INVESTIGATION OF MEMBRANE MATERIALS FOR SOLID-STATE, ION-SELECTIVE ELECTRODES.

by
Marie-Josée Rocheleau

A Thesis Submitted to the Faculty of Graduate Studies and
Research in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy.

Department of Chemistry
McGill University
Montréal,Québec.
Canada.

September 1990

Investigation of Membrane Materials for Solid-state, Ion-selective Electrodes.

ABSTRACT:

The preparation and characterization of new materials to make ion-selective membranes are described. The usefulness of zinc orthophosphate and zinc mercuric thiocyanate to make a carbon-support electrode responsive to zinc was investigated. Better results were obtained with zinc orthophosphate. However, the electrode response was lowered by the formation of acidic oxides on the surface of the electrode, and interferences from copper(II), lead(II), and cadmium(II) were observed. An indirect potentiometric method based on the selective monitoring of chlorozincate(II) or cyanozincate(II) anions with a coated-wire ion-selective electrode was proposed as an alternative for monitoring zinc ion. The application of quaternary ammonium, phosphonium, and alkyl phosphate ionic polymer membranes to potentiometric and voltammetric analysis was also studied. Ionic polymer membranes offer a number of advantages, namely improved membrane lifetime and enhanced adherence to solid-substrate electrodes, when compared to conventional ion-selective membranes. The last stage of this research focused on the application of ionic polymer membrane electrodes in flow injection analysis.

Etude de Diverses Membranes pour les Electrodes Sélectives.

RESUME:

Cette étude décrit la préparation et les caractéristiques de différents matériaux utilisés dans la composition de membranes sélectives. Dans un premier temps, la possibilité d'utiliser l'orthophosphate de zinc pour fabriquer une électrode de graphite sensible aux ions du zinc a été étudiée. Il est démontré dans cette étude, que la formation d'oxyde à la surface de l'électrode limite sérieusement la sensibilité de cette électrode. En plus, la présence d'ions tel que le Cu(II), le Pb(II) et le Cd(II) cause des interférences avec la mesure du zinc. Une méthode potentiométrique basée sur la mesure de certains complexes anioniques du zinc est proposée comme alternative pour la détermination du Zn(II). Dans la seconde étape de cette étude, le comportement et la sélectivité de certains polymères ioniques, modifiés avec des groupements d'ammonium quaternaires, de phosphonium ou de phosphate ont été étudiés par potentiométrie et voltamétrie. Les performances des membranes de polymère ionique et des membranes polymériques conventionnelles ont été comparées. Les membranes de polymère ionique ont notamment une longévité accrue et offrent une meilleure adhérence aux électrodes solides. L'utilisation d'une électrode à membrane de polymère ionique a aussi été appliquée à l'analyse en flot continu (flow injection analysis).

A mes parents, Huguette et Euclide,
avec tout mon amour.

TABLE OF CONTENTS:

List of Figures:

Chapter 1:

Chapter 2:

Chapter 3:

Chapter 4:

Chapter 5.

Chapter 6:

Chapter 7:

Appendices:

List of Tables:

Chapter 1:

Chapter 2:

Chapter 4:

Chapter 5:

Chapter 6:

Chapter 7:

Preface

After several decades of active research, the development of electrochemical sensors continues to be an exciting and expanding area of analytical research. The issue of selectivity remains central to the operation of electrochemical sensors. However, the development of potentiometric sensors with solid internal contact, namely coated wire electrodes and ion-sensitive field effect transistors, has also raised concerns about the integration of chemically sensitive membranes with solid-state electronic devices. In fact, the most commonly used ion-selective membranes are not well-suited for use with solid-state devices, and problems with membrane performance and lifetime arise. This thesis investigates the possibility of using alternative membrane materials with solid-state electrodes.

This thesis has been divided into 7 chapters: The first chapter reviews the theory of ion-selective electrodes, and the second chapter describes carbon-support and coated wire ion-selective electrodes. The characterization of ion-selective electrodes is detailed in chapter 3. Chapters 4, 5, 6 and 7 describe original research. Chapter 4 investigates membrane materials for making zinc-selective, solid-state electrodes. Chapter 5 describes the preparation of ionic polymer membranes. Following this, in chapter 6, the application of ionic polymer membranes to potentiometric and voltammetric analysis was investigated. Voltammetry was used to probe the charge-transport and response mechanisms within ionic polymer membranes. A brief description of the design, construction, and application of an ionic polymer membrane electrode-based flow injection system is given in chapter 7. The final section of this thesis presents a summary of the conclusions reached in chapters 4-7, and provides suggestions for further research in this area.

Acknowledgements:

I wish to express my gratitude to Professor William C. Purdy for his support and guidance during the course of this work. I am indebted to Dr. Thomas Gennett for his assistance in the preparation of this manuscript and for many helpful discussions. I am also indebted to Dr. Robert Moore III for assistance in the characterization of ionic polymers, and to Dr. Maria Teodorczyk for many helpful suggestions.

I would like to thank Fred Kluck and Bill Bastian for their assistance in building an electrochemical cell; the Department of Chemistry at McGill University for Summer Research Fellowships and Assistant Demonstratorships; the Natural Sciences and Engineering Research Council of Canada for post-graduate scholarships.

I also wish to extend special thanks to my family and friends, and especially to my parents, Huguette and Euclide, for their love and support throughout all these years.

CHAPTER I

INTRODUCTION TO ION-SELECTIVE ELECTRODES.

About 25 years ago, the pH glass membrane electrode was the only potentiometric sensor widely available [1]. The growth in the use of potentiometric methods started when attention was turned from glass membranes to polyvalent membrane systems such as, pellets of insoluble salts [2], ion exchange liquids [3,4], and polymeric membranes [5]. These investigations have led to the development of a variety of electrodes selective for inorganic ions such as, halides [6], nitrates [7], potassium [8] and calcium [9]. Further development has also resulted in the availability of Ion-Selective Electrodes (ISE's) for the monitoring of organic species, i.e. quaternary ammonium ions [10] and drugs of abuse [11].

An ion-selective electrode is a potentiometric sensing device which responds selectively towards one or several ionic species. A unique feature of ISE's is that the response to an ion occurs in a heterogeneous mixture of ions. Ion-selective electrodes therefore represent an interesting approach to the development of a simple analytical method requiring minimal sample preparation. ISE's can be used in direct determinations and as sensors for titrations [1]. Measurements with ISE's are simple, rapid and do not affect the composition of the test solution [12]. Further, ISE's possess wide response ranges, are also portable and inexpensive to use [1,12].

The membrane of the electrode is made of an electrically conducting material across which is developed a potential that depends on the activity of the analyte. This response is described by the Nernst equation [13]:

$$E = E^o + (RT/z_iF) \ln a_i \quad (1)$$

where E^o is the standard electrode potential, R is the universal gas constant (8.3144 J K^{-1} mol^{-1}), T is the absolute temperature in Kelvin, F is the Faraday's constant (96,487 C mol^{-1}), a_i and z_i are the activity and the charge of the analyte ion, respectively. The selectivity of this response can be modified through the modification of the chemical composition of the membrane.

Ion-selective electrodes find their principal applications in process control [14], clinical diagnostics [15], and environmental monitoring [16]. In fact, in many cases, ISE's have replaced spectrophotometric methods [12]. For example, over the past 20 years the number of clinical assays of sodium and potassium ions performed with ISE's has surpassed those done by flame photometry [12]. This is mainly attributed to the low cost and simplicity of the instrumentation required for potentiometric analysis.

However, further breakthroughs, especially in organic analysis, have been hindered by the apprehension expressed toward electroanalytical techniques in the scientific community. Limitations on wider use of electroanalytical methods are also imposed by the small number of reliable sensors available. Consequently, new types of sensors with better selectivity and stability are in greater demand, and a considerable amount of research is still required to expand the applications of ISE's.

1.1 CLASSIFICATION AND HISTORY OF ION-SELECTIVE ELECTRODES.

Ion-selective electrodes can be classified in the three following categories, as suggested by the International Union of Pure and Applied Chemistry (IUPAC) [17]:

-Noncrystalline electrodes.
-Crystalline electrodes.
-Sensitized electrodes.

1.1.1 Noncrystalline electrodes:

This category includes the glass membrane and liquid membrane electrodes. The pH glass electrode is certainly the most successful glass membrane electrode ever developed and the most widely applied ISE. Cremer is credited with the discovery of this electrode in 1906 [18]. Through variations of the chemical composition of the glass membrane, monovalent cation-responsive glass electrodes were obtained. These developments were based principally on the studies of Eisenman and his collaborators [19]. However, the usefulness of this electrode system is limited to the determination of a few monovalent cations such as Na^+, K^+, Li^+, and NH_4^+ [19].

A liquid membrane is usually composed of a water immiscible liquid ion exchanger. Alternatively, a solution of a neutral-carrier dissolved in an organic solvent can be used. The support for liquid membranes can be either an inert porous frit, or an inert polymeric material such as polyvinyl chloride [1]. The use of various ion-exchange materials and neutral-carriers allowed the extension of ISE's to the monitoring of a wider variety of ionic species. Information on selectivity is generally obtained from solvent extraction data [1]. The development, study, and application of liquid and polymer membrane ISE's remain the prime focus of many investigations [20-22].

1.1.2 Crystalline electrodes:

The membranes of this group either possess an homogeneous or heterogeneous structure [23]. Homogeneous membranes are made of single or mixed crystals, or are alternatively constituted of a pressed pellet of a crystalline material. Heterogeneous membranes, on the other hand are prepared by the dispersion of a solid compound in an inert binding material such as, silicon rubber, or polyvinyl chloride. In both cases, the crystals used are sparingly soluble salts [1], and the selectivity pattern can be predicted on the basis of the solubility product of the salt used [24]. While homogeneous membranes are found particularly useful, heterogeneous membranes are usually slow to respond and subject to poisoning [23]. The use of membranes made of silver halides [6] and metal sulfides [25] were found to provide excellent transition metal ion-sensitive electrodes.

One of the most successful examples of a crystalline solid-state electrode is the fluoride electrode [2] made of a single crystal of lanthanum fluoride, LaF_3. This electrode was first reported by Frant and Ross from Orion Research in 1966 [2]. Later, in the early seventies, Ruzicka and Lamm introduced an innovative multipurpose solid-state electrode made of hydrophobic graphite on which insoluble compounds can be applied directly [26]. This type of electrode will be further discussed in Chapter 2.

1.1.3 Sensitized electrodes:

Gas-sensing and bioselective membrane electrodes are a direct development from ISE's [23]. A biocatalyst or mediator is used to convert the substance to be measured to a species which can be detected by the membrane electrode. For example, a pH electrode or an ammonia-sensitive electrode is commonly used for this purpose [23].

1.2 THEORY OF MEMBRANE POTENTIAL.

1.2.1 The origin of membrane potential:

When two phases containing electrically charged particles are in contact, an electric potential difference develops at their interface. The composition of the phases are characterized by the electrochemical potential, $\tilde{\mu}$. For a system in equilibrium, and the charged species "i" in phases 1 and 2,

$$\tilde{\mu}_i(1) = \tilde{\mu}_i(2) \qquad (2)$$

Under ISE conditions, this equation [24] can be rewritten in terms of the standard chemical potentials, μ_i^o, the activity and the charge of the species present in both phases, a_i and z_i, and the inner potentials of the phases, φ:

$$\mu_i^o(1) + RT \ln a_i(1) + z_i F\varphi(1) = \mu_i^o(2) + RT \ln a_i(2) + z_i F\varphi(2) \qquad (3)$$

The potential difference at the interface

$$\Delta\varphi = \varphi(2) - \varphi(1) \qquad (4)$$

can then be described by the following expression:

$$\Delta\varphi = [\mu_i^o(1) - \mu_i^o(2)] / z_i F + RT/z_i F \ \ln [a_i(1) / a_i(2)] \qquad (5)$$

and

$$\Delta\varphi = \text{constant} + RT/z_i F \ \ln [a_i(1) / a_i(2)] \qquad (6)$$

where the constant is equal to $[\mu_i^o(1) - \mu_i^o(2)]/z_i F$. If the activity of the species of interest is known in one phase, the activity of the analyte in the other phase can therefore be determined by measuring $\Delta\varphi$.

However, the potential difference, $\Delta\varphi$, cannot be measured directly. The potential of an ISE must be measured against a reference electrode, an electrode which does not display a response to the analyte species, and the potential of which remains constant. In the conventional barrel configuration, the ion-selective membrane separates two electrolytic solutions; the sample solution is placed on one side, and a standard solution containing the tested species at a defined activity and 0.1M KCl, on the other [24].

$$\mathrm{Hg}\ \Big|\ \mathrm{Hg_2Cl_2}\ \Big|\ \begin{array}{c}\mathrm{KCl}\\ \text{saturated}\end{array}\ \Big\|\ \begin{array}{c}\text{test}\\ \text{solution}\end{array}\ \Big|\ \text{membrane}\ \Big|\ \begin{array}{c}\text{standard}\\ \text{solution}\\ +0.1\mathrm{M\ KCl}\end{array}\ \Big|\ \mathrm{AgCl}\ \Big|\ \mathrm{Ag}$$

$$\Delta\varphi_{L} \qquad\qquad \Delta\varphi_{M}$$

$\Delta\varphi_{M}$ is the membrane potential, and $\Delta\varphi_{L}$ is the liquid-junction potential. A silver/silver chloride reference system is commonly used inside the ISE, and the potential of the ISE is generally measured against a Saturated Calomel Electrode (SCE) [24]. The ISE and reference electrode form an electrochemical cell (Fig.1.1), and the potential difference is measured between the two reference electrodes.

The ion-selective membrane and the bulk of the solution are usually not in equilibrium. Nevertheless, if the interfaces are in equilibrium, which is normally the case, equation (3) still applies. In this case, potentials $\varphi(1)$ and $\varphi(2)$ correspond to the test and the standard solution, respectively, and their difference is equal to the membrane potential, $\Delta\varphi_{M}$ (equation (5)).

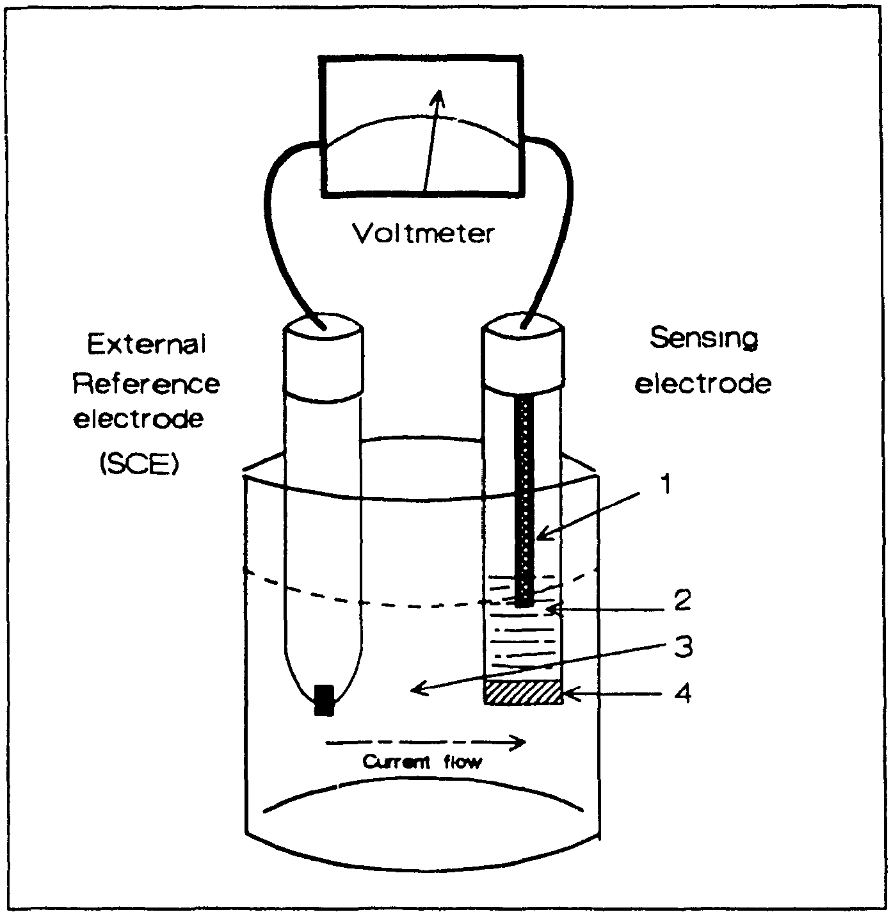


Fig.1.1 Electrochemical cell formed by an ion-selective electrode and a saturated calomel reference electrode (SCE): (1) Ag/AgCl internal reference electrode, (2) Standard solution, (3) Test solution, (4) Ion-selective membrane.

1.2.2 The liquid-junction potential:

When a membrane mechanically prevents the rapid mixing of two solutions without hindering the transport of electrolytes, a diffusion potential is developed across the membrane. This diffusion potential is called the liquid-junction potential, $\Delta\varphi_L$. Since the ions are free to move from one compartment to the other, a liquid-junction is a non-selective interface. When electrolytes with a common cation or anion are present in equal concentration on both sides of the liquid-junction,

$$\begin{array}{c||c} 0.1\text{M KCl} & 0.1\text{M HCl} \\ \text{solution 1} & \text{solution 2} \end{array}$$

the simplified Henderson [27] formula is applicable:

$$\Delta\varphi_L = -\frac{RT}{F} \ln \frac{U_{H^+}(2) + U_{Cl^-}(2)}{U_{K^+}(1) + U_{Cl^-}(1)} \qquad (7)$$

U is the particle mobility,

$$U = \lambda /(|z|F^2) \qquad (8)$$

where λ is the equivalent ionic conductivity.

In practical electrochemical cells (Fig.1.1), $\Delta\varphi_L$ appears at the porous frit of the external reference electrode. It is essential to minimize $\Delta\varphi_L$, or to keep its value constant during the potentiometric measurements, since ideally, only the potential of the ISE, $\Delta\varphi_M$, should change with changes in the solution composition. Fluctuations of $\Delta\varphi_L$ can be minimized by adding a large fixed concentration of an indifferent electrolyte to the test solution. The liquid-junction potential is then essentially a function of the composition of the electrolyte solution inside the reference electrode and the composition of the buffer of the test solution. A bridge can also be used between the indicator and reference electrode. Such a bridge is commonly filled with a saturated KCl solution. If the reference electrode is a saturated calomel electrode, usually no other bridge is required. In this case, the liquid-junction has normally a small value, see Table 1.1.

Table 1.1: Liquid-junction potentials for a saturated calomel electrode, at 25°C [28].

Electrolytes	$\Delta\varphi_L$ (mV)
0.1M KNO_3 | sat.KCl	+1.9
0.1M $NaNO_3$ | sat.KCl	+1.6
0.1M HCl | sat. KCl	+4.6
0.1M NaOH | sat. KCl	-0.4

1.2.3 The Donnan potential:

Consider a membrane made of a cation exchange material, and placed in a dilute solution of a particular electrolyte. There is a considerable difference between the concentration profile of the two phases, i.e. the membrane and the electrolyte solution. The concentration of cations is much larger in the membrane, whereas the concentration of mobile co-ions, anions in this case, is larger in the solution. This concentration profile causes the migration of cations into the solution, and of anions into the ion exchanger. This results in an accumulation of positive charges in the solution, as well as an accumulation of negative charges in the ion exchanger. This accumulation of charges builds up a potential difference between the two phases, which is called the Donnan potential, $\Delta\varphi_D$ [29].

The Donnan potential prevents the concentration of co-ions in the membrane from rising beyond an equilibrium value [29], a value which is usually much smaller than the concentration in the external solution. The electrolyte is at least partially excluded by the membrane which therefore exhibits a permselectivity for the counterions.

The Donnan exclusion is dependent on the ionic concentration of electrolytes in solution. When interposed between electrolyte solutions of low or moderate concentrations, a membrane contains a large number of counterions but only few co-ions, as previously discussed [29]. Counterions are admitted to the membrane, and have no difficulty in passing through from one solution to another. This migration from a solution of higher concentration to that of lower concentration produces a potential difference across the membrane, and an electrical double layer is simultaneously formed on both sides of the membrane (Fig.1.2).

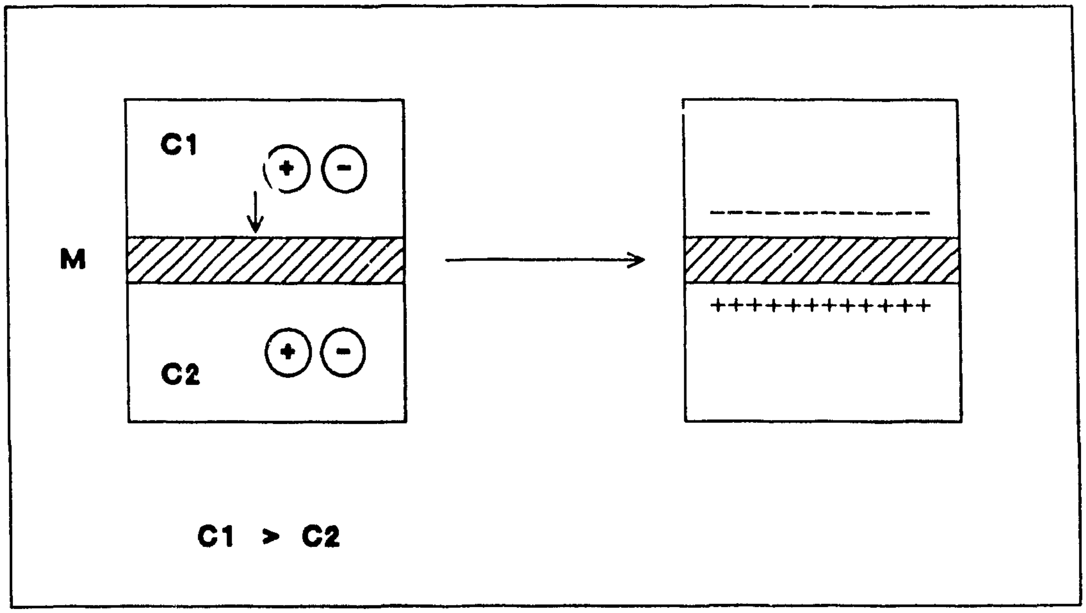


Fig.1.2 Diagram of an electrochemical membrane (M) selective to cationic species: A small number of ions to which the membrane is selective, pass from the solution of higher concentration (C1) through the membrane to that of lower concentration (C2), thus producing an electric potential difference.

For a system at equilibrium,

$$\tilde{\mu}_{I+}(1) = \tilde{\mu}_{I+}(2) \qquad (9)$$

and consequently,

$$\Delta\varphi_D = \varphi(2) - \varphi(1) = RT/F \ \ln [a_{I+}(1) / a_{I+}(2)] \qquad (10)$$

The situation with membranes made of anion exchangers is analogous, however the Donnan potential has the opposite sign [29].

However, when the concentrations of the solutions are increased, the Donnan exclusion becomes less effective and the permselectivity is consequently reduced [29]. This effect can result in deviations in the response of an ISE at high sample concentrations. Effects from co-ions impair the performance of several cation-responsive electrodes [30], particularly when the concentration of electrolytes reach a value above 1mM.

Both the liquid-junction and Donnan potentials constitute limiting cases for membrane potentials. The properties of most ion-selective membranes generally lie between these two limiting cases [24]. The overall potential difference across the membrane is therefore the sum of the two potential differences at the membrane-solution interfaces and the diffusion potential across the membrane. The resulting equation for $\Delta\varphi_M$ then consists of a combination of the Donnan and Henderson terms.

1.3 THEORY OF MEMBRANE TRANSPORT AND SELECTIVITY.

1.3.1 Membranes made of solid ion exchangers.

1.3.1.1 Glass membranes:

A glass membrane behaves as a simple cation exchange membrane which displays a high degree of selectivity for monovalent cations, and is almost solely permeable to cations [19,31]. The initial transport process is believed to be due to a rapid interfacial cation exchange, which may be followed by the diffusion of the cationic species through the bulk of the membrane to the other interface where an exchange process also takes place [31]. It is therefore possible to obtain an expression for the membrane potential in terms of the ion exchange equilibrium constants and mobilities of the cationic species [31]. If the number of cations in solution is limited to two, I^+ and J^+, the equation for the membrane potential $\Delta\varphi_M$ becomes

$$\Delta\varphi_M = \frac{RT}{F} \ln \frac{a_i(1) + [(U_j/U_i)\ K_{ij}]\ a_j(1)}{a_i(2) + [(U_j/U_i)\ K_{ij}]\ a_j(2)} \qquad (11)$$

for an ideal system at equilibrium. (1) and (2) refer to the solutions on the two sides of the membrane.

The selectivity between I^+ and J^+ is determined by the product of the mobility ratio of these species in the membrane (U_j / U_i) and the ion exchange equilibrium constant (K_{ij}) characteristic of their exchange between the aqueous phase and the membrane [31].

$$J^+_{(aq)} + I^+_{(membrane)} \overset{K_{ij}}{\rightleftharpoons} J^+_{(membrane)} + I^+_{(aq)}$$

However, the more strongly an ion is preferred by the ion exchange sites, the more poorly it would move within the membrane [31]. There are therefore opposing effects between mobilities and affinities of ions in solid membranes with fixed ion exchange sites.

1.3.1.2 Insoluble inorganic salts membranes:

Substances exhibiting purely electronic conductivity (metals and various forms of carbon) are excluded as potential ion-selective materials since they are sensitive to a multitude of ions, and do not exhibit any selectivity [24]. Substances suitable for use as ion-selective materials must also exhibit ionic conductivity. Working solid membranes can therefore be visualized as a bulk phase, through which charge is transported either by an ionic or an electronic mechanism, or by a combination of both [32]. The use of a membrane made of silver halide can serve as an example. A wafer of silver chloride behaves as a rapid ion exchanger for Ag^+ [32], and can therefore be used to measure the activity of Ag^+. It can also respond to the activity of chloride ions in solution since silver ions can also act as charge carriers inside the membrane [32].

In the presence of an interfering ion forming a less soluble precipitate with an ion of the membrane material, the membrane is gradually covered with this precipitate and the electrode becomes sensitive to the interfering ion [24]. Concurrent interfacial reactions involving redox species and complexing agents may distort the desired ion exchange equilibrium, and consequently affect the membrane selectivity [24].

1.3.2 Liquid membranes.

1.3.2.1 Liquid ion exchanger membranes:

A liquid ion exchange membrane is composed of a water immiscible solvent containing an appreciable concentration of ionizable species [1]. These species which are preferentially soluble within the membrane phase, selectively associate with some counterions. In this case, the ion exchange sites "S^-" are free to move within the membrane (Fig.1.3) [31].

In the example given, the analyte ion, I+, is permeable across the membrane-solution interfaces whereas the organophilic anion, S^-, is physically trapped within the membrane.

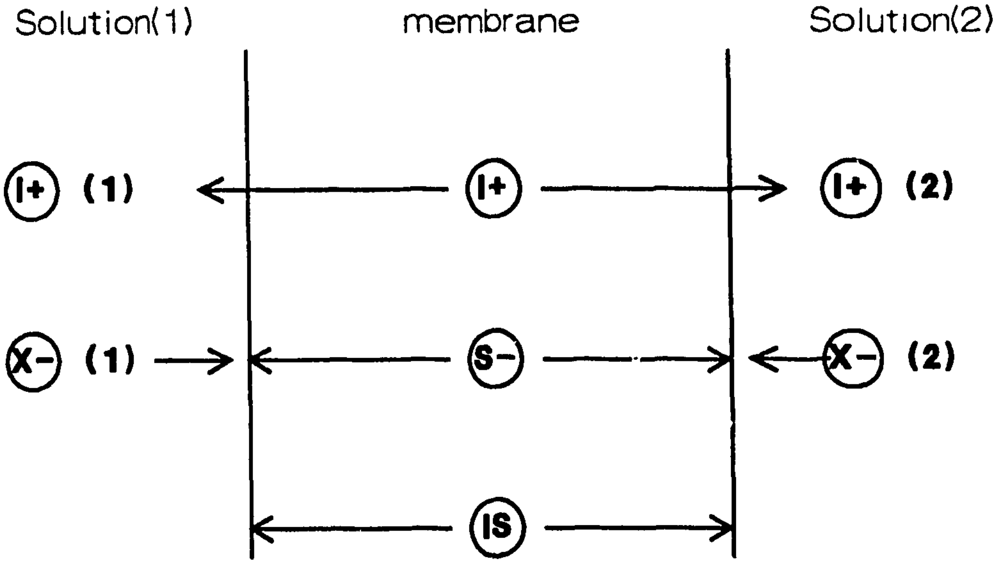


Fig.1.3 Diagram of a liquid ion exchanger membrane: I+, S- and X- refer to the counterion, the organophilic ion exchange site, and the co-ion species, respectively.

The equation for the membrane potential can be described for two limiting cases: negligible and strong association of the analyte with the ion-exchange sites. Eisenman and coworkers [31] showed that in the case of negligible association, the membrane potential can be expressed as

$$\Delta\varphi_M = \frac{RT}{F} \ln \frac{a_i(1) + [(U_j/U_i)(k_j/k_i)]\, a_j(1)}{a_i(2) + [(U_j/U_i)(k_j/k_i)]\, a_j(2)} \qquad (12)$$

U_i is the mobility of the dissociated I^+ species in the solvent phase, and k_i is the partition coefficient of I+ between water and the solvent of the membrane:

$$I^+_{(aq)} \overset{k_i}{\rightleftharpoons} I^+_{(membrane)}$$

while U_j and k_j are the mobility and partition coefficient of J+. The selectivity between species I+ and J+ is determined by the partition coefficients and mobilities of the dissociated ions [31],

$$K_{ij}^{pot} = (U_j/U_i)\,(k_j/k_i) \qquad (13)$$

and the selectivity coefficient, K_{ij}^{pot} is therefore determined by the properties of the solvent.

The strong association of the species I+ and S- within the membrane phase, results in the formation of a neutral pair IS [31]

$$I^+ + S^- \overset{K_{IS}}{\rightleftharpoons} IS$$

IS is freely mobile within the membrane. K_{IS} is the association constant for the formation of neutral pairs within the membrane phase.

For such a system, Eisenman and coworkers [31] have shown that the electrode potential, E is given by:

$$E = RT/F\,(1-\tau)\ln \frac{\{a_i(1) + [(U_j+U_s)k_j/(U_i+U_s)k_i]a_j(1)\}}{\{a_i(2) + [(U_j+U_s)k_j/(U_i+U_s)k_i]\,a_j(2)\}} + \tau \ln \frac{a_i(1) + [(U_{js}/U_{is})K_{ij}]a_j(1)}{a_i(2) + [(U_{js}/U_{is})K_{ij}]\,a_j(2)} \qquad (14)$$

U_{js}/U_{is} is the mobility ratio of the neutral pairs, K_{ij} is the ion exchange constant of the reaction

$$J^{+}_{(aq)} + IX_{(membrane)} \overset{K_{ij}}{\rightleftharpoons} JX_{(membrane)} + I^{+}_{(aq)}$$

and τ is given by

$$\tau = [U_s(U_{js}K_{js}-U_{is}K_{is})] / [(U_i+U_s)U_{js}K_{js} - (U_j+U_s)U_{is}K_{is}] \qquad (15)$$

The value of τ which can lie between 0 and 1, depending on the solvent and ion exchanger, determines the relative importance of the two logarithmic terms [31]. The selectivity coefficient for membranes with strongly associated and immobile sites (τ=0) therefore depends on the properties of the solvent:

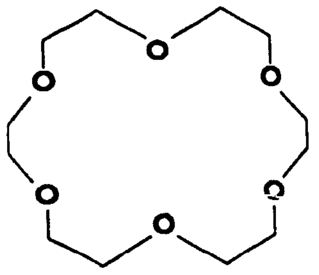
$$K_{ij}^{pot} = [(U_j+U_s)k_j] / [(U_i+U_s)k_i] \qquad (16)$$

However for membranes with strongly associated and highly mobile sites (τ=1), the selectivity depends both on the properties of the ion-exchange sites and the solvent:

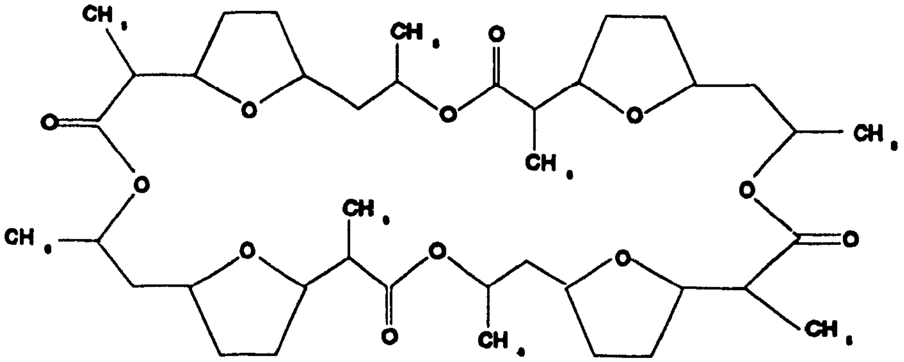
$$K_{ij}^{pot} = (U_{js}/U_{is}) K_{ij} \qquad (17)$$

1.3.2.2 Neutral carrier liquid membranes:

Neutral macrocyclic antibiotics and polyethers contain an arrangement of ring oxygens suitable, through ion-dipole interaction, for replacing the hydration shell around cations [33]. The ability of these neutral macrocyclic molecules to complex selectively ionic species and to solubilize cations in low dielectric constant solvents, lies in their ability to wrap around an ion and therefore to provide a cavity of the right size [34].



18-crown-6



Nonactin

Fig.1.4 Two examples of common neutral carriers: 18-crown-6 and nonactin [35].

The problem of the mechanism of neutral carrier-based membrane potential is complex. Eisenman and coworkers [31] demonstrated that a thin neutral carrier-based membrane potential is described by the equation:

$$\Delta\varphi_M = RT/F \; \ln \frac{a_i(1) + [(U_{js}/U_{is})(K_j/K_i)]\, a_j(1)}{a_i(2) + [(U_{js}/U_{is})(K_j/K_i)]\, a_j(2)} \qquad (18)$$

K_j / K_i is the ratio of the equilibrium constants for the extraction of I^+ and J^+

$$I^+X^- + S \overset{K_i}{\rightleftharpoons} IS^+ + X^-$$

$$J^+X^- + S \overset{K_j}{\rightleftharpoons} JS^+ + X^-$$

which measures the extent to which the neutral carrier, S, can extract the salt, I^+X^-, from water into an organic solvent phase. The scheme of Reusch and Cussler [35] provides a simple representation of the diffusion-controlled process (Fig.1.5).

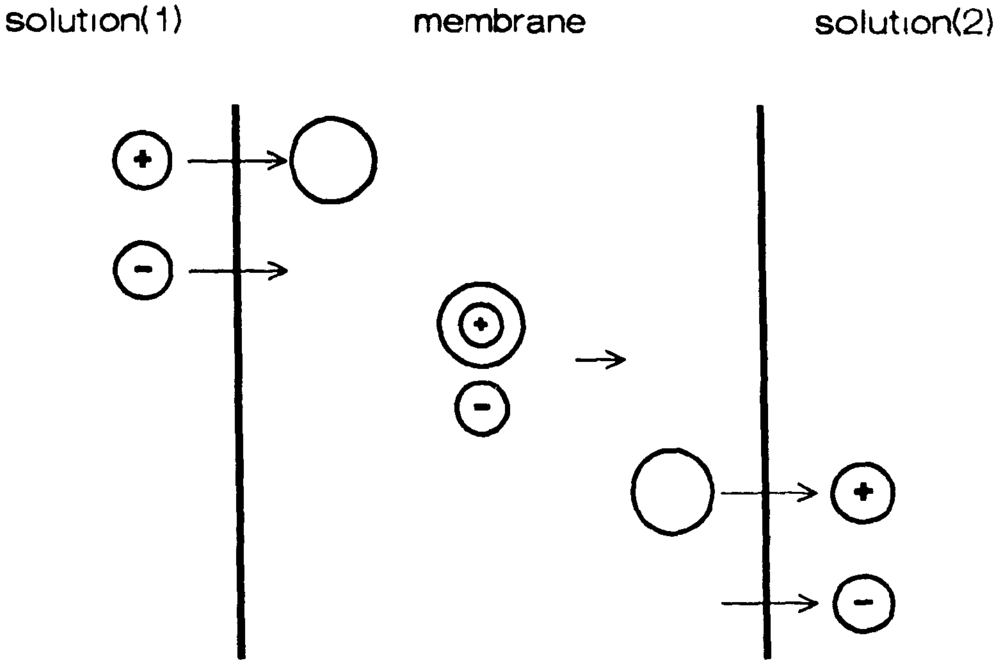


Fig.1.5 Diagram of a neutral-carrier membrane: The ions are complexed by the neutral-carrier at the membrane-solution interface. The complex thus diffuses across the membrane to the other interface where decomplexation occurs. The free carrier is therefore free to return.

The main problem with this model is the question of electroneutrality. Although the total system may contain regions which are not electroneutral in the form of double layers at the membrane interfaces and within the membrane, a membrane must be electrically neutral overall [34]. The space-charge regions extend outward into the aqueous solution and inward into the membrane, with a mean thickness which is called the Debye thickness [34]. Thin membranes of thickness less than or equal to the Debye thickness are not electroneutral. Since a large deviation from electroneutrality cannot be maintained, the use of thick membranes (>100μm) is preferable since they are necessarily electroneutral in their bulk [34]. However, the major mechanistic problem lies in understanding the nature of transport across the bulk of thick membranes considering the rapid response time obtained with this type of membrane electrode [34].

REFERENCES:

[1] A.K. Covington, Ed., "Ion-Selective Electrode Methodology", Vol.I, CRC Press, Boca Raton (Florida), 1979, Chapter 1.

[2] M.S. Frant and J.W. Ross, *Science*, **1966**, 154, 1553.

[3] K. Sollner and G.M. Shean, *J.Am.Chem.Soc.*, **1964**, 86, 1901.

[4] O.D. Bonner and D.C. Lunney, *J.Phys.Chem.*, **1966**, 70, 1140.

[5] A. Shatkay, *Anal.Chem.*, **1967**, 39, 1056.

[6] H. Adametzova and R. Vadura, *J.Electroanal.Chem.*, **1974**, 55, 53.

[7] B.M. Kneebone and H. Freiser, *Anal.Chem.*, **1973**, 45, 449.

[8] L.A.R. Pioda, V. Stankova, and W. Simon, *Anal.Lett.*, **1969**, 2, 665.

[9] J.W. Ross, *Science*, **1967**, 156, 1378.

[10] C.R. Martin and H. Freiser, *Anal.Chem.*, **1980**, 52, 562.

[11] H. Freiser, *J.Chem.Soc., Faraday Trans. 1*, **1986**, 82, 1217.

[12] J. Koryta, *AnnRevMaterSci.*, **1986**, 16, 13.

[13] G.D. Christian, "Analytical Chemistry", 3rd Ed., John Wiley & Sons, New York, 1980, pp.255-8.

[14] J. Polesuk, *AmLab.*, **May 1970**, 27.

[15] D. Amman, H.B. Jenny, P.C. Meier, and W. Simon, in: "Electroanalysis in hygiene, environmental, clinical and pharmaceutical chemistry", W.F. Smyth, Ed., Analytical Chemistry Symposia Series, Vol.2, Elsevier Scientific Publishing Company, New York, 1980, pp.3-10.

[16] H.Freiser, *Pure & Appl.Chem.*, **1987**, 59, 539.

[17] International Union of Pure and Applied Chemistry, Analytical Chemistry Division-Commission on Analytical Nomenclature, *Pure & Appl.Chem.*, **1976**, 48, 127.

[18] M.Cremer, Z. *Biol.*, **1906**, 47, 562.

[19] G.Eisenman, Ed., "Glass Electrodes for Hydrogen and Other Cations", Marcel Dekker, New York, 1967, Chapter 9.

[20] M.A. Arnold and M.E. Meyerhoff, *Anal.Chem.*, **1984**, 56, 20R.

[21] M.A. Arnold and R.L. Solsky, *Anal.Chem.*, **1986**, 58, 84R.

[22] R.L. Solsky, *Anal.Chem.*, **1988**, 60, 106R.

[23] G.D. Christian, "Analytical Chemistry", 3rd Ed., John Wiley & Sons, New York, 1980, pp.310-4.

[24] J. Vesely, D. Weiss, and K. Stulik, "Analysis with Ion-selective Electrodes", Halsted Press, John Wiley & Sons, New York, 1978, pp.1-28.

[25] A.K. Covington, Ed., "Ion-Selective Electrode Methodology", Vol.I, CRC Press, Boca Raton (Florida), 1979, pp.145-160.

[26] J. Ruzicka and C.G. Lamm, *Anal.Chim.Acta*, **1971**, 53, 206.

[27] A.J. Bard and L.R. Faulkner, "Electrochemical Methods: Fundamental and Applications", John Wiley & Sons, New York, 1980, p.71.

[28] J. Vesely, D. Weiss, and K. Stulik, "Analysis with Ion-selective Electrodes", Halsted Press, John Wiley & Sons, New York, 1978, pp. 71-74.

[29] J.A. Marinsky, Ed., "Ion Exchange: A Series of Advances", Vol.1, Marcel Dekker, New York, 1966, pp.284-286.

[30] J.H. Boles and R.P. Buck, *Anal.Chem.*, **1973**, 45, 2057.

[31] G. Eisenman, in: "Ion-Selective Electrodes", R.A. Durst, Ed., National Bureau of Standards, Special Pub. 314, U.S. Government Printing Office, Washington, D.C., 1969, Chapter 1.

[32] A.K. Covington, Ed., "Ion-Selective Electrode Methodology", Vol.I, CRC Press, Boca Raton (Florida), 1979, pp.176-178.

[33] T.E. Edmonds, Ed., "Chemical Sensors", Chapman and Hall, New York, 1988, pp.18-29.

[34] A.K. Covington, Ed., "Ion-Selective Electrode Methodology", Vol.I, CRC Press, Boca Raton (Florida), 1979, pp.94-97.

[35] C.F. Reusch and E.L.Cussler, *AIChE Journal*, **1973**, 19, 736.

CHAPTER 2

CARBON-SUPPORT AND COATED WIRE, ION-SELECTIVE ELECTRODES.

Recently, significant effort has been devoted to the preparation of electrodes with solid internal contacts [1]. These solid substrates can be divided into two broad classes, carbon [2], and metals such as, platinum, silver or copper [3]. These conductors can then be coated with a polymer membrane [3] or insoluble inorganic salts [4] to form an ISE. This configuration eliminates the aqueous internal reference system, and achieves considerable simplification and miniaturization of ion-selective electrodes [3,5]. This miniaturization of ISE's is particularly useful for measurements in small volumes such as *in-vivo* clinical monitoring [5].

The use of solid substrate electrodes was found to overcome some of the disadvantages encountered with the classical barrel configuration (refer to Chapter 1, section 1.2.1). For example, classical ion-selective membrane electrodes can rarely be used at high temperatures or pressures. Pressure difference between the inside and outside of the ISE can seriously impair the performance of the electrode [6], and even destroy the membrane. Therefore, the use of solid-support, ion-selective electrodes is more advantageous in flow injection analysis and liquid chromatography, where effects from pressure build-up at the membrane interface can be particularly important [7].

2.1 CARBON-SUPPORT ELECTRODES.

Carbon-based electrodes have found many applications in potentiometry [1] and voltammetry [8]. Carbon-support, ion-selective electrodes exist in multiple forms like their conventional counterparts: Liquid-state [2], solid-state [4], and pH [9] electrodes.

2.1.1 The Selectrode®

Important work on carbon-support electrodes has been done by Ruzicka and his coworkers. This work led to the development of a new type of commercial ion-selective electrode named Selectrode®, and manufactured by Radiometer in Denmark (Fig.2.1) [1,9]. The carbon-support electrodes are characterized by a simple and robust construction [9], which allows the easy renewal of the ion-sensitive surface.

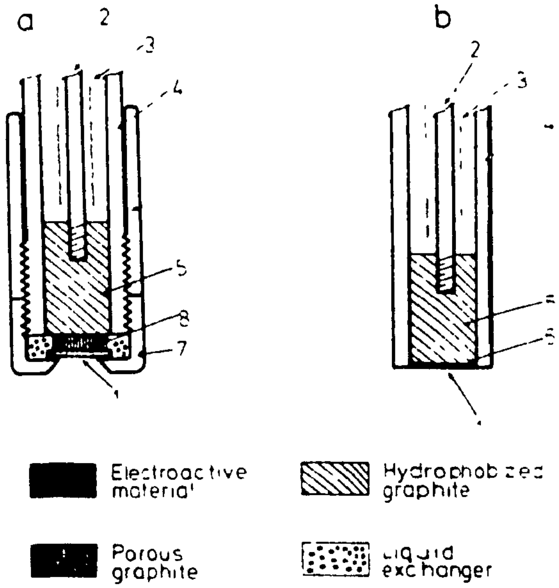


Fig.2.1 Selectrode® construction [9]: (a) Liquid-state electrode, (b) Solid-state electrode. (1) sensitive surface, (2) stainless steel contact, (3) screening, (4) teflon tubing, (5) cylinder pressed from hydrophobized graphite, (6) coating of electroactive material, (7) pool of liquid ion exchanger, (8) porous pellet.

The first report of the Selectrode® described a liquid-state electrode [2], Fig.2.1 a. The membrane consisted of a thin layer of a water immiscible organic liquid within which an electroactive material was dispersed. This membrane was coated on the surface of a porous carbon support to form an ISE. Various electroactive materials such as, valinomycin [9], and dithizone complexes of heavy metals [10] have been used. Valinomycin is an ionophore which displays a high selectivity for potassium ions [11]. Dithizone is a contraction for diphenylthiocarbazone, a complexing agent. Quinhydrones were also found useful for making pH-responsive Selectrodes® [9].

Subsequently, Ruzicka and his collaborators introduced the use of carbon-support electrodes coated with insoluble electroactive materials [4], Fig.2.1 b. Useful electrodes were obtained with silver halides [12],and sulfides of Ag [12], Cu [13], Cd [14], Pb [15], and Hg [9,16]. Typically, homogeneous mixtures of silver sulfide and other metal sulfides were employed [1,9]. The Ag_2S has good semiconducting properties and a stabilizing effect on the electrode behavior [12]. The presence of silver sulfide can notably reduce the light sensitivity of a silver chloride sensing surface [12]. Only few other insoluble inorganic salts have been used [9,17]. Notably, sodium antimonate [18] proved to be useful for making a Selectrode® sensitive to sodium ions [9].

The Solid-state Selectrode® proved to be as sensitive and applicable to real sample analysis as other solid-state pellet membrane electrodes commercially available [17]. In fact, the preparation of Selectrodes® is particularly advantageous, since the problems related to the pellet-pressing technique used to prepare classic solid-state electrodes are avoided [19]. The simplicity of the Selectrode® makes it an extremely versatile research tool to study new membrane materials, and therefore to develop new solid-membrane electrodes. The results of an investigation of membrane materials for making a zinc-selective, carbon-support electrode will be reported in Chapter 4.

2.1.2 Carbon paste electrodes:

The carbon paste electrode can be used as an alternative configuration to the Selectrode®. The paste is prepared with spectral-grade graphite powder, a low solubility compound, and a mulling agent such as Nujol oil or paraffin wax [20]. Alternatively, the paste can be combined with a liquid ion exchanger [21]. This type of electrode is constructed in a similar way to the Selectrode®.

2.1.3 Theory of electrode potential:

The response of a carbon-support electrode coated with an insoluble electroactive material [9] can be related to the behavior of a silver/silver chloride electrode:

$$Ag/AgCl_{(s)}/Cl^-$$

In this case, the half-reaction is

$$AgCl + e^- \rightleftharpoons Ag + Cl^- \qquad (19)$$

and the potential of this electrode [22] is defined by:

$$E = E^o_{AgCl,Ag} - (2.303\ RT)/F \log a_{Cl}. \qquad (20)$$

where $E^o_{AgCl,Ag}$ is the standard potential of Ag/AgCl, -20mV (vs SCE) [23], and a_{Cl^-} is the activity of chloride ions in solution. Since

$$a_{Cl^-} = K_{sp}(AgCl) / a_{Ag+} \qquad (21)$$

equation (20) can therefore be expressed to reflect the activity of Ag^+ in solution:

$$E = E^o_{AgCl,Ag} - (2.303\ RT)/F \log K_{sp} + (2.303\ RT)/F \log a_{Ag+} \qquad (22)$$

Therefore, $$E = E' + (2.303\ RT)/F \log a_{Ag+} \tag{23}$$

In this case,

$$E' = E^o_{AgCl,Ag} - (2.303\ RT)/F \log K_{sp} \tag{24}$$

and $$E' = E^o_{Ag+,Ag} = +557mV \text{ (vs SCE).} \tag{25}$$

At 25°C, the response of a carbon-support electrode (in millivolts) coated with an insoluble electroactive material, M_iX_j, is therefore given by the Nernst equation for cations, M^{j+}:

$$E = E' + 59/n \log a_{M^{j+}} \tag{26}$$

and for anions, X^{i-}:

$$E = E'' - 59/n \log a_{X^{i-}} \tag{27}$$

Table 2.1: E' values for various metal sulfides Selectrodes®.

Electroactive material	Measured ion	E' vs SCE (mV)		
		E'_{exp}[a]	E'_{theory}[b]	E'_{Sato}[c]
CuS/Ag_2S	Cu(II)	369	98	349
CdS/Ag_2S	Cd(II)	100	-645	83
PbS/Ag_2S	Pb(II)	100	-368	130

[a] measured at pM=3 and extrapolated to pM=0, ref. [9].
[b] calculated for the corresponding M/MS electrode.
[c] Ref. [24].

For a Selectrode® coated with silver chloride, E' and E" values are in good agreement with $E^o_{Ag^+,Ag}$ and $E^o_{AgCl,Ag}$ [12], respectively. However, it has been observed that with the copper(II) Selectrode (CuS/Ag_2S membrane), the E' value was about 270mV more positive than the theoretical value calculated for a Cu/CuS electrode (see Table 2.1) [9].

The difference observed between the E' values found for the Selectrode® coated with metal sulfides and the values of E' calculated for the corresponding M/MS electrode, was explained by Sato [24]. He has demonstrated that the electric potential of these materials depends not only on the activities of the ions in solution, but also on the activities of the component elements in the solid phase [24]. He found that the potential of the electroactive material, M_iX_j, which dissociates to give M^{j+} and X^{i-} ions in aqueous solutions, can be described by the general formula:

$$E_{M_iX_j} = E^o_{M_iX_j} + RT/2ijF \ln[((a_{M^{j+}})_l{}^i(a_X)_s{}^j)/((a_{X^{i-}})_l{}^j(a_M)_s{}^i)] \qquad (28)$$

where

$$E^o_{M_iX_j} = 1/2\ (E^o{}_{M,M^{j+}} + E^o{}_{X^{i-},X}) \qquad (29)$$

$E_{M_iX_j}$ is the potential of the Selectrode® coated with the electroactive material M_iX_j, $E^o_{M,M^{j+}}$ and $E^o_{X^{i-},X}$ are respectively the standard potential of the metal and of the anionic species, e.g. sulfide in this case. $a_{M^{j+}}$ and $a_{X^{i-}}$ represent respectively the activity of the metallic and anionic species in solution; "i" is the charge of the anionic species, and "j", the charge of the metallic species. The subscript "l" represents the activity of the component in the aqueous phase, and "s", the activity of the component in the solid phase.

If a solid membrane made of AgCl is saturated with silver, E' normally corresponds to the predicted value for a Ag/AgCl electrode [25]. However, if AgCl is saturated with chloride, the E' value is much more positive than the value expected [25]. When a platinum or carbon support is used, E' can be significantly different from the value expected, since it is not possible to know the activity of silver or chloride in the solid. Nevertheless, the E' values obtained from Sato's model for Selectrodes® coated with metal sulfides are in good agreement with the experimental values, Table 2.1.

2.2 COATED WIRE ELECTRODES:

A Coated Wire Electrode (CWE) consists of a membrane made of an electroactive species dispersed in a polymeric matrix, which is coated directly onto a metallic conductor. The inspiration for the discovery of CWE's came from the work of Hirata and Date [26]. They imbedded a copper wire in polyvinyl chloride (PVC) in which a thick slurry of finely divided cuprous sulfide had been incorporated. Subsequently, Henry Freiser et al. [27,28] developed a flexible and useful approach whereby the electroactive species was dissolved in the polymeric matrix. Electroactive species common to conventional liquid-membrane electrodes such as, phosphate [27], quaternary ammonium [28,29], sulfonate [30] ion-exchange sites, and neutral carriers [31] were used, Table 2.2.

Table 2.2: Common ionophores used for CWE's

Ionophore	Measured ion	Ref.
Didecylphosphate/ dioctylphenylphosphonate	Ca^{2+}	[27]
Aliquat 336S (tricaprylylmethylammonium chloride)	NO_3^-	[28,29]
Dinonylnaphtalenesulfonic acid	NR_4^+ *	[30]
Valinomycin	K^+	[31]

* High molecular weight quaternary amines.

This type of sensor often features better response characteristics and selectivity, than conventional ISE's [3]. Although further size reduction can be easily achieved, CWE's are usually 1-2 mm in diameter. They can be used at any angle, and their preparation is inexpensive [3,32].

2.2.1 Membrane components for coated wire electrodes:

A number of different polymers have been used such as, polyvinyl chloride, polymethylmethacrylate and epoxy resins. The effects on electrode performance due to the specific polymer base were usually found to be negligible [3]. Among these polymeric matrices, PVC is certainly one of the most popular matrices, mainly because of its mechanical strength and wide availability [33].

Before its incorporation into the membrane, the electroactive species must usually be converted to the desired form [3]. A simple method of preparing the electroactive material consists of an extraction procedure of the analyte to be measured. For example, the chloride of tricaprylylmethylammonium ion (commercial name: Aliquat 336S, available in the chloride form), can be exchanged with the desired anion X^{n-}. This procedure is done by successive extractions of a solution of Aliquat 336S. The Aliquat 336S is first dissolved in decanol or hexane, and this solution is extracted with appropriate portions of a concentrated aqueous solution of X^{n-}. The extraction is normally repeated until the final portion gives a negative test for Cl^-. Alternatively, the electrode could be prepared from Aliquat 336S in the chloride form, and conditioned by immersing it in the appropriate salt solution of the analyte species until complete conversion of the ion-exchange sites [3]. However, based on our observations, the first method usually provides more reliable sensors.

The PVC matrix membrane ISE's possess a similar response behavior to their liquid membrane counterparts [33]. Since CWE's are based on liquid membrane principles [3], the polymer film must exhibit some properties of a liquid phase. The temperature at which the electrode is employed should therefore be higher than the glass transition temperature, t_g, of the polymer matrix used [3]. The t_g is the temperature at which the rigid glassy solid material becomes a viscoelastic fluid and facilitates ionic transport [34]. For commercial grades of unplasticized polyvinyl chloride, t_g is approximately 80°C [3]. However, the use of such high temperatures for potentiometric measurements is not practical (for more details, consult Chapter 3, section 3.1.5). Plasticizers must therefore be used to make the polymer more viscoelastic at room temperature. A wide variety of organic compounds, most frequently aromatic esters such as phthalates, can be used as plasticizers [3,33]. The role of plasticizers is important for neutral carrier CWE's since the ionophore constitutes only 2 to 3% of the membrane [3,33]. In contrast, with anion-selective electrodes based on Aliquat 336S, a viscous liquid, the electroactive species is a major component of the membrane (60-70% of the membrane) [33]. Aliquat 336S seems to provide sufficient plasticizing action so that no additional plasticizer is needed [3].

2.2.2 Construction of coated wire electrodes:

A number of techniques have been used in the construction of coated wire electrodes. A platinum wire, soldered to the central conductor of a coaxial cable wire, can be conveniently used [3,5], Fig.2.2. The metal wire is normally coated with the polymer mixture constituted of the polymer, the electroactive species, and the plasticizer in appropriate proportions, dissolved in tetrahydrofuran [5]. It should then be allowed to dry in air for a minute or two, and dipped again until a visible polymer film is obtained on the platinum wire. Of course the coating must be free of bubbles, pinholes, and other texture inconsistencies [3].

The film coating cannot exceed a certain thickness (>300μm). Membranes which exhibit an electrical impedance higher than 50MΩ are usually rejected [3]. Impedance measurements are normally carried with an ac Wheatstone bridge [35] (the reader is directed to reference [35] for a description of this type of instrument). On the contrary, measuring very low impedances can be an indication of incomplete coverage of the metal wire. The junction of the platinum wire and the polymer coating is then sealed with parafilm (Fig.2.2).

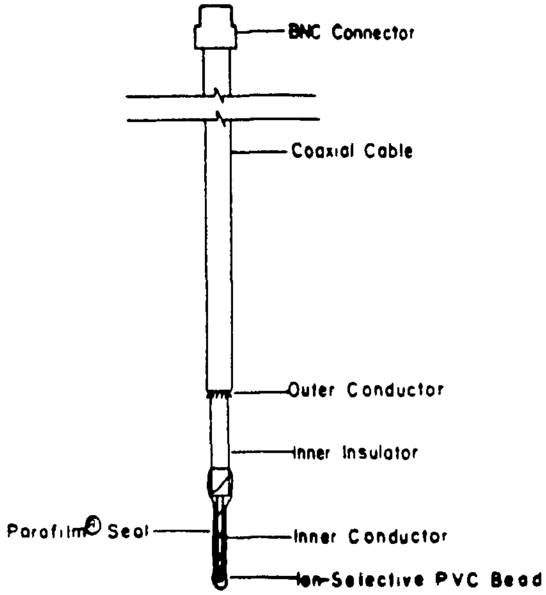


Fig.2.2 A coated wire electrode [3].

2.2.3 Mechanism of the response of coated wire electrodes:

With CWE's, the elimination of the aqueous internal reference system has brought some criticism [3,32]. Notably, the use of polymer-membrane coated-wire electrodes has raised fundamental questions concerning the charge conduction mechanism occurring in the membrane and at the polymer-substrate interface.

From fundamental studies carried out by Carmack and Freiser [36], it was observed that the conductivity behavior of the polymer-dispersed salts can be compared with the behavior of semiconductor thermistors. The temperature dependence of the conductivity of polymer membranes (Fig.2.3) follows the expression for organic semiconductors:

$$\sigma = \sigma_0 \, e^{-Ea/kT} \tag{30}$$

where σ and E_a are the conductivity and the activation energy of the system, respectively. The logarithm of the conductivity is usually plotted on the ordinate against the reciprocal of the absolute temperature on the abscissa. The slope of the straight line is taken as E_a/k, and the extrapolated intercept of the line on the ordinate at $T^{-1}=0$ yields the value of σ_0.

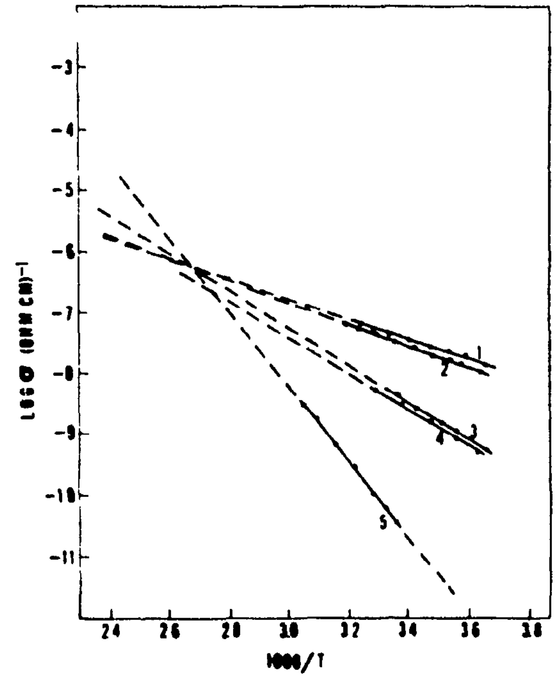


Fig.2.3 Temperature dependence of the conductivity of 0.3M Aliquat$^+$ClO$_4^-$ in different polymeric matrices [36]:
(1) Polyethylene, (2) polystyrene, (3) polymethylmethacrylate, (4) nylon-66, (5) epoxy.

However, a point of significant contrast in the behavior of the polymer-dispersed salts and the organic semiconductors, is their unusually high conductivity in relation to their activation energies (Fig.2.4) [3,36]. Furthermore, it was observed that as the concentration of the salt in the matrix increased, the increase in conductivity was accompanied by a decrease in E_a [3] (Table 2.3). These observations did not support the adoption of a single mechanism of electronic conduction.

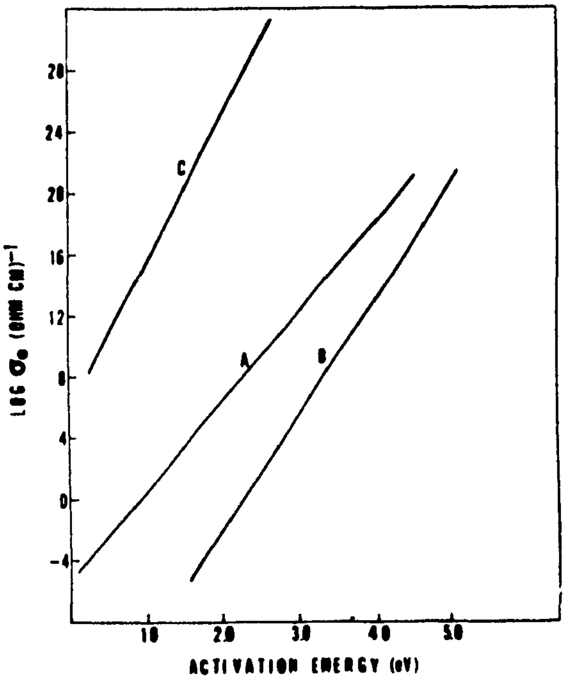


Fig.2.4 Comparison of the conductivity-activation energy relationships for organic systems and an Aliquat$^+$ClO$_4^-$ membrane [36]:
(A) Aromatics, (B) proteins, (C) Aliquat$^+$ClO$_4^-$.

Table 2.3: Conductivity of a polyvinyl chloride film as a function of the concentration of Aliquat 336S [3].

Aliquat-Cl (wt %)	$-\log \sigma_a$ $(\Omega cm)^{-1}$	E_a (eV)
1	13.4	2.34
5	9.3	1.70
11	7.2	1.08
50	6.9	0.58

To elucidate the mechanism of charge conduction, a study of the pressure dependence of the conduction was carried by Carmack and Freiser [37]. Activation volumes, Δv^*, for this process can be calculated from:

$$\Delta v^* = RT\,(\,\partial \ln\sigma / \partial P) \qquad (31)$$

Activation volumes involving electronic conduction commonly have negative values. This was attributed to the increase in the degree of orbital overlap between adjacent molecules with the increase in pressure [38]. On the other hand, large activation volumes were expected for ionic conduction processes. In the case of ionic conduction, the activation volumes should be related to the molar volume of an ion pair, or at least to the volume of the smaller of the two ions as a limiting case [39]. The large activation volume calculated for an Aliquat/PVC membrane, $\Delta v^* = 61 cm^3/mole$ [3,37], is therefore inconsistent with an electronic conduction. Therefore, this study gave strong evidence supporting the theory of an ionic conduction mechanism.

The results obtained from the charge conduction studies also suggested that the existence of some redox couple at the substrate polymer interface probably functions as an internal reference. This hypothesis was further reinforced by the observation that the standard electrode potential shifts significantly and reproducibly from one type of metal substrate to another [40].

2.2.4 Other coated solid-state devices:

Recent developments in electronic and computer technologies have led to the evolution of potentiometry toward the integration of chemically sensitive membranes with solid-state electronics. For example, a field effect transistor (FET) coated with an ion-sensitive membrane can be used in a manner similar to CWE's [41]. In this case, the membrane is directly coated on the gate of the FET (Fig.2.5), which is capable of monitoring the charge build-up in the ion-sensitive membrane [5].

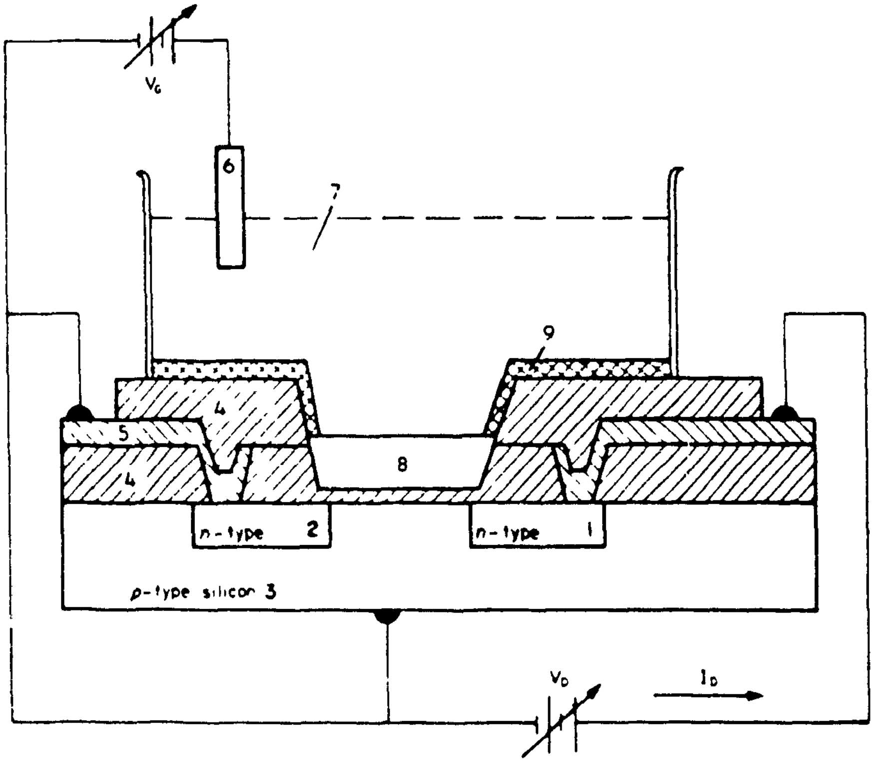


Fig.2.5 An ion-selective field effect transistor [41]: (1) Drain, (2) source, (3) substrate, (4) insulator, (5) metal layer, (6) reference electrode, (7) solution, (8) membrane, (9) encapsulant. V_g is the gate voltage, and V_D is the voltage difference between the source and drain.

A field effect transistor has the basic structure shown schematically in Figure 2.5. An n-channel device is shown, but p-channel devices work equally well. This n-channel FET consists of two n-type diffusions called the source and the drain in a p-type Silicon substrate. An n-type substrate refers to a semiconductor in which electrons are the charge carriers, while positive holes predominantly carry the current in p-type semiconductors. The p-type area of the FET is covered by a thin (50nm) insulator layer (silicon dioxide or silicon dioxide overlaid with silicon nitride) which is called the gate insulator. A metal layer achieves an electrical connection with the source and drain of the device. The remainder of the device is covered by a thick (200nm) layer of insulator.

The voltage applied between the gate and the substrate controls the current that flows between the source and the drain. The field produced across the insulator layer by the gate voltage causes an inversion to occur in a thin layer of silicon close to the gate insulator. This inversion alters the p-type silicon to n-type silicon, and causes a current to flow between the source and the drain of the FET. The inverted area of silicon is called the channel of the device. For a FET operating in the saturation region [41], the drain current, I_d, flowing through the channel is given by

$$I_d = (WC\mu / 2L)\,(V_g - V_T)^2 \tag{32}$$

where W and L are respectively the width and the length of the channel, C is the capacitance of the insulator layer, μ is the mobility of the charge carriers within the channel, V_g, is the gate voltage, and V_T is the threshold voltage. The threshold voltage is the smallest voltage that is required to be applied to the gate in order for a current to be able to flow through the channel of the FET.

In the ISFET, the gate of the electrode is coated with an ion-sensitive membrane. The charge density in this membrane changes because of the interaction with the ions in solution. This causes a current to flow between the source and drain of the transistor (Fig.2.5) [5]. The increased voltage required to bring the current to its initial value represents the response. This response is proportional to the logarithm of the activity of the ion of interest in solution, in a manner similar to conventional ISE's.

The advantages of FET's particularly reside in the possibility of preparing multisensors, due to their very small size, and in numerous possibilities of data-processing [41]. However, problems of compatibility between the electrochemical element (the membrane) and the electronic component (FET) have limited the expansion and application of FET's to real-sample analysis [41]. It became rapidly obvious that the requirements for the encapsulation materials are much more stringent for these electronic devices. Alternatives for the preparation of membranes must therefore be developed to solve this problem.

REFERENCES:

[1] A.K. Covington, Ed., "Ion-Selective Electrode Methodology", Vol.I, CRC Press, Boca Raton (Florida), 1979, pp.145-172.

[2] J. Ruzicka and J.Chr. Tjell, *Anal.Chim.Acta*, **1970**, 49, 346.

[3] H. Freiser, Ed., "Ion-selective Electrodes in Analytical Chemistry", Vol.2, Plenum Press, New York, 1980, Chapter 2.

[4] J. Ruzicka and C.G. Lamm, *Anal.Chim.Acta*, **1971**, 53, 206.

[5] J. Wang, "Electroanalytical Techniques in Clinical Chemistry and Laboratory Medicine", VCH Publishers, New York, 1988, pp.70-75.

[6] P. Van den Winkel, J. Mertens, and D.L. Massart, *Anal.Chem.*, **1974**, 46, 1765.

[7] T.K. Christopoulos and E.P. Diamandis, *Analyst*, **1987**, 112, 1293.

[8] P.T. Kissinger and W.R. Heineman, Eds., "Laboratory Techniques in Electroanalytical Chemistry", Marcel Dekker, New York, 1984, pp.289-317.

[9] J. Ruzicka, C.G. Lamm, and J. Chr. Tjell, *Anal.Chim.Acta*, **1972**, 62, 15.

[10] J. Ruzicka and C.G. Lamm, *Anal.Chim.Acta*, **1970**, 51, 1.

[11] L.A.R. Pioda, V. Stankova, and W. Simon, *Anal.Lett.*, **1969**, 2, 665.

[12] J. Ruzicka and C.G. Lamm, *Anal.Chim.Acta*, **1971**, 54, 1.

[13] E.H. Hansen, C.G. Lamm, and J. Ruzicka, *Anal.Chim.Acta*, **1972**, 59, 403.

[14] J. Ruzicka and E.H. Hansen, *Anal.Chim.Acta*, **1973**, 63, 115.

[15] E.H. Hansen and J. Ruzicka, *Anal.Chim.Acta*, **1974**, 72, 365.

[16] G.A. East and I.A. DaSilva, *Anal.Chim.Acta*, **1983**, 148, 41.

[17] D. Midgley and D.E. Mulcahy, *Ion-Selective Electrode Rev.*, **1983**, 5, 165.

[18] F. Girardi and E. Sabbioni, *J.Radioanal.Chem.*, **1968**, 1, 169.

[19] A.K. Covington, Ed., "Ion-Selective Electrode Methodology", Vol.I, CRC Press, Boca Raton (Florida), 1979, pp.176-178.

[20] S. Mesaric and E.A.M.F. Dahmen, *Anal.Chim.Acta*, **1973**, 64, 431.

[21] G. Ali Qureshi and J. Lindquist, *Anal.Chim.Acta*, **1973**, 67, 243.

[22] G.D. Christian, "Analytical Chemistry", 3rd Ed., John Wiley & Sons, New York, 1980, pp.288-289.

[23] J. Dean, Ed., "Lange's Handbook of Chemistry", 13th Ed., McGraw-Hill Book, New York, 1985, p. 6-16.

[24] M. Sato, *Electrochim. Acta*, **1966**, 11, 361.

[25] R.P. Buck and V.R. Shepard, *Anal.Chem.*, **1974**, 46, 2097.

[26] H. Hirata and K. Date, *Talanta*, **1970**, 17, 883.

[27] R.W. Cattrall and H. Freiser, *Anal.Chem.*, **1971**, 43, 1905.

[28] H. James, G. Carmack, and H. Freiser, *Anal.Chem.*, **1972**, 44, 856.

[29] B.M. Kneebone and H. Freiser, *Anal.Chem.*, **1973**, 45, 449.

[30] C.R. Martin and H. Freiser, *Anal.Chem.*, **1980**, 52, 562.

[31] R.W. Cattrall, S. Tribuzio, and H. Freiser, *Anal.Chem.*, **1974**, 46, 2223.

[32] H. Freiser, *J.Chem.Soc. Faraday Trans. 1*, **1986**, 82, 1217.

[33] A.K. Covington, Ed., "Ion-Selective Electrode Methodology", Vol.I, CRC Press, Boca Raton (Florida), 1979, pp.111-127.

[34] L. Holliday, Ed., "Ionic polymers", Halsted Press Book, John Wiley & Sons, New York, 1975, p.35.

[35] J. Braunstein and G.D. Robbins, *J.Chem.Ed.*, **1971**, 48, 52.

[36] G. Carmack and H. Freiser, *Anal.Chem.*, **1973**, 45, 1975.

[37] G. Carmack and H. Freiser, *Anal.Chem.*, **1975**, 47, 2249.

[38] P.K. Datta, *J.Sci.Ind.Res.*, **1971**, 30, 222.

[39] S.D. Hamann, *Aust.J.Chem.*, **1965**, 18, 1.

[40] H. Freiser, *Pure & Appl.Chem.*, **1987**, 59, 539.

[41] H. Freiser, Ed., "Ion-selective Electrodes in Analytical Chemistry", Vol.2, Plenum Press, New York, 1980, pp.107-131.

CHAPTER 3

CHARACTERIZATION OF ION-SELECTIVE ELECTRODES

3.1 MEASUREMENT TECHNIQUES AND PRACTICAL ASPECTS USING ION-SELECTIVE ELECTRODES.

3.1.1 Calibration procedures:

The most efficient calibration method for ISE's consists of measuring the potential between the ion-selective and reference electrodes for a series of standard analyte solutions of varying concentrations [1]. The potential readings are generally made in triplicate. The average of the readings obtained for each standard solution is plotted on a graph of potential versus the logarithm of the ionic activity of the analyte (for example, see Fig.3.2). This response is described by equation (1). An ISE is said to exhibit a Nernstian response over a given range of activity when the slope of the linear portion of the calibration curve has a value of

$$(2.303\ RT)/z_iF = 0.059/z_i\ \text{(volt)} \qquad (33)$$

per unit of pa_i at 25°C [2]. The precision or reproducibility of the measurements is taken as the standard deviation of a set of three potential readings.

3.1.2 Calculation of the activity coefficient:

ISE's are responsive to the activity of an ionic analyte in solution. Therefore, the activity coefficient of the analyte must be known to calibrate an ISE. The activity coefficient is a correction factor for inter-ionic attractions [3]. Cations of the analyte attract the anions of the dissolved electrolytes in solution and vice versa. This attraction effectively shields the ionic analyte species, decreasing their effective concentration or activity in solution. The activity of an ion a_i can be defined by the expression:

$$a_i = C_i\gamma_i \tag{34}$$

where C_i is the concentration of the ion "i", and γ_i is its activity coefficient. The activity of an ion is normally expressed in molarity.

The Debye-Huckel equation [4] can be used to calculate the activity coefficient of an analyte

$$-\mathrm{Log}\ \gamma_i = 0.51\ z_i^2\ I^{1/2} / (1+0.33\ \alpha I^{1/2}) \tag{35}$$

This equation takes into account the ionic strength, I, and the ion-size parameter, α. The ionic strength is a measure of total electrolyte concentration

$$I = 1/2 \sum C_i z_i^2 \tag{36}$$

where z_i is the charge of each ion present in solution [3]. The ion-size parameter is the effective diameter of the hydrated ion in Ångstrom [5]. It normally ranges from 3 to 6Å [5]. The constants 0.51 and 0.33 were calculated in aqueous solutions at 25°C [3]. This equation is considered valid to an ionic strength of about 0.2M.

For higher ionic strength, correction terms must be added to the Debye-Huckel equation (equation 35). The equation with the Davies modification [6]:

$$-\mathrm{Log}\ \gamma_i = 0.51\ z_i^2\ I^{1/2}/(1+0.33\ \alpha I^{1/2})\ -\ 0.1\ z_i^2 I \tag{37}$$

is valid to an ionic strength of about 0.6M.

In dilute solutions, less than 0.1mM, the activity coefficient of a simple electrolyte is almost unity, therefore the activity is approximately equal to the molar concentration. Above 0.1mM the activity coefficient decreases significantly, and its influence can no longer be neglected.

3.1.3 Sample conditionning: Ionic strength and pH adjustment.

Since the total ionic strength of the solution affects the activity coefficient (equation 37), variations of the activity coefficient of the analyte can be minimized by adding a large constant concentration of an indifferent electrolyte (an electrolyte to which the ISE does not respond). If γ is maintained constant, the activity of the analyte ion is directly proportional to its concentration in solution. In this case, the potential readings can then be plotted directly against the concentration of the analyte. The addition of a large concentration of an inert electrolyte is also helpful in reducing the liquid junction potential of the reference electrode, see Chapter 1, section 1.2.2.

The ISE response may also be affected by the pH of the solution being measured, usually it is preferable to maintain the pH of the solution in an appropriate range $3 < pH < 11$. It is also important to use similar experimental conditions, i.e. pH and ionic strength, both in the calibration of the electrode system and in the measurements of sample solutions.

3.1.4 Response time of ISE's:

The response time of an electrode is defined as the time required for the potential reading to be within a specified range of the final steady-state value; a limit of 1 mV within the steady-state value is commonly used [1]. Experimentally, the readings may be taken when the rate of potential drift has fallen below 1mV/min for low-precision experiments, or 0.1 to 0.2mV/min for highest precision [1]. The use of a chart recorder is a straightforward way of assessing drift rate.

When low concentrations near the limit of detection are being determined, the response time may be extremely long. In such cases, it is possible to make a measurement with non-stationary potentials at a fixed time, but this is at the expense of precision.

3.1.5 Temperature dependency of ISE's response:

The standard potential and the slope of the response of an ISE are both dependent on the temperature of the solution measured, see equation (1). From this equation, a variation of 0.198mV in the ISE response is expected after a temperature change of 1K. The variation of the concentration or the activity of the analyte with temperature is usually considered a small effect, and should not affect the ISE response. However, following an abrupt temperature change an ion-selective electrode may take as long as two hours to reach a stable potential and a reference electrode may take even longer [1]. The standard and sample solutions should therefore be thermostated at 25^{o}C to minimize temperature effects on the response of ISE's.

3.1.6 Quantitation by standard addition:

The standard addition technique is a very convenient method for the determination of the concentration of an analyte in real samples [7]. This technique avoids many of the difficulties typically encountered in solutions containing high concentrations of interfering ions and/or complexing agents. Also, with standard addition, a calibration procedure carried as a distinctive operation is not required. In order to apply this technique, the only requirement is a knowledge of the electrode response to the species of interest. The response is evaluated with standard solutions and should be determined with high precision. Once evaluated, the response or slope factor is generally quite stable and needs only periodic rechecking [1,8].

The initial potential of the unknown sample is given by the Nernst equation:

$$E_1 = E^o + RT/zF \ln C_x \gamma_x \qquad (38)$$

where E^o is the standard potential of the electrode, C_x and γ_x are the concentration and activity coefficient of the analyte ion, respectively. After the addition of a known amount of the analyte, a new potential is measured:

$$E_2 = E^o + RT/zF \ln (C_x + \Delta C) \gamma_x \qquad (39)$$

where ΔC is the increase in concentration of the analyte ion produced by the standard addition. The addition of a standard should be made in such a way that changes of the sample ionic strength are minimized; this keeps γ_x unchanged. If we take the difference between the initial and final potentials measured,

$$\Delta E = E_2 - E_1 \qquad (40)$$

we obtain the following expression:

$$\Delta E = RT/zF \ln [(C_x + \Delta C)/C_x] \qquad (41)$$

Equation (41) can then be solved for the concentration of the analyte in the unknown sample:

$$C_x = \Delta C \, (10^{\Delta E/S} - 1)^{-1} \qquad (42)$$

S is the slope of the electrode response, 2.303 RT/zF, and $\Delta C = C_s(V_s/V_x)$. C_s is the concentration of the analyte standard solution, V_s is the volume of the standard addition aliquot, and V_x is the volume of the unknown sample solution.

If we consider the changes in concentration of the unknown sample solution by the addition of an aliquot of the standard solution, the general form of the standard addition equation [8] becomes

$$C_x = C_s\,[V_s/(V_x+V_s)]\,[10^{\Delta E/S} - ((V_x+V_s)/V_x)]^{-1} \qquad (43)$$

3.2 INSTRUMENTATION AND FACTORS OF ERRORS.

The selection of a voltmeter is determined by the precision of measurement required and the maximum impedance of the cell. A direct-reading instrument, the Fisher Accumet 805MP which can be connected to a suitable recording instrument was used. This instrument can accept a voltage range from 0 to ±2000mV [9].

The input resistance of the meter causes errors due to the attenuation of the signal. The cell hooked up to the meter can be compared to a voltage divider (Fig.3.1)

$$E_{in} = E\,R_{in}/\,(R_{in} + R_e) \qquad (44)$$

where E_{in} is the input potential difference between the indicator and reference electrode, R_{in} is the input resistance of the meter, and R_e is the resistance of the ISE. The attenuation of the signal due to R_{in} is then expressed as

$$\Delta E = E - E_{in} \qquad (45)$$

$$\Delta E = E\,R_e\,/\,(R_{in} + R_e) \qquad (46)$$

The input resistance of the meter must be at least 1000 times that of the cell resistance, in order that the signal attenuation should not exceed 0.1%. With the Accumet 805MP (input impedance > $10^{12}\Omega$ [9]) an accuracy of 0.02% or 0.1mV can easily be achieved with a typical pH glass electrode (R_e=200MΩ, output potential vs SCE = ±414mV [10]). The stability of ±0.1mV/hour of the meter also allows the reliable monitoring of the potential readings of a given cell.

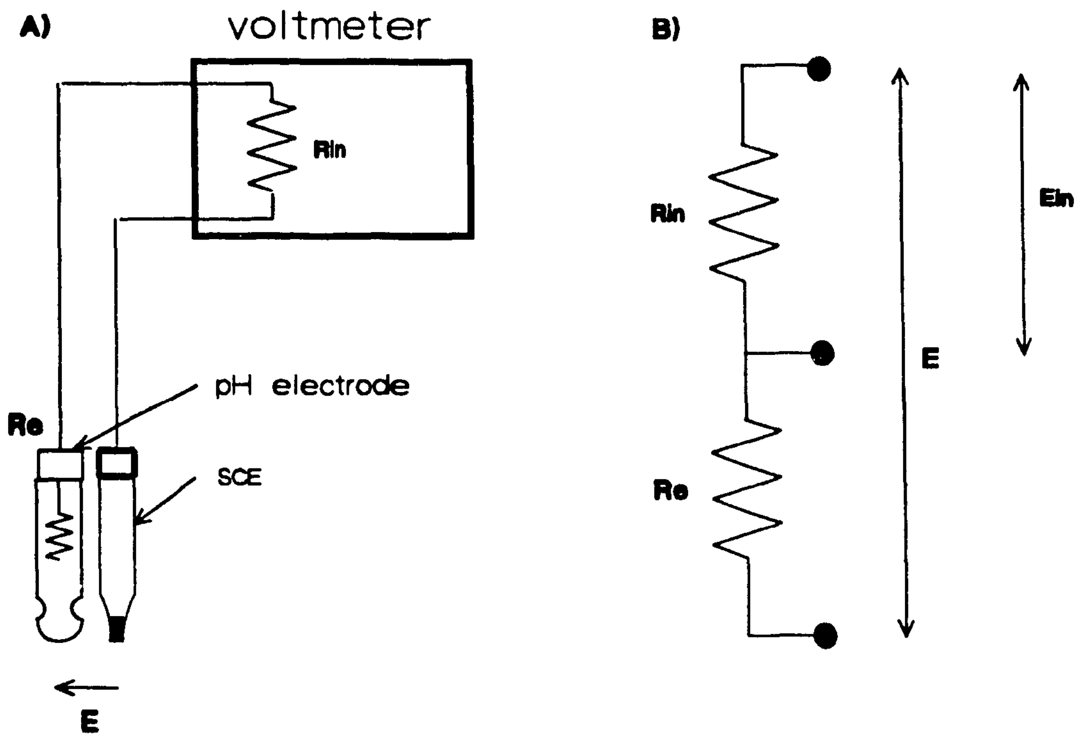


Fig. 3.1 Input resistance error: An electrochemical cell (A) hooked up to a voltmeter acts like a voltage divider (B).

The fluctuations of the voltmeter are usually not an important factor limiting the reliability of the measurements. In fact, the potential fluctuations caused by thermal non-equilibrium in the cell, or by the variations of the ISE characteristics, are usually much higher than the instrumental fluctuations.

A reproducibility of at least 1mV can typically be obtained with an ISE. Differentiation of equation (1) gives the following expression for the error on the measurements:

$$\partial E / \partial a_i = RT/z_iF \; 1/a_i \qquad (47)$$

If $\partial E = \Delta E$ and $\partial a_i = \Delta a_i$, equation (47) becomes:

$$\Delta E = 25.68 mV/z_i \; \Delta a_i/a_i \qquad (48)$$

where ΔE and Δa_i represents the error of the ISE reading and the corresponding error in activity of the ionic species measured, respectively. An error of 1mV with an ISE exhibiting a Nernstian response therefore corresponds to a relative error of 3.9% in activity for monovalent ions.

Significant potential drift over time can introduce serious errors in measurement. Since this non-random change in time is usually very slow [1], frequent calibrations of ISE's, as well as short time intervals between calibrations and sample measurements are recommended to minimize this problem.

If after the concentration has been changed and restored to its original value, there is a significantly different potential recorded, hysterisis has occured [1,2]. Consequently, the reproducibility of the ISE measurements will be quite poor. This problem is more frequently encountered when an electrode is used close to the limit of detection.

3.3 ION-SELECTIVE ELECTRODE PERFORMANCE.

3.3.1 Limit of detection:

A typical calibration curve is shown in Fig.3.2. The limit of detection for an ISE should be defined as the concentration at which the potential reading deviates from the average potential in the region "I", by some multiple ("2" or "3" are frequently used) of the standard deviation of multiple measurements [11]. However, a more convenient definition was recommended by IUPAC [2]. The practical limit of detection is determined as the activity of the analyte at the point of intersection of the extrapolated linear segments of the calibration curve (Fig.3.2). In other words, the limit of detection of an ISE is defined as the lowest activity at which a response for the analyte is observed.

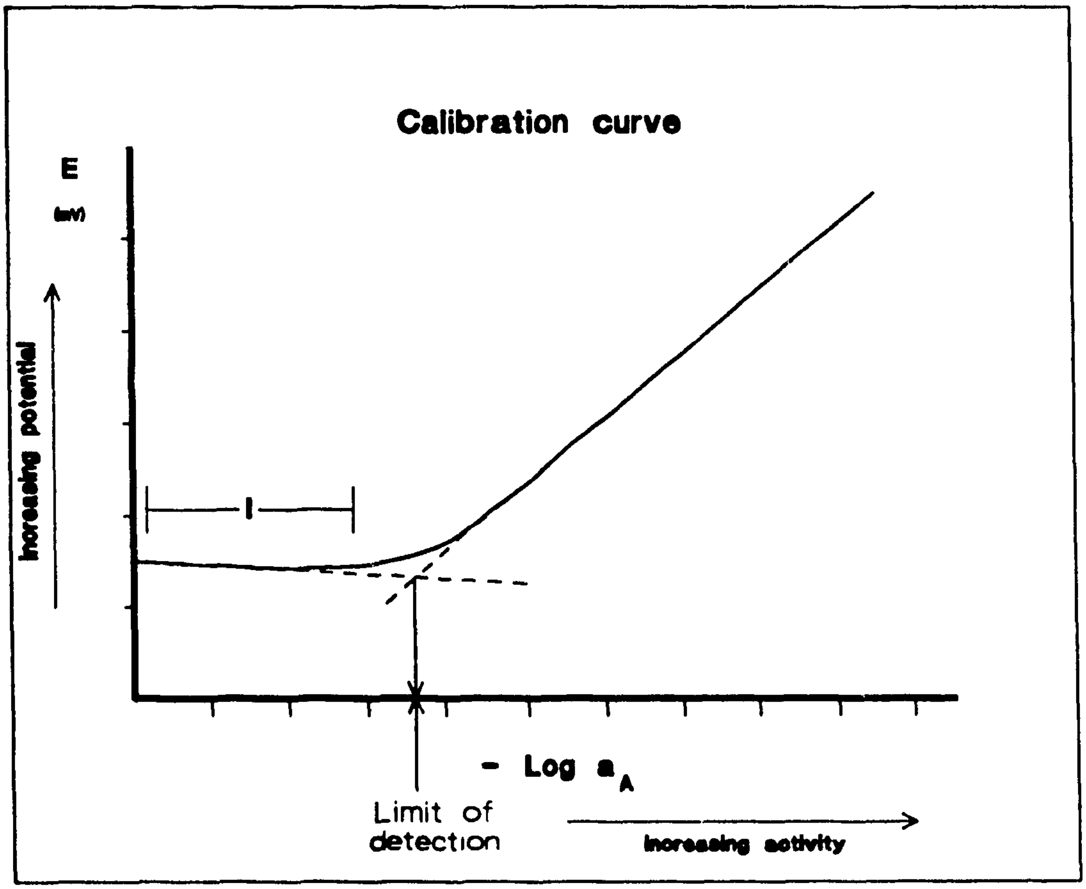


Fig.3.2 Determination of the limit of detection: Segments are extrapolated from the linear portions of the calibration curve. The limit of detection is then determined as the activity of the analyte at the point of intersection of the extrapolated linear segments.

Many factors can affect the limit of detection of an ISE [1]. Therefore, it is essential to report the experimental conditions, i.e. the composition of the solution and the preconditionning of the ISE, in which the ISE was used.

3.3.2 Calculation of the selectivity coefficient:

An electrode can never be considered as specific towards a given ion. It is rather considered selective for the conditions used. Interfering ions can cause the ISE to give a similar response to that of the analyte ion. This results in an apparent increase in the activity of the analyte ion. Consequently, the presence of interfering ions in solution can seriously impair the performance of an ISE.

The response of an ion-selective electrode in the presence of interfering species is described by the Nikolskii-Eisenman equation [12]:

$$E = E^o + (RT/z_iF) \ln [a_i + K_{ij}^{pot} a_j^{zj/zi}] \qquad (49)$$

where a_i and a_j represent the activity of the analyte and of the interfering species, z_i and z_j are the charge of the analyte and interfering ion, respectively.

The selectivity coefficient, K_{ij}^{pot}, defines the ability of an ISE to distinguish between different ions in an heterogeneous solution [12]. It is an approximative factor which can vary significantly with the concentration of interfering ion. It is nevertheless a very useful guide for the electrode performance. The selectivity coefficient is helpful for the prediction of the maximum concentration of interfering ion which can be tolerated in specific conditions.

Although other methods exist to evaluate the selectivity coefficient of an ISE, the fixed interference method usually gives more reliable results [12]. This method consists of measuring the potential of a cell in a series of solutions with a constant level of interference, a_j, while varying activity of the primary ion, a_i. The potential values obtained are plotted against the activity of the primary ion. The value of a_i which is to be used to calculate K_{ij}^{pot} is determined by the intersection of the extrapolation of the linear portions of the curve plotted, Fig.3.3.

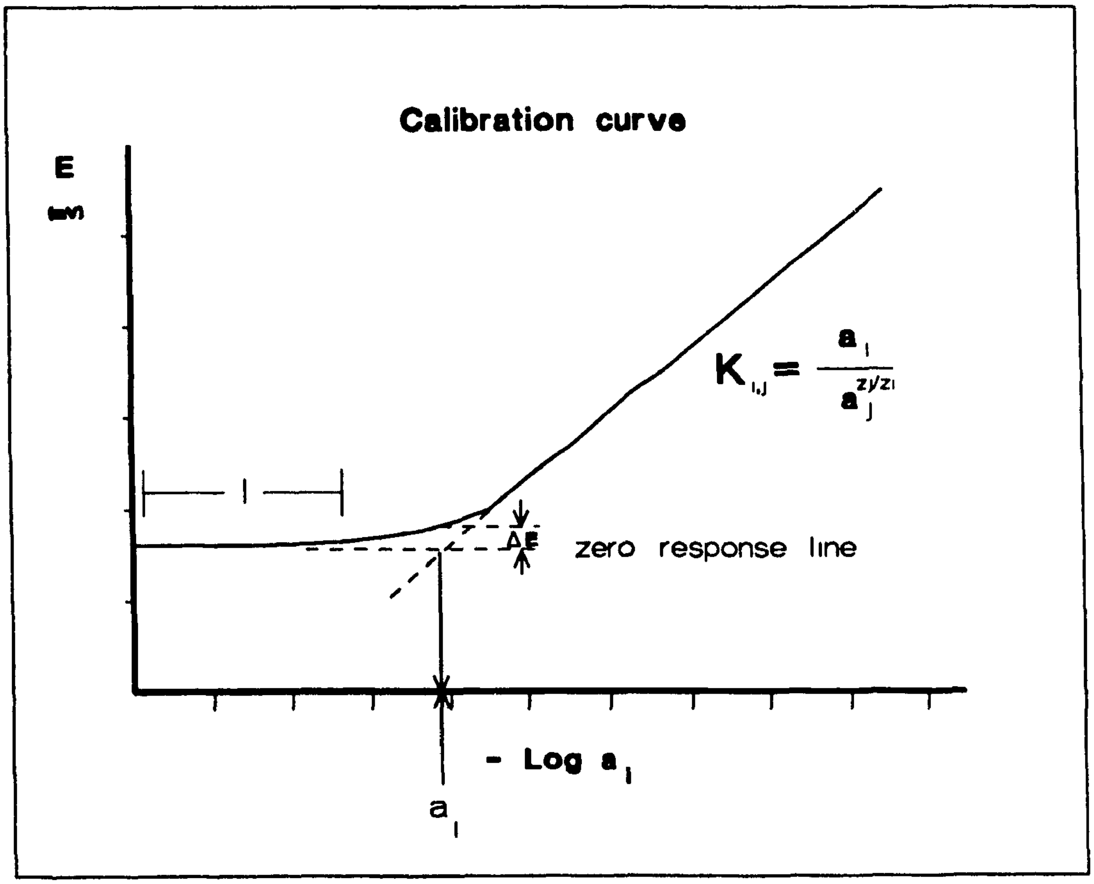


Fig.3.3 Determination of the selectivity coefficient by the fixed interference method (see text for explanations).

This value corresponds to the activity of the analyte at which a response for the analyte is observed, i.e. the limit of detection in the presence of interfering species. The smaller is the value of K_{ij}^{pot}, the greater is the preference of the ISE for the analyte.

As the horizontal part of the experimental plot in Fig.3.3 (region "I") is subject to irreproducibility and drift, it is more reliable to determine a_i as the point at which the difference between the experimental curve and the extrapolated Nernstian response is expressed as:

$$\Delta E = 59\text{mV}/z_i \quad [\underbrace{\log(a_i + K_{ij}^{pot}\, a_j^{zj/zi})}_{\text{response in presence of interfering ions}} \; - \; \underbrace{(\log a_i)}_{\text{Nernstian response}}] \qquad (50)$$

Therefore,

$$\Delta E = 59\text{mV}/z_i \log((a_i + K_{ij}^{pot}\, a_j^{zj/zi})/a_i) \qquad (51)$$

Since the selectivity coefficient is defined as, $K_{ij}^{pot} = a_i / a_j^{zj/zi}$ [2,12], this expression becomes:

$$\Delta E = 59\text{mV}/z_1 \log 2 = 18\text{mV}/z_1 \qquad (52)$$

With this method, a_i is determined as the concentration at which the potential difference, ΔE, between the experimental curve and the extrapolated Nernstian dependence is equal to $18\text{mV}/z_1$.

In fact, other substances can affect the response of an ISE. Some species can interact with the membrane, to change its chemical composition. For example, the presence of organic solvents can seriously impair and even destroy liquid or polyvinylchloride membrane electrodes. Complexing substances can also interact with the ion being measured, and therefore decrease the activity or apparent concentration of the analyte. In this case, the electrode continues to report the true activity of the analyte, but the result obtained is not the result expected.

REFERENCES:

[1] A.K. Covington, Ed., "Ion-Selective Electrode Methodology", Vol.I, CRC Press, Inc., Boca Raton (Florida), 1979, pp.44-58.

[2] International Union of Pure and Applied Chemistry, Analytical Chemistry Division-Commission on Analytical Nomenclature, *Pure & Appl.Chem.*, **1976**, 48, 127.

[3] G.D. Christian, "Analytical Chemistry", 3rd Ed., John Wiley & Sons, New York, 1980, pp.104-107.

[4] A.W. Adamson, "A textbook of Physical Chemistry", 2nd Ed., Academic Press, New York, 1979, p.476.

[5] J. Kielland, *J.Am.Chem.Soc.*, **1937**, 59, 1675.

[6] C.W. Davies, "Ion Association", Butterworths, London, 1962, pp.38-39.

[7] D.A. Skoog and D.M. West, "Principles of Instrumental Analysis", 2nd Ed., Saunders College, Philadelphia, 1980, p.558.

[8] R.A. Durst, Ed., "Ion-selective Electrodes", National Bureau of Standards, Special Pub. 314, U.S. Government Printing Office, Washington, D.C., 1969, pp.381-384.

[9] Fisher Accumet 805MP pH/mv meter, user manual.

[10] A.K. Covington, Ed., "Ion-Selective Electrode Methodology", Vol.I, CRC Press, Inc., Boca Raton (Florida), 1979, p.22.

[11] D.A. Skoog and D.M. West, "Principles of Instrumental Analysis", 2nd Ed., Saunders College, Philadelphia, 1980, p.319.

[12] A.K. Covington, Ed., "Ion-Selective Electrode Methodology", Vol.I, CRC Press, Inc., Boca Raton (Florida), 1979, pp. 15-18.

CHAPTER 4:

INVESTIGATION OF MEMBRANE MATERIALS FOR MAKING A ZINC-SELECTIVE ELECTRODE.

4.1 ZINC-SELECTIVE, CARBON-SUPPORT ELECTRODES:

4.1.1 Zinc: usefulness and applications.

Zinc, a transition metal, is a member of Group IIB in the periodic table of the elements. Zinc is usually found in nature as the sulfide (ZnS) [1], but is not as abundant as less familiar elements like zirconium, vanadium, and strontium. It is an essential trace constituent of plant and animal life, with zinc deficiency being the cause of various plant and animal diseases [2]. In human metabolism, it is notably an essential constituent of several enzymes. One of the largest and important industrial uses of zinc involves the protection of steel against corrosion [1,3].

Zinc and its compounds are relatively nontoxic, unless the associated ions with it are toxic [2]. Nevertheless, hazards do exist for the environment and government regulations in most industrial countries limit the amount of zinc permitted in plant effluents [4-6]. It is therefore essential to control the release of zinc in the environment, and to develop reliable and simple methods to detect zinc.

4.1.2 Choice of membrane materials for zinc-selective electrodes:

In the field of ion-selective electrodes, there have been only a few reports of zinc-selective electrodes [7-16]. Those based on ion exchangers or chelates [7-12] offer poor selectivity, and therefore suffered from strong interference effects. A common example of such an electrode is the polymeric membrane electrode based on organic phosphate ion exchange sites [7,9]. The choice of this liquid ion-exchanger was suggested by the observation that zinc(II) seriously interfered with a calcium-selective electrode [17] based on the same system. Although the solvent mediator and the ligand can be carefully selected to optimize the selectivity toward zinc, strong interferences from calcium, strontium, and lead remained an important problem [9].

Zinc solid-state electrodes based on zinc sulfide, zinc telluride or zinc selenide [13-15] were also found to be of limited usefulness, owing to their lack of stability and selectivity. Similarly, a Selectrode® coated with a polymer of tetracyanoethylene, which demonstrated the ability of complexing zinc ions, showed a limited sensitivity toward zinc and a long response time [16].

In light of the poor selectivity displayed by organic ion exchangers and chelates for zinc ions, the possibility of using other insoluble inorganic materials in the preparation of membranes sensitive to zinc was considered. As established by Ruzicka et al. [18], the choice of solid electroactive materials is governed by the following requirements:

-Low solubility in water ($pK_{sp}>6$).
-Ion exchange at selective functional groups.
-Sufficient conductivity of the electroactive material.

Although low solubility in water is simple to assess, the two other requirements are more difficult to establish. The choice of insoluble inorganic materials is therefore more or less, a matter of trial and error.

Three insoluble zinc inorganic complexes, zinc ferrocyanide ($Zn_2[FeCN_6]$), zinc orthophosphate ($Zn_3(PO_4)_2.XH_2O$), and zinc mercuric thiocyanate ($Zn[Hg(SCN)_4]$) were initially selected for this study. Notably, they are more stable than zinc sulfide, zinc telluride, and zinc selenide on exposure to light and air. Such inorganic complexes exhibit ion-exchange properties [19]. For example, the exchange reaction

$$Zn^* + Zn[Hg(SCN)_4] = Zn + Zn^*[Hg(SCN)_4]$$

is believed to proceed primarily through metathetical reactions in which the metal of the complex is displaced by appropriate ions in solution [20], i.e. the corresponding metal ion or an interfering metal ion. Studies conducted on the ion exchange behavior of ferrocyanides clearly demonstrated a high affinity for cesium ions [21]. This ion exchange behavior proceeds through a structural rearrangement [20]. These facts make the use of zinc ferrocyanide unsuitable for the monitoring of zinc. Therefore, this investigation was limited to the use of zinc orthophosphate and zinc mercuric thiocyanate.

4.1.3 Zinc orthophosphate and zinc mercuric thiocyanate membrane electrodes.

4.1.3.1 Construction of a carbon-support electrode:

A carbon-support electrode similar to the Selectrode® described by Ruzicka et al. [18] was prepared. A 10-cm long spectrographic grade graphite rod about 6mm in diameter (available from Ultra-carbon, Bay City, Michigan), was cleaned by soaking overnight in a 6M hydrochloric acid solution. The rod was then dried in an oven at 120°C for a minimum of 1 hour. A metal spring was fitted over one end of the rod to make the electrical connection (Fig.4.1a). The graphite rod and connector were then inserted into a length of heat-shrink tubing. A small amount of mercury can also be added in the tube to ensure better connection. The tube was sealed to prevent seepage of test solution.

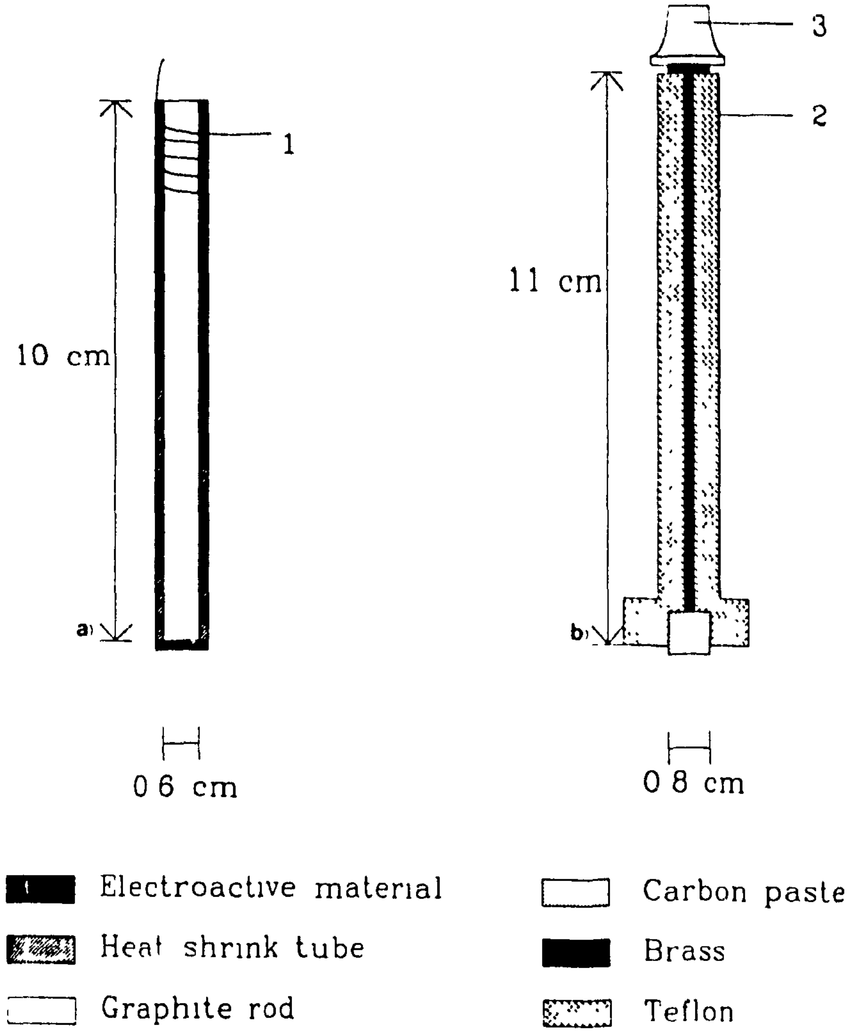


Fig.4.1 a)Graphite electrode. The graphite rod was inserted in a poly(vinyl chloride) heat shrink tube. The electroactive material was coated at the tip of the electrode and the electrical contact was effected with a metal wire spring (1).
b)Carbon paste electrode. The activated carbon paste is packed in the well of the electrode. The body (2) of the electrode was made of Teflon and contact between the paste and the connection jack (3) was made by a brass rod.

4.1.3.2 Preparation of membrane materials: zinc orthophosphate and zinc mercuric thiocyanate.

Zinc orthophosphate can be easily prepared by mixing the appropriate volumes of aqueous solutions of zinc sulphate and sodium phosphate dibasic [22]:

$$3ZnSO_4{\cdot}7H_2O + 2Na_2HPO_4{\cdot}2H_2O \rightarrow Zn_3(PO_4)_2{\cdot}4H_2O + 2Na_2SO_4 + H_2SO_4 + 21H_2O$$

The reaction is conducted at high temperature, above 80°C. A crystalline precipitate forms immediately which is analytically pure. $Zn_3(PO_4)_2 4H_2 0$ loses 2 molecules of water when dried at 100-110°C [22].

Zinc mercuric thiocyanate can be prepared by the precipitation of the zinc with ammonium mercuric thiocyanate [23]:

$$ZnSO_4 7H_2O + (NH_4)_2[Hg(SCN)_4] \rightarrow Zn[Hg(SCN)_4] + (NH_4)_2SO_4 + 7H_2O$$

Ammonium mercuric thiocyanate is itself prepared from mixing appropriate ratios of mercuric chloride, $HgCl_2$, and ammonium thiocyanate, NH_4SCN [22]. Prior to its use, zinc mercuric thiocyanate was dried at 100°C.

The tip of the electrode was cleaned, and coated with the electroactive materials by applying and rubbing in the dry powder. The thin layer of material was hand-polished on a hot (100°C) stainless-steel surface. This procedure was used to coat the carbon-support electrode with either zinc orthophosphate or zinc mercuric thiocyanate. Since the degree of coverage of the electrode surface does not appear to be very critical [18], electrodes can be prepared in a reproducible manner.

4.1.3.3 Response characteristics of the zinc orthophosphate, carbon-support electrode.

Calibration graphs were obtained for unbuffered solutions containing zinc in concentrations ranging from 10^{-6} to 10^{-1}M. A 0.1M zinc solution was prepared by dissolving 2.8754g of zinc sulphate heptahydrate ('Baker Analyzed' reagent) in 100ml of distilled-demineralized water. This solution was standardized by titration of zinc with ethylenediaminetetraacetic acid (EDTA) [24]. The solutions of lower zinc concentration (10^{-6}-10^{-2}M) were obtained by successive dilution.

The electrode coated with zinc orthophosphate showed a linear response to zinc activity in the concentration range from 10^{-5} to 10^{-2}M, with a Nernstian slope of 28.9±0.8 mV/decade (Fig.4.2a). The activity coefficients were calculated from equation (37). Note that each calibration point of Figure 4.2 represents the average of three potential readings. Since the reproducibility of this electrode is within 1mV, the error bar of each calibration point is in fact smaller than the symbol used.

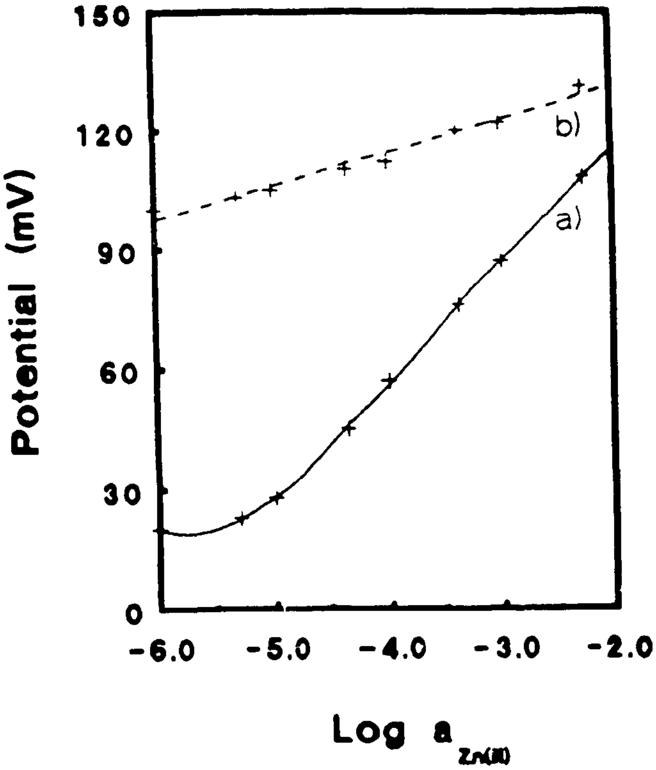


Fig.4.2 Typical response of the zinc orthophosphate, carbon-support electrode:
a) The straight-line portion has a slope of 28.9mV/decade; Zinc standard solutions were prepared in distilled-demineralized water.
b) Response of the same electrode after a brief exposure (5min.) to an acidic solution of 1mM zinc (pH 3.0). The sensitivity was reduced to 9.6mV/decade (same conditions as in a).

The slope of the straight-line portion of the calibration curve was calculated by the method of least-squares [25]. The other calibration graphs presented in this chapter were plotted in the same fashion. This electrode had a response time of 60 seconds. A limit of detection of 5.5×10^{-6}M was obtained. This limit of detection compares favorably with those of the zinc selective electrodes previously reported in literature [7-16]. The use of 0.1M potassium nitrate to maintain a constant ionic strength decreased the sensitivity of the zinc orthophosphate membrane electrode (Fig.4.3).

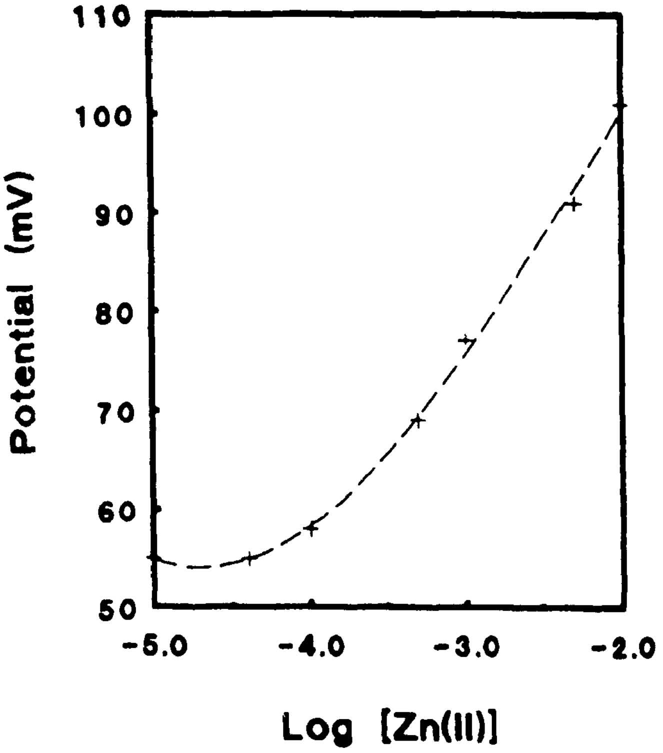


Fig.4.3 Response of the zinc orthophosphate, carbon-support electrode in 0.1M KNO_3. The straight-line portion has a slope of 23.6mV/decade.

The zinc orthophosphate carbon-support electrode was either stored dry or in a 1mM Zn(II) solution. However, it was noticed that after a few days of storage, the electrode demonstrated a strong shift in potential of about 100mV along with a reduced response. Brief exposure to a moderately acidic (pH≅3) solution or to a solution of a strong oxidant, resulted in a similar shift in potential readings and decrease in sensitivity (Fig.4.2b). Prolonged exposure to strongly acidic solution seriously deteriorates the electrode response, since zinc orthophosphate is soluble in acids [22]. Prolonged exposure of the zinc orthophosphate carbon-support electrode should therefore be avoided. Deterioration of the electrode response necessitates the renewal of the ion-sensitive surface.

Graphite exhibits some pH-sensitivity because of the presence of chemisorbed oxygen at its surface [18]. Oxygen forms acidic oxides of carbon such as acidic carboxyl groups, and the formation of these acidic oxides appears to be catalysed in acidic and oxidant solutions [18]. Further, the presence of oxygen compounds on the graphite surface makes the surface hydrophilic. The change of hydrophilic to hydrophobic surfaces can be achieved by impregnation of the graphite body with hydrocarbons. Ruzicka et al. [18] claimed that this procedure reduces both the pH-sensitivity and the memory effect caused by the hydrophilic character of graphite. However, the use of carbon tetrachloride to make graphite hydrophobic is clearly not sufficient to control the pH-sensitivity of the zinc orthophosphate electrode. This poorly reproducible pH-sensitivity of the carbon-support is reflected by the irreproducibility of measurements.

Similarly, East and Da Silva [26] found that hydrophobized spectro-grade graphite still demonstrates a response to pH. They proposed the use of the Williamson synthesis, known as an irreversible route to ethers, to modify the acidic carboxyl groups found at the graphite surface. This modification should reduce the pH sensitivity of the graphite support. The Williamson reaction consists of the reduction of the acidic groups at the graphite surface with lithium aluminium hydride and methylation of the reduced groups with dimethyl sulphate (Fig. 4.4).

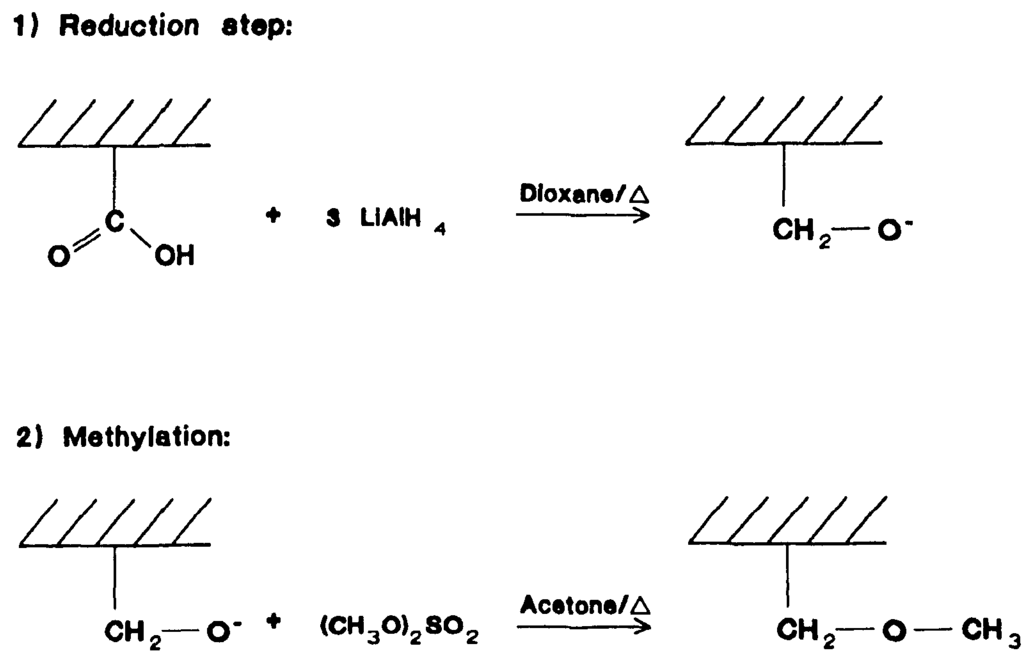


Fig.4.4 Reduction of the pH sensitivity of the carbon-support electrode, through the modification of acidic oxides.

The procedure was found quite effective, and the graphite body of the electrode was found less sensitive to the pH of the solution in the range 4-9 (Fig.4.5). Alternatively, other materials such as paraffin wax and poly(vinylchloride) were used to make graphite hydrophobic. However, all these treatments significantly reduced the electrode response to zinc activity. This was attributed to the increase of the impedance of the zinc orthophosphate electrode, related to the increased hydrophobicity of the graphite body.

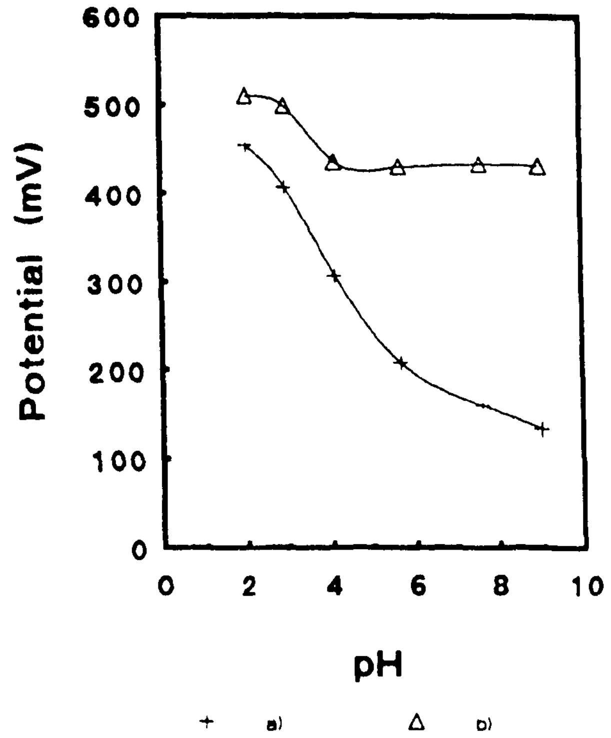


Fig.4.5 pH sensitivity of the carbon-support electrode before (a), and after modification (b) of the graphite surface.

Graphite electrodes coated with mixtures of zinc orthophosphate and silver sulfide demonstrated improved stability. This stabilizing effect of Ag_2S on the behavior of a $AgCl/Ag_2S$ electrode was also observed [27]. Mixtures of different ratios of zinc orthophosphate and silver sulfide (1:1, 3:1, 9:1) were used to coat a graphite electrode. Mixtures of the electroactive materials were obtained by carefully mixing the powders with a mortar and pestle. These mixtures were coated on the carbon-support electrode by the procedure described in section 4.1.3.2.

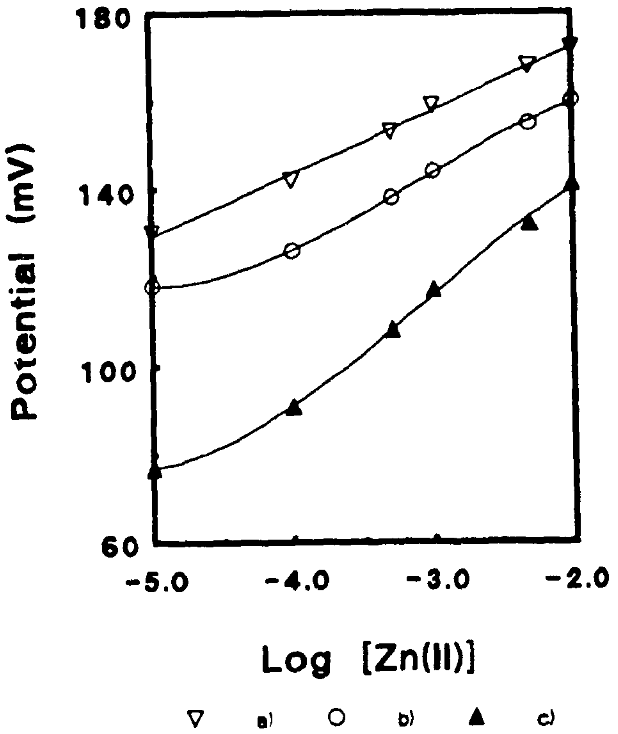


Fig.4.6 Typical response of the carbon-support electrode coated with zinc orthophosphate and silver sulfide:
a) 1:1 mixture (slope= 14.9mV/decade); b) 3:1 (slope= 16.9mV/decade);
c) 9:1 (slope= 24.6mV/decade). The ionic strength of the analyte solutions was maintained constant with 0.1M KNO_3.

The electrodes coated with the 1:1 and 3:1 mixtures demonstrated a low sensitivity to zinc ions. Better sensitivity was obtained with the graphite electrode coated with the 9:1 mixture (Fig.4.6). The use of a mixture of zinc orthophosphate and silver sulfide certainly helped to improve the stability of the electrode, but frequent calibration was still required to compensate for the potential drifts observed after several weeks of use.

4.1.3.4 Selectivity of the zinc orthophosphate, carbon-support electrode:

As previously mentioned for solid membrane electrodes (refer to Chapter 1, section 1.3.1.2), the presence of interfering species may cause potential drifts because of changes in the membrane surface when species enter the solid phase. The selectivity pattern can be predicted by calculating the free energies of formation of the compounds which can be formed from the interfering ions. The standard free energy of an inorganic salt, M_iX_j, in the reaction

$$M_iX_{j\,(s)} \rightleftharpoons iM^{j+}{}_{(l)} + jX^{i-}{}_{(l)}$$

is given by

$$\Delta G_f{}^o = -RT \ln K_{sp} \qquad (53)$$

where K_{sp} is the solubility product of the compound [28], and $\Delta G_f{}^o$ is directly proportional to the pK_{sp} of the material formed.

Interestingly, the metathesis of most potential interfering ions with zinc orthophosphate is not thermodynamically favorable, Table 4.1. This suggested that a zinc determination with the zinc orthophosphate membrane electrode would not significantly suffer from interferences. The values of $\Delta G_f{}^o$ in Table 4.1 were calculated from equation (53).

Table 4.1: Solubility products and values of ΔG_f^o of some orthophosphates.

Orthophosphates	Solubility product*	ΔG_f^o (KJ/mol)
Na_3PO_4	soluble	
K_3PO_4	soluble	
Ag_3PO_4	$1.4x10^{-16}$	90
Li_3PO_4	$3.2x10^{-19}$	106
$Ba_3(PO_4)_2$	$3.4x10^{-23}$	128
$Mg_3(PO_4)_2$	$1x10^{-23}$	131
$Ca_3(PO_4)_2$	$2x10^{-29}$	164
$Zn_3(PO_4)_2$	$9.0x10^{-33}$	183
$Cd_3(PO_4)_2$	$2.5x10^{-34}$	192
$Cu_3(PO_4)_2$	$1.3x10^{-37}$	210
$Pb_3(PO_4)_2$	$8x10^{-43}$	240

* These values were obtained from reference [29].

As predicted, the presence of alkaline and alkaline earth cations did not affect significantly the electrode response, Table 4.2. However, the presence of some transition metals was found to interfere much more than expected. The presence of silver gave rise to very strong interference effects, particularly with the response of the 9:1 zinc orthophosphate/silver sulfide carbon-support electrode.

The selectivity of the zinc orthophosphate electrode can be favorably compared to that of the zinc-selective electrodes based on ion-exchangers and chelating agents previously reported [7-12]. However, we observed a selectivity pattern similar to the one observed for other zinc solid-state electrodes [13-15]. The interferences caused by copper, cadmium, and lead still remain a problem.

Table 4.2: Selectivity coefficients for the zinc orthophosphate carbon-support electrode.

Interfering cations	Selectivity coefficients*
Li(I)	$<1\times10^{-4}$
Na(I)	$<1\times10^{-4}$
Mg(II)	0.072
Ca(II)	0.032
Ba(II)	0.21
Cu(II)	1.0
Cd(II)	8.9
Pb(II)	10

* The selectivity coefficients were determined by the fixed interference method ([interferent]= 1mM), and 0.1M KNO_3 as salt bridge.

4.1.3.5 Response characteristics of the zinc mercuric thiocyanate, carbon-support electrode:

The zinc mercuric thiocyanate membrane showed a non-linear response in the concentration range from 10^{-4} to 10^{-2}M (Fig.4.7). A limit of detection of 2.5×10^{-4}M was obtained with the zinc mercuric thiocyanate electrode, Table 4.3. After storage, no significant potential shift was observed, but the response of the electrode was reduced even further.

4.1.4 Zinc sensitive, carbon-paste electrodes:

The carbon-paste electrode was proposed as a useful alternative to the Selectrode®, to ease surface problems [30]. Carbon-paste electrodes activated with zinc orthophosphate were studied. Two carbon-pastes were obtained by mixing graphite powder (Ultracarbon, Bay City, Michigan) and paraffin oil in the ratio 5:1 (W/V), or graphite powder and paraffin wax in the ratio 3:1 (W/W).

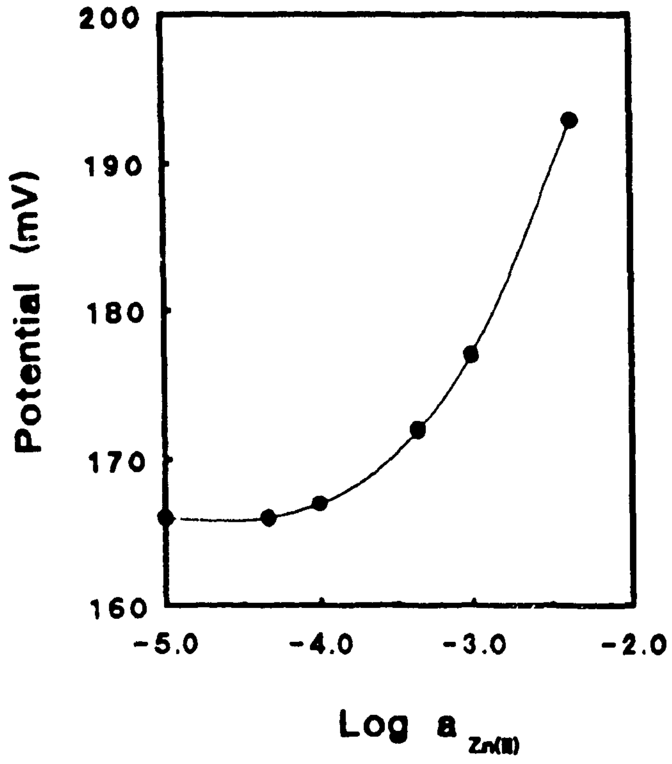


Fig.4.7 Response of the zinc mercuric thiocyanate, carbon-support electrode. Zinc standard solutions were prepared in distilled-demineralized water.

Table 4.3: Comparison of the detection limits and E' values for the zinc-selective electrodes studied.

Activating material	E' (V)	pD[a]
$Zn_3(PO_4)_2 \cdot 2H_2O$	+0.176	5.3
$Zn[Hg(SCN)_4]$	+0.245	3.6

[a] pD: -log (Detection Limit).

The ion-selective pastes were prepared by mixing appropriate ratios of carbon paste and the electroactive materials studied. The best results were obtained with pastes containing 30% electroactive material, that were packed into the well of a pool electrode (Fig4.1b). The carbon pastes activated with zinc orthophosphate showed a linear response at low zinc activity, which leveled off at concentrations above 1mM (Fig.4.8).

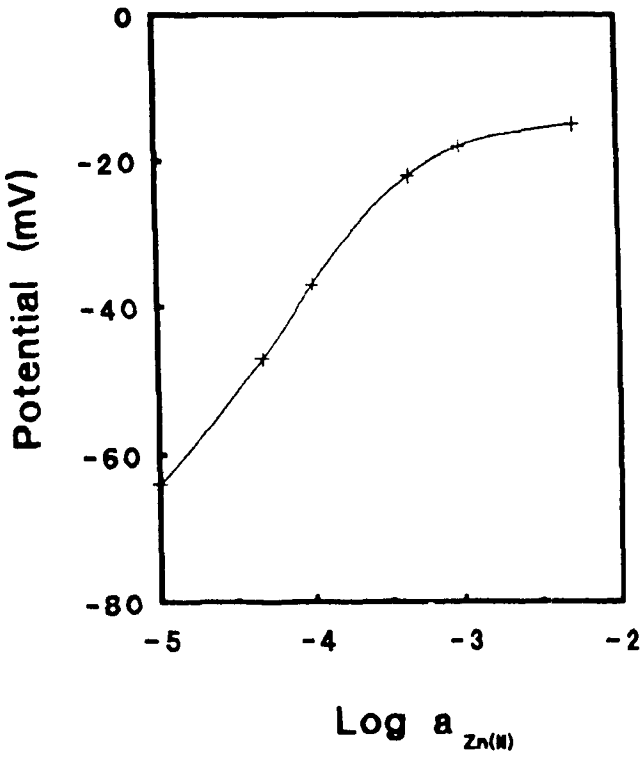


Fig.4.8 Response of the zinc orthophosphate carbon paste electrode. The straight-line portion has a slope of 25.8±0.6mV/decade.

In a theoretical treatment of the potentiometric response of ion-selective membrane electrodes, a Nernstian cation response is only obtained if the fluxes of all the anions within the membrane are minimized (see Chapter 1, section 1.2.3). An anion response can be observed in the presence of oil-soluble anions in the sample, due to their significant extraction by the membrane at high concentrations. Of course, this response to co-ions seriously impairs the response to cations.

Pre-conditioning of the zinc orthophosphate carbon-paste electrode in a dilute solution (1mM) of zinc nitrate or zinc sulfate was necessary to ensure sufficient membrane conductivity and to obtain a stable response. However, prolonged pre-treatments caused the membrane to swell, probably followed by the formation of pores which increases the unselective mobility of ions in the membrane, and seriously impairs the electrode lifetime. This was confirmed by the total loss of selectivity exhibited when other cations were present in tested solutions. This approach to prepare a zinc orthophosphate electrode was therefore not found very useful.

4.2 APPLICATION OF AN ALIQUAT 336S COATED WIRE ELECTRODE TO THE INDIRECT POTENTIOMETRIC MONITORING OF ZINC.

In the previous section, it was concluded that direct potentiometric methods for zinc determination suffer from many interferences, notably other transition metal ions. This problem necessitates either the inconvenient extraction of zinc from the sample matrix, or the use of chelating agents to mask the presence of interfering species. However, the use of these sample treatments are cumbersome, and alternatives must be found to selectively monitor zinc. An interesting possibility consists of using membranes based on long chain alkylammonium salts to monitor zinc anionic complexes such as, zinc chloro complexes, and zinc cyano complexes.

4.2.1 Preparation of an Aliquat 336S coated wire electrode, sensitive to zinc complexes:

The Aliquat salt of the zinc chloro complexes was prepared by solvent extraction. This method is described in Chapter 2, section 2.2.1 (see also Cattrall and Chin-Poh Pui [31,32]). The equilibrium for the formation of the anionic chloro complexes of zinc is not particularly favorable (Table 4.4). Therefore, quite large amounts of chloride must be used in the extraction procedure. In this case, 1M sodium chloride was used. The extraction coefficient of zinc anionic chloro complexes is high, around 10^6 [33]. The same method was used for the extraction of cyano complexes of zinc.

Table 4.4: Formation constants and ratios of zinc containing complexes[a]

	Cl^-		CN^-	
Log β_3[b]	0.53		----	
Log β_4	0.20		16.7	
$[L^-]$	0.2	1.0	0.4	1.0
$[ZnL_3^-]/[Zn^{2+}]$	0.3%	9.4%	---	---
$[ZnL_4^{2-}]/[Zn^{2+}]$	0.02%	3.0%	38%	52%

[a] Calculated by the method of Freiser and Fernando [34].

[b] Cumulative Formation constants [29]: $\beta_3 = [ML_3]/([M]\,[L]^3)$

$\beta_4 = [ML_4]/([M]\,[L]^4)$

The oil obtained after extraction of Aliquat 336S-zinc chloro complexes was mixed with PVC in the ratio 70:30 oil/PVC (W/W). The mixture was dissolved in tetrahydrofuran, and coated over the tip of a Beckman platinum wire electrode. The new electrodes were initially conditioned for a period of 3 hours in a 0.1M zinc solution which contained 1M of the appropriate complexing anions. Before measurement, the electrodes were immersed for 30 minutes in a solution containing an appropriate concentration of chloride or cyanide in the absence of zinc. Between use, the electrodes were reconditioned by soaking in the same solutions but for shorter periods of time, typically 30 minutes. The electrodes may require reconditioning if they are accidentally rinsed with water or exposed to strongly interfering species.

4.2.2 Measurements of the zinc complex anions:

Zinc chloride standard solutions (10^{-5}-10^{-1}M) were prepared by dissolving zinc oxide (Analar grade, BDH) in a small quantity of hydrochloric acid (final concentration of 0.2M), and an appropriate amount of sodium chloride (reagent grade, BDH) to yield a total chloride concentration of 1.0 or 3.0M. The solutions of lower zinc concentration were obtained by successive dilution with the appropriate standard acidified sodium chloride solution (pH about 1.0).

Zinc cyanide standard solutions (10^{-5}-10^{-1}M) were prepared by dissolving zinc cyanide (BDH) in an appropriate solution of potassium cyanide to produce a solution containing 0.1M zinc and either 0.4M or 1M total cyanide. The solutions of lower zinc concentration were obtained by successive dilution.

The response of the chlorozincate(II)-responsive electrode in 10^{-5}-10^{-1}M zinc standard solutions for various concentrations of total chloride is shown in Fig.4.9. The observed slope is close to the Nernstian value expected for a divalent anion. This indicates that the electrode responds preferentially to the anionic tetrachlorozincate(II) species. The tetrachlorozincate(II) complexes are not present in high concentrations in the solutions measured, see Table 4.4. For 1M free chloride, only about 3% of the zinc present in solution is complexed in this form. This certainly demonstrates the electrode sensitivity toward these species. The potential decreases systematically with increasing concentration of chloride at the same zinc concentration. This is consistent with the presence of increasing amounts of the anionic chlorozincate(II) species as the concentration of chloride increases. The limit of detection reaches a value of 1×10^{-5}M or 0.7ppm in 1.0M total chloride. In terms of anionic species, this detection limit represents a value as low as 0.3μM $ZnCl_4^{2-}$.

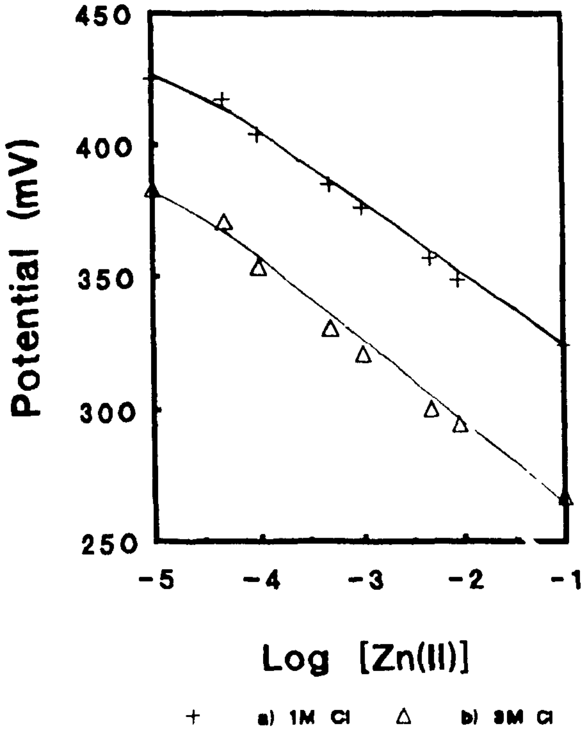


Fig.4.9 Response of a chlorozincate(II)-Aliquat 336S coated wire electrode:
a) in 1.0M total chloride (0.2M HCl-0.8M NaCl), slope: -27.4±0.4mV/dec.
b) in 3.0M total chloride (0.2M HCl-2.8M NaCl), slope: -30.8±0.3mV/dec.

The cyanozincate(II)-responsive electrode exhibits a similar behavior in a concentration range from 10^{-5} to 10^{-1}M Zn(II), Fig.4.10. The cyanozincate(II)-responsive electrode demonstrates an increased sensitivity in dilute cyanide solutions rather than in concentrated solutions. This was attributed to interference effects from cyanide when high concentrations of this species are used. In this case, the detection limit can reach a value as low as 2×10^{-5}M (1.3ppm) or 7.7μM $ZnCN_4^{2-}$ in 0.4M total cyanide.

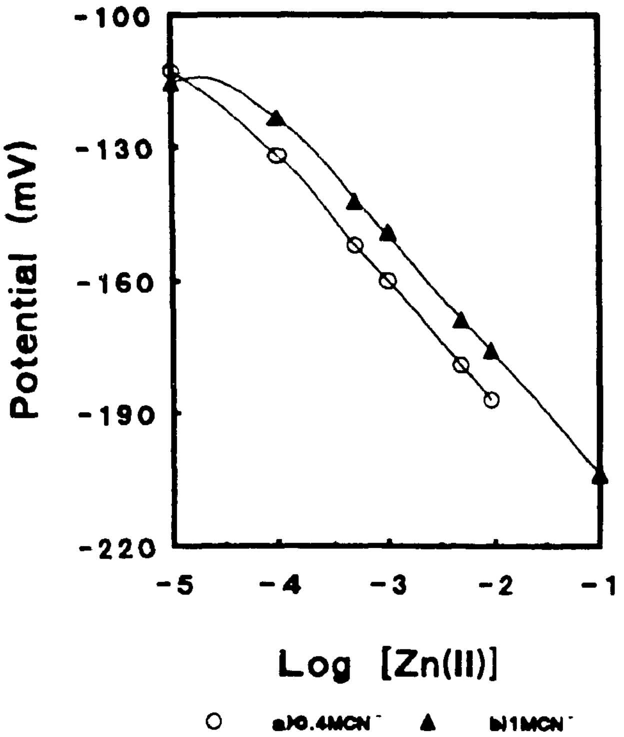


Fig.4.10 Response of a cyanozincate(II)-Aliquat 336S coated wire electrode: **a)** in 0.4M total cyanide, slope: -27.6±0.4mV/dec., b) in 1.0M total cyanide, slope: -26.9±0.4mV/dec.

The response time of both electrodes is very short, just a few seconds. However, about 3 to 5 minutes are required to reach a stable potential in solutions below 0.1mM. The reproducibility of the potential measurements is within 1mV at zinc concentrations above 0.1mM. Both electrodes were stored dry between use, and were used for a period exceeding four weeks. The sensitivity of the cyanozincate(II)-responsive electrode started to deteriorate after four weeks of use. The slow hydrolysis of the organic salt in alkaline conditions is believed to accelerate the degradation of the membrane.

These CWE's are simple, inexpensive, and easy to prepare. They also function well over the concentration range from 10^{-5} to 0.1M. However, they suffer from long-term stability problems, e.g. the potential of these sensors slowly drifts with time. This problem is common to all coated solid-state devices, and is related to the lack of internal reference components. Nevertheless, such devices have found important applications, but their operation necessitates periodic calibration to minimize this problem. The use of a Ag/AgCl rather than a simple conductor or interposing a layer of calomel paste between the membrane and the solid substrate surface [35], was proposed to improve the stability of CWE's. However, the use of a Ag/AgCl electrode coated with a membrane responsive to zinc chlorocomplexes did not appear to have any practical advantage, and did not improve the response stability of these zinc sensing electrodes.

4.2.3 Application to zinc monitoring in the electrogalvanizing process:

As mentioned in section 4.1.1, zinc is widely used to protect steel against corrosion. The electrogalvanizing process with zinc is gaining wide acceptance because it allows a better control of the plating efficiency and avoids the heavy losses of plating materials involved with older non-electroplating techniques [3]. Chloride-containing and cyanide-containing zinc electroplating baths [3,36] (see Table 4.5, 4.6, 4.7) are commonly used for this process, but their plating efficiency is dependent on the composition of the bath. Therefore, the level of zinc and the conditions used must be carefully controlled.

Table 4.5: The composition of some common concentrated chloride-containing zinc electrogalvanizing baths [36].

Chemicals	Concentrated chloride bath		
	KCl bath (M)	NH_4Cl bath (M)	Mixed bath (M)
$ZnCl_2$	0.50-0.66	0.25-0.37	0.25-0.37
KCl	2.51-3.21	---------	2.51-2.91
NH_4Cl	---------	2.80-3.50	---------
NaCl	---------	---------	0.51-0.77
H_3BO_3	0.42-0.67	---------	---------
Operating temperature	18-45°C	18-50°C	18-55°C

Table 4.6: The composition of some dilute chloride-containing zinc electroplating baths [3].

Chemicals	Dilute chloride baths			
	I (M)	II (M)	III (M)	IV (M)
$ZnSO_4.7H_2O$	0.84	1.25	0.56	1.67
NH_4Cl	0.28	0.56	----	----
Na_2SO_4	----	----	0.63	0.63
NaCl	----	----	0.51	0.51
$Al_2(SO_4)_3.18H_2O$	0.05	----	----	----
H_3BO_3	----	----	0.32	3.24
glucose	----	0.67	----	----

Table 4.7: The composition of some common cyanide-containing zinc electroplating baths [36].

Chemicals	Conventional bath (M)	Dilute bath (M)
$ZnCN_2$	0.52	0.26
NaCN or KCN	0.86	0.44
NaOH	1.87	1.87
Operating temperature:	20-45oC	20-45oC

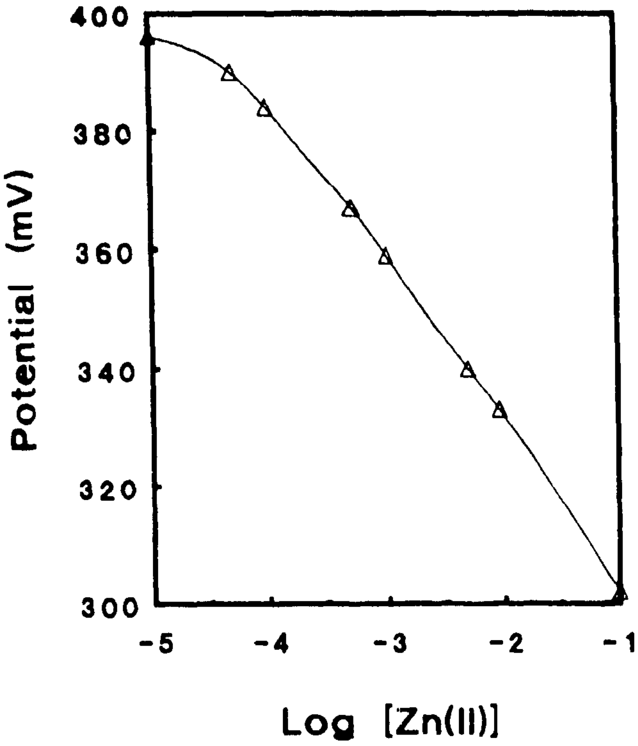


Fig.4.11 Response of a chlorozincate(II)-Aliquat 336S coated wire electrode: in 3.0M KCl-0.5M H_3BO_3, slope: -29.2mV/dec.

Calibration graphs for the chlorozincate(II)-responsive CWE were obtained in standard solutions reproducing the conditions used in the electrogalvanizing process (Table 4.5 and 4.6). These standard solutions were prepared from zinc chloride, and ammonium chloride or potassium chloride acidified with boric acid. The tetrachlorozincate(II)-responsive CWE showed a linear response in the concentration range from $5x10^{-5}$ to 0.1M Zn(II) in concentrated chloride ($[Cl^-]>3M$), see Fig.4.11 and Fig.4.12, while the linear response range is limited to $5x10^{-4}$ to 0.01M Zn(II) in dilute ammonium chloride (0.2M), Fig.4.13.

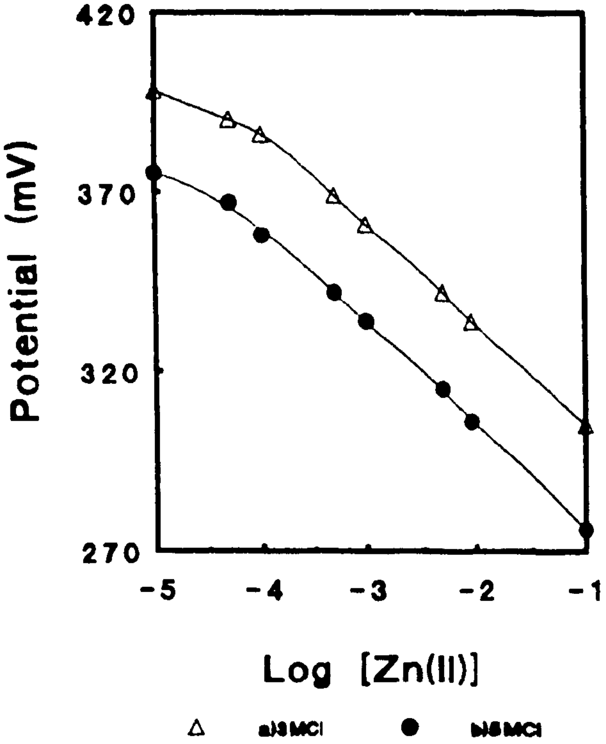


Fig. 4.12 Response of a chlorozincate(II)-Aliquat 336S coated wire electrode in ammonium chloride solutions:
a)in 3.0M NH_4Cl, slope: -27.2mV/dec., b)in 5.0M NH_4Cl, slope: -27.2mV/dec.

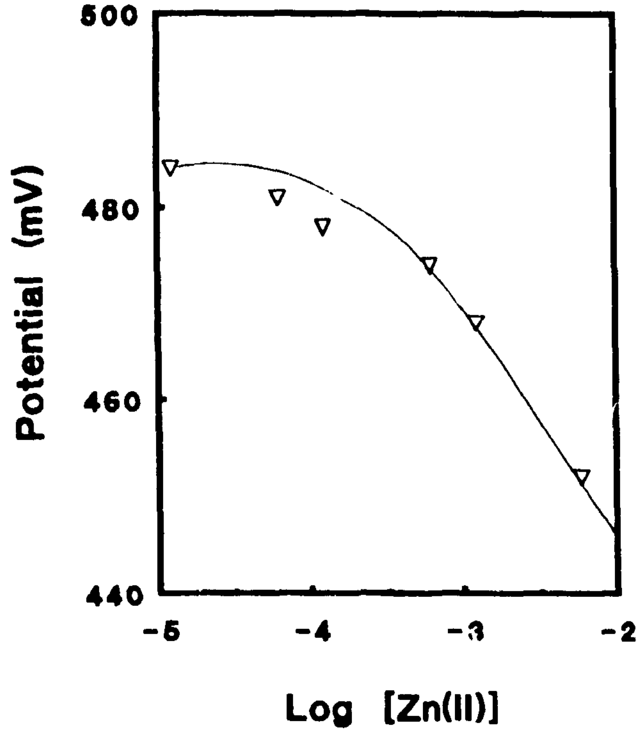


Fig. 4.13 Response of a chlorozincate(II)-Aliquat 336S coated wire electrode in a dilute solution of ammonium chloride (0.2M); slope: -23.3mV/dec.

The electrogalvanizing process is commonly carried at high temperatures (see Table 4.5). The behavior of the chlorozincate(II)-Aliquat 336S CWE at high temperatures was therefore studied to evaluate the temperature effect on its response profile. The response of the tetrachlorozincate(II) responsive CWE was studied at temperatures ranging from 25°C up to 40°C. Although no appreciable change in sensitivity was observed, the potential readings were drifting at high temperatures. This can be expected since the thermal time constants of ion-selective and reference electrodes are long (refer to Chapter 3, section 3.1.5). The use of these zinc sensors at room temperature (20-25°C) is therefore recommended, particularly since their use at high temperatures can accelerate the degradation of the membranes.

The composition of raw waste streams from electroplating plants can reach levels of zinc as high as 4mM [5]. Governmental regulations of industrialized countries commonly limit effluent discharge to 4ppm or 0.06mM [6]. Considering the sensitivity exhibited over a wide concentration range and the detection limits which can be reached (refer to Table 4.8), the use of an Aliquat 336S CWE demonstrates interesting features for the monitoring of zinc in the electrogalvanizing process and waste management. This method also constitutes an advantageous and economical alternative to Flame Atomic Absorption (FAA) for measuring zinc.

Table 4.8: Comparison of the detection limits of FAA and indirect potentiometry for zinc determination.

	FAA[a]	Chlorozincate(II) CWE	Cyanozincate(II) CWE
working range:	0.001-10ppm (0.015μM-0.15mM)	10μM-0.1M	10μM-0.1M
detection limit:	0.001ppm	0.7ppm[b]	1.3ppm[c]

[a] Air-acetylene flame, wavelength: 213.9nm [37].
[b] in 1.0M total chloride.
[c] in 0.4M total cyanide.

Despite the fact that FAA shows superior detectability for zinc, the presence of alkalis in high concentrations reduces the sensitivity and linearity of this method. Further, aspiration of high salt solutions causes severe problems due to the clogging of the nebulizer.

4.2.4 pH dependence of the response of the Aliquat 336S CWE's:

The response of the chlorozincate(II)-responsive electrode is relatively independent of the pH of the solution below pH 7. Above pH 7, zinc precipitates as the hydroxide. The pH of the solution in this case can also have a particular influence on the selectivity of the electrode, please see next section.

On the other hand, cyanide behaves as a Bronsted base and maintains the pH around 11. Of course, the presence of acids must be avoided since solutions of potassium cyanide liberate a poisonous gas, cyanuric acid, when in contact with acids. The presence of hydroxides in high concentrations must be masked since it causes the degradation of the membrane. The measurements must therefore be taken under mild alkaline conditions and in a well-ventilated area.

4.2.5 Interference studies:

The interference of various ions on the response of the chlorozincate(II)-responsive electrode was studied in 3M ammonium chloride. The selectivity coefficients reported in Table 4.9, were determined by the fixed interference method. For this study, the concentration of the interferent was maintained at 1mM, while the concentration of the analyte was varied from 0.01mM to 0.1M.

The only serious interferences arise from the presence of Cu(II), Cd(II) and Hg(II). Silver and lead precipitate as insoluble chlorides, and therefore do not interfere under these conditions. Although the strong interference of Fe(III) was reported in strong acidic chloride solutions [32], Fe(III) does not interfere if the pH of the tested solution is maintained above 4, conditions which are encountered in electroplating baths. These conditions lead to the precipitation of $Fe(OH)_3$. In dilute chloride solutions, the interference effects are more significant. Although the presence of Al(III), a common additive in electroplating baths, does not demonstrate an appreciable interfering effect in 3.0M ammonium chloride, the presence of Al(III) seriously interferes with zinc determination in dilute ammonium chloride solutions (0.2M).

Table 4.9: Selectivity of the chlorozincate and cyanozincate responsive CWE's in the presence of transition metal ions.

Interferents	Selectivity coefficients	
	Chlorozincate(II) CWE	Cyanozincate(II) CWE
Fe(III)	$<1\times10^{-4}$ *	strong shift in potential
Co(II)	$<1\times10^{-4}$	strong shift in potential
Ni(II)	$<1\times10^{-4}$	0.77
Cu(II)	0.09	shift in potential
Cd(II)	4.38	0.89
Hg(II)	7.60	0.92

* Value obtained at pH=4.0.

Solutions of 1M potassium cyanide were used to evaluate the interference effects on the response of the cyanozincate(II)-responsive electrode. In this case, serious interferences occurred from Fe(III), Co(II), Cu(II), as reported in Table 4.9. These metal ions interfere strongly with zinc response, and cause a strong shift in potential readings. The selectivity of the electrode is similar in 0.4M potassium cyanide solutions.

For both electrodes, simple inorganic anions do not significantly interfere with zinc determination. The results obtained indicated that zinc complexes can be monitored in the presence of a 10,000-fold amount of either sulphate, halides and nitrate anions. The only serious interference arises from perchlorate. The presence of electroplating additives such as glucose (Table 4.6) did not exhibit any interfering effect.

Since zinc anion complexes are strongly preferred by the liquid anion exchanger, it is possible to prepare an electrode which demonstrates a high selectivity for zinc with respect to other metals, metals that either do not form complexes or form weaker complexes than zinc. These electrodes therefore offer considerable advantages in eliminating certain interferences which impair the performance of zinc-selective electrodes.

REFERENCES:

[1] N.N. Greenwood and A. Earnshaw, "Chemistry of the Elements", Pergamon Press, New York, 1984, pp. 1395-97.

[2] A. White, P. Handler, and E.L. Smith, "Principles of Biochemistry", 3rd Ed., McGraw-Hill Book Company, New York, 1964, p.943.

[3] F.A. Lowenheim, "Electroplating", McGraw-Hill Book Company, New York, 1978, pp. 171-187.

[4] J.K. Walters and A. Wint, Eds., "Industrial Effluent Treatment, Water and Solid Wastes", Vol.1, Applied Science Publishers, London, 1981, pp. 108-110.

[5] L.L. Tavlarides, "Process Modifications for Industrial Pollution Source Reduction", Industrial Waste Management Series, Lewis Publishers, Chelsea (Michigan), 1985, p.27.

[6] M.D. La Grega and D.A. Long, Eds., "Toxic and Hazardous Wastes: Proceedings of the Sixteenth Mid-Atlantic Industrial Waste Conference", Technomic Publishing Company, Lancaster, 1984, p. 263.

[7] L. Gorton and U. Fiedler, *Anal.Chim.Acta*, **1977**, 90, 233.

[8] M. Uchida, E. Ikeda, I. Ohba, and T. Kashima, *Kyoritsu Yakka Daigaky Kenkyu Nempo*, **1978**, 23, 19; *Chem.Abst.*, **1979**, 91, 44573x.

[9] U. Fiedler-Linnersund and K.M. Bhatti, *Anal.Chim.Acta*, **1979**, 111, 57.

[10] A.G. Rodichev, T.P. Ushangishvili, V.A. Dolidze, and V.G. Krunchak, *Otkrytiya, Izobret.*, **1986**, 8, 263; *Chem.Abst.*, **1986**, 104, 218326y.

[11] A. Viksna, E. Jansons, S. Pastare, and A. Klajse, *Otkrytiya, Izobret.*, **1986**, 15, 154; *Chem.Abst.*, **1986**, 105, 71788k.

[12] O.A. Lebedeva and E. Jansons, *Latv. PSR Zinat. Akad. Vestis, Kim. Ser.*, **1987**, 4, 483; *Chem.Abst.*, **1987**, 107, 189732g.

[13] H. Hirata and K. Higashiyama, *Talanta*, **1972**, 19, 391.

[14] A.F. Zhukov, A.V. Vishnyakov, Y.L. Kharif, Y.I. Urusov, F.K. Volynets, E.I. Ryzhikov, and A.V. Gorievskii, *Zh.Anal.Khim.*, **1975**, 30, 1761; *Chem.Abst.*, **1976**, 84, 97045p.

[15] S. Zhang, *Zhongguo Kexue Jishu Daxue Xuebao*, **1982**, 12, 124; *Chem.Abst.*, **1983**, 98, 136652v.

[16] M. Sharp, *Anal.Chim.Acta*, **1975**, 76, 165.

[17] G.J. Moody, R.B. Oke, and J.D.R. Thomas, *Analyst*, **1970**, 95, 910.

[18] J. Ruzicka, C.G. Lamm, and J.Chr. Tjell, *Anal.Chim.Acta*, **1972**, 62, 15.

[19] D.E. Ryan and M.T. Cheung, *Anal.Chim.Acta*, **1976**, 82, 409.

[20] V. Pekarek and V. Vesely, *Talanta*, **1972**, 19, 1245.

[21] V. Kourim, J. Rais, and B. Millon, *J.Inorg.Nucl.Chem.*, **1964**, 26, 1111.

[22] G. Brauer, Ed., "Handbook of Preparative Inorganic Chemistry", Vol.2, 2nd Ed., Academic Press, New York, 1965, p.1081.

[23] F.D. Snell and C.L. Hilton, Eds., "Encyclopedia of Industrial Chemical Analysis", Vol.5, Interscience Publishers, New York, 1967, p.148.

[24] W.E. Harris and B. Kratochvil, "Chemical Separation and Measurements: Background and Procedures for Modern Analysis", Saunders College, Philadelphia, 1974, p.237.

[25] J.H. Kennedy, "Analytical Chemistry: Principles", 2nd Ed., Saunders College, New York, 1990, pp.46-51.

[26] G.A. East and I.A. Da Silva, *Anal.Chim.Acta*, **1983**, 148, 41.

[27] J. Ruzicka and C.G. Lamm, *Anal.Chim.Acta*, **1971**, 54, 1.

[28] W.H. Waggoner, *J.Chem.Educ.*, **1958**, 35, 339.

[29] J. Dean, Ed., "Lange's Handbook of Chemistry", 13th Ed., McGraw-Hill, New York, 1985.

[30] S. Mesaric and E.A.M.F. Dahmen, *Anal.Chim.Acta*, **1973**, 64, 431.

[31] R.W. Cattrall and Chin-Poh Pui, *Anal.Chem.*, **1975**, 47, 93.

[32] R.W. Cattrall and Chin-Poh Pui, *Anal.Chim.Acta*, 1975, 87, 419.

[33] G. Scibona, F. Orlandini, and P.R. Danesi, *J.Inorg.Nucl.Chem.*, **1966**, 28, 1313.

[34] H. Freiser and Q. Fernando, "Ionic Equilibria in Analytical Chemistry", John Wiley & Sons, New York, 1963, pp.144-165.

[35] A.K. Covington, Ed., "Ion-Selective Electrode Methodology", Vol.I, CRC Press, Inc., Boca Raton (Florida), 1979, pp. 149-160.

[36] H. Geduld, "Metal Finishing", Vol.85, No.1A, 55th Guidebook-Directory Issue, Metal and Plastics Publications, Hackensak (New Jersey), 1987, pp.299-308.

[37] G.D. Christian, Analytical Chemistry, 4th Ed., John Wiley & Sons, New York, 1986, pp.409-420.

CHAPTER 5:
IONIC POLYMER MEMBRANES

Improvement of the selectivity of polymeric ion-selective membranes through systematic studies of various ionophores and membrane additives remains an important area of research [1-3]. However, there are limitations to the usefulness of polymeric membranes because of their limited lifetime [4]. This is especially true when they are used with semiconductor devices such as field effect transistors [5,6] (please refer to Chapter 2, section 2.2.4).

The limited lifetime of polymeric membranes has been attributed to the loss of the plasticizer and the ionophore from the membrane phase [4]. The plasticized polymer forms a molecular network into which the ionophore permeates [7]. In the presence of water, the polymeric membrane swells and slowly releases the membrane components to the external solution [4]. The plasticizer and the ionophore are essential components of the membrane which are promoting the selective, ionic mobility in the membrane [7]. Therefore, the loss of these components is detrimental to the performances of the membrane electrode [4]. Serious limitations of membrane lifetime are to be expected, especially in chemically or physically hostile environment. In order to eliminate the limitations associated with leaching of the active components, it is necessary to incorporate the ion-sensing species as an integral part of the polymer membrane.

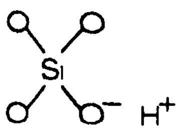
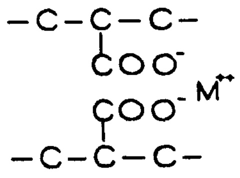
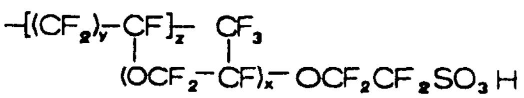
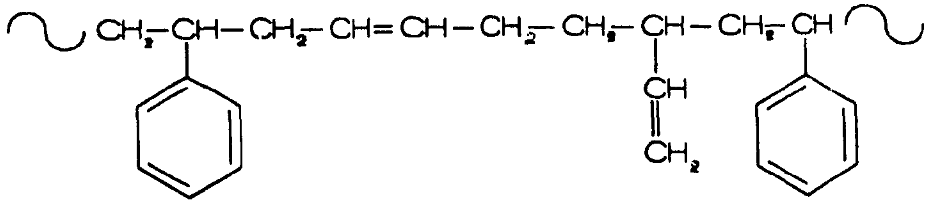
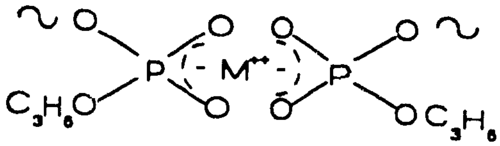
5.1 IONIC POLYMERS AND THEIR APPLICATION TO ISE's:

An ionic polymer is a polymer either organic or inorganic in nature, which contains both covalent and ionic bonds [8]. These polymers containing ions have also been referred to as "ion-containing polymers" and "ionomeric polymers" [8,9]. The name Ionomer is a DuPont trademark originally used to designate a metal salt of a carboxylated polyethylene [9]. However, it has become a common designation for ionic polymers in general [8].

With ionic polymer membranes, the ion exchange-groups are covalently bound to the polymer network rather than physically entrapped within a polymer matrix, as compared to conventional polymeric ion-selective membranes. In contrast, the counterions associated to these ionic groups are free to move. This mobility depends on the strength of the ionic bond and on the presence of liquids in the polymer matrix, such as water, which promote the dissociation of ionic bonds. Hence, a mechanism of ionic transport without plasticizing the polymer apparently exists in ionic polymers. The mechanism of charge transport in ionic polymer membranes will be further investigated in Chapter 6. Therefore, the use of ionic polymers seems particularly attractive to prepare ion-selective membranes with non-leachable components.

By definition, the family of ionic polymers includes very different materials such as, glass (silicates), DuPont ionomers, and carboxylated rubbers. Silicates and carboxylated rubbers were used in the composition of ion-selective membranes, see Table 5.1. Although glass membranes were found useful for the monitoring of pH in aqueous solutions [10], the selectivity of the carboxylated rubbers for divalent cations was found too low for practical analytical applications [11]. Membranes of poly(acrylic acid) were also found to exhibit poor selectivity for divalent cations [12]

Table 5.1: Ionic polymers used in ISE technology.

Ionomeric polymers	Structure	Ions monitored	Ref.
Glass		H+	[10]
Carboxylated rubber, Poly(acrylic acid)		Divalent cations	[11,12]
Perfluorosulfonate Nafion Ionomer		Large organic cations: Quaternary Ammoniums	[13]
Poly(styrene-b-butadiene-b-styrene)			
with phosphate groups:		Calcium	[14,15]
with ammonium groups:	$\sim NR_3^+\ X^-$	Nitrate	[16]

Martin and Freiser [13] have reported that a polymeric membrane made of Nafion 120 exhibits a high selectivity for large organic, hydrophobic cations (Table 5.1). The Nafion polymers are a family of perfluorosulfonate cation-exchange polymers developed by DuPont which exhibit outstanding chemical and thermal stabilities [17]. Their ability to promote ionic or charge transport has led to the application of perfluorosulfonate ionomers (PFSI's) in fuel cells, water electrolyzers, batteries, and more recently in electroanalysis [18]. A membrane electrode made of Nafion 120 was used to potentiometrically monitor large quaternary ammonium cations such as tetrabutylammonium [13].

Only a few other attempts were made to prepare ion-selective polymeric-membrane electrodes with immobilized ion-exchange sites. Ebdon et al. [14] have prepared membranes by cross-linking a styrene-butadiene-styrene (SBS) triblock copolymer with ion-exchange groups, using free radical initiation with ultraviolet irradiation. Phosphate [14,15] and quaternary ammonium ion exchange groups [16] have been immobilized in this fashion (see Table 5.1). However, there are disadvantages associated with this approach; this immobilization procedure is 1) limited to photopolymerizable materials and 2) a high yield of cross-linking was found detrimental to the membrane response.

5.2 STRUCTURAL AND PHYSICAL PROPERTIES OF IONIC POLYMERS.

5.2.1 Concentration of ionic bonds:

The concentration of covalently bound ions in the polymeric structure is an important parameter in ionic polymers and is used as a guide for classification [8]. For this purpose, the concept of relative number of ionic (N_{ir}) and covalent network (N_{cr})

bonds per volume unit (cm^3) can be used:

$$N_{ir} = \rho / M_i \tag{54}$$

$$N_{cr} = \rho \chi (CN)/(2M_{ru}) \tag{55}$$

ρ is the density of the polymer, M_i is the average molecular weight of the chain between ion groups, χ is the number of covalent network atoms in repeat unit, and M_{ru} is the molecular weight of covalent repeat unit. CN is the average connection number of network atoms:

$$CN = \frac{2a + 3b + 4c}{a + b + c} \tag{56}$$

a is the number of 2-connected, b is the number of 3-connected, and c is the number of 4-connected atoms in the chain. For example, the network atoms of poly(vinyl chloride), $-CH(Cl)-CH_2-$, are 2-connected, while a network atom which represents a cross-linking point may be 3- or 4-connected.

For univalent bound ions, the relative number of total network bonds [8], N_r, is given by

$$N_r = N_{(c+i)r} = \rho \left(1/M_i + \chi (CN)/(2M_{ru}) \right) \tag{57}$$

The proportion of bound ions in several ionic polymers is given in Table 5.2.

Table 5.2: Proportion of bound ions in ionic polymers.

Polymer	$N_{ir}/(N_{cr} + N_{ir}) \times 100$ *
Carboxylated rubbers	0.5-2%
Metal polyacrylates	20%
Linear silicates	33%

* These values were obtained from reference [8].

The range of ionic bonds normally falls between the extreme values of 0% for PVC and 100% for an ionic salt like sodium chloride.

5.2.2 Aggregation of ions in ionic polymers:

Ion association takes place in liquid media of low dielectric constant. For example, salts such as Bu_4NCl and KCl aggregate to form ion-pairs in organic solvents of low dielectric constant. Similarly, ionic association or aggregation should occur in ionic polymers [8]. However, aggregation of ions in a polymeric matrix is more difficult. In this case, the ion is bound to a chain. Therefore, it is necessary that the conformation of this chain is accommodated to the arrangement of ion-pairs. Ion-pairs are also termed "multiplets" [19]. These multiplets consist of small numbers of ion dipoles, dispersed in the hydrocarbon matrix [19]. Multiplets can therefore act as ionic crosslinks. For example, in a polymer containing neutralized carboxylic acid groups, hydrogen bonds act as ionic crosslinks, Fig.5.1.

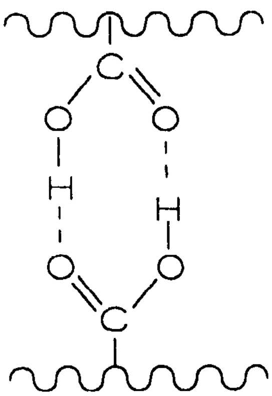


Fig.5.1 Hydrogen bonds in an ionic polymer containing carboxylic acid groups act as ionic crosslinks.

At this stage, it was assumed that multiplets are randomly distributed throughout the polymer matrix [8]. However, it is necessary to address the possibility that these ion-pairs can further aggregate in domains called "clusters". Studies of DuPont's Nafion polymers have yielded more information about the formation and the physical characteristics of ionomeric polymers [20,21]. These studies have clearly demonstrated that ionic clusters are formed in Nafion ionomers [21]. These clusters contain the polymer-attached ion, its counterion, and water of hydration, as well as some of the polymer chain material [8]. The ionic clusters, approximately 40Å in diameter, are randomly distributed throughout the backbone of the polymer. These clusters are connected by small channels, about 10Å in diameter [21]. Counterions and neutral species may apparently diffuse from cluster to cluster via these small channels [22], while co-ions should be excluded (Donnan exclusion, refer to Chapter 1, section 1.2.3).

The following factors [8] must be considered in the aggregation of ions:

-Work is involved to stretch the segment of the polymer chain so that ionic aggregation becomes possible.
-Electrostatic energy is released when ions aggregate.
-The cluster is not infinitely stable, and above some temperature T_c, the cluster decomposes.

At low ion concentrations, the space between the ionic groups is large. Of course, large space between ions will oppose their aggregation. The nature of the polymer chain, its stiffness, and the presence of bulky side chain will also play a role in ionic aggregation [8]. The dielectric constant of the media in which the salt groups are immersed also influences ionic aggregation. In a polymer with a high dielectric constant, no particular driving force to induce formation of clusters exists. The higher the concentration of ionic groups, the more polar is the media. In systems based on polyacrylates, the proportion of bound ions is large (N_{ir}/N_T=20%, Table 5.3), and evidence of cluster formation was not observed [8].

5.2.3 Glass transition in ionic polymers.

Ion-pairs or multiplets which act as ionic crosslinks strongly influence the glass transition temperature of the polymer [8]. The transition from a glassy to a rubbery consistency is a characteristic of many polymeric systems. As the temperature increases, the segmental mobility increases in such a way that rubber-like deformations become possible. The segmental mobility depends upon the nature of the inter-chain forces, the degree of ionisation and the presence of ionic bonds. In very highly cross-linked polymers and in polymers with a high concentration of ionic groups, the t_g is high. In these cases, there is often even no indication of a t_g below the temperature of decomposition of the polymer [8].

As the temperature is further increased, ionic polymers may melt, and this process should be reversible. It was shown that polymers with a low concentration of ionic bonds generally melt. On the contrary, polymers with a high concentration of ionic groups rather decompose on heating. This is attributed to the higher degree of cross-linking or crystallinity in the polymer matrix. While multiplets act as ionic crosslinks, the crystalline domains play a role as physical crosslinks [23]. Studies have demonstrated that the ionic groups are absent from the crystalline domains [23]. This involves the presence along the backbone of the polymer of many long hydrophobic segments containing only hydrocarbon chains.

Differential scanning calorimetry (DSC) is commonly used to determine the glass transition temperature of a polymeric system [24]. DSC measures the heat energy occurring in a substance as a function of temperature. With this technique, it is possible to detect any physical transition or chemical reaction that is accompanied by a heat-energy change [24].

5.3 STUDY OF THE IMMOBILIZATION OF ION-EXCHANGE SITES WITHIN POLY(VINYL BENZYL CHLORIDE).

Two main synthetic routes can be adopted for the immobilization of ion-exchange sites: a) copolymerization of a functionalized monomer with an olefinically unsaturated monomer or b) direct functionalization of a preformed polymer. The second approach seems more advantageous. It is synthetically more simple, and it does not require the use of photopolymerizable material and radical initiators as in the first synthetic approach (a).

In a study initiated by Lawton and Yacynych [12], it was demonstrated that poly(vinylbenzyl chloride), PVBC, offers promise as a precursor for chemically modified polymer-film electrodes. The chloromethyl group is extremely reactive to a variety of nucleophilic reagents [25]. Therefore, it appears possible to functionalize PVBC with various ion exchange groups. The immobilization of several ionic groups, quaternary ammonium, phosphonium, and alkyl phosphates was studied, Table 5.3.

Table 5.3: Immobilization of ion-exchange sites investigated.

Ion exchange sites	Reagent	Solvent	Reflux time
$-CH_2-NR_3^+Cl^-$			
R_1:$-CH_2-CH_3$	triethylamine	methanol	5 hours
R_2:$-(CH_2)_4-CH_3$	tripentylamine	methanol	5 hours
R_3:$-(CH_2)_5-CH_3$	trihexylamine	methanol	6 hours
R_4:$-(CH_2)_7-CH_3$	trioctylamine	chloroform	24 hours
$-CH_2-PR_3^+Cl^-$			
R_1:$-(CH_2)_7-CH_3$	trioctylphosphine	chloroform	6 hours
R_2:$-C_6H_5$	triphenylphosphine	methanol	6 hours
$-CH_2-PO_2(OC_2H_5)^-K^+$	triethylphosphite	50:50 methanol chloroform	72 hours
	+hydrolysis	1% KOH in methanol	5 hours
$-CH_2-C_6H_5-B(C_6H_5)_3^-K^+$	tetraphenylborate	chloroform	

Poly(vinylbenzyl chloride) was obtained from Aldrich Chemicals, and used as received. It is a 60/40 mixture of 3- and 4- isomers of poly(vinylbenzyl chloride), and has a molecular weight of approximatively 50,000. The use of PVBC is interesting because of the similarity of its properties with those of PVC. Notably, it is soluble in organic solvents such as tetrahydrofuran and chloroform.

5.3.1 Characterization of modified polymers.

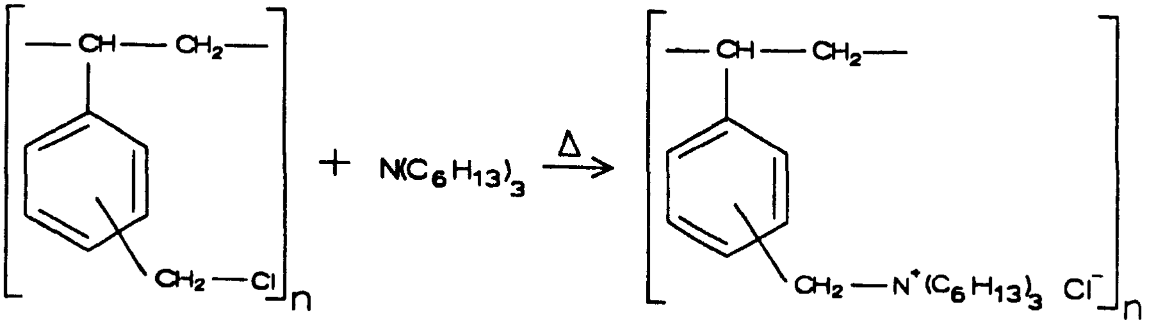
After functionalization with ion-exchange groups, the modified PVBC was characterized by infrared spectroscopy. Infrared spectroscopy is a technique commonly used to obtain structural information [26]. An Analect AQS18 Fourier Transform Infrared (FTIR) spectrometer was used for this investigation. This spectrometer basically consists of two modules: an optical system which uses an interferometer, and a dedicated computer. The computer controls optical components, collects and stores data, performs computation on data, and displays spectra [27]. FTIR offers many advantages compared with conventional dispersion infrared spectroscopy. These advantages include higher signal-to-noise ratio and higher accuracy in frequency for spectra taken over a wide range of frequencies [28]. The reliability and superior performances notably allow the analysis of smaller samples.

Several sample preparation techniques can be used with polymeric systems. These techniques include using a solution of the polymer dissolved in an appropriate organic solvent, casting thin films on InfraRed (IR) transmitting plates, preparing melt samples between plates, etc. The preparation of KBr pellets or Nujol mulls is probably the simplest method [29]. However, differences in refractive index between the sample and the suspending medium may give rise to poor quality spectra. Good quality spectra can be obtained from thin films of polymers which are cast either on spectral plates, or on glass from which they can be peeled and then mounted in the IR beam of the spectrometer [29]. This is a very satisfactory method for samples that are soluble in a volatile solvent. Alternatively, polymeric samples which are not soluble in organic solvents, can be handled by melting a small amount of the material between two plates in order to obtain a thin film [29].

5.3.2 Immobilization of anion exchange sites:

The immobilization of various quaternary ammonium and quaternary phosphonium ion-exchange groups was investigated, see Table 5.3. Reagents were obtained from Aldrich chemicals, except for tripentylamine and trioctylphosphine which were obtained from Alfa Chemicals. Reagent grade chemicals were obtained, and were used as received.

In the first reaction scheme, 1.5g of PVBC was suspended in 20 ml of a 25% (v/v) solution of the amine in methanol. The above suspension was then heated to reflux, to about 70-80°C. In the following example, trihexylamine reacts with poly(vinylbenzyl chloride) to form poly(trihexylvinylbenzylammonium chloride):

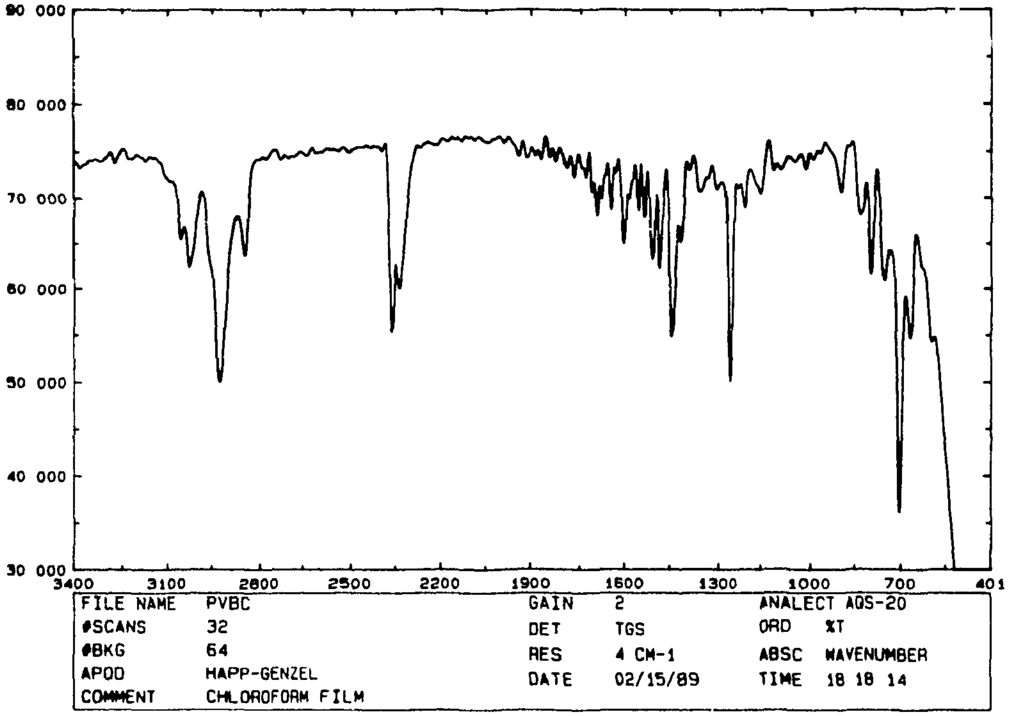


Since poly(vinylbenzyl chloride) is insoluble in methanol, and the modified PVBC is soluble in methanol, the end of the reaction was indicated by the dissolution of PVBC. A reflux time of 5 to 6 hours was usually required for the completion of the reaction. The nucleophilicity of amines decreases with alkyl substitution and hydrocarbon chain length. Hence, nucleophilic reactions with trioctylamine required a long reflux time (24 hours). In this case, chloroform was used as the solvent. The specific conditions used for the immobilization of these quaternary ammonium ion-exchange groups are shown in Table 5.3.

After quaternization of PVBC with trihexylamine, the modified polymer was precipitated by addition of water, and filtered. The product obtained was redissolved in chloroform and dried over anhydrous sodium sulphate or sodium acetate. The chloroform solution was then concentrated by evaporation, and the polymer was precipitated by the addition of hexane. After filtration, the polymer was rinsed with additional hexane. The entire procedure was repeated to ensure proper purification of the modified polymer.

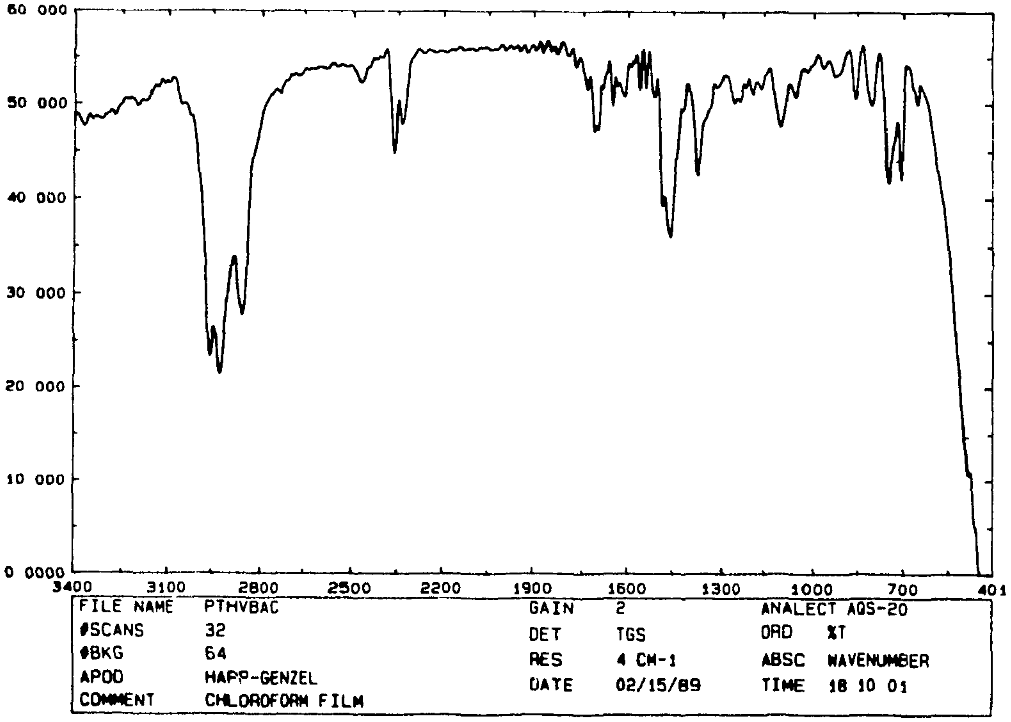
Infrared spectra of PVBC before and after modification were obtained from thin films cast on NaCl spectral plates, see Fig. 5.2 and 5.3. The spectrum of PVBC displays only a few peaks: alkane C-H stretch occurred in the region 2850-3000cm^{-1}, and aromatic C-H stretch occurred to the left of 3000cm^{-1}. A characteristic -CH_2- bend absorption was recorded at 1447 cm^{-1}. The absorption at 1266cm^{-1} is attributable to CH_2-Cl. Note that the band at 2400cm^{-1} is due to absorption of atmospheric CO_2.

An infrared spectrum taken after the reaction of trihexylamine with PVBC confirms the modification of the polymer, see Fig.5.3. The C-H stretch alkane and aromatic absorption bands are intense. A characteristic, medium C-N stretching absorption was also recorded at 1376cm^{-1}. Note that the infrared absorption of CH_2-Cl at 1266cm^{-1} disappeared after functionalization of PVBC with the quaternary ammonium groups, as expected. This indicates that the reaction was successful.



FILE NAME	PVBC	GAIN	2	ANALECT AQS-20	
#SCANS	32	DET	TGS	ORD	%T
#BKG	64	RES	4 CM-1	ABSC	WAVENUMBER
APOD	HAPP-GENZEL	DATE	02/15/89	TIME	18 18 14
COMMENT	CHLOROFORM FILM				

Fig.5.2 Infrared spectrum of poly(vinylbenzyl chloride).



FILE NAME	PTHVBAC	GAIN	2	ANALECT AQS-20	
#SCANS	32	DET	TGS	ORD	%T
#BKG	64	RES	4 CM-1	ABSC	WAVENUMBER
APOD	HAPP-GENZEL	DATE	02/15/89	TIME	18 10 01
COMMENT	CHLOROFORM FILM				

Fig.5.3 Infrared spectrum of poly(trihexylvinylbenzylammonium chloride).

The results of a quantitative elemental analysis performed on poly(trihexylvinylbenzylammonium chloride), PTHVBAC, are reported in Table 5.4. These results confirm the modification of PVBC, and indicate a yield of immobilization of quaternary ammonium groups superior to 80%. The molecular weight of PTHVBAC was also calculated from the results of the quantitative elemental analysis.

Table 5.4: Quantitative elemental analysis of PTHVBAC[a].

Element	%(w/w)
C	74.7±0.1
H	9.7±0.1
N	2.5±0.2
Cl	<13.0[b]
M.W.	140,000
ρ	1.4g/cm^3

[a] Analysis performed by Guelph Chemical Laboratories, Ontario.
[b] %Cl = 100 - (%C+%H+%N)

The density of PTHVBAC was evaluated by dividing the mass of a sample of the polymer, by the volume of water displaced when it was submerged in a graduated cylinder. It is a simple method to calculate the density of a solid [30]. A density of 1.4g/cm^3 was obtained for PTHVBAC at room temperature (21°C).

DSC measurements were performed on poly(trihexylvinylbenzylammonium chloride); these measurements were carried in the laboratory of Professor Adi Eisenberg. The first scan, Fig.5.4, clearly indicated that an endothermic reaction occurred between 410 and 480 Kelvin. The maximum of this peak was recorded at 452.7K or 179.7°C.

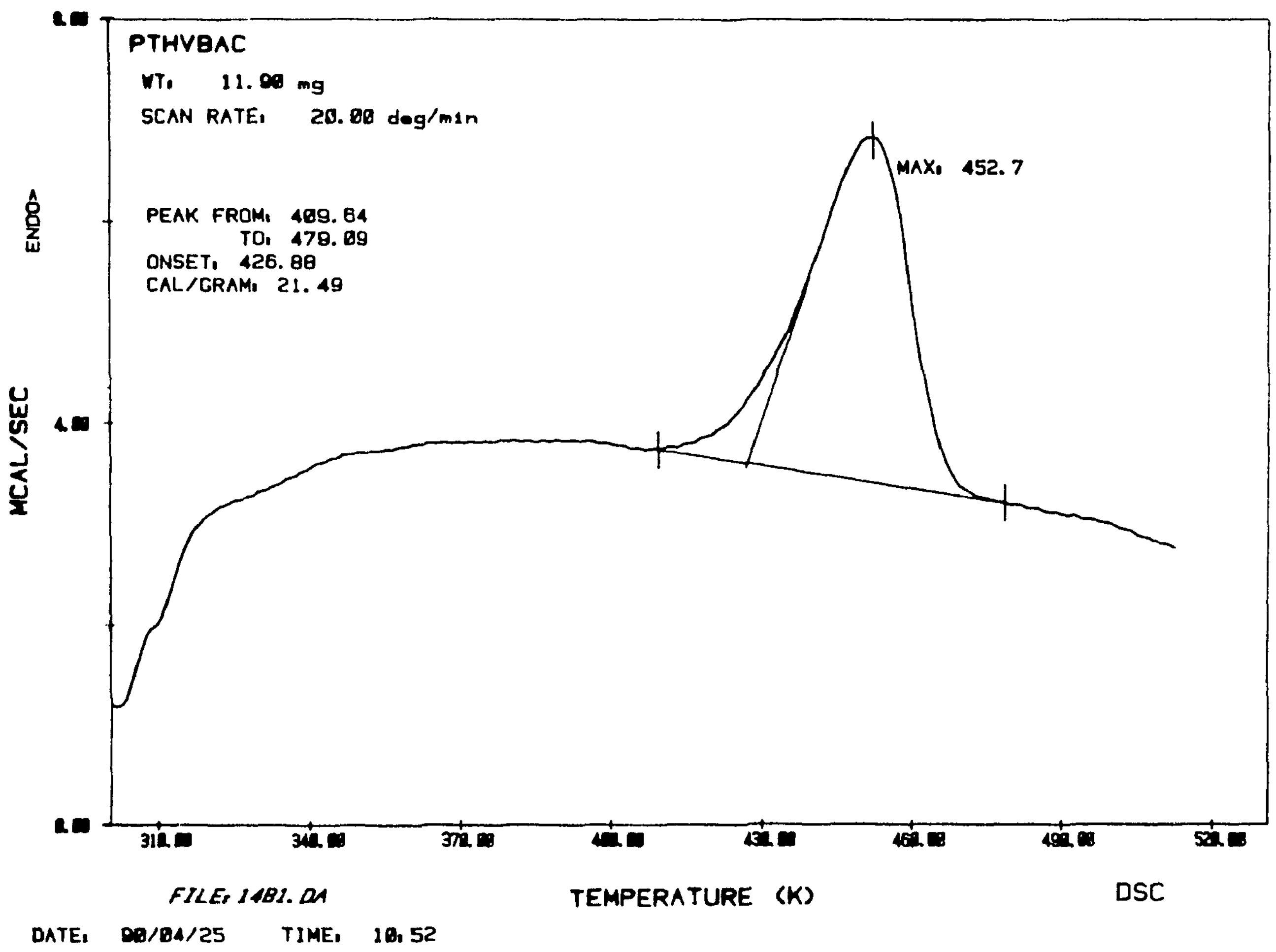


Fig. 5.4 Differential scanning calorimetry of PTHVBAC, first scan.

After this first scan, the sample of PTHVBAC was quickly cooled down, and a second scan was performed. The second scan, Fig.5.5, demonstrated that the endothermic reaction monitored in the first scan was not reversible. These measurements indicate that there is no glass transition temperature for PTHVBAC, and that decomposition seems to occur at 179.7°C. These results seem to indicate that a high degree of cross-linking and crystallinity exist in the PTHVBAC matrix (refer to section 5.2.3).

In poly(trihexylvinylbenzylammonium chloride) and poly(trioctylvinylbenzylammonium chloride), the proportion of bound ions is large, $N_{ir}/(N_{cr} + N_{ir}) \cong 0.25$ or 25%. The proportion of bound ions was evaluated from equations (54) and (57). Considering the high proportion of bound ions in poly(trihexylvinylbenzylammonium chloride) and poly(trioctylvinylbenzylammonium chloride), the formation of clusters is not probable in these polymeric systems. As discussed in section 5.2.2, ionic aggregation is influenced by the polarity of the media.

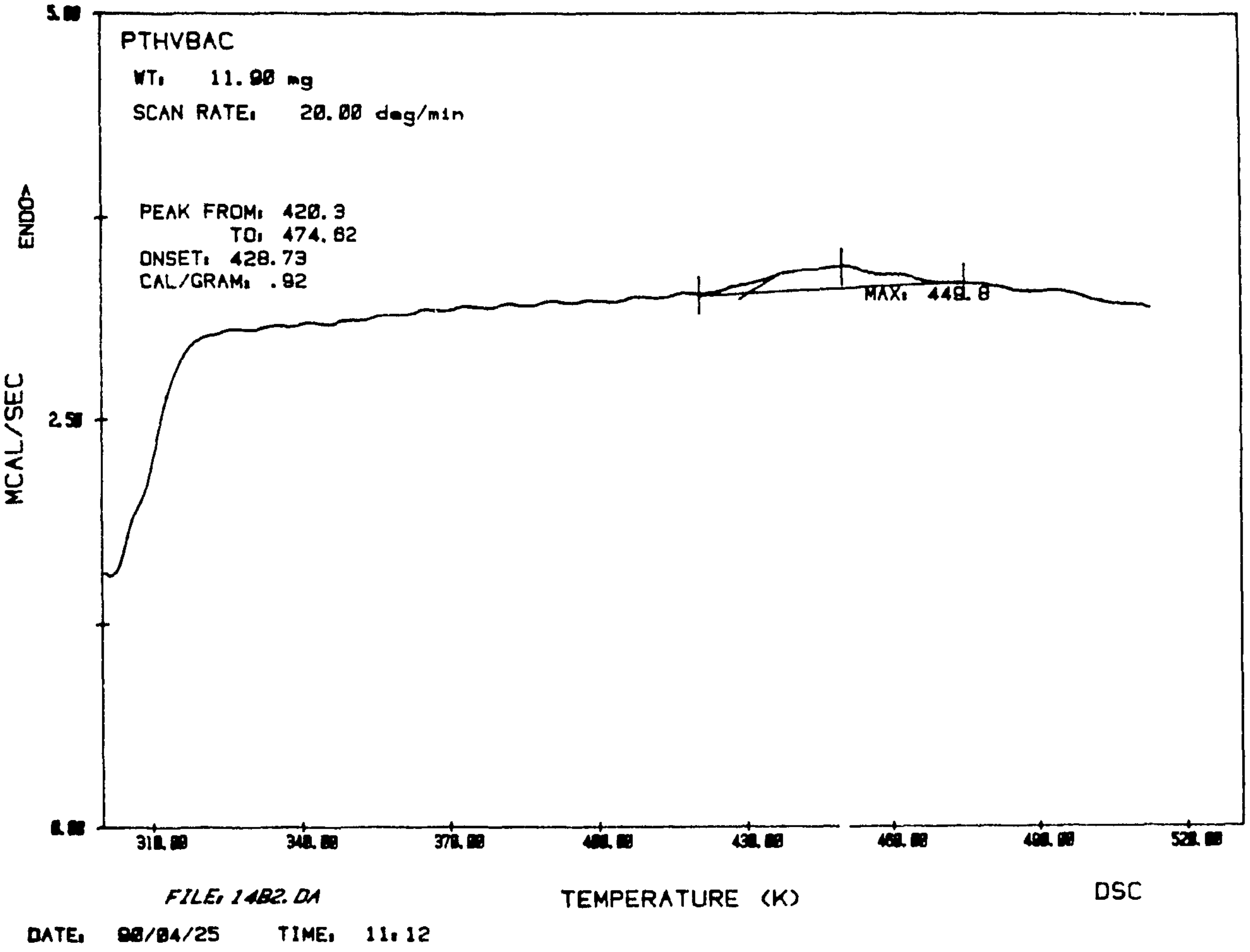


Fig. 5.5 Differential scanning calorimetry of PTHVBAC, second scan.

The same experimental procedures used to immobilize quaternary ammonium groups within PVBC were employed to immobilize the quaternary phosphonium groups. Phosphines are characterized by their high nucleophilic reactivity with alkyl halides to produce phosphonium salts. An infrared spectrum was obtained for poly(trioctylvinylbenzylphosphonium chloride), see Fig.5.6.

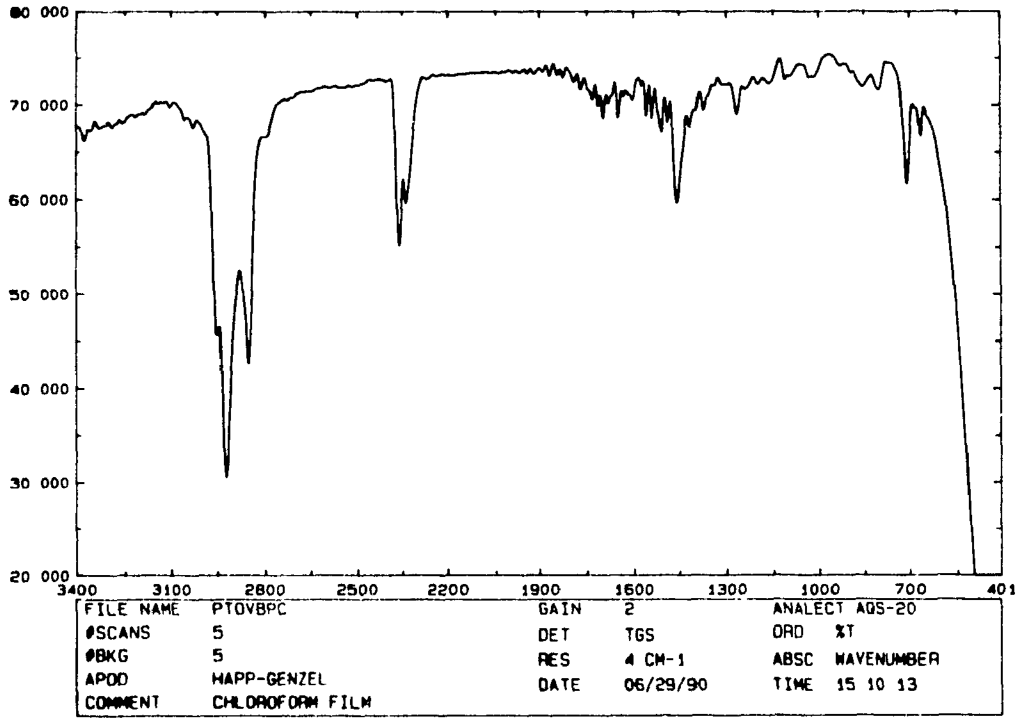
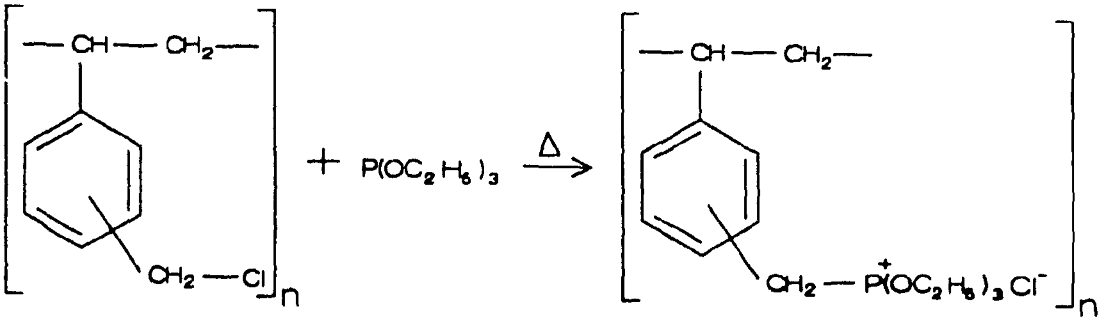


Fig.5.6 Infrared spectrum of poly(trioctylvinylbenzylphosphonium chloride).

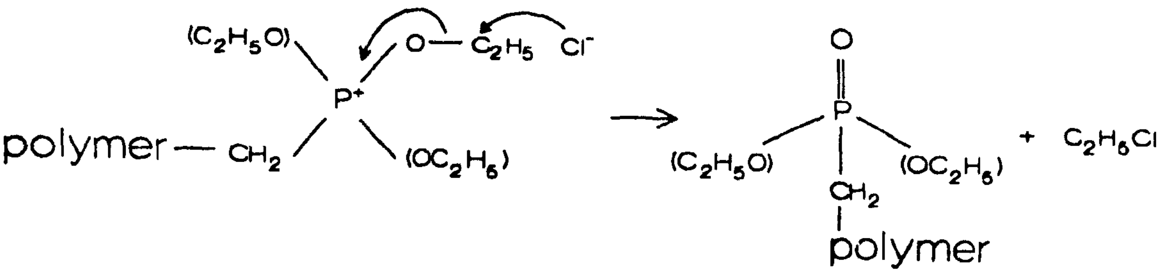
The phosphorus-carbon linkage does not display any characteristic band. However, the functionalization of PVBC with quaternary phosphonium groups was indicated by the disappearance of the characteristic CH_2-Cl absorption band of PVBC at 1266cm^{-1}. Quantitative elemental analysis indicates a yield of immobilization of the quaternary phosphonium groups superior to 80%.

5.3.3 Immobilization of cation exchange sites:

PVBC was reacted with triethylphosphite to produce a phosphonate ester which can be hydrolyzed to obtain alkyl phosphate ion exchange groups. The first step of this reaction is one of the most useful and best known reactions in phosphorus chemistry, the Arbusov reaction [31]. The initial reaction of triethylphosphite with poly(vinylbenzyl chloride) yields an unstable phosphonium ion:

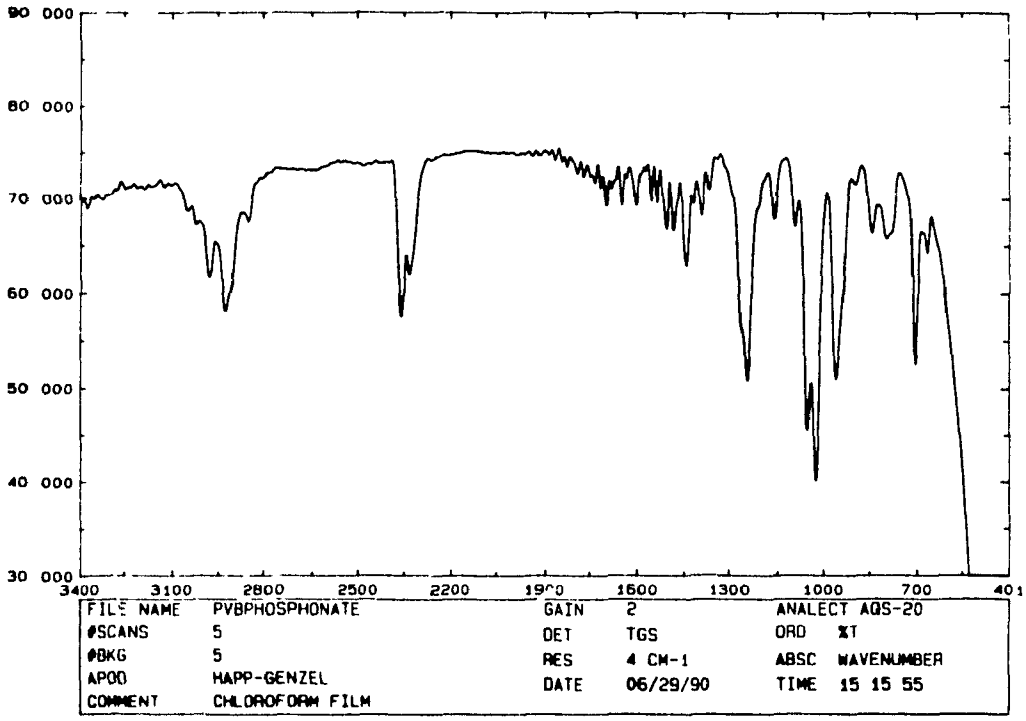


The halide ion can displace one of the alkyl group to yield a phosphonate ester:



The second step is favorable because of the stability of the leaving group with a phosphorus-oxygen double bond. Phosphites with their electron withdrawing alkoxy groups on the phosphorus are much less reactive or nucleophilic than phosphines [31]. Therefore, such alkylation reactions often require long reflux times. After 6 hours of reflux, only about 1% of immobilization was achieved. A reflux of 72 hours was necessary to allow completion of the reaction.

The infrared spectrum of PVBC functionalized with phosphonate groups, Fig.5.7, displays characteristic P-O-C absorption bands between 1000-1100cm^{-1}. Also associated with the P-O-C groups is a strong intensity band at 963cm^{-1}. The P=O groups absorb strongly near 1250cm^{-1}.

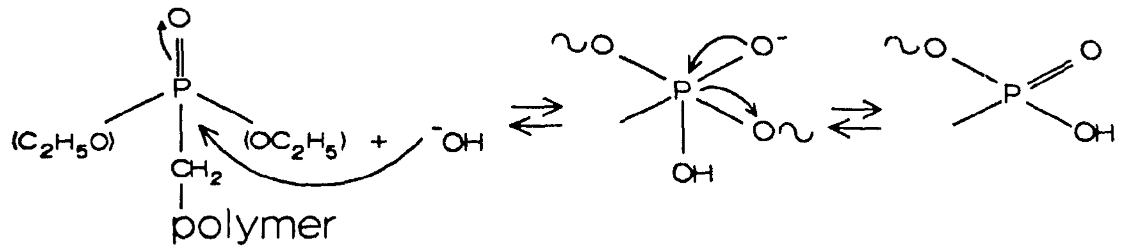


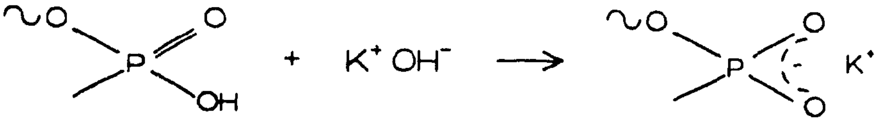
FILE NAME	PVBPHOSPHONATE	GAIN	2	ANALECT AQS-20	
#SCANS	5	DET	TGS	ORD	%T
#BKG	5	RES	4 CM-1	ABSC	WAVENUMBER
APOD	HAPP-GENZEL	DATE	06/29/90	TIME	15 15 55
COMMENT	CHLOROFORM FILM				

Fig.5.7 Infrared spectrum of the phosphonate functionalized polymer.

It is necessary to hydrolyse the alkyl groups with alkali to obtain a suitable sensor unit, i.e. alkyl phosphate groups. Two options can be used in the hydrolysis step. The first option consists of a strong alkaline hydrolysis in aqueous media, but this might result in the attack of the polymer itself. The use of milder alkaline conditions in methanol (see Table 5.3) is more convenient.

In mild alkaline conditions, the attack of the hydroxide ions on the phosphonate ester site results in the formation of a dialkyl phosphate salt.

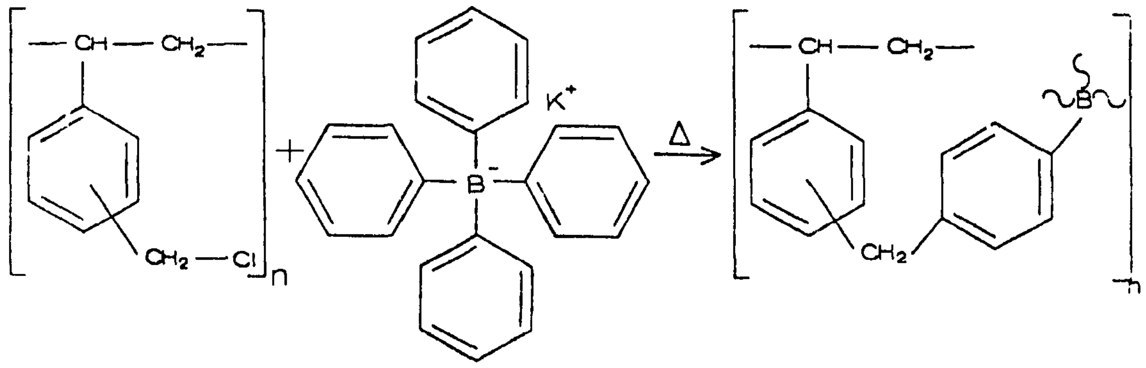




The stability of this salt is such that further hydrolysis to remove other alkyl groups is very difficult and will not proceed under the conditions used (Table 5.3).

Tetraphenylborate is a large lipophilic ionophore, useful for the determination of potassium ions and alkaloids such as ephedrine [32]. In this case, a Friedel-Crafts reaction scheme [33] was used in an attempt to immobilize tetraphenylborate (TPB) within PVBC structure.

Under these conditions, one of the phenyl groups of TPB should act as the nucleophile attacking the chloromethyl group of PVBC.



A catalyst such as aluminium chloride ($AlCl_3$) or titanium tetrachloride ($TiCl_4$) must be used to promote the reaction. Therefore, anhydrous conditions must be used, since both catalysts react violently with water. Unfortunately, even after prolonged reflux, for periods extending over 12 hours, no evidence of significant immobilization of tetraphenylborate was obtained. Apparently, the electron withdrawing character of boron seems to inhibit the nucleophilic reactivity of the phenyl groups.

5.4 PROCEDURES FOR PREPARING IONIC POLYMER FILMS AND MEMBRANES.

5.4.1 Dissolution of ionic polymers.

Studies carried on the characteristics of Nafion polymers provided information regarding the solubility parameters of ionic polymers. Ionic polymers interact much more strongly with an appropriate binary solvent systems than with a single solvent [34]. An appropriate binary solvent means a system composed of an organic solvent which can solubilize hydrocarbon chains of the polymer, and a polar solvent which can solubilize more effectively the ionic moeities.

However, many ionic polymers would not dissolve at room temperature, even in binary solvent systems [34]. High temperatures seem to favor the dissolution of ionic polymers. This difficulty is related to the nature of the inter-chain forces, and to regions of crystallinity in the polymer.

The dissolution of quaternary ammonium functionalized PVBC was found more effective in a 50:50 methanol-chloroform system. As the length of the alkyl chain of the ammonium groups was increased, the functionalized polymer became more soluble in chloroform. We also observed that with the aging of the polymer, its dissolution became more difficult.

5.4.2 Preparation of membranes:

Ionic polymer films or membranes can be easily cast at room temperature from a solution of the polymer dissolved in a volatile organic solvent. The procedure is simple; it consists of depositing a small drop of the solution on a glass plate (or any other suitable surface). The solvent which slowly evaporates, leaves a film of polymer on the plate. However, resulting films are often hard and brittle, and cannot be peeled easily from the surface. Furthermore, the solution-cast films often swell considerably in the presence of water. This was notably the case for poly(triethylvinylbenzylammonium chloride) and poly(tripentylvinylbenzylammonium chloride) films.

A high temperature solution processing procedure was developed by Moore and Martin [35] to produce high quality Nafion films which were found insoluble in polar solvents. Changes in the morphology of the ionic polymers seem to be at the origin of the difference observed in the properties of these films, compared to the films cast at room temperature.

A similar procedure was used to cast a film of poly(triethylvinylbenzylammonium chloride). The polymer was first dissolved in methanol and an equal volume of dimethylformamide was added to this solution. The majority of the methanol was removed by heating on a hot plate at 80°C. The solution was then placed in an oil bath, which had been preheated at 160°C, and evaporated to dryness. At this temperature, no damage was inflicted to the polymer. However, this procedure did not significantly reduce the swelling of the film in presence of water.

On the other hand, long chain quaternary ammonium functionalized polymers, i.e. poly(trihexylvinylbenzylammonium chloride) and poly(trioctylvinylbenzylammonium chloride) were found to hold structural integrity and minimum swelling in water was observed. This was related to the high degree of crystallinity and cross-linking found in both polymers. A high degree of cross-linking imposed rigidity to the polymer matrix, and reduced swelling in water.

We have also observed that these functionalized polymers demonstrated enhanced adherence to solid substrates. The adherence of these membranes to a glass or silicate substrate was investigated qualitatively from a peel test. While plasticized PVC membranes are easily removed from the substrate, a membrane cast from PTHVBAC shows no sign of peeling when subjected to the same test. The enhanced adhesive properties of PTHVBAC to silicate substrates is believed to be primarily due to electrostatic attraction of the positively charged quaternary ammonium groups, and the negatively charged silicates. Significant enhancement of Chemically Sensitive Semiconductor Devices (CSSD's) lifetime can be expected to result from improved membrane adhesion. In that matter, the future integration of ionic polymer membranes with semiconductor devices seems particularly attractive.

REFERENCES:

[1] M.A. Arnold and M.E. Meyerhoff, *Anal.Chem.*, **1984**, 56, 20R.

[2] M.A. Arnold and R.L. Solsky, *Anal.Chem.*, **1986**, 58, 84R.

[3] R.L. Solsky, *Anal.Chem.*, **1988**, 60, 106R.

[4] U. Oesch and W. Simon, *Anal.Chem.*, **1980**, 52, 692.

[5] G. Blackburn and J.Janata, *J.Electrochem.Soc.*, **1982**, 129, 2580.

[6] D.J. Harrison, A. Teclemariam and L.L. Cunningham, *Anal.Chem.*, **1989**, 61, 246.

[7] A.K. Covington, Ed., "Ion-Selective Electrode Methodology", Vol.I, CRC Press, Boca Raton (Florida), 1979, pp.111-121.

[8] L. Holliday, Ed., "Ionic polymers", Halsted Press-John Wiley & Sons, New York, 1975, Chapter 1.

[9] A. Eisenberg and M. King, "Ion-Containing Polymers: Physical properties and structure", Academic Press, New York, 1977, pp.1-14.

[10] F. Haber and Z. Klemensiewicz, *Z.Physik.Chem.*, 1909, 67, 385.

[11] E. Pungor and J. Havas, *Acta Chim.Hung.*, **1966**, 50, 77.

[12] R.S. Lawton and A.M. Yacynych, *Anal.Chim.Acta*, **1984**, 160, 149.

[13] C.R. Martin and H. Freiser, *Anal.Chem.*, **1981**, 53, 902.

[14] L. Ebdon, A.T. Ellis, and G.C. Corfield, *Analyst*, **1979**, 104, 730.

[15] L. Ebdon, A.T. Ellis, and G.C. Corfield, *Analyst*, **1982**, 107, 288.

[16] L. Ebdon, B.A. King and G.C. Corfield, *Analytical Proceedings*, **1985**, 22, 354.

[17] A. Eisenberg, H.L. Yeager, Eds., "Perfluorinated Ionomer Membranes", American Chemical Society, Washington, D.C., 1982; ACS Symposium Serie No. 180, pp.1-6.

[18] R.W. Murray, in: "Electroanalytical Chemistry", A.J. Bard, Ed., 13th Ed., New York, Vol.13, 1984, pp.330-333.

[19] R.A Weiss, W.J. MacKnight, R.D. Lundverg, D.A. Mauritz, C. Thies, and D.A. Brant, in: "Coulombic Interactions in Macromolecular Systems", A. Eisenberg and F.E. Bailey, Eds., American Chemical Society, Washington, D.C., 1986, pp.1-19.

[20] S.C. Yeo, A. Eisenberg, *J.Appl.Polym.Sci.*, **1977**, 21, 875.

[21] T.D. Gierke, *J.Electrochem.Soc.*, **1977**, 124, 319C.

[22] H.L. Yeager and B. Kipling, *J.Phys.Chem.*, **1979**, 83, 1836.

[23] M. Pineri, in: "Coulombic Interactions in Macromolecular Systems", A. Eisenberg and F.E. Bailey, Eds., American Chemical Society, Washington, D.C., 1986, pp.159-160.

[24] N.M. Bikales, Ed., "Characterization of Polymers", Wiley-Interscience, New York, 1971, pp.191-192.

[25] N.L. Allinger, M.P. Cava, D.C. De Jongh, C.R. Johnson, N.A. Lebel, and C.L. Stevens, "Organic Chemistry", Worth Publishers, New York, 1971, pp.259-260.

[26] D.L. Pavia, G.M. Lampman, and G.S. Kriz, "Introduction to Spectroscopy", Saunders College, Philadelphia, 1979, pp.13-18.

[27] AQS-18 Analect FTIR spectrometer user manual.

[28] J.R. Ferraro and L.J. Basile, Eds., "Fourier Transform Infrared Spectroscopy: Applications to Chemical Systems", Vol.1, Academic Press, New York, 1978, Chapter 1.

[29] E.G. Brame and J.G. Grasselli, Eds., "Infrared and Raman Spectroscopy", Marcel Dekker, New York, 1977, pp. 875-881.

[30] J.E. Brady, G.E. Humiston, "General Chemistry: Principles and Structure", 4th Ed., John Wiley & Sons, New York, 1986, pp.21-22.

[31] N.A. Allinger, M.P. Cava, D.C. De Jongh, C.R. Johnson, N.A. Lebel, and C.L. Stevens, "Organic Chemistry", Worth Publishers, New York, 1971, pp.864-866.

[32] G.E. Baiulescu and V.V. Cosofret, "Applications of Ion-Selective Membrane Electrodes in Organic Analysis", Halsted Press, John Wiley & Sons, New York, 1977, Chapter 9.

[33] S.H. Pine, J.B. Hendrickson, D.J. Cram, and G.S. Hammond, "Organic Chemistry", 4th Ed., McGraw-Hill, New York, 1980, pp.637-639.

[34] C.R. Martin, T.A. Rhoades, J.A. Ferguson, *Anal.Chem.*, **1982**, 54, 1639.

[35] R.B. Moore III and C.R. Martin, *Anal.Chem.*, **1986**, 58, 2569.

CHAPTER 6:

THE APPLICATION OF IONIC POLYMERS TO ELECTROANALYSIS.

6.1 QUATERNARY AMMONIUM FUNCTIONALIZED POLYMERS.

6.1.1 Potentiometric response characteristics of quaternary ammonium functionalized polymer membrane electrodes.

With conventional ion-selective polymeric membrane electrodes, organic ion exchangers are incorporated into a plasticized polyvinyl chloride matrix. Electrodes selective to thiocyanate, salicylate, and nitrate were developed in this fashion using long chain alkyl ammonium salts [1,2]. The main disadvantage with this approach is that the ion exchanger and the plasticizer tend to be leached from the polymer matrix. Over time, this results in deterioration of the membrane performance. As discussed in chapter 5, the preparation of polymeric ion-selective membranes with non-leachable materials is possible when a polymer functionalized with ion-exchange sites is used. An enhancement of membrane lifetime is therefore expected from the use of ionic polymer membranes.

The properties and usefulness of membranes prepared from poly(trihexylvinylbenzylammonium chloride), PTHVBAC, were investigated. PTHVBAC membranes about 100µm thick were cast on a carbon-support electrode (see Fig.4.1a). This configuration is analogous to the coated-wire electrode described by Freiser [3]. Prior to coating the graphite electrode with PTHVBAC, the counterions of the bound quaternary ammonium groups were exchanged for the analyte species through a liquid-liquid extraction procedure. The functionalized polymer was first dissolved in chloroform, and extracted with an aqueous solution of the analyte. Response characteristics of PTHVBAC membrane electrodes to thiocyanate, nitrate and salicylate are illustrated in Fig.6.1. Note that each calibration point of Figure 6.1 represents the average of three potential readings. Since the reproducibility of this electrode is within 0.2mV, the error bar of each calibration point is much smaller than the symbol.

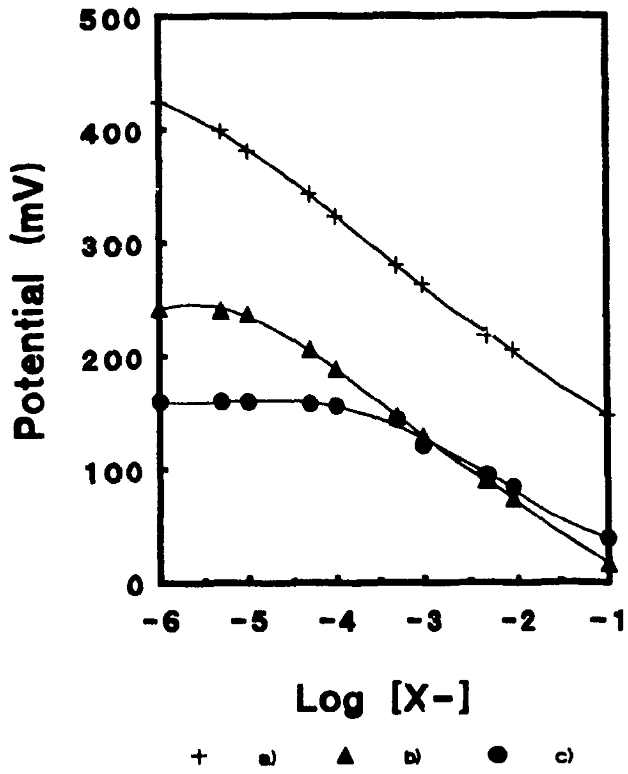


Fig.6.1 Typical potentiometric response of PTHVBAC coated carbon-support electrodes:
a) thiocyanate: slope, -59.1mV/decade; linear response range, 5µM-0.1M; 0.1M phosphate buffer, pH 6.5.
b) salicylate: slope, -58.2mV/decade; linear response range, 10µM-0.1M; 0.1M phosphate buffer, pH 8.0.
c) nitrate: slope, -43.2mV/decade; linear response range, 1mM-0.1M; 0.1M phosphate buffer, pH 7.0.

The carbon-support electrode coated with a film of poly(trihexylvinylbenzylammonium thiocyanate), PTHVBASCN, yielded a selective potentiometric response to thiocyanate (Fig.6.1). The logarithmic response extended from 5×10^{-6}M to 0.1M SCN^-, with a Nernstian slope of -59.1mV/decade. The slope of the straight-line portion of the calibration curve was calculated by least squares. The useful range of the electrode extended to 1×10^{-6}M thiocyanate. The standard solutions were buffered with 0.1M potassium dihydrogen phosphate, adjusted to pH 6.5. Phosphate ions had no observable effect on the response of the PTHVBASCN membrane electrode. Thiocyanate can, in fact, be monitored in the presence of a 10,000-fold excess of phosphate. The influence of pH on the potential of this electrode was also investigated. The potential of the electrode was measured in solutions of pH varying in the range 4-10. No variation of potential was noted in this pH range. These results are similar to the ones obtained by Lawton and Yacynych with a similar membrane electrode [4].

The PTHVBASCN membrane electrode showed fast response, and continued to function well for several months, Fig.6.2. Only a small deterioration of the membrane response was observed after 42 weeks of use. Comparatively, a typical lifetime of 12 weeks was reported for Aliquat 336S-PVC coated wire electrodes [1]. The PTHVBASCN coated carbon-support electrode was stored dry, and was pre-conditioned in 0.1M KSCN for 30 minutes prior to reuse.

The selectivity of this membrane electrode was evaluated in the presence of other anions. The selectivity coefficients were measured by the fixed interference method, with concentration of interfering anions fixed at 1mM. The results of this investigation are presented in Table 6.1.

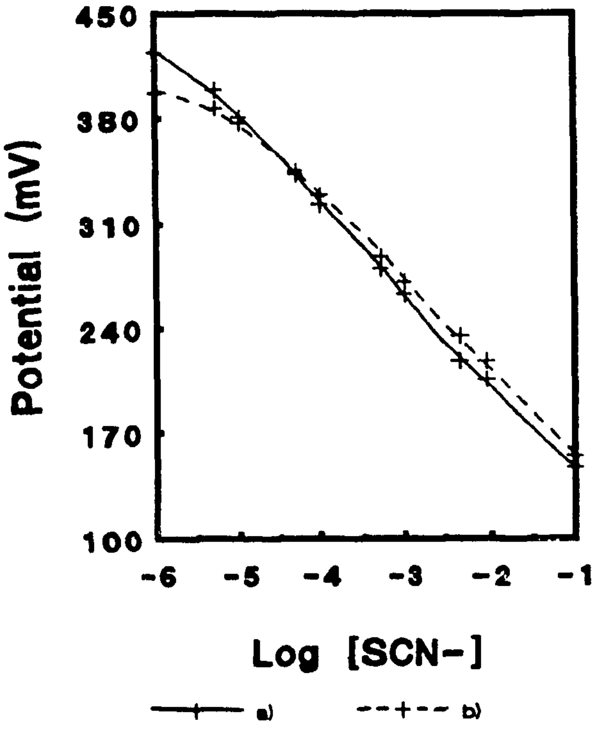


Fig.6.2 Response of a PTHVBASCN coated carbon-support electrode after several weeks of use: a) after 4 weeks of use, slope: -59.1±0.2mV/decade; b) after 42 weeks of use, slope: -57.3±0.1mV/decade.

It is interesting to note that the PTHVBASCN membrane electrode offers a greater selectivity for thiocyanate than a conventional coated wire electrode based on Aliquat 336S [1]. The selectivity of this PTHVBASCN membrane electrode can also be favorably compared to the behavior of a solid-state AgSCN heterogeneous membrane electrode. In this case, iodide, bromide and chloride react with the AgSCN precipitate, and therefore strongly interfere with the measurement of thiocyanate [5]. On the other hand, the PTHVBASCN membrane electrode demonstrated better selectivity for thiocyanate in presence of bromide and iodide (refer to Table 6.1), as compared to the solid-state AgSCN heterogeneous membrane electrode.

Table 6.1: Selectivity coefficients for some thiocyanate ion-selective electrodes.

Interfering anions	$K_{i,j}^{pot}$	$K_{i,j}^{pot}$	$K_{i,j}^{pot}$
	PTHVBASCN membrane	Aliquat 336S membrane[1]	AgSCN heterogeneous membrane[2]
phosphate	<0.0001		
acetate	<0.0001		
sulphate	<0.0001	0.001	
chloride	0.001	0.001	0.003
cyanide	0.003		
bromide	0.009		1.4
nitrate	0.01	0.046	
salicylate	0.10		
iodide	0.12	0.34	270
perchlorate	0.99		

[1] Ref.[1]
[2] Ref.[5]

Thiocyanate ISE's main applications are in kinetic analysis and in the investigation of chemical reaction kinetics [6]. However, thiocyanate ISE's could also be used for the determination of thiocyanate in various industrial processes and plant effluents. Notably, ammonium and alkali thiocyanates are used in photography, catalysis, agricultural chemicals, and dyeing of textiles [7]. Though not as toxic as cyanide, thiocyanate is harmful to aquatic life.

With conventional ion-selective membranes, the slightest modification of the ion exchanger can have a significant influence on the sensitivity and selectivity of the membrane. For example, better sensitivity and selectivity for salicylate were obtained when tetraoctylammonium salts were used instead of tetraheptylammonium salts [8]. Therefore, bulkier quaternary ammonium compounds apparently display better affinity for salicylate. Salicylate (*o*-hydroxybenzoic acid) is used in the composition of a wide variety of pharmaceutical preparations for its pain-relieving action [8,9].

Similarly, poly(trihexylvinylbenzylammonium chloride) and poly(trioctylvinylbenzyl ammonium chloride) were evaluated for salicylate selectivity. This study indicated that poly(trioctylvinylbenzylammonium salicylate) (PTOVBAS) membrane electrode displayed poorer sensitivity for salicylate than the poly(trihexylvinylbenzylammonium salicylate) (PTHVBAS) membrane electrode, see Fig.6.3.

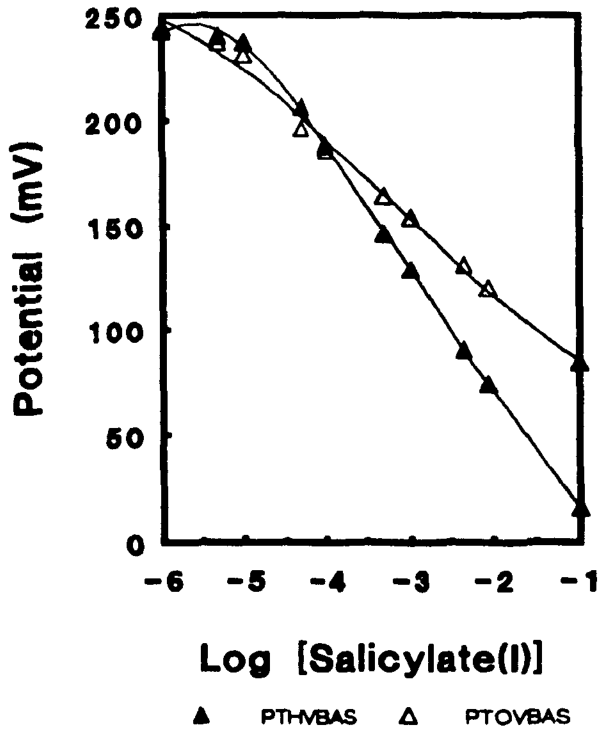


Fig.6.3 Comparison of the potentiometric response of PTHVBAS and PTOVBAS membrane electrodes to salicylate:
a)PTHVBAS membrane: slope, -58.2±0.2mV/decade; linear response range, 10μM-0.1M.
b)PTOVBAS membrane: slope, -34.1±0.6mV/decade; linear response range, 0.1mM-0.1M. Supporting electrolyte, 0.1M phosphate buffer (pH 8.0).

Further, the response of the PTOVBAS membrane electrode is significantly slower. The slower response of the PTOVBAS membrane electrode may be related to the slower fluxes or diffusion of ionic species within the membrane (the diffusion of ionic species within poly(trioctylvinylbenzylammonium chloride) and poly(trihexylvinylbenzyl ammonium chloride) films will be discussed in section 6.1.2.2). The selectivity pattern of the PTOVBAS membrane was found comparable to the selectivity of the PTHVBAS membrane, see Table 6.2. With quaternary ammonium functionalized polymers, variation in selectivity through structure, particularly through the length of the hydrocarbon substitutions, is apparently vitiated by covalent bonding of the ammonium groups.

Table 6.2: Comparison of the selectivity of PTHVBAS and PTOVBAS membrane electrodes for salicylate.

Interfering anions	$K_{i,j}^{pot}$ PTHVBAS membrane	$K_{i,j}^{pot}$ PTOVBAS membrane
phosphate	<0.0001	<0.0001
nitrate	0.11	0.25
thiocyanate	10	16.7

[a] PTHVBAS: Poly(trihexylvinylbenzylammonium salicylate)
[b] PTOVBAS: Poly(trioctylvinylbenzylammonium salicylate)

The selectivity of conventional polymeric membrane electrodes is also influenced by the solvent mediator, i.e. the plasticizer. Notably, the properties of the solvent influence the partition coefficient of the analyte ion in the membrane phase (refer to Chapter 1, section 1.3.2.1), with consequent effects on the electrode selectivity. Ionic polymer membranes prepared with poly(trihexylvinylbenzylammonium salicylate) were impregnated with mediators, i.e. 1-decanol, and *o*-nitrophenyl octyl ether. However, impregnation with these materials resulted in a loss of physical strength of the polymer. Further, the use of mediators conferred no additional selectivity to the poly(trihexylvinylbenzylammonium salicylate) membrane.

Polymer membrane electrodes prepared from poly(trihexylvinylbenzylammonium chloride) show a number of advantages, namely speed of response, long lifetime, and robustness. However, a better understanding of the response mechanism of PTHVBAC membranes is required to fully exploit these advantages. A better understanding of the response mechanism of ionic polymer membranes should also point out means of modifying their selectivity.

6.1.2 Voltammetric studies with a quaternary ammonium functionalized polymer-coated electrode.

Ionic polymers are found useful in the electroanalysis of ionic species because of their conducting and ion-exchange properties. Thus, an ionic polymer coated onto an electrode surface can be used to separate and preconcentrate an analyte ion prior to voltammetric determination at the substrate-electrode surface [10]. The use of cyclic voltammetry is particularly useful for the mechanistic study of electroactive systems. Cyclic voltammetry and the theory associated with this technique are described in Appendix B.

An EG&G Princeton Applied Research Model 273 Potentiostat/Galvanostat, in conjunction with a Hewlett Packard Model 7815B X-Y recorder was used for cyclic voltammetry. The potentiostat controls the potential of the electrode and measures the current at the electrode. The electrochemical cell contained three electrodes, a working, a reference and a counter electrode, which were immersed in an electrolytic solution. The working electrode is the electrode where the electrochemical reaction occurs. A glassy carbon electrode, 2.5mm in diameter, available from Bioanalytical Systems (BAS MF2012) was used. This electrode was coated with a thin film of the functionalized polymer. The reference electrode provides a stable potential with which the potential of the working electrode is compared. A saturated calomel electrode (Fisher 13-639-51) was used. The counter electrode is a conductive material that is chemically inert; a platinum electrode was used. With this configuration, the current in the cell is passed between the counter and working electrodes, and no current passes through the reference electrode.

Glassy carbon working electrodes are more commonly used than spectrographic graphite electrodes for voltammetric measurements. This is because the porosity of spectrographic graphite electrodes causes rather large, nonreproducible residual currents. On the contrary, the structure of glassy vitreous carbon has been described as compact thin ribbons of graphite sheets, highly resistant to chemical attack [11]. Prior to its coating, the working glassy carbon electrode was hand-polished with alumina slurries of 1 and 0.05μm. This procedure is necessary to remove any material which could be adsorbed at the electrode surface. After each polishing procedure, residual polishing material was removed from the surface by sonication in a water bath for 5 minutes.

The glassy carbon electrode was modified by coating its surface with a few microliters of a dilute solution of the functionalized polymer. A dilute solution (0.1% W/V) of poly(trihexylvinylbenzylammonium chloride) was prepared in chloroform. The evaporation of the volatile solvent leaves a thin film of polymer on the electrode surface. This method of film preparation is useful for electrodes with a modest surface area. The thickness of the polymer film was estimated from the density of the functionalized polymer ($\rho_{PTHVBAC}=1.4 g/cm^3$). PTHVBAC films exhibited good adhesion to the carbon substrate.

Various electroactive species, i.e. gold tetrachlorocomplexes, mercury chlorocomplexes, ferrocyanide, iodide, uric and ascorbic acid, served as test analytes. Voltammograms were obtained as follows: The polymer film-coated electrode was immersed into a standard solution of the analyte, and the solution was stirred for 10 minutes. This equilibration period allowed the ionic analyte to partition into the film, Fig.6.4.

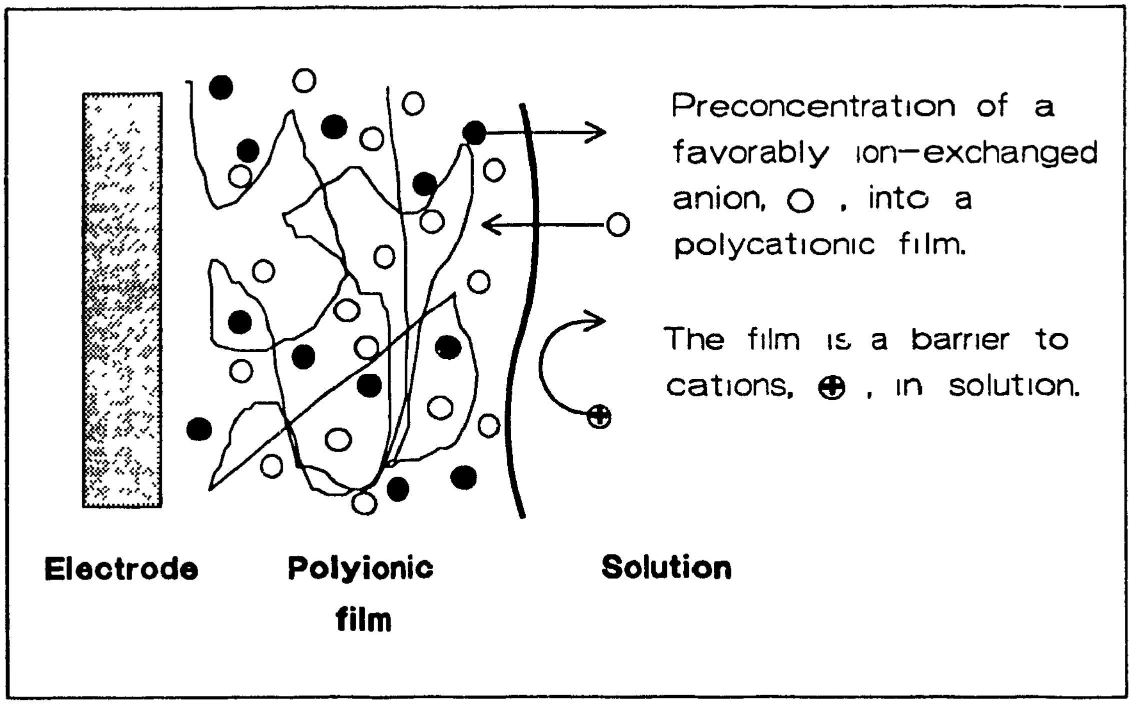


Fig.6.4 Schematic illustration of a polycationic polymer film coated electrode.

Preconcentration of analytes proceeds through ion exchange, and ionic redox species are therefore incorporated into the polyelectrolyte polymer film as the counterions of the film. On the other hand, the polycationic polymer film should act as a barrier to co-ions, as expected from the Donnan exclusion theory (please refer to Chapter 1, section 1.2.3). After 10 minutes of equilibration, the stirring was stopped and a voltammogram was recorded.

Quaternary ammonium ion-exchange sites are expected to demonstrate high affinity for anionic inorganic complexes such as gold and mercury complexes [12]. A 1mM gold stock solution was prepared in 0.1M hydrochloric acid (Baker acid for trace analysis) and 0.9M sodium chloride (BDH, analytical grade reagent), from sodium tetrachloroaurate(III) (Aldrich Chemicals). A mercury stock solution (1mM) was also prepared in 0.1M hydrochloric acid-0.9M sodium chloride, from mercuric chloride (Fisher, analytical grade reagent). In high concentrations of chloride, anionic chlorocomplexes of mercury, i.e. $HgCl_3^-$ and $HgCl_4^{2-}$ are formed. These standard solutions were prepared with distilled-demineralized water obtained from a Milli-Q Millipore system. Solutions of lower concentrations were prepared by dilution just before use.

The voltammograms obtained for charged inorganic complexes, clearly demonstrated that these complexes are adsorbed at the PTHVBAC polymer film surface. Adsorption waves frequently appear as very sharp current spikes [13], as shown in Fig.6.5 for chlorocomplexes of mercury. Sharp current spikes may also be caused by strong interactions of the ionic sites with the analyte [14]. A cathodic current spike was recorded at -0.07V vs SCE which was attributed to the reduction of mercury complexes, please refer to Table 6.3, p.123. Provided the scan rate is sufficiently rapid, part of the mercury is reoxydized while the rest of the mercury diffuses back in solution. A reoxydation wave was recorded at +0.05V, and ΔE_p=120mV. This large potential scan-rate-dependent ΔE_p was attributed to slow electron transfer kinetics (please refer to Appendix B) at the PTHVBAC film-coated electrode.

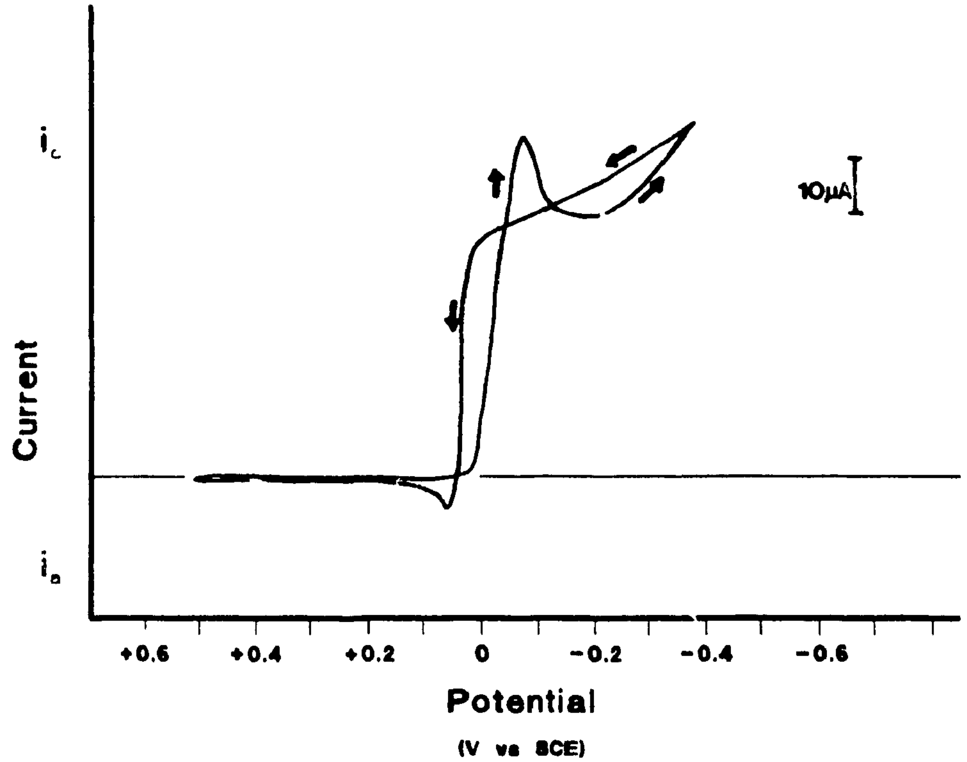
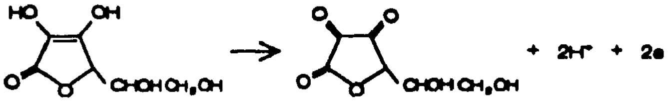
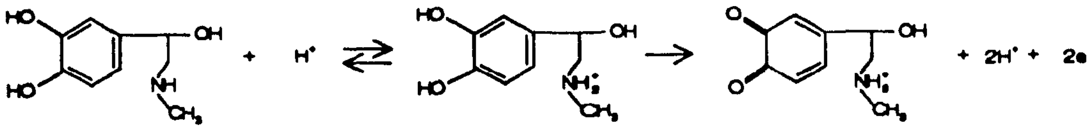
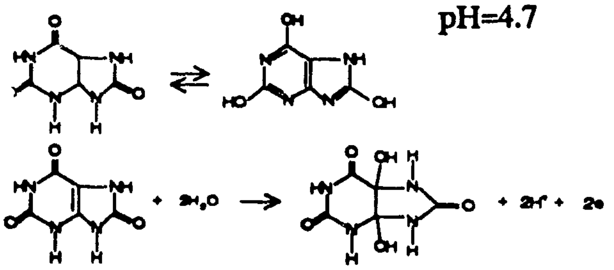


Fig.6.5 Cyclic voltammogram for mercury chlorocomplexes at a PTHVBAC film-coated electrode: Test solution, 1mM Hg(II) and 1.0M Cl^- (0.1M HCl-0.9M NaCl); Film thickness, 1μm; preconcentration time, 10min.; scan rate, 50mV/s.

Gold(III) tetrachlorocomplexes also exhibit a high affinity for quaternary ammonium ion-exchange sites, and $AuCl_4^-$ was accumulated at the PTHVBAC film electrode. Differential pulse voltammetry (DPV) was used to measure $AuCl_4^-$. The application of a potential pulse waveform helps reduce the background current, thus leading to significantly improved detection limits compared to cyclic voltammetry. Differential pulse voltammetry is described in Appendix C. An EG&G PAR Model 174A polarographic analyzer, in conjunction with an EG&G PAR Model RE0089 X-Y recorder, was used for differential pulse voltammetric measurements.

Table 6.3: Standard and peak potentials of the species studied.

Half-reaction	Buffer solution	Potential vs SCE	Ref.
Ascorbic acid: 	phosphate buffer pH=7.0	$E_{p/2}=+0.41V$	[15]
Epinephrine: 	phosphate buffer pH=3.0	$E_{p/2}=+0.64V$	[15]
$AuCl_4^- + 3e^- \rightleftharpoons Au + 4Cl^-$		$E^o=+0.76V$	[16]
$I_2(aq) + 2e^- \rightleftharpoons 2I^-$		$E^o=+0.38V$	[16]
$Fe(CN)_6^{3-} + e^- \rightleftharpoons Fe(CN)_6^{4-}$		$E^o=+0.31V$	[16]
$HgCl_4^{2-} + 2e^- \rightleftharpoons Hg + 4Cl^-$		$E^o=+0.24V$	[16]
$Ru(NH_3)_6^{3+} + e^- \rightleftharpoons Ru(NH_3)_6^{2+}$		$E^o=-0.24V$	[16]
Uric acid: 	acetate buffer pH=4.7	$E_p=+0.47V$	[17]

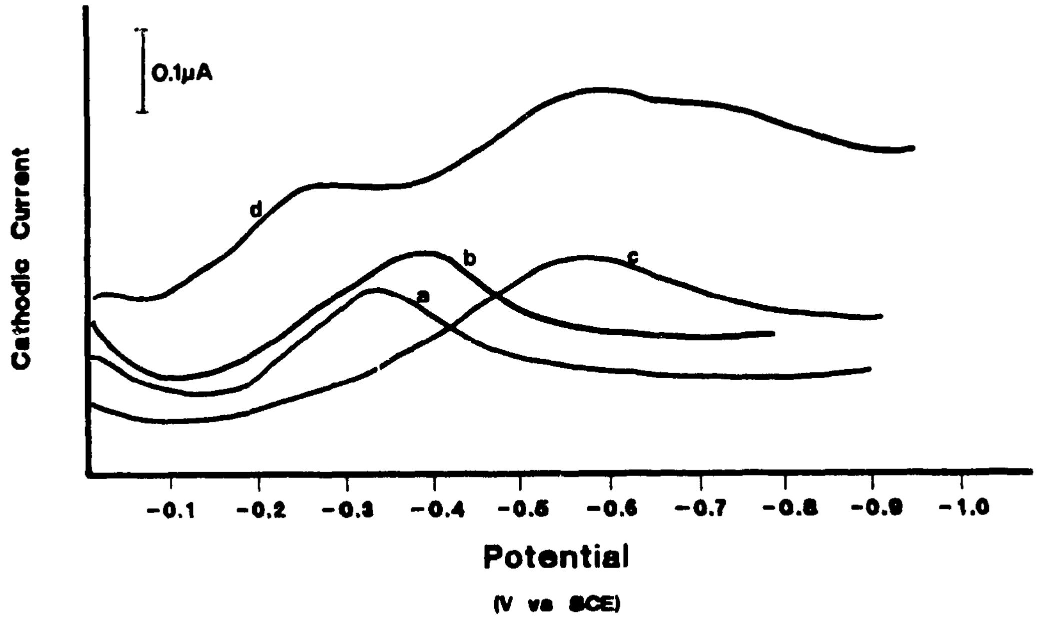


Fig.6.6 Differential pulse voltammogram for $AuCl_4^-$ at a PTHVBAC film-coated electrode:
[$AuCl_4^-$]: (a) 1μM, (b) 10μM, (c) 30μM, (d) 50μM. Supporting electrolyte, 1.0MCl^- (0.1M HCl-0.9M NaCl), film thickness, 1μm; pulse amplitude, 50mV; scan rate, 5mV/s.

The peak potential for reduction of $AuCl_4^-$ in differential pulse voltammetry lies at -0.34V vs SCE for a solution concentration of 1μM, Fig.6.6. $AuCl_4^-$ was reduced to the metal during the voltammetric measurement in a 3-electron reaction (see Table 6.3). As the concentration of $AuCl_4^-$ was increased, the cathodic peak potential shifted significantly. The cathodic wave split into two distinct broad peaks when the concentration of $AuCl_4^-$ reached 50μM. These shifts in peak potential are typical of adsorption waves. A similar behavior was observed for multiple-charged inorganic complexes, such as ferrocyanide (data not shown). Although these adsorption phenomena may be interesting for mechanistic studies, they unfortunately give analytically undesirable data. At this point, it is also interesting to note that a PTHVBAC membrane electrode did not yield a potentiometric response to these inorganic complexes.

While inorganic charged complexes were adsorbed at the PTHVBAC film-coated electrode, a cyclic voltammogram obtained for uric acid, Fig.6.7, indicated that this species was incorporated into the polymer film. A 1mM standard solution of uric acid was prepared in 0.01M phosphate buffer at pH 7.0. Under these conditions, the ionization of uric acid occurs ($pK_{a1}=5.5$, $pK_{a2}=10.3$) [18]. Uric acid is singly charged, and preconcentration in the PTHVBAC film coated electrode can therefore proceed through an ion-exchange process. Uric acid is oxidized in a single rapid 2-electron process (Table 6.3), see Fig.6.7.

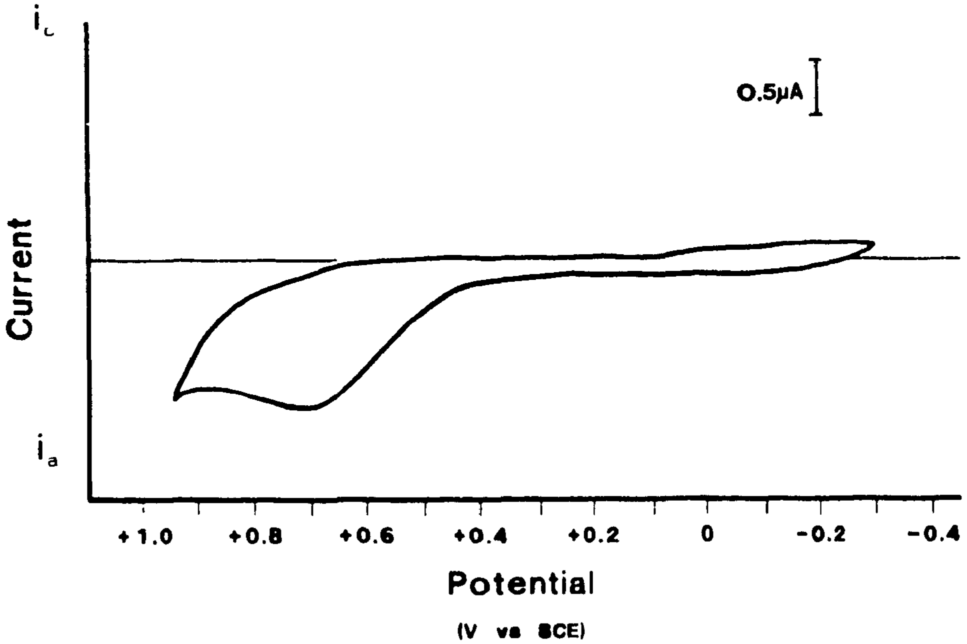


Fig.6.7 Cyclic voltammogram for 0.1mM uric acid at a PTHVBAC film-coated electrode: Supporting electrolyte, 0.01M phosphate buffer pH 7.0; film thickness, 1μm; preconcentration time, 10min.; scan rate, 50mV/s.

This oxidation proceeds via a primary uric acid-4,5-diol product which predominantly fragments to allantoin [17]. Provided the scan rate is sufficiently rapid, part of the 4,5-diol can be reduced back to uric acid. At 50mV/s, no cathodic peak was recorded, Fig.6.7. A well defined anodic peak was recorded at +600mV vs SCE (Fig.6.8), using differential pulse voltammetry.

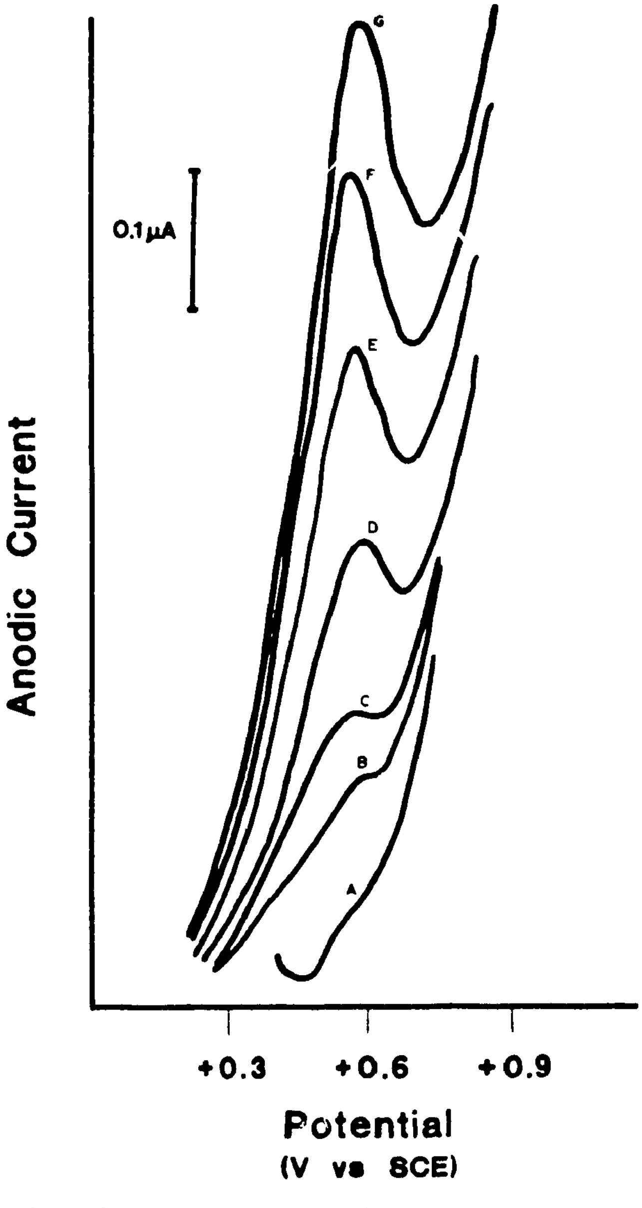


Fig. 6.8 Differential pulse voltammograms for uric acid at a PTHVBAC film-coated electrode. Uric acid concentration: (A) 0, (B) 1μM, (C) 2μM, (D) 4μM, (E) 6μM, (F) 8μM, (G) 10μM. Supporting electrolyte, 0.01M phosphate, pH 7.0; film thickness, 1μm; preconcentration time, 10min.; pulse amplitude, 50mV; scan rate, 5mV/s. The zero current of the individual curves is displaced for clarity.

From the calibration shown in Fig.6.9, it is clear that as the concentration of uric acid increases in solution, more uric acid is incorporated into the film. When the response of a PTHVBAC film electrode and a bare glassy carbon electrode are compared, a positive shift in the anodic peak potential of about +200mV is recorded. This shift in peak potential was attributed to slow electron transfer kinetics. Changes in pH in the interior of the polymer coating may also account for these shifts [19]

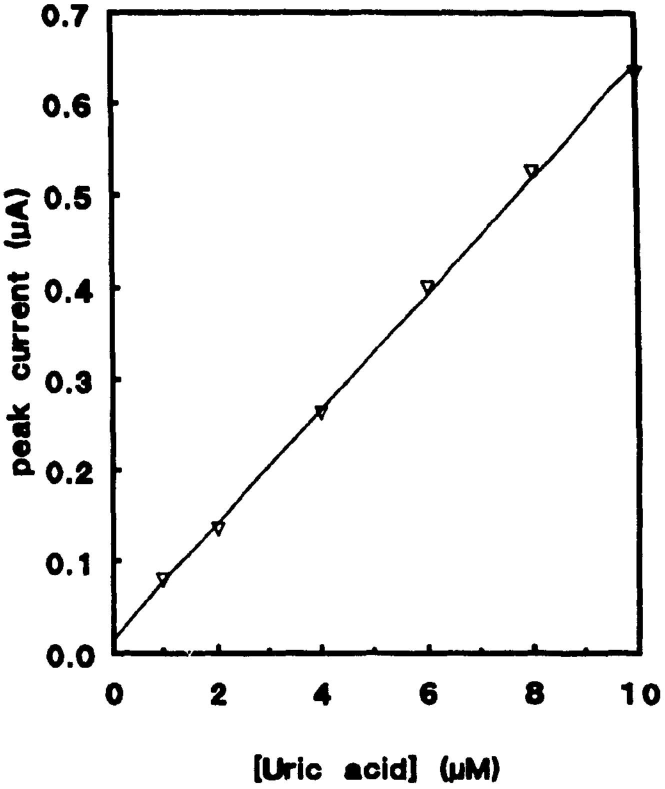


Fig.6.9 DPV response of a PTHVBAC film electrode to uric acid: Slope, 0.063µA/µM; y-intercept, 0.015µA. (Experimental conditions as described in Fig.6.8.)

In potentiometry, the use of thick membranes, typically 100µm thick, is essential to preserve the electroneutrality of the membrane (refer to Chapter 1, section 1.3.2.2). On the other hand, the voltammetric response of an electrode is affected by the thickness of the polymer film. Thin films (1µm thick) coated onto a glassy carbon electrode exhibited attractive permselectivity to uric acid. Repetitive preparations of a PTHVBAC film result in relatively reproducible response. For example, a series of three different PTHVBAC films yielded a response to 0.1mM uric acid with a relative standard deviation of 12%.

The anodic peak current for the oxidation of uric acid decreases upon decreasing the pH of the analyte solution from 7.0 to 4.0. At pH 4.0, uric acid is unionized, and neutral uric acid is excluded from the polymer film. Figure 6.10 shows cyclic voltammograms for both epinephrine and $Ru(NH_3)_6^{2+}$ at modified and bare glassy carbon electrodes in 0.01M phosphate buffer, at pH 7.0. As can be seen, the positively charged film effectively excludes cationic species such as epinephrine and $Ru(NH_3)_6^{2+}$. Exclusion of cationic species by the PTHVBAC polymer-film electrode was expected from Donnan exclusion principles (Chapter 1, section 1.2.3).

6.1.2.1 Investigation of charge-transport mechanisms in polymer films.

An important question in the behavior of polymer film coated electrode involves the mechanism of charge transport through the film layer. Electrochemical transport is thought to occur by electron self-exchange reactions between neighboring oxidized and reduced centers. This mechanism is called "electron hopping process" [10]. For example, during the reversible electrochemical oxidation of species "Red" at a glassy carbon electrode,

$$\mathrm{Red} \rightleftharpoons \mathrm{Ox}^{n+} + n\,e^- \tag{58}$$

Red can be brought to the electrode by the electron-transfer reaction:

$$\mathrm{Ox}^{n+} + \mathrm{Red} \rightarrow \mathrm{Red} + \mathrm{Ox}^{n+} \tag{59}$$

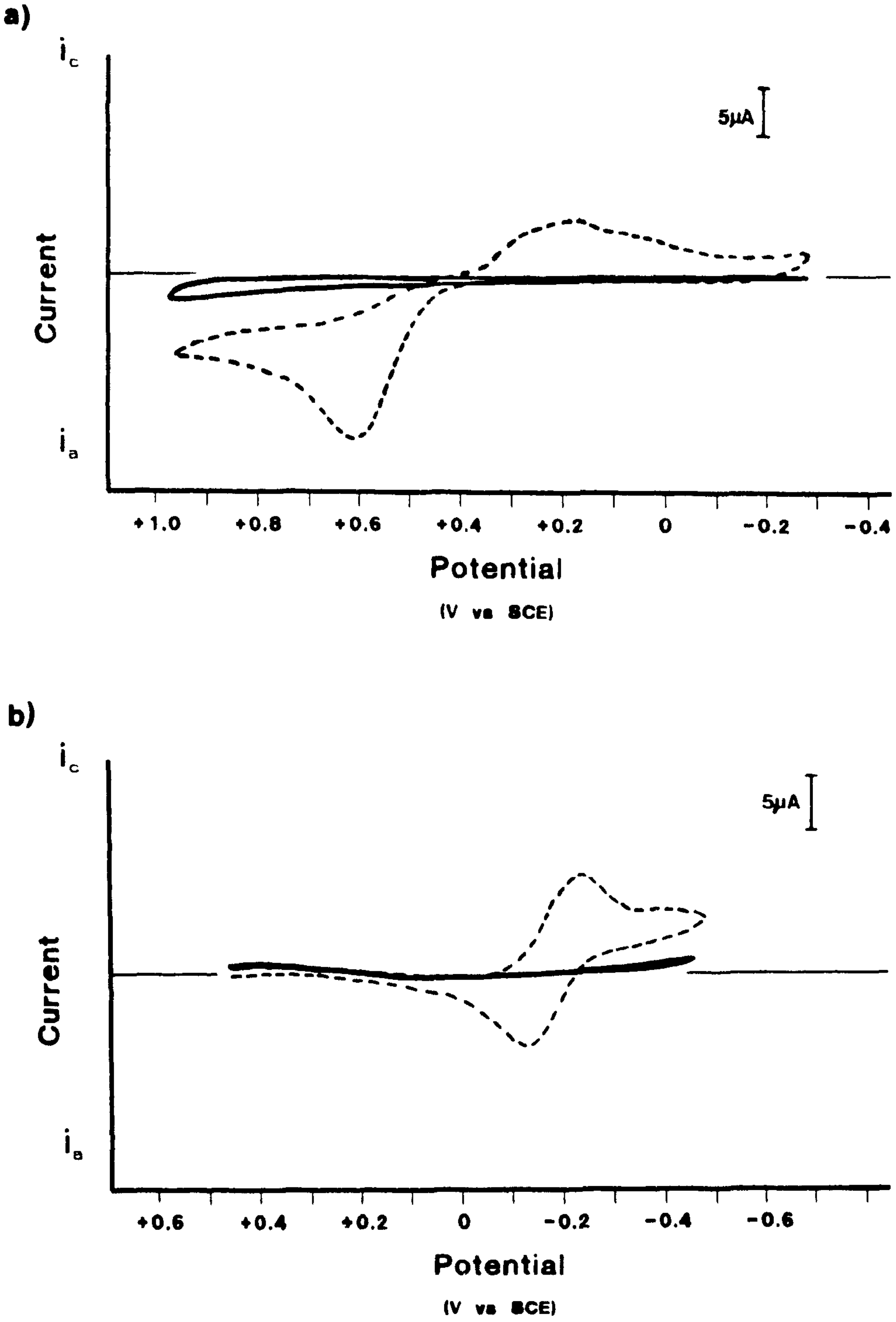


Fig.6.10 Cyclic voltammograms for 1mM epinephrine (a), and 1mM $Ru(NH_3)_6^{2+}$ (b) at bare and coated glassy carbon electrodes (dotted and solid lines, respectively). Supporting electrolyte, 0.01M phosphate buffer, pH 7.0; PTHVBAC film thickness, 1µm; scan rate, 50mV/s.

Fig. 6.11 is a good illustration of the electron-hopping process in a polymer film.

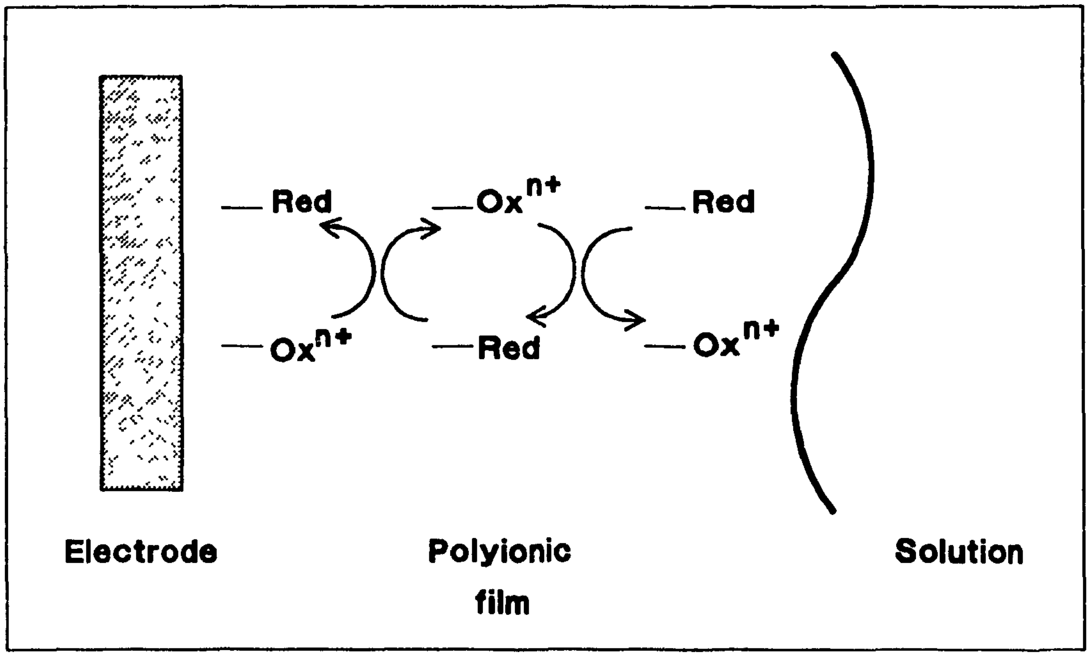


Fig.6.11 Schematic illustration of the electron hopping process in a polymer film.

Red can also be brought to the electrode by diffusion of the electroactive species, driven by the concentration gradient. Motions of polymer chains, charge-compensating counterions, and the presence of water of solvation may also contribute to the transport of electrochemical charge in the polymer film [20].

Voltammetric studies with uric acid at a PTHVBAC film-coated electrode exhibited a diffusion-controlled behavior, e.g. the cyclic voltammetric anodic peak current was proportional to the square root of the scan rate (refer to Appendix B for explanation of the diffusional-controlled behavior in cyclic voltammetry). However, the actual nature of the charge transport or diffusion process within polymer films is still the object of several investigations, and has not been determined yet. The diffusion coefficient of uric acid in PTHVBAC and PTOVBAC films, as determined from chronoamperometric experiments, will be discussed in the next section.

6.1.2.2 Determination of extraction and diffusion coefficients of ionic species in PTHVBAC and PTOVBAC polymer films:

Values for the diffusion coefficient of ionic species in PTHVBAC and PTOVBAC polymer electrodes were determined from chronoamperometric experiments (chronoamperometry is described in Appendix D). In chronoamperometry, the current is described by the Cottrell equation:

$$i_t = nFAD_{app}^{1/2}C_p / \pi^{1/2}\, t^{1/2} \qquad (60)$$

where i_t (A) is the current at time t, n is the number of electrons (eq/mol), F is the Faraday's constant (96,485 C/eq), A is the area of the electrode (cm^2), C_p is the concentration of electroactive species incorporated within the polymer film (mol/cm^3), D_{app} is the apparent diffusion coefficient of electroactive species (cm^2/s), and t is time (seconds). D_{app} is composed of contributions from actual diffusion of electroactive species and electron transfer. The concentration of electroactive material incorporated into the polymer film is defined as

$$C_p = N_p/Al \qquad (61)$$

N_p is the amount of electroactive species incorporated within the polymer film, l is the film thickness. N_p can be determined from the charge, Q, consumed in complete coulometric consumption of the film species:

$$Q = nFN_p \qquad (62)$$

An EG&G Princeton Applied Research Model 273 Potentiostat/Galvanostat interfaced with an IBM model AT computer was used for the chronoamperometric experiments. The interface of the potentiostat and computer is completed through an IEEE-488 National Instruments General Purpose Interface Bus (GPIB) which was installed in the computer. A software designed to run chronoamperometric experiments was used. This software and the hardware set-up is thoroughly described in reference [21]. Direct computer control of the potentiostat allows points to be taken as quickly as 100μsec per point, and as many as 3072 points were taken. The user can control the potential settings, the number of points collected, and the time per point. The coulometer of the potentiostat was used for coulometric experiments [22].

Modified electrodes were soaked 10 min in the uric acid solution buffered with 0.01M phosphate at pH 7.0, prior to the electrochemical measurement. This equilibration time ensured proper equilibrium between the polymer and solution, although no appreciable change in polymer concentration was observed after 4-5 minutes. The rate of equilibration of species between the solution and the polymer film is relatively rapid. When the electrode is immersed in a solution of supporting electrolyte, appreciable loss of uric acid from the loaded polymer film occurs over only a few minutes. If the electrode is immersed for more than 30 minutes, most of the uric acid is lost from the polymer layer. The concentration of uric acid incorporated within the film was varied over 2 orders of magnitude, by varying the concentration of the soaking solution. Coulometric measurements were made in triplicate, and were found to be reproducible in the working concentration range used. Each point of Figure 6.12 represents the average of each set of three measurements.

Plots of log C_p vs log C_s (Fig.6.12) were linear over the range of solution concentration varying from $1x10^{-6}$ to $1x10^{-5}$M. C_p and C_s are the concentration of electroactive species in polymer and solution, respectively. C_p was calculated from equations (61) and (62). Curvature of the plot for the PTHVBAC polymer film-electrode was observed at solution concentrations above 10μM, indicating saturation of the uric acid concentration in the polymer film. A saturation limit of 3.5mM was found. This value is a 1000 times lower than the calculated limit based on the quaternary ammonium groups present in the film. The concentration of quaternary ammonium ion-exchange sites was obtained from the results of elemental analysis performed on PTHVBAC. From these results, a concentration of 2.5M was calculated.

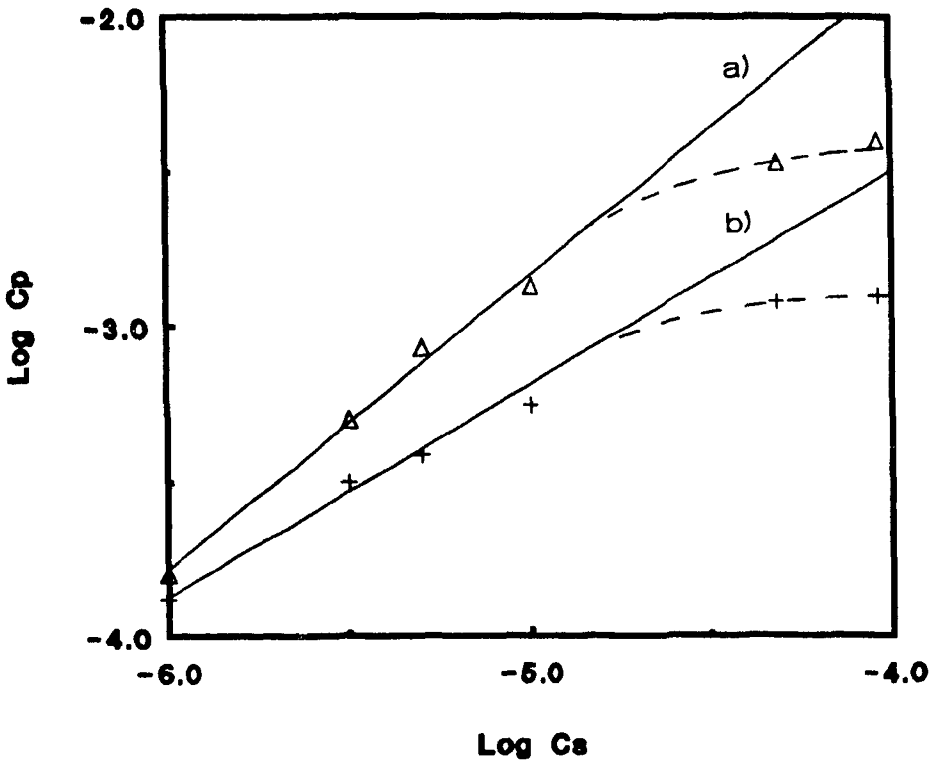


Fig.6.12 Concentration of uric acid incorporated in PTHVBAC (a) and PTOVBAC (b) film electrodes vs the concentration of uric acid in solution. The incorporated uric acid was determined coulometrically in 0.01M phosphate buffer, at pH 7.0.

The saturation limit for a PTOVBAC film is lower. In this case, a saturation limit was obtained at a concentration of 1mM uric acid. This was related to the high degree of cross-linking and crystallinity of PTHVBAC and PTOVBAC. These results seem to indicate that only a small fraction of the quaternary ammonium groups present in the membrane phase are available as ion-exchange sites.

The extraction coefficient, $K=C_p/C_s$, of uric acid in PTHVBAC and PTOVBAC films was evaluated from the slope of these plots in the linear segments. The extraction coefficients of iodide and ascorbic acid are also presented in Table 6.4. Ascorbic acid is oxidized in a 2-electron process, see Table 6.3. The acidity of ascorbic acid is due to dissociation of the enolic hydrogen on carbon-3 (pK_a=4.17) [23]. Since a solution of ascorbic acid degrades rapidly, it must be prepared, just prior its use.

Table 6.4: Extraction coefficients of ionic species in PTHVBAC and PTOVBAC films.

Ionic species	$K_{PTHVBAC}$	$K_{PTOVBAC}$
Uric acid	135	64
Ascorbic acid	47	17
Iodide	26	<10

In both PTHVBAC and PTOVBAC film electrodes, the extraction coefficient of uric acid is relatively large, compared to the values obtained for ascorbic acid and iodide. Further, the extraction coefficients for uric acid, ascorbic acid and iodide are systematically lower for the PTOVBAC film than for the PTHVBAC film electrode.

The diffusion coefficient of uric acid within PTHVBAC and PTOVBAC films was determined from chronoamperometric experiments. Typical Cottrell plots of current vs $t^{-1/2}$ are shown in Fig.6.13. These plots are linear with zero intercepts, as expected for a diffusion-controlled process [24].

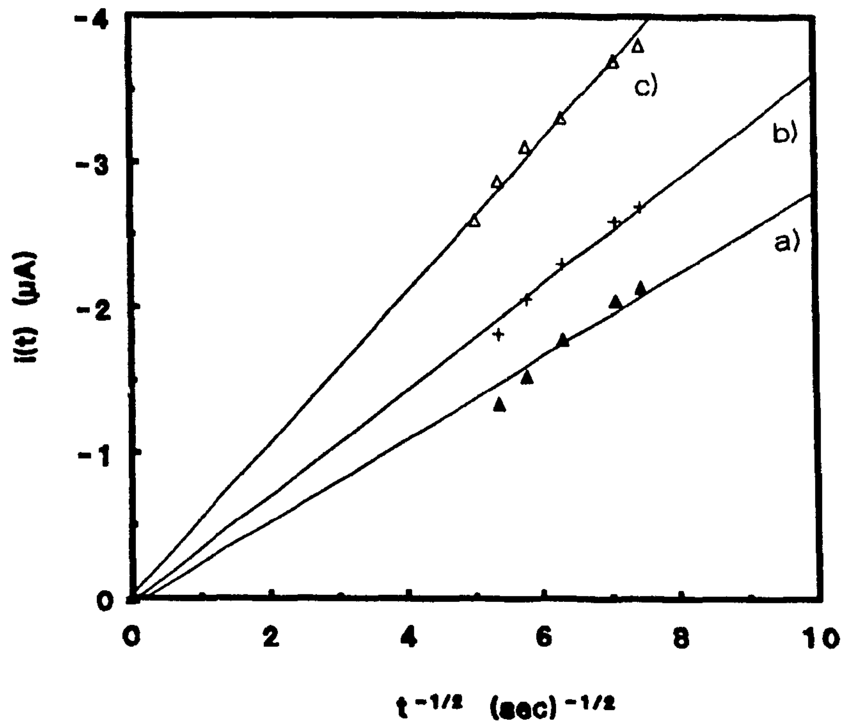


Fig.6.13 Cottrell plots resulting from oxidation of uric acid incorporated in a PTHVBAC film electrode, in 0.01M phosphate buffer, at pH 7.0.
Uric acid concentration: (a) 5μM, (b) 10μM, (c) 50μM. Film thickness, 1μm.

D_{app} values were determined from the slope of the Cottrell plots and equation (60). A D_{app} value of $3.2\pm0.9 \times 10^{-9}$ cm^2/s for the PTHVBAC film electrode, and a slightly lower value of $1.1\pm0.2 \times 10^{-9}$ cm^2/s for the PTOVBAC film electrode were found. Although considerable scatter existed in the values of D_{app} obtained, the apparent diffusion coefficient seems to be relatively independent of the total film concentration over the range 0.1mM-1.7mM. A similar independence of D_{app} with concentrations has been reported for other polymer modified electrodes [20].

6.1.3 Electrochemical measurement of uric acid with a PTHVBAC polymer-coated electrode:

Uric acid is a waste product, derived from purines of the diet. An healthy adult body contains about 1.1g of uric acid; one-sixth of this amount is present in the blood, the remainder being in other tissues [25]. Normally, about one-half of the total uric acid in the body is eliminated each day by urinary excretion. An abnormal level of uric acid in biological fluids is the symptom of several diseases. Determination of serum uric acid levels are most helpful in the diagnosis of gout, in which serum levels are frequently between 6.5 and 10mg/100ml. Normal serum levels vary from 2.6 to 7.2mg/100ml (0.16-0.43mM).

Several methods for the determination of uric acids in biological fluids have been described. The phosphotungstate method is most widely used clinically. With this method, uric acid is oxidized to allantoin and carbon dioxide by a phosphotungstic acid reagent in alkaline solution. Phosphotungstic acid is reduced in this reaction to tungsten blue, and the resultant blue color is measured by spectrophotometry [25]. Although this method gives good reproducible results, it is time-consuming and requires considerable sample manipulation. Direct voltammetric measurement of uric acid in body fluids constitutes an interesting alternative method [26]. However, direct electrochemical measurements of uric acid are typically limited by the presence of other oxidizable compounds. Notably, the presence of ascorbic acid constitutes a positive interference in the electrochemical determination of uric acid [26,27].

Poly(trihexylvinylbenzylammonium chloride) shows a high ion-exchange affinity for uric acid relative to simple inorganic anions such as, chloride and phosphate ions. Typically, the extraction coefficient of uric acid is about 135 in 0.01M phosphate buffer at pH 7.0, while the extraction coefficient of ascorbic acid is 3 times lower under the same conditions (refer to Table 6.4). PTHVBAC will preferentially incorporate uric acid from a contacting aqueous solution phase, even when this solution contains a high concentration of inorganic anions. Thus, an electrode coated with PTHVBAC can separate and preconcentrate an organic analyte such as uric acid, from a contacting sample solution phase. Because of this preconcentration effect, the detection limit for uric acid can be as much as two orders of magnitude lower at the PTHVBAC film-coated electrode than at a bare glassy carbon electrode. Typically, a cyclic voltammetric response to uric acid cannot be observed at a concentration below 1×10^{-4}M, while a response below 1×10^{-6}M can be monitored at a PTHVBAC film coated electrode. This detection limit is well below the concentration of uric acid found in human serum.

The enhanced selectivity obtained as a result of excluding cationic species such as epinephrine could be quite significant in the development of a sensor for the determination of uric acid in biological fluids and tissues. Epinephrine is a neurotransmitter, oxidized at +0.65V vs SCE, which can seriously interfere with the direct electrochemical measurement of uric acid. The selective retardation of ascorbic acid is also of great significance for the reduction of its interfering effect.

6.1.4 Selectivity pattern of PTHVBAC and PTOVBAC.

The factors operative in the ion-exchange behavior of PTHVBAC and PTOVBAC membranes can be described by simple thermodynamics. The Gibbs-Donnan equation

[28] for the exchange of a pair of monovalent ions

$$X^-_{(aq)} + Y^-_{(membrane)} \rightleftharpoons X^-_{(membrane)} + Y^-_{(aq)}$$

is given by

$$RT \ln K_{X,Y} = -RT \ln (\gamma_X^* \gamma_Y)/(\gamma_X \gamma_Y^*) + P\Delta V \qquad (63)$$

$K_{X,Y}$ is the ion selectivity coefficient of the ionic polymer membrane, γ is the activity coefficient of the respective ions, * refers to ions in the membrane phase, P is the pressure difference between the phases, and ΔV is the partial molar volume difference of the membrane ion-counterion salts in the membrane phase.

If both X^- and Y^- are simple inorganic ions of approximately the same size, the term $P\Delta V$ is considered negligible, and the ion exchange selectivity is attributed to the ratio of the activity coefficients, equation (63). These activity coefficients arise from electrostatic interactions in the membrane and solution phase. Apart from their nonspecific electrostatic interactions with ion exchange sites, ions can produce specific effects on the conformation of these macromolecular sites. If we refer to Table 6.1 and 6.2 (p.115 and 117, respectively), the selectivity pattern of PTHVBAC and PTOVBAC membranes tends to follow the Hofmeister series:

$$SCN^- > I^- > Br^- > NO_3^- > Cl^- > SO_4^{2-}$$

The Hofmeister series is an arrangement of anions in order of decreasing ability to produce coagulation of macromolecules [29].

If the main difference between X- and Y- is the size of the ion, then the term $P\Delta V$ dominates equation (63). For example, the smaller ion, Cl^-, is energetically favored in the membrane phase because of the increase in ionic volume resulting from the incorporation of a larger ion such as $AuCl_4^-$. Although gold tetrachlorocomplexes are not easily admitted within a PTHVBAC membrane phase, $AuCl_4^-$ can interact with ion exchange sites located at the membrane surface. Consequently, voltammetric adsorption waves were monitored for these inorganic complexes, Fig.6.6.

When X^- and Y^- have different hydrophobic properties, i.e. X^- is a large organic ion and Y^-, a small inorganic anion, another term must be added to the Gibbs-Donnan equation:

$$RT \ln K_{X,Y} = -RT \ln (\gamma_X^* \gamma_Y)/(\gamma_X g_Y^*) - P\Delta V - \Delta G_H \qquad (64)$$

ΔG_H describes the contribution of the hydrophobic nature of an ion to the free energy change associated with the incorporation of this ion into the membrane [28,30]. The hydrophobic interactions between uric acid and the membrane phase seems to be the driving force for the rate of the ion-exchange process.

6.2 QUATERNARY PHOSPHONIUM FUNCTIONALIZED POLYMERS:

6.2.1 Potentiometric response characteristics of quaternary phosphonium functionalized polymer membrane electrodes:

A membrane prepared from poly(trioctylvinylbenzylphosphonium chloride), PTOVBPC, demonstrated an enhanced sensitivity to nitrate ions compared to a membrane prepared from poly(trihexylvinylbenzylammonium chloride), see Fig.6.14. A carbon-support electrode coated with 100µm thick membranes was used. Note that prior to coating the carbon-support electrode with PTOVBPC, the counterions of the bound quaternary phosphonium groups were exchanged for nitrate through the previously described liquid-liquid extraction procedure (Section 6.1.1). The useful response of the carbon-support electrode coated with a film of $PTOVBPNO_3$ extended from 1×10^{-5}M to 0.1M NO_3^- with a slope of -53.4±0.5mV/dec. The standard solutions were buffered with 0.1M phosphate, pH 7.0.

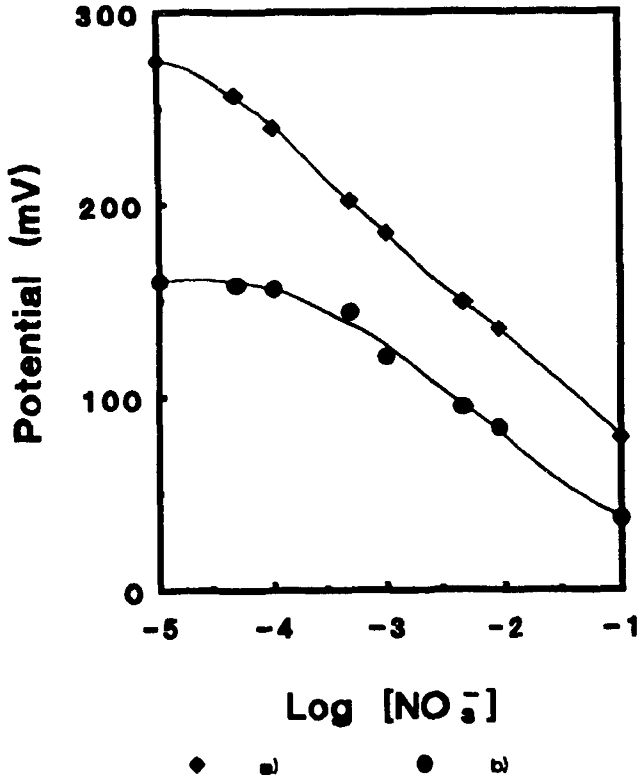


Fig.6.14 Comparison of the potentiometric response of PTOVBPNO$_3$ and PTHVBANO$_3$ membrane electrodes to nitrate:
a) PTOVBPNO$_3$ membrane: slope, -53.4±0.5mV/decade; linear response range, 0.01mM-0.1M.
b) PTHVBANO$_3$ membrane: slope, -43.2±0.6mV/decade; linear response range, 1mM-0.1M.

The selectivity coefficients for the PTHVBANO$_3$ and PTOVBPNO$_3$ membrane electrodes were measured by the fixed interference method; the concentration of interfering anions was fixed at 1mM, while the concentration of nitrate was varied from 1×10^{-5} to 0.1M. The selectivity coefficients for both electrodes are presented in Table 6.5.

Table 6.5: Selectivity coefficients for the nitrate ion-selective membrane electrodes.

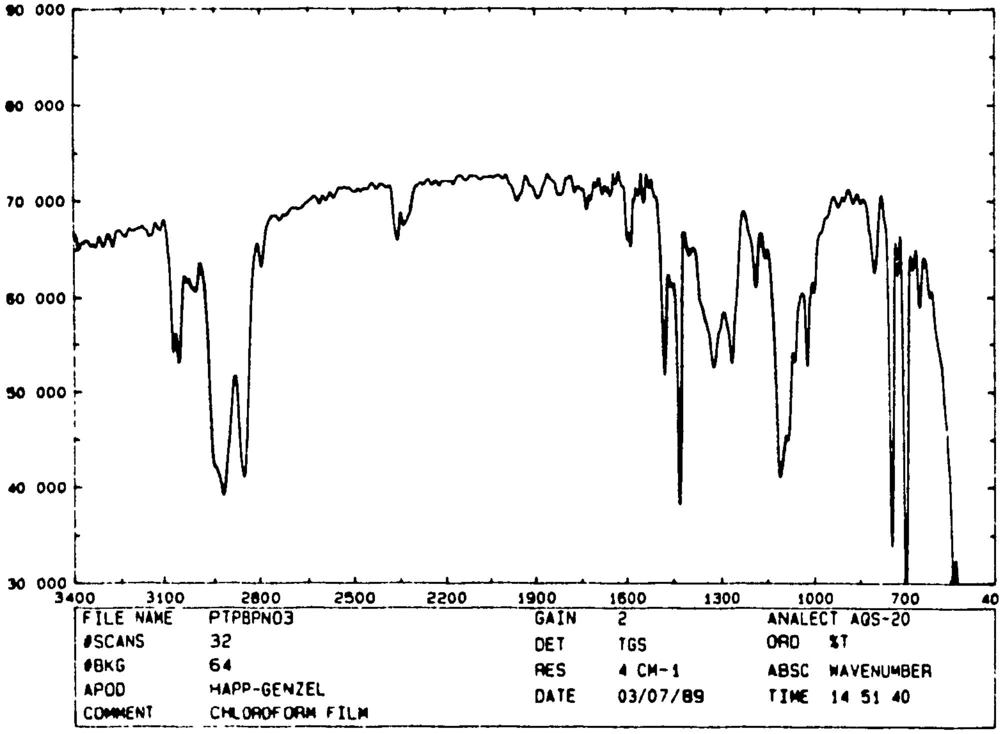
Interfering anions	$K_{i,j}^{pot}$ $PTOVBPNO_3$ membrane	$K_{i,j}^{pot}$ $PTHVBANO_3$ membrane
phosphate	<0.0001	0.0005
acetate	0.0005	0.0008
sulphate	0.003	0.005
chloride	0.008	0.01
nitrite	0.05	0.25
bromide	0.25	0.3
iodide	3.2	1.0
perchlorate	10	15.8

The $PTOVBPNO_3$ membrane clearly exhibits an increased sensitivity and selectivity to nitrate ions compared to the $PTHVBANO_3$ membrane. These results indicate that the selectivity of an ionic polymer membrane depends on the nature of the ion-exchange sites bound to the polymeric structure.

The selectivity of the $PTOVBPNO_3$ membrane can be favorably compared to conventional nitrate ion-selective electrodes (based on tridodecylhexadecylammonium nitrate). Perchlorate constitutes the most serious interferent of commercial nitrate ISE's, typically $K_{NO_3^-,ClO_4^-} = 1000$ for a Corning No.476134 ISE [31]. A significant improvement of selectivity for nitrate in presence of perchlorate was obtained with the $PTOVBPNO_3$ membrane electrode, $K_{NO_3^-,ClO_4^-} = 10$. This represents an improvement of 2 orders of magnitude.

The results obtained with this $PTHVBANO_3$ membrane electrode and a nitrate ion-selective electrode with covalently bound sites reported by Ebdon et al. [32], were also compared. The latter was prepared from a poly(styrene-b-butadiene-b-styrene) matrix cross-linked with allyl substituted quaternary ammonium salts (SBS-QAS membrane). This SBS-QAS membrane electrode displayed near-Nernstian response to nitrate, but poor selectivity for this species in presence of other ions. For example, chloride interferes seriously with the response of the SBS-QAS membrane electrode, $K_{NO_3^-,Cl^-} = 0.16$, while the response of the PTHVBANO$_3$ membrane is less seriously affected by the presence of chloride, $K_{NO_3^-,Cl^-} = 0.01$.

Poly(triphenylvinylbenzylphosphonium chloride), PTPVBPC, also demonstrated high affinity for nitrate ions. This was confirmed by an infrared spectrum, Fig.6.15, taken after extraction of a PTPVBPC dissolved in chloroform with an aqueous solution of 0.1M KNO$_3$.



FILE NAME	PTPBPNO3	GAIN	2	ANALECT AQS-20	
#SCANS	32	DET	TGS	ORD	%T
#BKG	64	RES	4 CM-1	ABSC	WAVENUMBER
APOD	HAPP-GENZEL	DATE	03/07/89	TIME	14 51 40
COMMENT	CHLOROFORM FILM				

Fig. 6.15 Infrared spectrum of poly(triphenylvinylbenzylphosphonium nitrate).

A characteristic N=O stretching absorption was recorded in the region 1250-1400cm^{-1}. A strong absorption band at 1116cm^{-1} and a medium band at 1026cm^{-1} are associated with the presence of aromatic quaternary phosphonium groups within the polymeric structure.

Despite the selectivity exhibited for nitrate ions, a PTPVBPNO$_3$ membrane electrode did not demonstrate any sensitivity to nitrate. For polymer membranes with fixed ion-exchange sites, not only is selectivity involved in the membrane response mechanism but so is the mobility of the counterion species within the membrane. Therefore, there are opposing effects between mobilities and affinities of ions in ionic polymer membranes. This constitutes the principal limitation of this membrane system.

6.2.2 Analysis of nitrate in fertilizers with a PTOVBPNO$_3$ membrane electrode:

Nitrogen is an essential constituent of natural ecosystems. However, an undesirable level of nitrate in natural waters as a result of man's activities is becoming a serious source of pollution. The extensive use of artificial fertilizers in agriculture has been implicated as a major cause of the increasing nitrate concentration in natural waters, and as an important factor in the growing problems of eutrophication of lakes [33]. The rapidly increasing consumption of artificial fertilizers has stimulated the development of efficient, inexpensive analytical methods for the determination of nitrate.

The PTOVBPNO$_3$ membrane electrode was applied to the determination of nitrogen-nitrate in two samples of fertilizers. These fertilizers were obtained from local stores. The RaPidGro Evergreen Fertilizer (RAPIDGRO Corporation, Dansville, New York) is a granule concentrate, while the Jobe's Sunsplash Fertilizer (International Spike, Inc., Lexington, Kentucky) is a dilute aqueous preparation. They both contain all three of the main plant nutrients, i.e. nitrogen, phosphate and potassium, Table 6.6. The

RaPidGro fertilizer also contains 5 micronutrients, Boron, Copper, Iron, Manganese, and Zinc.

Table 6.6: Chemical composition of commercial fertilizers analyzed.[a]

Elements	RaPidGro Evergreen	Jobe's Sunsplash
Total Nitrogen:	32%	1%
Ammoniacal nitrogen	1.9%	0.6%
Nitrate nitrogen	2.9%	0.4%
Urea Nitrogen	27.2%	----
Phosphoric acid[b] (P_2O_5)	10%	3%
Soluble potash[c] (K_2O)	10%	2%
Others:		not specified
Chelating agent (EDTA)	0.08%	
Boron (B)	0.02%	
Copper (Cu)	0.05%	
Iron (Fe)	0.10%	
Manganese (Mn)	0.05%	
Zinc (Zn)	0.05%	

[a] Guaranteed minimum analysis, as specified by the manufacturer.
[b] P_2O_5 is soluble in water. It decomposes to H_3PO_4 [34].
[c] K_2O is readily hydrolyzed by water to form potassium and hydroxyl ions [35].

A 5g sample of the RaPidGro Evergreen fertilizer was finely ground, and dried in an oven for at least 2 hours at 100°C. At this temperature, no degradation of the sample occurs. Three portions of about 0.1g of the dry sample was then dissolved in 50ml of 0.1M phosphate buffer (pH 7.0). The Jobe's sunsplash fertilizer liquid was readily used without any dilution.

An interference suppressor composed of 0.01M aluminium sulphate, 0.01M silver sulphate, 0.02M boric acid, 0.01M sulphamic acid, and adjusted to pH 3.0 with 0.1M sulphuric acid was used. This solution effectively reduces the interfering effect of many common inorganic ions. Chloride ions are quantitatively precipitated as silver chloride. Traces of bromide, cyanide, suphide and phosphate are also removed by precipitation with Ag(I). Further, aluminium ion strongly complexes anions of organic acids, and nitrite is quantitatively destroyed by reaction with sulphamic acid [36]. Equal volumes (2ml) of this interference suppressor and the sample solution were mixed. After precipitation of the interfering species, the solution was filtered, and diluted with 50ml of 0.1M phosphate (pH 7.0). The use of this interference suppressor was found particularly useful for the analysis of the Jobe's sunsplash fertilizer. Without the use of the interference suppressor, an unspecified component of the sample caused a positive interference with nitrate measurements.

The nitrate-nitrogen content of each sample was quantitated by standard addition using the PTOVBPNO$_3$ membrane electrode, and the results are reported in Table 6.7.

Table 6.7: Potentiometric determination of nitrate in commercial fertilizers.

Sample	NO_3-N%	
	claimed	found
RaPidGro Evergreen	2.9%	2.7 ± 0.1%
Jobe's Sunsplash	0.4%	0.44 ± 0.02%

In both cases, these results are in good accordance with the amount of nitrate-nitrogen guaranteed by the manufacturer. The electrode potentials obtained by repeated measurements on a 1mM nitrate solution fall within ±1mV. This variability in the electrode response and sampling errors account for the standard deviation observed. Thus, this newly described electrode proved to be a simple, reliable and sensitive method for the determination of nitrate in samples of fertilizers.

6.3 POLY(VINYLBENZYL DIALKYL PHOSPHATE) MEMBRANES:

Poly(vinylbenzyl dialkyl phosphate) film cast on a carbon-support electrode was conditioned and used as an ion-selective membrane for calcium. The use of dialkyl phosphate ion exchanger in the composition of a calcium selective electrode was first introduced by Ross [37] in 1967. The best membrane resulted from PVBC functionalized with 5% mole/mole dialkyl phosphate/polymer repeat unit. Higher levels of immobilized dialkyl phosphate groups resulted in water-soluble membranes. However, the membrane electrode with 5% dialkyl phosphate groups exhibited a sub-Nernstian response to calcium in the concentration range from 1×10^{-4}M to 0.01M, Fig.6.16. The electrode was stored in 10^{-2}M Ca^{2+} solution.

The response of the electrode was not dependent on the pH of the solution in the range pH 5-8. The pH of the solution was changed by using 0.1M hydrochloric acid and 0.1M sodium hydroxide. Selectivities studies performed on a limited number of cations showed the general order of selectivity to be:

$$Pb^{2+} > Ca^{2+} > Mg^{2+} > K^{+}$$

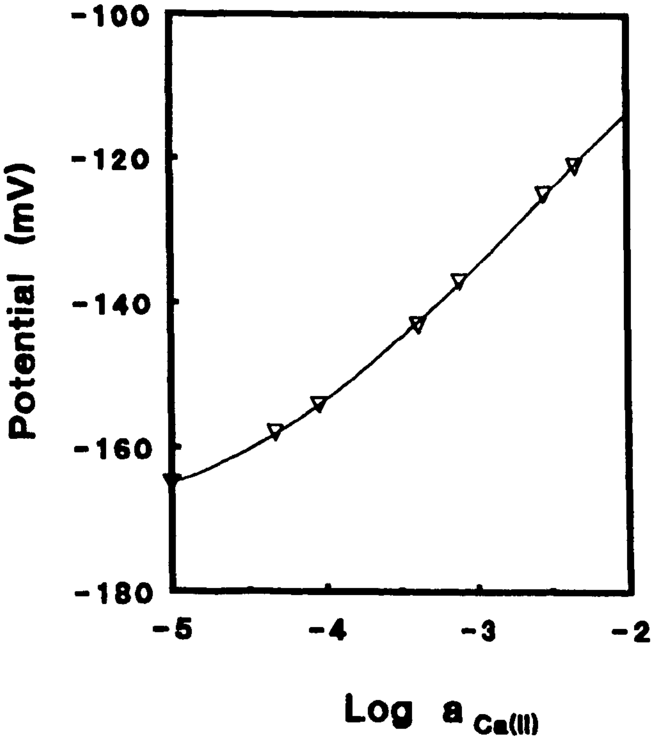


Fig.6.16 Response of a poly(vinylbenzyl dialkyl phosphate) coated carbon-support electrode to calcium ions: Slope, 19±1mV/dec.; response range, 0.01mM-0.01M.

Further, this electrode yielded a poor reproducible response, and potential drifts were of the order of several millivolts/day.

REFERENCES:

[1] H. James, G. Carmack, and H. Freiser, *Anal.Chem.*, **1972**, 44, 856.

[2] B.M. Kneebone and H. Freiser, *Anal.Chem.*, **1973**, 45, 449.

[3] H. Freiser, *J.Chem.Soc.Faraday Trans.1*, **1986**, 82, 1217.

[4] R.S. Lawton and A.M. Yacynych, *Anal.Chim.Acta*, **1984**, 160, 149.

[5] M. Mascini, *Anal.Chim.Acta*, **1972**, 62, 29.

[6] C.E. Efstathiou, M.A. Koupparis, and T.P. Hadjiiannou, *Ion-Selective Electrode Revs.*, **1985**, 7, 203.

[7] W.J. Williams, "Handbook of Anion Determination", Butterworths, Boston, 1979, pp.228-239.

[8] A. Mitsana-Papazoglou, E.P. Diamandis, and T.P. Hadjiioannou, *Anal.Chim.Acta*, **1984**, 159, 393.

[9] N.W. Tietz, Ed., "Fundamentals of Clinical Chemistry", W.B. Saunders, Philadelphia, 1976, pp.1147-48.

[10] R.W. Murray, A.G. Ewing, and R.A. Durst, *Anal.Chem.*, **1987**, 59, 379A.

[11] P.T. Kissinger and W.R. Heineman, Eds., "Laboratory Techniques in Electroanalytical Chemistry", Marcel Dekker, New York, 1984, pp.290-312.

[12] K. Kalcher, *Anal.Chim.Acta*, **1985**, 177, 175.

[13] P.T. Kissinger and W.R. Heineman, Eds., "Laboratory Techniques in Electroanalytical Chemistry", Marcel Dekker, New York, 1984, pp.46-48.

[14] A.J. Bard, Ed., "Electroanalytical Chemistry", Marcel Dekker, New York, Vol.13, 1984, p.206.

[15] L. Meites and P.Zuman, "Handbook Series in Organic Electrochemistry", Vol.I, CRC Press, Cleveland (Ohio), 1976, Table I.

[16] J.A. Dean, Ed., "Lange's Handbook of Chemistry", 13th Ed., McGraw Hill, New York, 1985, pp.6-6 - 6-19.

[17] G. Dryhurst, *J.Electrochem. Society*, **1969**, 116, 1411.

[18] A. White, P. Handler, and E.L. Smith, "Principles of Biochemistry", 3rd Ed., McGraw-Hill Book Company, New York, 1964, p.165.

[19] J. Wang and T. Golden, *Anal.Chem.*, **1989**, 61, 1397.

[20] H.S. White, J. Leddy, and A.J. Bard, *J.Am.Chem.Soc.*, **1982**, 104, 4811.

[21] M.E. Perry, "Interface of an IBM-AT with a Model 273 Potentiostat/Galvanostat", B.A. Honour Degree Thesis, Mount Holyoke College, South Hadley, Massachusetts, May 1987.

[22] PAR 273 Potentiostat/Galvanostat user manual.

[23] A. White, P. Handler, and E.L. Smith, "Principles of Biochemistry", 3rd Ed., McGraw-Hill Book Company, New York, 1964, p.973-74.

[24] P.T. Kissinger and W.R. Heineman, Eds., "Laboratory Techniques in Electroanalytical Chemistry", Marcel Dekker, New York, 1984, pp.56-61.

[25] N.W. Tietz, Ed., "Fundamentals of Clinical Chemistry", W.B. Saunders, Philadelphia, 1976, pp.999-1002.

[26] J. Wang and B.A. Freiha, *Bioelectrochemistry and Bioenergetics*, A section of *J. Electroanal.Chem.*, **1984**, 12, 225.

[27] G. Park, R.N. Adams, and W.R. White, *Anal.Lett.*, **1972**, 5, 887.

[28] I.F. Miller, F. Bernstein, and H.P. Gregor, *J.Chem.Phys.*, **1965**, 43, 1783.

[29] S.P. Parker, Ed., "McGraw-Hill Dictionary of Chemical Terms", McGraw-Hill Book, New York, 1984, p.204.

[30] J.A. Marinsky, Ed., "Ion Exchange: A Series of Advances", Vol.2, Marcel Dekker, New York, 1969, pp.139-151.

[31] J.E.W. Davies, G.J. Moody, and J.D.R. Thomas, *Analyst*, **1972**, 97, 87.

[32] L. Ebdon, B.A. King, and G.C. Corfield, *Analytical Proceedings*,**1985**, 22, 354.

[33] N.N Greenwood and A. Earnshaw, Chemistry of the Elements, Pergamon Press, New York, 1984, pp.469-470.

[34] R.C. Weast, M.J. Astle, and W.H. Beyer, Eds., "CRC Handbook of Chemistry and Physics", 64th Ed., CRC Press, Boca Raton (Florida), 1983, p.B-119.

[35] F.A. Cotton and G. Wilkinson, "Basic Inorganic Chemistry", John Wiley & Sons, New York, 1976, p.220.

[36] L. Meites, Ed., "Handbook of Analytical Chemistry", First Ed., McGraw-Hill Book Company, New York, 1963, p.12-162.

[37] J.W. Ross, *Science*, **1967**, 156, 1378.

CHAPTER 7:

FLOW INJECTION ANALYSIS WITH AN IONIC POLYMER MEMBRANE ELECTRODE.

Potentiometric detection has a number of advantages in flowing stream analysis. Notably, automatization of potentiometric measurements in flow injection systems increases the number of samples which can be determined in a given period of time and reduces the consumption of reagents and sample manipulations [1]. Furthermore, the measuring surface of the electrode is continuously in contact with fresh reagent in flowing solutions. Therefore, the electrode cannot affect the composition of the sample solution. This can result in an increase in sensitivity of the potentiometric measurements. The flowing solution stream also ensures a small diffusion layer thickness, and thus a quicker electrode response is attained [2]. These advantages all contribute to the utilization of ion-selective electrodes in Flow Injection Analysis (FIA).

Since ionic polymer membrane electrodes have displayed enhanced lifetime and rapid response in static solutions, their application in flow injection analyzers seems particularly promising. An ionic polymer membrane electrode-based flow injection system suitable for the measurement of salicylic acid is described; a poly(trihexylvinylbenzylammonium salicylate) polymer coated carbon-support electrode was used. There is a particular need for salicylate measuring systems for application in pharmaceutical analysis.

7.1 FLOW INJECTION ANALYSIS SYSTEM:

Flow Injection Analysis involves the injection of a sample into a flowing stream which carries the sample to a suitable analytical detector [3]. The flow injection system used is illustrated in Fig.7.1.

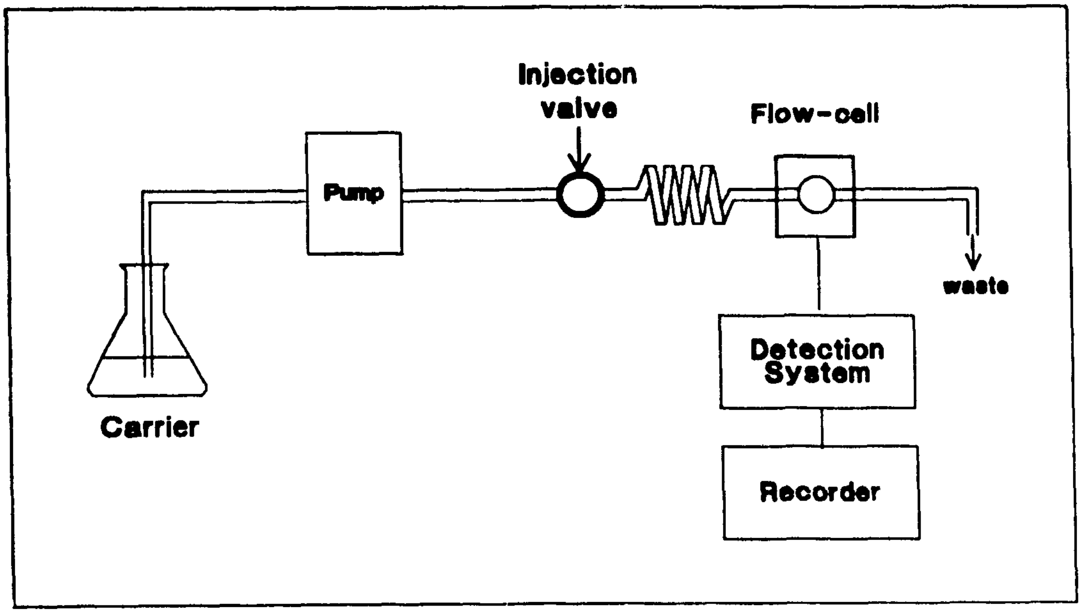


Fig.7.1 Components of the FIA system: A propelling unit, an injection system, a tube or reaction chamber, an electrochemical flow-cell, a detection system, and a recorder.

It basically consists of a dual-piston pump (Waters Model 6000A) used to propel the carrier stream through the reaction chamber; an injection port (Rheodyne 7125 rotary valve), by means of which a defined volume of a sample solution is injected to the carrier stream; a piece of tubing (Teflon tubing 0.8mm ID, Chromatography Sciences Company) along which the transport of the sample takes place; and a flow-cell which accommodates a detector transducing some property of the analyte monitored by the detection unit, i.e. the Fisher Accumet Model 805MP pH/mV meter with a Servogor 120 recorder (The characteristics of the 805MP pH/mV meter were already described in chapter 3, section

3.2). The specifics of the electrochemical flow-cell are described in section 7.1.4.

A typical FIA recorder output has the form of a peak (Fig.7.2), i.e the analytical signal as a function of time. This type of transient signal is similar to the signal obtained in liquid chromatography. The peak height is related to the concentration of the component in the injected sample.

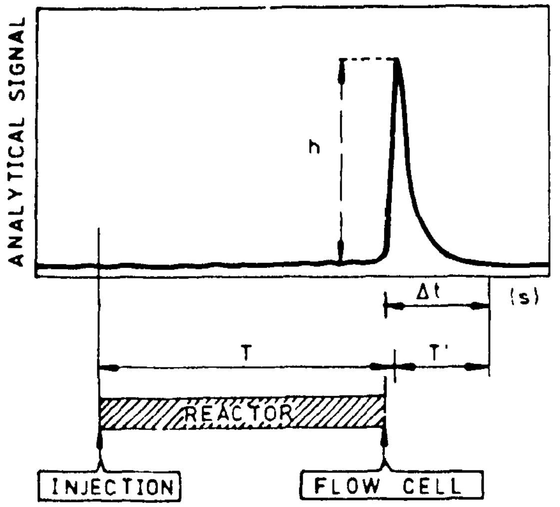


Fig.7.2 Typical FIA recorder output [3]: T is the residence time, Δt, the peak width at the baseline, and h, the peak height. The time scale is in seconds.

The maximum attainable sampling frequency [4], S_{max}, in FIA is defined as

$$S_{max} = 3600/\Delta t \text{ (samples/hour)} \tag{65}$$

7.1.1 Propelling unit:

The flow rate of the carrier stream should be constant and reproducible in order to give a predictable residence time. This function can be performed by a peristaltic pump, a gas-pressure system or a piston-driven pump. With piston-driven pumps, the regularity of the pump flow depends on the number of pistons. Dual-piston units give a significantly smoother flow than single-piston pumps [3]. Flow-rate pulses can be damped by use of a suitable attenuator. A coiled tube placed before the injection port is commonly used for this purpose [3].

In automated potentiometric systems, oscillations of potential readings are generally caused by the propelling unit. These oscillations are ascribed to several causes such as changes in liquid-junction potential at the reference electrode or to static electricity effects [5,6]. These oscillations may also be caused by change in streaming potentials [7,8]. When a liquid is forced through a narrow tube by a pressure gradient, a potential difference is formed between the ends of the tube [7]. This potential difference is called the streaming potential, E_s, and is given by the Helmholtz-Smoluchowski equation:

$$E_s = D\xi\Delta P/(4\pi\eta\lambda) \tag{66}$$

where D is the dielectric constant (dimensionless), ξ is the electrokinetic potential (volt), ΔP is the pressure gradient (dyne cm^{-2}), η and λ are the viscosity (poise) and the conductivity (ohm^{-1} cm^{-1}) of the media, respectively.

Assuming a Poiseuille velocity profile in the carrier stream [7],

$$\Delta P = 8d\eta l/(\pi r^4) \tag{67}$$

where d is the flow rate (ml/sec), l is the length of the tubing (cm), and r is the radius of the tube (cm). Substitution of equation (66) in (67) yields:

$$E_s = 2dD\xi l/(\pi^2 r^4 \lambda) \tag{68}$$

If all the parameters are kept constant, E_s is constant and it is simply added to the potential of the cell. However, the flow rate "*d*" usually oscillates to a certain extent. This leads to oscillation of the value of E_s which appears in the measured signal as periodic noise.

Different methods can be used to minimize the effects of streaming potential oscillations. The most practical solution is to add a large quantity of electrolyte. The addition of a large quantity of indifferent electrolyte to the carrier stream increases the conductivity, and consequently reduces E_s, equation (68). The careful choice of the pump can also help to reduce flow-rate pulses.

7.1.2 Injection system:

A suitable injection system should allow the reproducible introduction of an accurately measured sample volume into the carrier flow. The most common injection device employed is a rotary valve [3]. Rotary valves give high reproducibility in injected volume, and offer a wide range of injection volumes with the use of injection loops of different sizes.

In the filling mode (Fig.7.3a), the sample enters the valve through port 2, fills the loop between ports 1 and 4, and goes to waste through port 3. Meanwhile the carrier stream enters the valve through port 6 and passes out through port 5. In the injection mode (Fig.7.3b), port 6 is connected internally with port 1, sweeping the sample plug towards the detector through ports 4 and 5.

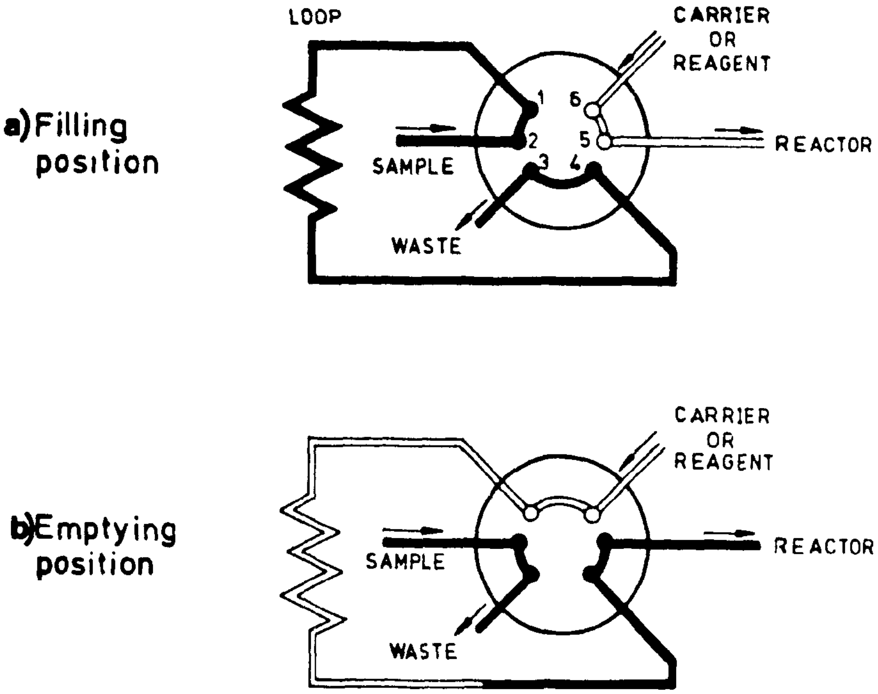


Fig.7.3 Operational scheme for a four-way rotary injection valve [3]:
a) Filling position, b) injection mode.

7.1.3 Reaction chamber:

In the flow injection system described in Figure 7.1, the reaction chamber is simply defined as a length of tubing along which the transport of sample takes place. When a sample zone moves through an open tube in a laminar flow, dispersion of the injected sample occurs. The dispersion coefficient [4], D, is defined as:

$$D = C_0/C \tag{69}$$

where C_0 is the original sample concentration prior to injection, and C is the concentration of the dispersed sample solution measured. From its definition, it follows that the dispersion coefficient always exceeds unity.

There are two mechanisms contributing to the dispersion of the injected sample: convective and diffusional transport, Fig.7.4. Convective transport occurs under laminar flow conditions [3]. Laminar flow yields a parabolic velocity profile with sample molecules near the tube walls having zero linear velocity, while the molecules at the centre of the tube having twice the average velocity. Diffusional transport is due to the presence of concentration gradients in the convective transport regime. This gives rise to axial and radial diffusion [3]. Axial dispersion resulting from concentration difference perpendicular to the direction of the flow makes an important contribution to the dispersion of the sample.

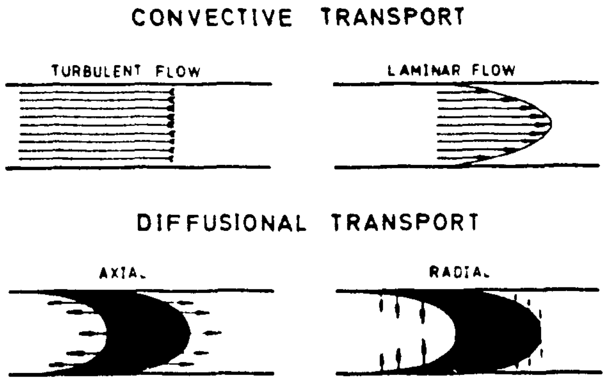


Fig.7.4 Convective and diffusional transport in a straight open tube [3].

Any deviation of geometry from a circular straight pipe will disturb the laminar pattern of the liquid flowing through the tube. Relaxation of the laminar profile in the radial direction is best achieved by creating a local turbulence where the direction of flow is suddenly changed. The elements of fluid that are lagging because they are close to the walls of the channel are then moved into the rapidly advancing central stream. The dispersion factor therefore decreases as the increased radial dispersion changes the character of the flow.

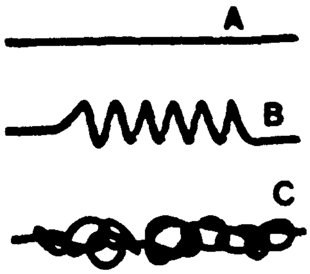


Fig.7.5 Geometries of some frequently used microreactors in FIA [9]: A, straight open tube; B, helical coiled tube; C, 3-D coiled or knitted reactor.

As expected from this model, the dispersion factor decreases systematically from a circular straight tube to an helical coiled reaction chamber to a 3-D coiled tube, Table 7.1. This is attributed to the intensification of the dispersion-reducing effect introduced by coiling the tube.

Table 7.1: Comparison of dispersion factors for reaction chambers with different geometry [4].

Reaction chamber[a]	Dispersion factor[b]
Straight tube	0.41
Helical coiled tube	0.34
3-D coiled tube	0.23

[a] 75cm long, 0.5mm I.D.

[b] Dispersion factor: $S_{1/2}/V_r$.
$S_{1/2}$: injected sample volume necessary to reach 50% of steady state signal.
V_r: volume of the channel.

Therefore, a 100cm long 3-D coiled microreactor with a narrow bore of 0.8mm was used. Accordingly, the channel volume between the point of injection and the flow cell was 500μl.

In FIA with potentiometric detection, the flowing stream system serves merely as a reproducible means of transport. An FIA system with limited dispersion (D <3) will operate at a higher sampling rate, with better limit of detection and economy of reagent and time. The dispersion of sample solution can best be controlled by choice of a suitable sample volume, pumping rate, and geometry of the carrier flow [3].

7.1.4 Electrochemical flow-cell:

A flow-through cell was designed to accommodate a carbon-support electrode, Fig.7.5. This thin-layer flow-cell was based on designs previously used in this laboratory [10,11]. The cell body was made of Kef-F, a mechanically stable material which retains its properties after exposure to organic solvents. The lower cell body was a 4cm-long hemicylindrical piece of Kel-F. The graphite rod, positioned in the middle, was press-fitted in the cell body. A copper wire was used as the electrical connection. The ion-sensitive membrane, about 100μm thick, was cast directly on the graphite surface. The upper cell body had two tapped holes for the solution inlet and outlet. A rectangular flow channel was defined by an opening cut into a 1mm-thick piece of Teflon, which was clamped between the cell pieces. With this configuration, the carrier solution flows tangentially over the membrane surface of the ion-selective electrode, and from there to the reservoir where the terminal part of the reference electrode is submerged. A constant and small level of liquid is maintained in the reservoir, and the carrier flow emerging from the outlet of the reservoir directly goes to waste.

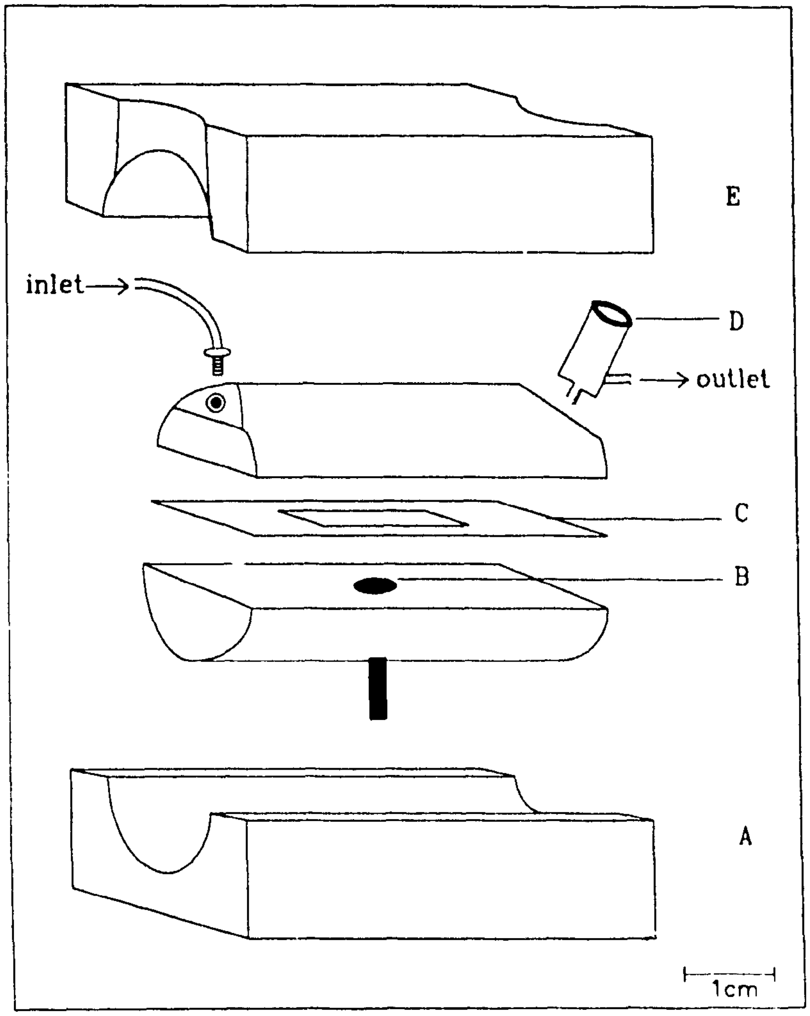


Fig.7.6 Electrochemical flow-cell: A, bottom holder, B carbon-support electrode, C, Teflon spacer, D, reference electrode reservoir, E, upper holder.

This flow-cell has a relatively small holdup volume of 168μL which allows the analysis of small sample volumes. The detector units can be easily cleaned, and the sensing element, easily replaced. Since the reference electrode is mounted downstream from the ion-selective electrode, interferences caused by the leakage of filling solution from the reference electrode are minimized. From the cell geometry and holdup volume, geometry and holdup volume, an injection sample size of 100µl was selected.

7.2 RESPONSE CHARACTERISTICS OF A PTHVBAS MEMBRANE ELECTRODE IN FLOW INJECTION ANALYSIS.

The flow injection system incorporated a salicylate ion-selective membrane electrode based on poly(trihexylvinylbenzylammonium chloride). The preparation and performances of this membrane electrode were already described in Chapter 6, section 6.1.1. In static systems, the PTHVBAS membrane electrode exhibits a near-Nernstian response of -58.2mV/decade, and has a limit of detection of 1×10^{-5}M (refer to Fig.6.1), while the limit of Nernstian response is 5.5×10^{-5}M. On the basis of the selectivity coefficients presented in Table 7.2, a phosphate buffer was selected as the carrier solution. In order to obtain adequate conductance of the flowing stream, it was necessary to use a phosphate concentration of 0.1M, otherwise the base line signal became very noisy (refer to section 7.1.1). Optimum operating conditions were obtained when the pH of the carrier was adjusted to 8.0

Table 7.2: Selectivity coefficients of a PTHVBAS[a] coated carbon-support electrode.

Interfering ions	$K_{i,j}^{pot}$ [b]
phosphate	<0.0001
acetate	<0.0001
chloride	0.0065
bromide	0.044
benzoate	0.095
nitrate	0.11
iodide	0.93
thiocyanate	10

[a] Poly(trihexylvinylbenzylammonium salicylate)
[b] Determined by the Fixed Interference method, [interferent]=1mM.

Fig.7.7 shows the FIA response of the PTHVBAS membrane electrode for salicylate standards in the concentration range from 1x10^{-5}M to 0.1M. The standards were prepared in 0.1M phosphate buffer at pH 8.0, and were injected in triplicate.

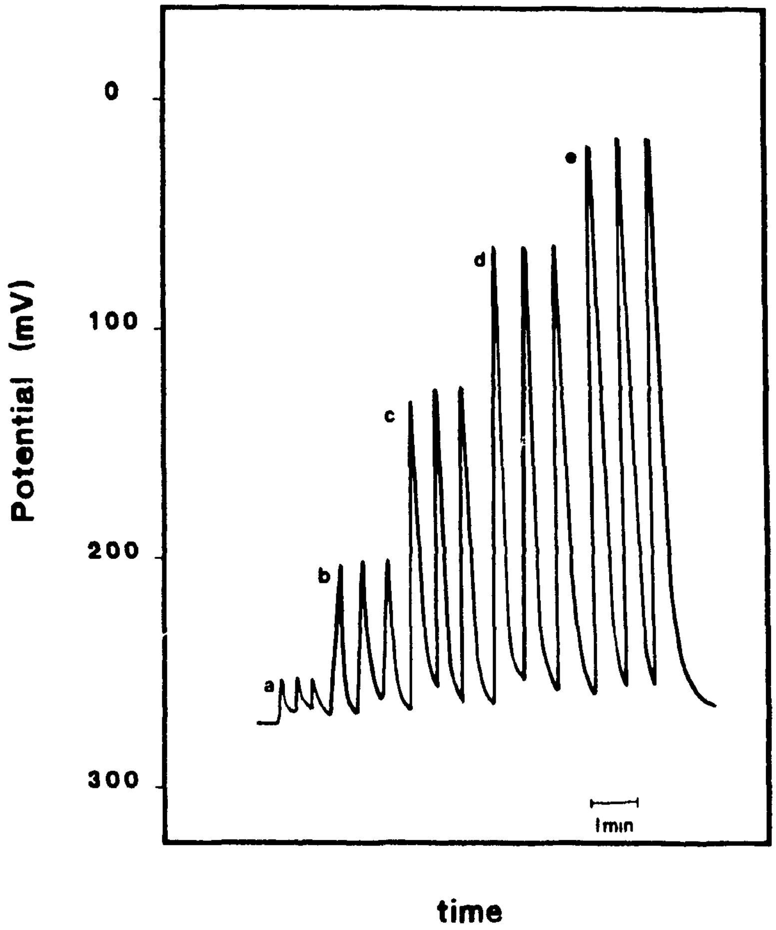


Fig.7.7 Illustrative FIA recordings for a PTHVBAS membrane electrode. Concentration of salicylate: (a) 1x10^{-5}M, (b) 1x10^{-4}M, (c) 1x10^{-3}M, (d) 1x10^{-2}M, (e) 0.1M. 0.1M phosphate buffer pH 8.0, as the carrier stream; sample size, 100μL; flow-rate, 1mL/min.

A rapid near-Nernstian potentiometric response to salicylate was obtained. The calibration curve obtained from the FIA data for the PTHVBAS membrane electrode response to salicylate is showed in Fig.7.8. The near-Nernstian response of the PTHVBAS membrane electrode in flowing streams is similar to the response obtained in stationary systems. Since the electrode is subject to drift, the system should be calibrated frequently. The electrode was stored dry between use, and immersed in a 0.1M salicylate-containing buffer before use.

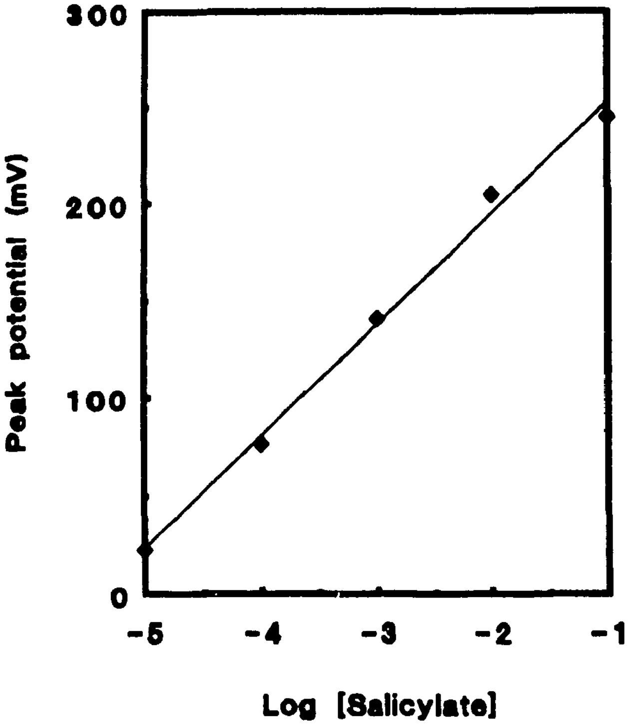


Fig.7.8 Calibration graphs from FIA data for a PTHVBAS coated carbon-support electrode. Slope, 57.3±0.5 mV/decade. The experimental conditions are the same as in Fig.7.7.

The dispersion coefficient of this FIA system was measured by the following procedures: 100μl of 1mM salicylate was injected into the carrier, and the height "h" of the resulting peak was measured. Then, the carrier was replaced with the standard solution which gave a time-independent signal of the height "h_o" corresponding to the undiluted sample. Since the signal height is directly proportional to the sample concentration, the dispersion coefficient was calculated from equation (69). This yielded a dispersion coefficient of 1.38. With a carrier flow rate of 1ml/min, a maximum sampling frequency of 110 samples/hour can be attained. Improvements of the dispersion and sampling frequency of this FIA system could be expected from optimization of the flow-cell geometry, i.e the reduction of the dead volume of the connections.

Potentiometric measurements of salicylate with a poly(trihexylvinylbenzylammonium salicylate) membrane electrode in flowing streams are certainly superior and more convenient than measurements in stationary systems, especially if the analysis of a large number of samples is involved. This study has also demonstrated that an ionic polymer membrane electrode can be conveniently used as a detector for Flow Injection Analysis.

REFERENCES:

[1] T.S. Ma and S.S.M. Hassan, "Organic Analysis using Ion-selective Electrodes", Vol.1, Academic Press, New York, 1982, pp.30-40.

[2] A.K. Covington, "Ion-selective Electrode Methodology", Vol.II, CRC Press, Boca Raton (Florida), 1979, pp.87-92.

[3] M. Valcarcel and M.D. Luque de Castro, "Flow Injection Analysis: Principles and Applications", Ellis Horwood, Chichester (London), 1987, pp.40-128.

[4] J. Ruzicka and E.H. Hansen, *Anal.Chim.Acta*, **1984**, 161, 1.

[5] P. Van den Winkel, J. Mertens, G. De Baenst, and D.L. Massart, *Anal.Lett.*, **1972**, 5, 567.

[6] J. Mertens, P. Van den Winkel, and D.L. Massart, *Anal.Lett.*, **1973**, 6, 81.

[7] P. Van den Winkel, J. Mertens, and D.L. Massart, *Anal.Chem.*, **1974**, 46, 1765.

[8] T.K. Christopoulos and E.P. Diamandis, *Analyst*, **1987**, 112, 1293.

[9] J. Ruzicka and E.H. Hansen, "Flow Injection Analysis", John Wiley & Sons, New York, 1981, p.31.

[10] B.R. Hepler and W.C. Purdy, *Anal.Chim.Acta*, **1980**, 113, 269.

[11] S.A. McClintock and W.C. Purdy, *Anal.Chim.Acta*, **1983**, 148, 127.

CONCLUSION

Ideally, an ion-selective electrode should be simple to operate, highly selective for the species of interest, and offer a rapid and reproducible response. Also, the ideal ion-selective electrode should be robust with long operating lifetime. Most solid-state inorganic salt membrane electrodes fulfil these requirements. However, there are only a few of these devices available for the monitoring of a limited number of ions. At the present time, only very few materials, i.e. the rare-earth fluorides, silver salts, and metal sulfides, are known to show sufficient ionic conductivity to be useful as membrane materials. Unfortunately, our understanding of ionic conduction in inorganic salts or crystals is still limited, making it difficult to predict if a known salt will show useful properties to be used in the composition of ion-selective membranes. The number of untried materials is vast, and the experimental process of evaluation is slow.

The usefulness of zinc orthophosphate and zinc mercuric thiocyanate to make a carbon-support electrode responsive to zinc was investigated. The best results were obtained with zinc orthophosphate, which produced a Nernstian response to zinc in the concentration range from 10^{-5} to 10^{-2}M. However, the electrode response was lowered by the formation of acidic oxides on the surface of the electrode, and interference effects from copper(II), cadmium(II), and lead(II) were observed. An indirect potentiometric method based on the selective monitoring of chlorozincate(II) or cyanozincate(II) anions with an Aliquat 336S coated-wire electrode demonstrated improved selectivity in zinc monitoring. The applicability of this method to zinc monitoring in the electrogalvanizing process is particularly interesting.

Polymeric membrane electrodes based on ion exchangers, crown ethers and various other ionophores extend the applicability of ion-selective electrodes to the monitoring of a large number of important ions such as, Ca^{2+}, K^+, NO_3^-, and quaternary amines. However, there are limitations to the usefulness of polymeric membranes, especially when they are used with solid-state devices. Difficulties arise from poor adhesion of the membrane to solid substrates, and from the leaching of the membrane sensing components, i.e. the ion exchange material and the plasticizer, physically entrapped in the polymeric matrix.

This work has shown that it is possible to make solid-state ion-selective electrodes using an ionic polymer as the ion-sensitive membrane. The main advantage of ionic polymer based electrodes is that the membrane contains no leachable components. Therefore, robust polymeric membranes with long operating lifetime can be obtained. The robustness and rapid response of ionic polymer membrane electrodes make their use particularly interesting in flow injection analysis. Further, this study has shown that the selectivity of the ionic polymer based electrodes can be quite high, when compared to that of conventional polymer membrane electrodes.

Ionic polymer-modified electrodes also hold promise for increasing the selectivity, sensitivity, and reproducibility of voltammetric measurements. A glassy carbon electrode coated with a thin film of poly(trihexylvinylbenzylammonium chloride) was shown to exhibit attractive permselective and ion-exchange properties. In particular, this polymer effectively excludes cations while it binds organic counterionic species such as uric acid. Thus, an electrode modified with an ionic polymer film can be used to separate and preconcentrate an analyte from a contacting sample solution phase prior to electrochemical measurement. Because this technique involves a preconcentration step, it is similar to anodic stripping voltammetry (please refer to Appendix C for a description of this technique). In fact, the two techniques are complementary in that anodic stripping voltammetry is used for analyses of inorganic ions, i.e. metal cations, whereas the latter is best suited for analyses of organic ions.

The use of ionic polymers appears to open many new opportunities for future sensor developments. Notably, ionic polymers exhibit good adhesion to many solid substrates. Significant enhancement of Chemically Sensitive Semiconductor Devices lifetime can be expected to result from improved membrane adhesion. In that connection, the future integration of ionic polymer membranes with semiconductor devices seems particularly attractive. Nevertheless, a better understanding of the microstructure of polymeric ion exchange membranes is required to explain membrane characteristics such as, permselectivity, ionic conductivity, and the charge transport mechanism.

Contributions to original knowledge:

The properties and usefulness of zinc orthophosphate and zinc mercuric thiocyanate to make a carbon-support electrode sensitive to zinc were investigated. The best results were obtained with zinc orthophosphate. However, deterioration of the electrode response due to the formation of acidic oxides at the electrode surface was demonstrated. Several methods of minimizing this problem were proposed.

An indirect potentiometric method based on the selective monitoring of chlorozincate(II) or cyanozincate(II) anions with a coated-wire electrode was studied. The applicability of this method to zinc monitoring in the electrogalvanizing process was established.

We have studied the immobilization of several ionic groups such as, quaternary ammonium, phosphonium, and alkyl phosphates, with poly(vinylbenzyl chloride). These functionalized polymers were used as ion-sensitive membranes for solid-state electrodes. The response characteristics and the selectivity of ionic polymer membranes and conventional polymeric membranes were compared.

The permselectivity and ion-exchange properties of poly(trihexylvinylbenzylammonium chloride) coated on glassy carbon electrodes were described.

The apparent diffusion coefficients, D_{app}, of uric acid within polymer-modified electrodes, i.e poly(trihexylvinylbenzylammonium chloride) and poly(trioctylvinylbenzylammonium chloride) film-coated electrodes, were measured by chronoamperometry.

A poly(trioctylvinylbenzylphosphonium nitrate) membrane electrode was applied to the determination of nitrogen-nitrate in samples of fertilizers.

An ionic polymer membrane electrode-based flow injection system was designed and applied to the monitoring of salicylate.

APPENDIX A:

Abbreviations, symbols and constants.

Abbreviations:

AC: Alternating Current
CSSD: Chemically Sensitive Semiconductor Device
CV: Cyclic Voltammetry
CWE: Coated Wire Electrode
DC: Direct Current
DPASV: Differential Pulse Anodic Stripping Voltammetry
DPV: Differential Pulse Voltammetry
DSC: Differential Scanning Calorimetry
EDTA: EthyleneDiamineTetraacetic Acid
FAA: Flame Atomic Absorption
FET: Field Effect Transistor
FIA: Flow Injection Analysis
FTIR: Fourier Transform Infra-Red
IR: Infra-Red
ISE: Ion-Selective Electrode
IUPAC: International Union of Pure and Applied Chemistry
PFSI: PerFluoroSulfonate Ionomer
PTEVBAC: Poly(TriEthylVinylBenzylAmmonium Chloride)
PTHVBAC: Poly(TriHexylVinylBenzylAmmonium Chloride)
PTOVBAC: Poly(TriOctylVinylBenzylAmmonium Chloride)
PTOVBPC: Poly(TriOctylVinylBenzylPhosphonium Chloride)
PTPVBAC: Poly(TriPentylVinylBenzylAmmonium Chloride)
PTPVBPC: Poly(TriPhenylVinylBenzylPhosphonium Chloride)
PVBC: PolyVinylBenzyl Chloride
PVC: PolyVinyl Chloride
QAS: Quaternary Ammonium Salt
SBS: Styrene-Butadiene-Styrene
SCE: Saturated Calomel Electrode

Symbols and constants:

a_i: Activity of an ion
A: Area of an electrode (cm^2)
α: Ion-size parameter
a: number of 2-connected atoms in a polymer chain
β: Cumulative formation constant
b: number of 3-connected atoms in a polymer chain
C: Capacitance
C_i: Concentration of an ion
c: number of covalent network in repeat unit of an ionic polymer
c: number of 4-connected atoms in a polymer chain

c:	number of 4-connected atoms in a polymer chain
CN:	average connetion number of network atoms
C_p:	Concentration of Electroactive species incorporated in a polymer film
C_s:	Concentration of species in solution
d:	Flow rate (ml/sec)
D:	Detection limit
D:	Dielectric potential
D_{app}:	Apparent diffusion coefficient
E:	Electrode potential
E^o:	Standard electrode potential
E_a:	Activation energy
E_{in}:	Input potential difference between the indicator and reference electrodes
E_s:	Streaming potential
F:	Faraday's constant (96 487 Cmol^{-1})
ΔG:	Free-energy change
γ:	Activity coefficient
h:	Peak height
η:	Viscosity
I:	Ionic strength
I_d:	Drain current
i_t:	Current at time t (A)
φ:	Inner potential of a phase
$\Delta\varphi_M$:	Membrane potential
$\Delta\varphi_L$:	Liquid-junction potential
$\Delta\varphi_D$:	Donnan potential
k_i:	Partition coefficient of I^+
K_i:	Equilibrium constant for the extraction of I^+
K_{ij}:	Ion exchange equilibrium constant
$K_{i,j}^{pot}$:	Selectivity coefficient of an Ion-selective Electrode
K_{IS}:	Association constant for the formation of a neutral pair IS
K_{sp}:	Solubility product
$K_{X,Y}$:	Ion selectivity coefficient of an ionic polymer membrane
l:	Thickness of a polymer film
L:	Length of a FET channel
L^-:	Ligand
l:	Length of tubing (cm)
λ:	Equivalent ionic conductivity
M:	Metal
M_i:	Average molecular weight of the chain between ion groups
M_{ru}:	Molecular weight of covalent repeat unit in ionic polymer chain
μ:	Mobility of the charge carriers within a FET channel
$\tilde{\mu}$:	Electrochemical potential of a phase
μ^o:	Standard chemical potential
n:	number of electrons (eq/mol)
N_{cr}:	Relative number of covalent network bonds per volume unit (cm^3) in ionic polymers
N_{ir}:	Relative number of ionic bonds per volume unit (cm^3) in ionic polymers
N_p:	Amount of electroactive species incorporated within a polymer film
N_r:	Relative number of total network bonds in ionic polymers
P:	Pressure
Q:	Charge (in coulombs)
R:	Universal gas constant (8.3144 JK^{-1}mol^{-1})
R_e:	Resistance of an Ion-selective Electrode
R_{in}:	Input resistance of the pH/voltmeter

r:	Radius (cm)
ρ:	Density
σ:	Conductivity of a media
t:	Time (in seconds)
T:	Absolute temperature (in Kelvin)
t_g:	Glass transition temperature
T:	Residence time in a FIA system
Δt:	Peak width at the baseline
U:	Particle mobility
V_D:	Drain voltage
V_g:	Gate voltage
V_s:	Volume of a standard solution
V_T:	Threshold voltage
V_x:	Volume of an unknown solution
Δv^*:	Activation volume
W:	Width of a FET channel
ξ:	Electrokinetic potential (volt)
z_i:	Charge of an ion

APPENDIX B:

Cyclic Voltammetry

Cyclic voltammetry is a versatile electroanalytical technique used for the mechanistic study of electroactive systems [1]. The electrode potential is rapidly scanned in search of redox couples. A repetitive triangular potential excitation signal is applied, Fig.B1 a. This causes the potential of the working electrode to sweep back and forth between two designated values: The positive potential scan from the initial potential, a, to the switching potential, b. At this point, the direction of the scan is reversed, and the negative potential scan from b to c. Although the potential scan can be interrupted at the end of the first cycle, it can be continued for any number of cycles. Of course, the potential values and scan profile are determined by the redox couple of interest. The current at the working electrode is measured during the potential scan to obtain a cyclic voltammogram.

For example, a typical cyclic voltammogram obtained with a carbon paste electrode immersed in a 1.0mM Fe^{2+} solution with 1.0M sulfuric acid supporting electrolyte,is shown in Fig.B1 b. The potential scan applied is identical with the profile depicted in Fig.B1 a. During the positive scan, the applied potential becomes sufficiently positive at +0.4V to cause the oxidation of Fe^{2+}. The anodic current caused by this oxidation process increases rapidly until the surface concentration of Fe^{2+} approaches zero. The current then decays as the concentration of Fe^{2+} at the electrode surface decreases. This depletion of Fe^{2+} and accumulation of Fe^{3+} during the positive scan is described by the concentration distance profiles a to d in Fig.B1 b. When profile d is reached, the anodic current depends on the diffusion of Fe^{2+} from the bulk of the solution to the electrode surface. After the direction of potential scan is reversed, oxidation of Fe^{2+} continues until the applied potential becomes sufficiently negative to cause the reduction of Fe^{3+} accumulated at the electrode surface. The cathodic current increases as the potential moves increasingly negative until the reduction of Fe^{3+} causes a depletion of the concentration of Fe^{3+} at the electrode surface, and the current decays correspondingly.

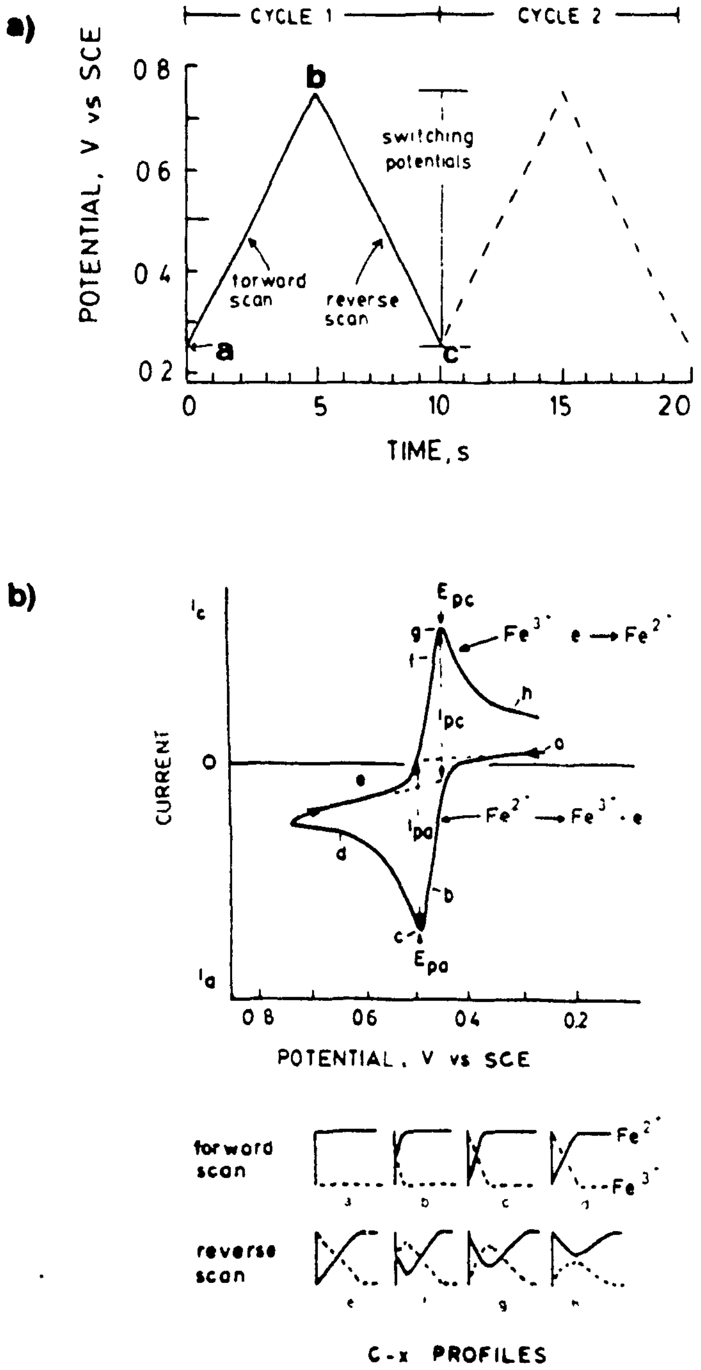


Fig.B1 a) Typical potential-time excitation signal for cyclic voltammetry.
b) Cyclic voltammogram of 1.0mM Fe^{2+} in 1M H_2SO_4, and concentration-distance profiles during potential scan [1].

A redox couple in which both species rapidly exchange electrons with the working electrode is termed an electrochemically reversible couple. The reversibility of a redox couple can be assessed by the measurement of the potential difference between the two peak potentials, E_{pa} and E_{pc} [1]. For a reversible system, ΔE_p should be given by:

$$\Delta E_p = E_{pa} - E_{pc} = 0.059V/n \qquad (70)$$

where n is the number of electrons transferred, E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively. This 0.059/n volt separation of peak potentials is independent of the scan rate. For such a system, the peak current is defined by the Randles-Sevcik equation [2]:

$$i_p = (2.69x10^5)\ n^{3/2}\ A\ D^{1/2}\ C\ v^{1/2} \qquad (71)$$

i_p is the peak current (A), A is the electrode area (cm^2), D is the diffusion coefficient of the species being oxidized or reduced (cm^2/s), C is the concentration of the electroactive species in solution (mol/cm^3), and v is the scan rate (V/s).

Electrochemical irreversibility is characterized by a separation of peak potentials that is greater than 0.059/n volt, and it is caused by slow electron exchange of the redox species with the working electrode. In this case, the separation of peak potentials is no longer independent of the scan rate [1]. For an irreversible system, the equation for i_p is

$$i_p= (2.99x10^5)\ n\ (\alpha n_a)^{1/2}\ A\ D^{1/2}\ C\ v^{1/2} \qquad (72)$$

where α is the transfer coefficient and n_a is the number of electrons in the rate-determining step of the electrode process. For reversible and irreversible systems, the voltammetric peak current is then proportional to $v^{1/2}$, and a diffusion-controlled behavior prevails.

REFERENCES:

[1] P.T. Kissinger and W.R. Heineman, Eds., "Laboratory Techniques in Electroanalytical Chemistry", Marcel Dekker, New York, 1984, pp.86-93.

[2] A.J. Bard and L.R. Faulkner, "Electrochemical Methods: Fundamental and Applications", John Wiley & Sons, New York, 1978, p.218.

APPENDIX C:

Differential Pulse Voltammetry

The use of cyclic voltammetry is normally limited to the mechanistic study of redox systems. It is rarely used for quantitative purposes because of the difficulty of obtaining accurate peak currents [1]. This difficulty is related to the establishment of a correct baseline which is essential for the accurate measurement of peak currents. Differential Pulse Voltammetry (DPV) overcomes some of these problems. The application of a pulse waveform rather than a linear waveform notably helps reduce the largest portion of the dc background current, Fig.C1.

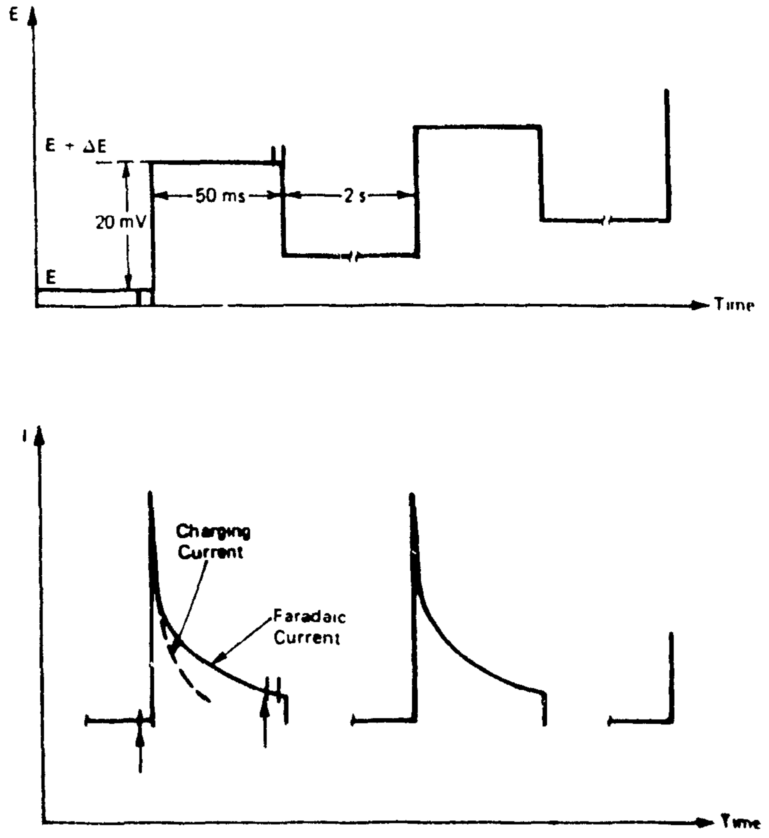


Fig.C1 Typical differential pulse excitation waveform, and resulting charging and faradaic current-time behavior [2].

A staircase potential waveform is applied in DPV, Fig.C1. Relatively large amplitude pulses (25-50mV) are periodically superimposed on a linear potential ramp, normally about 5mV/sec. Just prior to the application of the pulse, a current sample is taken, and a second sample is monitored at the end of the pulse [2], see Fig.C1. Since the charging current decays faster than faradaic current, measurement of the current at the end of the pulse lifetime reduces contributions of nonfaradaic current. Using small potential steps and scan rates, excellent sensitivity and resolution can be achieved with Differential Pulse Voltammetry. This method is well-suited for detecting small amounts of analytes (<0.1μM) [3].

Differential Pulse Anodic Stripping Voltammetry:

Electrochemical stripping techniques involve the deposition or "preconcentration" of the analyte at the electrode surface by controlled-potential electrolysis. This preconcentration step is followed by a "stripping" step in which the deposited analyte is removed from the electrode surface by a potential scan, and the accompanying electrochemical signal is used to determine the concentration of each analyte species in the sample. For example, in Differential Pulse Anodic Stripping Voltammetry (DPASV) of heavy metals, preconcentration is caused by reduction of the metal ions to the elemental state at a mercury electrode, and the stripping step is accomplished by a positive potential scan that gives an anodic current when the preconcentrated metals are oxidized [4]. The combination of electrochemical preconcentration and Differential Pulse Voltammetry provides a very sensitive technique for the detection of metals such as, copper, lead, and cadmium.

REFERENCES:

[1] P.T. Kissinger and W.R. Heineman, Eds., "Laboratory Techniques in Electroanalytical Chemistry", Marcel Dekk New York, 1984, pp.86-93.

[2] T.R. Copeland and R.K. Skorgerboe, *Anal.Chem.*, **1974**, 46, 1257A.

[3] P.T. Kissinger and W.R. Heineman, Eds., "Laboratory Techniques in Electroanalytical Chemistry", Marcel Dekker, New York, 1984, pp.152-154.

[4] H. Siegerman and G. O'Dom, *Am.Lab.*, **June 1972**, 59.

APPENDIX D:

Chronoamperometry

The waveform signal applied in chronoamperometry is a square-wave voltage [1], as shown in Fig.D1. In chronoamperometry, the potential of the working electrode step from a value at which no faradaic current occurs, E_1, to a potential, E_s, at which the surface concentration of the electroactive species is depleted. The potential is then stepped to a final potential E_f after some interval of time τ has passed.

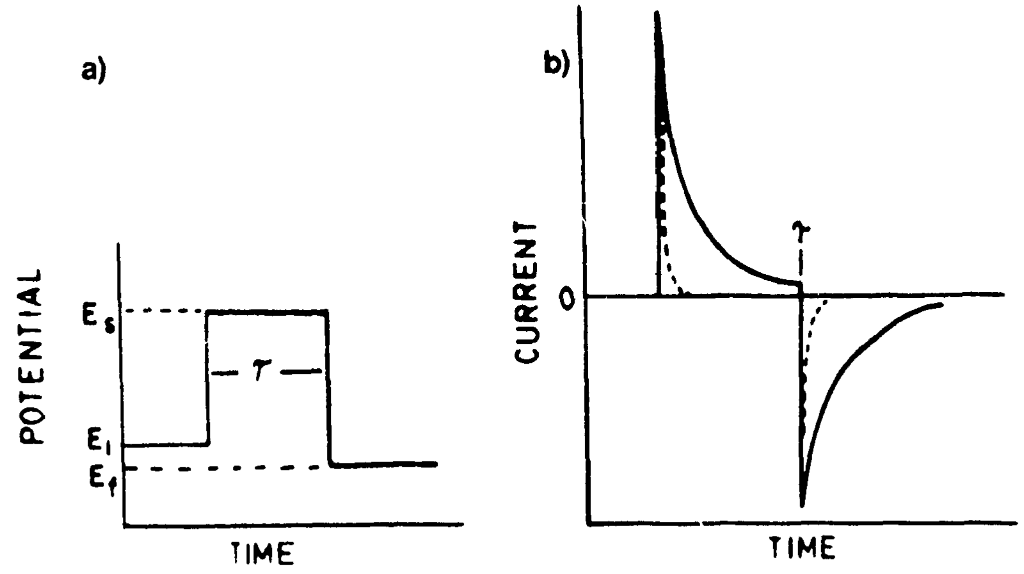


Fig.D1 Potential excitation waveform used for chronoamperometry (a), and resulting chronoamperogram (b).

A typical double potential-step chronoamperogram is shown in Fig.D1 b. The dashed line shows the background response to the excitation signal for a solution containing only the supporting electrolyte. This current decays rapidly when the electrode has been charged to the applied potential. The potential step initiates an instantaneous current as a result of the oxydation or reduction of the electroactive species [1]. The current then drops as the electrolysis proceeds. The current decays smoothly and approaches zero with increasing time as described by the Cottrell equation [1] for a planar electrode:

$$i_t = nFAD^{1/2}\, C / (\pi^{1/2} t^{1/2}) \qquad (73)$$

where i_t (A) is the current at time t, n is the number of electrons (eq/mol), F is the Faraday's constant (96 485 C/eq), A is the area of the electrode (cm^2), C is the concentration of electroactive species in solution (mol/cm^3), D is the diffusion coefficient of electroactive species (cm^2/s), and t is time (sec). Chronoamperometry has proven particularly useful for the measurement of diffusion coefficients of electroactive species [1,2].

REFERENCES:

[1] P.T. Kissinger and W.R. Heineman, Eds., "Laboratory Techniques in Electroanalytical Chemistry", Marcel Dekker, New York, 1984, pp.56-61.

[2] H.S. White, J. Leddy, and A.J. Bard, *J.Am.Chem.Soc.*, **1982**, 104, 4811.