - light from a projector is reflected from a mirror onto the electrode surface so obviously the position of the lamp and mirror are crucial but not one hundred per cent reproducible. For this reason, any results obtained can only be treated in a qualitative fashion. It was also observed that thinner films gave rise to a faster attainment of the plateau current state as illustrated in Figure 5.9. This effect was also observed when Cobalt oxalate was used as a substrate. For this substrate similar photocurrents were obtained as for $[Fe(C_2O_4)_3]^{3-}$ but it took a longer time to achieve their maximum value. Apart from the disubstituted complex, $[Ru(bipy)_2(PNVI)Cl]^+$ was used but in the presence of ferrous oxalate as external quencher, no photocurrent was observed. Only a slight deflection of the pen resulted and was attributed to the presence of trace amounts of disubstituted complex as confirmed by cyclic voltammetric studies. The use of the aqua complex, $[Ru(bipy)_2(PNVI)H_2O]^{2+}$, for this purpose was also studied and again no photocurrent was observed in the presence of suitable quenchers. No photocurrent was observed substantiating the conclusion that the photocurrents obtained were a result of the irreversible oxidative quenching of the excited state of the ruthenium polymer by the quencher
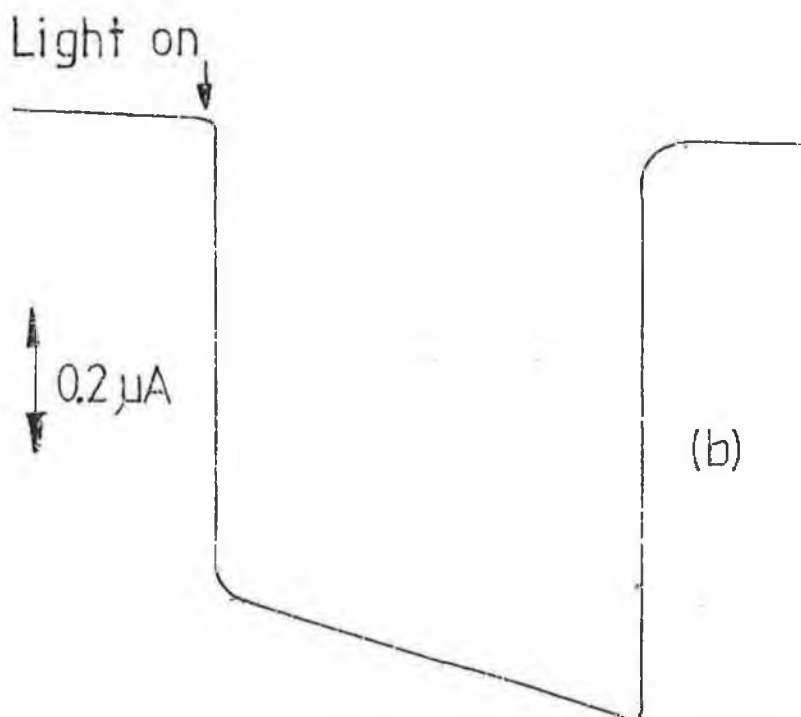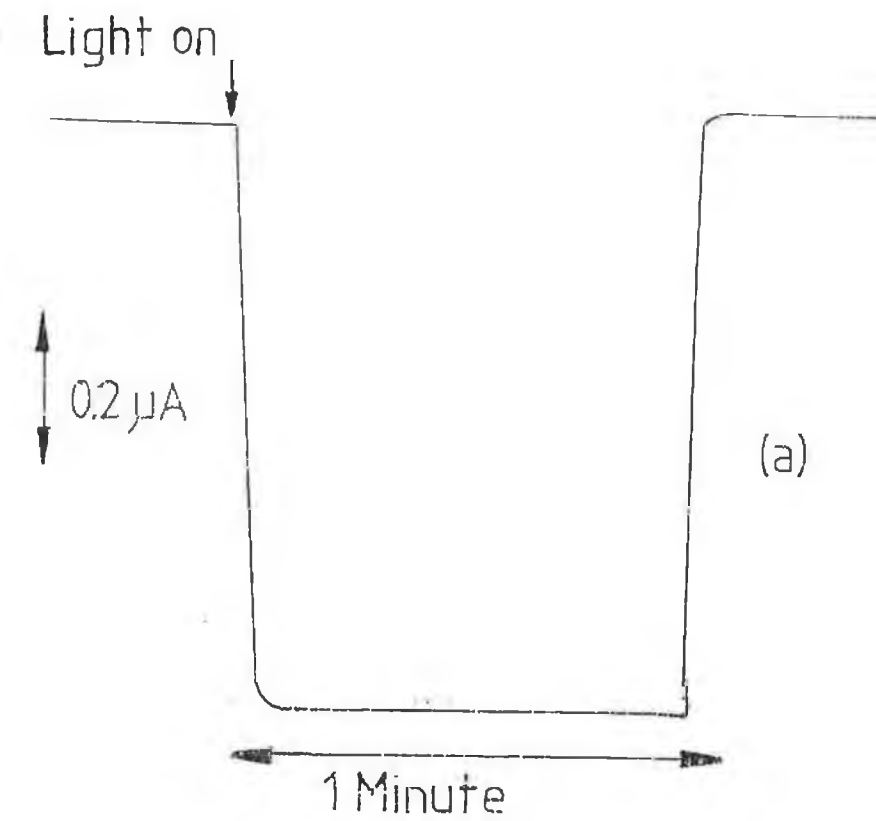
169

FIGURE 5.9. Effect of surface coverage on photoresponse.

(a) Surface coverage = 1.5×10^{-8} moles / cm^{-2}.

Substrate concentration = 2.0×10^{-3} moles/L.

(b) Surface coverage = 2.4×10^{-8} moles / cm^{-2}.

Substrate concentration = 2.0×10^{-3} moles/L.

ELECTROLYTE : 0.9M $NaClO_4$ + 0.1M $HClO_4$.

which diffuses in the film. Another parameter which was varied during the course of these experiments was the potential at which the electrode was held. It was necessary that the electrode be maintained at a potential where the ruthenium is in the 2+ oxidation state so it was varied between +0.2V and +0.5V. It was found that a maximum current was observed at +0.3V so this potential was used for all other experiments in this section. The effect of electrode rotation on the photocurrent response was subsequently investigated. It was expected that electrode rotation would lead to an increase in photocurrent but the opposite effect was observed.

The only possible explanation which I could propose for this strange effect was that as the light is reflected from a mirror through the solution onto the surface, the swirling motion of the electrolyte due to electrode rotation does in fact decrease the amount of light reaching the film. If this were true the photocurrent would be expected to decrease with increased rotation speed. This effect was observed and is illustrated in Figure 5.10. To investigate the true effect of electrode rotation on the photoresponse, an optically transparent electrode would be required, so that irradiation can take place through the electrode from the top.

Figure 5.10. Effect of rotation speed on the magnitude of the photoresponse.

Surface coverage $= 2.4 \times 10^{-8}$ moles / cm^2.

Substrate concentration $= 0.01mM [Fe(C_2O_4)_3]^{3-}$ in 0.9 M NaCl +0.1M HCl.

Electrode potential $= 0.3$ V.

Although the nature of these studies has only been qualitative it has been demonstrated that this system can be used in the generation of a photocurrent. Increases in film thickness and quencher concentration give rise to an increase in photocurrent produced, up to a certain limit of film thickness. Decreases in the magnitude of the photoresponse is primarily attributed to the substrate being irreversibly used up and not due to the loss of metallopolymeric film from the electrode surface as determined by cyclic voltammetry. The unexpected result relating to the effect of electrode rotation has already been mentioned and explained to some extent. The significance of optimizing the light source in this system and cannot be overemphasised.

V.3   CONCLUDING REMARKS

The work discussed in this chapter has illustrated
some of the interesting photochemical properties
associated with the synthesised materials with a view
to some potential applications.   One of the most
interesting reactions was the photolysis of
$[Ru(bipy)_2(PNVI)Cl]Cl$ in sulphuric acid leading to the
formation of two photostable products.   As explained
this system could possible function as a switching
device.   The instability of the materials in various
electrolytes did, as before, present certain problems,
particularly for the disubstituted complex where the
material under photolysis was just leached off the
electrode surface with continuous scanning in
different electrolytes.   Photochemical substitution in
the case of the monosubstituted complex led to the
formation of the corresponding aqua species which
could not be prepared by any other means.   Studies of
the photoresponsive properties of $[Ru(bipy)_2(PNVI)]^{2+}$
using a suitable substrate demonstrated how light
energy could be converted into redox energy and in
turn into electrical energy with the generation of a
photocurrent.

REFERENCES

1. V. Balzani, L. Moggi, M. F. Manfrin, F. Bolletta
   and M. Gleria,
   Science 189, 1975, 852.

2. G. Sprintschnik, H. W. Sprintschnik, P. P. Kirsch
   and D. G. Whitten,
   J. Am. Chem. Soc., 98, 1976, 2337.

3. G. Sprintschnik, H. W. Sprintschnik, P. P. Kirsch
   and D. G. Whitten,
   J. Am. Chem. Soc., 99, 1977, 4947.

4. S. J. Valenty and G. L. Gaines,
   J. Am. Chem. Soc., 99, 1977, 1285.

5. J. M. Clear, J. M. Kelly, D. C. Pepper and J.
   G. Vos,
   Inorg. Chim. Acta, 33, 1979, L 139.

6. J. M. Clear, J. M. Kelly, C. M. O'Connell and J.
   G. Vos,
   J. Chem. Res., (M), 1981, 3039.

7. M. Ito and T. Kuwana,
   J. Electroanal. Chem., Interfacial Electro-
   chem, 32, 1971, 415.

8. C. D. Ellis, M. Eckhoff and V. D. Neff,
   J. Phys. Chem., 85, 1981, 1225.

9. K. Itaya, H. Akahoshi and S. Toshima,
   J. Electrochem. Soc., 129, 1982, 762.

10. A. Desbene - Monvernay, P. C. Lacaze, J. E. Dubois
    and P. L. Desbene,
    J. Electroanal. Chem., Interfacial Electro-
    chem, 152, 1982, 87.

11. K. Kalyanasundaram,
    J. Chem. Soc., Chem. Comm., 628, 1978.

12. J. M. Calvert, J. V. Caspar, R. A. Binstead, T. D.
    Westmoreland and T. J Meyer,
    J. Am. Chem. Soc., 104, 1980, 6620.

13. J. M. Clear, J. M. Kelly, C. M. O'Connell J. G.
    Vos, C. J. Cardin, S. R. Costa and A. J. Edwards,
    J. Chem. Soc., Chem. Commun., 1980, 750.

14. O. Haas, M. Kriens and J. G. Vos,
    J. Am. Chem. Soc., 103, 1981, 1318.

15. J. M. Kelly and J. G. Vos,
    Angew Chemie, 21, 1982, 628.

16. O. Haas and J. G. Vos,

    J. Electroanal. Chem., Interfacial Electro-
    chem, 113, 1980, 139.

17. J. M. Calvert and T. J. Meyer,
    Inorg. Chem., 21, 1982, 3978.

18. O. Haas, H. R. Zumbrunnen and J. G. Vos,
    Electrochim. Acta, 30, 1985, 1551.

19. B. Durham, J. L. Walsh, C. L. Carter and T. J.
    Meyer,
    Inorg. Chem., 19, 1980, 860.

20. J. Van Houten and R. J. Watts,
    Inorg. Chem., 17, 1978, 3381.

21. M. Kaneko, S. Nemoto, A. Yamada and Y. Kurimura,
    Inorg. Chim. Acta, 44, 1980, 289.

22. D. P. Rillema, W. J. Dressick and T. J. Meyer,
    J. Chem. Soc., Chem. commun., 1980, 247.

23. B. Durham and T. J. Meyer,
    J. Am. Chem. Soc., 100, 1978, 6286.

24. B. Durham, W. J. Dressick and T. J. Meyer,
    J. Chem. Soc., Chem. Commun., 1979, 381.

25. J. M. Calvert and T. J. Meyer,
    Inorg. Chem., 20, 1981, 27.

26. N. Oyama, S. Yamaguchi, M. Kaneko and A Yamada,
    J. Electroanal. Chem., Interfacial Electro-
    chem, 139, 1982, 215.

27. M. Kaneko and A Yamada,
    Makromol. Chem. Rapid Commun., 3, 1982, 769.

28. M. Kaneko and A Yamada,
    Electrochim. Acta., 31, 1986, 273.

29. T. D. Westmoreland, J. M. Calvert, R. M. Murray
    and T. J. Meyer,
    J. Chem. Soc., Chem. Commun., 1983, 65.

30. L. D. Margerum, T. J. Meyer and R. W. Murray,
    J. Electroanal. Chem., Interfacial Electro-
    chem, 149, 1983, 279.

31. M. Krishnan, X. Zhang and A. J. Bard,
    J. Am. Chem. Soc., 106, 1984, 7371.

32. S. Cosnier, A. Deronzier and J. C. Moutet,
    J. Phys. Chem., 89, 1985, 4895.

33. C. P. Andrieux, J. M. Dumas Bouchiat and J. M. Saveant,

    J. Electroanal. Chem., Interfacial Electrochem, 114, 1980, 159.

34. K. A. O'Hill, N. J. Walton and D. Whitford,

    J. Electroanal. Chem., Interfacial Electrochem, 187, 1985, 109.

35. I. Rubinstein and A. J. Bard,

    J. Am. Chem. Soc., 102, 1980, 6641.

36. H. D. Abruna and A. J. Bard,

    J. Am. Chem. Soc., 104, 1982, 2641.

37. P. K. Ghosh and A. J. Bard,

    J. Electroanal. Chem., Interfacial Electrochem, 169, 1984, 113.

38. M. Majda and L. R. Faulkner,

    J. Electroanal. Chem., Interfacial Electrochem, 137, 1982, 149.

39. C. D. Ellis and T. J. Meyer,

    Inorg. Chem., 23, 1984, 1748.

40. U. T. Mueller-Westerhoff and A. Nazzal,

    J. Am. Chem. Soc., 106, 1984, 5381.

41. K. Rajeshwar, M. Kaneko, A. Yamada and N. Rommel,
    J. Phys. Chem., 89, 1985, 806.

42. P. C. Lacaze, J. E. Dubois, A. Desbene-Monvernay,
    P. L. Desbene, J. J. Basselier and D. Richard,
    J. Electroanal. Chem., Interfacial Electro-
    chem, 147, 1983, 107.

43. H. Akahoshi, S. Toshima and K. Itaya,
    J. Phys. Chem., 85, 1981, 818.

44. F. B. Kaufman, A. H. Schroeder, E. M. Engler and
    V. V. Pabel,
    Appl. Phys. Lett., 36, 1980, 422.

45. C. M. Elliot and J. G. Redpenning,
    J. Electroanal. Chem., Interfacial Electro-
    chem, 197, 1986, 219.

CHAPTER VI

Mediating Properties of Poly-N-Vinylimidazole Based Metallopolymers

VI.1   INTRODUCTION

A great deal of information on the electrochemical properties and the catalytic applications of coated electrodes can be obtained by observing their behaviour towards redox systems in solution using rotating disk electrodes [1-19]. Polymer films on electrodes do provide a convenient narrowly defined spatial region in which redox centres may be immobilised for electrocatalysis or sensing of electrochemically inaccessible analytes. Polymeric films can act as 3-dimensional redox catalysts and in this manner increase the amount of catalyst, by comparison with monolayer coverage of the electrode. This will thus increase the catalytic efficiency or the signal in the case of a sensor. Within the film the availability of substrate for reaction with the catalyst depends on both the ability of the substrate to partition into the film and to freely diffuse to catalyst centres. In this situation an immobilised reversible redox centre can act as a fast electron transfer mediator for a solution species which is oxidized or reduced slowly or not at all at the bare electrode. This concept is illustrated in Figure 6.1. Mediated electron transfer is only possible when the polymer half-reaction is appropriate to cause the reduction or oxidation of the solution species. The overall intention of the process is to diminish the

182

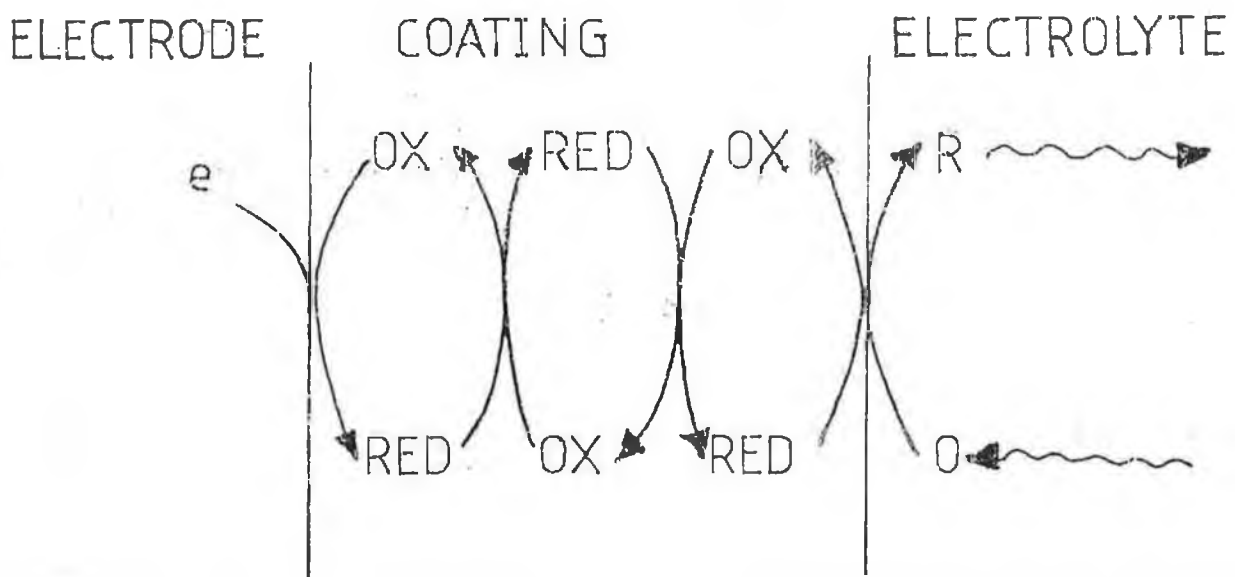ELECTRODE   COATING   ELECTROLYTE

Figure 6.1   Schematic diagram illustrating
mediated electron transfer at
a modified electrode.

overpotential required for direct oxidation/ reduction of the substrate and also to prevent poisoning of the electrode surface, as often occurs in the presence of various substrates. In redox catalysis the catalyst couple is involved in an outer sphere electron transfer reaction within the substrate, playing then simply the role of an electron carrier between the electrode and substrate and preventing at the same time direct reaction of the substrate with the bare electrode. Theoretical models for such reactions have been developed by Saveant and co-workers [8] and also by Albery's group [9a,b]. In our case we are dealing with an irreversible oxidation process and the reversible case will therefore not be discussed. The models described by Saveant and Albery are overall very similar and give results of a similar nature. In the Albery model, reaction of the substrate at the bare electrode is included. In this chapter the results obtained will be discussed using the Saveant/Andrieux model.

The kinetics of electrochemical reactions mediated by redox polymer films have been studied for the case of a reversible as well as an irreversible cross-exchange reaction using rotating disk electrode voltammetry [20-31]. The irreversible process can be illustrated as in

P

D_E

Q

$Q + A \xrightarrow{k_1} B + P$

A

B

A

ϕ

δ
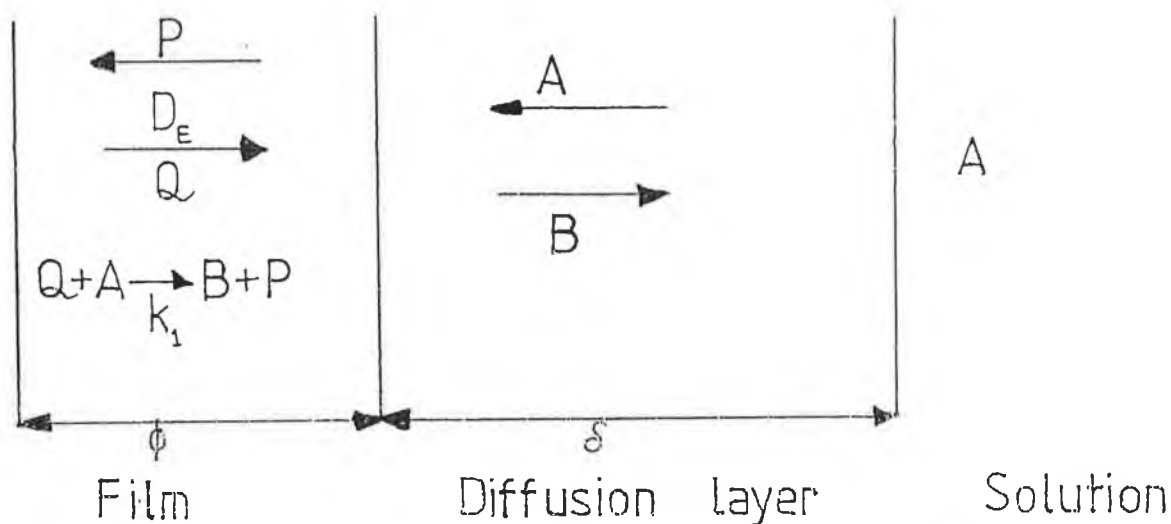
Film   Diffusion layer   Solution

FIGURE 6.2. Schematic diagram illustrating irreversible cross-exchange reactions at a modified electrode.

P/Q is the mediator couple incorporated in the film. A is the substrate and B the initial product after reduction or oxidation. In this system the electrochemical reaction can be illustrated as follows:-

(1) $P \pm e^{-} \rightleftharpoons Q$ attached mediator couple.

(2) $Q + A \rightarrow P + B$ A/B is the substrate couple.

- reaction (2) can be considered as the mediation reaction. In such studies a kinetic zone diagram is applied, as illustrated in Figure 6.3, which shows the possible factors governing kinetic control. S indicates substrate diffusion control, R corresponds

185

Figure 6.3 . Kinetic zone diagram.

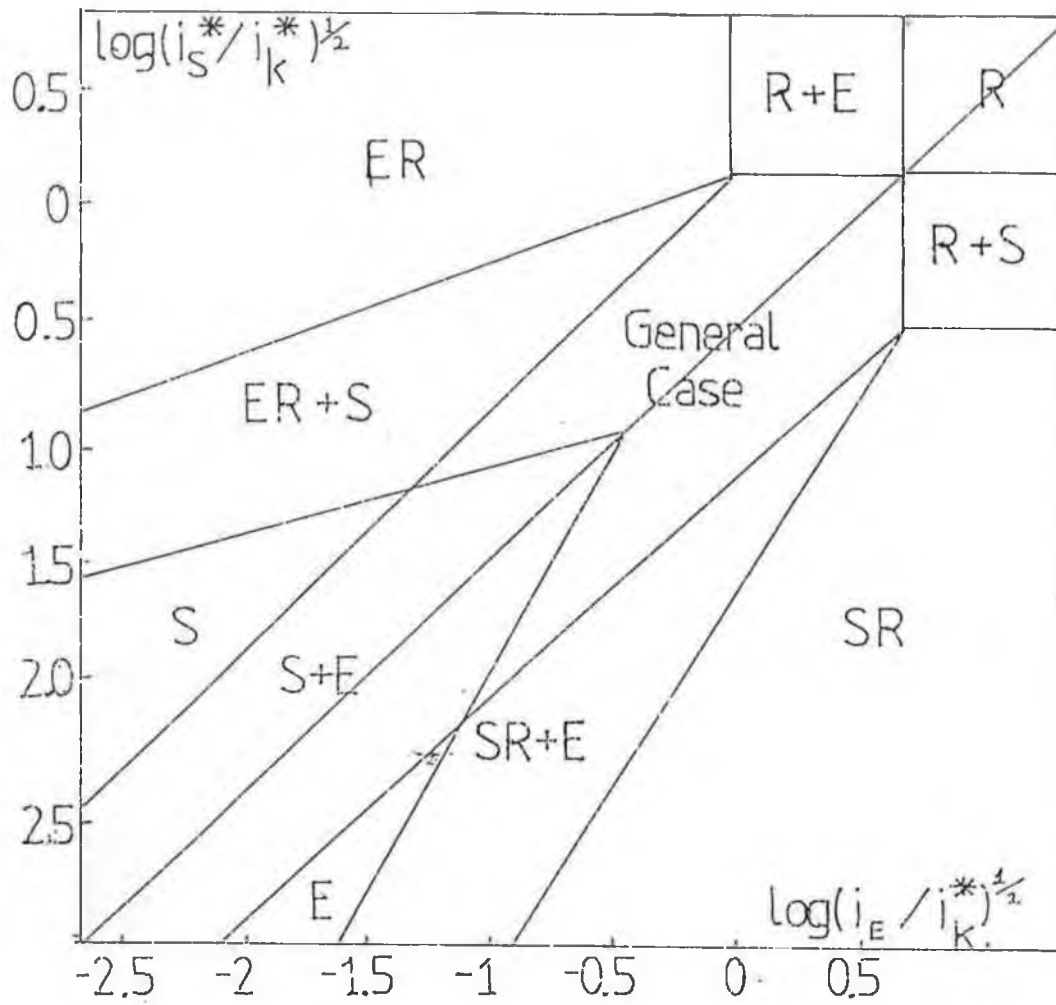to kinetic control determined by the speed of electron cross-exchange and E relates to control by electron diffusion through the layer. This approach has been applied to many systems. For example, when the catalytic reaction is very fast compared to the diffusion of the substrate in the film, the reaction takes place in a thin reaction layer, at the film-solution interface. The irreversible treatment is valid for cases where the current corresponding to the reduction of B at the electrode surface is negligible compared to the mediated current i.e. for the irreversible oxidation of A at the coated electrode.

In the Saveant model different criteria can be used to classify the nature of the mediating process [8]. The plateau current i for the mediated process can be expressed in terms of four characteristic currents (i) to (iv).

(i) $i_A = FSC_A^O D/\delta$ Substrate solution diffusion current which is equal to the plateau current at a bare electrode of the same surface area.

(ii) $i_S = FSC_A^O kD_S/\phi$ Substrate film diffusion current.

187

(iii) $i_E = FSC_p^O D_E / \phi = FS \Gamma^O D_E / \phi^2$

Film electron diffusion like transport current.

(iv) $i_k = FSC_A^O kK_1 C_p^O \phi = FSC_A^O kK_1 \Gamma^O$

Cross-exchange reaction current.

The film thickness ϕ is considered as constant. D_E is the diffusion co-efficient for the diffusion like propagation of electrons in the film, D_S represents the diffusion of substrate in the film, k is the partition co-efficient of the substrate between the film and solution, and K_1 is the second order rate constant of the reaction between the substrate and the active form of the mediator in the film. Using the above expressions the mechanism and kinetics can be characterized. These factors can be studied as functions of film thickness or substrate concentration via Koutecky-Levich plots which help in determining the nature of the kinetic control involved in this type of mediated electrocatalysis.

The Saveant model employs Koutecky-Levich treatment for its analysis. Diffusion of the substrate from the bulk of the solution to the film-solution interface is regarded as stationary with a diffusion layer thickness (δ) given in equation (3)(a).

$$\delta = 4.98 D^{1/3} \, \nu^{1/6} \omega^{-1/2} \qquad (3)(a)$$

D can be calculated according to equation $\qquad$ (3)(b)

$$D = \left(\frac{4.98 \nu^{1/6}}{nFASC_{Fe}} \right)^{3/2} \qquad (3)(b)$$

where D = diffusion coefficient of substrate in solution.

ν = kinematic viscosity $(cm^2 s^{-1})$

A = electrode area (cm^2)

S = slope of Koutecky-Levich plot

C_S = substrate concentration $(mol \, L^{-1})$

The Koutecky-Levich treatment is based on equation (4)

$$\frac{1}{i_{lim}} = \frac{1}{i_A} + \frac{1}{i_F} \qquad (4)$$

where i_A is the current due to substrate diffusion to the electrode surface and i_F is the current due to the kinetic limitations of the modified electrode surface. Also in the treatment of these results Andrieux, Saveant and co-workers have presented some diagnostic criteria for the determination of rate limiting factors, as illustrated in Table 6.1. As a general comment it can be said that for the study of mediated substrate oxidation, the use of Koutecky-Levich plots,

Table 6.1.

Diagnostic criteria for the determination of rate limiting factors for charge transport.

Limiting behaviour	Second wave	1/i_CAT vs. 1/ω^(1/2)				
		Linear	Slope		Intercept	
			Variation with c_A^0	Expression[a]	Variation with c_A^0	Expression
(R)	Yes	Yes	Inversely proportional	$\gamma/FSDc_A^0$	Inversely proportional	$1/FSc_A^0 k\,\Gamma^0 k_1$
(S+E)	No	Yes	Yes	$\gamma kD_S/FSD(kc_A^0 D_S + \Gamma^0/\phi D_E)$	Yes	$\phi/FS(kc_A^0 D_S + \Gamma^0/\phi D_E)$
(E)	No	Yes	Independent	0	Independent	$\phi^2/FS\,\Gamma^0 D_E$
(S)	No	Yes	Inversely proportional	$\gamma/FSDc_A^0$	Inversely proportional	$\phi/FSc_A^0 kD_S$
(SR)	No	Yes	Inversely proportional	$\gamma/FSDc_A^0$	Inversely proportional	$\phi^{1/2}/FSc_A^0 kD_S^{1/2}\,\Gamma^{01/2} k_1^{1/}$
(ER)	Yes	No	$i_{CAT}i_A^{1/2}/(i_A-i_{CAT})^{1/2} = FSc_P^0 c_A^{1/2} k^{1/2} D_E^{1/2} k_1^{1/2}$ is independent of ω and proportional to $(c_A^0)^{1/2}$			

[a] $\gamma = 4.98D^{1/3}\nu^{1/6}$ [γ in cm (rpm)$^{1/2}$, D and ν in cm^2 s^{-1}].

in conjunction with the Andrieux Saveant model, is valuable and results obtained can be interpreted using existing models [20].

Protonated poly (L-lysine) films containing $[Fe^{II}(edta)]^{2-}$ as counterions have been used for the development of a new model for the interior of poly-electrolyte coatings on electrode surfaces [21]. The purpose was to demonstrate the viability of the two-phase model for the interior of polyelectrolyte films. The coating was divided conceptually into two regions. The first, termed the "Donnan domains" represents the region where the counterions are confined by electrostatic forces; the second comprises the remaining volume of the coating which is assumed to be occupied by the supporting electrolyte solution. This concept is illustrated in Figure 6.4. Two modes of charge transport within the film, and the importance of coupling them, are considered. The coupling served to increase the overall charge transport rate by accentuating the role of the more rapid of the two transport modes. Charge propagation in the two-phase coating can be explained in terms of the characteristic currents (i) to (iv) listed earlier. The authors studied the current-potential curves for the reduction of $[Fe(III)(edta)]^{-}$ using the polymer coated electrode, with a subsequent evaluation of D, D_E and k as a function of film thickness and
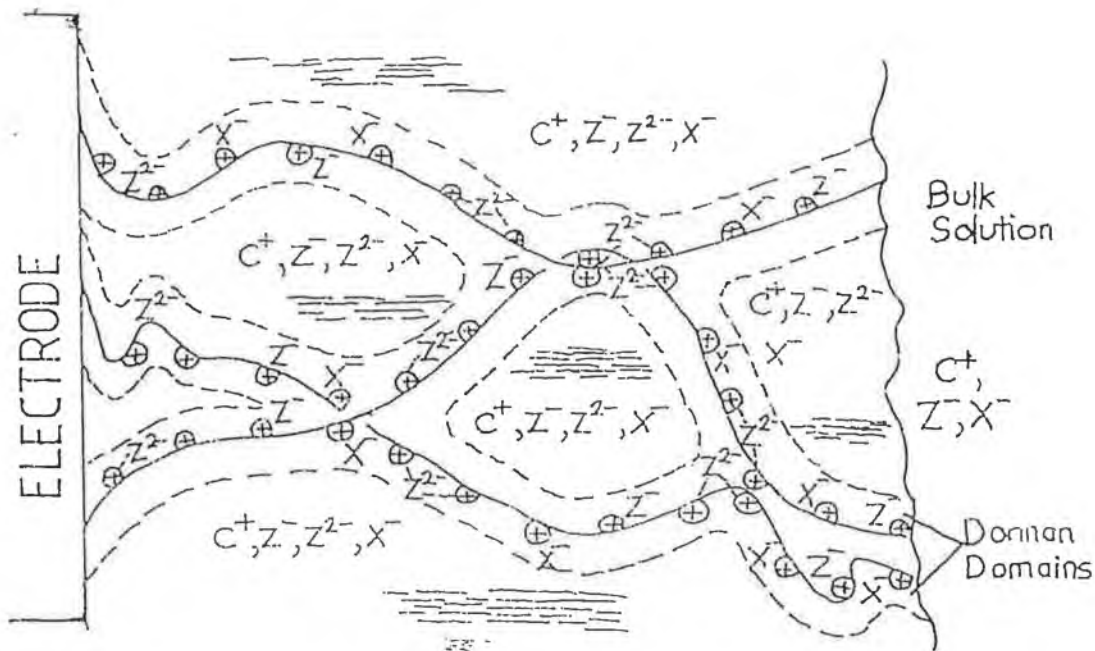
FIGURE 6.4.

A schematic model for a portion of a swollen
cationic film on an electrode surface. The film
has been equilibrated with a solution containing
an electroinactive supporting electrolyte composed
of $C^+ X^-$ and the oxidised half of an electroactive
couple , Z^-/Z^{2-}. The electrode potential is adjusted
to the limiting current plateau for the reduction of
Z^- to Z^{2-}. Solid lines represent the polyelectrolyte
chains. The dashed lines indicate the regions of
extension of the " Donnan Domains " containing the
electrostatic fields generated by the fixed cationic
sites on the chains . The remaining empty space is
filled by the supporting electrolyte solution that
permeates the coating.

substrate concentration. Chronoamperometry and chronocoulometry were used here to study charge transport in the Donnan domains.

Several different types of polymer-modified electrode systems have been studied in this way. Andrieux and co-workers have examined the effect of film thickness on values of diffusion co-efficients previously examined [32] for systems, where the reduction of 1,2-dibromo-1,2 diphenyl ethane was catalyzed at poly-p-nitrostyrene coated electrodes [26]. It was found that the catalytic efficiency increased to a limiting value as the amount of chargeable polymer increased. In a first approach the movement of electrons and diffusion of substrate through the film were considered to be fast enough not to interfere kinetically. It was considered here that at a monolayer derivatized electrode bearing the same catalyst couple in both cases, the possibility of the catalytic efficiency being increased with film thickness was somewhat contradicted by the fact that it would be more difficult for substrates to cross the film and for electrons to propagate in the opposite direction. For the polyvinyl ferrocene or poly(p-nitrostyrene) system, the electron diffusion co-efficient was determined to be in the range of $1 - 3 \times 10^{-10}$ cm^2/sec. The authors attributed three major governing factors to the control of the catalytic

process. These are the rate of electron transfer between the electrode and first layer of redox molecules, the propagation of electrons through the film and the migration of counterion resulting in ohmic drops. Several other such systems have also been the subject of such investigations.

Degrand and Miller have studied an electrode modified with polymer-bound dopamine which catalyses NADH oxidation. It was found that the response obtained was not dependent on the concentration of catalyst bound to the electrode surface [19]. Chemically modified electrodes have been employed as potentiometric sensors in which they investigated the pH response of a poly (1,2 diaminobenzene) coated electrode in a phosphate buffer [32]. The response of this film- coated platinum electrode to Co(II) was also investigated. However, no change in electrode response to varying concentration of Co(II) was obtained.

Oyama and Anson have prepared adherent coatings of a cationic polyelectrolyte on pyrolytic graphite electrodes [33]. $[IrCl_6]^{2-}$ was incorporated in the PVP film and the system was found to catalyse the oxidation of Fe^{2+} to Fe^{3+} present in solution. They describe the successful acceleration of a simple electrode reaction using electrostatically as well as

co-ordinatively bound catalysts. The main purpose of this work was to explore the diagnostic utility of voltammetry with rotating disc electrodes in studies of electrode surfaces and electrode coatings. It was found that such measurements can be quite valuable especially when they are analysed by means of reciprocal plots of (limiting current)$^{-1}$ versus $\omega^{-1/2}$, (rotation speed)$^{-1/2}$. Thus it was possible for this system to distinguish between currents limited by the rate of a redox reaction between a dissolved substrate and a catalyst anchored to an electrode coating from those limited be electron transfer through the coating. At low rotation rates, the transfer of Fe^{2+} through the rather thick Levich layer, controls the current so that linear i vs $\omega^{1/2}$ behaviour results. At higher values of ω, the thickness of the Levich layer decreases and the magnitude of the current is controlled by the rate of the redox reaction between Fe^{2+} and $[IrCl_6]^{2-}$ confined in the polyelectrolyte film. In this case the reciprocal plot, i^{-1} vs $\omega^{-1/2}$ is used.

Peerce and Bard have studied reactions between films of poly(vinylferrocene) and solution species [34]. The authors studied the effect of poly(vinylferrocene) films on the cyclic voltammetric behaviour of dissolved substrates as a function of sweep rate and film thickness. They also studied channels in films

on electrode surfaces and the diffusional behaviour of the electrons through the film by chronoamperometry. They concluded that the movement of ions through the film also plays a role in the electrochemical oxidation and reduction of the polymer film itself. The kinetics and electrocatalysis of dibromoalkyl reductions using electrodes coated with covalently immobilized metallotetraphenylporphyrin have been studied by Rocklin and Murray [35]. There have been several reports of successful qualitative approaches to mediated electrocatalysis [16-19, 33, 36-41] but there have been few quantitative electrocatalytic reduction measurements by using rotating disk electrode voltammetry. The rate of reaction for the above system [35] was found to be independent of the amount of metalloporphyrin on the electrode surface, a feature found in other systems. Results obtained did suggest that the rate of diffusion of electrochemical charge through the layer is faster than the rate of diffusion of substrate through the layer. However, comparison of electrocatalytic rates for the different mediation involves specific interactions between substrate and metalloporphyrin rather than being a simple outer-sphere electron transfer event.

The treatment of the data is based largely on equation (5) [33, 39]

$$\frac{1}{i_{max}} = \frac{1}{nFAk_{ch} \; C_s} + \frac{1}{0.62nFADs^{2/3} \; \nu^{-1/6} \; \omega^{1/2} \; C_s} \quad (5)$$

where i_{max} represents the limiting current for electrocatalytic current. This implies that when the intercept of a $1/i_{max}$ vs $1/\omega^{-1/2}$ plot is zero, the current is limited solely by the rate of mass transport of substrate from the solution to the rotating electrode, and not by the rate of substrate-reduced porphyrin chemical reaction. This treatment has been commonly used in modified electrode studies [33, 39, 42]. In most cases it has been found that charge transport is likely to control the current. As illustrated in the work of Rocklin and Murray [35], for electrocatalysis by a polymer-films with control by the rate of the chemical step, whether the quantity of catalyst sites corresponds to the outermost layer of the film or to that in the total film (Γ_t) is predicted by panels of A and B in Figure 6.5 to depend on the ordering of chemical flux charge transfer flux and substrate flux.

When the species incorporated in the coating is also present in the solution being studied [43], the current
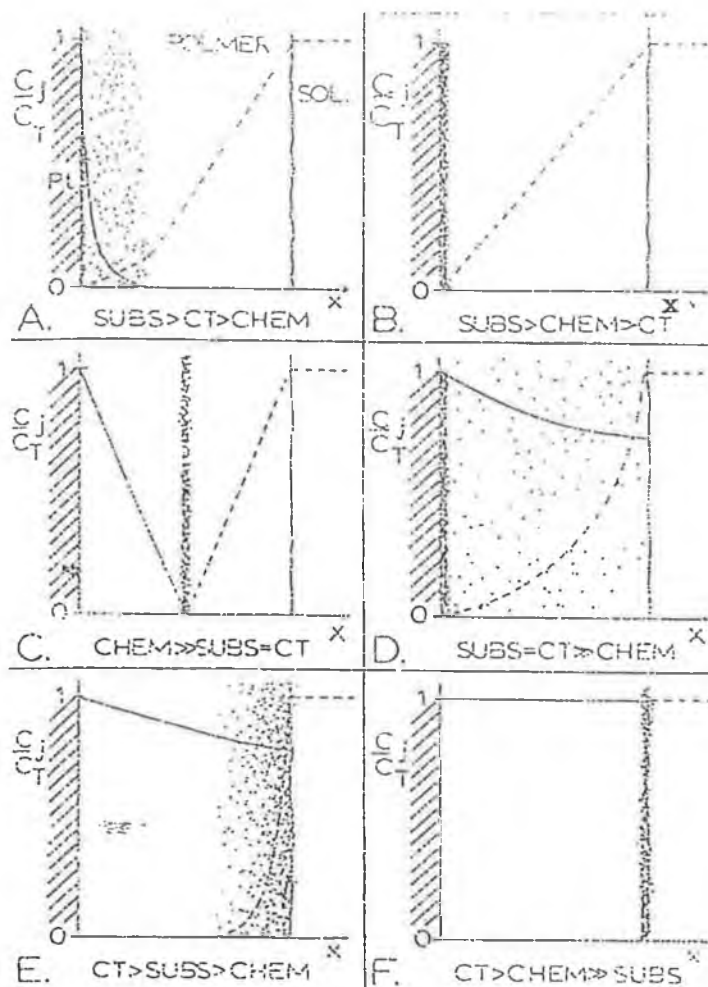
FIGURE 6.5:

Schematic concentration – distance profiles for metal deposition at a reducing polymer – coated electrode. C_j = concentration of reduced polymer sites (——) or concentration of metal ions (– – –) C_T = total concentration of polymer redox sites or bulk concentration of metal ions outside polymer Dots represent distribution of metal particles,

SUBS = rate of diffusion of metal ions through the polymer (step 1); CT = rate of charge transport through the polymer (step 2); CHEM = rate of reduction of metal ions by the reduced polymer sites (step 3).

flowing at such electrodes was found to be limited by the rate of electron exchange reaction between the solution-phase reactant and its oxidized or reduced counterpart present in the film on the electrode surface. Anson and co-workers have measured such self-exchange rates for $[IrCl_6]^{2-/3-}$ and $[Fe(CN_6]^{3-/4-}$ incorporated by poly(4-vinylpyridine). Their analysis of the results included the use of Koutecky-Levich plots previously mentioned. The thickness of the Levich layer was found to be inversely proportional to the rate of rotation of the electrode. The Levich plot exhibited expected linearity at an uncoated electrode but increased deviations appeared as the quantity of polyelectrolyte coating is increased. The slopes of these plots were found to be inversely proportional to the concentration of the reactant. Intercepts of the plots were therefore identified with values of the limiting current density $(i_L)_\infty$ where $(i_L)_\infty = F(K_{ex})app \ \Gamma \ Ir(III) \ c^b \ Ir(IV)$ solution and K_{ex} is the expected second order rate constant. The methods used here are of general applicability to multiply charged reactants.

The permeation of electroactive solutes such as ferrocene or diquat through ultra thin polymeric films of electropolymerized $[Ru(vbipy)_3]^{2+}$ on electrode surfaces has been investigated [44]. Specifically, rates of permeation of electroactive solutes through

redox polymer films to the electrode have been measured as a function of film polymeric structure and of solute size and charge. Thorough understanding of solute transport through thin films is important in describing the catalytic or inhibitory behaviour of such films, so much attention was addressed to this area. It was found in these studies that different substrates exhibited different permeation rates through the same film of poly[Ru(vbipy)$_3$]$^{2+}$. Koutecky-Levich treatment and the data obtained for the system confirmed the membrane-diffusion model i.e. that a solute diffused to an electrode through a membrane diffusion barrier with diffusion constant D_s or that the reciprocal limiting current is equal to the sum of the reciprocal kinetic and reciprocal limiting currents. The authors have also addressed the problem of film imperfections in relation to the transport of electrochemical charge.

Anson and co-workers have investigated the kinetics of electron-transfer cross-reactions within polylysine co-polymer with incorporated electroactive anions [45]. The authors employed the normal Koutecky-Levich treatment of results as described by Andrieux and co-workers [20]. Anson and co-authors have employed chronocoulometry and chronoamperometry as mentioned previously in Chapter IV.

While several different modified electrodes have already been reported in the literature [1-45], electroactive coatings containing $[Ru(bipy)_3]^{2+}$ continue to be of interest because of the fast kinetics of electron exchange and the very favourable excited state and ground state properties of the redox couple [46]. An important reaction in the design of efficient photoanodes is the Co(II) catalyzed oxidation of H_2O by $[Ru(bipy)_3]^{2+}$ where the latter is incorporated into polymeric films. Ghosh and Bard have investigated hydrogen evolution at electrodes described above [46]. However, no catalysis of this reaction was observed. Still considering the use of pyridyl based materials, electrodes coated with polystyrene sulphonate as a matrix for mediated oxidation of ferrocene-1-1' disulfonate in acetonitrile by electrostatically bound tris(s,2'bipyridine)osmium (III) have been studied [47]. The author studied the rate-limiting factors controlling the system and Koutecky-Levich plots and chronocoulometric experiments were employed. The response was studied as a function of substrate concentration. Using the Andrieux/Saveant treatment of kinetics and the experiments mentioned above, charge transport was reported to follow the SR mechanism i.e. a rapid cross-exchange reaction and slow substrate diffusion through the film. Pyridyl based complexes have also been investigated by Morris

[48]. She and her co-workers have studied the physical nature of poly(4-vinylpyridine) films loaded, at pH3, with a ferricyanide (catalyst) in an ion exchange process. Molecular oxygen was used as the substrate due to its advantages of electroactivity, neutral charge and nearly universal solubility. Koutecky-Levich analysis for this system indicated a rotation-independent substrate penetration current.

Niwa and Doblhoffer have studied the inter-relation between the electrochemical behaviour of polyvinylpyridinium coated electrodes and the ion exchange properties of the coating [6]. The $[Fe(CN)_6]^{3-/4-}$ charge transfer reaction was studied with the anion exchange polymer-coated electrodes. Analysis of the results indicated that the redox ions were practically not admitted to the electrode surface and the film acted as a barrier for the $[Fe(CN)_6]^{3-/4-}$ charge transfer reaction. On the other hand $[Fe(CN)_6]^{3-}$ was found to replace $[Fe(CN)_6]^{4-}$ and $[SO_4]^{2-}$ in the film. Consequently in this situation the system acts as an efficient barrier for the oxidation of $[Fe(CN)_6]^{4-}$ while the $[Fe(CN)_6]^{3-}$ reduction proceed inhibited.

Protonated poly-4-vinylpyridine films containing electroactive anions, $[IrCl_6]^{3-}$ have been studied for the purpose of catalysing or mediating the transfer of

charge between the electrode and a dissolved substrate [49]. The kinetics of Fe(II) oxidation by this system has been examined. The charge transport through these films was studied in terms of apparent current density or apparent electron diffusion co-efficient, D_E [50-51]. The values were derived from slopes of chronocoulometric experiments.

In this section it will be demonstrated how ruthenium-containing poly-N-vinylimidazole based polymers coated on the surface of graphite or glassy carbon electrodes can be used for the mediated catalysis of Fe(II) oxidation in aqueous solution. In this investigation rotating disk experiments have been analysed using the Saveant model. The results obtained are discussed with respect to the nature of the charge-transport process and the polymer-electrolyte interface.

VI.2 RESULTS AND DISCUSSION

The mechanisms and kinetics of various catalytic reactions have been discussed in the introduction to this chapter. Studies on the mediator properties of ruthenium-containing poly-N-vinylimidazole were concentrated in the following areas:

1. Effect of film thickness on the catalytic efficiency.

2. Effect of substrate type and concentration on the results obtained.

3. Determination of the rate limiting factors; substrate diffusion (D), electron diffusion (D_e) or speed of electron cross-exchange.

4. Effect of electrolyte concentration, nature and pH on the mechanism and kinetics observed.

In the following series of experiments the catalytic properties of $[Ru(bipy)_2(PNVI)Cl]Cl$ modified glassy-carbon electrodes towards the catalysis of the oxidation of Fe(II) in aqueous solution have been investigated as a function of the parameters mentioned above.

The two iron-containing substrates investigated were $(NH_4)_2Fe(SO_4)_2$ which exists as $[Fe(H_2O)_6]^{2+}$ in aqueous solution and $K_4[Fe(CN)_6]$ also in aqueous solution. The difference in the nature of these two complexes and their electrochemical behaviour is expected to be a function of their overall charge.

VI.2.1   Mediation   of $(NH_4)_2Fe(SO_4)_2$ Oxidation   by
          $[Ru(bipy)_2(PNVI)Cl]Cl$ (Sample   C)   Coated
          Glassy Carbon Electrodes

Using rotating disk electrodes coated with different
concentrations of the mediator (metallopolymer) the
electrochemical response of the iron containing
substrate was studied at varying electrode rotation
speeds.   A typical example of such a response is
illustrated in Figure 6.6.   Analysis of these results
is achieved by employing Koutecky-Levich plots where
$(i_{lim})^{-1}$ is plotted against $(\omega)^{-1/2}$.   These plots
allow calculation of D, the diffusion co-efficient of
the substrate in solution, and K_S.   Results are
treated according to the Andrieux-Saveant treatment of
kinetics as discussed above.   Values of D were
obtained using equation (3) already listed.   As
illustrated in the kinetic zone diagram there are
certain models which can be applied.   Koutecky-Levich
plots were linear and a single oxidation wave observed
except for extremely thin films, Koutecky-Levich plots
showed slopes and intercepts which are inversely
proportional to the concentration of the substrate.
Based on these facts, an 'SR' mechanism was assumed.
One other criterion is that i_A (equivalent to plateau
current observed at a bare electrode) is less than i_E
(charge propagation current density).   This was
observed for this system as there was no plateau

current observed for a bare electrode. For
illustration refer to Figure 6.6. On the basis of
this assumption, values of the surface rate constant,
K_s, could be calculated according to equation (6) [49]

$$K_S = \frac{i_k}{nF \; c_{Fe} \Upsilon_{Ru}} \tag{6}$$

where i_k is the reciprocal of the intercept of the
Koutecky-Levich plot.

For the experiments described here, sulphate,
perchlorate and chloride based electrolytes were used.
Considering first perchlorate based electrolytes it
was found that no oxidation of $[Fe(H_2O)_6]^{2+}$ was
observed at the modified electrode. This was not due
to the loss of the film from the electrode surface as
confirmed by cyclic voltammetry. This result was
attributed to the fact the the polymer is insoluble in
perchlorate solutions and will therefore not swell.
Because of this the metallopolymer film presents a
closed structure thus preventing penetration of the
positively charged Fe(II) substrate. This phenomenon
was found to occur regardless of the pH. For these
reasons the perchlorate-based electrolytes were
unsuitable for these studies. Next a sulphate based
electrolyte, namely 0.9M Na_2SO_4 + 0.1M H_2SO_4, with a
pH of approximately 1.8, was used. A typical response
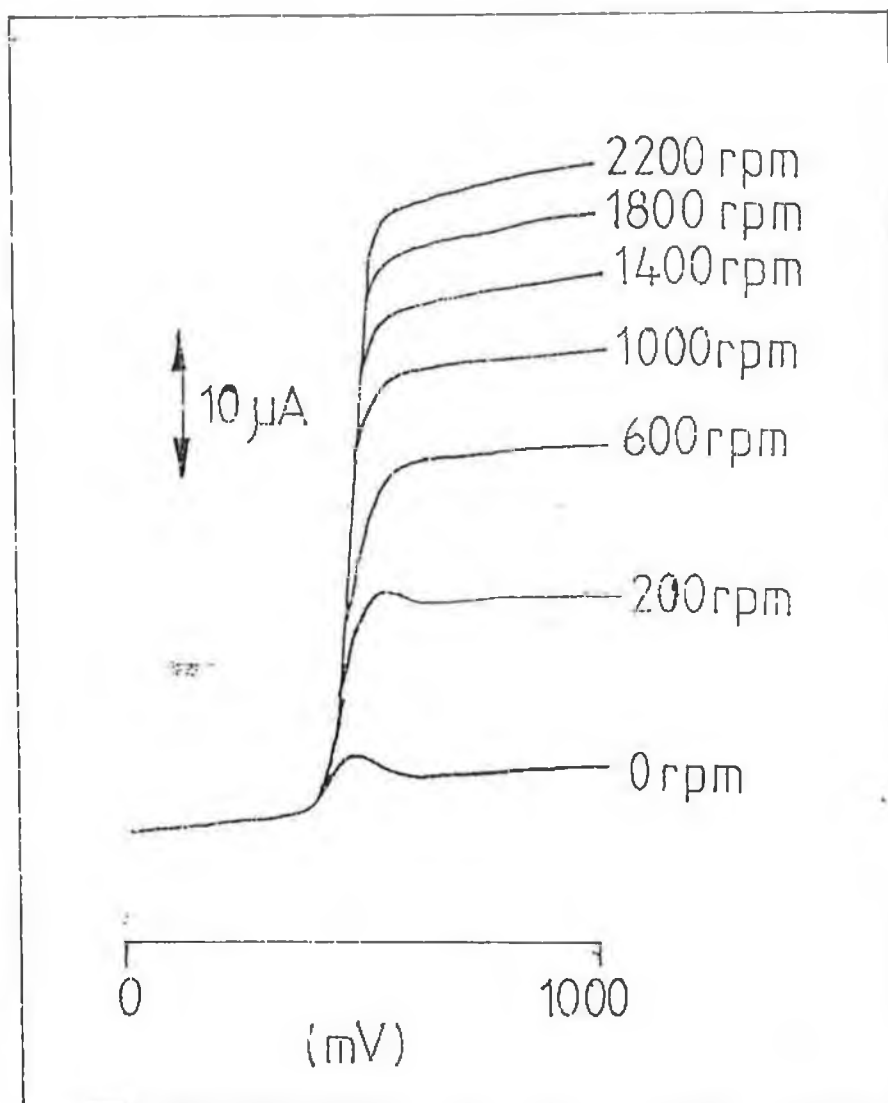using these conditions is illustrated in Figure 6.7.

FIGURE 6.6. Current-potential response for a
RDE coated with $[Ru(bipy)_2(PNVI)Cl]^+$
Film thickness = 7.2×10^{-9} moles/cm^2.
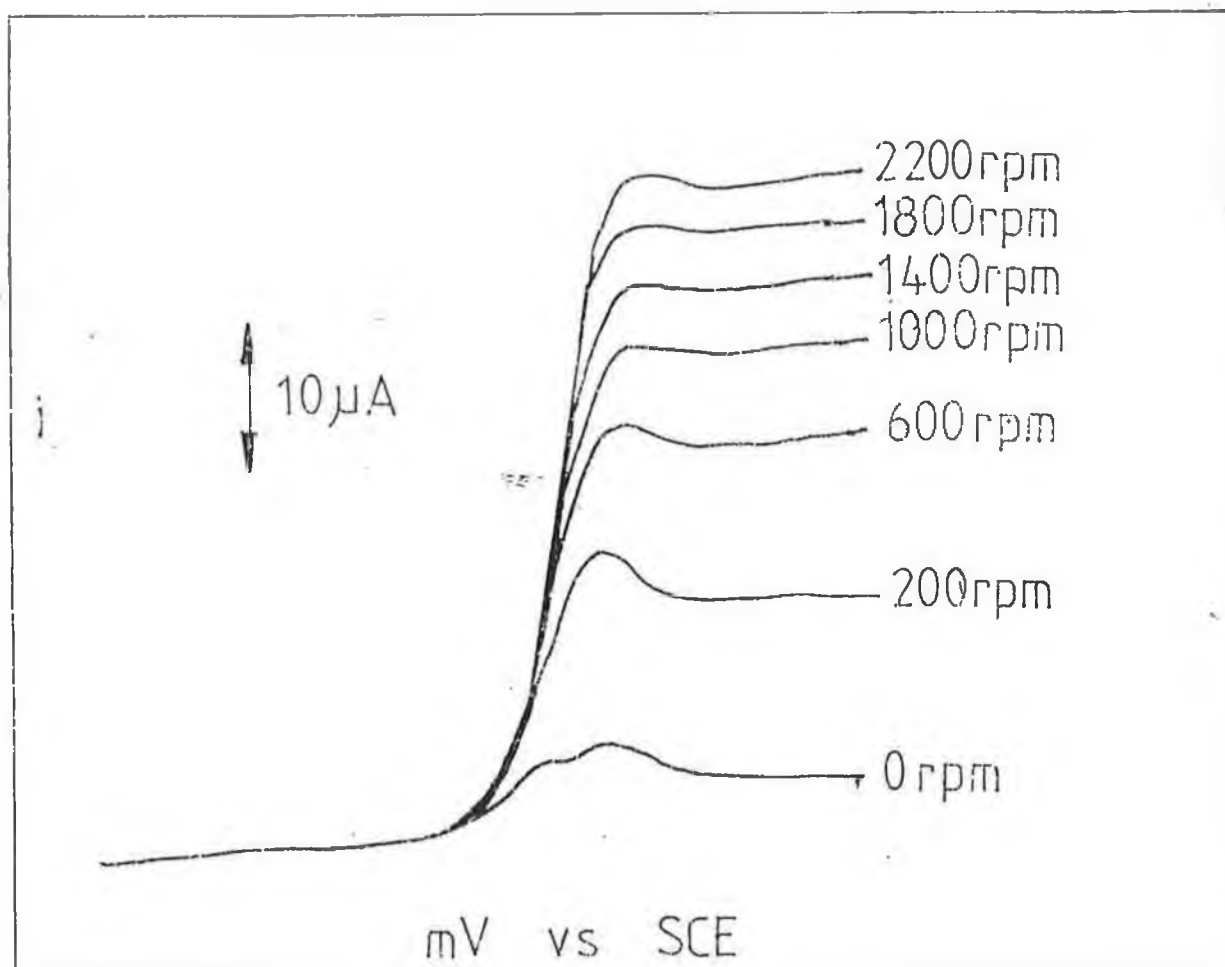Substrate : 1.5mM $(NH_4)_2Fe(SO_4)_2$.
Sweep rate : 5mV/sec.

Electrolyte : 0.9M NaCl + 0.1M HCl.

FIGURE 6.7. Current-potential response curve for a RDE coated with $[Ru(bipy)_2(PNVI)Cl]^+$. Film concentration = 1.2×10^{-8} moles/cm^2. Substrate : 1mM $(NH_4)_2Fe(SO_4)_2$. Electrolyte : 0.9M Na_2SO_4 + 0.1M H_2SO_4. Sweep rate : 5mV/sec.

However, with time the response is found to tend towards that of a bare electrode surface. So although a good response is obtained initially, the instability of the film in this electrolyte rules this system out for extensive studies. It was decided to employ chloride based electrolytes as previous electrochemical studies indicated the stability of the metallopolymer film in this electrolyte. The response of ferrous ammonium sulphate was studied at different sweep rates and using different film thicknesses. The reproducibility of these results and the stability of the metallopolymer film were two important factors which were assigned due consideration.

Studies on the subject of the catalysis of the oxidation of Fe(II) in aqueous chloride solutions require also an investigation into the cyclic voltammetric behaviour of the polymeric film in such electrolyte. This served two purposes; namely the determination of the film concentration per unit area and also the study of the condition of the film i.e. whether any changes were incurred during the course of the experiments. The two pH values used here were pH1.0-pH2.0 and pH5.0-pH6.0. The former condition is achieved using a 0.9M NaCl/0.1M HCl electrolyte. The higher pH media were obtained using NaCl solutions, particularly 1.0M NaCl. Very different results were obtained in these two situations. At the higher pH

values response for the Fe(II) oxidation is hindered. An initial response is obtained but after a few minutes the response stops. One could attribute this result to a loss of product from the electrode surface. However, this idea was ruled out by running a cyclic voltammogram before and after the experiment. The shape of the voltammogram was however found to change after the experiment. The band corresponding to the Ru(II) to Ru(III) oxidation was found to be broader but on immersion in HCl the previous response i.e. with a narrower, sharper band, returned. This would seem to indicate that the polymeric film was effected by the high pH but previous experiments in this electrolyte in the absence of any substrate showed no change on continuous scanning in 1M or 0.2M NaCl. This suggests that the layer was effected by the presence of $(NH_4)_2Fe(SO_4)_2$ in the electrolyte.

Experiments run in more acidic chloride based electrolytes i.e. 0.1M HCl or 0.001M HCl exhibited different responses. Considering firstly the 0.1M HCl electrolyte having a pH of approximately 1.3 a response was obtained is illustrated in Figure 6.8. The Koutecky-Levich plot, Figure 6.9, shows a linear response over most of the rotation speeds except at 200rpm, a feature which is common in such experiments. Cyclic voltammograms run before and after the experiment show a loss of a small amount of product
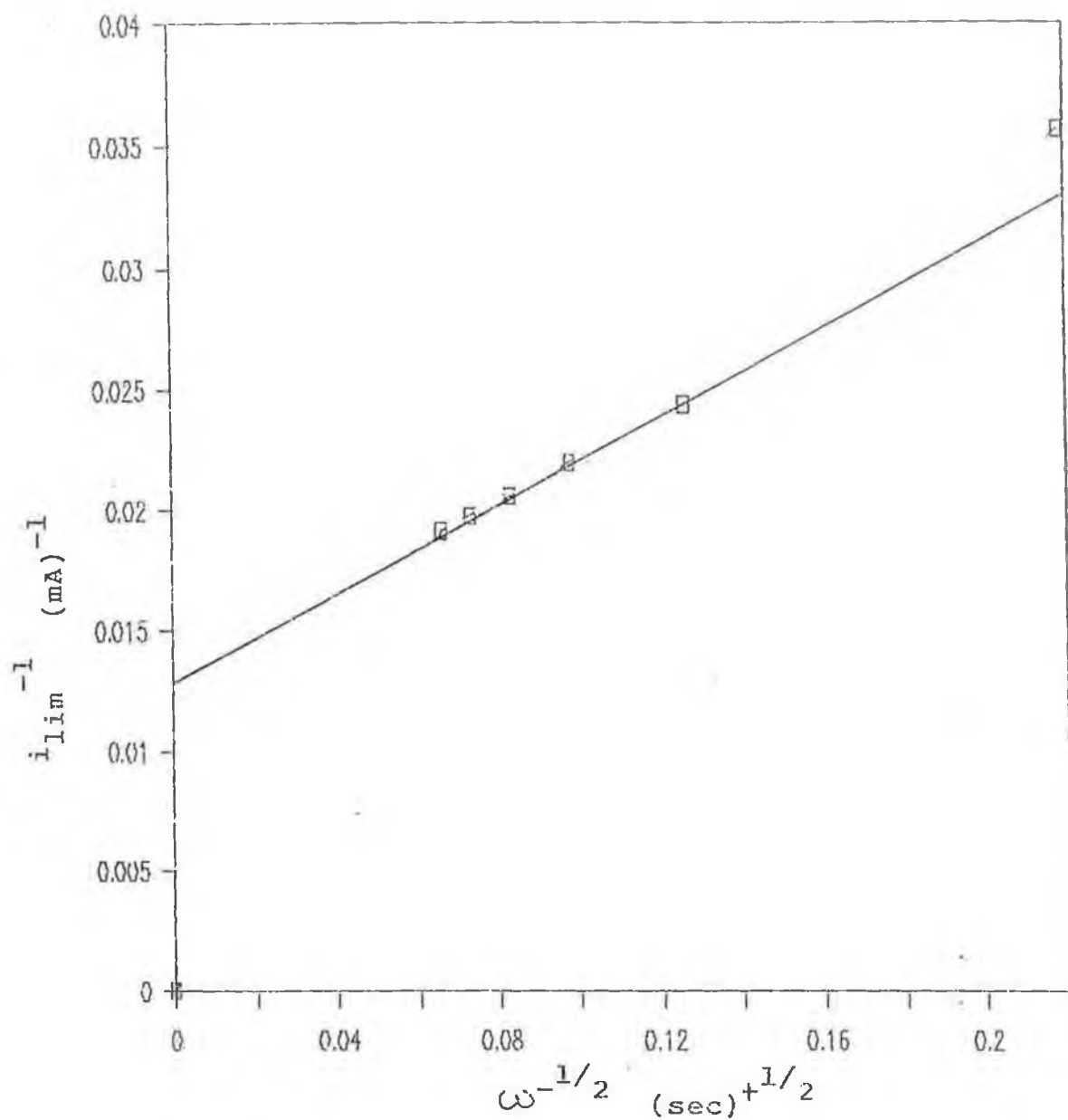
FIGURE 6.9. Koutecky-Levich plot corresponding to Figure 6.8.

FIGURE 6.8. Current-potential response curve for a RDE coated with 0.9×10^{-9} moles/cm^2 of sample C.
Sweep rate : 5mV/sec.
Electrolyte : 0.1M HCl.
Substrate : 2mM $(NH_4)_2Fe(SO_4)_2$.

FIGURE 6.10. Current-potential response curve for a RDE coated with 0.95×10^{-9} moles/cm^2 of sample C.
Electrolyte : 0.001M HCl.
Sweep rate : 5mV/sec.
Substrate : 1.5mM $(NH_4)_2Fe(SO_4)_2$.

213

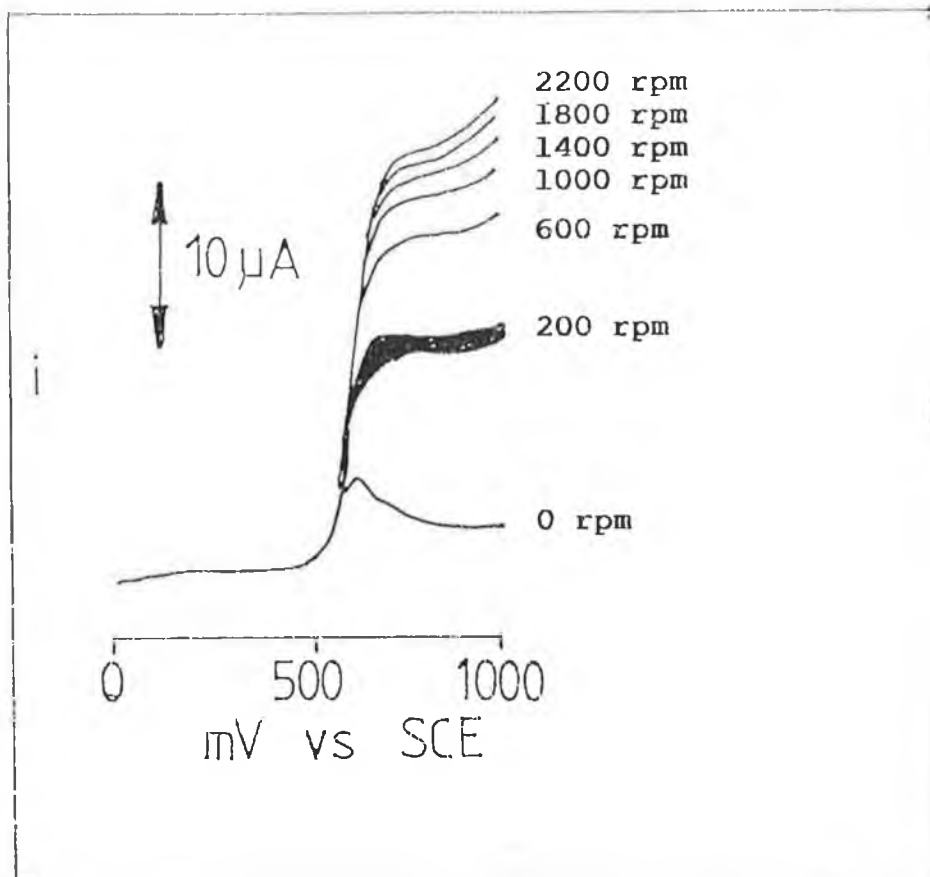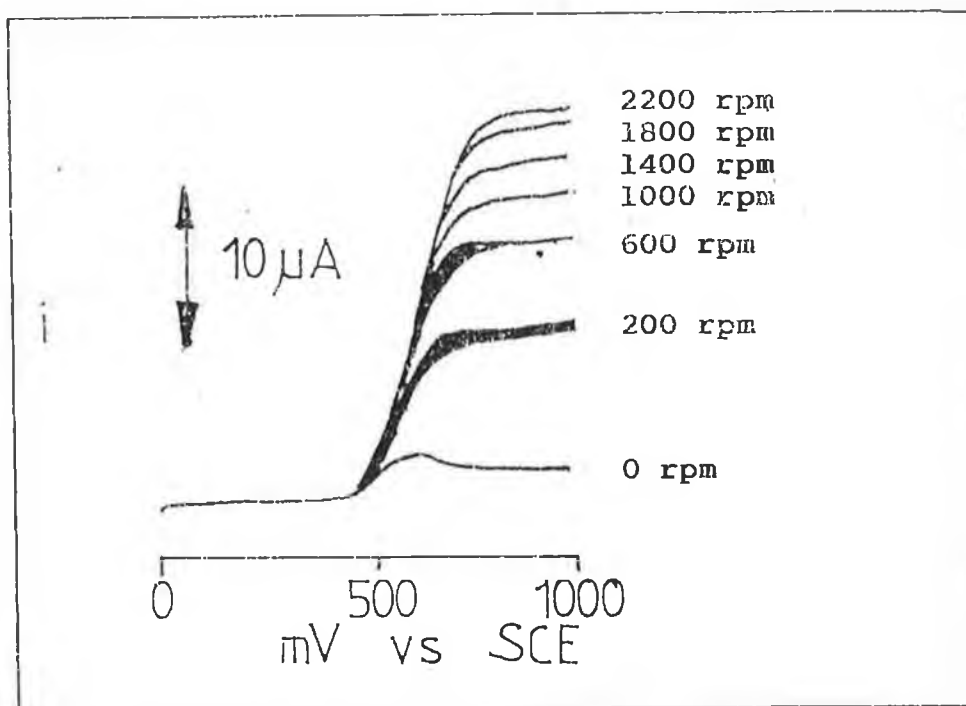(~10%) from the electrode surface. This can be explained by some instability incurred in the film due to the strongly acidic nature of the electrolyte. This phenomenon was previously observed in cyclic voltammetric studies. Using a 0.001M HCl electrolyte, pH3.0, different responses were obtained, an example of which is given in Figure 6.10. Firstly it should be noted that the polymeric film was found to be more stable at this pH. One important factor to realise here is that the electrolyte concentration here is very low so the experimental conditions are very different in this case from the other electrolytes used. Current-potential responses were recorded for different concentrations of substrate. Calculations of D and K_S for the two systems indicate that values of D do not significantly change and are of the order $6 \times 10^{-6} cm^2 s^{-1}$. It should also be noted that for calculation of K_S using equation (2) values of Γ_{Ru} (surface coverage) are very important but the integrated area under a cyclic voltammogram run immediately before in the appropriate electrolyte at a scan rate of 50mV/s. We will consider now a pH2.0, 0.9M NaCl + 0.1M HCl, electrolyte. This electrolyte was found to be the most suitable for systematic experiments of this nature due to the stability of the film. A series of experiments were run using different concentrations of substrate and different film thicknesses. Film thicknesses of 1.2×10^{-9}, 3.5

214

X 10^{-9} and 7.12 X 10^{-9} moles/cm^2 were used mainly for these studies using as a substrate, $(NH_4)_2Fe(SO_4)_2$, with concentrations ranging from 0.5 X 10^{-3} to 2.0 X 10^{-3}M solutions. Examples of the types of responses obtained are illustrated in Figures 6.11 - 6.12. All experiments were carried out in duplicate and fairly good agreement was obtained between different runs. Tables of results including values of D and K_S are presented accompanied by representative Koutecky-Levich plots, see tables 6.2 - 6.4. One very important feature to note is that at the lowest film thickness of 1.2 X 10^{-9} moles/cm^2 a second wave is visible particularly at higher concentrations of substrate and higher rotation speeds. This is illustrated in Figure 6.12. This is attributed to the reaction of the substrate at the bare electrode i.e. unmediated oxidation of the Fe(II) in solution. Koutecky-Levich plots are illustrated in Figure 6.13. This feature had been observed previously by Oyama and Anson [33] in the study of the catalysis of Fe(II) oxidation of PVP (poly-4-vinylpyridine) with incorporated $[IrCl_6]^{3-}$ coated pyrolytic graphite electrodes. Here two oxidation waves were observed except at low rotation speeds (100rpm) where the rate of the catalytic cycle is apparently adequate for all Fe(II) reaching the electrode surface to be oxidized at the potential of the first wave. In these situations the second wave, appearing at higher

Table 6.2 - Results of Koutecky-Levich plot analysis.

[Fe] (X 10^3) moles L^{-1}	*Intercept^{-1} mAcm^{-2}	K_S (X 10^{-4}) mol^{-1}Ls^{-1}	a_D (X 10^{-5}) cm^{2}s^{-1}	b_D (X 10^{-5}) cm^{2}s^{-1}
0.5	1.76	3.04	2.41	3.07
0.75	1.76	2.03	2.95	3.36
1.0	4.33	3.74	2.25	2.99
1.5	4.695	2.7	2.45	3.44
2.0	9.39	4.055	2.74	3.68

*:- (Intercept)$^{-1}$ for first oxidation wave.

a Diffusion co-efficient for first oxidation wave.

b Diffusion co-efficient for second oxidation wave.

It should be noted that the intercept for the second wave was equal to zero implying $K_S \to \infty$.

$(NH_4)_2Fe(SO_4)_2$ was used as a substrate and 0.9M NaCl + 0.1M HCl electrolyte at pH 2.0.

$[Ru(bipy)_2(PNVI)Cl]Cl$ concentration was 1.2 X 10^{-9} moles/cm^2.

Table 6.3 - Results of Koutecky-Levich plot analysis.

[Fe]	Slope	Inter-cept^{-1}	D_S	K_S
moles L^{-1}	mA^{-1}s^{-1}	mAcm^{-2}	cm^{2}s^{-1}	mol^{-1}Ls^{-1}
0.5 X 10^{-3}	602.37	2.35	3.76 X 10^{-5}	1.33 X 10^4
0.75 X 10^{-3}	368.66	2.82	4.265 X 10^{-5}	1.545 X 10^4
1.0 X 10^{-3}	280.17	7.04	4.18 X 10^{-5}	2.21 X 10^4
1.5 X 10^{-3}	206.32	6.335	3.6 X 10^{-5}	1.35 X 10^4
2.0 X 10^{-3}	162.33	9.4	3.35 X 10^{-5}	1.56 X 10^4

All experiments were carried out using the substrate $(NH_4)_2Fe(SO_4)_2$ at a sweep rate of 2mV/s.

The electrolyte used was 0.9M NaCl + 0.1M HCl at a pH of 2.

[Ru(bipy)$_2$(PNVI)Cl]Cl concentration was 3.5 X 10^{-9} moles cm^{-2}.

Table 6.4 - Results of Koutecky-Levich plot analysis.

[Fe] moles L^{-1}	Slope $mA^{-1}s^{-1}$	Inter-cept^{-1} $mAcm^{-2}$	D_S cm^2s^{-1}	K_S $mol^{-1}Ls^{-1}$
0.5×10^{-3}	537.95	4.5	4.39×10^{-5}	1.395×10^4
0.75×10^{-3}	364.65	5.0	4.32×10^{-5}	0.945×10^4
1.0×10^{-3}	260.43	6.67	4.66×10^{-5}	0.935×10^4
1.5×10^{-3}	180.8	20	4.385×10^{-5}	1.955×10^4
2.0×10^{-3}	137.37	20	4.30×19^{-5}	1.46×10^4

All experiments were carried out using the substrate $(NH_4)_2Fe(SO_4)_2$ at a sweep rate of 2mV/s.

The electrolyte used was 0.9M NaCl + 0.1M HCl at a pH of 2.
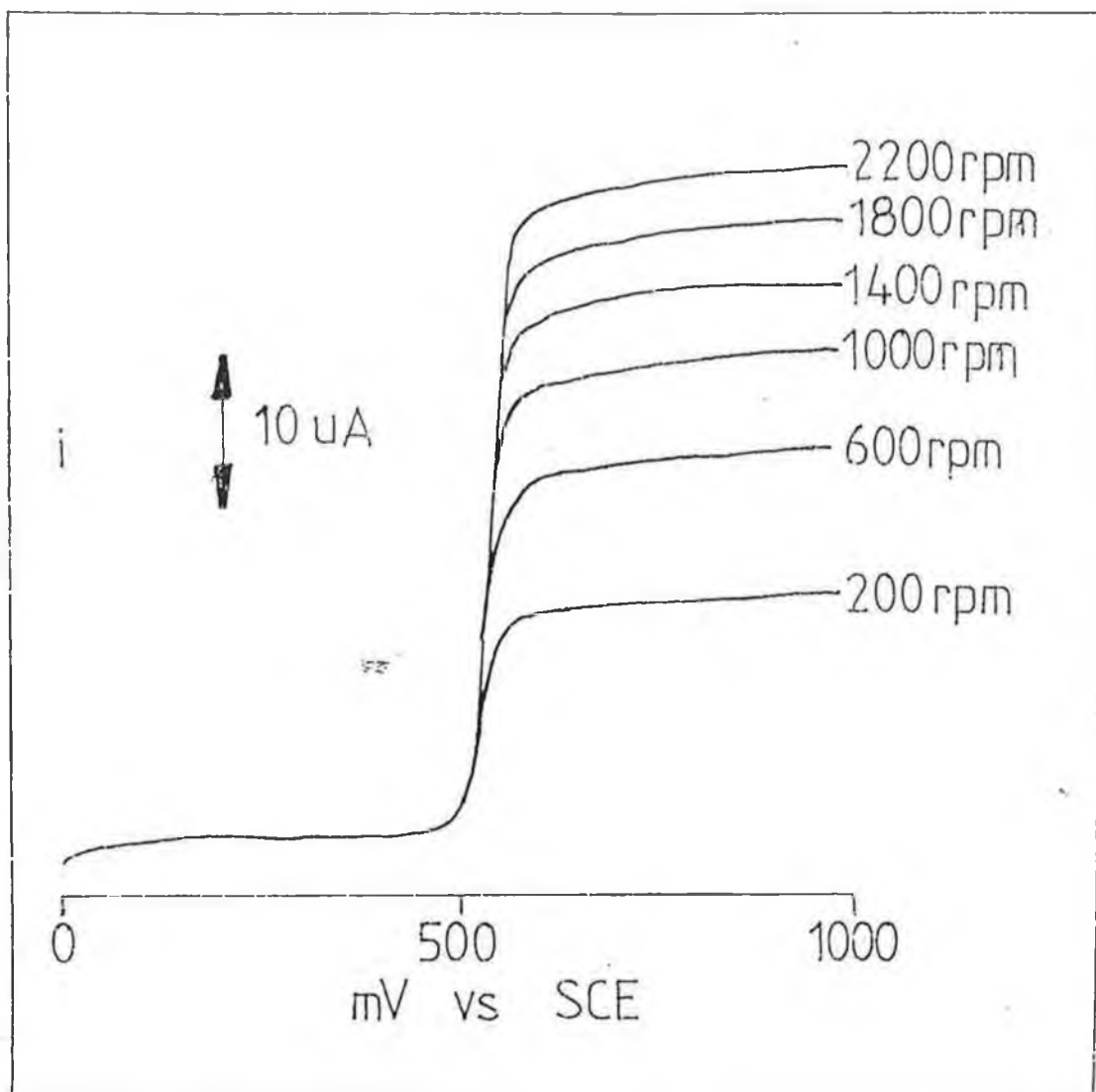
[Ru(bipy)$_2$(PNVI)Cl]Cl concentration was 7.12×10^{-9} moles cm^{-2}.

FIGURE 6.11.   Current-potential response curve for a RDE coated with 7.2×10^{-9} moles/cm^2 of sample C.

Electrolyte : 0.9M NaCl + 0.1M HCl.

Sweep rate : 5mV/sec.

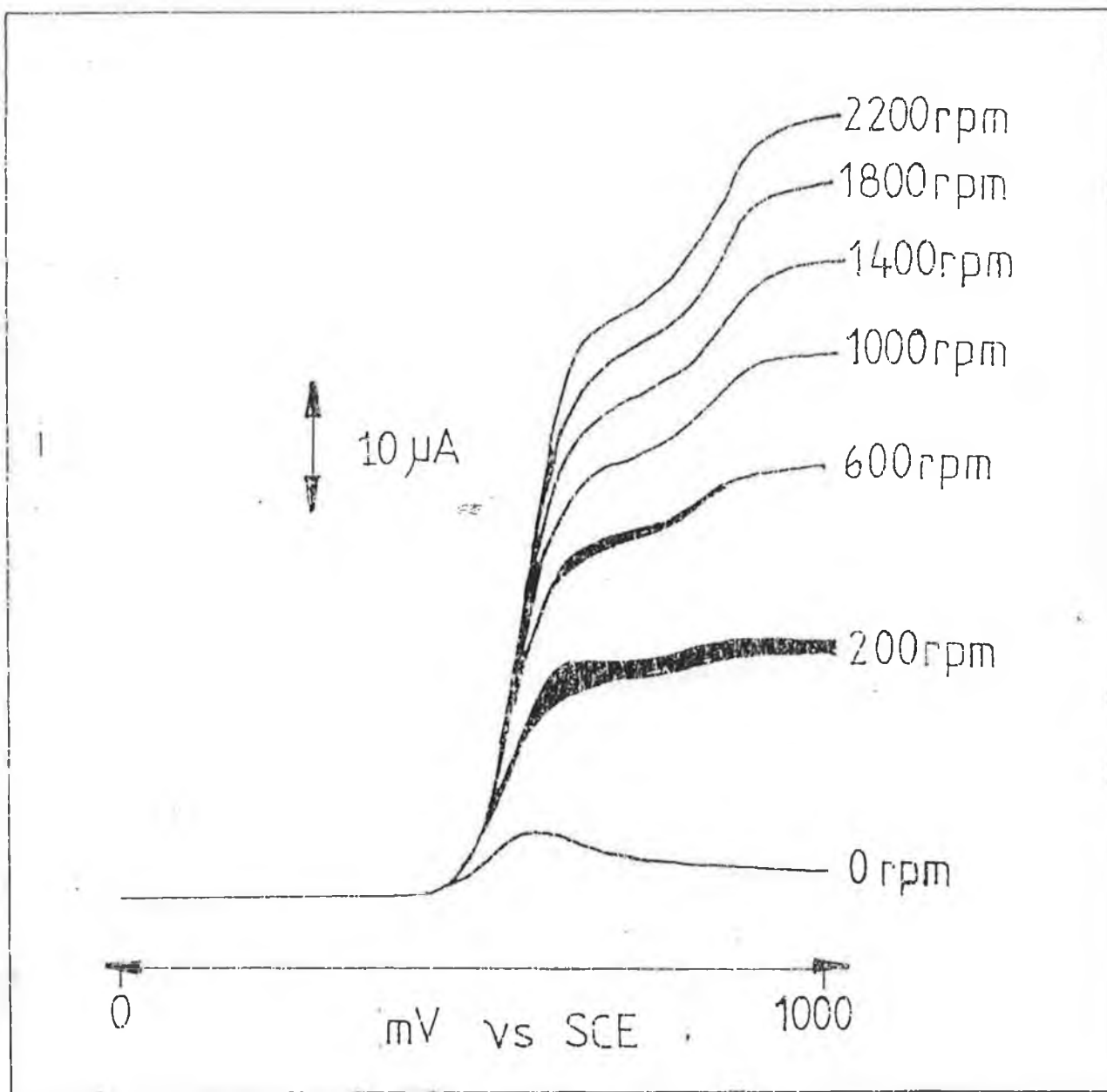Substrate : 1.5mM $(NH_4)Fe(SO_4)_2$.

FIGURE 6.12. Current-potential response curve for a RDE coated with 1.2×10^{-9} moles/cm^2 of Sample C.
Electrolyte : 0.9M NaCl + 0.1M HCl.
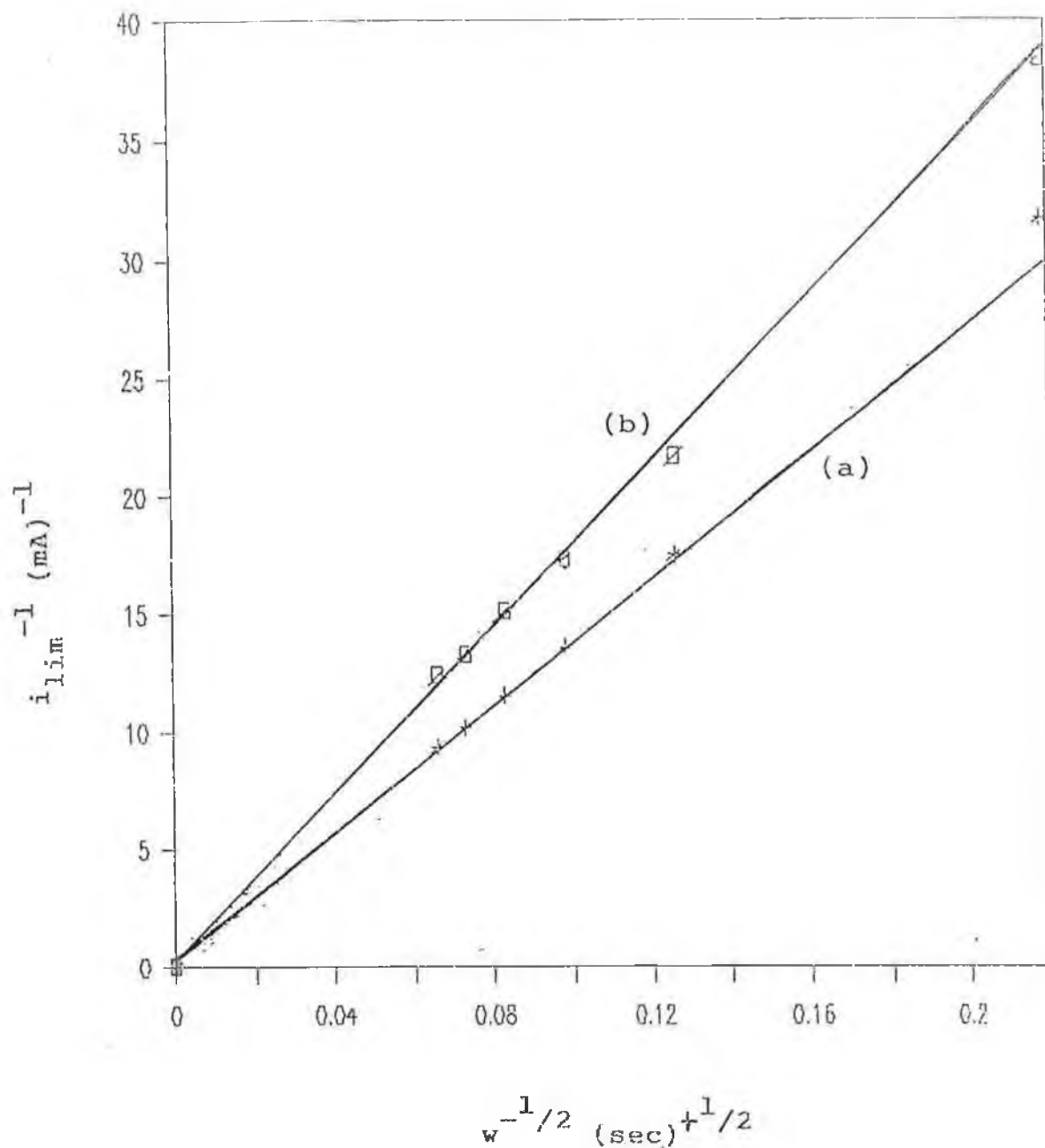Sweep rate : 5mV/sec.
Substrate : 2mM $(NH_4)_2Fe(SO_4)_2$.

FIGURE 6.13. Koutecky-Levich corresponding

to Figure 6.12.

(a) Corresponds to first oxidation wave (~560mV)

(b) Corresponds to second oxidation wave (~900mV)

rotation rates, has a limiting current similar to that observed at a bare electrode and was found to vary linearly with $\omega^{-1/2}$. The ratio of Fe(II) oxidized by means of the Ru(III) catalyst to that oxidized by penetration of the polyelectrolyte film was found to decrease with increasing rotation speed as would be expected, see Figure 6.14. This conclusion was also drawn by the authors mentioned above. This feature is explained by the fact that with an open structure (the polymer is soluble in choride media and thus swells) and a thin film facilitate fast penetration of the substrate to the electrode surface. Representative Koutecky-Levich plots and accompanying results indicate that the intercepts corresponding to the second wave are all zero. According to equation (6) this implies and uncontrolled rate of surface reaction, i.e. K_s approaches infinity.

One other important feature to note in this regard is that at very thin coatings i.e. 6 X 10^{-10} moles/cm^2 two waves were observed again. However, Koutecky-Levich plots indicate that the two intercepts are zero. Only the slopes vary as illustrated in Figure 6.15, so again K_s approaches infinity. As illustrated by the presence of two waves we do observe reaction at the bare electrode. A very thin film allows penetration of the substrate to the bare electrode.

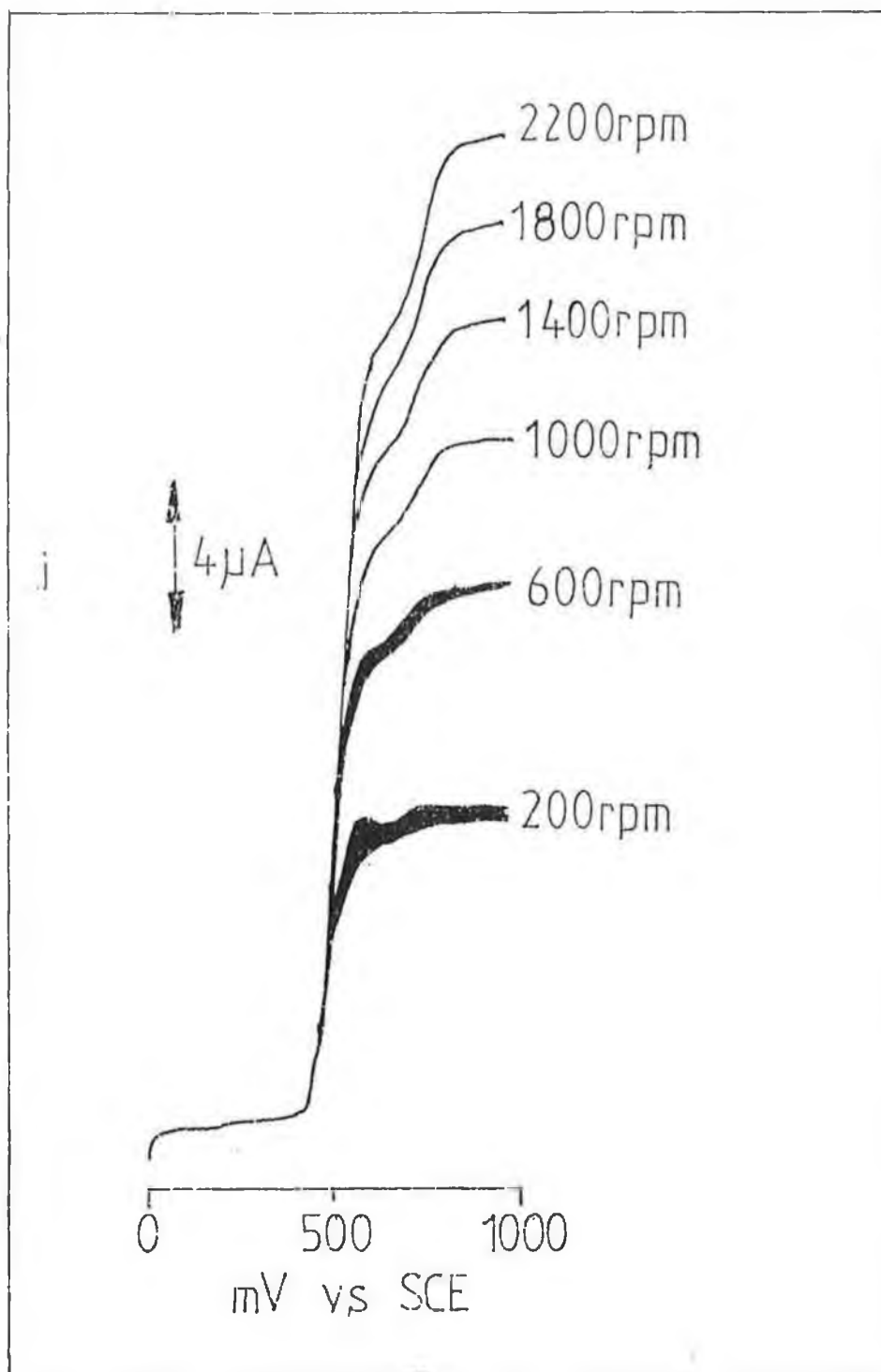FIGURE 6.14. Current-potential curve for a RDE coated with 6×10^{-10} moles/cm^2 of Sample C.

Electrolyte : 0.9M NaCl + 0.1M HCl.

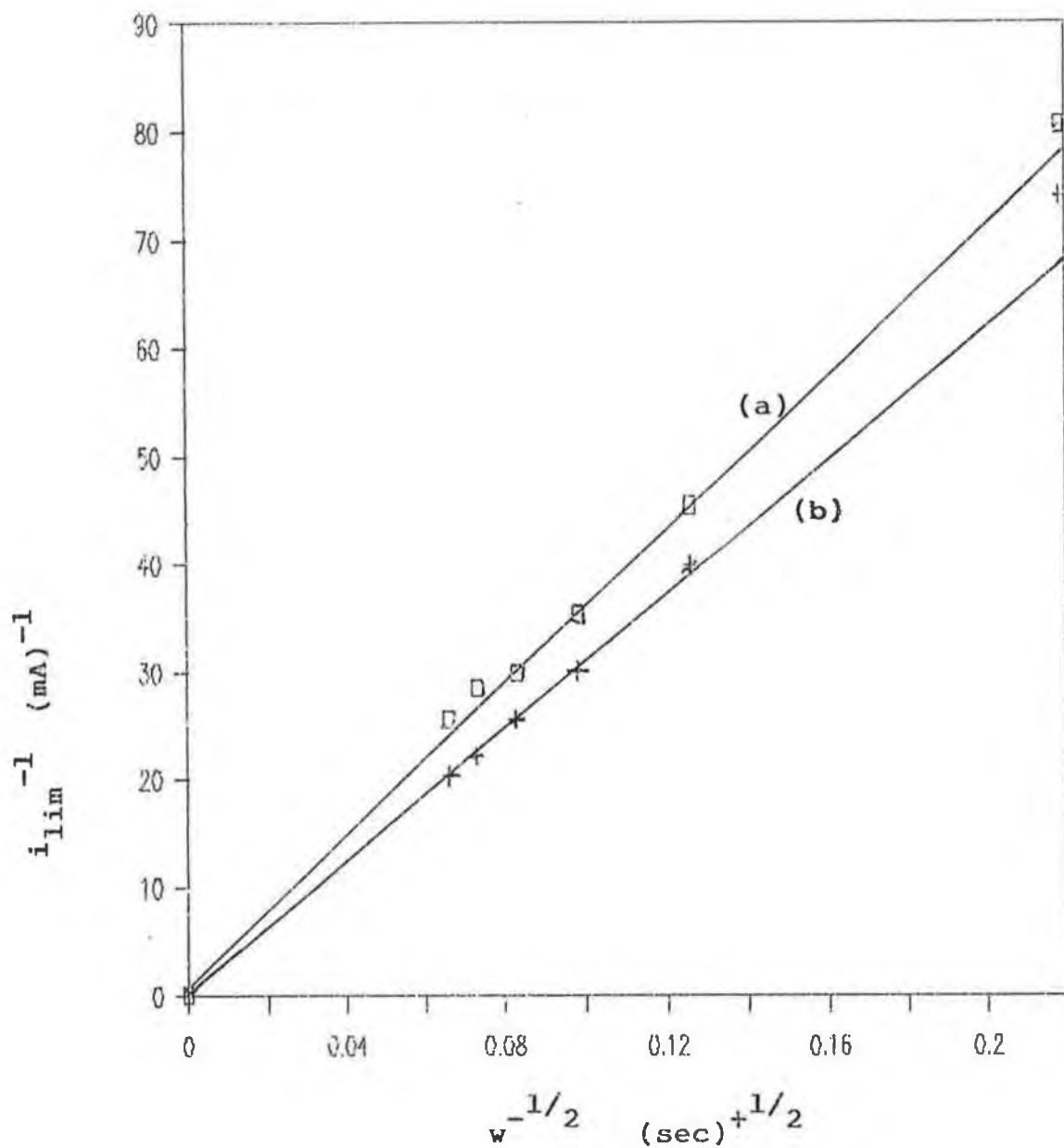Sweep rate : 5mV/sec.

Substrate : 1.0mM $(NH_4)Fe(SO_4)_2$.

223

FIGURE 6.15. Koutecky-Levich plot corresponding to Figure 6.14.

(a) Response corresponding to reduction wave occuring at 900 mV.

(b) Response corresponding to reduction wave occuring at 560 mV.

VI.2.2 Mediation of $K_4[Fe(CN_6)]$ Oxidation by $[Ru(bipy)_2(PNVI)Cl]Cl$ Sample C, Coated Glassy Carbon Electrodes

Using rotating disk electrodes coated with different polymer thicknesses, the electrochemical response of the modified electrode towards $[Fe(CN)_6]^{4-}$ was studied. A typical example of such a response is illustrated in Figure 6.16. The results obtained were analysed using Koutecky-Levich plots as described previously. The reaction in this case was in fact found to be faster than observed for $[Fe(H_2O)_6]^{2+}$. It should of course be noted that the substrate has an overall negative charge and thus is not repelled by the positively charged film. This implies that the problems encountered in the $[Fe(H_2O)_6]^{2+}$ case with respect to electrolyte penetration are avoided. To optimize the stability of the film, chloride and perchlorate based media were used.

Because the reaction is so fast one could speculate that the substrate oxidation is unmediated. However, in contradiction to this the response obtained using a coated electrode differs from that obtained using a bare electrode as illustrated in Figure 6.17.

Clearly, a much clearer plateau is seen using a film coated electrode. At very low concentrations of
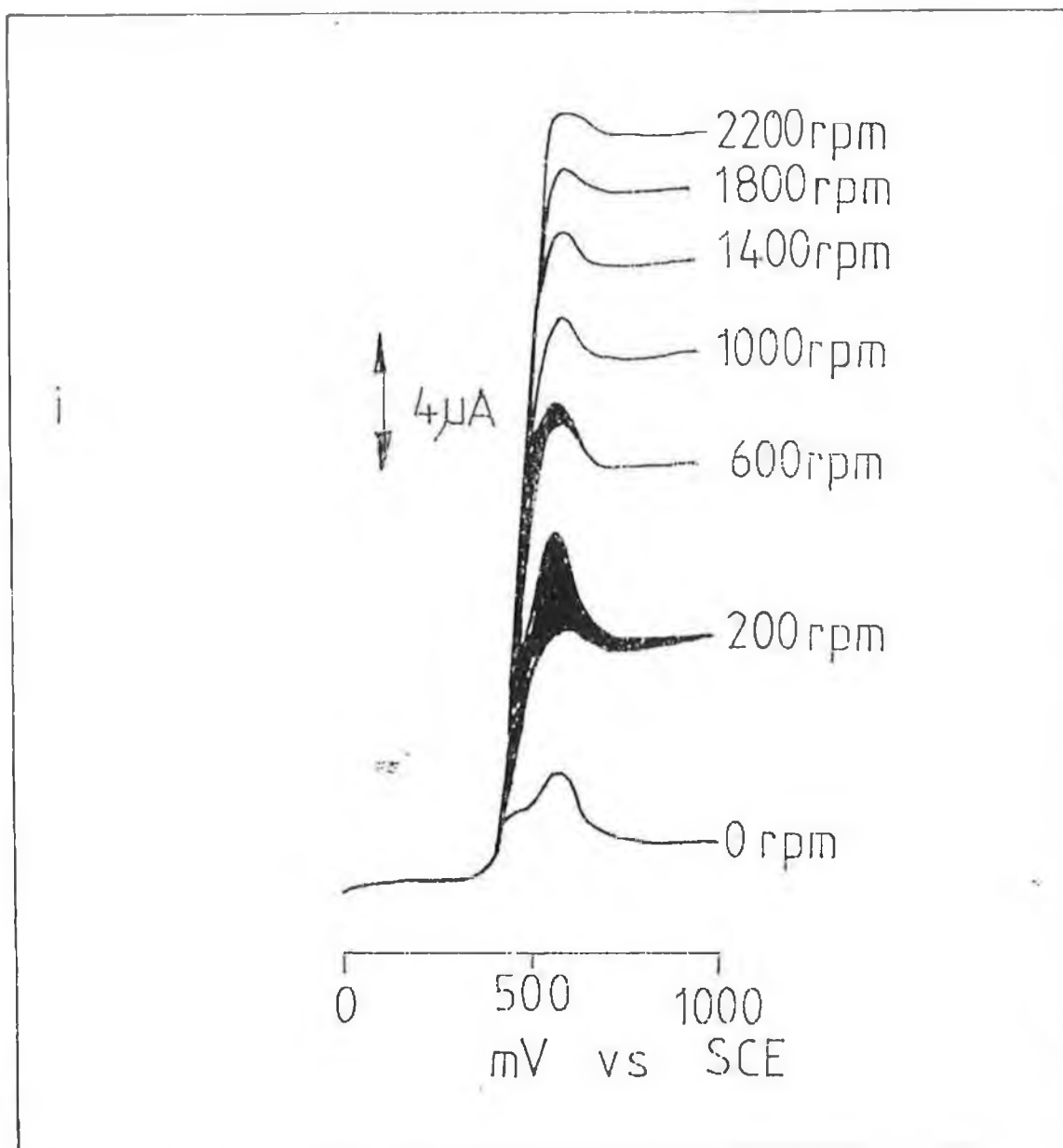
225

FIGURE 6.16. Current-potential response curve for a RDE coated with 9.4×10^{-9} moles/cm^2 of sample C.

Electrolyte : 0.2M NaClO$_4$.

Sweep rate : 5mV/sec.

Substrate : 1.0mM K$_4$[Fe(CN)$_6$].

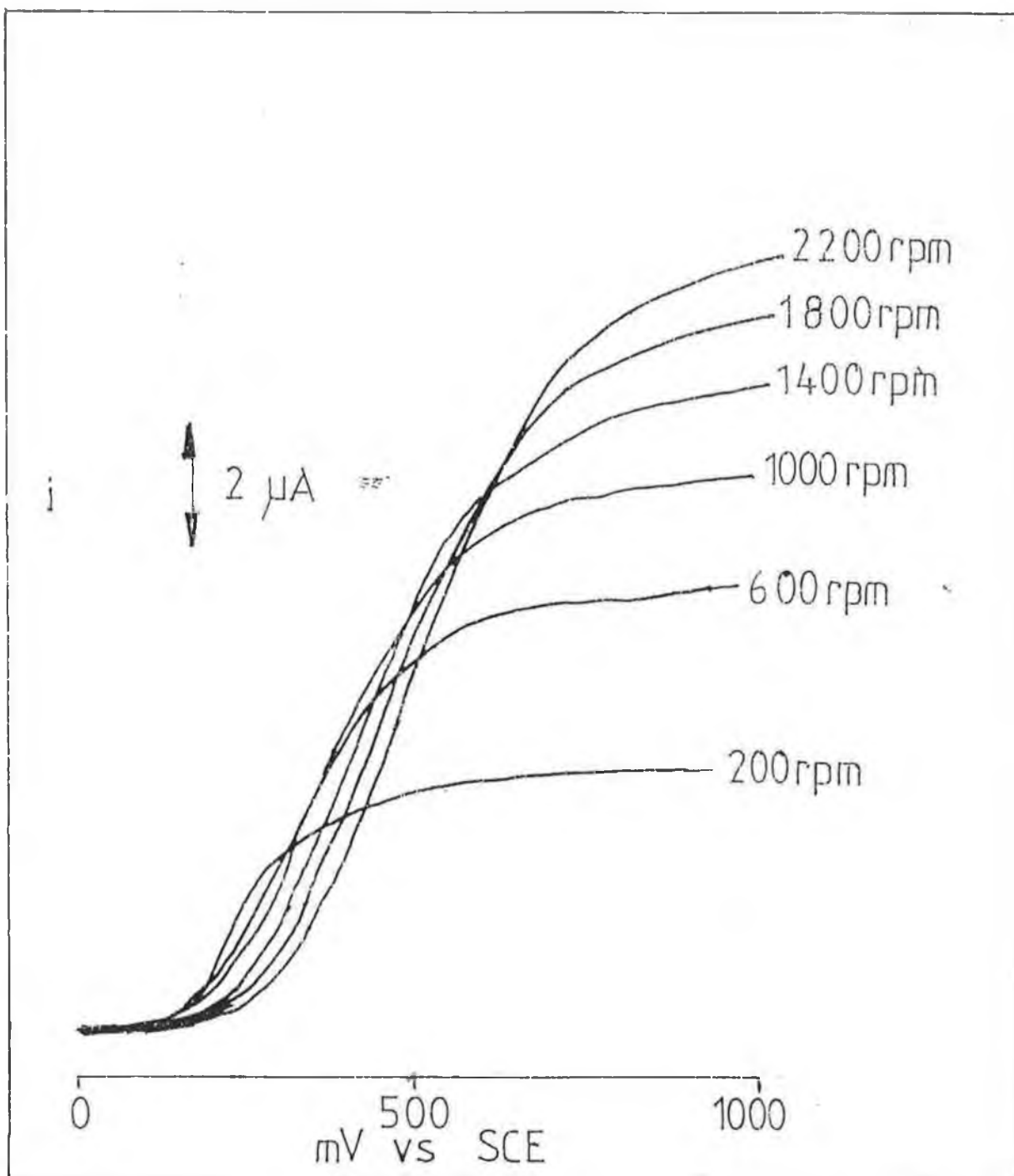FIGURE 6.17. Current-potential response curve for an uncoated RDE. Electrolyte : 0.2M $NaClO_4$. Substrate : 0.5mM $K_4Fe(CN)_6$

substrate $1 \times 10^{-5}M$ to $5 \times 10^{-4}M$ $K_4[Fe(CN)_6]$ the oxidation wave for the Ru(II)/Ru(III) couple is observed before any plateau as illustrated in Figure 6.18. This feature supports the idea that we are looking at a mediated reaction.

The oxidation potential of the substrate in the absence of the film was observed to be approximately 320 mV. This value did not vary significantly with pH. For the catalysis of $[Fe(CN)_6]^{4-}$ oxidation, the potential at which the current started to rise was found to depend on the film thickness and not on pH as was first thought. This observation was made using aqueous perchlorate electrolytes at pH of 2.0 or 5.6.

This result can be explained by the fact that even though the polymer is not soluble in this electrolyte and does not swell the negatively charged substrate penetrates the layer easily, independent of pH. At film thicknesses of 1.8×10^{-8} moles/cm^2 or greater the current was found to rise at 500mV corresponding to the Ru(II) oxidation. However, at film thicknesses of 3×10^{-9} moles/cm^2 or less, this rise in current was found to occur at approximately 300 mV implying some reaction of the substrate with the bare electrode. This feature of the system is illustrated in Figure 6.19. The thinner film, as well as acting as a mediator, also provides a smaller barrier to the

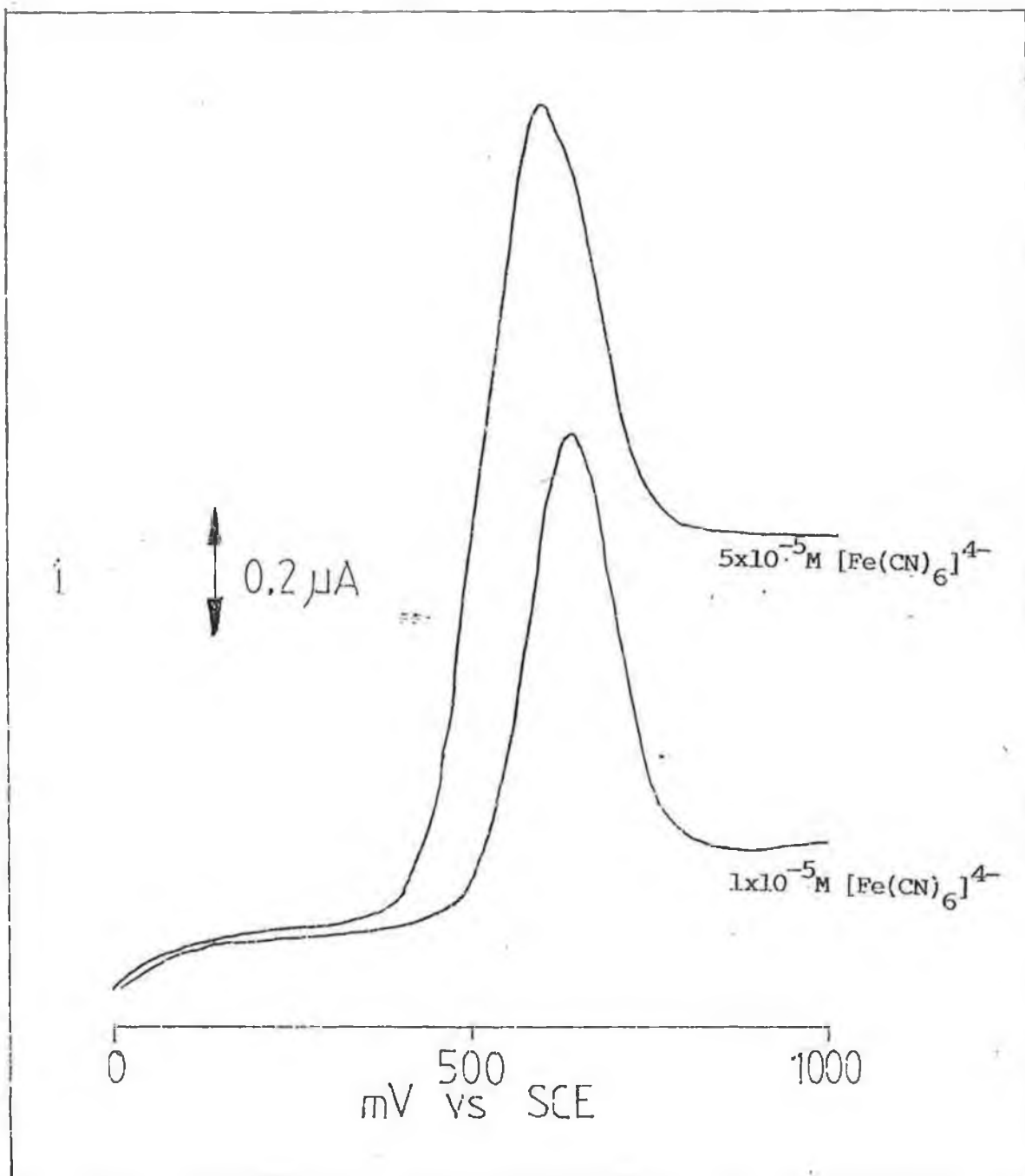FIGURE 6.18.   Current-potential   response   curves   for   a
RDE   coated   with 1.8×10^{-8}moles/cm^2 of
sample C.
Electrolyte : 0.2M NaClO$_4$(pH 2)
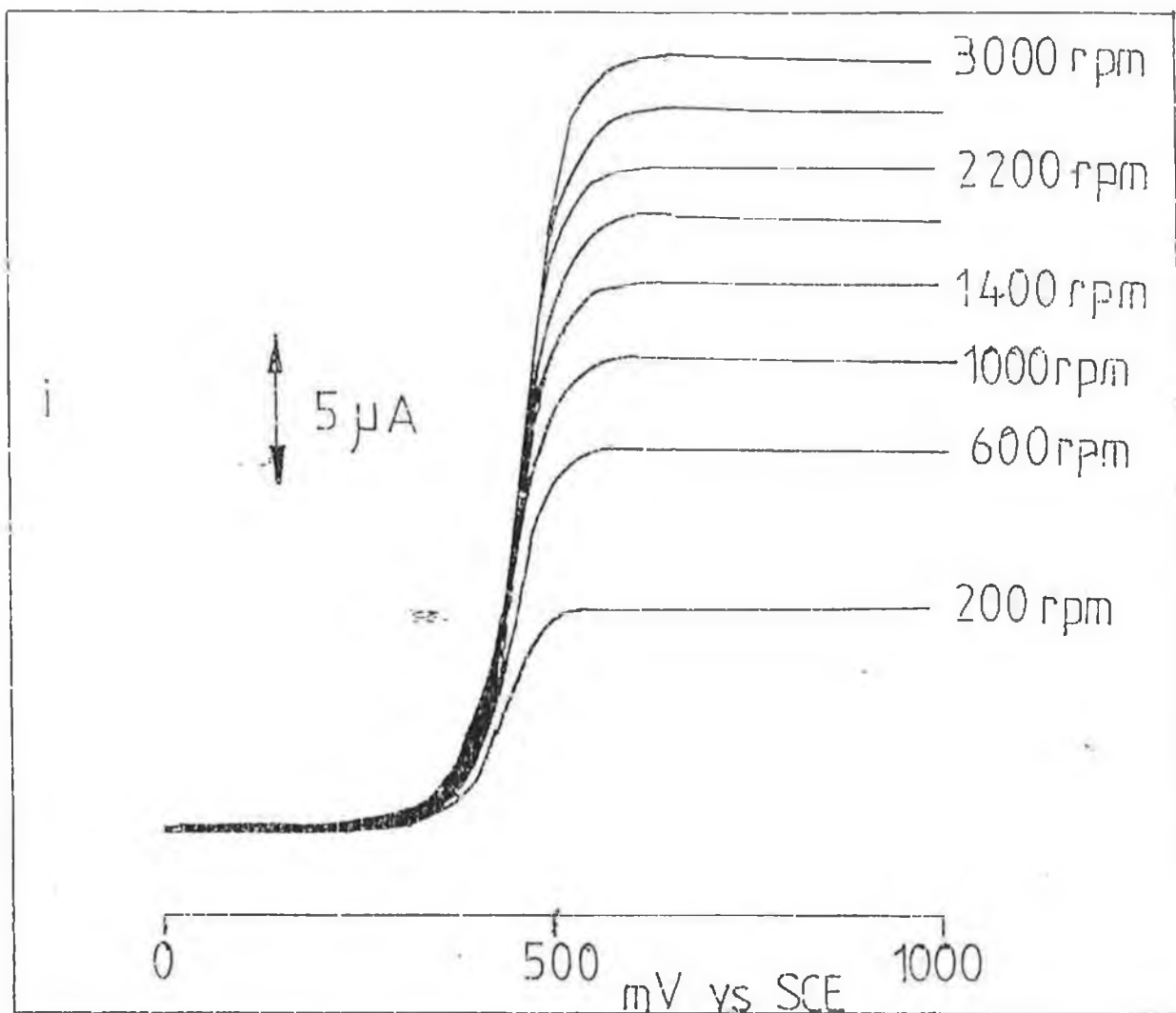Sweep   rate : 5mV/sec.
Rotation   speed : 600 rpm.

FIGURE 6.19. Current-potential response for a RDE coated with 3×10^{-9} moles/cm^2 of Sample C.

Electrolyte : 0.2M NaClO$_4$.
Sweep rate : 5mV/sec.
Substrate : 1.0mM K$_4$Fe(CN)$_6$.

penetrating substrate. An important distinction between results obtained here and those obtained for the sulphate-based substrate is contained in the fact that for $K_4[Fe(CN)_6]$ the intercept of the Koutecky-Levich plots is always found to approach zero implying that K_S always tends towards infinity. This is shown in Figure 6.20. As with the other system, the slopes of the Koutecky-Levich plots were found to vary inversely with substrate concentration as were the intercepts at higher substrate concentration even though they still approached infinity.

Due to the fact that the reaction in this case is so fast, studies carried out here were not as extensive as for the previous system. An important point to note is that when $(NH_4)_2Fe(SO_4)_2$ was studied in perchlorate based electrolyte, no response was obtained as was previously explained. If subsequently $K_4[Fe(CN)_6]$ was added to the solution, again no response was obtained, even though normally a response would be obtained for the latter substrate in these media. This would seem to imply that the layer was actually effected by the sulphate based substrate in the perchlorate medium. Penetration of $K_4[Fe(CN)_6]$ into the layer was actually hindered. This condition could however be rectified by continuous scanning of the coated electrode in a chloride medium. After about a half hour the second experiment was tried
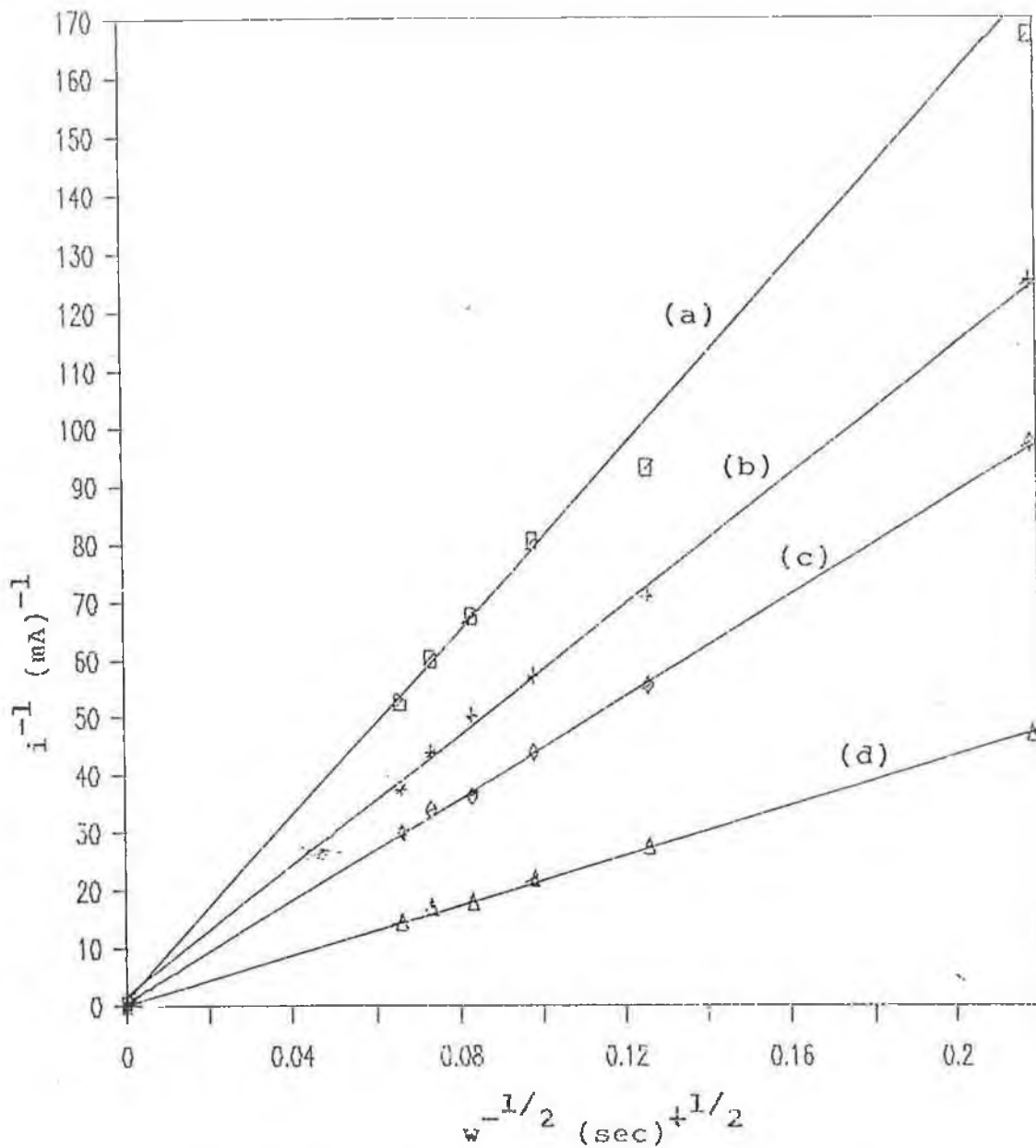
FIGURE 6.20. Koutecky-Levich plots for different substrate concentrations.
(a) 0.5mM $K_4Fe(CN)_6$; (b) 0.75 mM $K_4Fe(CN)_6$;
(c) 1.0mM $K_4Fe(CN)_6$; (d) 2.0 mM $K_4Fe(CN)_6$.
Film concentration : 1.1 x 10^{-8} moles/cm^2.

again with the result of obtaining a normal response. With respect to the possible analytical applications of this type of system the change in limiting current response was studied as a function of substrate concentration. Results are illustrated in Figure 6.21. The limiting current was found to vary linearly with substrate concentration in the range 5×10^{-6} M to 3×10^{-3} M $K_4[Fe(CN)]_6$. A similar response was obtained for the sulphate-based substrates. This implies that these systems can actually be used for the analytical determination of Fe(II) in aqueous solution.
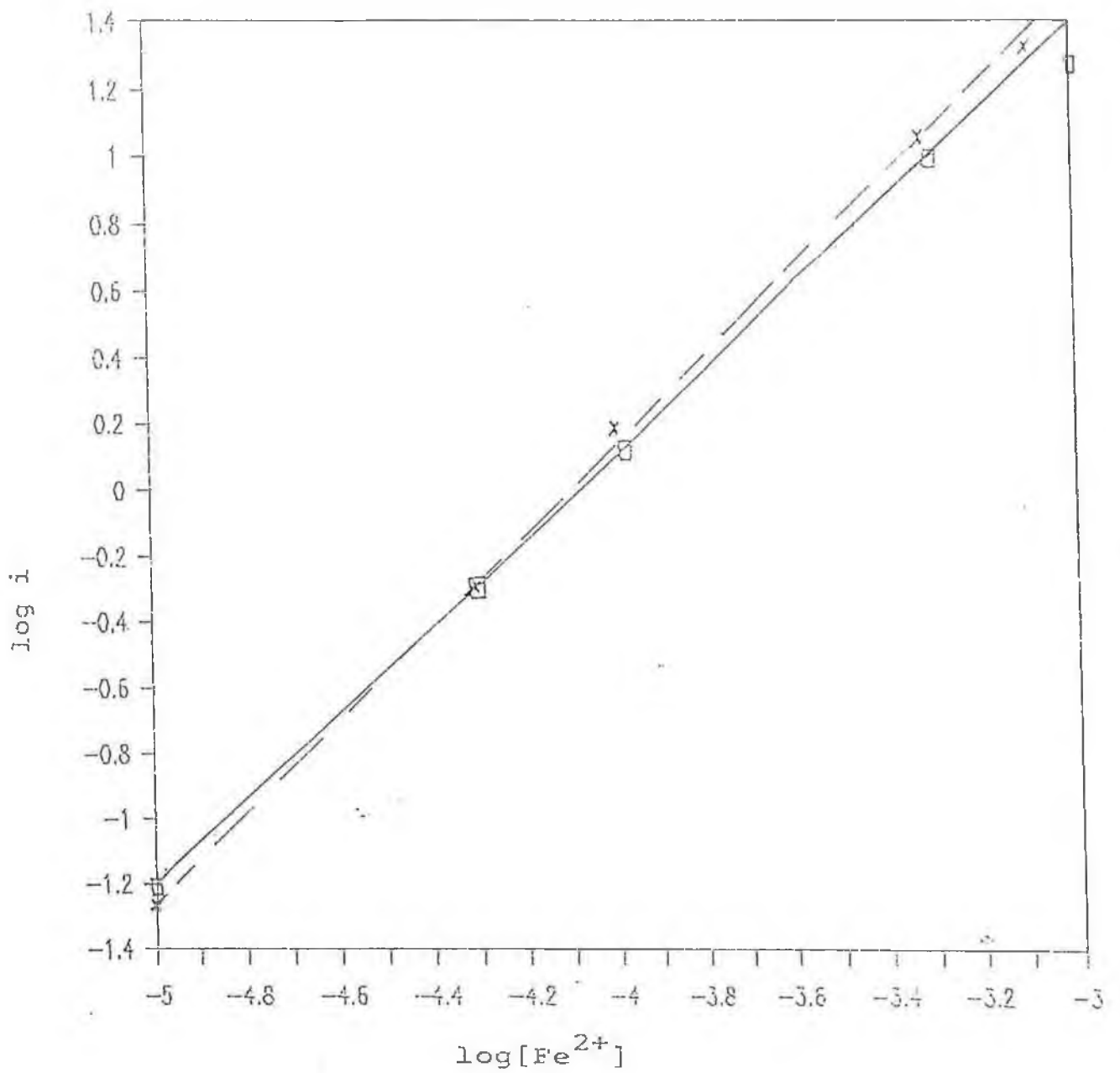
FIGURE 6.21.

Log-Log plot illustrating the linear range
for the analytical determination of :
(——),$K_4[Fe(CN)_6]$ and (— — —),$(NH_4)_2Fe(SO_4)_2$
in aqueous solution.
Film concentration : 1.8×10^{-8} moles/cm^2.
Electrolyte : 0.2M NaClO$_4$.

CONCLUDING REMARKS

Results obtained here show the application of $[Ru(bipy)_2(PNVI)_5Cl]Cl$ coated electrodes for the mediated catalysis of $[Fe(H_2O)_6]^{2+}$ oxidation. One important point to note is that surface coverages were calculated by integrating the area under a cyclic voltammogram obtained at a scan rate of 50mV/s. However, it was since considered that this sweep rate was too fast in order to see a more complete oxidation/reduction of the ruthenium (II) contained in the film. It should be noted that the $E_{1/2}$ value of the substrate, $(NH_4)_2Fe(SO_4)_2$, in the absence of mediator film, occurs at 440mV in aqueous chloride media. However, no oxidation of hydrated Fe(II) is observed before 500 mV, when a film coated electrode is used, corresponding to the start of Ru(II) oxidation. This indicates the catalytic capacity of the metallopolymer film. The unsuitability of perchlorate based media is also an important feature of this system and contrasts with results obtained for a different substrate $K_4[Fe(CN)]_6$. This is due to the fact that the film is, overall, positively charged. The sulphate-based substrate is also positively charged and is therefore probably repelled. Also the lack of swelling of the film due to its insolubility in this electrolyte yields a closed system. However, in chloride based media the polymer swells and

presents an open structure to the penetrating substrate. As illustrated in Figures 6.8 and 6.10, different chloride-based electrolytes give rise to different current-potential responses in the presence of iron-containing substrates. In this case, pH is likely to be the deciding factor. Figures 6.11 and 6.12 illustrate the effect of film thickness on the response obtained in the presence of $(NH_4)_2Fe(SO_4)_2$. The existence of a second wave at ~ 900 mV in Figure 6.12 is attributed to substrate reaction at the bare electrode, a feature which was previously observed by Oyama and Anson [33]. Results given in Table 6.2 indicate that the intercepts of the Levich plots were inversely proportional to the substrate concentration but there is no trend observed for values of K_s. The two sets of diffusion coefficients (D) were found to exhibit only marginal differences. As we are only studying the diffusion co-efficient of the substrate in solution, this would be the expected result.

Marked differences were noted between the two iron-containing substrates with respect to their current-potential response in the presence of a film-coated electrode. The important feature is the lack of response for the substrate $[Fe_2(H_2O)_6]^{2+}$ in perchlorate based electrolyte; whereas $[Fe(CN)_6]^{4-}$ exhibits a very stable response. This is attributed, as stated previously, to the differences in substrate

charge. The latter of the two substrates was found to have a much faster response. However, the linear range for the two substrates was found to be similar and both systems were found to exhibit irreversible electrode cross-exchange reactions.

REFERENCES

1. N. Oyama and F. C. Anson,

    J. Electrochem. Soc., 127, 1980, 247.

2. N. Oyama and F. C. Anson,

    J. Electrochem. Soc., 127, 1980, 640.

3. G. J. Samuels and T. J. Meyer,

    J. Am. Chem. Soc., 103, 1981, 307.

4. O. Haas, M. Kriens and J G Vos,

    J. Am. Chem. Soc., 1O3, 1981, 139.

5. M. Sharp, D. D. Montgomery and F. C. Anson,

    J.   Electroanal.   Chem.   Interfacial   Electro-
    chemistry, 194, 1985, 247.

6. K. Niwa and K. Doblhofer,

    Electrochim. Acta, 31, 1986, 549.

7. K. Doblhofer, H. Braun and R. Lange,

    J.   Electroanal.   Chem.   Interfacial   Electro-
    chemistry, 209, 1986, 93.

8. C. P. Andrieux, J. M. Dumas Bouchiat and J. M. Saveant,

    J. Electroanal. Chem., Interfacial Electrochemistry, 131, 1982, 1.

9a. W. J. Albery, M. G. Boutelle and A. R. Hillman,

    J. Electroanal. Chem., Interfacial Electrochemistry, 182, 1985, 99.

9b. W. J. Albery and A. R. Hillman,

    J. Electroanal. Chem. Interfacial Electrochemistry, 170, 1984, 27.

10. R. J. Mortimer and F. C. Anson,

    J. Electroanal. Chem. Interfacial Electrochemistry, 138, 1982, 325.

11. H. D. Abruna, P. Denisevich, M. Umana, T. J. Meyer and R. W. Murray,

    J. Am. Chem. Soc., 103 (1981), 1.

12. A. Bruce and M. S. Wrighton,

    J. Am. Chem. Soc., 104, 1982, 74.

13. L. D. Margerum, T. J. Meyer and R. W. Murray,

    J. Phys. Chem., 90, 1986, 2696.

14. J. M. Saveant.

    J. Electroanal. Chem. Interfacial Electro-
    chemistry, 201, 1986, 211.

15. P. Daum, J. R. Lenhard, D. Rolison and R. W.
    Murray,

    J. Am. Chem. Soc., 102, 1980, 4649.

16. M. R. Van de Mark and L. L. Miller,
    J. Am. Chem. Soc., 100, 1978, 3223.

17. J. B. Kerr and L. L. Miller,
    J. Electroanal. Chem. Interfacial Electro-
    chemistry, 101, 1979, 263.

18. J. B. Kerr, L. L. Miller and M. R. Van de Mark,
    J. Am. Chem. Soc., 102, 1980, 3380.

19. C. Degrand and L. L. Miller,
    J. Am. Chem. Soc., 102, 1980, 5728.

20. C. P. Andrieux, J. M. Dumas Bouchiat and J. M.
    Saveant,
    J. Electroanal. Chem. Interfacial Electro-
    chemistry, 142, 1982, 1.

21. F. C. Anson, J. M. Saveant and K. Shigehara,
    J. Am. Chem. Soc., 105, 1983, 1096.

22. C. P. Andrieux and J. M. Saveant,
    J. Electroanal. Chem. Interfacial Electro-
    chemistry, 134, 1982, 162.

23. C. P. Andrieux and J. M. Saveant.
    J. Electroanal. Chem. Interfacial Electro-
    chemistry, 93, 1978, 163.

24. C. P. Andrieux, J. M. Dumas Bouchiat and J. M.
    Saveant,
    J. Electroanal. Chem. Interfacial Electro-
    chemistry, 87, 1978, 39.

25. C. P. Andrieux, J. M. Dumas Bouchiat and J. M.
    Saveant,
    J. Electroanal. Chem. Interfacial Electro-
    chemistry, 87, 1978, 55.

26. C. P. Andrieux, J. M. Dumas Bouchiat and J. M.
    Saveant,
    J. Electroanal. Chem. Interfacial Electro-
    chemical, 114, 1980, 159.

27. K. Shigehara, N. Oyama and F. C. Anson.
    J. Am. Chem. Soc., 103, 1981, 2552.

28. F. C. Anson, J. M. Saveant and K. Shigehara,
    J. Phys, Chem., 87, 1983, 214.

29. C. P. Andrieux, J. M. Dumas Bouchiat and J. M. Saveant,

    J. Electroanal. Chem. Interfacial Electro-chemistry, 169, 1984, 9.

30. J. Leddy, A. J. Bard, J. T. Maloy and J. M. Saveant,

    J. Electroanal. Chem. Interfacial Electro-chemistry, 187, 1985, 205.

31. C. P. Andrieux, in

    "Electrochemistry, Sensors and Analysis", M. R. Smyth and J. G. Vos, Editors, p. 269, Elsevier Pub. Co. Amsterdam, 1986.

32. W. R. Heineman, H. J. Wieck and A. M. Yacynych

    Anal. Chem., 52, 1980, 345.

33. N. Oyama and F. C. Anson,

    Anal. Chem., 52, 1980, 1192.

34. P. J. Peerce and A. J. Bard,

    J. Electroanal. Chem. Interfacial Electro-chemistry, 112, 1980, 97.

35. R. D. Rocklin and R. W. Murray,

    J. Phys. Chem., 85, 1981, 2104.

36. J. F. Evans, T. Kuwana, M. T. Henne and G. P. Royer,

    J. Electroanal Chem., Interfacial Electro-chemistry, 80, 1977, 409.

37. A. Bettelheim, R. J. H. Chan, T. Kuwana,

    J. Electroanal, Chem., Interfacial Electro-chemistry, 99, 1979, 391.

38. N. S. Lewis, A. B. Bocarsly and M. S. Wrighton,

    J. Phys. Chem., 84, 1980, 2033.

39. F. C. Anson,

    J. Phys. Chem., 84, 1980, 3336.

40 J. P. Collman, M. Marrocco, P. Denisevich, C. Koval and F. C. Anson,

    J. Electroanal, Chem. Interfacial Electro-chemistry, 101, 1979, 117.

41. P. Denisevich, H. D. Abruna, M. Umana, T. J. Meyer and R. W. Murray,

    J. Am. Chem. Soc., 103, 1981, 1.

42. W. J. Albery, W. R. Bowen, A. W. Foulds, K. J. Hall, A. R. Hillman, R. J. Egdell and A. F. Orchard,
J. Electroanal. Chem. Interfacial Electro-chemical, 107, 1980, 37.

43. K. Shigehara, N. Oyama and F. C. Anson,
Inorg. Chem., 20, 1981, 518.

44. T. Ikeda, R. Schmehl, P. Denisevich, K. Willman and R. W. Murray,
J. Am. Chem. Soc., 104, 1982, 10.

45. F. C. Anson, T. Ohsaka and J. M. Saveant,
J. Am. Chem. Soc., 105, 1985, 4883.

46. P. K. Ghosh and A. J. Bard,
J. Electroanal, Chem. Interfacial Electro-chemistry, 169, 1984, 113.

47. E. Tracy Turner Jones,
J. Electrochem. Soc., 132, 1985, 245C.

48. S. E. Morris,
J, Electrochem. Soc., 132, 1985, 478C.

49. B. Lindholm and M. Sharp,

   J. Electroanal. Chem. Interfacial Electro-
   chemistry, 198, 1986, 37.

50. C. P. Andrieux and J. M. Saveant,

   J. Electroanal. Chem. Interfacial Electro-
   chemistry, 111, 1980, 377.

51. E. Laviron,

   J. Electroanal. Chem. Interfacial Electro-
   chemistry, 112, 1980, 1.

CHAPTER VII

Concluding Remarks

CONCLUDING REMARKS

The first part of this work involved an investigation of the preparation and characterisation of ruthenium-containing poly-N-vinylimidazole based metallopolymers as discussed in chapter III. Results of the characterisation studies illustrated how the product or ratios of products obtained could be dictated by the reaction conditions, i.e. reflux time, polymer to metal ratio etc. As mentioned previously, the isolation and subsequent solubility for the synthesised complexes proved to be a problem for the disubstituted complex $[Ru(bipy)_2(PNVI)_2]^{2+}$ and the monosubstituted complex $[Ru(bipy)_2(PNVI)Cl]^+$ respectively. Following the preparation and characterisation of these materials, the properties, (electrochemical, photochemical and catalytic) of these systems were studied.

Investigation of the electrochemical properties of the prepared complexes, by comparison to monomeric or polyvinylpyridyl based analogues, constituted a very important aspect of this research. Prior to these studies, spectroscopic characterisation studies were carried out. As illustrated in chapter III, it was found possible to distinguish between the synthesised complexes on the basis of absorption and emission maxima. The monosubstituted complex,

247

$[Ru(bipy)_2(PNVI)Cl]^+$, was found to exhibit an absorption maximum at approximately 502nm and an emission maximum at 680nm (at 77K). At room temperature the emission maximum for this complex was found to occur at 640nm but this was attributed to the presence of small amounts of the disubstituted complex. The disubstituted complex, $[Ru(bipy)_2(PNVI)_2]^{2+}$, was found to have an absorption maximum at 485nm and emission maxima at 640nm and 628nm at room temperature and at 77k respectively. These deductions were drawn by comparison to monomeric analogues. Similar studies on poly-4-vinylpyridine based analogues have been carried out, largely by Kelly and co-workers [1-5]. In a series of experiments by Kelly and co-workers in which the PVP:Ru stoichiometry was varied from 80:1 to 2:1, the only product obtained was the monosubstituted complex, $[Ru(bipy)_2(PVP)Cl]^+$ [1]. At higher polyvinylpyridine concentrations and a reaction stoichiometry of 20:1, a product identified as $[Ru(bipy)_2(PVP)_2]^{2+}$, by spectroscopic studies, was obtained. The wavelengths of maximum absorption for the monosubstituted and disubstituted complexes were found to be 494nm and 459nm respectively. The trend of these values is comparable to those obtained for the poly-N-vinylimidazole based analogues. Results obtained from synthesis using poly-N-vinylpyridine where $[Ru(bipy)_2(PVP)Cl]^+$ was the only product obtained up

to PVP:Ru ratios 100:1 [3].

Study of the electrochemical properties of the synthesised complexes was considered to be of particular importance to this research. This is due to the fact that potential applications would depend largely on the electrochemical properties. Results obtained here could be compared to analogous polypyridyl complexes. Considering firstly the sweep rate dependence, values of ΔE_p were found to decrease with decreasing sweep rate. This effect had previously been observed for polyester [6] and polypyridyl based complexes [2,7]. Miller and Van de Mark have studied the sweep rate dependence on ΔE_p for polyester, with incorporated ferrocene, coated platinum electrodes [6]. The fact that ΔE_p increased with increasing sweep rate led to the conclusion that the film did impede normal electron transfer. Similar results were found by Haas and Vos using electrodes coated with poly(4-vinylpyridine) bound ruthenium complexes [2]. The overall conclusion to be drawn here is that when ΔE_p decreases with decreasing sweep rate then the electrochemical behaviour is kinetically controlled. Electrochemical properties were found to be largely dependent on the nature of the electrolyte used. Effects on the redox potentials obtained were observed as a result of the electrolyte used for the prepared poly-N-vinylimidazole based complexes. Using

electrolytes in which the polymer was soluble, for example, 1M H_2SO_4, lower values of ΔE_p and narrower bands were obtained. Haas and Vos [2] and Calvert and Meyer [8] have also examined the electrolyte dependence of the electrochemical response of electrodes coated with films of poly(4-vinylpyridine) bound ruthenium bipyridyl complexes. It was found, using electrodes coated with $[Ru(bipy)_2(PVP)Cl]^+$, that the electrolyte used governed the electrochemical response for this system [2]. This feature was observed in this research project where the redox potential of the $Ru^{II/III}$ couple in $[Ru(bipy)_2(PNVI)Cl]^+$ and $[Ru(bipy)_2(PNVI)_2]^{2+}$ varied with choice of electrolyte. This has been illustrated in Table 4.1. Electrochemical response in the presence of the substrate $K_4[Fe(CN)]_6$ was also investigated in this research. This is comparable to work carried out by Doblhoffer and co-workers [9] who studied the diffusion of the substrate $[Fe(CN)_6]^{4-}$ across a poly(4-vinylpyridinium) film. By comparison to the work of the above mentioned authors, it would appear that the negatively charged iron complex, $[Fe(CN)_6]^{4-}$ was drawn into the polymer layer in order to balance out the positive charge resulting from the oxidation of Ru(II). Chronoamperometric experiments were carried out in order to determine the electron diffusion rate in the film. Results obtained here were found to depend on the film thickness as shown in Table 4.3.

The linearity of the Cottrell plot was found to depend on the electrolyte used. Values of D_e for this system were found to be of the order of magnitude of $10^{-10}cm^2s^{-1}$, a value which is comparable to those obtained previously for poly(4-vinylpyridinium) analogues. Doblhoffer and co-workers have found that diffusion co-efficients (D_e) were found to be $10^{-9}cm^2s^{-1}$ [9]. Lindholm and Sharp have also determined electron diffusion co-efficients for cross-linked PVP films, containing $[IrCl_6]^{3-}$, on glassy carbon electrodes [15]. These values were determined using chronocoulometric experiments and were of the order of magnitude of $10^{-9} - 10^{-10}cm^2s^{-1}$.

Following on from here one can discuss the catalytic properties of poly-N-vinylimidazole based metallopolymers. As discussed in chapter VI, the main theoretical models used for treatment of such systems are those developed by Saveant and co-workers [10] and also by Albery's group [11], [12]. For the purpose of this research, results obtained were discussed using the Saveant/Andrieux model. As mentioned in chapter VI, there are several factors which govern kinetic control of such mediated electron transfer systems, see Figure 6.3 and Table 6.1. For reasons already mentioned in chapter VI, an SR controlled mechanism was proposed for this system. Pyrolytic graphite or glassy carbon electrodes coated with films of

[Ru(bipy)$_2$(PNVI)Cl]$^+$ were used for these catalytic studies. The metallopolymer film was found to act as a mediator for the oxidation of Fe(II) in aqueous solution. Several comparable studies were carried out using poly-4-vinylpyridine based complexes [13-18]. Oyama and Anson [14] have studied the catalysis of electrode processes by coatings of PVP with incorporated [IrCl$_6$]$^{2-}$. These coated electrodes were found to catalyse the oxidation of Fe^{2+} to Fe^{3+}. They also found that the electrode reactions of ferro and ferricyanide were impeded at electrodes coated with unprotonated films of PVP but the reduction of [Fe(CN)$_6$]$^{3-}$ was catalyzed by the Ru^{II}(edta) which could be co-ordinatively attached to the films. Rotating disk measurements showed that the catalyzed current was limited by the rate of reaction between [Fe(CN)$_6$]$^{3-}$ and Ru^{II}(edta), not by the electronic conductivity of the polymer film. As with this research project, Oyama and Anson employed Koutecky-Levich analysis for studies of reaction mechanisms. This treatment does allow a means to distinguish currents limited by the rate of a redox reaction between a dissolved substrate and a catalyst anchored to an electrode coating from those limited by electron transfer through the coating.

Lindholm and Sharp have studied substrate permeation through cross-linked PVP films [15]. As found in this

project, the authors have observed that the facility with which substrate species diffuse into and within the film to encounter the relatively immobile catalyst sites largely determines whether the reaction zone occupies a large part of the polymer phase. The above authors have studied the rate of oxidation of Fe^{2+} by $[IrCL_6]^{2-}$ bound to cross-linked PVP coatings [15]. They have also employed Koutecky-Levich analysis and also the theoretical treatments of Andrieux and Saveant and also assigned an "SR" mechanism to the process.

It has been shown previously that the oxidation of $[Fe(H_2O)_6]^{2+}$ and $[Fe(CN)_6]^{4-}$ are mediated $[Ru(bipy)_2(PVP)Cl]^+$ or $[Ru(bipy)_2(PNVI)Cl]^+$ coated electrodes [16a], [17], [18a], [18b]. From results obtained in these cases it was clear that the charge of the substrate ($[Fe(H_2O)_6]^{2+}$, or $[Fe(CN)_6]^{4-}$) is of major importance in the electrochemical behaviour of the modified electrode. For the study of the mediated oxidation of $[Fe(H_2O)_6]^{2+}$, the use of Koutecky-Levich plots proved valuable and the results obtained could be interpretated using existing models. For $[Fe(CN)_6]^{4-}$, however, the mediation process is very fast and is limited by the diffusion of the substrate from the bulk solution, in which case Koutecky-Levich plots were less useful since the intercepts were zero for all concentrations of substrate.

For both substrates under investigation in this research, i.e., $[Fe(CN)_6]^{4-}$ and $[Fe(H_2O_6]^{2+}$, no reduction signal was observed under the conditions used. This implies that the catalysed oxidation of Fe(II) was irreversible. This is comparable to results obtained previously for poly-4-vinylpyridine based analogues [17] and is contrary to results obtained previously by Niwa et al. [19] for quarternised PVP, where $[Fe(CN_6)]^{3-}$ or $[Fe(H_2O)_6]^{2+}$ cannot reach the electrode surface in this case. The dependence of the response obtained here on the choice of supporting electrolyte was also an important factor. Indeed the use of high pH ($\geq$ 5) perchlorate based electrodes was found to inhibit any response for the $[Fe(H_2O)_6]^{2+}$ substrate due to the insolubility of the polymer layer (i.e. layer does not swell to facilitate penetration of the positively charged layer). As stated previously the linear range for the determination of Fe(II) in aqueous solution extended from 5×10^{-6} to 3×10^{-3} M Fe(II). This served to illustrate that these modified electrodes have potential applications as potentiometric sensors but much more work is required for their further development.

Marked differences were noted between the two iron-containing substrates with respect to their current-potential response in the presence of a film-coated electrode. One important feature is the lack of

response for the substrate $[Fe_2(H_2O)_6]^{2+}$ in perchlorate based electrolyte, whereas $[Fe(CN)_6]^{4-}$ exhibits a very stable response. This is attributed, as stated previously, to the differences in substrate charge. The latter of the two substrates was found to have a much faster response. However, the linear-range for the two substrates was found to be similar and both systems were found to exhibit irreversible electrode cross-exchange reaction.

Calculations of the kinetic parameters involved in these catalytic systems have been illustrated in Tables 6.2 - 6.4. It was evident here that values of D and K_S do not vary considerably with substrate concentration or film thickness. One could predict that the catalytic efficiency at the polymer-coated electrode would increase as the film thickness is made larger and larger. However, as previously stated by Andrieux and co-workers [20], increasing the film thickness will, at the same time, result in more difficulty for the substrate to cross the film from the solution side toward the electrode and for the electrons to propagate in the opposite direction thus limiting or cancelling out the beneficial effect of increasing the number of layers. The hopping of electrons possibly associated with counter-ion movements can be regarded formally as a diffusion process [21, 22]. It has been found that diffusion co-

efficients of substrates in the film seems to depend on the size of the substrate molecules and the structure of the polymer [23]. It has also been found by Kerr and co-workers [23] that when the film thickness is increased, the catalytic efficiency reaches a maximum and then decreases. This feature was observed when Kerr et al studied the catalysis of 1,2-dibromo-1,2,diphenylethane reduction at poly-p-nitrostyrene coated electrodes.

Although the $K_4[Fe(CN)_6]$ system was found to exhibit much faster responses than the $[Fe(H_2O)_6]^{2+}$ system, the differences observed between the two systems were minimal with the exception of the choices of electrolyte. In the case of $[Fe(H_2O)_6]^{2+}$, there were several limitations imposed by; 1) the charge of the metallopolymer and 2) the charge of the substrate. Ikeda, Schmehl and co-workers have studied the rate of solute permeation in relation to the reaction site, the number of waves and the potential at which the waves occur [24]. If the rate solute permeation is very fast, the reaction site is the electrode surface, only one wave is produced and the potential is the same as the naked electrode. If the rate of solute permeation is very slow, the reaction site is the film/solution interface. Only one wave is produced and occurs at the polymer potential as is the case of the $[Fe(H_2O)_6]^{2+}$ system. If the rate of solute permeation is

measurable, two reaction sites can exist:- 1) electrode surface and 2) film/solution interface. Two waves are produced occurring at 1) the potential equivalent to that of the bare electrode and 2) the polymer potential. Results obtained here are also tied in with those obtained from the chronoamperometric studies already discussed where electron diffusion within the film was also found to depend on electrolyte and film thickness. Also, from comparing valued of T_{Ru} (see Table 4.3) it can be seen that only a portion of the film is actually involved in the catalytic reaction which may limit its efficiency. Overall it can be said that the observation made in these studies is significant in that the ruthenium polymers have redox properties making them potential oxidation catalysts for electro-organic reactions.

The photochemical properties of ruthenium bipyridyl based metallopolymers have provided much of the impetus for their investigation. This is largely as a result of their potential applications in, for example, the photodissociation of water by visible light [1, 3, 25, 26]. For the purpose of this research, the effect of light on the electrochemical response of the film-coated electrodes and the use of these materials in the generation of a photoresponse. Considering firstly the former of these two studies, the synthesised poly-N-vinylimidazole based materials were found to exhibit

interesting   photochemical/photoelectrochemical
properties,   particularly   for   the   monosubstituted
complex.

As   illustrated   in   Figures   5.2   to   5.6,   the
photoelectrochemical properties of the monosubstituted
complex were found to depend totally on the electrolyte
used. Photolysis of this complex in 1M H_2SO_4 was found
to   exhibit   a   particularly   interesting   effect.   A
photostable sulphate complex was determined to have
formed, by comparison with results obtained by Haas,
Zumbrunnen and Vos [27]. This result seemed to indicate
the possibility of using this system for information
storage   or   switching   devices.   Photolysis   of   this
complex in 1M $HClO_4$ was found to give rise to a
photosubstitution reaction where total conversion to
the aqua species $[Ru(bipy)_2(PNVI)H_2O]^{2+}$ could be
achieved. This reaction in itself allowed preparation
of the above complex which could not be prepared by
any other means.

Perhaps   the   most   interesting   area   of   these
photochemical studies was in the investigation of the
photosensitizing properties of poly-N-vinylimidazole
based complexes. These type of studies had previously
been carried out by Murray [28] and Cosnier [29] where
similar results to those obtained here, were found.
Murray and co-workers [28], using systems composed of

polypyridyl based ruthenium complexes and Cosnier [29], using electrodes coated with polypyridyl complexes of ruthenium(II)-containing pyrrole groups in the presence of suitable substrates (oxalates and tetrafluoroborates respectively) found it possible to generate photocurrents of the order of $10 - 100 \, \mu A/cm^2$. These are comparable with results obtained in this research. The magnitudes of the photocurrents were found to depend on film thickness and quencher concentration, see Table 5.1. Although much of this work is still rather qualitative, it has exhibited some interesting possibilities with respect to potential applications of the poly-N-vinylimidazole based complexes. However, as found with the catalytic studies, experiments were found to be very much limited by the choice of supporting electrolyte. With this in mind, it would be of importance to study these properties with a more stable metallopolymer complex. It is possible that substituting osmium for ruthenium might be an answer to some of these limitations.

Although much of this research is still in very early stages of development, it has been shown that a variety of poly-N-vinylimidazole based metallopolymers can be prepared and satisfactorily characterised. They have been found to exhibit interesting electrochemical properties, many of which were found to be similar to polyvinylpyridine analogues. Also in the

electrochemical area, some interesting potential applications have been noted and are indicative of the rapid development of electrochemistry as an in-depth area of chemistry.

REFERENCES

1. J. M. Clear, J. M. Kelly, D. C. Pepper and J. G. Vos,

   Inorg. Chim. Acta., 33, 1979, L.139.

2. O. Haas and J. G. Vos,

   J. Electroanal. Chem., Interfacial Electro-
   chemistry 113, 1980, 139.

3. J. M. Clear, J. M. Kelly, C. M. O'Connell and J. G. Vos,

   J. Chem. Research, (M), 1981, 3039.

4. O. Haas, M. Kriens and J. G. Vos,

   J. Am. Chem. Soc., 103, 1981, 1318.

5. J. M. Clear, J. M. Kelly and J. G. Vos,

   Makromol. Chem., 184, 1983, 613.

6. L. L. Miller and M. R. Van de Mark,

   J. Electroanal. Chem., Interfacial Electro-
   chemistry, 88, 1978, 437.

7. C. D. Ellis and T. J. Meyer,

   Inorg. Chem., 23, 1984, 1751.

8. J. M. Calvert and T. J. Meyer,

    Inorg. Chem., 20, 1981, 27.

9. K. Doblhofer, H. Braun and R. Lange,

    J. Electroanal. Chem., Interfacial electro-
    chemistry, 206, 1986, 93.

10. C. P. Andrieux, J. M. Dumas-Bouchiat and J. M. Saveant,

    J. Electroanal. Chem., Interfacial Electro-
    chemistry 131, 1982, 1.

11. W. J. Albery, M. G. Boutelle and a. R. Hillman,

    J. Electroanal. Chem., Interfacial Electro-
    chemistry, 182, 1985, 99.

12. W. J. Albery and A. R. Hillman,

    J. Electroanal. Chem., Interfacial electro-
    chemistry, 170, 1984, 27.

13. B. Lindholm and M. Sharp,

    J. Electroanal. Chem., Interfacial Electro-
    chemistry, 235, 1987, 41.

14. N. Oyama and F. C. Anson,

    Anal. Chem., 52, 1980, 1192.

15. B. Lindholm and M. Sharp,

   J. Electroanal. Chem., Interfacial Electro-
   chemistry, 198, 1986, 37.

16a. J. F. Cassidy and J. G. Vos,

   J. Electroanal. Chem., Interfacial Electro-
   chemistry, 235, 1987, 41.

16b. J. F. Cassidy and J. G. Vos,

   J. Electrochem. Soc., 135, 1988, 863.

17. J. F. Cassidy, A. G. Ross and J. G. Vos,
   "Electrochemistry, Sensors and Analysis",
   M. R. Smyth and J. G. Vos, Editors, p.269,
   Elsevier Pub. Co. Amsterdam, 1986.

18a. S. M. Geraty, A. G. Ross and J. G. Vos,
   Proceedings of the International Society of
   Electrochemistry Meeting, Salamanca, Spain,
   September 1985, p.02200.

18b. S. M. Geraty, D. W. M. Arrigan and J. G. Vos, in
   "Electrochemistry, Sensors and Analysis",
   M. R. Smyth and J. G. Vos, Editors, p.269,
   Elsevier Pub. Co. Amsterdam, 1986.

19. K. Niwa and K. Doblhofer,
   Electrochim. Acta, 31, 1986, 549.

20. C. P. Andrieux, J. M. Dumas Bouchiat and J. M. Saveant,

    J. Electroanal. Chem., Interfacial Electro-chemistry, 114, 1980, 159.

21. E. Laviron,

    J. Electroanal. Chem., Interfacial Electro-chemistry, 112, 1980, 1.

22. C. P. Andrieux and J. M. Saveant,

    J. Electroanal. Chem., Interfacial Electro-chemistry, 111, 1980, 377.

23. J. B. Kerr, L. L. Miller and M. R. Van de Mark,

    J. Am. Chem. Soc., 102, 1980, 3380.

24. T. Ikeda, R. Schmehl, P. Denisevich, K. Willman and R. W. Murray,

    J. Am. Chem. Soc., 10, 1982, 2683.

25. G. Sprintschnik, H. W. Sprintschnik, P. P. Kirsch and D. G. Whitten,

    J. Am. Chem. Soc., 98, 1976, 2337.

26. S. Valenty and G. L. Gaines,

    J. Am. Chem. Soc., 99, 1977, 1285.

27. O. Haas, H. R. Zumbrunnen and J. G. Vos,
    Electrochim. Acta, 30, 1985, 1551.

28. T. D. Westmoreland, J. M. Calvert, R. W. Murray
    and T. J. Meyer,
    J. Chem. Soc., Chem. Commun., 65, 1983, 3.

29. S. Cosnier, A. Deronzier and J. C. Moutet,
    J. Phys. Chem., 89, 1985, 4895.

APPENDIX

LIST OF PUBLICATIONS

1. S. M. Geraty and J. G. Vos,
   J. Electroanal. Chem., Interfacial Electro-
   chemistry, 179, 1984, 389.

2. S. M. Geraty, A. G. Ross and J. G. Vos
   Proceedings of the International Society of
   Electrochemistry Meeting, Salamanca, Spain,
   September 1985, p. 02200.

3. S. M. Geraty, D. W. M. Arrigan and J. G. Vos, in
   "Electrochemistry, Sensors and Analysis", M. R.
   Smyth and J. G. Vos, Editors, p. 269, Elsevier
   Pub. Co. Amsterdam, 1986.

4. S. M. Geraty and J. G. Vos,
   J. Chem. Soc., Dalton Trans., 1987, 3073.