

CARBON PASTE ELECTRODES MODIFIED
BY ADMIXING WITH NOVEL
REDOX MEDIATORS

BY

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CHAPTER I

INTRODUCTION

Research on and the application of chemically modified electrode systems possessing specifically functionalized surfaces represent an important area of today's electroanalytical chemistry.

The origins of the field of chemically modified electrodes can be traced to adsorption, chemisorption and electrodeposition. However, chemically modified electrodes diverge sharply from adsorption on electrode surfaces. The most essential difference is that in chemically modified electrodes one deliberately seeks, in some hopefully rational fashion, to immobilize a chemical on an electrode surface so that the electrode thereafter displays the chemical, electrochemical, optical, and other properties of the immobilized species. This means that one selects chemicals to immobilize on the basis of known and desired properties such as, for instance, fast outer-sphere electron transfer agents, chiral centers, electron transfer mediator-catalysts, functionalities which can concentrate trace species or ions from solutions for determination in preconcentrated form, photosensitizers for a semiconductor electrode, and corrosion inhibitors. That is, the electrode

can be tailor-made to exhibit desired properties.

Since the immobilized species are confined to the electrode surface, they provide an opportunity for the study of electrochemical reactions. These are the motivations associated with much of the recent and current research on electrodes bearing immobilized chemicals. They are called chemically modified, derivatized, functionalized, electrochemically deposited, and polymer-coated electrodes [1].

Recently there have been many studies on chemically modified electrodes. Property-dependent applications have been suggested in various fields, such as catalysis, protection of materials, microelectronics, electrochromic devices, potentiometric sensors, and amperometric sensors [2]. Among all these studies, the development of chemical- and bio-sensors has specially attracted the analysts' attention. Among the different types of modified electrodes, the chemically modified carbon paste electrode is the most scrutinized one. Several recent reviews on chemically modified electrodes have been presented by Abruña [3], Fujihira [4] and Murray [5].

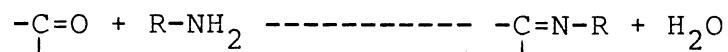
Immobilization by covalent bonding, electropolymerization, and direct admixing with carbon pastes are the three main avenues used to modify carbon surfaces. Although it has been questioned as a "true" modification [6], direct admixing for modifying carbon paste electrodes is particularly attractive because of the

simplicity of electrode preparation and surface renewal, the possibility to control very simply the degree of modification, and the wide range of chemical species that are potentially useful for modification. An important requirement, particularly if the sensor is for use under continuous-flow conditions, is the need for a modifier fairly insoluble in the carrier (supporting electrolyte) used.

The chelating functionality =N-C-C-N=, present in 1,10-phenanthroline, its substituted derivatives, and some other analytical ligands forms complex cations when reacted with iron(II) and some other metal ions. A detailed discussion about the electroanalytical chemistry of complex compounds of 1,10-phenanthroline has been presented by Prokhorova [7]. The iron(II) and iron(III) complexes have the attractive feature that, under given experimental conditions, they constitute a redox couple in which oxidation and reduction can be accomplished, chemically or electrochemically, by changing the oxidation state of the central metal ion only. The organic moiety is left unaffected. This property invites the incorporation of chemical species of this type on carbon surfaces for their use in amperometric sensing in continuous-flow systems. Successful application of carbon paste-modified electrodes for sensing in continuous-flow systems [e.g. liquid chromatography and continuous-flow sample or reagent processing] ideally should involve a permanently immobilized

reversible redox mediator exhibiting fast electron exchange with analyte and with graphite itself. Salts of iron(II) and iron(III) complexes with ligands of the 1,10-phenanthroline family have been found useful redox mediators for continuous-flow detection and determination of redox species [8-10]. Although tris[4,7-diphenyl-1,10-phenanthroline]iron(II) exhibits reasonably low solubility in most common aqueous electrolytes [8], it slowly leaches out under prolonged use in continuous-flow systems and is also fairly soluble in organic solvents. Therefore, the search for highly insoluble ligands and iron complexes of the same family becomes important and necessary.

Interaction of primary amines with aldehydes results in imine bond formation via carbon-nitrogen double bond linkages:



The presence of an aryl group on the nitrogen (or the carbon) prevents rapid decomposition or polymerization; the reaction products in such a case are usually called Schiff bases [11]. This chemical route has been extensively exploited for the attachment of proteins, especially enzymes, to inert supports using glutaraldehyde as the aldehyde [12] because the Schiff-type reaction can occur at

room temperature and under mild conditions conducive to retention of the protein structure (i.e. retention of enzyme activity).

In this research, with the intention to link two phenanthroline units via aggregates of a dialdehyde molecule and obtain a flexible tetradentate ligand and highly insoluble metal complexes, the reaction between 5-amino-1,10-phenanthroline and ethanedial (glyoxal) was studied and the corresponding complexes were prepared. Results from spectrochemical studies of the products, the electrochemical behavior of the resulting electrodes, and evaluation of their analytical applications in continuous-flow sensing, are reported here. A kinetic interpretation of the amperometric response as a function of applied electrode potential is also discussed in some detail.

CHAPTER II

REVIEW OF CHEMICALLY MODIFIED CARBON

PASTE ELECTRODES

Carbon Electrodes

The earliest carbon-based electrode was in graphite rod form and was described by Gaylor in 1957 [13]. From the beginning, carbon as an electrode has exhibited three major advantages over other conventional materials such as platinum or mercury. First, carbon is a much less expensive material than either platinum or mercury. Second, unlike mercury, carbon is not a poison and does not contaminate the environment. Third, the most important practical advantage inherent in carbon is that it can provide a wider range of working potential than conventional electrode materials. Figure 1 shows a comparison of the potential windows for carbon, platinum, and mercury electrodes. As shown in the current-potential plots, when the potential of the electrode is negative enough (in the reduction region), the hydrogen ions in the solution are reduced at the electrode and give reduction currents. When the potential of the electrode is positive enough (in the oxidation region), water is oxidized at the electrode and an oxidation current results. In between the oxidation region and the reduction region, there

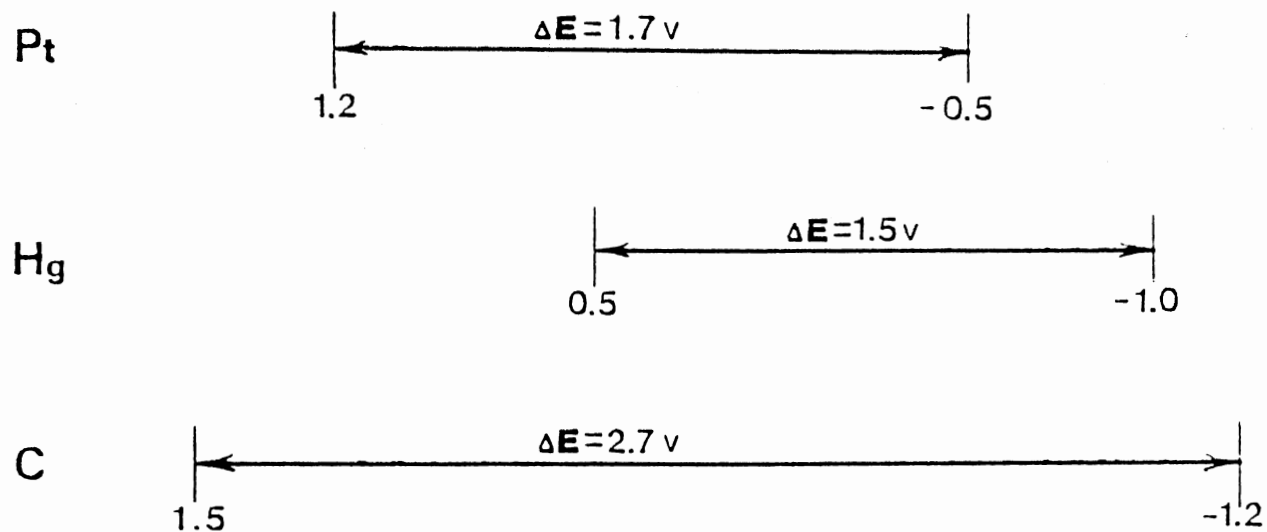
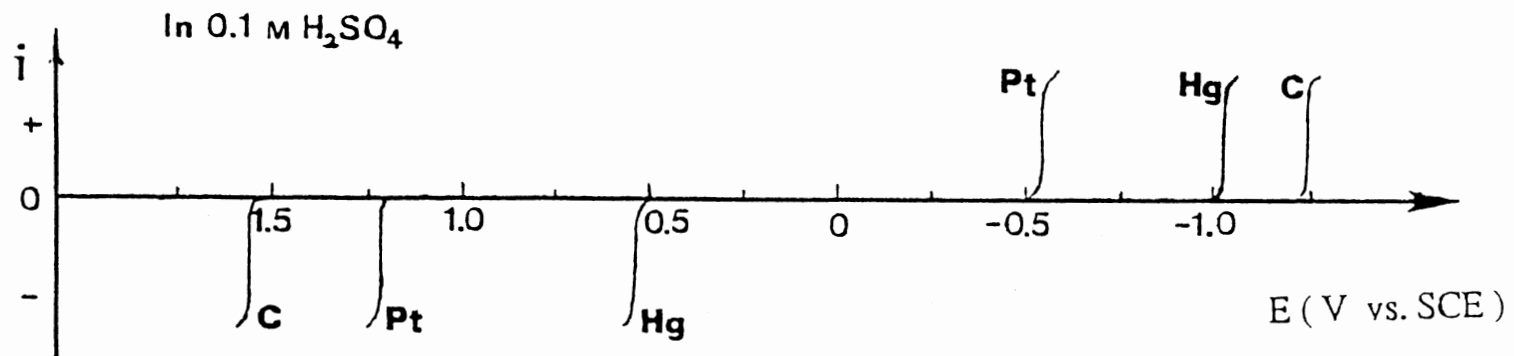


Figure 1. Potential Windows of Different Electrode Materials

is a potential range with very low background current, defined as the potential window of the electrode. In electroanalytical chemistry, all experiments have to be performed within this potential range to avoid interference from the background currents. The larger the potential window provided, the better the material is for use as electrode. In 0.10 M H_2SO_4 supporting electrolyte solution, while a platinum electrode has a potential window range of 1.7 V, from 1.2 V to -0.5 V vs. SCE (more suitable for oxidation than for reduction), a mercury electrode offers a 1.5 V-potential window, from 0.5 V to -1.0 V vs. SCE (more suitable for reduction). Under the same conditions, a carbon electrode can provide up to 2.7 V as a potential window (from 1.5 V to -1.2 V vs SCE) which, simultaneously, covers both the oxidation and the reduction regions. Perusal of tables of standard potentials shows that about 90% of metal ions and many other chemical species have their formal standard electrode potentials within this range. This means that carbon electrodes can provide wider opportunities for electrochemical research and for application than other conventional electrode materials.

Carbon Paste Electrodes

The earliest carbon electrode, which was in graphite rod form, was not convenient to prepare and use [13]. This electrode required a few hours of pretreatment with a wax material such as ceresin to fill the micropores in the

graphite rod. Absorption of the wax into the pores prevents unwanted adsorption and thus greatly reduces the residual current [10]. Since then, many different forms of carbon materials have been developed such as graphite particles, highly ordered graphite rod and discs, pyrolytic graphite, carbon black, glassy carbon, and carbon paste electrodes. In 1958, Adams introduced the carbon paste electrode (CPE) [14]. This new type of electrode possessed the same characteristics as the graphite rod but was more easily prepared.

Generally a carbon paste electrode is constructed by mixing graphite with a liquid binder, which can be a silicone grease or a mineral oil. When well mixed, such electrode material has the consistency of a paste which can be packed into the well of a glass or nylon tube to form an electrode. Electrical contact can be made by using a copper rod that is in contact with the paste as shown in Figure 2. Besides the simplicity of preparation, another advantage of these electrodes is that since they are pasty in nature, the electrode surface can be easily renewed by polishing, which exposes a fresh electrode surface for use.

Chemically Modified Carbon

Paste Electrodes

Using a carbon paste electrode, Kuwana first introduced the concept of chemically modified carbon paste electrodes in 1964 by separately dissolving several organic compounds

Carbon Paste Composition

65% graphite powder

35% mineral oil

Area of CPE Surface : 0.20 cm^2

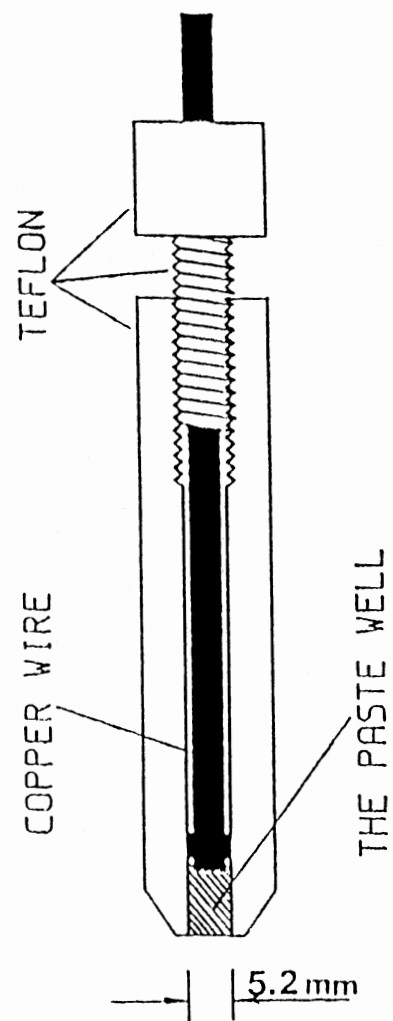


Figure 2. A Typical Example of Carbon Paste Electrode

in the binder used to prepare the carbon paste electrodes to add some new redox properties to the electrodes [15].

As already mentioned and in general, chemically modifying an electrode consists in incorporating a desired electroactive substance onto the surface of the electrode. This electroactive substance, called the "modifier", constitutes a new redox agent on the surface. The new redox center can work as a catalyst to change the mechanism of the electrochemical process and to accelerate the electron exchange at the surface of the electrode. In Figure 3 the modifier attached on the surface of the carbon paste electrode could be in either the oxidized or the reduced form depending on the actual experimental needs. If the reactant is originally in the oxidized form (as in Figure 3), the modifier can act in its reduced form in a chemical reaction with a given reactant. After this chemical reaction, and while the reactant is reduced, the modifier attached on the surface of the carbon paste electrode becomes oxidized and immediately undergoes an electrode reaction which reduces it and makes it ready for the next reaction with the reactant species. Since the modifier is not consumed, the net result of the chemical-electrode reaction cycle is only the continuous reduction of the reactant. This reduction process does not directly happen on the working electrode but through an attached chemical ("modifier") as a mediator. Working in this mode, the modifier can make some difficult reactions possible, and

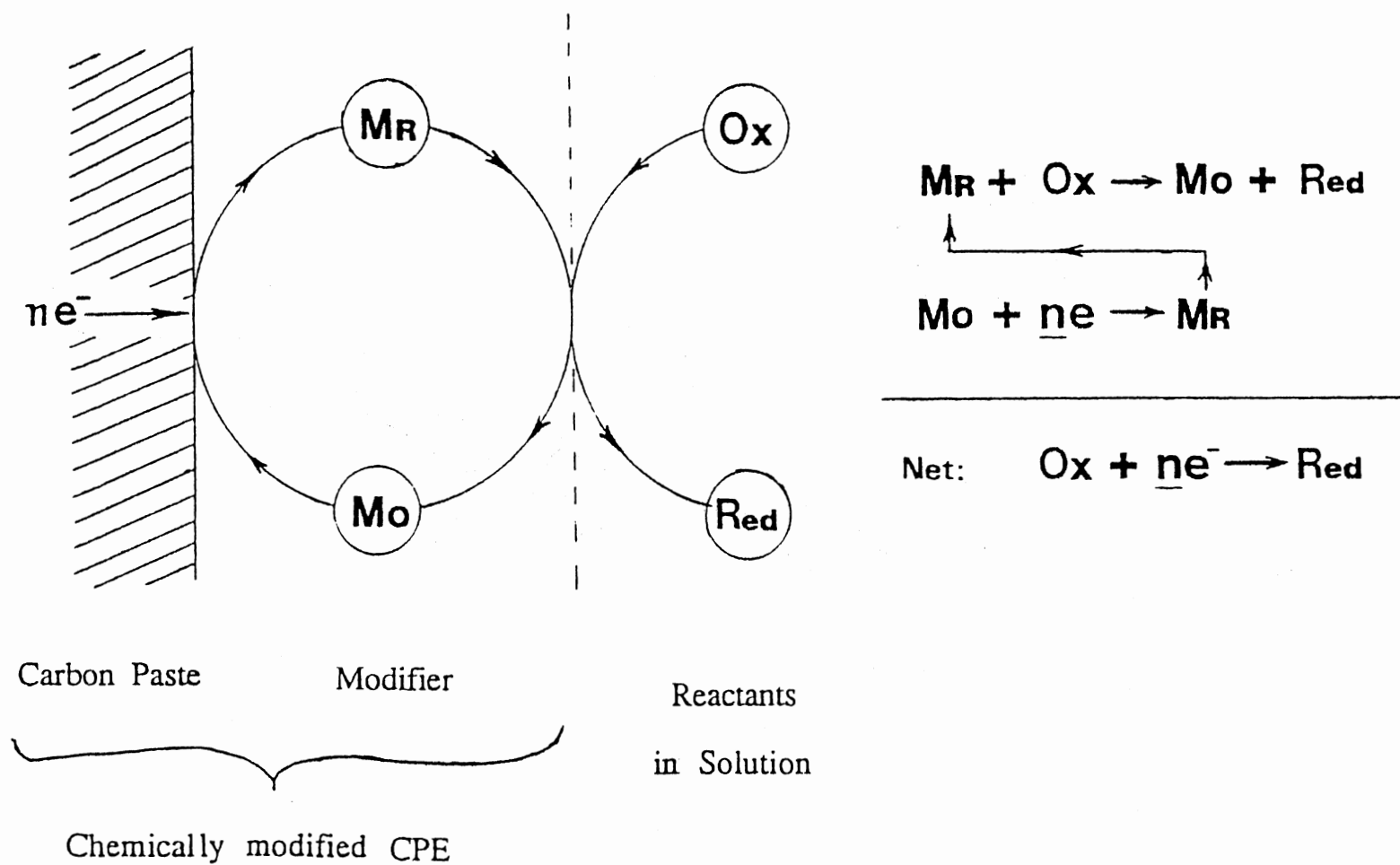


Figure 3. Illustration of Redox Mediation in a Chemically Modified Electrode

make some ordinarily irreversible or quasi-reversible processes reversible. Analytically this would result in desired selectivity and enhanced sensitivity.

Approaches for the Chemical Modification of Carbon Paste Electrodes

To modify an electrode, the key is to successfully attach the modifier to the surface of the electrode. According to the most common methods used to attach modifiers, there are three kinds of approaches to modify a carbon paste electrode; they are: 1) chemically immobilizing the modifier on the surface of the graphite powder, 2) covering the surface of the CPE with a film of insoluble material containing the modifier moiety, and 3) direct admixing of the modifier into the carbon paste. By choosing different types of electroactive species, one is able to design different kind of modified electrodes with different electrochemical properties to satisfy different research and application purposes. A brief overview of each of these approaches is given below.

Chemical Immobilization

In this type of modification, chemical reactions are used to couple the modifier to the surface of the CPE. Albahadily's work [16] provides a good example to illustrate chemical immobilization of a modifier as shown in Figure 4. In this example, the modifier is

5-amino-1,10-phenanthroline. To attach it on graphite, the graphite surface first needs a pretreatment. On a carbon graphite surface there are originally some residual functional groups such as hydroxyl, carbonyl, and carboxyl groups which can work as bridge piers at which to connect the modifier with the graphite via a chemical reaction. In order to obtain a high loading of modifier on the graphite surface, it is advantageous to further oxidize the graphite surface and increase the amount of oxygen functionalities, especially, the amount of carboxyl groups. After oxidation by heating the graphite in an oxygen atmosphere at about 400°C for 12 h, the other oxygenated sites are, hopefully, converted to carboxyl groups. Then thionyl chloride is used to convert the carboxyl groups to form chlorocarbonyl groups (acyl chlorides) on the surface of the carbon. Finally, the 5-amino-1,10-phenanthroline is reacted with the poly(acyl chloride) to attach the ligand onto the graphite.

Besides thionyl chloride coupling, carbodiimide coupling and cyanuric chloride coupling are also popularly used in chemical immobilization [1]. The chemical immobilization method was the earliest approach developed for modifying CPE. The main problem of this modifying avenue is that in some cases the degree of modification is too low and not easily controlled.

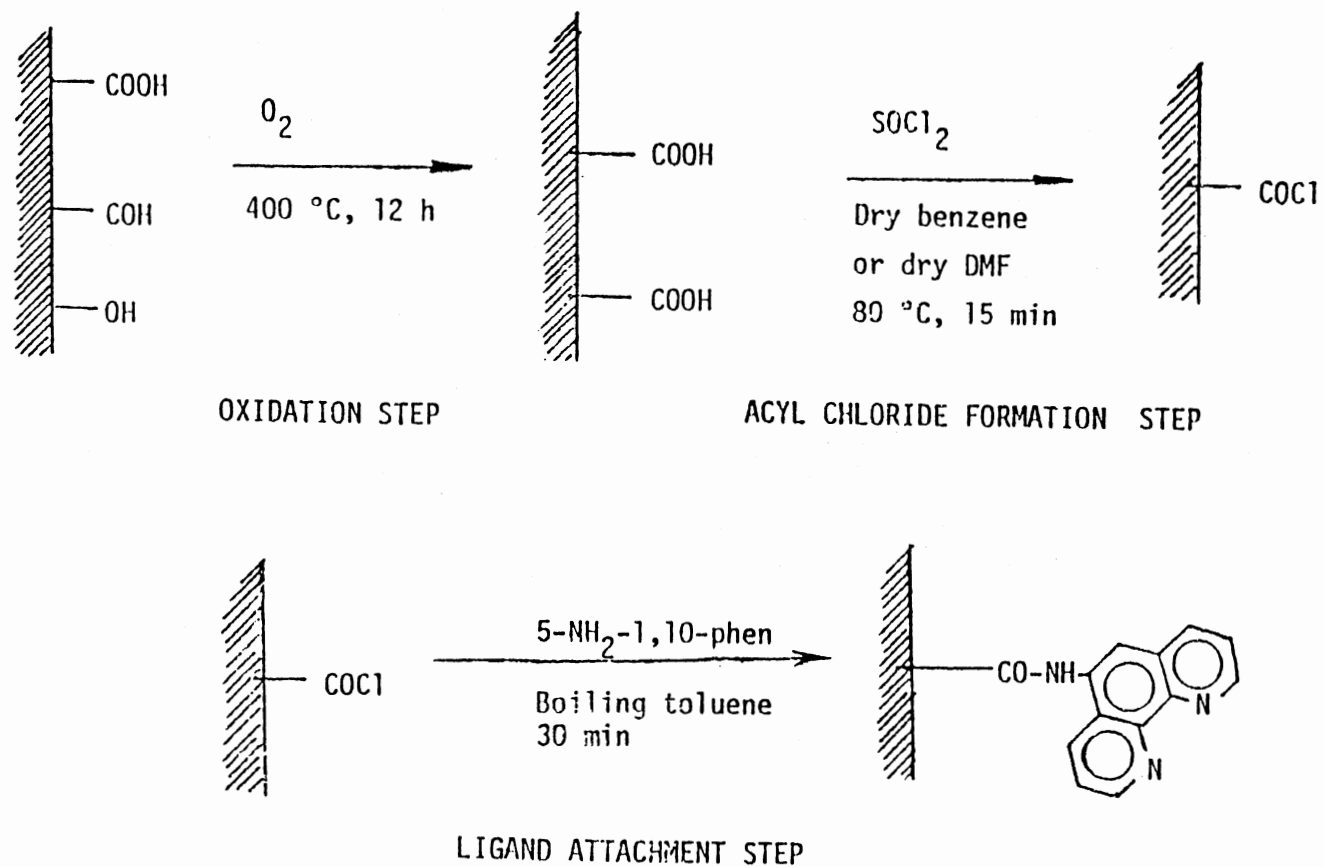


Figure 4. Modification by Chemical Immobilization
 [Adapted from Albahadily, F. N., Ph.D. Thesis, OSU, 1989]

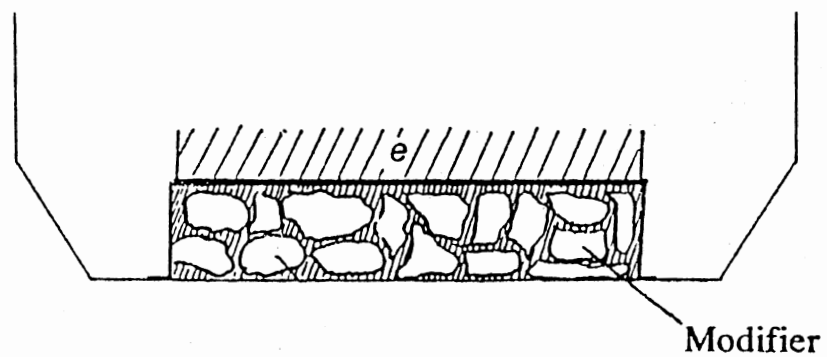
Electrochemical Polymerization

The formation of a polymer film on the electrode surface and the use of polymer-film-coated electrodes for analytical purposes has been known for some time and has been discussed in detail in reference 1. In this kind of modification approach, the advantages for carbon paste electrodes such as ease of preparation and renewal of the modified surface have been replaced by the relatively tedious procedure of polymerization; hence the most work was performed with glassy carbon electrodes, which it was hoped could provide good stability. The essential characteristic of modern polymer-coated electrodes is that the polymer film contains electrochemically or chemically reactive centers. The electrochemically active centers can undergo electron transfer reactions with the electrode, and since the films generally contain the equivalent of many monomolecular layers' worth of electroactive sites, their electrochemical responses are larger and more easily observed than those of immobilized monomolecular layers. According to the reaction mechanism, such polymers on electrodes can be alternatively classified as redox polymers and ion-exchange polymers. Redox polymers contain the electroactive centers as part of the polymer chain backbone while ion-exchange polymer films on electrodes depend on drawing ionic redox substances from the solutions into the film as counterions having favorable ion-exchange partition coefficients.

The most important and useful method to apply polymer films to electrodes is electrochemical polymerization, in which the modifiers are electrochemically deposited on the surface of the electrode and form multilayer polymer films. Some other methods are also used to make polymer films such as dip coating, droplet evaporation, spin coating, and RF plasma polymerization. Generally, the polymer-film-modified electrodes show very stable and reproducible electrochemical behavior. However, there are two major problems which limit the application of this method of modification. First, not many modifiers can be easily converted to a polymer film form. Second, even when a polymer film has been obtained, the poor ionic conductivity of the film and the large overpotential for the analyte on the polymer-coated electrodes may result in serious difficulties. Recently, some researchers have tried to use electrochemical pretreatment to solve this problem [17, 18].

Direct Admixing

Another approach to modify carbon paste electrodes is the direct admixing method, in which about 2-15 % (sometimes more) by weight of solid sample of the electroactive species (modifier) is simply mixed with the carbon powder and the mineral oil to make a carbon paste electrode which is then employed in the usual way [Figure 5]. After smoothing of the surface of the electrode, the electroactive species becomes exposed at the carbon powder-solvent interface and



Typical Composition :

| | |
|--------|-----------------|
| 2-15% | modifier |
| 63-50% | graphite powder |
| 35% | mineral oil |

Figure 5. Electrode Modified by Direct Admixing of Modifier to Carbon Pastes

exhibits its characteristic chemical and electrochemical reactivities. Their electrochemical responses are usually very reproducible but can be improved when necessary by removing an outer layer of the paste and smoothing the electrode surface again. The cyclic voltammetric peak currents obtained from carbon paste electrodes modified by direct admixing are very distinct and are much too large to be accountable by reaction of a monolayer film [19].

Compared with chemical immobilization and electropolymerization methods, carbon paste electrodes modified by direct admixing have several advantages that make them popular. A detailed discussion on this topic will be given in the following section. The only requirement for admixing, as already noted, is that the modifier should be fairly insoluble in the supporting electrolyte solution to be used for electrochemical measurement.

Advantages of Direct Admixing

Modification of carbon paste electrodes by direct admixing has four major advantages over the other two previously mentioned approaches. First, it is very easy to make a modified carbon paste electrode by this means. Here one does not need to perform chemical reactions or arrange for some electropolymerization in order to obtain a modified electrode surface. The only thing one needs is simply mixing the modifier with the carbon paste when preparing the electrodes. Second, by controlling the percentage weight of

the modifier added one can easily control the degree of modification. Another advantage is that by extruding a little bit of paste from the electrode well and resmoothing the electrode surface one can easily renew the modified surface. Surfaces renewed by this way always give good reproducible electrochemical responses. The fourth advantage of direct admixing is that although many chemical species are known as very effective modifiers for some special applications, many of them are difficult to immobilize on the surfaces of electrodes either by chemical reactions or by polymerization techniques. Most of these chemicals, however, can be incorporated into carbon pastes by admixing. This property ensures a wide range of applications and good flexibility in the selection of modifiers.

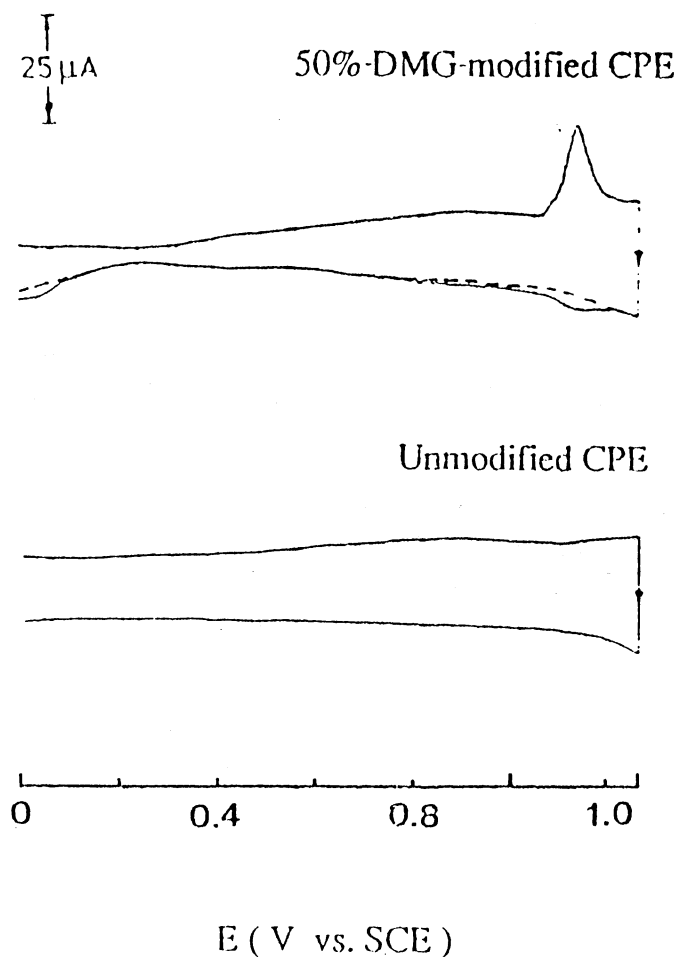
Types of Modifiers Used in Direct Admixing

As indicated above, due to versatility in modification, simplicity in preparation, and competitive performance, carbon paste electrodes modified by direct admixing have attracted attention. A considerable number of studies have focused on this type of modification and have been reported [21]. According to the chemical property of the admixed modifier, all these studies can be grouped into three categories: (a) incorporation of ligands, (b) incorporation of metal complexes, and (c) incorporation of enzymes. A

brief overview of each is given below.

Incorporation of Ligands

Different types of ligands have been incorporated as modifiers into carbon paste electrodes by admixing. Their applications include: a phenanthrenequinone-modified CPE for the detection of ascorbic acid [20], a 1,2-naphthoquinone-modified CPE for the detection of NADH [20], an ethylenediamine-modified CPE for the determination of silver ions [21], a crown-ether-modified CPE for measurement of mercury [22], and others. A typical example of application was given by Baldwin: a carbon paste electrode modified by admixing with dimethylglyoxime has been characterized and successfully used for preconcentrating and determining traces of nickel(II) [23]. Figure 6 shows a comparison of cyclic voltammograms of unmodified CPE and a 50%-dimethylglyoxime-modified CPE. In a 1 μM nickel ion solution, the modified CPE shows a current peak at 1.15 V vs SCE while the unmodified one gives no response. When this dimethylglyoxime-modified CPE was used to determine traces of nickel(II) with the standard addition method, a linear range of nickel(II) concentration from 0.050 μM to 5.00 μM was obtained (Figure 7). The detection limit can be estimated as 0.050 μM with a 3% relative standard deviation based on 20 replicates. Good selectivity was observed in excess concentrations of bismuth, cadmium, copper, cobalt, lead, palladium, platinum and zinc, which



Admixing Modifier: Dimethylglyoxime (DMG)

Species determined: Ni (II)

Cyclic Voltammogram Condition:

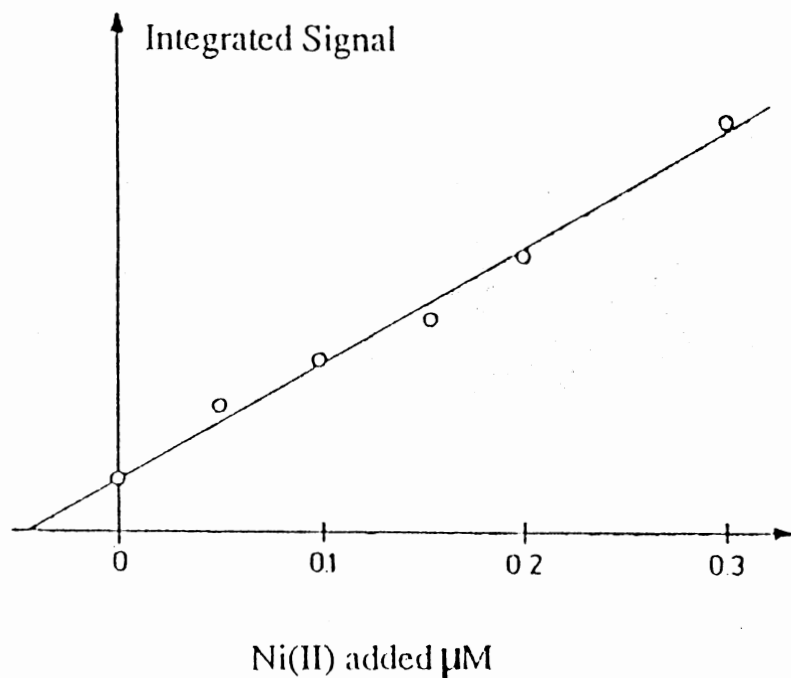
Sample: 1 μ M- Ni(II)

Electrolyte: ammonia buffer, pH 8.0

Scan rate: 59 mV/s

Figure 6. Example of Results Obtained after Incorporation of a Ligand into Carbon paste
 [Adapted from Baldwin, R. P., Christensen, J.K. and Kryger, L., Anal. Chem.
 58, 1790 (1986)]

Standard Addition Method:



Linear range: 0.050--5.00 μM Ni(II)

Detection limit: 0.05 μM Ni(II)

RSD: 3%

Excess Concentrations of Bi, Cd, Cu, Co, Pb,

Pd, Pt, Zn did not influence the Ni response.

Figure 7. Application of a Dimethylglyoxime-Modified Carbon Paste Electrode in the Determination of Ni(II)

[Adapted from Baldwin, R. P., Christensen, J. K. and Kryger, L., Anal. Chem. 58, 1790 (1986)]

did not influence the response of nickel(II).

Incorporation of Metal Complexes

Compared to work with ligand-modified carbon paste electrodes, more research has been focused on admixing metal complex modifiers into the carbon paste to build up new catalytic centers on the surface of the electrode. For example, Murray's research group has investigated $[\text{Ru}(\text{trpy})(\text{phen})\text{OH}_2](\text{ClO}_4)$ (trpy = 2,2',2''-terpyridine; phen = 1,10-phenanthroline) as a modifier [24], as well as iron(III) meso-tetraphenylporphyrin chloride, $[\text{Fe}(\text{II})\text{TPPCl}]$ -modified carbon paste electrodes and $[\text{Mn}(\text{III})\text{TPPCl}]$ -modified carbon paste electrodes [25]. Mottola's research group has exploited tris[4,7-diphenyl-1,10-phenanthroline]iron(II) perchlorate-modified carbon paste electrodes for the determination of NO_2 , SO_2 , H_2S , and Cl_2 gaseous species [8, 10], while Baldwin's group have developed a cobalt phthalocyanine (CoPC)-modified carbon paste electrode for the determination of organic compounds such as cysteine, glutathione [26], glucose, galactose, maltose, lactose, ribose, sucrose, fructose [27], and also hydrazine [28]. For the determination of hydrazine, 0.5% w/w of CoPC was mixed into a carbon paste to prepare the modified electrode. Hydrazine gave a signal at -0.200 V (vs. SCE) on the modified electrode while it gave no response on an unmodified CPE as indicated in the cyclic

voltammograms of Figure 8. When this CoPC-modified CPE is used in a continuous-flow system as an amperometric sensor, it gives very reproducible signals with trace amounts of hydrazine while the unmodified electrode does not show a response (Figure 9). An unusually wide linear range of 5 orders of magnitude in concentration (from 10^{-8} M to 10^{-3} M of hydrazine) was obtained [28].

Incorporation of Enzymes

Biochemical sensors comprise a relatively new branch in chemically modified electrodes. In order to construct a bioelectrode, enzymes or other bio-active species are immobilized on the surface of carbon paste electrodes via admixing. For example, Yao and Musha [29] have admixed nicotinamide adenine dinucleotide (NAD^+), an important coenzyme, into carbon paste electrodes for the determination of ethanol and L-lactic acid. During the determination, NAD^+ is first converted to NADH by oxidation of ethanol and L-lactic acid catalyzed by their respective dehydrogenases. Then the NADH formed is electrochemically oxidized to the original NAD^+ for repeated use. Mottola's research group has developed a bioamperometric sensor for detecting and determining phenol based on direct admixing of tyrosinase (E.C. 1.14.18.1) and hexacyanoferrate ions which have been electrostatically immobilized on poly(4-vinylpyridine) [30]. The tyrosinase used was either a purified commercial preparation or naturally immobilized

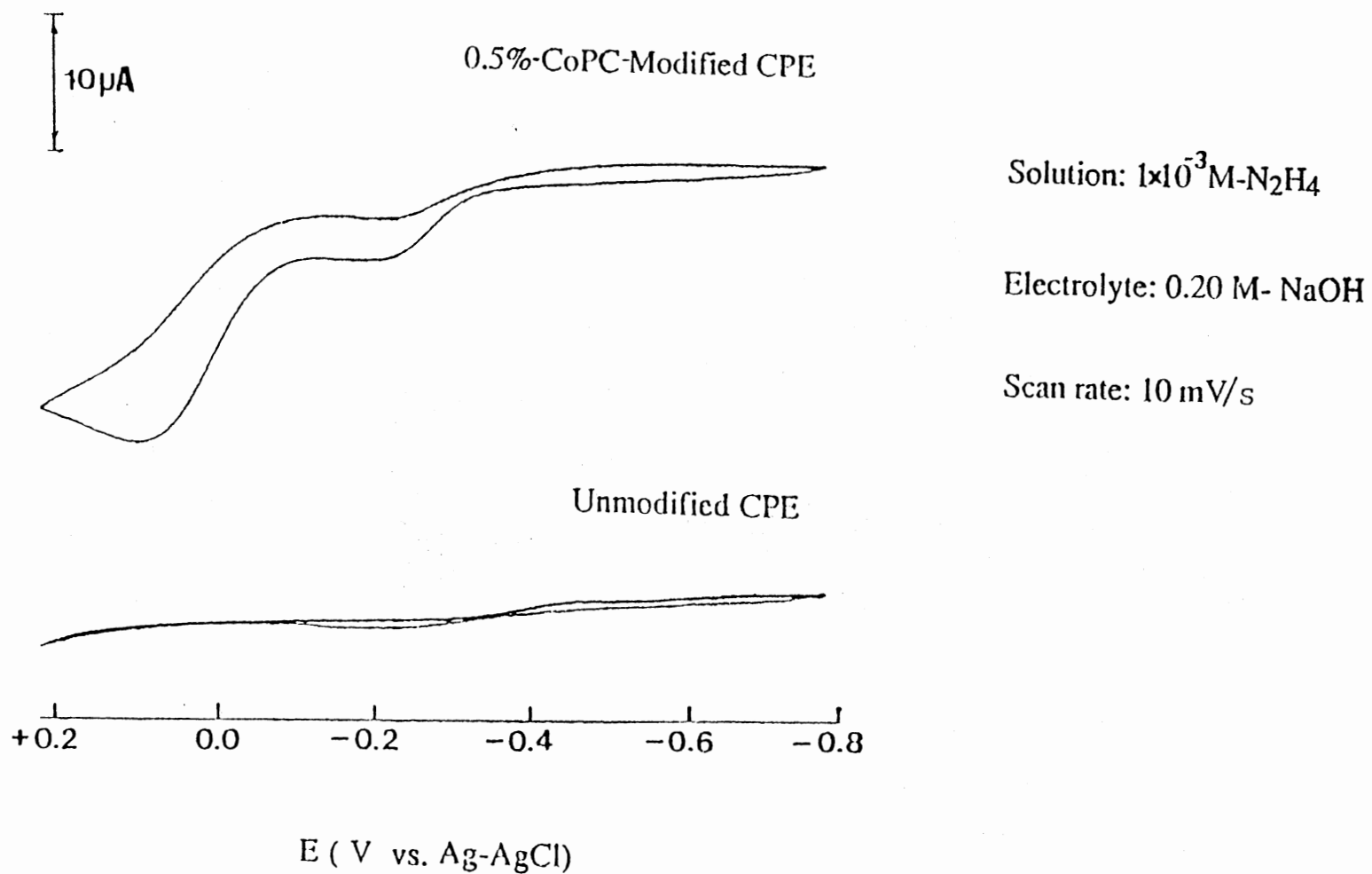


Figure 8. Cyclic Voltammetry of a Carbon Paste Electrode Modified with Cobalt Phthalocyanine Complex

[Adapted from Korfhage, K.M., Ravichandran, K. and Baldwin, R.P., Anal. Chem. , 56, 1517 (1984)]

2 μ A

0.5% CoPC Modified CPE



Flow injection sample: 16 pM N_2H_4

carrier: 0.20 M-NaOH

Flow rate: 0.5 mL/min

Controlling Potential: -1.0V (vs. Ag-AgCl)

Unmodified CPE



Linear Range: 1×10^{-8} — 1×10^{-3} M- N_2H_4

Figure 9. Application of a Cobalt Phthalocyanine-Modified Carbon Paste Electrode in a Flow Injection System

[Adapted from Korfhage, K.M., Ravichandran, K. and Baldwin, R.P., Anal. Chem., 56, 1517 (1984)]

in edible mushrooms. Wang's research group also have reported the admixing of some plant tissues into carbon paste electrodes to take advantage of naturally immobilized enzymes, such as incorporation of horseradish root (which contains horseradish peroxidase) into carbon paste matrix to build a bioelectrode for sensing hydrogen peroxide [31] and the admixing of banana tissue into carbon paste electrodes to provide the biocatalytic activity at the electrode surface for selective detection of dopamine [32]. A recent report from University of Hawaii has described a polyphenol oxidases-modified carbon paste electrode obtained by admixing eggplant tissue with carbon paste for the detection of trace amount of catechol [33]. In addition to the direct admixing of enzymes with graphite, Abu Nader and his co-workers [34] have recently reported the modification of carbon paste electrodes by direct admixing of the enzyme sulfite oxidase from chicken liver [EC 1.8.3.1] that was previously immobilized on crosslinked agarose gels activated with 1,1'-carbonyldiimidazole for the selective determination of sulfite ion in aqueous solutions and $\text{SO}_2(\text{g})$ in air.

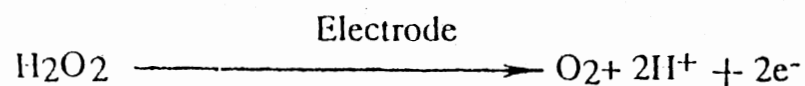
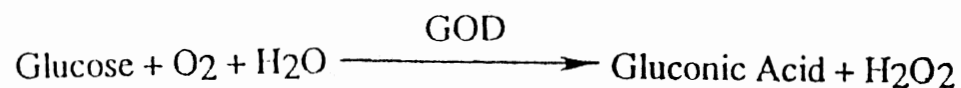
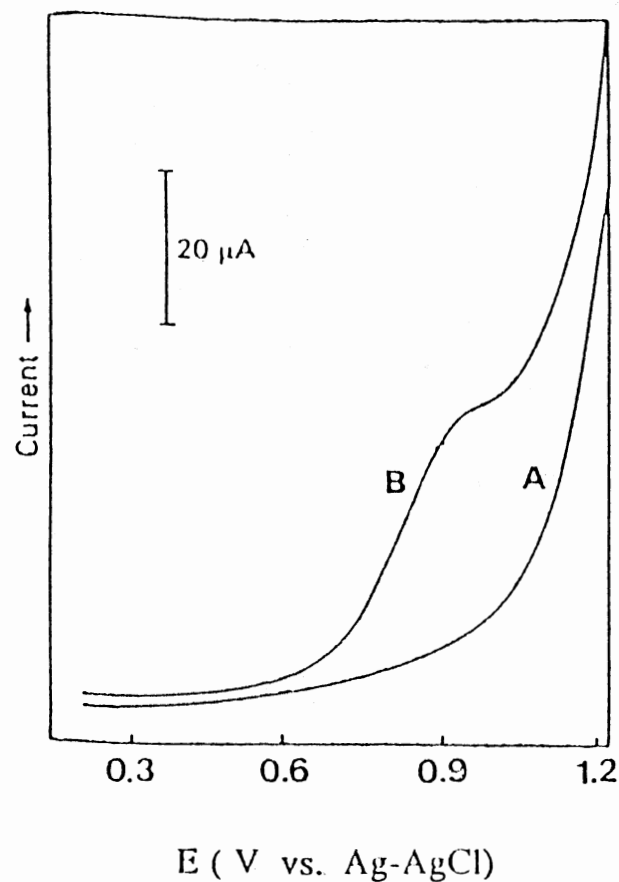
A typical example of application of enzyme-modified CPE in analytical chemistry was provided by Matuszewski and Trojanowicz [35]. They mixed 5% glucose oxidase (E.C. 1.1.3.4) into carbon pastes to prepare a modified CPE for the determination of glucose. During the reaction the admixed enzyme, some of which exists at the surface of the

electrode, works as a catalyst to accelerate the chemical oxidation of glucose and produce an equivalent amount of hydrogen peroxide on the surface of the electrode. The hydrogen peroxide formed immediately undergoes electrode reaction and gives a current signal. Figure 10 shows hydrodynamic voltammograms comparing the responses of the glucose oxidase-modified CPE: (A) background solution, (B) 2 mM glucose solution. The peak on curve B shows that the enzyme-modified CPE developed a very good current signal response in the glucose solution at 0.90 V (vs. Ag-AgCl). When this enzyme-modified CPE was used as an amperometric sensor in continuous-flow systems for determining glucose, a linear range of 20 μ M to 30 mM, with good reproducibility, was obtained, as shown in Figure 11. The electrode lifetime can be as long as three weeks.

From the brief discussion given above, two points become clear. First, chemically modified carbon paste electrodes make it possible to construct different types of microstructures and attach different functional groups on the surface of the electrodes. This results in surfaces which can work as redox-selective electrodes. Secondly, admixing is the most versatile as well as effective and easy approach to modify carbon paste electrodes.

Admixing Modifier: 5% w/w Glucose Oxidase (GOD) (E.C.1.1.3.4)

Species determined: Glucose

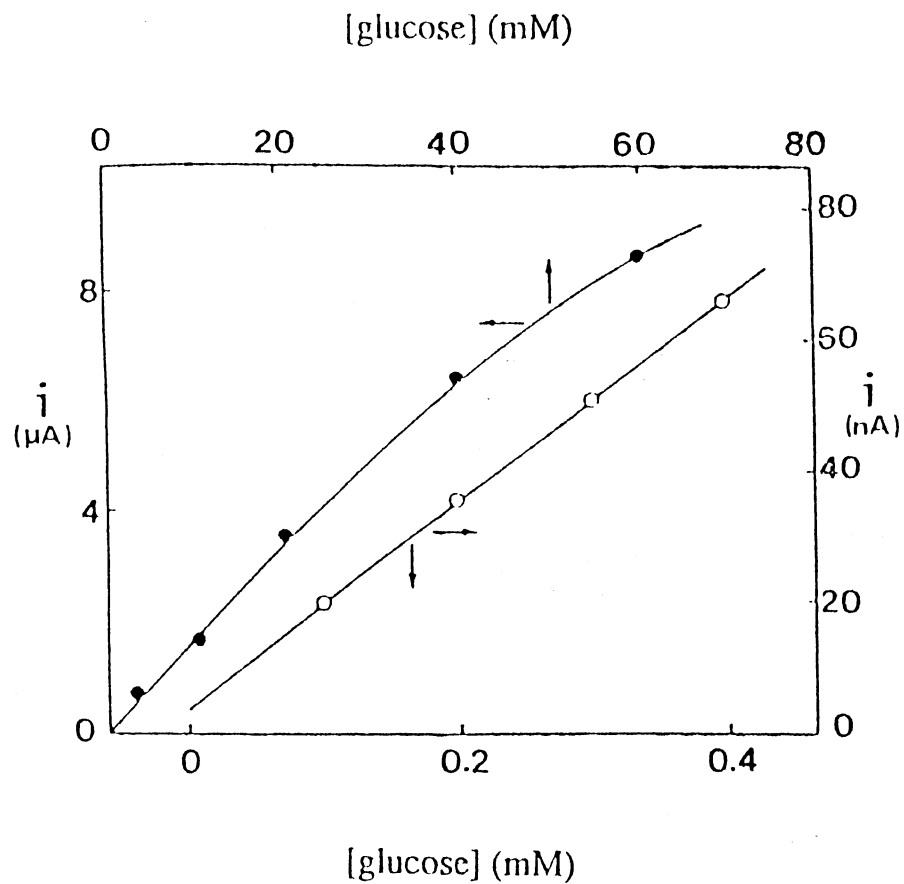


A-----0.1 M phosphate buffer pH 6.50

B-----2 mM glucose in 0.1 M phosphate buffer pH 6.50

Figure 10. Example of Incorporation of an Enzyme into a Carbon Paste Electrode

[Adapted from Matuszewski, W. and Trojanowicz, M., Analyst, 113, 735 (1988)]



Linear Range: 20 μM –30 mM glucose

Detection Limit: 20 μM glucose

Carrier: 0.1 M phosphate buffer pH 6.50

Control Potential: +0.90 V vs. Ag-AgCl

Electrode Life-time: 3 weeks

Figure 11. Application of Glucose Oxidase-Modified Carbon Paste Electrode in a Flow Injection System

[Adapted from Matuszewski, W. and Trojanowicz, M., Analyst, 113, 735 (1988)]

CHAPTER III

EXPERIMENTAL

The goal of this research was to develop a new type of amperometric sensor for use in continuous-flow systems such as flow injection analysis or liquid chromatography. According to the above discussion chemically modified electrodes are good candidates for this purpose. Since carbon paste electrodes modified by direct admixing with metal ion complexes possess several advantages over other types of modified electrodes, they have been chosen as the main object of this research.

The first step of the research was to try to prepare a modifier containing a suitable redox center. This center should work as a "catalyst" and at the same time exhibit very low solubility in common electrolyte solutions.

It is known that the iron(II) complexes with ligands of the 1,10-phenanthroline family are useful redox mediators in electrochemistry. These complexes and their ligands, however, are somewhat soluble in aqueous solution and this limits their use as modifiers in carbon paste electrodes. To overcome this problem, the basic idea was to attach a chemical species onto the 5-amino-1,10-phenanthroline ligand through the amino group. This attached chemical species

should not interfere with the chelating function of 5-amino-1,10-phenanthroline with iron(II) and should help, at least, to increase the molecular weight or even serve as a bridge to link two 1,10-phenanthroline moieties together retaining hydrophilic properties to facilitate counter-ion mobility. This should result in a decrease in solubility and also an increase in the density of modifier on the electrode surface with rapid charge transfer. After the preparation of the new compounds, a series of spectroscopic and electrochemical studies were performed to characterize the new modifiers and examine the electrochemical behavior of the resulting modified CPE. The application of the modified carbon paste electrodes as amperometric sensors in continuous-flow systems was also experimentally examined.

Reagents and Solutions

All reagents used were of reagent grade except as noted. The 5-amino-1,10-phenanthroline was obtained from Polysciences, Inc. (Warrington, PA) and the ethanedial was from Aldrich Chemical Co. (Milwaukee, WI) in the form of a 40% weight percent solution in water. The 4-nitrobenzyl alcohol used as solvent in preparing samples for mass spectrometry was a 97% sample, also from Aldrich. Deionized-distilled water was used for preparation of all aqueous solutions.

Apparatus and Electrodes

Elemental analysis data on carbon, hydrogen, and nitrogen content were obtained from Guelph Chemical Laboratories (Guelph, Ontario, Canada), MultiChem Laboratories Inc. (Lowell, MA), and by courtesy of CONOCO Inc. (Ponca City, OK). Data from CONOCO were obtained with a Perkin-Elmer 240A unit. Elemental analysis of the residue left after ashing at about 550°C, by inductively coupled plasma (ICP) emission spectrometry, was performed with a Jarrell Ash ICAP 61 instrument. Thermogravimetric data were obtained with a Du Pont 9900 unit (Du Pont Co., Wilmington, DE).

UV-Vis spectra were obtained with a Perkin-Elmer Lambda 3840 linear diode array spectrophotometer operated by a Perkin-Elmer 7300 computer (Perkin-Elmer Inc., Norwalk, CT) and in a 1-cm quartz cell.

Infrared spectra (in pellets prepared with KBr powder from pure single crystals and of infrared quality from Spectra-Tech Inc., Stamford, CT, containing 2% w/w of ligand or complex) were collected in a Perkin-Elmer 681 spectrophotometer.

Liquid secondary ion mass spectrometry was performed with a ZAB-2SE high resolution mass spectrometer (VG Instruments Inc., Danvers, MA). The mass spectrometer was operated in a nominal mass mode with unit resolution at m/z 1000. The primary ion gun was operated to provide a 2- μ A

beam of +35 KeV Cs⁺ ions to the sample surface. Spectra were acquired on a 11-250J data system (VG instruments Inc.) at a scan rate of ten seconds per decade. The data system was operated in a multichannel analyzer mode and five to ten scans were typically averaged for each spectrum.

Electrochemical measurements (cyclic voltammetry) were performed with a BAS-100 electrochemical analyzer (Bioanalytical Systems, West Lafayette, IN). The carbon paste electrodes (3 mm in radius) were prepared by thoroughly mixing UCP-1-M graphite (Ultra Carbon, Bay City, MI) with light mineral oil (Sargent Welch, Skokie, IL) and the insoluble ligands or complexes. Typically the degree of modification, at a 10% level, was achieved by mixing well 0.16 g of ligand or complex, 0.84 g of graphite, and 0.6 mL of mineral oil. The dry ligand or complex and the graphite were first thoroughly mixed. The resulting fine powder was finally blended with the mineral oil. The paste so formed was pressed into the well of a Teflon body and its surface smoothed against a clean stiff paper card. The paste was in contact with a copper wire to provide direct contact with the measuring circuit. The electrode surface was easily renewed by screwing in the thick copper wire (3 mm o. d.) used for electrical contact. The resulting modified paste electrode was characterized electrochemically as the working electrode in a three-electrode cell with a Ag-AgCl(s), Cl⁻ (3.0 M KCl) electrode as reference and a platinum wire as auxiliary electrode.

Scanning electron micrographs were obtained with a Cambridge Stereoscan 250 Mark II instrument.

The continuous-flow system included a thin-layer cell with a working electrode and a reference electrode compartment, with an auxiliary electrode in the form of the metal tube serving as the exit to waste (Figure 12). Gravity was used for propulsion of the carrier solution. The current signal was measured with LC4B Amperometric Detector (Bioanalytical System, West Lafayette, IN).

All pH measurements were made with a model 601A Orion digital pH meter equipped with an epoxy-body combination electrode (Sensorex, Westminster, CA).

Synthetic Procedures for Ligands and Iron Complexes

To search for a suitable chemical species to anchor and bridge 5-amino-1,10-phenanthroline molecules, several organic compounds including palmitoyl chloride, glutaraldehyde, tris(2-aminoethyl)amine, and ethanedial were tested. Since the compounds from the reaction between ethanedial and 5-amino-1,10-phenanthroline did show the best electrochemical behavior by cyclic voltammetry, ethanedial was chosen as the attaching chemical. The synthesis procedures used are indicated in Figure 13.

To prepare the ligands, ethanedial in a 20-fold molar excess was reacted with the 5-amino-1,10-phenanthroline for 1 h at about 100°C. The pH of the reacting solution was

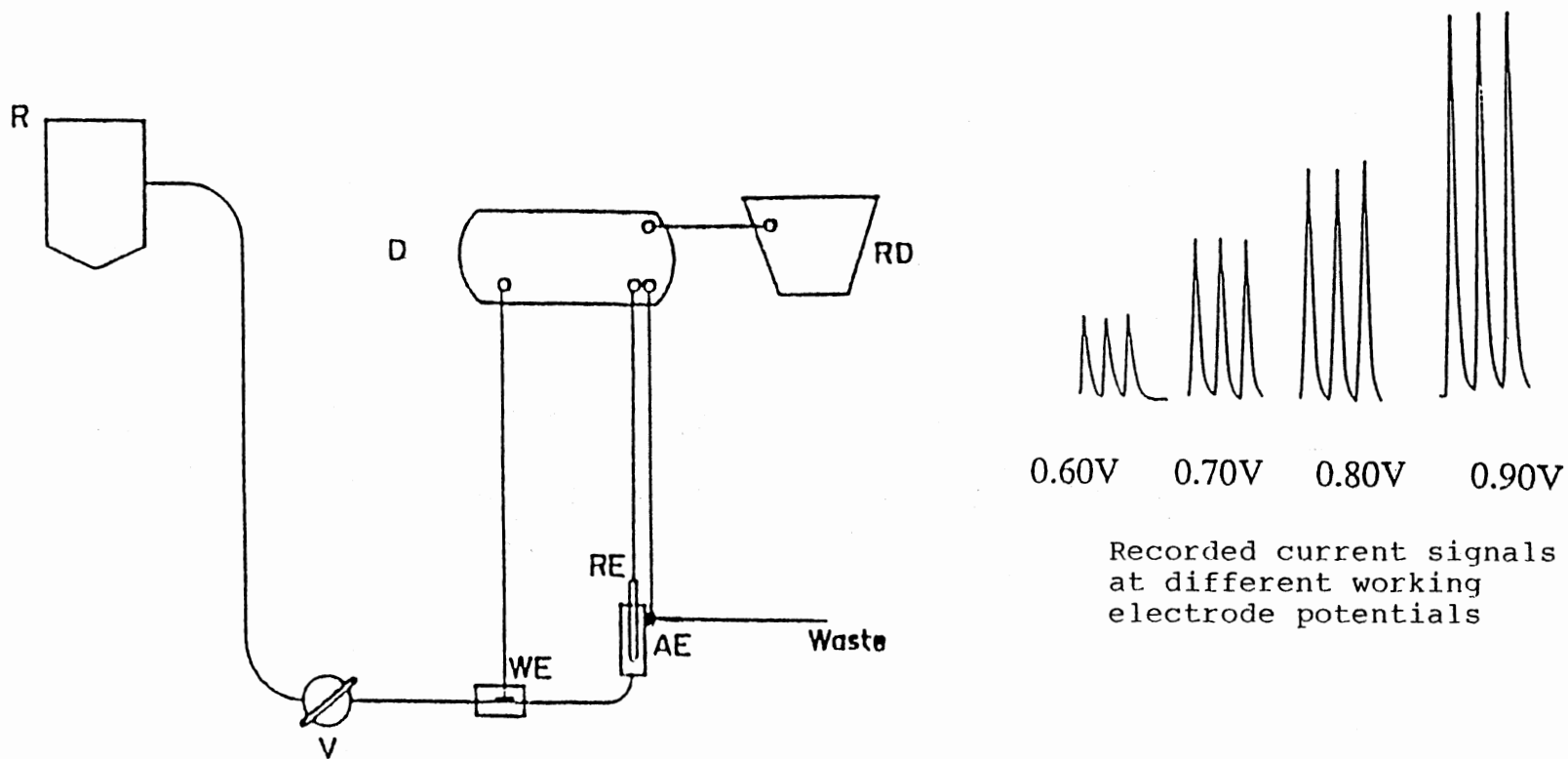


Figure 12. Diagram of Continuous-Flow System
 R--reservoir, V--rotary valve, WE--working electrode,
 RE--reference electrode, AE--auxiliary electrode,
 D--potentiostat-amplifier detector, RD--recorder.

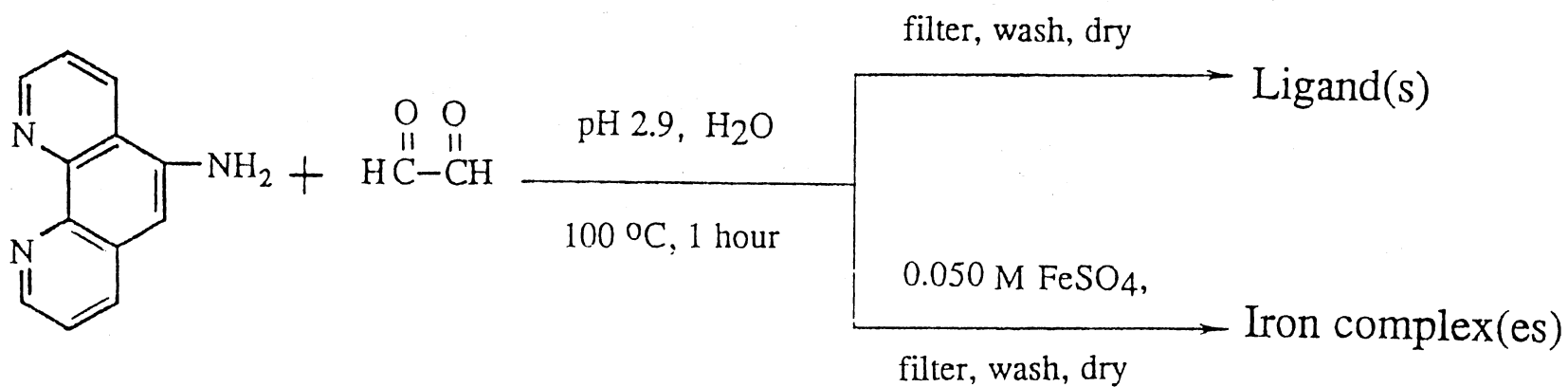


Figure 13. Preparation of Ligands and Iron Complexes

2.90. The insoluble dark brown material produced in this manner was filtered out and repeatedly washed with deionized-distilled water. After washing, the resulting solid was dried at 60°C for about 4 h. The iron complex(es) were obtained by reacting a 0.050 M FeSO_4 solution with the mixture obtained before separation of the solid ligand for 1 h at 90°C. The resulting solid was then filtered out, washed, and dried as indicated for the ligand.

CHAPTER IV
CHEMICAL AND SPECTROMETRIC STUDIES OF
LIGANDS AND IRON COMPLEXES

Elemental Analysis and
Thermal Stability

To characterize the products of the reaction between ethanedial and 5-amino-1,10-phenanthroline, elemental analysis of the products was carried out; a summary of the experimental data is listed in Table 1. Figure 14 also gives a typical thermogravimetric response of the same products. This thermogravimetric information indicated that the preparations typically have between 2 and 3% w/w moisture and start decomposing above 160°C. A residue of 20.6% w/w remained after heating at 550°C; 13% w/w was left after heating at 760°C for 24 h (the residue was insoluble in cold concentrated sulfuric or nitric acid and in polar and nonpolar organic solvents and mixtures of them and was evidently mostly carbonized). After heating for 1 h at 850°C the residue amounted to 12.3% w/w. Inductively coupled plasma analysis of the residue left after heating at 550°C indicated that except for C, H, N, and O there was no element present in more than 0.1% w/w. A 4.0 to 4.5% iron content was measured in the residue of

TABLE 1
 ELEMENTAL ANALYSIS DATA
 (all results in % w/w)

| | | | |
|----------|--|-------|------|
| Ligands | [reaction in absence of Fe(II)] ^a | | |
| CARBON | 57.5; | 57.7; | 57.5 |
| NITROGEN | 9.81; | 9.84; | 9.78 |
| HYDROGEN | 3.1; | 3.2; | 2.78 |

| | | | |
|-----------|---|-------|--|
| Complexes | [reaction in presence of Fe(II)] ^b | | |
| CARBON | 48.03; | 47.92 | |
| NITROGEN | 8.30; | 8.33 | |
| HYDROGEN | 3.51; | 3.49 | |
| IRON | 5.23; | 5.16 | |

a: Average oxygen (by difference) after subtracting moisture content: 27.2%

b: Average oxygen (by difference) after subtracting moisture content: 32.0%

NOTE: Direct elemental analysis for oxygen gave results of 17.6% for the ligands.

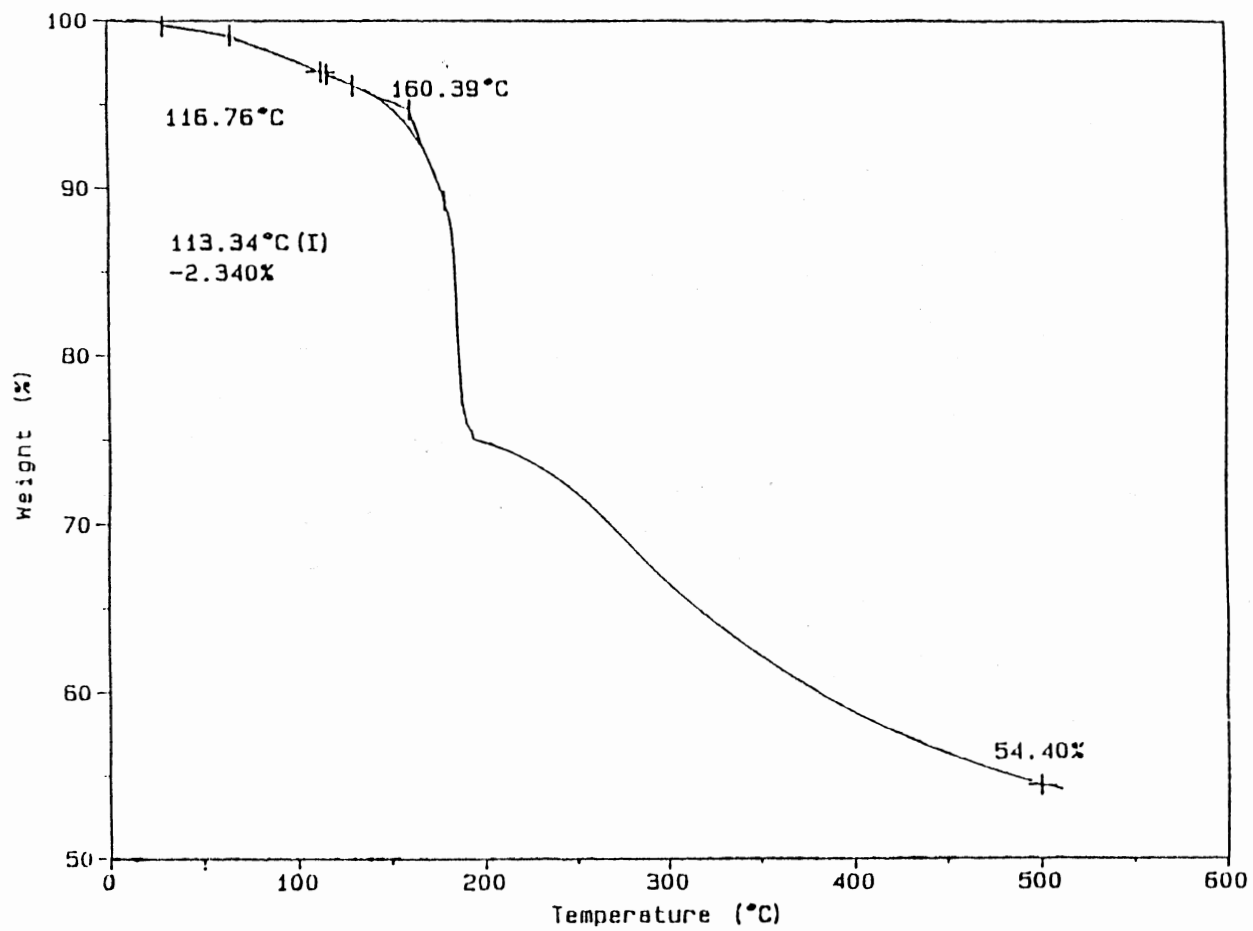


Figure 14. Thermogravimetric Response of Ligands

the iron complexes. Consequently, about 10-12% of the ligand and complexed iron preparations, after intensive heating, remained as a highly insoluble and refractory material. This 10-12% agree with the fact that direct elemental analysis performed for C, H, N, and O accounted only for about 90% of the material in the ligand(s) preparation.

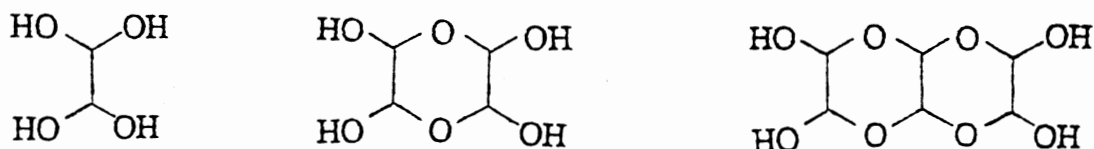
Colorimetric Determination of Iron

The iron content in the iron complex(es) was determined after destruction of the organic matter by digesting with sulfuric-nitric acid mixture and replenishing the nitric acid until total destruction of the carbonaceous material. After digestion, the clear liquid was evaporated almost to dryness. The concentrated sulfuric acid residue containing the iron was quantitatively transferred to a 25-mL volumetric flask with deionized-distilled water and made up to volume with the same solvent. A 5-mL aliquot of this solution was used for colorimetric determination of iron using the 1,10-phenanthroline method [36]. Each determination was performed on a 10-mg sample.

Infrared Spectra

Whipple has thoroughly investigated the behavior of ethanedial [37] and has indicated that ethanedial in aqueous solution is believed to exist primarily as a mixture of hydrated oligomers; the lower-order oligomers are believed

to be a hydrated monomer, a hydrated dimer, and a hydrated trimer as illustrated below:



In direct infrared spectra of the 40% w/w solution of ethanedial, a broad band between 3300 and 3500 cm^{-1} is observed, as expected. It indicates the presence of hydrogen-bonded -OH groups (it should be noted, however, that the sample contains 60% w/w water). Also rather weak but distinct absorption peaks at 1650 cm^{-1} and 1070 cm^{-1} can be seen due to the carbonyl group and the C-O stretching, respectively.

Potassium bromide pellets with 2% w/w ligand (or iron complexes) gave infrared spectra with very strong absorbance at 1100 cm^{-1} revealing an abundance of C-O bonds. Weak absorptions at 1640 cm^{-1} and 1300 cm^{-1} may well be due to C=N and aryl-NH bonds, respectively. Although both KBr and sample were carefully dried before preparing the pellets, a broad absorption band at 3300 cm^{-1} confirms the presence of hydrogen-bonded -OH groups. Absorption due to carbonyl groups was, however, weak.

Table 2 gives a summary of the infrared absorption for ethanedial, 5-amino-1,10-phenanthroline, and both ligands and complexes prepared according to the procedure given in

TABLE 2
 INFRARED ABSORPTION SPECTROSCOPIC FEATURES

5-Amino-1,10-phenanthroline

| | | |
|--------------------------------------|----------------------|---------------------------------|
| 3340 and 3420 cm^{-1} | $-\text{NH}_2$ | (primary amine coupled doublet) |
| 3050 and 600 to 900 cm^{-1} | $=\text{C}-\text{H}$ | (aromatic rings) |
| 1400 and 1600 cm^{-1} | $\text{C}=\text{C}$ | (aromatic rings) |

Ethanedial

| | | |
|-------------------------------|------------------------------|-------------------------------------|
| 3300 to 3500 cm^{-1} | $-\text{OH}$ | (hydrogen bonded, broad absorption) |
| 1650 cm^{-1} | $\text{C}=\text{O}$ | (conjugated) ^a |
| 1070 cm^{-1} | $\text{C}-\text{O}-\text{C}$ | |

Ligands

| | | |
|-----------------------|-----------------------|-------------------|
| 3470 cm^{-1} | $-\text{OH}$ | (hydrogen bonded) |
| 2950 cm^{-1} | $-\text{C}-\text{H}$ | (aliphatic) |
| 1750 cm^{-1} | $\text{C}=\text{O}$ | (unconjugated) |
| 1640 cm^{-1} | $>\text{C}=\text{N}-$ | |

Iron Complexes

Same absorption peaks and bands as for ligands.

a: Because of conjugation effect, carbonyl absorption shifted to lower wavenumbers.

the experimental section. The infrared absorption data point to differences between the starting materials and the products of the reaction. The ligand characteristics, however, dominate the absorption features of the iron complexes.

Ultraviolet-Visible Spectra

Figure 15 shows UV-Vis absorption spectra in the 190-450 nm region for reactants and products. The absorption spectra were obtained for samples of: (A) 0.40 mg.mL⁻¹ ethanedial, (B) 0.020 mg.mL⁻¹ 5-amino-1,10-phenanthroline, (C) 0.020 mg.mL⁻¹ ligand(s), and (D) 0.020 mg.mL⁻¹ iron complex(es) with a solvent mixture of dimethyl sulfoxide 1.0 M in H₂SO₄ and 1.0 M in acetic acid as solvent. The different electronic configurations of the products and the reactants are clearly revealed in the differences observed among the absorption spectra. Again the absorption characteristics of the ligand(s) predominate in the iron complex(es); this agrees with the fact that for the ligands of the 1,10-phenanthroline family the UV spectra of the various metal chelates closely resemble these of the corresponding protonated ligands. The apparent absorptivity, \underline{a} (concentration expressed in g.L⁻¹), at the wavelength of maximum absorption (about 285 nm) for the complex(es) is roughly twice that of the ligand(s).

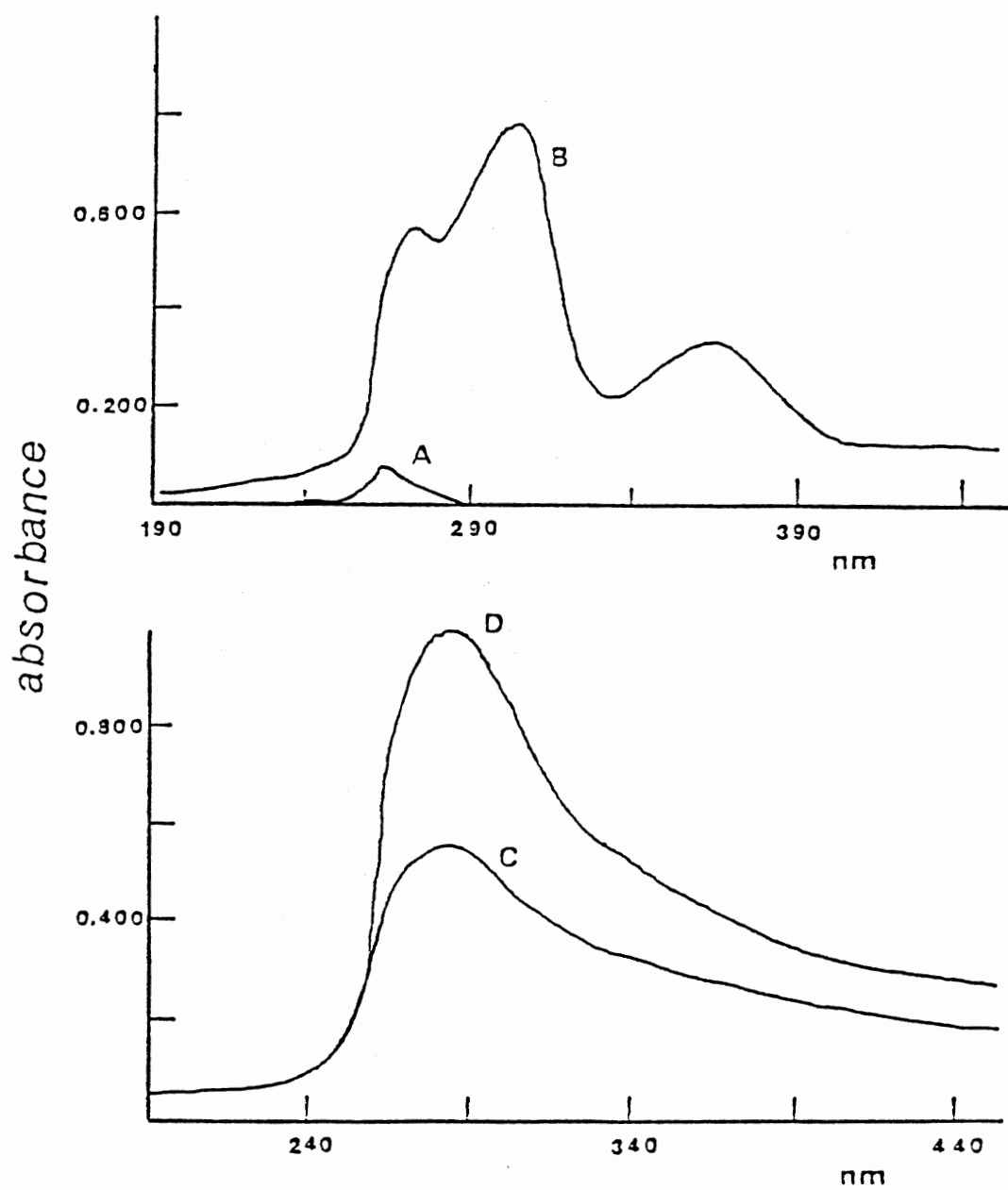


Figure 15. Ultraviolet-Visible Absorption Spectra
A-- 0.40 mg/mL ethanedial,
B-- 0.020 mg/mL 5-amino-1,10-phenanthroline,
C-- 0.020 mg/mL ligand(s),
D-- 0.020 mg/mL iron complex(es).

Comparative Solubility Tests

A comparison is shown in Figure 16 that indicates the difference of absorbance changes with time depicting the rate of leaching into 0.10 M H_2SO_4 (pH 2.0) of tris[4,7-diphenyl-1,10-phenanthroline]iron(II) perchlorate [curve A, absorbance monitored at 315 nm] and the iron complexes of the ligands obtained by reacting ethanedial and 5-amino-1,10-phenanthroline [curve B, absorbance monitored at 305 nm]. The insert reproduced from reference 8 shows the same change, depicting the rate of bleeding from a carbon paste into a 1.00 M KCl solution (under stirring). Curve C was obtained from tris[1,10-phenanthroline]iron(II) perchlorate in a carbon paste prepared with 16.8% (w/w) iron complex and the absorbance monitored at 512 nm. Curve D was obtained from tris[4,7-diphenyl-1,10-phenanthroline]iron(II) perchlorate in a carbon paste with the same proportions as in curve C and the absorbance monitored at 543 nm.

It is clear that the increase in molecular weight decreases the solubility considerably and that the iron complexes obtained in this work offer a very satisfactory long-term stability for use in sensors in continuous-flow systems (e.g. chromatography and flow injection procedures). All absorbance measurements were performed at the wavelength of maximum absorbance in the corresponding medium. Data for curves A and B were obtained by direct contact of solid and aqueous solutions with intermittent shaking; the point on the Y-axis corresponds to a reading obtained 2 h after

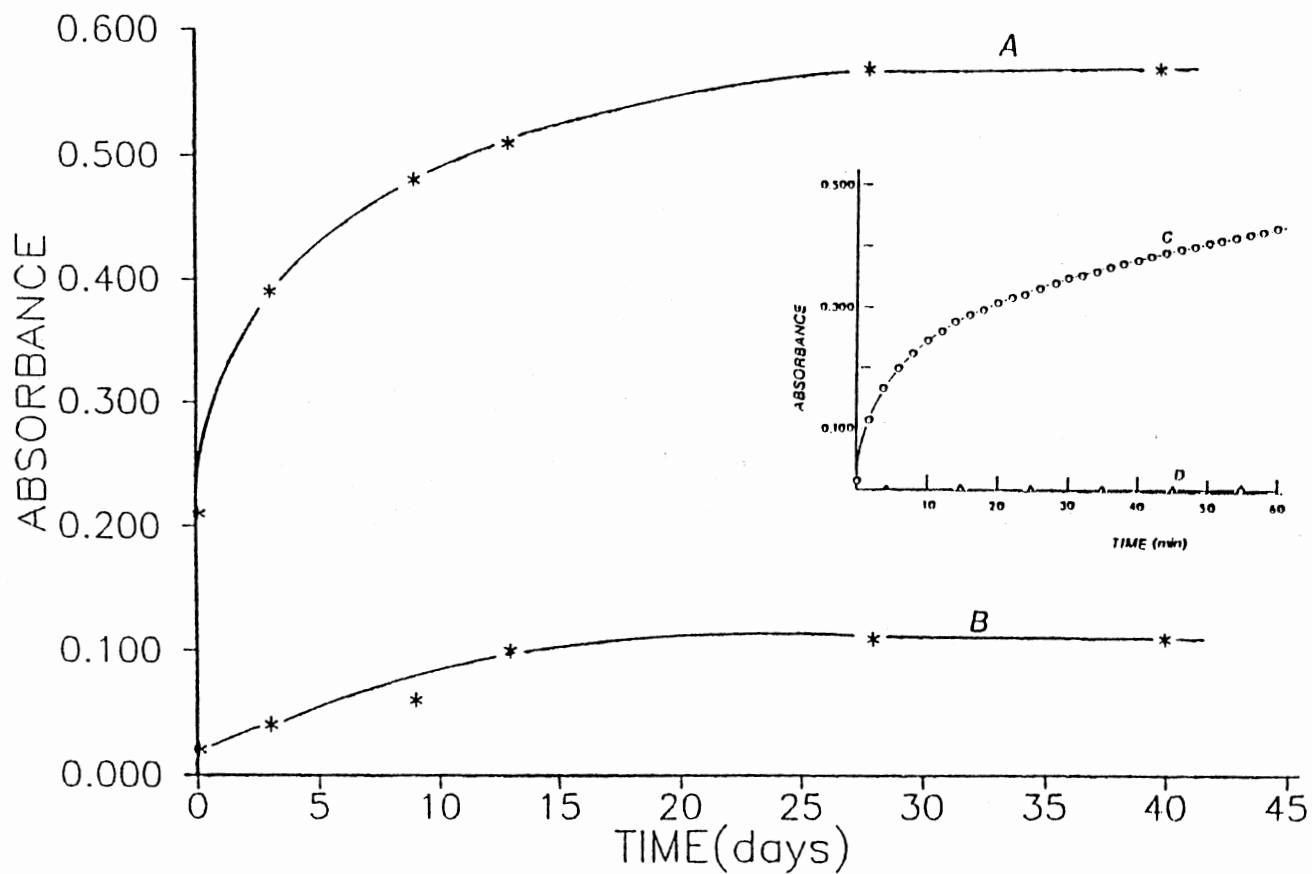


Figure 16. Aborbance Change with Time Depicting the Rate of Leaching
 A, D-- tris[4,7-diphenyl-1,10-phenanthroline]iron(II) perchlorate,
 B---- iron(II) complexes of ligands obtained by reacting
 ethanedial and 5-amino-1,10-phenanthroline,
 C---- tris[1,10-phenanthroline]iron(II) perchlorate,

contact. Although the insert in Figure 16 cannot be directly compared with curves A and B, since absorbance readings should be expected to be higher in the case of these curves, it serves to emphasize the usefulness of the iron complexes discussed here as redox mediators for amperometric detection under continuous flow. Particularly relevant to chromatographic use is the fact that the low solubility of these complexes applies also in several commonly used organic solvents, namely: acetonitrile, chloroform, ethanol, propanone, octane, toluene, benzene, dibutylamine, hexane, nonane, 1-octanol, methyl isobutyl ketone, butyl alcohol, dimethyl sulfoxide, isopropyl ether, and tetrahydrofuran. These solvents represent a wide range of "polarity" from ethanol (solubility parameter = 12.7) to isopropyl ether (solubility parameter = 7.0) and n-octane (solubility parameter = 7.5).

About 60% of the ligand mixture is constituted of the species with molecular weights of 480 and 524 (see next section on liquid secondary ion mass spectrometry). These species contain two chelating moieties per molecule, and even if both moieties are coordinated to the same iron, the resulting complexes are of considerably greater molecular weight than the iron complexes formed by 4,7-diphenyl-1,10-phenanthroline. Since molecular models show certain steric stress if these ligands act as tetradentate units, the possibility of each ligand molecule coordinating with two irons cannot be ruled out, and this should result in

even higher molecular weights for the complexes.

Liquid Secondary Ion Mass Spectrometry

Samples for liquid secondary ion mass spectrometry (LSIMS) were dissolved in a matrix of p-nitrobenzyl alcohol containing 1% trifluoroacetic acid. The LSIMS spectrum of ligands (Figure 17) revealed the following predominant peaks after subtraction of the matrix spectrum: 340 m/z (78%), 372 m/z (55%), 481 m/z (100%) and 525 m/z (85%). Normalizing the abundance to 100% gives a ratio of 25:17:31:27 for the species with molecular weights of 339, 371, 480 and 524, respectively. The same ratio can be obtained from the average of elemental analysis data taking into account that direct elemental analysis performed on C, H, N and O corresponds to 90% of the material in the ligands. Assignment of molecular weight to the species responsible for the peaks, as elaborated below, is based on the assumption that the sample undergoes proton transfer to produce primarily pseudomolecular ions $(M + H)^+$ [38]. The LSIMS spectrum of ethanedial (Figure 18), acquired in a glycerol matrix, showed a series of peaks at 165 (100%), 227 (64%), 243 (41%), 285 (18%), 303 (32%), 319 (38%), 361 (22%) and 395 (13%) m/z . The multiple peaks observed with ethanedial reflect the fact that it exists in different degrees of polymerization in aqueous solution [37, 39] and the absence of these peaks in the spectra for the ligands

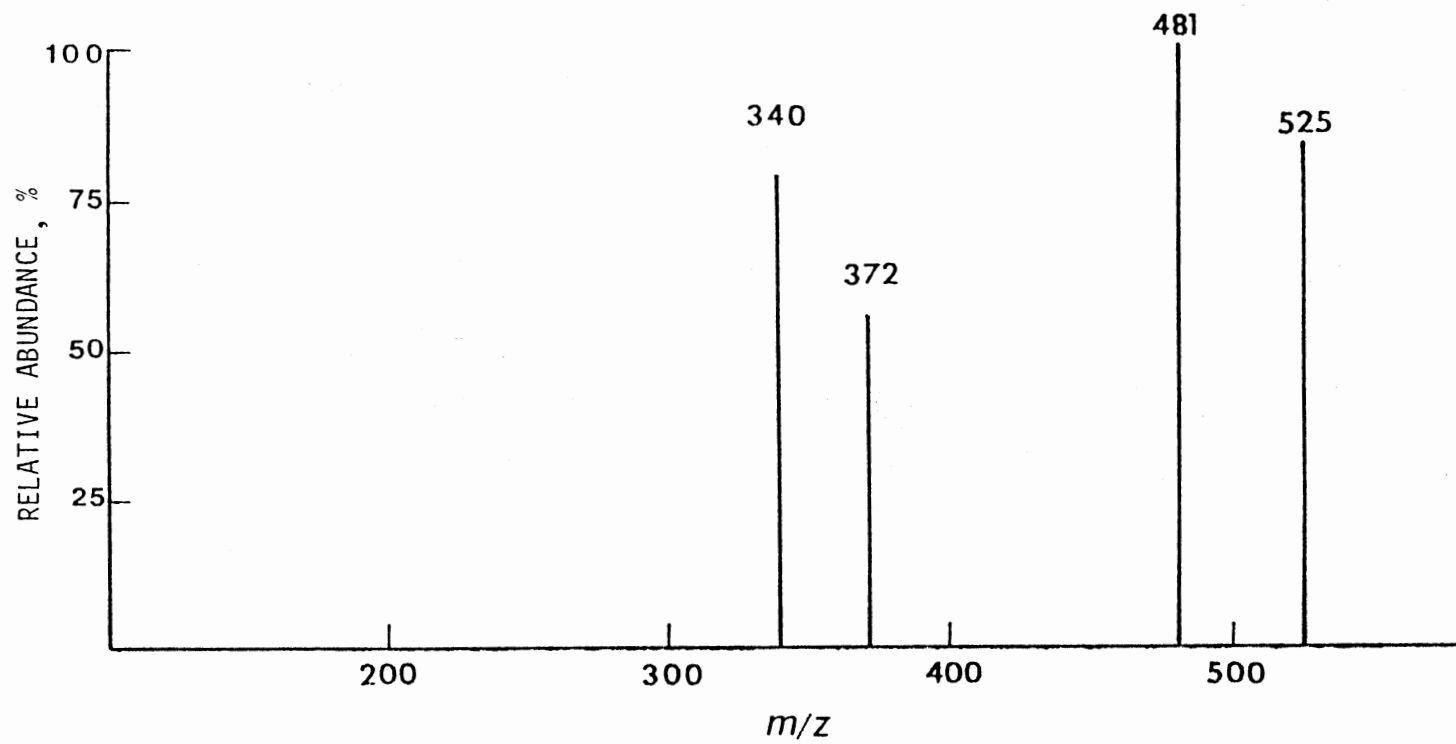


Figure 17. Liquid Secondary Ion Mass Spectrum of Ligands

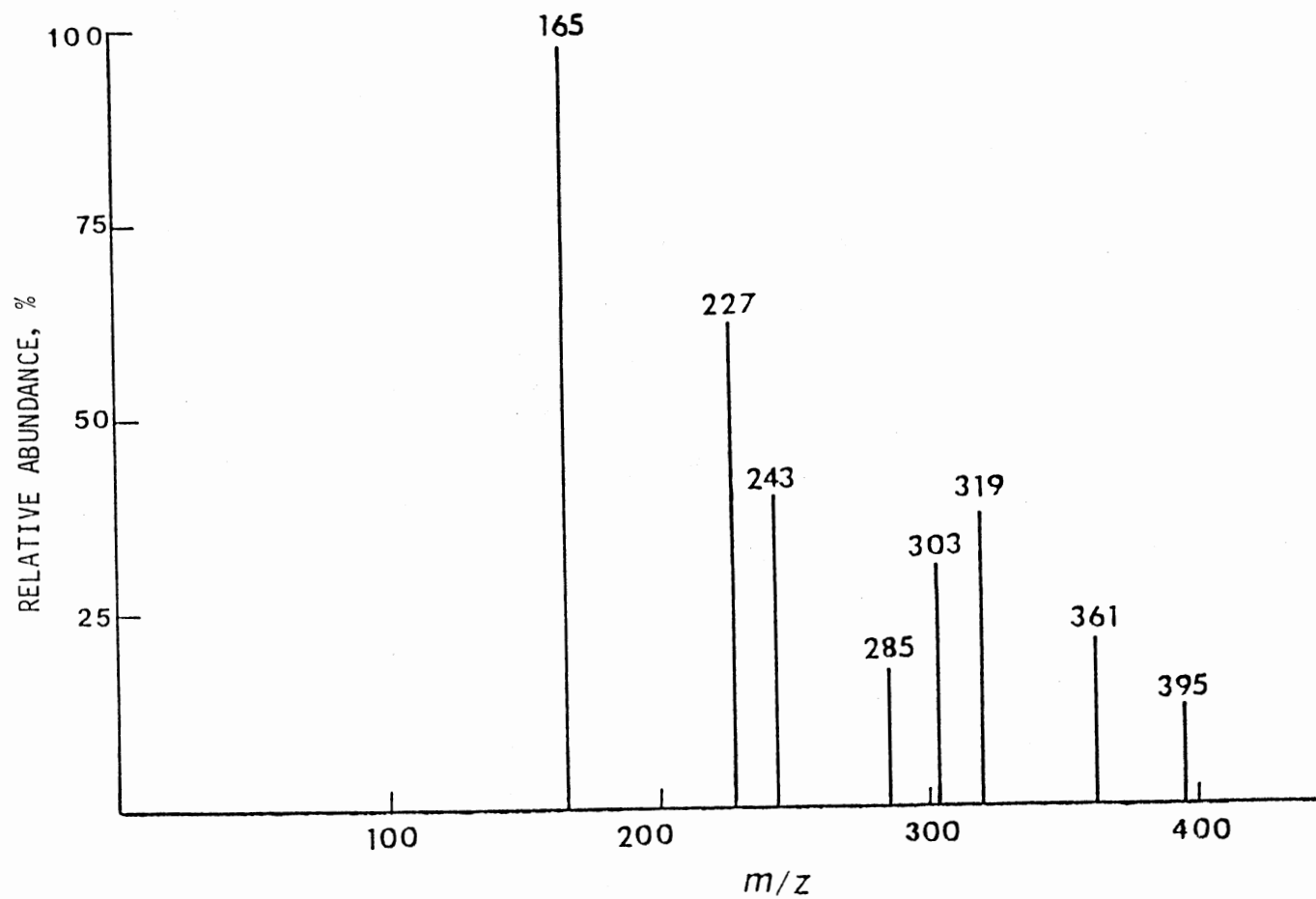
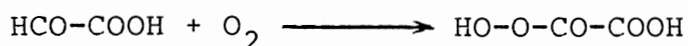


Figure 18. Liquid Secondary Ion Mass Spectrum of Ethanedial

indicates total reaction with the 5-amino-1,10-phenanthroline, as would be expected. The excess, unreacted dialdehyde is expelled during washing after preparation of the ligands; the presence of free (reactive) aldehyde groups in the ligands was clearly revealed, however, by applying the Tollens' reagent test [40].

Structural Formulation and Reaction
Mechanism for Preparation
of Ligands

By combining and utilizing the information reported above one can formulate structures that are not in contradiction but supported by such information. Some basic assumptions were taken into consideration, namely: (a) C=N linkages are favored over C-N, when feasible, in the bridging of the 5-amino-1,10-phenanthroline moiety and the ethanedial oligomeric portion of the molecules in consideration of the Schiff-base type reaction, (b) a ring structure with alternate -C-O-C- bonds is favored in the oligomeric ethanedial units over chain structures, (c) chemical species such as HCO-COOH and HO-O-CO-COOH can be derived from the dialdehyde by reactions such as:



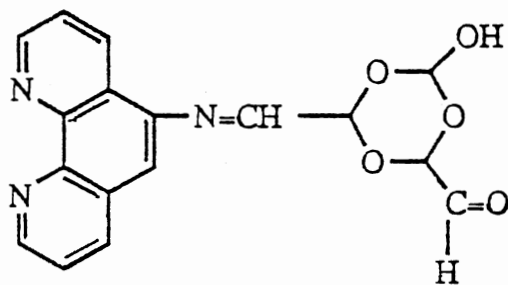
The four molecular ion peaks in the LSIMS spectrum

indicates a mixture of four species with molecular weights of 339, 371, 480 and 524 mass units. For each of these species a proposed structure and a reaction path leading to their formation is indicated below.

Ligand I

MW = 339 mass units

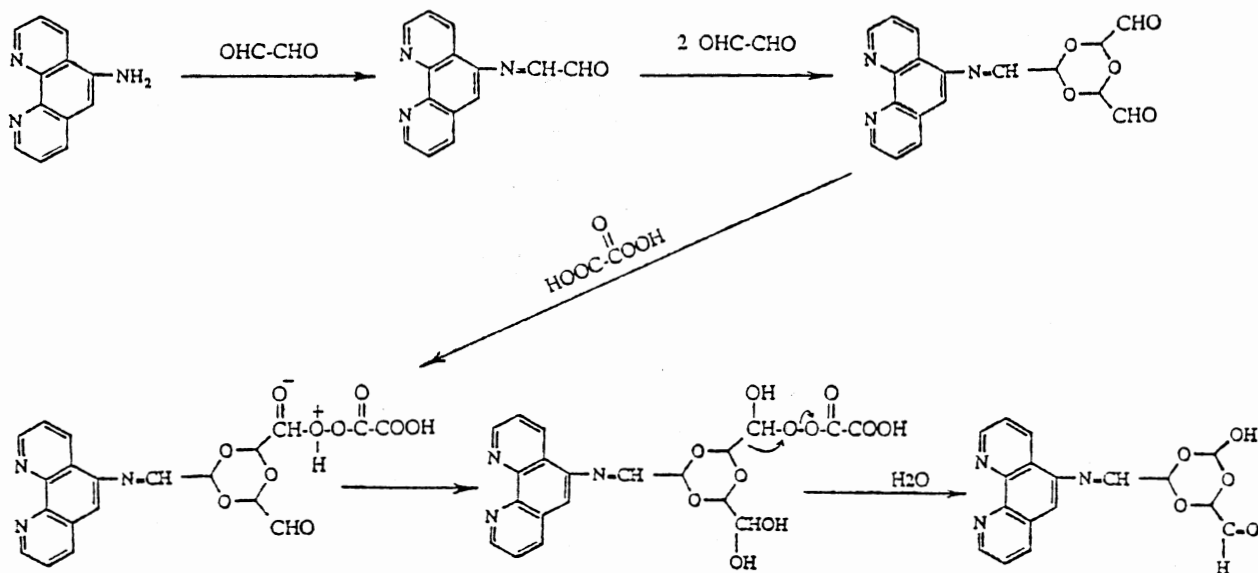
Structure:



Elemental composition:

C, 60.2%; H, 3.8%; N, 12.4%; O, 23.6%.

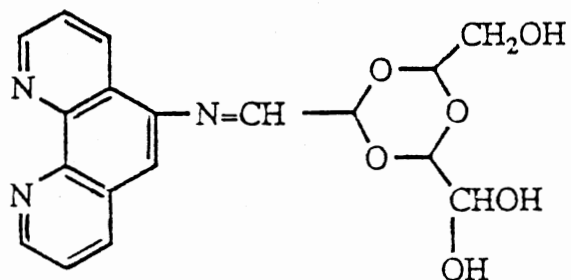
Chemical reactions leading to its formation:



Ligand II

MW = 371 mass units

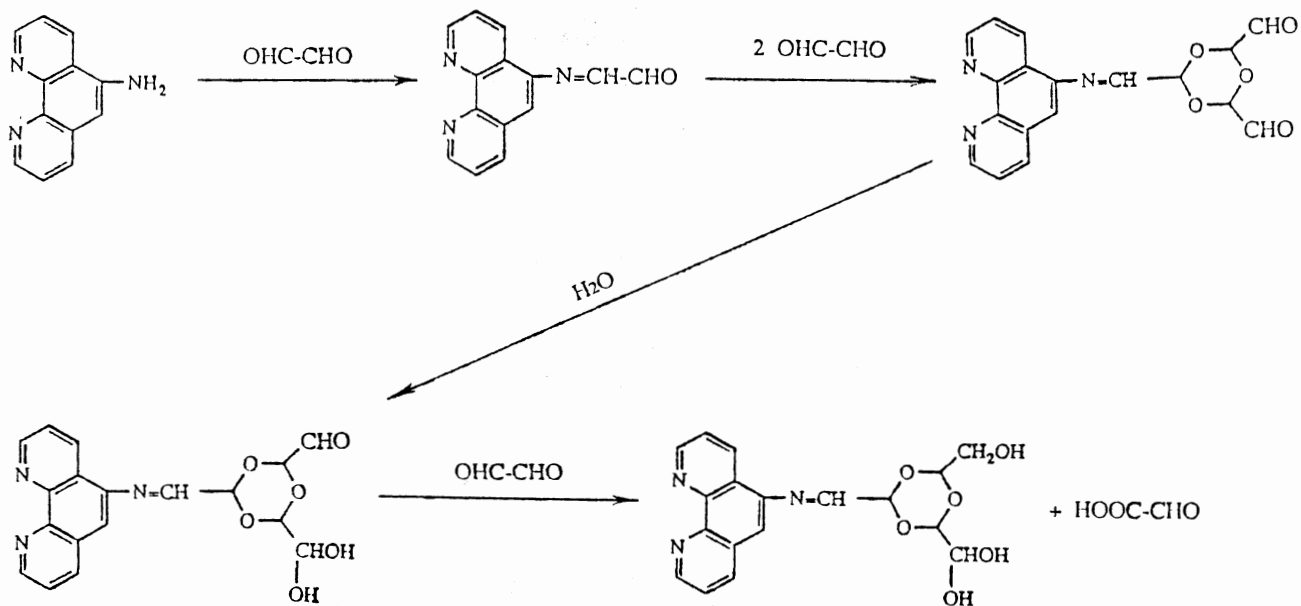
Structure:



Elemental composition:

C, 58.2%; H, 4.6%; N, 11.3%; O, 25.9%.

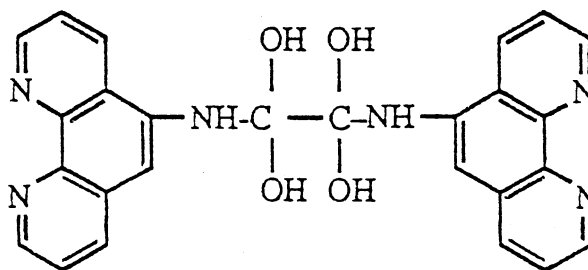
Chemical reactions leading to its formation:



Ligand III

MW = 480 mass units

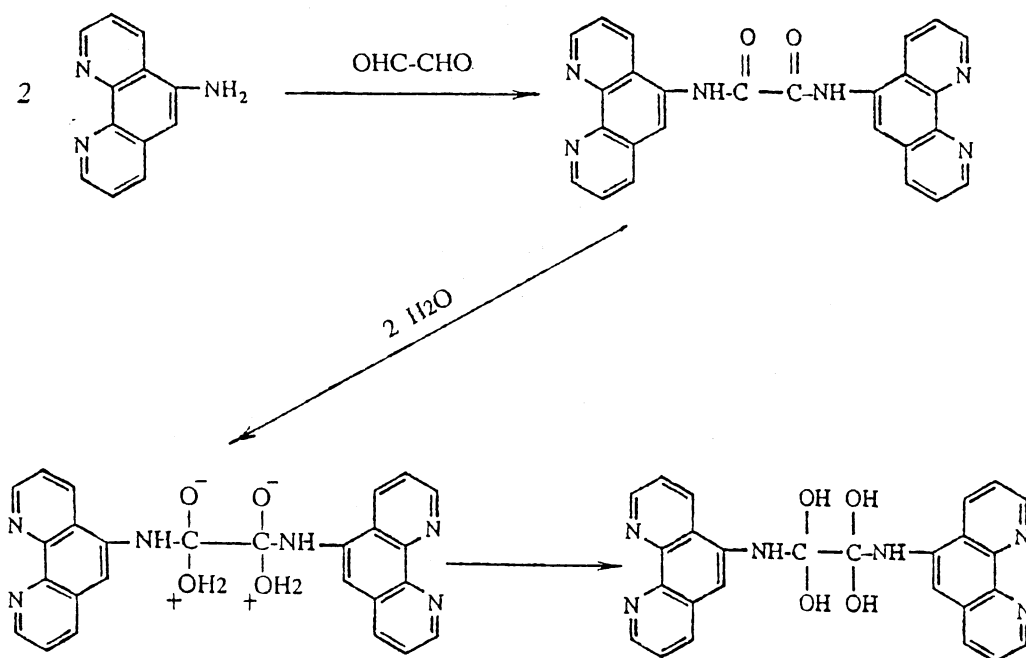
Structure:



Elemental composition:

C, 57.5%; H, 4.2%; N, 11.7%; O, 26.7%.

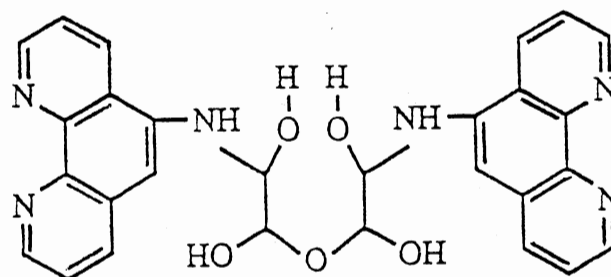
Chemical reactions leading to its formation:



Ligand IV

MW = 524 mass units

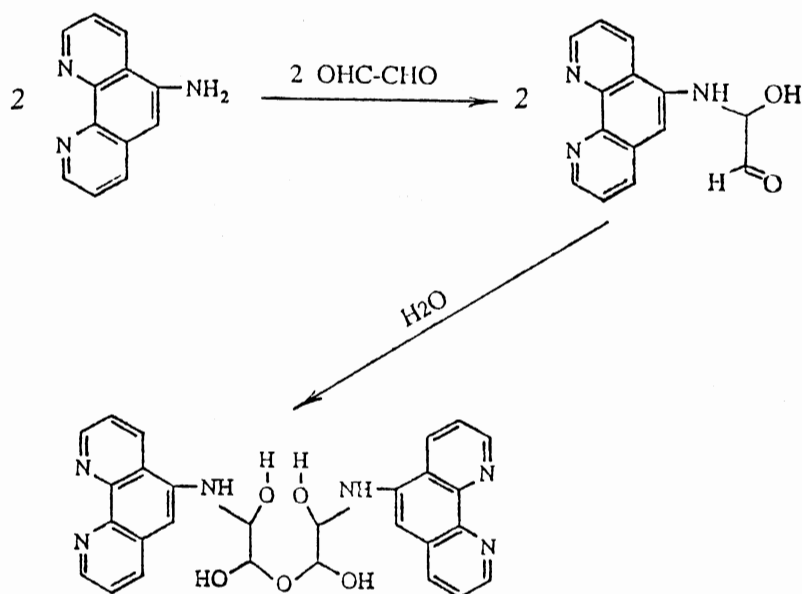
Structure:



Elemental composition:

C, 64.1%; H, 4.6%; N, 16.0%; O, 15.3%.

Chemical reactions leading to its formation:



Although bridging of two 1,10-phenanthroline moieties has been experimentally rather elusive (present only in two of the four structures proposed for the ligands) the reaction of ethanedial and 5-amino-1,10-phenanthroline has resulted in ligands involving a 1,10-phenanthroline moiety and oligomeric units derived from the dialdehyde. As expected, however, the iron complexes of these species are highly insoluble but hydrophilic in nature and useful as redox mediators when incorporated, by direct admixing, into carbon paste formulations. The electrochemistry and analytical application of these redox mediators for detection and determination in continuous-flow systems is discussed in subsequent chapters.

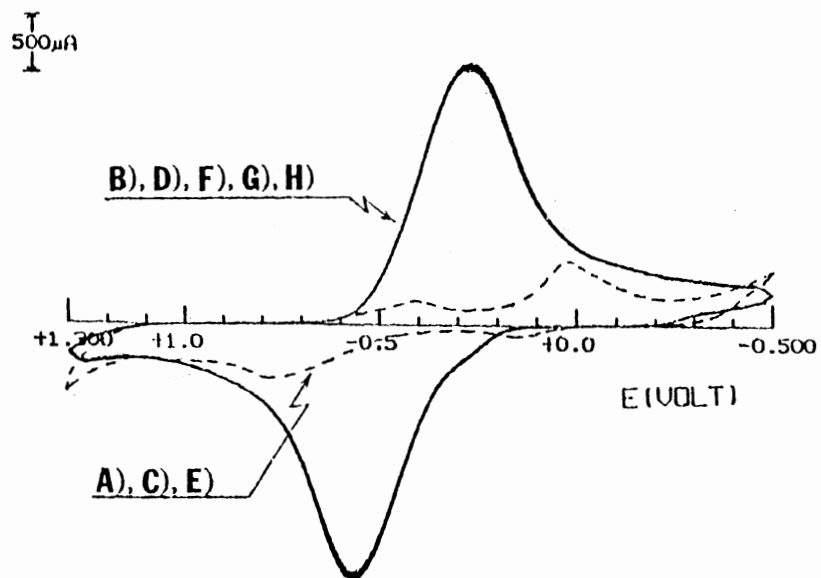
CHAPTER V
OBSERVATIONS ON CARBON PASTE ELECTRODES
MODIFIED BY ADMIXING WITH LIGANDS
AND IRON COMPLEXES

Attachment and Removal of Metal Ions

Ligand-modified (10%) carbon paste preparations were used as working electrodes, under different experimental conditions, to obtain cyclic voltammetric information in the -0.500 V to +1.300 V range and at a scan rate of 100 mV/s. Figure 19 shows the cyclic voltammetric behavior of carbon paste electrodes modified by direct admixing of 10% (w/w) ligands or iron complexes of the same ligands with 55% graphite powder and 35% mineral oil in a supporting electrolyte solution of 0.10 M H_2SO_4 .

- (A) was obtained with the ligand-modified carbon paste electrode directly immersed in supporting electrolyte solution,
- (B) same as in (A) but after immersion in a 0.050 M $FeSO_4$ solution at pH 5.0 for one h,
- (C) same as in (B) but after polishing the electrode surface on a clean card,
- (D) same as in (C) but after reimmersion in iron(II) solution as in (B),

10% modified CPE — { 10% modifier
55% graphite powder
35% mineral oil



A) 10% ligand CPE

B) after treating with 0.050 M FeSO_4 solution

C) after being polished on a card

D) after treating with 0.050 M FeSO_4 solution again

E) after treating with 0.10M EDTA

F) after treating with 0.050M FeSO_4 solution again

G) 10% iron complex CPE

H) after being polished on a card

Figure 19. Cyclic Voltammetric Behaviors of Ligand-Modified CPE after Attachment and Removal of Iron(II)

- (E) same as in (D) but after immersion in a 0.10 M EDTA solution at pH 7.00 for three h,
- (F) same as in (E) but after reimmersion in iron(II) solution as in (B),
- (G) carbon paste electrode modified by direct admixing of the iron(II) complexes of the ligands used in (A)-(F),
- (H) same surface as in (G) but after polishing on a clean card.

From Figure 19 it can be seen that no redox peaks are observed in absence of iron(II) but a pair of sharp peaks ($E_{pc} = 0.320$ V, $E_{pa} = 0.540$ V) appear on contact with solutions of Fe(II) and these are the same peaks observed when modification is performed by direct admixing of the corresponding iron complexes. The superficial complexes can be removed by polishing the surface on a clean card or by immersing in a 0.10 M EDTA solution of pH 7.00. As shown in Figure 19, the process of attaching iron(II) ions and removing them is a reversible one. A similar trend was observed when the iron sulfate was replaced with a 0.10 M CuSO_4 solution. Values of $E_{pcathodic}$ at -0.240 V and $E_{panodic}$ at $+0.175$ V were obtained in this case but the peaks were not as well developed as in the case of iron.

Other metal ions were similarly tested [nickel(II), cobalt(II), cadmium(II) and manganese(II)], but no redox peaks were observed in the voltage region explored. The presence of these ions in the electrolyte solution did not significantly affect the response of the iron

complex-modified or copper complex-modified preparations.

Figure 20 shows cyclic voltammograms of (A) a ligand-modified electrode after immersion in 0.50 M copper(II) solution for 30 min and (B) an iron complex-modified electrode after immersion in a copper(II) solution. Evidently there is partial replacement of the iron center by copper and the voltammogram represents the electrochemistry of both redox couples, and indicates the presence of a surface with two different redox centers, Fe(II)/Fe(III) and Cu(I)/Cu(II), immobilized on it.

Effect of Electrolyte Solution

To assess the effects of different supporting electrolytes and select a suitable supporting solution, nine commonly used electrolyte solutions were divided into three groups according to their chemical composition and examined by cyclic voltammetry using a 10% iron complexes-modified carbon paste electrode as working electrode, a Ag-AgCl (3.0 M KCl) as reference electrode, a platinum wire as auxiliary electrode, and a scan rate of 100 mV/s.

Figure 21 shows a comparison of cyclic voltammograms produced in these different supporting electrolyte solutions:

- a) 0.10 M K_2SO_4 , b) 0.10 M KCl, c) 0.10 M $KClO_4$,
 d) 0.050 M K_2SO_4 + 0.050 M H_2SO_4 , e) 0.050 M KCl
 + 0.050 M HCl, f) 0.050 M $KClO_4$ + 0.050 M $HClO_4$,
 g) 0.10 M H_2SO_4 , h) 0.10 M HCl, i) 0.10 M $HClO_4$.

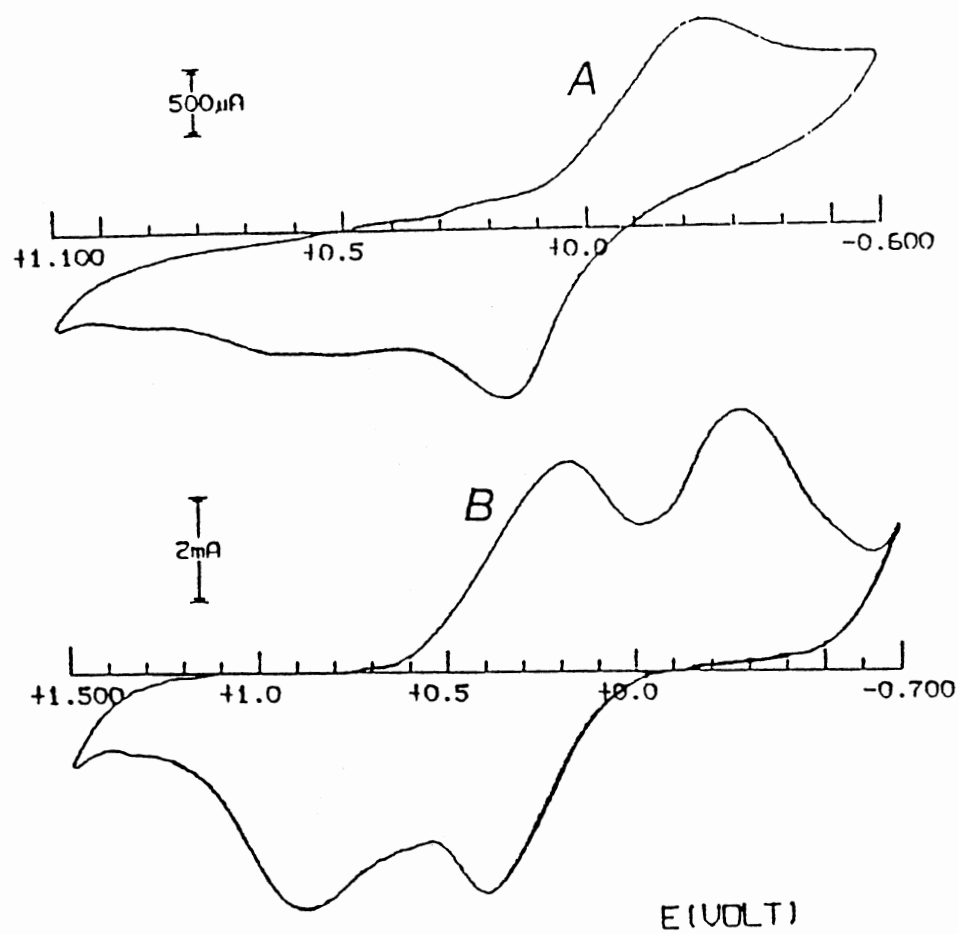


Figure 20. Cyclic Voltammetric Behavior of Copper(II) Attached to a Ligand Modified Carbon Paste Electrode

A--ligand-modified electrode,
B--iron complex-modified electrode.

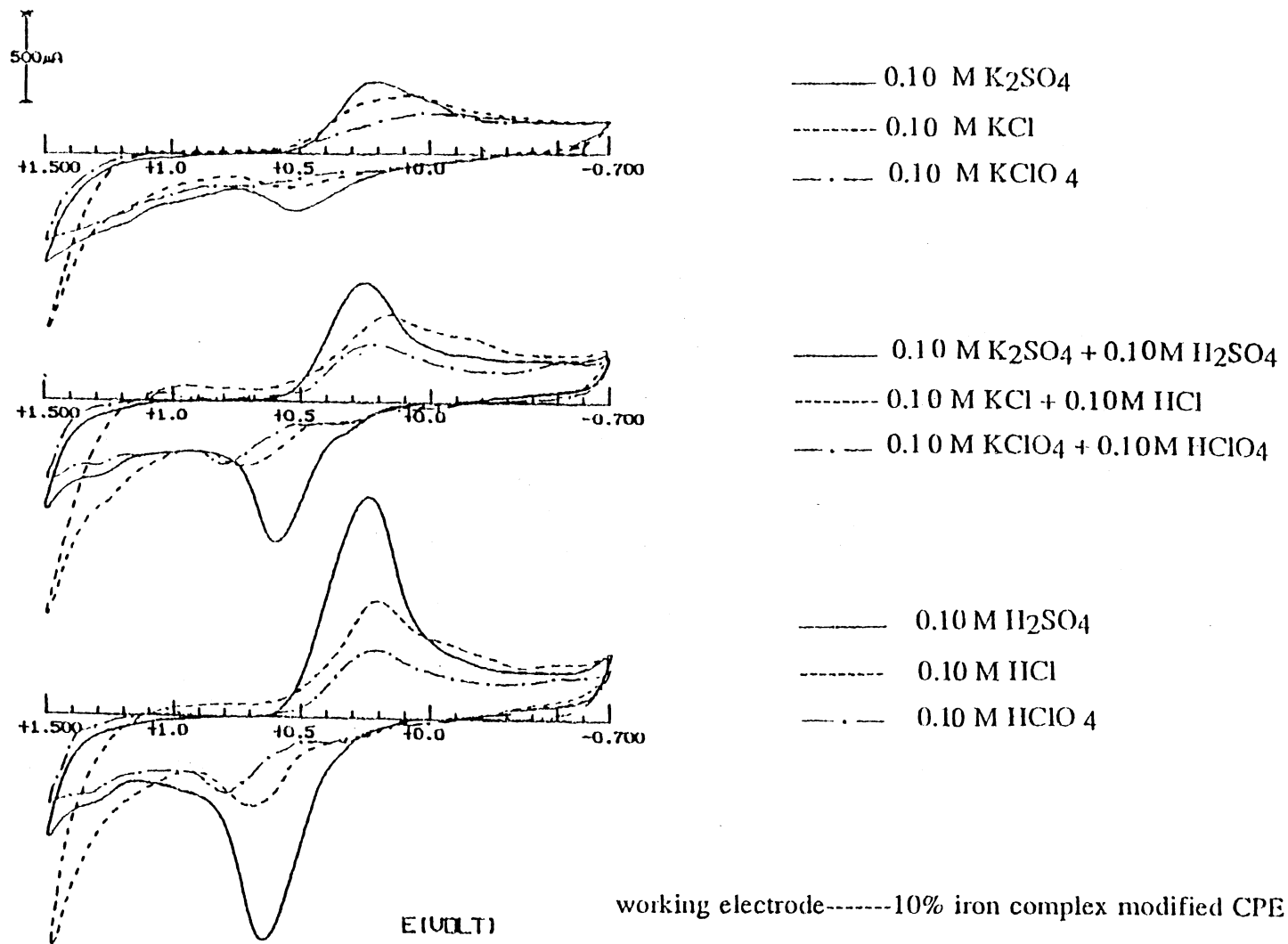


Figure 21. Cyclic Voltammograms Obtained in Different Supporting Electrolyte Solutions

This comparison indicates that in electrolytes containing SO_4^{2-} anions the working electrode can give better current response than in the other anion media and in 0.10 M H_2SO_4 solution (pH 2.0) the Fe(II)/Fe(III) redox centers in the modified electrode shows the best electrochemical behavior among all nine electrolytes. Hence, the 0.10 M H_2SO_4 was chosen as supporting electrolyte solution for subsequent electrochemical studies.

Stability Studies

Although incorporation of redox Fe(II)/Fe(III) centers is very conveniently done by the immersion procedure, the long-term stability is not as good as when modification is performed by admixing with the pre-formed iron complexes instead of ligands. For electrodes modified by admixing of the ligands and superficial complexing of iron(II) ions, the ratio of peak current to background current decreases 30% after three days and 50% after five days. For electrodes obtained by admixing with iron complexes good stability is achieved as indicated in Figure 22. Storing in air resulted in a loss of peak current of only 20% after 18 days and the signal remained constant after this for at least 32 days.

10% Ligand CPE (after treating with Fe(II)):

| | | | | | | |
|----------------------|------|------|------|------|------|------|
| storing time (hour): | 0 | 20 | 44 | 72 | 92 | 120 |
| signal/background: | 4.82 | 2.32 | 3.79 | 3.54 | 1.56 | 2.67 |

10% iron complex CPE:

A---fresh preparation
B---after storing in air for 32 days

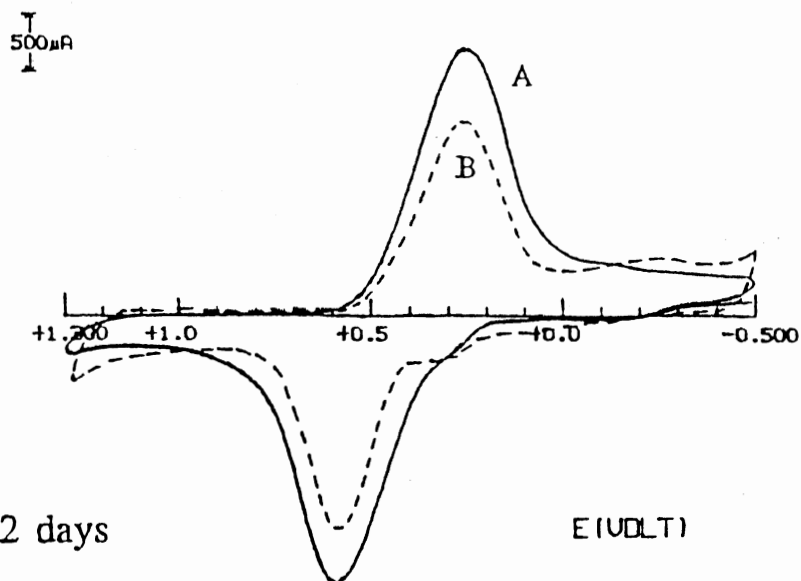


Figure 22. Stability Test of the Modified Carbon Paste Electrode

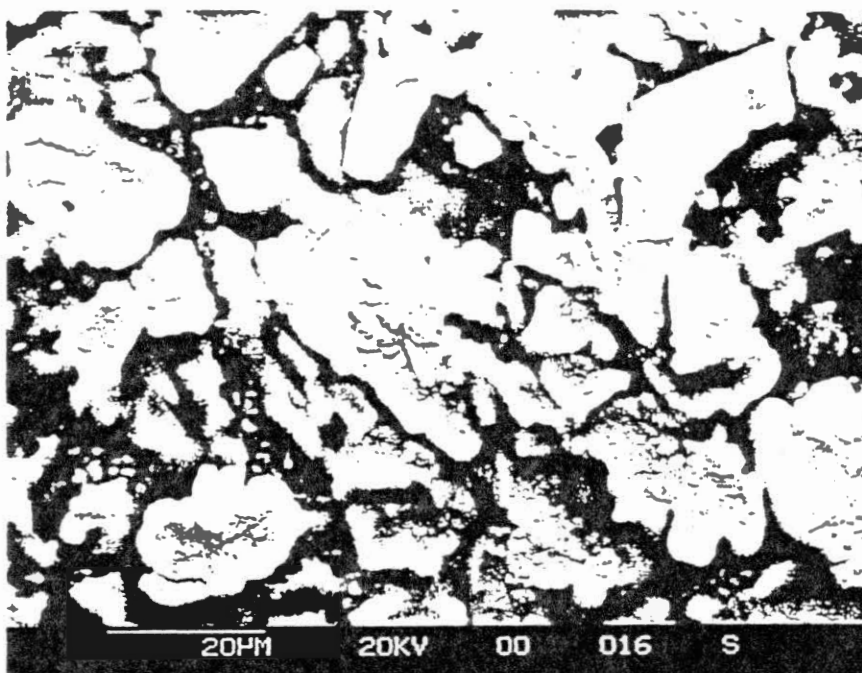
Scanning Electron Microscopy of Electrode Surfaces

Figure 23 shows scanning electron micrographs (SEM) of the surfaces of unmodified, ligand-modified, and iron complex-modified carbon paste preparations, obtained at 1000 times amplification. The surfaces of the ligand-modified and iron complex-modified carbon paste in photographs B and C look very similar but seem a little less rough than that of unmodified ones.

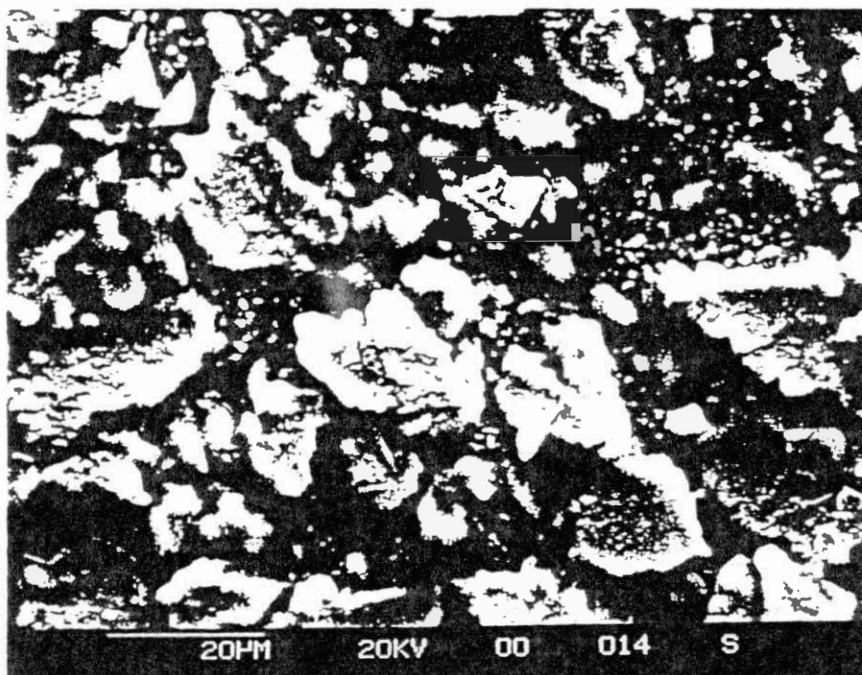
Effects of Potential Scan Rate

Cyclic voltammetry with 2% (w/w) iron complex-modified carbon paste electrode in 0.10 M H_2SO_4 supporting solution has been performed to investigate the effect of scan rate.

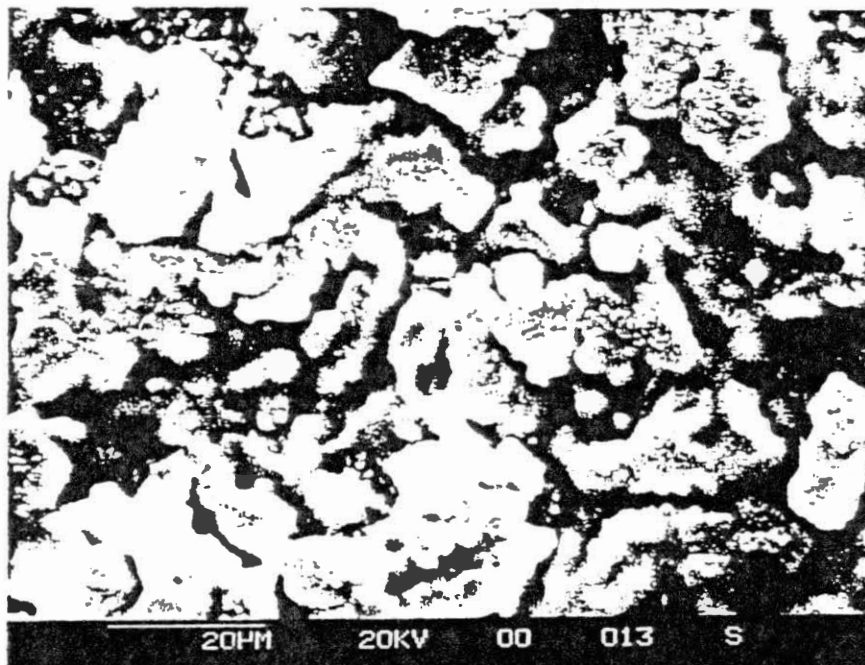
Cyclic voltammetry is a form of linear sweep voltammetry that is used principally to characterize the redox properties of chemical species and to study the mechanisms of redox reactions. In cyclic voltammetry, the triangular wave form in Figure 24-a is applied to the working electrode. The portion between times t_0 and t_1 represents a linear voltage ramp. However, unlike ordinary single sweep voltammetry, in which the ramp is applied over a period of a few minutes, cyclic voltammetry uses time of just a few seconds. Furthermore, in cyclic voltammetry the ramp is then reversed to bring the potential back to its initial value at time t_2 . The cycle may be



A --- Surface of Unmodified Electrode



B --- Surface of Ligand-Modified Electrode



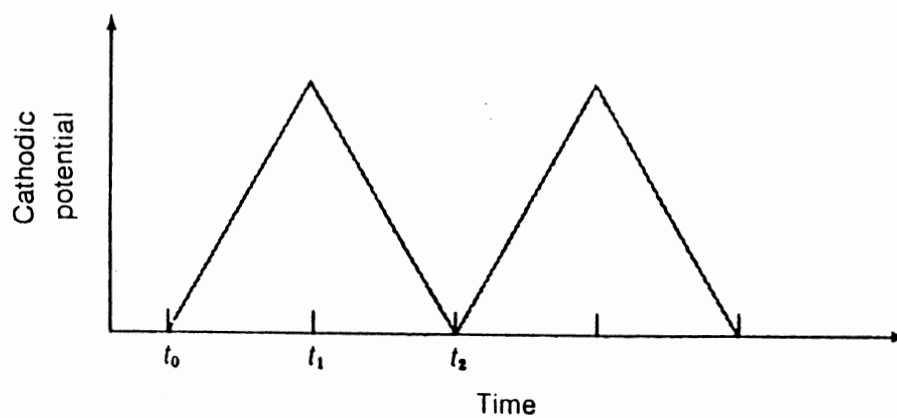
C— Surface of Iron Complex modified Electrode

Figure 23. Scanning Electron Micrographs of Carbon Paste Electrode Surfaces

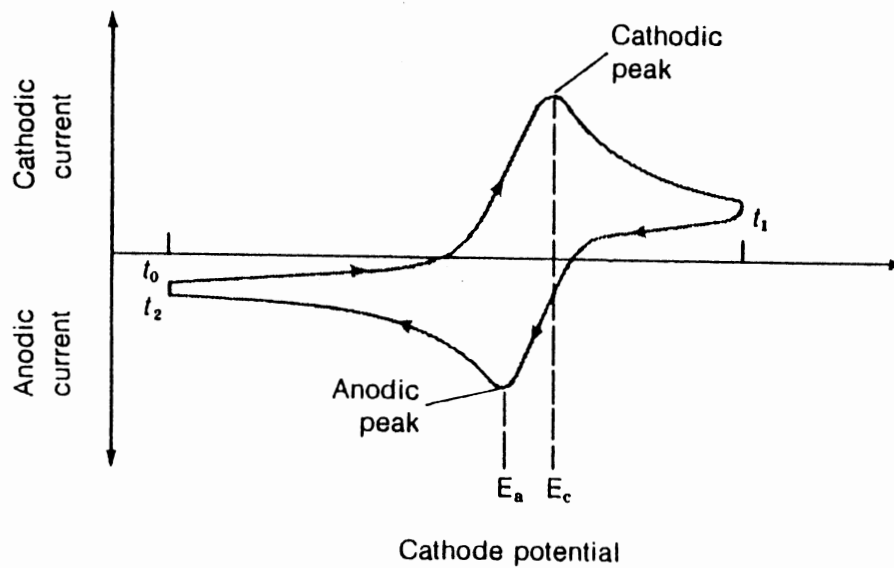
repeated many more times. In a typical cyclic voltammogram (Figure 24-b) the initial portion of the current-potential curve looks like that of an ordinary voltammogram, with a residual current followed by a cathodic wave. Instead of leveling off at the top of the wave, the current decreases as the potential is increased further. This happens because the electroactive species becomes depleted in the region around the electrode surface. In this example, at the time of the maximum voltage (t_1), the cathodic current has decayed to a fairly small value. After t_1 , the potential change is reversed, but a cathodic current continues to flow because the potential is still negative enough to reduce the analyte. When the potential becomes sufficiently less negative, the reduced analyte in the layer around the electrode surface begins to be oxidized. This gives rise to a corresponding anodic current peak. Finally, as the reduced species is depleted, the anodic current decays back toward the initial value of the residual current. For a reversible electrode reaction, the difference in potential between the anodic and cathodic peaks is

$$E_{pa} - E_{pc} = 0.059/\underline{n} \quad (\text{Volt, at } 25^\circ\text{C})$$

where \underline{n} is the number of electrons in the half-reaction. With a quasi-reversible reaction, the cathodic and anodic peaks become more drawn out and more separated. For an



(a) Waveform Used in Cyclic Voltammetry



(b) A Schematic Cyclic Voltammogram for a Reversible Process

Figure 24. Waveform Used and Typical Voltammogram in Cyclic Voltammetry

irreversible process, where the oxidation is very slow, no anodic peak would be seen.

A study of the peak currents and potentials as functions of the scan rate of applied potential in cyclic voltammetry permits evaluations of several important electrochemical properties of the modified electrodes. Table 3 lists the current and potential data of interest as functions of scan rate. According to these experimental results, the effect of potential scan rate is discussed below.

Effect on Peak Current

It is found that when the scan rate increases both anodic and cathodic peak currents increase too. The relation between cathodic peak current and the scan rate is not linear as would be expected for a truly immobilized or adsorbed species, which are characterized by peak currents directly proportional to the scan rate [41]. However, linear relationships between the peak currents and the square root of the scan rate are obtained and can be described by the following linear regression equations:

$$i_{pa} (\mu A) = (36 \pm 2) + (1.5 \pm 0.1) v^{1/2}$$

$$i_{pc} (\mu A) = (19 \pm 2) + (1.8 \pm 0.1) v^{1/2}$$

with v in $\text{mV}\cdot\text{s}^{-1}$. According to the cyclic voltammetry

TABLE 3

DEPENDENCE OF PEAK CURRENT AND PEAK SEPARATION ON SCAN RATE FOR COMPLEX-MODIFIED CARBON PASTE ELECTRODE

| Scan Rate (mV/s) | i_{pc} (μ A) | i_{pa} (μ A) | E_{pc} (V) | $(E_{pa}-E_{pc})$ (mV) | $(E_{pa}+E_{pc})/2$ (V) |
|---------------------|------------------------|------------------------|-----------------|---------------------------|----------------------------|
| 5 | 2.1 | 1.8 | 0.42 | 60 | 0.44 |
| 10 | 7.1 | 6.3 | 0.41 | 65 | 0.44 |
| 50 | 19.0 | 24.6 | 0.36 | 155 | 0.44 |
| 100 | 29.2 | 39.6 | 0.32 | 230 | 0.44 |
| 150 | 39.2 | 51.7 | 0.29 | 270 | 0.43 |
| 200 | 42.5 | 57.5 | 0.28 | 300 | 0.43 |
| 250 | 48.3 | 61.7 | 0.27 | 320 | 0.43 |
| 300 | 51.2 | 64.2 | 0.26 | 340 | 0.43 |
| 350 | 52.5 | 65.0 | 0.25 | 360 | 0.43 |
| 400 | 53.3 | 65.8 | 0.24 | 380 | 0.43 |
| 500 | 58.3 | 70.0 | 0.22 | 410 | 0.43 |
| 600 | 61.7 | 73.3 | 0.21 | 430 | 0.43 |
| 700 | 65.0 | 75.0 | 0.20 | 450 | 0.43 |

response function, this indicates that the reactions taking place at the electrode surface are controlled by a semi-infinite diffusion which occurs within a thin solvent layer (2 to 50 μm) at the electrode surface [41]. This relation is in agreement with the linear potential sweep current-potential equation which is characterized by i being directly proportional to $v^{1/2}$.

Effect on the Peak Potential Difference

As the scan rate decreases, the difference between the anodic peak potential, E_{pa} , and the cathodic peak potential, E_{pc} , decreases and tends to a value of 0.059 V. This indicates that when the scan rate decreases, the reaction process is allowed more time to finish and it changes from quasi-reversible to a reversible one.

Effect on the Average Peak Potential

No matter if the scan rate is changed or not, the average potential between the anodic and the cathodic peaks, E° , is always constant. This allows a convenient evaluation of an important electrochemical parameter, the formal electrode potential E°_f , according to the following equations [42]:

$$E^{\circ} = (E_{pa} + E_{pc})/2 = 0.435 \text{ (Volt)}$$

$$E^{\circ}_f = (E_{pa} + E_{pc})/2 + (0.029/n) \text{Log}(D_{ox}/D_{red}) = E^{\circ}$$

provided that D_{ox} and D_{red} , the diffusion coefficients for oxidized and reduced species, are very close and can be considered equal. This should be the case with the modifier used in this work.

Evaluation of Cathodic Transfer Coefficient

As can be seen from Table 3, as the scan rate increases, the cathodic peak potential E_{pc} shifts to more negative values. A plot of E_{pc} vs $\log v$ is linear with a slope of $-(138 \pm 3)$ and the following equation applies [42]:

$$E_{pc} = C - (30/\alpha n) \log v$$

in which C is a constant related with E^0 , and α is the transfer coefficient for the cathodic process, which serves as a measure of the symmetry of the energy barrier of the electrode reaction and ranges between $0 < \alpha < 1$. From this relation, since n equals 1 for Fe(II)/Fe(III) redox center, a value of 0.22 was extracted for α in the example discussed here. It is known [42] that in cyclic voltammetry for symmetric peaks, $\alpha = 0.5$ and $i_{pc} = i_{pa}$, and for asymmetric peaks, $\alpha > 0.5$ with $i_{pc} > i_{pa}$ or $\alpha < 0.5$ with $i_{pc} < i_{pa}$. In our case, we have $\alpha = 0.22$ which is less than 0.5 and is in agreement with the experimental observation that i_{pc} is less than i_{pa} .

Analytical Application

Amperometric Sensor

An important application of chemically modified carbon paste electrodes is their use as amperometric sensors in continuous-flow systems. Chemical species which can undergo oxidation or reduction with iron(II) or iron(III) will respond by generating a current signal at the modified electrode and thus can be detected and determined amperometrically.

The diagram of the continuous-flow system used in this work is as shown in Figure 12. The electrolyte solution carried by gravity from reservoir (R) continuously feeds into the system. The sample is injected via a Teflon rotary valve (V). A carbon paste electrode modified with 10% (w/w) iron complexes is used here as the working electrode (WE) and is arranged in a thin-layer cell form (Figure 25). A 0.10-mm-thick Teflon spacer provides the gap for passage of solution in the thin-layer cell compartment. The sample and carrier also pass in front of a reference electrode (RE) and an auxiliary electrode (AE) to complete a three-electrode cell. A potentiostat-amplifier unit (D) is used to control the potential applied to the working electrode and to detect the resulting current signal. For each injection of sample, a sharp current peak will be obtained at the recorder (RD). As indicated in Figure 12, for the same sample, the peak current will keep the same height for repeated injections at

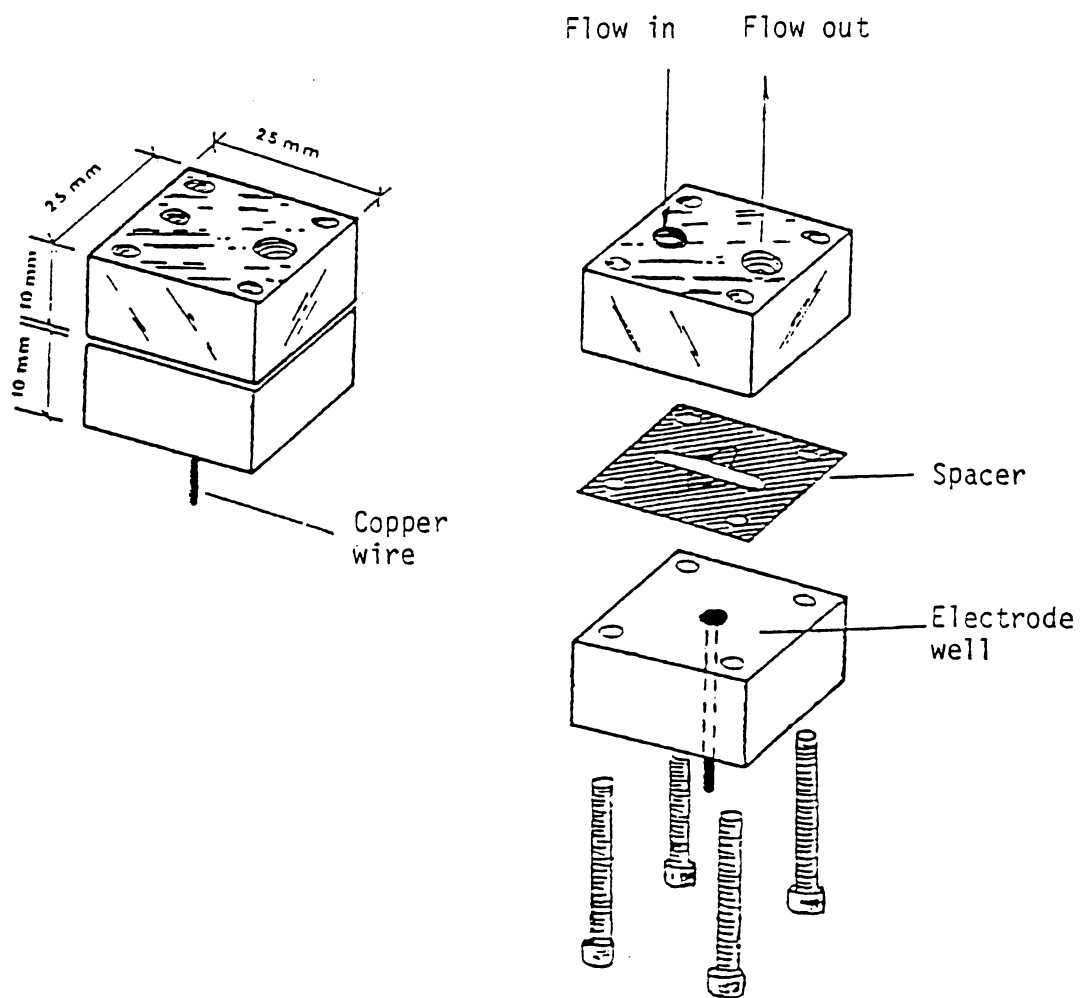


Figure 25. Diagram of Thin-Layer Cell

a fixed electrode potential but will change as the electrode potential is changed. If we record the amperometric responses at each different potential applied to the working electrode and then make a plot of peak current vs electrode potential, a graph called a "hydrodynamic voltammogram" can be obtained which permits identification of the optimum experimental conditions for amperometric determination.

Electrode Responses to Sulfite,
Sulfide, and Nitrite Ions

Figures 26-28 show hydrodynamic voltammograms obtained with 1.0×10^{-5} M sulfite anion, 1.0×10^{-4} M sulfide anion, and 1.0×10^{-4} M nitrite anion solutions, respectively, at the iron complex-modified carbon paste electrodes and at an unmodified surface. The injected sample size was 250 μ L with a 0.10 M H_2SO_4 solution as supporting electrolyte and a flow rate of 2.0 $\text{ml}\cdot\text{min}^{-1}$.

The comparison of amperometric responses shown in Figures 26-28 indicates that sulfite, sulfide, and nitrite anions can be detected by both the unmodified and the modified electrodes but with different sensitivity. At lower electrode potentials, for example, 0.60 V to 1.00 V, which represent favorable experimental conditions because of less interference from other redox species, the iron complex-modified carbon paste electrodes give higher signal currents than the unmodified electrodes. The largest

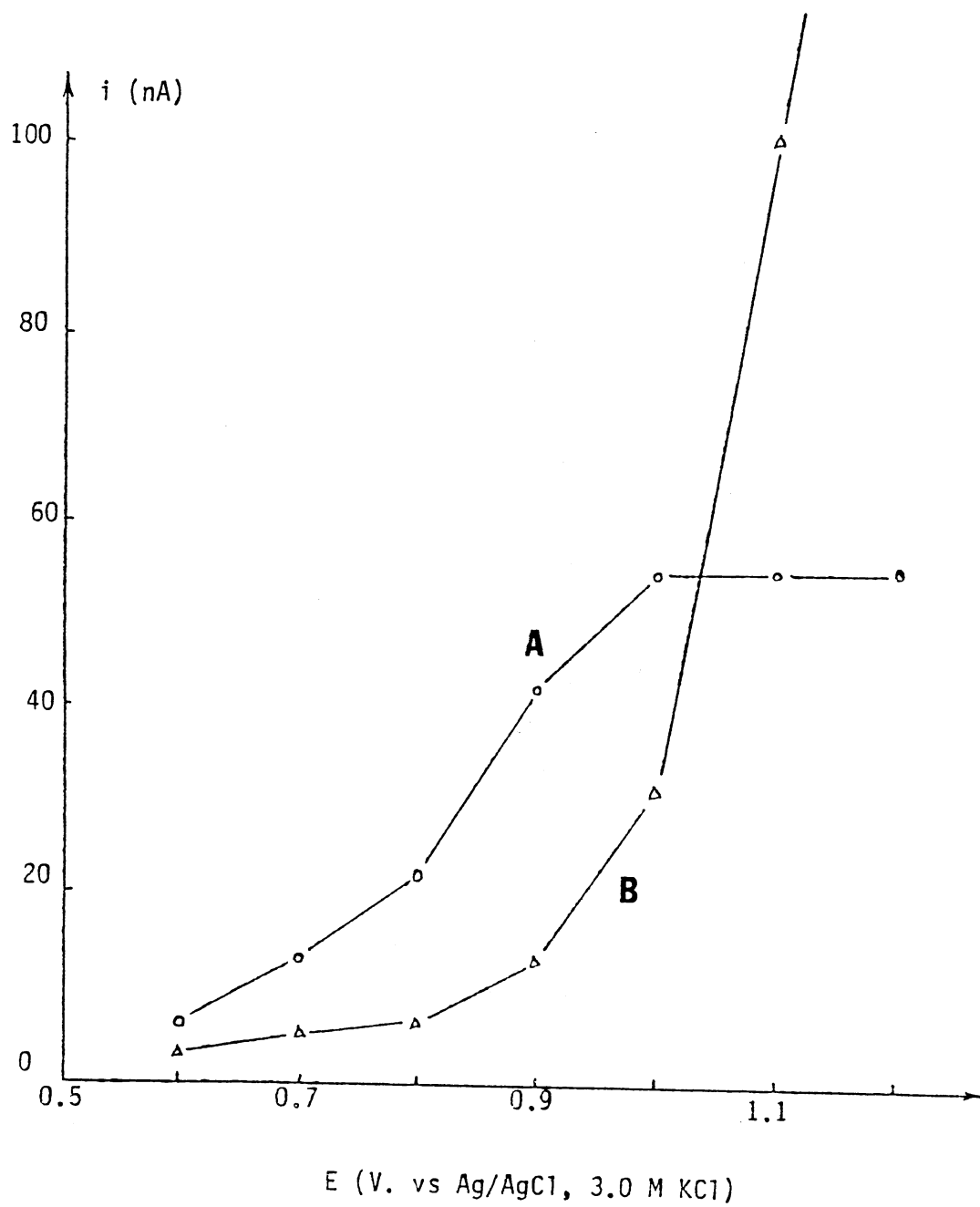


Figure 26. Hydrodynamic Voltammogram for Sulfite Ion
A--- iron complex-modified CPE
B--- unmodified CPE

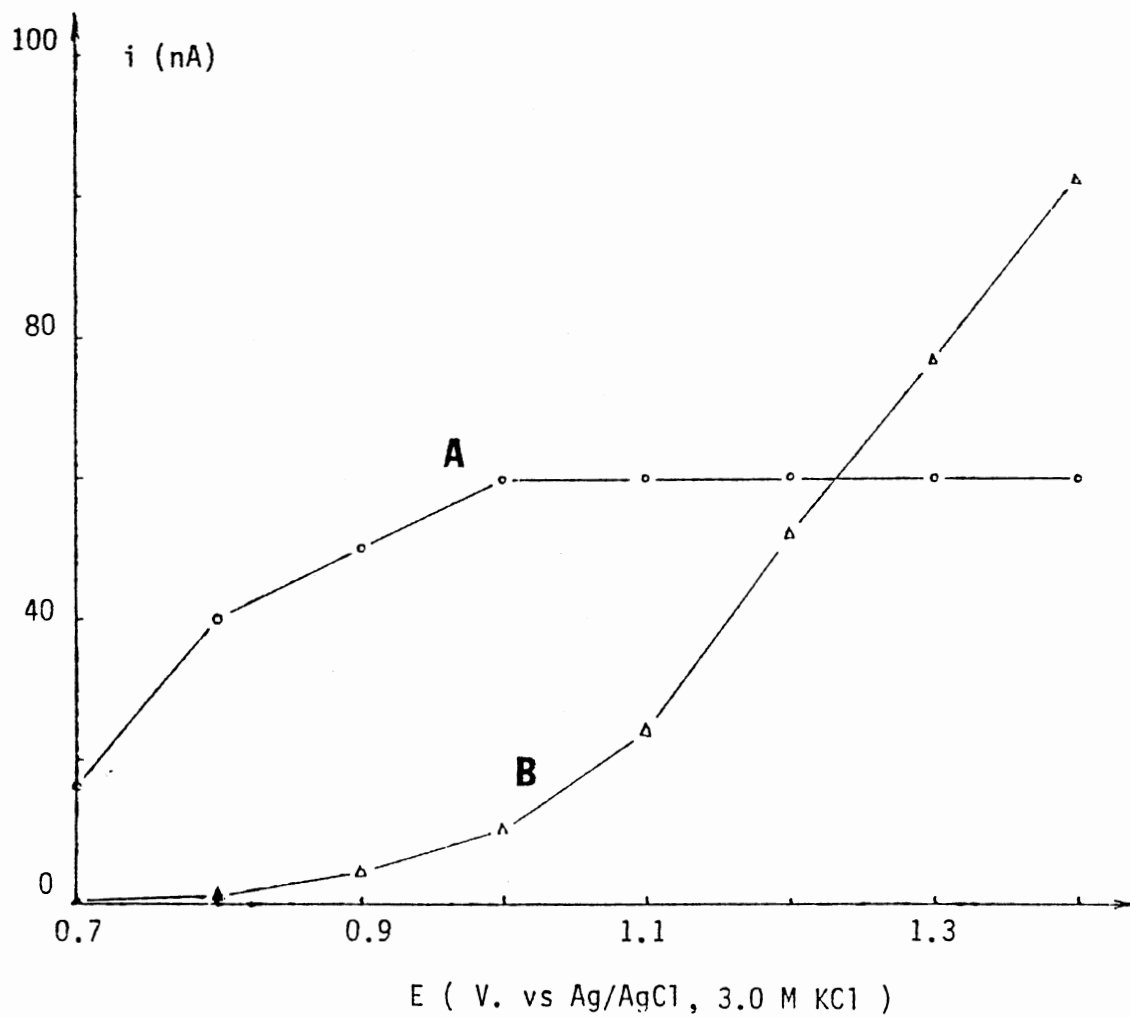


Figure 27. Hydrodynamic Voltammogram for Sulfide Ion
A--- iron complex-modified CPE
B--- unmodified CPE

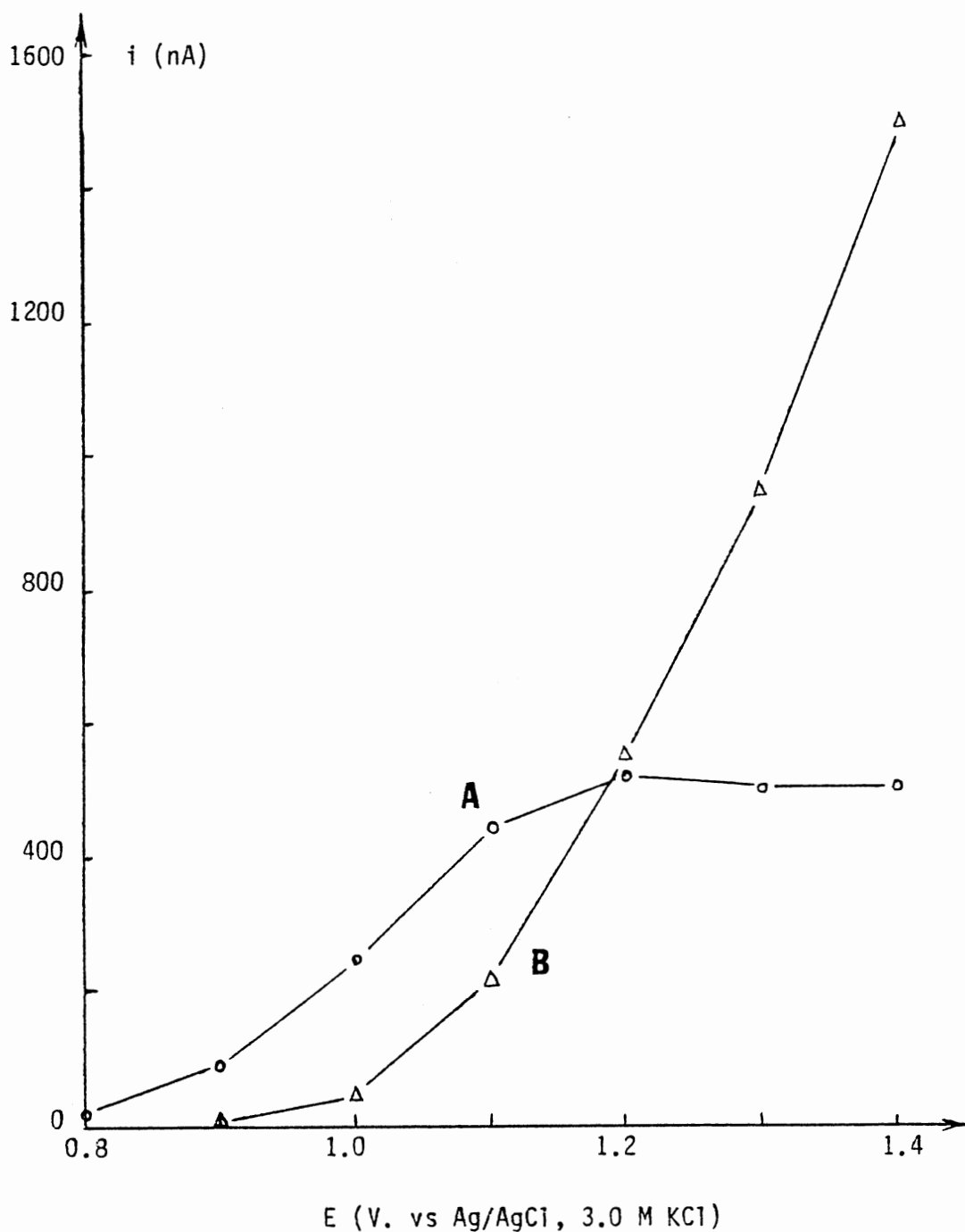


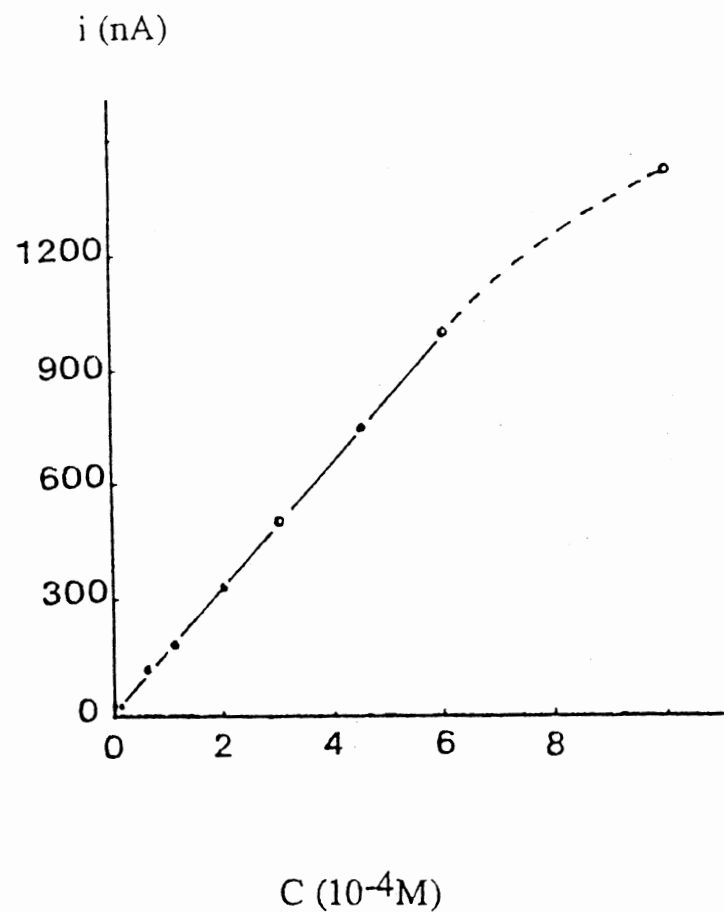
Figure 28. Hydrodynamic Voltammogram for Nitrite Ion
A--- iron complex-modified CPE
B--- unmodified CPE

differences occur at applied electrode potential of 0.95 V for sulfite ion, 1.00 V for sulfide ion, and 1.10 V for nitrite ion. For detection and determination purposes the electrode potential was controlled within this range. Beyond these potential values the signals of the unmodified electrodes increase rapidly and soon become higher than that of modified electrodes. This interesting phenomenon has been repeatedly observed in comparing hydrodynamic voltammograms for modified and unmodified carbon paste electrodes. A more detailed discussion of this observation is given in the next chapter.

Linear Range of Sulfite

Ion Concentration

Flow injection analysis for sulfite ions provides an example of using the modified carbon paste electrode as an analytical probe for the determination of chemical species. In present, the most commonly used approach for determination of sulfite is iodimetric method. This method has a determining limitation around 10^{-4} M and is not accurate, because low results are obtained as a result of air oxidation of the sulfurous acid or its salts during the titration [43]. In flow injection analysis, at an applied electrode potential of 0.95 V and with a 10% iron complex-modified carbon paste electrode as an amperometric sensor and in a continuous-flow system (0.10 M H_2SO_4 as carrier solution), a linear concentration response over



Sample: SO₂

Carrier: 0.10 M H₂SO₄

Electrode Potential: 0.950 V(vs. Ag-AgCl)

Linear Range: 6×10⁻⁶M-----6×10⁻⁴M SO₂

Limit of Detection: 3×10⁻⁶M (from 13 measurements)

Figure 29. Typical Calibration Curve for the Determination of Sulfite

two orders of magnitude for sulfite ion from 6.0×10^{-6} M to 6.0×10^{-4} M was obtained (Figure 29). The linear dependence can be described by the following equation:

$$i = (14 \pm 4) + (1.64 \pm 0.02) \times 10^6 C$$

where i is the peak current of the transient peak obtained under continuous-flow operation in nA, and C is the sulfite ion concentration in molarity. From three times the standard deviation of 13 blank readings, a limit of detection of 3.0×10^{-6} M sulfite was obtained.

The results presented above provide evidence that direct admixing of the complexes prepared in this work into carbon paste preparations can result in useful sensing surfaces. The electrode reaction at these surfaces is governed by a semi-infinite diffusion process and the very low solubility of the complexes in most commonly used solvents make them useful as modifiers for amperometric monitoring under continuous-flow operation.

CHAPTER VI

SOME KINETIC ASPECTS OF BEHAVIOR OF MODIFIED CARBON PASTE ELECTRODES

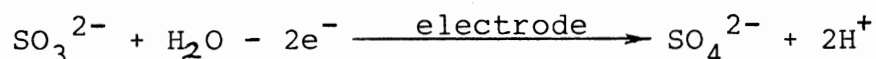
Observations from Hydrodynamic Voltammograms

As already mentioned, the comparison of hydrodynamic voltammograms of modified and unmodified carbon paste electrodes reveals an interesting phenomenon. As indicated in Figures 26-28, between 0.60 V and 1.00 V (vs. Ag-AgCl, 3M KCl) the carbon paste electrodes modified with the complexes of iron have higher signal response than the unmodified ones. The largest signal difference between the modified and unmodified surfaces occurs at 0.950 V for sulfite ion, at 1.00 V for sulfide ion, and at 1.10 V for nitrite ion. Beyond these potential values, however, while the signal at the modified carbon paste electrode tends towards a plateau, the response at the unmodified surface continually increases and becomes higher and higher than that at the modified one, as has been noted. This somewhat unexpected situation has been repeatedly observed and this observation is not unique to the modifier prepared in this work. Some other modifiers, such as cobalt phthalocyanine (CoPC)-modified carbon paste electrode [28], have also shown the same trend. The cobalt

phthalocyanine-modified electrode, for example, when tested in 0.15 M NaOH carrier for detection of nitrite ions gave the responses presented in Figure 30. This phenomenon can also be observed in work reported by Wang et al. [44] in research concerned with a metalloporphyrin-coated glassy carbon electrode for detecting acetaminophen. Up to now, however, no explanation has been advanced to explain this phenomenon.

A Qualitative Interpretation

Before a proper interpretation can be given, four basic concepts should be defined to aid the understanding. First, according to the mechanism operation at chemically modified electrodes, the modifier, which is immobilized on the surface of the electrode and then exists between the electrodes and the reactants as a "medium", can deliver electrons between the electrode and the reactants so that the direct electrode reaction of the reactants at the electrode is avoided. Working in this manner, the modifier can change the mechanism of the electrochemical path from the path normal at unmodified electrode surfaces. For example, in the hydrodynamic voltammogram of sulfite ion, the direct electrode reaction which occurs at the unmodified carbon paste electrode is:



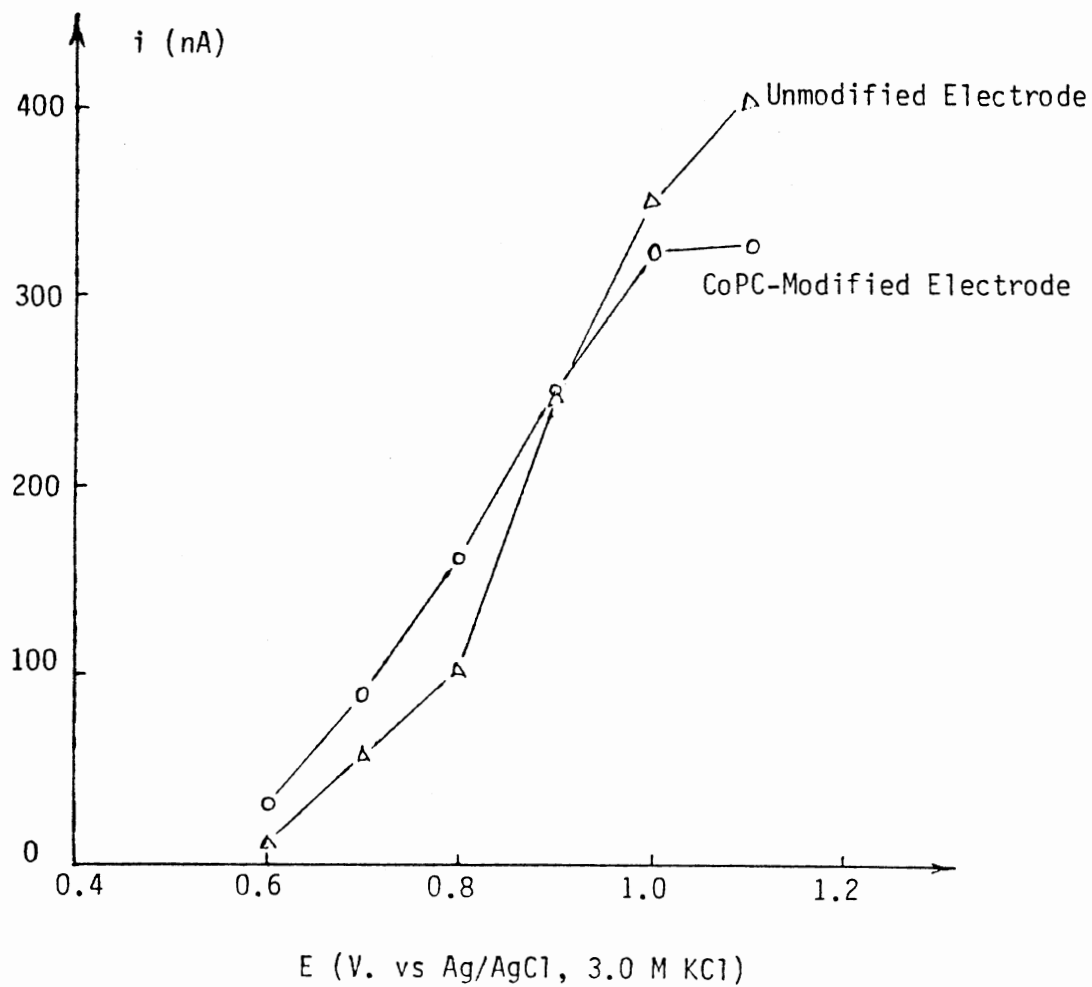
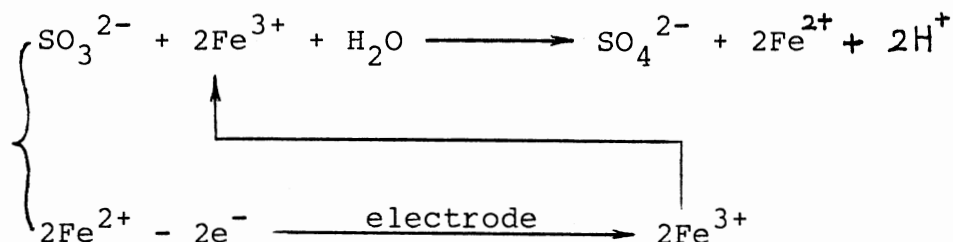


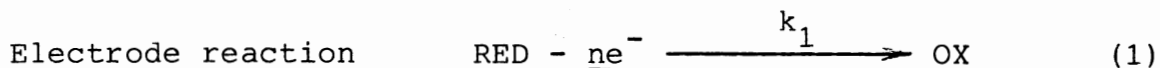
Figure 30. Hydrodynamic Voltammogram of Nitrite Ion with a Cobalt Phthalocyanine-Modified Electrode

The catalytic cycle which occurs at the carbon paste electrode modified with Fe(II)/Fe(III) centers can be illustrated as follows:

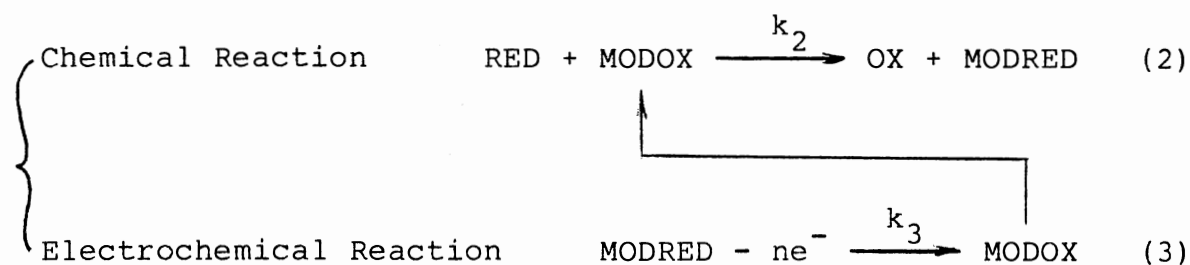


In a general manner, one can rewrite the above scheme as shown below:

UNMODIFIED ELECTRODE:



MODIFIED ELECTRODE:



where RED and OX are the reduced and oxidized forms, respectively, of the sensed analyte and MODRED and MODOX are the reduced and oxidized forms, respectively, of the modifier. The response at the modified electrode can be envisioned then as due to a catalytic mechanism similar to

the CE type in homogeneous electrocatalysis (Figure 31) and taking place in an integrated pre-electrode/reaction layer [10].

The second basic concept is that there are two preconditions for operation of a catalytic cycle. First, both $k_2 > k_1$ and $k_3 > k_1$. This condition ensures that the modifier can function as a "catalyst". Second, $k_2 > k_3$; this condition is not necessary but is generally the case for relatively fast chemical reactions. Combining these two conditions gives the order of the rate coefficients in the modified cycle and direct electrode reaction as: $k_2 > k_3 > k_1$.

The third concept indicates that the anodic current in the electrochemical reaction is given by:

$$i = nFAk[\text{RED}]$$

where k is the rate coefficient of the rate-determining step if more than one process is involved, as in a modified electrode situation.

Fourth, according to the kinetics of electrode reactions [45] the rate coefficients for electrochemical reactions, such as those represented by equations 1 and 3 on page 90, are functions of the applied electrode potential and can be expressed as:

$$k_{\text{ox}} = k_{\text{ox}}^{\circ} \exp[(1-\alpha)E(nF/RT)]$$

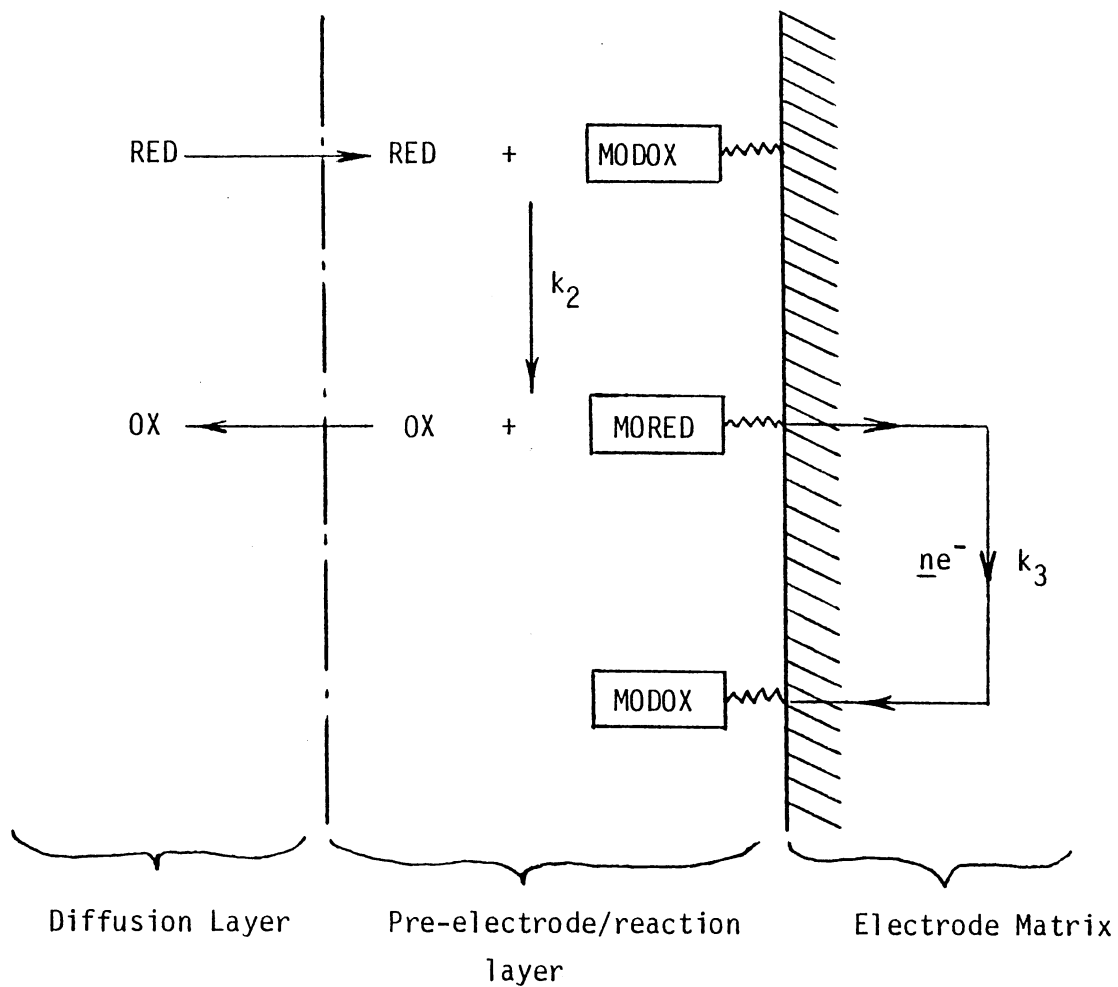


Figure 31. CE-Type Mechanism of Electrocatalysis at Chemically Modified Electrodes

Hence, when E increases, k_1 and k_3 both increase exponentially provided electrolysis takes place. The rate coefficient for the chemical reaction, k_2 , however, is independent of the applied potential and will be constant as long as the temperature is constant and the medium is not changed.

Based on the above four basic concepts, a kinetic interpretation for the phenomenon can be presented. For an unmodified carbon paste electrode, the analyte directly takes part in the electrode reaction 1. Since the rate coefficient k_1 is an exponential function of the applied potential, the current signal i_{un} can be written as:

$$i_{un} = nFAk_1[RED]$$

$$= nFAk_1^0 \exp[(1-\alpha)E(nF/RT)] * [RED]$$

Hence, i_{un} will always increase with the increase of applied electrode potential, provided that electrolysis can take place.

For a modified carbon paste electrode, the analyte first takes part in the chemical reaction 2 with the modifier (pre-immobilized on the surface of the electrode) which exists in the oxidized form in the example discussed here. After this chemical reaction, the modifier is in the reduced form and immediately undergoes electron exchange with the electrode material at the surface of the electrode

to undergo regeneration to the oxidized form (electrode reaction 3) for repeated use in the next catalytic cycle. For the modified cycle as a whole, the current signal i_{mod} is controlled by the slower step, the rate-determining step, which depends on the relative rates of the chemical reaction 2 and the subsequent electrode reaction 3. When the applied electrode potential is low (such as 0.60 V to 0.90 V in this example), k_3 is smaller than k_2 as postulated by the second basic concept discussed above. Then electrode reaction 3 becomes the rate-determining step in the modified cycle and i_{mod} is given by the equation:

$$i_{\text{mod}} = nFAk_3[\text{MODRED}]$$

$$= nFAk_3^{\circ} \exp[(1-\alpha)E(nf/RT)] * [\text{MODRED}]$$

Since $k_3 > k_1$, the i_{mod} is larger than i_{un} , while both increase with the increase of the applied electrode potential. This is shown in the hydrodynamic voltammogram in the region of 0.60 V to 0.90 V in this example (Figure 26). If the applied electrode potential is continually increased and becomes larger than a certain value, such as 0.95 V in the given example, k_3 will be greatly increased and eventually become larger than k_2 , which as already noted is independent of a potential change. At that point the chemical reaction 2 becomes the

rate-determining step instead of the electrode reaction 3 in the modified cycle and now i_{mod} is proportional to k_2

$$i_{\text{mod}} = Ck_2[\text{RED}]$$

with C as proportionality constant. If the applied electrode potential continually increases, i_{mod} will no longer change and will reach a signal plateau while i_{un} will keep increasing and eventually equal and then become larger than i_{mod} . This can be seen in the hydrodynamic voltammograms (Figures 26-28) in the potential region beyond 0.95 V. This explains how the applied electrode potential plays a key role in the kinetics of modified carbon paste electrodes to decide whether a modifier works as a catalyst to facilitate the electrode reaction or behaves as a "cruise control" to fix the reaction rate at a saturated level.

Evaluation of the Intrinsic Rate Coefficient for the Electrode Reaction

In the third basic concept the following equation has been cited:

$$i = nFAkC$$

Since C, n, F, A and i are all known, the rate coefficient k can be calculated. As indicated above, the rate coefficient k is a function of the applied electrode potential for the

unmodified electrode reaction and also for the modified catalytic cycle if the current signal in the modified cycle has not reached the plateau region. Hence, by combining with the equation:

$$k_{\text{ox}} = k_{\text{ox}}^{\circ} \exp[(1-\alpha)E(nF/RT)]$$

one can calculate the apparent intrinsic rate coefficient k_{ox}° from different k_{ox} values at different potentials. If the calculated k_{ox}° proves to be constant, it would provide a justification, at least indirectly, for the validity of the interpretation presented above.

Tables 4-11 list the results of the calculations for four different experiments. For each experiment both $k_{\text{ox(mod)}}^{\circ}$ and $k_{\text{ox(un)}}^{\circ}$ were calculated. In the first three experiments the iron complex-modified carbon paste electrodes described in this research were used to detect sulfite, sulfide and nitrite ions, respectively. In the fourth experiment the modified carbon paste electrode was prepared by admixing with 2.0% (w/w) cobalt phthalocyanine complex as reported by Baldwin [28] and was used to detect nitrite ion in a basic electrolyte carrier. From the results of the calculations it can be seen that with coefficients of variation (CV) between 5 to 27%, all of the k_{ox}° from the different experiments can be considered constant. This adds support to the qualitative

interpretation regarding the kinetic roles of the applied electrode potential and the catalytic function of modified carbon paste electrodes.

TABLE 4

RATE COEFFICIENT OF THE ELECTRODE REACTION FOR SULFITE
ION OXIDATION AT IRON COMPLEX-MODIFIED CPE

| E (V) | i (nA) | k_{ox} (cm/sec) | k_{ox}° (cm/sec) |
|----------|-----------|-----------------------------|-------------------------------------|
| 0.60 | 6 | 8.8×10^{-5} | 5.4×10^{-7} |
| 0.65 | 9 | 1.3×10^{-4} | 5.3×10^{-7} |
| 0.70 | 13 | 1.9×10^{-4} | 5.1×10^{-7} |
| 0.75 | 17 | 2.5×10^{-4} | 4.3×10^{-7} |
| 0.80 | 22 | 3.2×10^{-4} | 3.6×10^{-7} |
| 0.85 | 31 | 4.5×10^{-4} | 3.3×10^{-7} |
| 0.90 | 42 | 6.2×10^{-4} | 3.0×10^{-7} |

* Sample: 1×10^{-5} M Na_2SO_3

Carrier: 0.10 M H_2SO_4

Temperature: 293 ± 1 °K

RESULT OF CALCULATION:

$$\bar{k}_{\text{ox(mod)}}^{\circ} = 4.3 \times 10^{-7} \text{ (cm/sec)}$$

with Standard Deviation (SD) = 1.0×10^{-7}

Coefficient of Variation (CV) = 23%

95% Confidence Limits (CL) = $(4.3 \pm 0.9) \times 10^{-7}$

TABLE 5
 RATE COEFFICIENT OF THE ELECTRODE REACTION FOR
 SULFITE ION OXIDATION AT UNMODIFIED CPE

| E (V) | i (nA) | k_{ox} (cm/sec) | k_{ox}° (cm/sec) |
|----------|-----------|-----------------------------|-------------------------------------|
| 0.80 | 6 | 8.8×10^{-5} | 1.0×10^{-7} |
| 0.85 | 9 | 1.3×10^{-4} | 9.3×10^{-8} |
| 0.90 | 13 | 1.9×10^{-4} | 9.3×10^{-8} |
| 0.95 | 20 | 2.9×10^{-4} | 9.4×10^{-8} |
| 1.00 | 31 | 4.6×10^{-4} | 9.5×10^{-8} |
| 1.05 | 55 | 8.1×10^{-4} | 1.3×10^{-7} |

* Sample: 1×10^{-5} M Na_2SO_3

Carrier: 0.10 M H_2SO_4

Temperature: 293 ± 1 °K

RESULT OF CALCULATION:

$$\bar{k}_{\text{ox(un)}}^{\circ} = 1.0 \times 10^{-7} \text{ (cm/sec)}$$

with Standart Deviation (SD) = 0.14×10^{-7}

Coefficient of Variation (CV) = 14%

95% Confidence Limits (CL) = $(1.0 \pm 0.1) \times 10^{-7}$

TABLE 6

RATE COEFFICIENT OF THE ELECTRODE REACTION FOR SULFIDE
ION OXIDATION AT IRON COMPLEX-MODIFIED CPE

| E (V) | i (nA) | k_{ox} (cm/sec) | k_{ox}° (cm/sec) |
|----------|-----------|-----------------------------|-------------------------------------|
| 0.70 | 16 | 2.35×10^{-5} | 6.22×10^{-8} |
| 0.75 | 28 | 4.10×10^{-5} | 7.10×10^{-8} |
| 0.80 | 40 | 5.87×10^{-5} | 6.66×10^{-8} |
| 0.85 | 45 | 6.60×10^{-5} | 4.90×10^{-8} |
| 0.90 | 50 | 7.33×10^{-5} | 3.56×10^{-8} |

* Sample: 1×10^{-4} Na₂S
Carrier: 0.10 M H₂SO₄
Temperature: 293 ± 1 °K

RESULT OF CALCULATION:

$$\bar{k}_{\text{ox(mod)}}^{\circ} = 5.7 \times 10^{-8} \text{ (cm/sec)}$$

with Standard Deviation (SD) = 1.45×10^{-8}
Coefficient of Variation (CV) = 25%
95% Confidence Limits (CL) = $(5.7 \pm 1.2) \times 10^{-8}$

TABLE 7
 RATE COEFFICIENT OF THE ELECTRODE REACTION FOR
 SULFIDE ION OXIDATION AT UNMODIFIED CPE

| E (V) | i (nA) | k_{ox} (cm/sec) | k_{ox}° (cm/sec) |
|----------|-----------|-----------------------------|-------------------------------------|
| 0.90 | 4 | 5.87×10^{-6} | 2.85×10^{-9} |
| 0.95 | 6 | 8.80×10^{-6} | 2.80×10^{-9} |
| 1.00 | 10 | 1.46×10^{-5} | 3.04×10^{-9} |
| 1.05 | 15 | 2.20×10^{-5} | 3.00×10^{-9} |
| 1.10 | 24 | 3.52×10^{-5} | 3.13×10^{-9} |
| 1.15 | 38 | 5.57×10^{-5} | 3.25×10^{-9} |
| 1.20 | 52 | 7.62×10^{-5} | 2.91×10^{-9} |

* Sample: 1×10^{-4} M Na_2S

Carrier: 0.10 M H_2SO_4

Temperature: 293 ± 1 °K

RESULT OF CALCULATION:

$$\bar{k}_{\text{ox(un)}}^{\circ} = 3.0 \times 10^{-9} \text{ (cm/sec)}$$

with Standard Deviation (SD) = 0.16×10^{-9}

Coefficient of Variation (CV) = 5%

95% Confidence Limits (CL) = $(3.0 \pm 0.1) \times 10^{-9}$

TABLE 8

RATE COEFFICIENT OF THE ELECTRODE REACTION FOR NITRITE
ION OXIDATION AT IRON COMPLEX-MODIFIED CPE

| E (V) | i (nA) | k_{ox} (cm/sec) | k_{ox}^o (cm/sec) |
|----------|-----------|-----------------------|------------------------|
| 0.85 | 50 | 7.33×10^{-5} | 5.44×10^{-8} |
| 0.90 | 85 | 1.25×10^{-4} | 6.07×10^{-8} |
| 0.95 | 170 | 2.40×10^{-4} | 7.60×10^{-8} |
| 1.00 | 250 | 3.66×10^{-4} | 7.62×10^{-8} |
| 1.05 | 360 | 5.28×10^{-4} | 7.20×10^{-8} |
| 1.10 | 445 | 6.52×10^{-4} | 5.82×10^{-8} |

* Sample: 1×10^{-4} M NaNO_2

Carrier: 0.10 M H_2SO_4

Temperature: 293 ± 1 °K

RESULT OF CALCULATION:

$$\bar{k}_{ox(mod)}^o = 6.6 \times 10^{-8} \text{ (cm/sec)}$$

with Standard Deviation (SD) = 0.96×10^{-8}

Coefficient of Variation (CV) = 14%

95% Confidence Limits (CL) = $(6.6 \pm 0.8) \times 10^{-8}$

TABLE 9
 RATE COEFFICIENT OF THE ELECTRODE REACTION FOR
 NITRITE ION OXIDATION AT UNMODIFIED CPE

| E (V) | i (nA) | k_{ox} (cm/sec) | k_{ox}° (cm/sec) |
|----------|-----------|-----------------------------|-------------------------------------|
| 1.00 | 44 | 6.45×10^{-5} | 1.34×10^{-8} |
| 1.05 | 120 | 1.76×10^{-4} | 2.40×10^{-8} |
| 1.10 | 215 | 3.15×10^{-4} | 2.81×10^{-8} |
| 1.15 | 340 | 4.98×10^{-4} | 2.91×10^{-8} |
| 1.20 | 525 | 7.70×10^{-4} | 2.94×10^{-8} |
| 1.25 | 740 | 1.09×10^{-3} | 2.73×10^{-8} |
| 1.30 | 950 | 1.39×10^{-3} | 1.64×10^{-8} |

* Sample: 1×10^{-4} M NaNO_2

Carrier: 0.10 M H_2SO_4

Temperature: 293 ± 1 °K

RESULT OF CALCULATION:

$$\bar{k}_{\text{ox(un)}}^{\circ} = 2.4 \times 10^{-8} \text{ (L/s.m}^2\text{)}$$

with Standard Deviation (SD) = 0.65×10^{-8}

Coefficient of Variation (CV) = 27%

95% Confidence Limits (CL) = $(2.4 \pm 0.5) \times 10^{-8}$

TABLE 10
RATE COEFFICIENT OF THE ELECTRODE REACTION FOR NITRITE ION
OXIDATION AT COBALT PHTHALOCYANINE-MODIFIED CPE

| E (V) | i (nA) | k_{ox} (cm/sec) | K_{ox}° (cm/sec) |
|----------|-----------|-----------------------------|-------------------------------------|
| 0.60 | 28 | 8.2×10^{-6} | 8.1×10^{-9} |
| 0.65 | 50 | 1.5×10^{-5} | 8.3×10^{-9} |
| 0.70 | 88 | 2.6×10^{-5} | 8.1×10^{-9} |
| 0.75 | 125 | 3.7×10^{-5} | 6.5×10^{-9} |
| 0.80 | 160 | 4.7×10^{-5} | 4.6×10^{-9} |

* Sample: 5×10^{-4} M NaNO_2

Carrier: 0.15 M NaOH

Temperature: 293 ± 1 °K

RESULT OF CALCULATION:

$$\bar{k}_{\text{ox(mod)}}^{\circ} = 7.1 \times 10^{-9} \text{ (cm/sec)}$$

with Standard Deviation (SD) = 1.58×10^{-9}

Coefficient of Variation (CV) = 22%

95% Confidence Limits (CL) = $(7.1 \pm 0.7) \times 10^{-9}$

TABLE 11

RATE COEFFICIENT OF THE ELECTRODE REACTION FOR NITRITE
ION OXIDATION AT UNMODIFIED CPE IN BASIC MEDIUM

| E (V) | i (nA) | k_{ox} (cm/sec) | k_{ox}° (cm/sec) |
|----------|-----------|-----------------------------|-------------------------------------|
| 0.60 | 10 | 2.9×10^{-6} | 2.9×10^{-9} |
| 0.65 | 25 | 7.4×10^{-6} | 4.1×10^{-9} |
| 0.70 | 50 | 1.5×10^{-5} | 4.7×10^{-9} |
| 0.75 | 70 | 2.1×10^{-5} | 3.7×10^{-9} |
| 0.80 | 100 | 2.9×10^{-5} | 2.9×10^{-9} |
| 0.85 | 175 | 5.1×10^{-5} | 2.8×10^{-9} |
| 0.90 | 250 | 7.4×10^{-5} | 2.3×10^{-9} |

* Sample: 5×10^{-4} M NaNO_2

Carrier: 0.15 M NaOH

Temperature: 293 ± 1 °K

RESULT OF CALCULATION:

$$\bar{k}_{\text{ox(un)}}^{\circ} = 3.3 \times 10^{-9} \text{ (cm/sec)}$$

with Standard Deviation (SD) = 0.85×10^{-9}

Coefficient of Variation (CV) = 25%

95% Confidence Limits (CL) = $(3.3 \pm 0.3) \times 10^{-9}$

CHAPTER VII

CONCLUSIONS

The work described in this thesis demonstrates the advantages of carbon paste electrodes modified by direct admixing of novel redox modifiers with graphite in carbon paste preparations. They are (1) easily prepared, (2) easily renewed, (3) easily changed as to degree of modification, and (4) easily changed to incorporate a wider range of chemical species.

The mixture of ligands obtained by reacting ethanedial (glyoxal) and 5-amino-1,10-phenanthroline has been investigated and reaction mechanism of their formation and formulation of their structure are suggested. The complexes formed from these ligands and iron(II) are highly insoluble in most liquid media, particularly those of relevance in flow-injection procedures and in liquid chromatography, and exhibit almost ideal and typical redox electrochemical behavior. Consequently, they provide a new kind of modifier with which to prepare chemically modified carbon paste electrodes.

Direct admixing of these complexes into carbon paste preparations results in sensing surfaces that are useful for amperometric monitoring under continuous-flow operation.

The work reported here has also provided a qualitative and semiquantitative interpretation of the hydrodynamic voltammetric behavior of both modified and unmodified carbon paste electrodes. This interpretation reveals that the applied electrode potential as well as the rate coefficient for the chemical reaction play key roles in deciding the catalytic mechanism responsible for an enhancement of signal response, within certain potential range, at the modified surface.

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2
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