DEVELOPMENT OF MACROCYCLICS BASED ELECTROCHEMICAL SENSORS

Thesis

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By

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Dedicated to the memory of my parents,
K. C. Mathew and Thankamma Mathew

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Certificate

*Certified that the present work entitled "**Development of Macrocyclics based Electrochemical Sensors**", submitted by Mrs. Sobhana Mathew, in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry to Cochin University of Science and Technology, is an authentic and bonafide record of the original research work carried out by her under my supervision at the Department of Applied Chemistry. Further, the results embodied in this thesis, in full or in part, have not been submitted previously for the award of any other degree.*

K. Girish Kumar
(Supervising guide)

Declaration

I hereby declare that the work presented in this thesis entitled, ''Development of Macrocyclics based Electrochemical Sensors'', is based on the original research work carried out by me under the guidance of Dr. K. Girish Kumar, Professor of Analytical Chemistry, Department of Applied Chemistry, Cochin University of Science and Technology and has not been included in any other thesis submitted previously for the award of any degree.

Sobhana Mathew

Kochi

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Preface

Electroanalytical techniques represent a class of powerful and versatile analytical method which is based on the electrical properties of a solution of the analyte when it is made part of an electrochemical cell. They offer high sensitivity, accuracy, precision and a large linear dynamic range. The cost of instrumentation is relatively low compared to other instrumental methods of analysis. Many solid state electrochemical sensors have been commercialised nowadays.

Potentiometry is a very simple electroanalytical technique with extraordinary analytical capabilities. Since valinomycin was introduced as an ionophore for K^+, Ion Selective Electrodes have become one of the best studied and understood analytical devices. It can be used for the determination of substances ranging from simple inorganic ions to complex organic molecules. It is a very attractive option owing to the wide range of applications and ease of the use of the instruments employed. They also possess the advantages of short response time, high selectivity and very low detection limits. Moreover, analysis by these electrodes is non-destructive and adaptable to small sample volumes. It has become a standard technique for medical researchers, biologists, geologists and environmental specialists.

This thesis presents the synthesis and characterisation of five ionophores. Based on these ionophores, nine potentiometric sensors are fabricated for the determination of ions such as Pb^{2+}, Mn^{2+}, Ni^{2+}, Cu^{2+} and Sal^- ion (Salicylate ion). The electrochemical characterisation and analytical application studies of the developed sensors are also described. The thesis is divided into eight chapters. A brief idea of the chapters is given below.

Chapter1 presents a general introduction on the various electroanalytical techniques and their application. This chapter gives a brief idea of the various types of electrochemical sensors and discusses in detail the different types of potentiometric sensors. A brief review of the important macrocyclics based potentiometric sensors developed for the studied ions are also given in this chapter.

Chapter 2 describes in detail the materials and methods used in the investigation. It describes the synthesis and characterization of all ionophores. The general method for the preparation of the different types of sensors, preparation of solutions of metal salts, buffer solutions, effluent samples and real samples taken for analysis are also discussed. Details about the instruments used in the investigations are also discussed in this chapter.

Chapter 3 explains the response characteristics of two types of sensors based on 1,3,7,9-tetraaza-2,8-dithia-4,10-dimethyl-6,12-diphenyl cyclododeca-4,6,10,12-tetraene for the determination of Pb^{2+} ions. The developed sensors were successfully applied as an indicator electrode in the potentiometric titration of Pb^{2+} against EDTA and in the determination of Pb^{2+} in 'Eveready battery waste'.

Chapter 4 focuses on the sensors fabricated for Mn^{2+} based on 2,8,14,20-tetrakis(naphthyl)calix[4]resorcinarene. The response characteristics of two types of sensors were investigated in detail. The analytical application of the developed sensors as an indicator electrode in the potentiometric titration of Mn^{2+} against EDTA has also been discussed in this chapter.

Chapter 5 deals with the fabrication of PVC type and carbon paste type sensors for Ni^{2+} ions based on 2,8,14,20-tetrakis(3,4-dimethoxyphenyl)calix[4]resorcinarene. The selectivity, shelf life, response time, effect of pH and effect of non- aqueous media were investigated and its analytical application as an indicator electrode in EDTA titration and also for the direct determination of the Ni^{2+}content in chocolates, edible oil and effluent sample is discussed.

Chapter 6 details on the response characteristics of the sensors developed for Cu^{2+}. The fabrication of PVC membrane and carbon paste sensors based on the ionophore 5,10,15,20-tetrakis(3-methoxy-4-hydroxyphenyl)porphyrin (TMHPP) and application of these sensors in the potentiometric titration of copper with EDTA are included in this chapter. The application of the developed sensors in the determination of Cu^{2+} in waste water samples collected from electroplating units is also discussed.

Chapter 7 deals with the fabrication of PVC membrane sensor based on 5,10,15,20-tetrakis(3-methoxy-4-hydroxyphenyl)porphyrinato Manganese(III) chloride for salicylate ions. The response characteristics of the sensor were investigated in detail. The application of the developed sensor for the determination of salicylate content of hydrolyzed pharmaceutical preparations is also discussed.

***Chapter* 8** presents the summary and important conclusions of the work done.

References are given under separate head as the last part of the thesis.

Contents

Chapter 1

INTRODUCTION

Analytical chemistry is a scientific discipline that develops and applies methods, instruments and strategies to obtain information on the composition and nature of matter in space and time. Both qualitative information and quantitative information are required in an analysis. Qualitative analysis establishes the chemical identity of the species in the sample. Quantitative analysis determines the relative amounts of these species. Its applications extend to all parts of an industrialised society. An increasing concern with the well-being of individuals and life in general has led to initiatives for improvements in medicine and the world environment and in these areas analytical chemistry has particularly vital roles to play[1].

Analytical methods can be classified into classical and instrumental, the former comprising 'wet chemical methods' such as gravimetry and titrimetry. However the general application of these classical methods is decreasing with the passage of time and with the advent of instrumental methods to supplant them. Highly efficient chromatographic and electrophoretic techniques began to replace distillation, extraction and precipitation for the separation of components of complex mixtures prior to their qualitative or quantitative determination. These newer methods for separating and determining chemical species are known collectively as instrumental methods of analysis. Classical analysis and instrumental analysis are similar in many respects, such as in the need for proper sampling, sample preparation, assessment of accuracy and precision[2]. Instrumental methods of chemical analysis have become the principal means of obtaining information in diverse areas of science and technology. The speed, high sensitivity, low limits of detection, simultaneous detection capabilities and automated operations, when compared to classical methods created this predominance.

The information gathered from analytical chemical processes comes under the three classes – chemical, biochemical and biological. There is a growing trend to expand the boundaries of Analytical Chemistry into the microbiological and allergological fields[3]. Analytical Chemistry has wide applications in the field of pharmaceutical, food and environmental analysis[4-16].

Instrumental methods were developed in the early twentieth century, with the development of computer and electronic industries. The first instrumental analysis was flame emissive spectrometry developed by Robert Bunsen and Gustav Kirchhoff who discovered Rubidium (Rb) and Cesium (Cs) in 1860[17]. But Major developments in instrumental analysis took place only after 1900. Instrumental methods are classified as

1. Spectroscopic methods
2. Scattering Methods
3. Thermal Methods
4. Electro Analytical Methods

1.1. Electroanalytical chemistry

Electroanalytical chemistry is that branch of chemical analysis that employs electrochemical methods to obtain information related to the amounts, properties and environment of chemical species. Issac Maurits Kolthoff defined electroanalytical chemistry as the application of electrochemistry to analytical chemistry. It is preferable to consider electroanalytical chemistry as that area of analytical chemistry in which the electrode is used as a probe, to measure something that directly or indirectly involves the electrode[18].

1.2. Electroanalytical techniques

Electroanalytical techniques is an analytical tool in which electrochemistry provides analytical methodology[19]. Electroanalytical measurements can only be carried out in situations in which the medium between the two electrodes making up the electrical circuits be sufficiently conducting[20]. Electroanalytical measurements offer a number of important potential benefits [21].

1. Selectivity and specificity
2. Selectivity resulting from choice of material
3. High sensitivity and low detection limit
4. Possibility of giving results in real time
5. Application as miniaturized sensors in situations where other sensors may not be usable

Electroanalytical methods are divided into interfacial methods and bulk methods. Interfacial methods are based on phenomena that occur at the interface between electrode surfaces and the thin layer of solution just adjacent to these surfaces. Bulk methods, in contrast, are based on phenomena that occur in the bulk of the solution; every effort is made to avoid interfacial effects. Examples for bulk methods are conductometry and conductometric titrations. Conductometric sensors quantitate the changes of electrical properties between two electrodes.

Interfacial methods can be divided into two major categories, static methods and dynamic methods, depending on whether there is a current in the electrochemical cells[22].

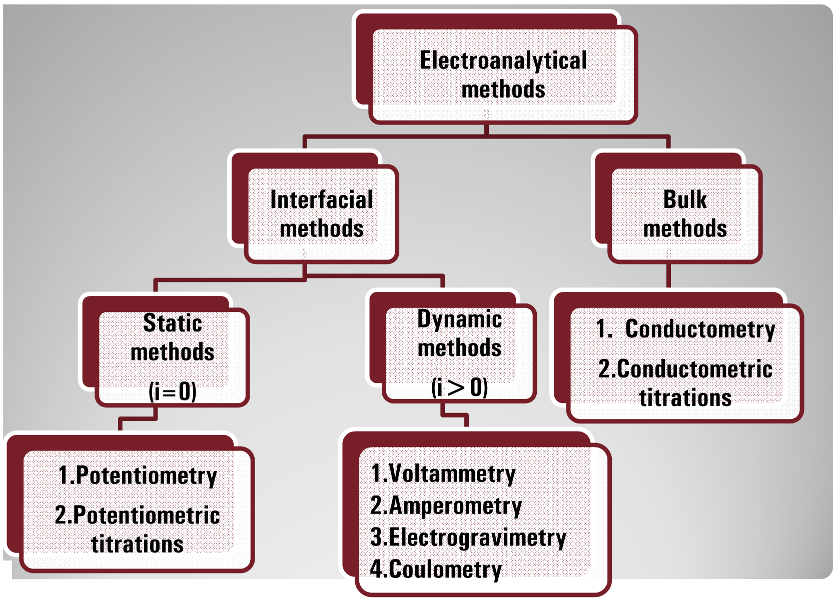
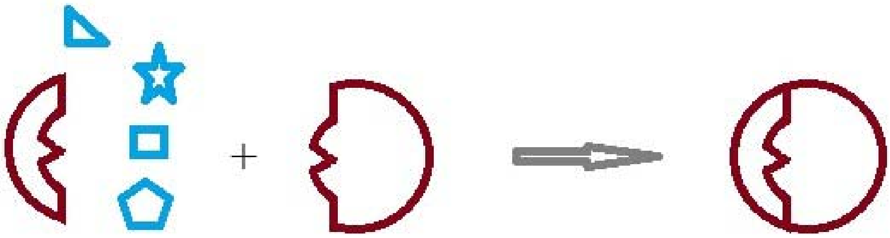


Figure 1.1 shows classification of electroanalytical methods

In Potentiometric methods the equilibrium potential difference between an indicator electrode and a reference electrode is measured. Ideally no current flows through the system at equilibrium. In general, the potential difference shows a linear relationship with the logarithm of the activity of the analyte, as in the Nernst equation. Voltammetric sensors measure the current from the charge transport of an electrochemical reaction on a working electrode when a varying potential (or a constant potential as in Amperometric detection) is applied between the working electrode and the solution. Voltammetric sensors use an auxiliary (counter) electrode to control the solution potential and as an electron source or sink for the counter reaction to the one at the working electrode. Voltammetric sensors use a nonpolarizable electrode to monitor the solution potential[23]. Coulometric and Electrogravimetric analysis are based on the electrolytic oxidation or reduction of an analyte for a sufficient period to assure its quantitative conversion to a new oxidation state. In electrogravimetric methods the product of the electrolysis is weighed as a deposit on one of the electrodes. On the other hand in coulometric analysis, the quantity of electricity needed to complete the electrolysis is a measure of the amount of the analyte present[23].

1.3. Electrochemical sensors

An overview of development of analytical chemistry demonstrates that electrochemical sensors represent the most rapidly growing class of chemical sensors. Sensors can be generally categorised into two general groups. There are physical sensors which are sensitive to physical responses such as temperature, pressure, magnetic field etc. Then there are chemical sensors which rely on a particular chemical reaction for their response[24]. Chemical sensors can be defined as a small device that as a result of a chemical interaction or process between the analyte and the sensor device, transforms chemical or biochemical information of a qualitative or quantitative type into an analytically useful signal[25]. A schematic representation of the working of a chemical sensor is shown below.



There are two parts to a chemical sensor. Firstly, there is the region where the selective chemistry takes place and then there is the transducer. The chemical reaction produces a signal such as a colour change, the emission of fluorescent light, a change in the electrical potential at a surface, a flow of electrons etc. The transducer responds to this signal and translates the magnitude of the signal into a measure of the amount of the analyte.

Depending upon the transducer type, chemical sensors are categorized into the following types

1. Electrochemical. These include potentiometric sensors and voltammetric/amperometric sensors.
2. Optical sensors. In these sensors there is a spectroscopic measurement associated with the chemical reaction. Optical sensors are often referred to as optodes. Absorbance, reflectance and luminescence measurements are used in the different types of optical sensors.
3. Mass sensitive sensor. They rely on a change in mass on the surface of an oscillating crystal which shifts the frequency of oscillation.
4. Heat sensitive sensor. These are often called calorimetric sensors in which the heat of a chemical reaction involving the analyte is monitored with a transducer.

Compared to optical, mass and thermal sensors electrochemical sensors are especially attractive because of their remarkable detectability, experimental simplicity and low cost. They have a leading position among the presently available sensors that have reached the commercial stage and which have found a vast range of important applications in the fields of clinical, industrial, environmental and agricultural analysis[26]. Many solid state electrochemical sensors have been commercialised, such as glucose monitors for diabetes and ion sensors for blood electrolytes.

1.4. Potentiometric Sensors

Potentiometric sensors are the simplest type of electrochemical sensors with extraordinary analytical capabilities [27]. It is a very attractive option for numerous analysis owing to the low cost and ease of use of the instruments employed. Potentiometry also has other interesting properties, such as short response times, high selectivity, and very low detection limits. Moreover, the instrumental response does not depend on the area of the electrode. Therefore, potentiometric devices could be readily miniaturized without, in theory, losing their determination capabilities[28].

The common glass electrodes[29-33] for pH measurements were the first developed potentiometric sensors. The membrane in a glass electrode is a sodium silicate glass made by fusing a mixture of Al_2O_3, Na_2O and SiO_2. Increasing the amount of Al_2O_3 in the glass leads to an increasing response to other monovalent cations such as Na^+, K^+ and Li^+. The selectivity of glass electrodes to alkali metal ions was studied by Eisenman et al. In all cases however the glass membrane also responds to pH[34]. Later it was discovered that a slice of a single crystal of LaF_3 attached to the end of an electrode barrel could be used to sense the fluoride ion in aqueous solution[35]. Different independent achievements in the mid-1960s marked the starting point of modern potentiometry[36]. During the last decade, the capabilities of potentiometric analysis have changed fundamentally in that the lower limit of detection (LOD) of ion selective electrodes has improved by a factor of up to one million. Nowadays, Ion selective electrodes (ISE) can be used for trace level measurements in environmental samples[37].

In 1967, Ross described the first membrane electrode based on a liquid ion exchanger[38] and compact ion exchange membranes were obtained by Frant and Ross[39]. Bloch and co-workers introduced the first ionophore-based polymeric membrane using PVC[40]. The major breakthrough occurred in 1970 when a number of PVC plasticized membranes have been developed in the laboratory of Prof. J. D. R. Thomas[41]. This matrix is still widely used today. Finally host-guest chemistry played an important role in novel ion selective ionophores[42,43].

The most important practical aspect and commercial success of potentiometric sensors is that it has become the standard technique in the clinical analysis of ions, including Na^+, Ca^{2+}, K^+ and Cl^- ions. Today more than 10 companies sell blood gas analysers with potentiometric detectors for relevant ions using of the order of 100µl blood serum or plasma[44]. Potentiometric sensors are also now widely used for the trace level detection of drugs[45-52]. The different types of potentiometric devices are coated wire electrodes (CWEs), carbon paste electrodes (CPEs), field effect transistors (FETs) and ion selective electrodes (ISEs).

1.4.1. Coated wire electrodes

Coated wire electrodes were designed in 1972 in an effort to miniaturize the ion selective electrodes. Coated wire electrodes are a type of ISE in which an electro active species is incorporated in a thin polymeric support film coated directly on a metallic conductor. The response of the coated wire electrode is similar to that of classical ISEs, with regard to detectability and range of concentration. Its main advantage is that it is dispensed with the internal filling solution. The substrate in the wire type electrode is usually platinum wire, but silver, copper and graphite rods have also been used. Cattrall et al developed a coated wire electrode based on valinomycin for potassium ions and applied it to the analysis of potassium ions in blood and in sea water[53]. Pungor and his co-workers developed an iodide ion selective electrode by incorporating finely dispersed silver iodide into a silicone rubber monomer and then carrying out polymerisation[54]. A tungsten oxide coated wire electrode as a pH sensor in a flow injection potentiometry was reported by Dimitrakopoulos et al which was employed to determine the pH of various alcoholic beverages and environmental water samples[55]. A number of coated wire electrodes have been developed for the trace level analysis of anions and cations[56-59].

1.4.2. Carbon paste electrodes

Carbon Paste Electrodes (CPE) belong to a group of heterogeneous carbon electrodes[60,61]. In the year 1958 Adams, from the University of Kansas in Lawrence, published a short page report[62] in which he had introduced a new type of electrode, the carbon paste electrode. His research group were the first to publish an extensive study on carbon paste electrodes comprising numerous test measurements[63,64]. The CPE is closely connected with Heyrovsky polarography and classical dropping mercury electrode (DME). Adams has later revealed that his original idea was to develop a dropping carbon electrode (DCE). The experiments with DCE performed by Adams's student Kuwana[65] led to the invention of the new electrode material. CPE is represented by carbon paste which is a mixture of graphite powder and a binder pasting liquid, packed into a suitably designed electrode body[66]. They have been successfully applied as potentiometric sensors for the potentiometric determination of various species[67,68]. These sensors possess the advantages of ease of preparation, ease of regeneration and very stable response in addition to very low ohmic resistance which is probably due to the formation of a very thin film of the pasting liquid coated on to small particles of carbon powder[69-72]. They have found direct applications in potentiometric, amperometric and voltammetric experiments[73-75].

1.4.3. Field effect transistors (FETs)

The FET is a solid state device that exhibits high input impedance and low output impedance and therefore is capable of monitoring charge build up on the ion sensing membrane. Ion selective field effect transistors (ISFET) work as an extension of coated wire electrode. ISFET incorporate the ion sensing membrane directly on the gate area of the field effect transistor. The construction is based on the technology used to fabricate microelectronic chip[76-77].

1.4.4. Ion Selective Electrodes (ISEs)

Membrane indicator electrodes are called as ion selective electrodes. They are commonly referred to as potentiometric chemical sensors since some selective chemistry takes place at the surface of the electrode producing an interfacial potential. Species recognition is achieved with a potentiometric chemical sensor through a chemical equilibrium reaction at the sensor surface. Thus the surface must contain a component which will react chemically and reversibly with the analyte.

1.5. Classification

Based on the physical state of the substances forming the electrode membrane[78,79] potentiometric sensors are classified into

1. **Ion selective electrodes with solid membranes**

The membrane can be either homogeneous (a single crystal, a crystalline substance or a glass which is considered to be a solid with regard to the immobility of the anionic groups) or heterogeneous, where a crystalline substance is built into a matrix made from a suitable polymer.

2. **Ion selective electrodes with liquid membranes**

In these types of membrane electrodes the sensor membrane is represented by a water immiscible liquid in which the electroactive species is dissolved.

Another classification based on the categories of membranes used in potentiometric chemical sensors are

1. ***Glass membranes*.**

These are selective for ions such as H^+, Na^+ and NH_4^+.

2. ***Sparingly soluble inorganic salt membranes.***

This type consists of a slice of a single crystal of an inorganic salt such as LaF_3 or a pressed powdered disc of an inorganic salt or mixture of salts such as $Ag_2S/AgCl$. Such membranes are selective for ions such as F^-, S^{2-} and Cl^-.

3. ***Polymer immobilised ionophore membranes.***

In these types an ion selective complexing agent or ion-exchanger is immobilised in a plastic matrix such as poly(vinyl chloride).

4. *Gel-immobilised and chemically bonded enzyme membranes.*

These membranes use the highly specific reactions catalysed by enzymes. The enzyme is incorporated into a matrix or bonded on to a solid substrate surface.

1.6. Development of potential

The potential of ion selective membrane electrode is not generated by the electrode reaction of exchanging electron but arises from the diffusion of mobile ionophore-ion complexes in the sensing membrane and the selective ion exchange between the ions in the complexes and the sample solution, and between the ions in complexes and the internal reference solution. The latter interaction will produce two interface potentials on both sides (the inner and outer sides) of the sensing membrane and the former one will generate the diffusion potential across the membrane. The membrane potential is the algebraic sum of the three potentials[80]. The Nernst equation relates the membrane potential to the activities of ions in sample phase (s) and in the electrode phase (β)

$$E = E^0 + RT/z_iF \ln a_i^s/a_i^\beta$$

E^0 = the standard potential of the sensor

a_i = the activity of the ions

z_i = the charge of the ion

1.7. Aspects of potentiometric sensors

1.7.1. Ionophore

The critical step in the development of a chemical sensor is the rational choice and preparation of the electroactive material. Most of the important properties of a sensor, such as sensitivity and selectivity, strongly depend on the characteristics of this sensing material. This electroactive species enable the sensor to respond selectively to a particular analyte, thus avoiding interferences from other substances. Schiff bases, ion association complexes, macrocyclic compounds, porphyrins, calixarenes, calixresorcinarenes, crown ethers etc. have been studied for their use as ionophores. The application of supramolecular compounds as ionophores in ion selective electrodes is getting more attention because of its molecular recognition properties which can be attributed to the three dimensional nature of their molecular chemistry[81]. Calixarenes and Calixresorcinarenes were studied as hosts for an extensive spectrum of guests. Calixarenes are used in commercial applications as Na^+ selective electrodes for the measurement of sodium levels in blood. Metalloporphyrins offer almost unique opportunities to design artificial receptors for chemical sensors[82]. Electrochemical molecular recognition is an expanding research area at the interface of electrochemistry and supramolecular chemistry[83,84].

1.7.2. Performance factors

1. Selectivity

Selectivity is one of the basic characteristics of the sensor. It depends on the composition of the membrane, ratio between the activities of the main and interfering ions in solution. Conditions such as pH, temperature and non aqueous content also affect the selectivity of the sensor.

2. Linear concentration range and detection limit

The linear concentration range refers to the concentration for which the sensor behaves in a Nernstian manner. The reproducibility of the linear range depends on the working condition of the electrode such as pH, composition of the solution, preconditioning of the electrode, temperature etc. According to the IUPAC recommendations, the detection limit of an ion selective electrode is defined as the activity of the analyte ion at the point of intersection of the extrapolated linear segments of the calibration curve[85].

3. Response of the electrode (slope)

The slope also called the response of the electrode is the main characteristic of a potentiometric sensor. The potentiometric response, the emf, is a linear function of the logarithm of the activity of the free ions in solution, Its slope is described by the Nernst equation as $59.2/z_i$ mV decade $^{-1}$. Below the detection limit, it has a constant value which is ideally defined by the response of the sensor to another interfering ion[86].

4. Influence of pH

The pH can influence the formation of protonated and unprotonated species of the same substance. The pH plays a very important role in the response of the potentiometric sensors. Special care must be accorded to the buffering of solutions, because a small difference in pH may cause a significant change in the potential, and that will result in an error in the measurement.

5. Response time

IUPAC defined the response time as the average time for the sensor to reach a potential within ± mV of its final equilibrium value[87]. For ISE the response time depends on concentration as well as on the stability of the compound formed between the ion that has to be determined and the ligand at the membrane solution interface.

6. Life time or Shelf life

The life time of a sensor refers to the period of time during which the sensor can be used for the determination of the analyte and it is determined by the stability of the selective material. After this time the slope and detection limit of the sensor decrease or increase. It is accepted that the loss of plasticizer, carrier or ionic site from the polymeric film, as a result of leaching into the sample, is the primary reason for the limited life time of the carrier based sensors.

1.8. A brief review on potentiometric sensors based on macrocyclics

As part of the present investigations, potentiometric sensors have been developed for the Pb^{2+}, Mn^{2+}, Ni^{2+}, Cu^{2+} and salicylate based on macrocyclic ionophores. A brief review on the potentiometric sensors based on macrocyclic compounds as ionophores for the mentioned ions is presented below.

1.8.1. Lead

A. K. Singh et al developed a Polystyrene-based potentiometric sensor with ionophore 2,3,4:10,11,12-dipyridine-1,3,5,9,11,13-hexaazacyclohexadeca-2,10-diene[88]. The sensor exhibited a linear concentration range 1.4×10^{-6} - 1.0×10^{-1} M with a Nernstian slope of 29.0 mV $decade^{-1}$ of concentration between pH 3.0 and 6.0.

A lead selective electrode based on 3,15,21-triaza-4,5:13,14-dibenzo-6,9,12-trioxabicycloheneicosa-1,17,19-triene-2,16-dione was developed by S. Y. Kazemi etal[89]. The electrode exhibited a Nernstian response for lead ions over the concentration range 1.3×10^{-2} - 3.6×10^{-6} M with a limit of detection 2.0 × 10^{-6} M. The proposed sensor could be used in the pH range 3.7 - 6.5.

Crown ethers bearing 18C6 unit 18-crown-6(18C6), dicyclohexyl-18-crown-6 (DC18C6) and dibenzo-18-crown-6(DB18C6) have been examined[90] as ion selective electrodes for lead by Zamani et al. The linear response range of the electrode based on 18C6 (1 × 10^{-6} - 1 × 10^{-3} M) differs from that exhibited by the DC18C6 and DB18C6 based electrodes (1 × 10^{-5} - 1 × 10^{-2} M).

M. A. F. Elmosallamy et al fabricated a potentiometric sensor based on 1,4,8,11-tetrathiacyclotetradecane as a neutral ionophore[91]. The sensor exhibited linear potentiometric response over the concentration range 1.0 × 10^{-5} - 1.0 × 10^{-2} M.

A PVC membrane sensor based on hexathia-18-crown-6-tetraone was reported by M. Shamsipur et al[92]. It exhibited a linear response in the concentration range 1.0 × 10^{-6} - 8.0 × 10^{-3} M and showed best response in the pH range 3.0 - 6.0.

X. Yang et al reported PVC membrane sensors based on dithiophene diazacrown ether derivatives, such as 7,16-dithenoyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane, 7,16-di-(2-thiopheneacetyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane, and 4,7,13,16-tetrathenoyl-1,10-dioxa-4,7,13,16—tetraazacyclooctadecane(TTOTC). Compared to the first two reported sensors, TTOTC showed much better selectivity, particularly in presence of alkali and alkaline earth metals towards lead ions[93-96].

Gupta and Jain reported sensors for the determination of Pb^{2+} ions based on macrocyclic compounds 15-crown-5 and 4-t-butyl calix[4]arene as ionophores. The membrane using 15-crown-5 exhibited a good response for lead(II) ions over a wide concentration range and response time was 30 s. The electrode based on 4-t-butyl calix[4]arene worked well in the concentration range 1.0×10^{-5} - 1.0×10^{-1} M with a Nernstian slope 30 mV decade^{-1}. The working pH range is 2.1 - 4.0[97-98].

The group Malinowska and Brzózka developed sensors for Pb^{2+} ions where potential carriers were di and tetrathiamide functional calix[4]arene derivatives and thiophosphorylated calix[6]arene[99,100].

A lead sensor based on mono benzo-15-crown-5-phosphomolybdic acid was fabricated by Sheen and Shih[101] which has a very good pH range of 3.0 - 9.0.

Attiyat et al reported a silver wire coated sensor using benzo-18-crown-6 as ionophore[102]. The group of Shamsipur reported a series of sensors for lead using dibenzopyridino -18-crown-6, 4'-vinylbenzo-15-crown-5 homopolymer, and 18 membered thia crown derivative as ionophores[103-105]. Cadogan and co-workers fabricated lead sensors using calixarene phosphine oxide derivative as ionophore[106].

Mousavi et al[107] fabricated a potentiometric sensor for lead ions based on 1,10,-dibenzyl-1,10-diaza-18-crown-6. The sensor exhibited a Nernstian response for lead ions over a concentration range of 1.0×10^{-2} - 5.0×10^{-5} M.

Zareh et al studied the effect of the presence of 18-crown-6 on the response of 1-pyrrolidine dicarbodithioate based lead sensor and it was observed that the response of the sensor with the immobilised 18-crown-6 was Nernstian[108].

Lu et al[109] reported a lead sensor based on calixarene carboxyphenyl azo derivative which showed a good Nernstian response in the concentration range 1.0×10^{-6} - 1.0×10^{-2} M.

Amini et al[110] developed a potentiometric sensor using cryptand (222) which showed a good response in the concentration range 1.0×10^{-5} - 1.0×10^{-1} M with a detection limit of 5×10^{-6} M. Its response time was about 30 s.

A lead selective polymeric membrane sensors based on selected thiacrown ethers[111] was developed by H. Radecka et al.

Ganjali et al[112] developed a membrane sensor based on N, N0-dimethylcyanodiaza-18-crown-6 for the determination of ultra-trace amounts of lead which showed a Nernstian response over a concentration range 1.0×10^{-2} – 1.0×10^{-7} M with a detection limit of 7×10^{-8} M.

A PVC membrane electrode based on meso-tetrakis(2-hydroxy-1-naphthyl)porphyrin was developed by Lee et al[113]. It displayed a good Nernstian response over the linear range of 3.2×10^{-5} - 1×10^{-1} M and its limit of detection was 3.5×10^{-6} M and it has a fast response time of 10 s.

Macrocyclic amides as ionophores for lead selective membrane electrodes were used by Malinowska et al. The electrodes exhibited a linear response in the concentration range $10^{-4.5}$-$10^{-1.7}$ M and showed a slope of 25-30 mV decade^{-1}. But the life time of the electrode does not exceed two weeks[114].

PVC based membranes of N, N'-bis(2-hydroxy-1-naphthalene)-2,6-pyridiamine was prepared by Gupta et al[115]. The electrode showed a good response in the concentration range 3.2×10^{-6} - 1.0×10^{-1} M with a Nernstian slope between a pH range 3.5 - 7.5.

1.8.2. Manganese

An exhaustive literature survey revealed only few reports on manganese sensors[116-124]. Among this there is only one sensor reported for manganese based on Macrocyclic compound as ionophore.

A PVC membrane electrode based on a pentaazamacrocyclic manganese complex (Manganese complex of 14,16-dimethyl-1,4,7,10,13 pentaazacyclohexadeca-13,16-diene) was fabricated for Mn^{2+} ions by Singh et al[125]. The sensor worked well in the concentration range of 1.3×10^{-5} - 1.0×10^{-1} M. It worked well in the pH range 3.0 - 8.0.

1.8.3. Nickel

Membrane sensors for Ni^{2+} ions based on macrocyclic compounds in PVC and polystyrene binders were prepared by Jain et al[126]. The PVC membranes showed near Nernstian response in the concentration range 1.0×10^{-5} - 1.0×10^{-1} M while polystyrene based membranes exhibited linearity in the concentration range 1.0×10^{-6} - 1.0×10^{-1} M. These electrodes worked well in the pH range 1.7 – 5.4.

PVC membrane sensor was constructed by Mousavi and his co-workers using 1,10-dibenzyl-1,10-diaza-18-crown-6 as a neutral carrier[127]. The sensor exhibited a Nernstian response over a concentration range 2.0×10^{-5} - 5.5×10^{-3} M. It could be used in the pH range of 4.0 – 8.0.

A polymeric membrane electrode (PME) and coated graphite electrode (CGE) for Ni^{2+} ion based on macrocyclic ligand 2,9-(2-methoxyaniline)$_2$-4,11-Me$_2$-[14]-1,4,8,11-tetraene-1,5,8,12-N$_4$ as a neutral ionophore was by fabricated by Singh et al[128].

A PVC based selective sensors for Ni^{2+} ions using carboxylated and methylated porphine was reported by Singh and Bhatnagar[129]. Carboxylated based porphine exhibited a linear concentration range $2.0 \times 10^{-6} – 1.0 \times 10^{-1}$ M with a slope of 29.6 mV decade^{-1} and methylated porphine showed linear potential response in the concentration range 1.0×10^{-5} - 1.0×10^{-1} M with a Nernstian slope of 29.0 mV decade^{-1}. The electrode could be used in the pH range 2.0 – 7.0.

Pentacyclooctaaza as a neutral carrier in coated wire ion selective electrode for Ni^{2+} ions was reported by Mazloum et al[130]. The electrode exhibited a near Nernstian response in the concentration range of 1.0×10^{-6} - 1.0×10^{-1} M. The electrode was suitable for use in aqueous solutions in the pH range 3.0 – 6.0.

Gupta and his co-workers reported a PVC membrane sensor based on Dibenzocyclamnickel(ll) as electroactive material[131]. It exhibited a linear response in the concentration range 7.0×10^{-6} - 1.0×10^{-1} M with a slope of 29.8 mV decade^{-1}. The sensor worked well in the pH range 2.0 - 7.6.

A PVC membrane sensor based on 3,4:12,13-dibenzo1,6,10,15-tetraazacyclooctadecane was fabricated by A. K. Singh and R. Singh[132]. The sensor worked well in the concentration range 2.8×10^{-6} - 1.0×10^{-1} M with a near Nernstian slope of 30.5 mV decade^{-1} and in the pH range 2.5 – 7.5.

A polystyrene based membrane using a tetraaza macrocyclic ligand as ionophore was fabricated by Singh et al[133]. The membrane worked well over a concentration range of 3.1×10^{-6} - 1.0×10^{-1} M with a near Nernstian slope of 30.7 mV decade^{-1} and in the pH range 2.5 – 7.0.

A PVC membrane electrode based on a tetraazamacrocycle as an ionophore was developed by Singh and Saxeena[134] for Ni^{2+} ions. It worked well in the concentration range 3.9 × 10^{-6} - 1.0 × 10^{-1} M with a Nernstian slope of 29.5 mVdecade^{-1} and in the pH range 2.5 – 7.7.

PVC based membranes incorporated with meso-tetrakis-{4-[tris-(4-allyl dimethylsilyl-phenyl)-silyl]-phenyl}porphyrin as an electroactive material was developed by Gupta et al[135]. The sensor exhibits a Nernstian response in the concentration range 2.5 × $10^{−6}$ - 1.0 × $10^{−1}$ M and performs satisfactorily over the pH range 2.5 - 7.7.

Gupta et al fabricated a PVC membrane sensor incorporating 5,10,15,20-tetra(4-methylphenyl) porphyrin as an electroactive material[136]. The sensor exhibited a Nernstian response in the concentration range 5.6 × 10^{-6} - 1.0 × 10^{-1} M in the pH range 2.5-7.4.

A PVC membrane sensor for Ni^{2+} ions incorporating dibenzodiaza-15-crown-4 as ionophore was fabricated by Shamsipur and Kazemi[137]. The sensor exhibited a Nernstian response in the concentration range 7.1 × 10^{-7} - 1.2 × 10^{-2} M in the pH range 3.0-6.0.

1.8.4. Copper

A copper (ll) selective membrane electrode was reported by Shamsipur et al based on a 23-member macrocyclic diamide[138]. The electrode exhibited a Nernstian response over the concentration range 3.2 × 10^{-5} - 1.0 × 10^{-1} M and the potential response remains almost unchanged over the pH range 3.5 - 6.0.

The group of Shamsipur[139] reported a sensor based on aza-thioether crowns containing a 1,10- phenanthroline sub unit, that showed a Nernstian slope over a wide concentration range of 2.0 × 10^{-1} - 1.0 × 10^{-5} M with a detection limit of 8.0 × 10^{-6} M. It could be used in the pH range of 2.5 – 5.5.

Park et al synthesized five novel 1,3-alternate calix[4]azacrown ethers having 2-picolyl, 3-picolyl and benzyl unit on the nitrogen atom and used as ionophores for copper selective polymeric membrane electrodes[140]. The electrode based on 2-picolyl armed 1,3- alternate calix[4]azacrown ether exhibited Nernstian response over a wide concentration range.

Copper (II) selective sensors have been fabricated from PVC matrix membranes containing porphyrin as neutral carriers by Gupta et al[141]. The sensor showed a linear response over the concentration range 4.4×10^{-6} - 1×10^{-1} M. The working pH range of the sensor is between 2.8 and 7.9 and it has a fast response time of 8 s.

Singh et al fabricated a copper incorporated $Me_2(15)dieneN_4$ Macrocyclic complex for copper ions[142]. The sensor worked well over the concentration range 1.1×10^{-6} - 1.0×10^{-1} M between the pH range 2.1 - 6.2 and it has a life time of six months.

Oliveira et al reported a PVC membrane sensor incorporating a thiophosphoril-containing macrocycle as neutral carrier[143]. The electrode exhibited a Nernstian response over the concentration range 3.0×10^{-6} - 1.0×10^{-2} M and the potential response remains almost unchanged over the pH range 3.9 - 6.4.

A highly selective and sensitive membrane sensor for copper ions based on a Benzo-substituted macrocyclic diamide was reported by Shamsipur and his co-workers[144]. They developed a PVC membrane electrode (PME) and a coated graphite electrode(CGE) with a Nernstian behaviour over a wide concentration range 1.0×10^{-7} – 1.0×10^{-1} M for PME and 1.0×10^{-8} - 1.0×10^{-1} M for CGE. The potentiometric responses are independent of pH in the range 2.7 – 6.2.

Chandra and his co-workers developed a poly(vinyl chloride) sensor based on 1,2,5,6,8,11-hexaazacyclododeca-7,12-dione-2,4,8,10 tetraene as ionophore[145]. The sensor showed a linear response of 29.5 mV decade^{-1} over the concentration range 2.0×10^{-7} - 1.0×10^{-1} M with a detection limit of 8.1×10^{-8} M. The working pH range of the sensor is between 3.0-11.0.

A novel macrocyclic calix[4]arene derivative was examined as an ionophore for PVC membrane electrode towards copper ions by Kamel et al[146]. It showed a near Nernstian response over a concentration range 8.1×10^{-6} - 1.0×10^{-2} M with a slope of 34.2 mV decade^{-1}.

A PVC membrane based Copper (II) selective electrode was constructed by Sindhu et al using 8,11,14-triaza-1,4-dioxo,5(6),16(17)-dibenzocycloseptadecane(TADOBCSD) as a neutral carrier[147]. It showed a linear response over the concentration range 1.0×10^{-8} – 1.0×10^{-1} M with a Nernstian slope of 29.5 mV decade^{-1}.

A copper (ll) electrode was reported by Sun et. al. which was based on a molecular deposition technique in which water soluble copper phthalocyanine tetrasulfonate was alternatively deposited with a dipolar pyridine salt on a 3-mercaptopropionic acid modified gold electrode[148]. It had a linear concentration range from 1.0×10^{-5} – 1.0×10^{-1} M with a slope of 29.0 mV decade^{-1} in the pH range 1.0 – 5.0.

1.8.5. Salicylates

A salicylate selective electrode based on the complex (2-[(E)-2-(4nitrophenyl) hydrazono]-1-phenyl-2-(2-quinolyl)-1-ethanone) Cu(ll) as the membrane carrier was developed by Ardakani et al[149]. The electrode exhibited a good Nernstian slope of 59.6 mV decade^{-1} and a linear range of 1.0 × 10^{-6} – 1.0 M.

The potential response of salicylicate electrode based on complex 1, 8-diamino-3,6-dioxaoctane Ni(ll) was studied by Ardakani et al[150]. The sensor gave a Nernstian response of 59.5 mV decade^{-1} over the concentration range of 7.0 × 10-7 - 1.0 × 10-1 M and can be used over a pH range of 6.0 – 9.5.

A liquid membrane electrode based on lutetium(lll) porphyrin were developed by Messik et al and the electrode showed preferential selectivity towards salicylate anions, discriminating thiocyanate and iodide ions[151].

Comparative study of the metal phthalocyanates as active components in salicylate selective electrodes was made by Leyzerovich et al. Tetrakis-tert-butylphthalocyanates of Al(lll), Sn(lV), Cu(ll), Lu(lll) and Dy (lll) were tested for salicylate membrane electrodes. The most significant deviation of potentiometric selectivity from Hofmeister series is observed for the membranes doped with Al(lll) complex[152].

A membrane electrode based on N, N'-(aminoethyl)ethylenediamide bis(2-salicylideneimine)binuclear copper(ll) complex as an ionophore was developed by Sun et al[153]. The electrode had a linear range of 5.0 × 10^{-7} - 1.0 × 10^{-1} M with a near Nernstian slope of 55 mV decade^{-1} in phosphate buffer solution of pH 5.0.

The potential response properties of a membrane electrode based on chromium(lll)tetraphenylporphyrin chloride was studied by S. Shahrokhian et al[154]. The electrode showed a near Nernstian slope over a concentration range of 1.0 × 10^{-6} - 1.0 × 10^{-1} M and can be used over a pH range 3.0 – 9.0.

The response properties of a PVC membrane electrode with selectivity towards salicylate ions was reported by Chaniotakis et al. The electrode was prepared by incorporating 5, 10, 15, 20-tetraphenyl (porphyrinato)tin(IV)dichloride into a plasticized PVC membrane. The sensor exhibited an anti Hofmeister selectivity pattern with selectivity for salicylate ions over other anions[155].

Electrodes based on vanadyl and molybdenyl phthalocyanines as ionophores were developed by Firooz et al[156]. The electrodes demonstrated Nernstian response over the concentration range 1.0×10^{-7} - 1.0×10^{-1} M and can be used over the pH range 6.0 – 9.0.

A membrane electrode based on the complex N,N’-1,4-butylene bis(3-methyl salicylidene iminato)copper(ll) was developed by Ardakani et al[157]. and the sensor exhibited a Nernstian slope of 59.1 mVdecade^{-1} and a linear range of 1.0×10^{-6} - 1.0 M and could be used in the pH range of 4.5 – 10.5.

An electrode was developed by Ardakani et al[158] based on the complex (2,3;6,7;10,11;14,15-tetraphenyl-4,9,13,16-tetraoxo-1,5,8,12-tetraazacyclohexadecane)copper(ll) as the membrane carrier and it showed a Nernstian slope of 60.9 mV decade^{-1} and a linear concentration range of 1.0×10^{-6} - 1.0×10^{-1} M and the pH range of the electrode is 3.5 – 10.5.

Ardakani et al[159] developed a coated wire ion selective based on zinc(ll)acetylacetonate as ionophore which exhibited a linear response with a Nernstian slope of 59.6 mV decade^{-1} over a concentration range 1.0×10^{-5} - 1.0×10^{-1} M and the electrode is suitable for use in aqueous solution in the pH range of 3.5 - 10.5.

A PVC membrane electrode based on a tin(lV) complex, tricyclohexyl-tin-1,2,4-trioxide was developed by Ganjali et al[160] which showed a Nernstian response in the concentration range of 1.0×10^{-6} - 1.0×10^{-1} M and the sensor could be used in the pH range 6.5 – 11.5.

1.9. Scope of the present investigation

Environmental pollution is the main threat faced by humanity in this century and human beings are exposed continuously to toxic metals. Hence the toxic level determinations of metal ions in the environment and in biological materials are increasingly required by the society. Electrochemical sensors hold a leading position among the different methods available for the trace level determination of metals. They have reached the commercial stage and have important applications in the fields of clinical, industrial, environmental and agricultural analysis. In continuation of our work in the area of low level monitoring of metal ions[161-165], the present work focused on the fabrication of potentiometric sensors for the determination of ions such as Pb^{2+}, Mn^{2+}, Ni^{2+}, Cu^{2+} and Sal^{-}(salicylate ions). A Total of 9 sensors have been fabricated for these ions. Two types of sensor fabrications have been adopted-PVC membrane sensor and carbon paste sensor. For all the developed sensors, the principal analytical parameters have been studied including response time, pH range of the sensor, selectivity, linear response range, calibration slope and detection limit. The developed sensors have been applied for the analysis of respective ions in real samples. It is hoped that the developed sensors can be used for the determination of respective ions with high accuracy and precision.

* * *

Chapter 2

MATERIALS AND METHODS

Contents

A brief sketch of the materials and methods used in the investigations is presented in this chapter. The synthesis and characterization of each ionophore and also the fabrication of the two types of sensors, viz., PVC membrane sensor and carbon paste sensor are described in detail. Details about the general reagents and the instruments used in the investigations are also discussed in this chapter. It also deals with the preparation of solutions of metal salts, buffer solutions, effluent samples and real samples taken for analysis.

2.1 Reagents

High molecular weight PVC, dibutyl sebacate (DBS), perchloric acid and all the metal salts were obtained from Merck, Germany and were used as received. The other plasticizers; dioctyl phthalate (DOP), dioctyl sebacate (DOS), dioctyl adipate (DOA), dimethyl sebacate (DMS), dibutyl phthalate (DBP), tributyl phosphate (TBP) and sodium tetraphenylborate (NaTPB) were obtained from Lancaster, UK and were used without further purification. High purity graphite powder was purchased from Sigma Aldrich Corporation, USA. Benzoyl acetone, thiourea, methyltrioctylammonium chloride (MTOAC), resorcinol, p-toluene sulphonic acid, 1-naphthaldehyde, veratraldehyde, pyrrole, 3-methoxy-4-

hydroxy benzaldehyde, tributyl phosphate (TBP) tetrahydrofuran (THF) and other solvents were all of Analar grade and were procured from local vendors.

2.2 Synthesis and characterization of the ionophores

Four types of electroactive substances are used for developing the sensors - 12-membered macrocyclic ligand, calix[4]resorcinarenes, substituted porphyrin, manganese complex of porphyrin. The synthesis of the electroactive substances are discussed in sections 2.2.1 to 2.2.5. They have been characterized by elemental analysis and spectroscopic methods.

2.2.1 1,3,7,9-tetraaza-2,8-dithia-4,10-dimethyl-6,12-diphenyl cyclododeca-4,6,10,12-Tetraene (TDDDCT)

The macrocyclic ligand 1,3,7,9-tetraaza-2,8-dithia-4,10-dimethyl-6,12-diphenylcyclododeca-4,6,10,12-tetraene was synthesised by microwave assisted method[166]. A finely mixed benzoyl acetone (3.24 g. 0.02 mol) and thiourea (1.52 g, 0.02 mol) was irradiated in a microwave oven at 360W for 2 minutes. After the reaction was completed, the reaction mixture was cooled, the organic layer was washed with water and then with ethanol. It was then dried in vacuo. The structure of TDDDCT was confirmed by analytical and spectroscopic methods and is depicted in Chapter 3 as Figure 3.1.

CHN analysis-

Found (%)	:	C - 65.66, H - 5.12, N - 13.78, S - 15.14
Calculated (%)	:	C - 65.30, H - 4.90, N - 13.91, S - 15.80
IR (KBr) νcm^{-1}	:	1234 (C=S); 1562 (C=N) methyl; 1620 (C=N) phenyl; 1438-85 (C-H)

UV- Visible spectrum in DMS, λ (nm) : 413

^{1}H NMR in $CDCl_3$, δ ppm: 1.4 (s, 6H), 2.23 (s, 4H) and 7.31 (m, H)

2.2.2 2,8,14,20-tetrakis(naphthyl)calix[4]resorcinarene (TNCR)

The ionophore 2,8,14,20-tetrakis(naphthyl)calix[4]resorcinarene was synthesized by the solvent free method[167]. A 1:1 mixture of 1-naphthaldehyde and resorcinol (0.5 to 1.0 g scale) along with a catalytic amount of p-toluene sulphonic acid (ca. 5%) were mixed together in a mortar and pestle and ground vigorously. Within seconds a viscous paste forms, this hardens on further grinding. The paste was left to stand for up to 1 hour, during which time it solidifies. The solid was reground, washed with water to remove any acid, filtered and the pure product recrystallised from hot methanol. It was then dried in vacuo. The structure of TNCR was confirmed by analytical and spectroscopic methods. It is shown as Figure 4.1 in Chapter 4.

CHN analysis-

Found (%) : C - 81.72, H - 4.64

Calculated (%) : C - 82.25, H - 4.83

IR (KBr) νcm^{-1} : 1499 (aromatic C=C), 3367 (phenolic OH)

UV- Visible spectrum in DMS, λ(nm) : 467

^{1}H NMR in $CDCl_3$, δ ppm: 4.8 (b,8H), 5.5 (b,4H), 6-6.5 (m,8H), 7.1-7.7 (m,28H)

2.2.3 2,8,14,20-tetrakis(3,4-dimethoxyphenyl)calix[4]resorcinarene (TDPCR)

The ionophore 2,8,14,20–tetrakis(3,4-dimethoxypheny l)calyx [4] resorcinarene was prepared by taking a 1:1 mixture of veratraldehyde and resorcinol (0.5 to 1.0 g scale) along with a catalytic amount of p-toluene sulphonic acid (ca. 5%) and they were mixed together in a mortar and pestle and ground vigorously. A viscous paste forms which hardens on further grinding. The paste was left to stand for up to 1 hour, during which time it solidifies [167]. The solid was reground, washed with water to remove any acid, filtered and the pure product recrystallised from hot methanol. It was then dried in vacuo. The structure of TDPCR was confirmed by analytical and spectroscopic methods. Its structure is depicted in Chapter 5 as Figure 5.1.

CHN analysis-

Found (%) : C - 69.81, H - 5.42

Calculated (%) : C - 69.76, H - 5.51

IR (KBr) νcm^{-1} : 3400 (OH), 3060 (CH), 1521 (C=C), 1259 (ether)

UV- Visible spectrum in DMS, λ (nm): 297, 475, 514

^{1}H NMR in CDCl$_3$, δ ppm : 3.45 (s, 24 H), 4.8 (d, 8H), 5.3 (s, 4H), 6.7-6.9 (s, 20 H)

2.2.4 5,10,15,20–tetrakis(3-methoxy-4-hydroxyphenyl)porphyrin (TMHPP)

The synthesis of 5,10,15,20–tetrakis(3-methoxy-4-hydroxyphenyl) porphyrin was performed according to Alder Method[168]. Freshly distilled pyrrole (1.04 mL, 0.015 mol) and 3-methoxy-4-hydroxy benzaldehyde (2.282 g, 0.015 mol) were added to 30 mL of boiling propionic acid. The mixture was refluxed for 30 minutes and allowed to cool. The filter cake was washed thoroughly with methanol. The resulting purple crystals were further purified by column chromatography. The structure of TMHPP is shown in Chapter 6 as Figure 6.1. Its structure is confirmed by spectroscopic and analytical methods.

CHN analysis-

Found (%) : C - 72.08, H - 4.66, N - 6.97

Calculated (%) : C - 72.18, H - 4.76, 7.01

IR (KBr) νcm^{-1} : 3000 (CH), 3363 (NH), 3539 (OH)

UV- Visible spectrum in DMS, λ (nm): 411, 445, 514, 647

^1H NMR in $CDCl_3$, δ ppm: 8.9 (s, 8H), 5.9 (s, 4H), 3.9 (s, 12H), 2.7 (s, 2H), 8.2 – 7.3 (m, 12H)

2.2.5 5,10,15,20-tetrakis(3-methoxy-4-hydroxyphenyl)porphyrinato Manganese(III) chloride (TPMC)

The ionophore 5,10,15,20–tetrakis(3-methoxy-4-hydroxyphenyl) porphyrinato Manganese(III) chlorid**e** was prepared by refluxing TMHPP (2 g, 3.22 mmol) and Manganese acetate $Mn(C_2H_3O_2)_2.4H_20$ in 500 mL glacial acetic acid for 72 hours. The solvent was then stripped off and the residue was then extracted into 250 mL methanol. The filtered methanol solution was treated with 250 mL conc. HCl and then 250 mL of water. The green precipitate formed is separated by filtration. The crude sample was then dissolved in 100 mL of benzene, filtered, treated with petroleum ether. The green precipitate is separated by filtration. It was then dried in vacuo[169]. The ionophore TPMC was characterized by elemental analysis and spectroscopic methods and its structure is shown in Chapter 7 as Figure 7.1.

CHN analysis-

Found (%)	:	C - 67.1, H – 4.15, N – 6.1, Mn – 6.87
Calculated (%)	:	C - 67.7, H – 4.23, N – 6.6, Mn – 6.5
IR (KBr) νcm^{-1}	:	3484 (OH), 1625 (NH), 472 (Mn-N)

UV- Visible spectrum in DMSO, λ(nm): 473

^{1}H NMR in $CDCl_3$, δppm : 3.8 (s, 12H), 5.7 (b, 4H), 8.3 – 7.2 (m, 12H), 8.8 (s, 8H)

2.3 Preparation of the metal salt solution

The stock solution (1.0×10^{-1}) of the metal salt was prepared by dissolving the appropriate amount of metal salt in a titrimetric flask and the solution was quantitatively diluted using distilled water. All the other solutions of different concentrations were made by serial dilution of the stock solution.

2.3.1 Lead (II) nitrate stock solution

8.28 g of lead nitrate was weighed accurately, transferred into a 250 ml titrimetric flask and dissolved in distilled water. 5 mL of HNO_3 (2M) was added and diluted to the mark. As the compound is a primary standard, further standardisation was not carried out.

2.3.2 Manganese (II) chloride stock solution

4.95 g of manganese chloride tetrahydrate was weighed accurately, transferred to a 250 ml titrimetric flask and was diluted to the mark with distilled water. The stock solution was standardised by EDTA titration method[170].

2.3.3 Nickel (II) nitrate stock solution

7.27 g of nickel nitrate hexahydrate was weighed accurately, transferred to a 250 ml titrimetric flask and was diluted to the mark with distilled water. The stock solution was standardised by EDTA titration method[170].

2.3.4 Copper (II) nitrate stock solution

6.04 g of cupric nitrate trihydrate was weighed accurately, transferred to a 250 ml titrimetric flask and was diluted to the mark with distilled water. The stock solution was standardised by iodometric method[170].

2.3.5 Sodium salicylate stock solution

4.0 g of sodium salicylate was weighed accurately, transferred to a 250 ml titrimetric flask and was diluted to the mark with distilled water. As the compound is a primary standard, further standardisation was not carried out.

2.4 Preparation of buffer solutions

Buffer solutions were used to maintain the pH of the test solutions and also during the EDTA titrations. They were freshly prepared according to the Robinson Table[171].

2.4.1 pH 5.0

To 100 mL 0.1 M potassium hydrogen phthalate solution, 45.2 mL of 0.1 M NaOH solution was added to give the buffer having pH 5.0

2.4.2 pH 6.0

To 100 mL 0.1 M potassium dihydrogen phosphate**,** 11.2 mL of 0.1 M NaOH solution was added to give the buffer having pH 6.0

2.4.3 pH 7.0

To 100 mL 0.1 M potassium dihydrogen phosphate, 58.2 mL of 0.1 M NaOH solution was added to give the buffer having pH 7.0

2.5 Preparation of the real samples

The practical utility of the developed sensors were tested by the determination of the metal ions in real samples and salicylates in tablets.

2.5.1 Chocolate samples

Ten grams of chocolate sample was heated in a silica crucible at 400°C on an electric bunsen burner till ash is obtained. The residue was dissolved in 2 mL conc. HNO_3 and again heated at 350°C for 2 hours; the process was repeated till no traces of carbon are left. The final residue was treated with 0.5 mL conc. HCl and 1-2 mL 70 % perchloric acid and then evaporated to fumes. The solid residue was dissolved in water, filtered and then transferred quantitatively to a 100 mL titrimetric flask. The pH was adjusted to 5.0 by adding 10 mL buffer solution and then the solution was quantitatively diluted.

2.5.2 Edible oil sample

Ten grams of the hydrogenated edible oil (Dalda) was heated at 500°C for one hour. The residue was completely dissolved in 5 mL of 0.1 M HNO_3. The solution was then transferred into a 100 mL titrimetric flask, the pH was adjusted to 5.0 by adding 10 mL buffer solution and then the solution was quantitatively diluted.

2.5.3 Effluent sample solutions (Electroplating wastes, Eveready battery waste)

A small volume of the effluent sample (from electroplating unit) was taken in a 100 mL titrimetric flask, the pH was adjusted to 5.0 by adding 10 mL buffer solution and then the solution was quantitatively diluted.

The ‘Eveready battery’ waste sample was initially treated with a few drops of conc. HNO_3, dissolved in distilled water, filtered and then the solution was transferred into a 100 mL titrimetric flask. The pH was adjusted to 5.0 by adding 10 mL buffer solution and then the solution was quantitatively diluted.

2.5.4 Pharmaceutical samples

For the preparation of pharmaceutical samples, tablets of three different companies were taken and finely powdered. A precisely weighed portion of each sample was refluxed with 50 mL of 0.5M NaOH for one hour. It is filtered and the solution was adjusted to pH 7.0 by adding buffer solution and then the solution was quantitatively diluted.

2.6 Fabrication of the sensors

Ionophore is the most important part of an ion selective sensor. Two different types of sensors were fabricated for the studied metal ions and one type of sensor for salicylate ions, using the synthesized ionophores. A brief description of the stages involved in the fabrication of the two types of sensors is given.

2.6.1Fabrication of the PVC membrane sensor

The general method for the fabrication of PVC membrane sensor was first reported by Cragg's and Moody[172]. PVC membrane electrodes belong to the class of liquid membrane electrodes. The main components of PVC membrane sensor are ionophore, PVC and plasticizer. Lipophilic additives are also added to the membrane which increases the response behaviour and selectivity of the electrode. Ionophore, PVC, plasticizer and ionic additives were taken in percentage-weight ratios of approximately 1-7 : 30-33 : 60-69 : 2-5 (Ionophore : PVC : plasticizer : ionic additive). All the components were taken in the specified ratios and dissolved in THF. The solution was poured into glass rings struck on to a glass plate. It was left to dry by allowing the slow evaporation of the solvent. Small disc shaped membranes formed were cut out and glued to one end of a hollow Pyrex glass tube. The Pyrex glass tube was filled with the internal filling solution which is a suitable concentration of the standard solution. The membrane was conditioned by dipping it in a 1.0×10^{-1} M solution. Figure 2.1 represents the stages involved in the fabrication of a PVC membrane sensor.

2.6.2 Fabrication of the carbon paste sensor

The carbon paste electrodes belong to the group of solid state ion selective electrodes. High purity graphite and the ionophore were mixed thoroughly in the appropriate percentage – weight ratios, using a mortar and pestle to give a homogeneous mixture. To this mixture a weighed amount of binder was added and mixed thoroughly to form a paste. The main function of the binder is to link mechanically the graphite particles and the ionophore. The mixing is repeated several times in order to obtain a mixture as homogeneous as one can get. This paste was then packed to one end of the Teflon holder in which electrical contact was made with a copper rod that runs through the centre of the electrode holder. Its filling is made in small portions when each of them being pressed intimately before adding the next one. Appropriate packing and a smooth surface was achieved by pressing the surface of the sensor against a smooth filter paper or butter paper. The prepared sensor is then kept as such for 1 or 2 hours. The carbon paste sensor was then conditioned by dipping in corresponding solutions of suitable concentrations. The main advantage of a carbon paste sensor is that it does not require an internal filling solution and the electrode surface could be polished using a filter paper to produce reproducible working surface. Figure 2.2 represents the stages involved in the fabrication of a carbon paste sensor.

2.7 Potential measurement and calibration

The potential measurements were carried out at 25 ± 1^{o}C on a Metrohm 781 ion meter. A Ag | AgCl (silver-silver chloride) or Hg | Hg_2Cl_2, KCl (sat.) (calomel) reference electrode was used in conjunction with the developed sensor. The cell assembly for potentiometric measurements can be represented as follows

For PVC membrane sensor,

External reference electrode | analyte solution | membrane | metal salt solution 0.1M (internal solution) | Internal reference electrode

For carbon paste electrode,

Reference electrode | analyte solution | carbon paste electrode

The performance of the sensor was investigated by measuring the emf of the cell comprising the analyte solution in the concentration range

1.0×10^{-8} - 1.0×10^{-1} M. The solutions were stirred and the stable potential reading was taken.

2.8 Selectivity study of the developed sensor

Selectivity is one of the basic characteristics of an electrochemical sensor. In a potentiometric sensor the cell potential is mainly influenced by the ion of interest (primary ion), but the cell potential may also be influenced by other ions which can interact with the sensor membrane. Selectivity represents to what extend the electrode is selective to a specified analyte in presence of various interfering species. The selectivity of the developed sensor is determined using the Fixed Interference Method (FIM) which is a mixed solution method and the selectivity coefficient values are evaluated[173]. In this method, the potential of a cell comprising an ion selective electrode and a reference electrode is measured with solutions of constant activity of the interfering ion, a_B and varying activity of the primary ion, $a_{A.}$ The potential values obtained are plotted versus the logarithm of the activity of the primary ion. The intersection of the extrapolation of the linear portions of the curve gives the value of a_A and is used to calculate potentiometric selectivity coefficient $K_{\mathbf{A,B}}^{\mathbf{Pot}}$ from the following equation.

$$K^{pot}_{A,B} = \frac{a_A}{(a_B)^{z_A/\,z_B}} \qquad \text{————} \qquad (1)$$

were ${}^{Z}{}_{A}$ and ${}^{Z}{}_{B}$ are the charge numbers of the primary ion, A and the interfering ion, B respectively. The selectivity coefficient indicates the extent to which a foreign ion interferes with the response of the electrode to the primary ion. A value of selectivity coefficient that is close to one suggests that the sensor is almost equally selective to the interfering ion as to the primary ion. If selectivity coefficient is larger than one, the electrode responds to the interfering ions more selectively than to the primary ions.

2.9 Instruments used

All the potential measurements were carried out on a Metrohm 781 ion pH meter. The CHN analysis was done on a CHN analyzer, Elementar Vario ELIII at Sophisticated Test and Instrumentation Centre (STIC), Kochi. The UV-Visible spectra were recorded using Spectro UV-Visible Double Beam UVD-3500 instrument. FT-IR spectra were recorded on JASCO 4100 FT-IR spectrometer using KBr discs. SEM analysis was done on JOEL 6300 LV at STIC, Kochi. ^{1}H NMR spectra were recorded using JEOL GSX 400 NB FT NMR spectrometer. The standard method used for the determination of metal content in real samples was the ICP-AES technique and the instrument used was Thermo Electron IRIS INTREPID II XSP DUO spectrometer. Spectrophotometric method was used as the standard method for salicylate.

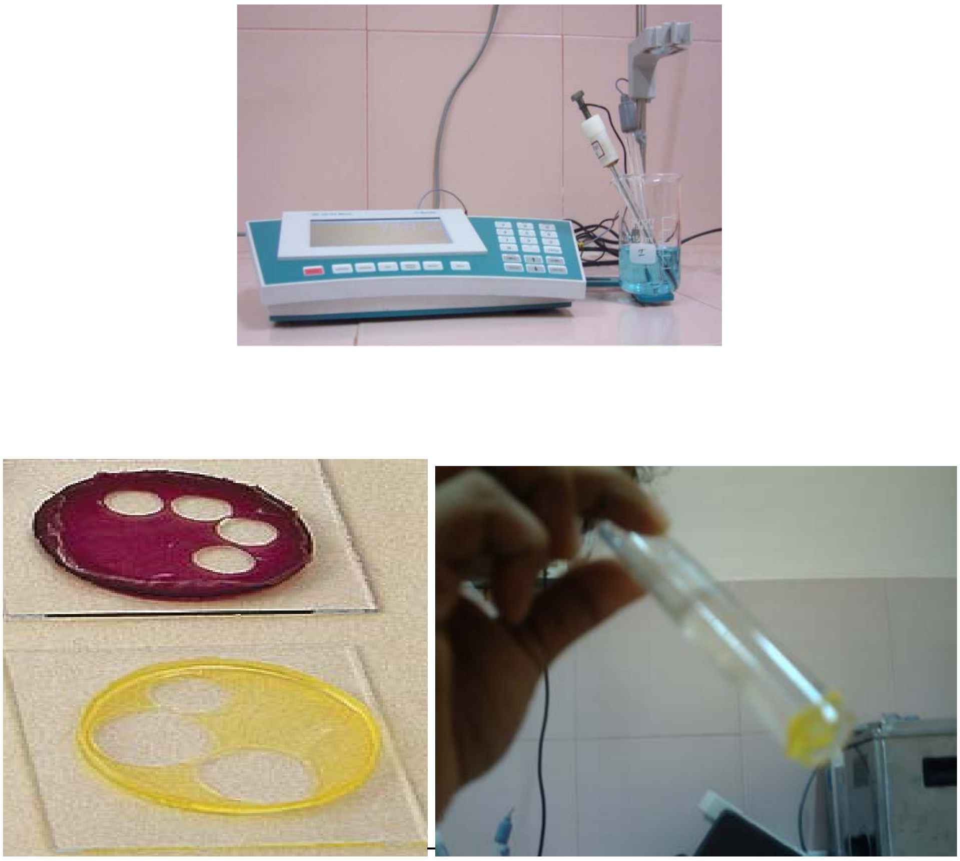


Figure 2.1 Stages involved in the fabrication of a PVC membrane sensor

Figure 2.2 Stages involved in the fabrication of a carbon paste sensor

* * *

Chapter 3

SENSORS FOR LEAD

This chapter deals with the fabrication of two types of sensors – a carbon paste sensor and a PVC membrane sensor – based on a macrocyclic ligand for the determination of Pb^{2+} *ions. The sensors worked well over a wide concentration range and with a fast response time. The analytical application of the developed sensors, in the determination of* Pb^{2+} *ions in battery waste and its application as an indicator electrode in the potentiometric titration of* Pb^{2+} *ions against EDTA have also been discussed.*

Lead is an extremely soft, highly malleable and ductile and a poor electrical conductor which is resistant to corrosion. It is a bluish white metal that tarnishes to dull gray in air. Lead is the only metal in which there is zero Thomson effect. Lead is the ultimate product of the various radioactive decay series. It occurs naturally as galena (PbS) and cerussite ($PbCO_3$). Lead is mainly used in alloys, storage batteries, paints, high quality glass, in solder for electronics and is used as shielding from radiation. Lead is the traditional base metal of organ pipes. Molten lead is used as a coolant for lead cooled fast reactors.

In spite of these advantages lead is an environmental pollutant and is cycled in the environment through the biogeochemical cycle. It accumulates with toxic effects in blood, liver, kidney and in the central nervous system of exposed mammals[174-176]. It is highly toxic and causes brain damage, nephropathy, sluggishness, restlessness, loss of skin colour and appetite. Chronic lead intoxication decreases the biosynthesis of haemoglobin[177-179]. Lead acetate (known as sugar of lead) was used by the Roman Empire as a sweetener for wine; and that is believed to be the cause of the dementia which affected many Roman Emperors.

Hence the determination of trace amounts of lead is a continuing research interest due to its toxicity and accumulation in the environment and living organisms. Spectrophotometric methods, Atomic Absorption Spectroscopy (AAS), AAS-ETS (electro thermal atomization)[180-184], Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES), Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) or the Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS)[185], Chromatography[186], Gravimetric determination and Photometry[187-190] are used for the trace level determination of lead ions in solution. But these methods generally require sample pre-treatment and infrastructure back up and hence are not convenient for routine analysis. But potentiometric sensors are better suited as they offer advantages such as high selectivity, sensitivity and good precision. This chapter describes the fabrication of a PVC membrane sensor and a carbon paste sensor using a macrocyclic ligand.

3.1 Synthesis of the Ionophore

Ionophore is the most important part of an ion selective sensor. It is the electroactive ingredient which is responsible for the selective recognition of the analyte in the developed sensor. The synthesis and characterization of the ionophore, 1,3,7,9-tetraaza-2,8-dithia-4,10-dimethyl-6,12-diphenyl cyclododeca-4,6,10,12-tetraene (TDDDCT) has been discussed under section 2.2.1 in chapter 2. The structure of TDDDCT is shown as Figure 3.1.

3.2 Sensors based on TDDDCT

The PVC and carbon paste sensors were fabricated using TDDDCT as ionophore. The potential responses of the two types of sensors towards different cations are shown as Figure 3.2 and Figure 3.3. It was found that the sensors showed a Nernstian response to lead ions. This may be attributed to the selective complexation behaviour of the ionophore for lead ions over other metal ions as well as the rapid exchange kinetics of the resulting complex.

3.3 Fabrication of the Sensors

The general method for the fabrication of the PVC membrane sensor has been discussed under section 2.6.1 and the fabrication of the carbon paste type sensor has been discussed under section 2.6.2 in Chapter 2.

The PVC membrane sensor was fabricated using TDDDCT, PVC, plasticizers and additive in THF. The optimised membrane composition that gave the best response in terms of slope, concentration range and response time was found to be 3 : 32 : 62 : 3 for TDDDCT : PVC : DOP : NaTPB (w/w%) where the plasticizer used was dioctyl phthalate (DOP) and the anion excluder was sodium tetraphenylborate (NaTPB). For the fabrication of PVC membrane sensor small disc shaped membranes were cut out and glued to one end of a hollow Pyrex glass tube and it was filled with an internal solution of 1.0 × 10^{-1} M lead nitrate solution and conditioned by dipping in 1.0 × 10^{-1} M lead nitrate solution for about 24 hours.

For the preparation of carbon paste sensor the ionophore was mixed with spectroscopic grade graphite powder. Binder was added to this mixture and it was again thoroughly mixed until it was uniformly wetted. This paste was then packed to one end of the Teflon holder in which electrical contact was made with a copper rod that runs through the centre of the electrode holder. The electrode surface was polished using a filter paper to produce reproducible working surface. The best composition ratio for carbon paste sensor was found to be 85 : 15 (graphite : TDDDCT).

The two types of sensors were conditioned by dipping it in a 1.0 × 10^{-1} M ($PbNO_3$) solution. The equilibrium time was 2 days for PVC membrane sensor and just 24 hours for carbon paste sensor.

3.4 Potential measurement and calibration

A Metrohm 781 ion meter was used for potential measurements. All emf measurements were carried out at 25 ± 1^{o}C. A saturated calomel electrode was used as the external as well as the internal reference electrode. The electrochemical cell assembly may be represented as follows:

For PVC membrane sensor:

External reference electrode | test solution | PVC membrane based on TDDDCT | internal filling solution (0.1M Pb^{2+}) | Internal reference electrode

For carbon paste sensor

Reference electrode | test solution | carbon paste electrode based on TDDDCT

Standard solutions of the analyte were prepared by serial dilution of the stock solution. The emf of the cell was directly measured by the developed sensors using the previously mentioned cell assembly. Calibration graph was obtained by plotting EMF (mV) versus $p[Pb^{2+}]$. The calibration graph was used for subsequent determination of unknown solutions.

The performance characteristics of a developed sensor are described in terms of its linear concentration range, detection limit, slope, response time and shelf life. These factors are discussed in detail in the next section.

3.5 Optimization studies of the two types of sensors

The key component of the sensor is the ionophore**.** The performance of the sensor is also influenced by some other important features such as nature of the solvent (plasticizer), amount of the ionophore, plasticizer/PVC ratio and nature of the additives. Optimization of the membrane composition is presented in Table 3.1.

The nature of the plasticizer has a marked influence on the response slope, linear domain and also on the selectivity of PVC membrane electrodes[191,192]. The PVC membrane without the plasticizer was stiff, with unequal thickness and the sensor, Tp_1 gave a sub Nernstian slope but on addition of the plasticizing agent, the membrane surface became smooth and the sensor showed improved response characteristics. The plasticizer which is compatible should exhibit high lipophilicity to avoid leaching and also possess adequate viscosity and dielectric constant[193,194]. From the results it was found that among the six different plasticizers used DOP was the most effective solvent mediator in the preparation of the PVC membrane sensor while others gave a Non Nernstian slopes. Hence the membrane with DOP was selected for further studies. The amount of the ionophore was also found to affect the sensitivity of the sensors. 3% was found to be the optimum amount of ionophore and further addition of ionophore content results in a diminished response from the sensors which may be due to the saturation of the membrane [195].

The presence of lipophilic negatively charged additives (anionic excluders) improves the potentiometric behaviour of the PVC membrane sensor. Such anionic excluders are beneficial for both neutral and charged carrier-based sensors[196-201]. These anionic excluders help to reduce the membrane resistance[202] and improve the selectivity[203-205] and reduce the interference from sample anions[206-209]. A 3% of NaTPB was found to be the optimum amount of anionic excluder for the best response of the sensor. Hence the sensor Tp_3 with TDDDCT : PVC : DOP : NaTPB (w/w%) ratio as 3 : 32 : 62 : 3 was used for further studies.

The surface morphology of the developed membrane was analyzed using SEM. This technique allows the study of membrane surface characteristics, such as morphological homogeneity and chemical composition. Homogeneity of the membrane may affect the response characteristics of a sensor. The SEM image of the membrane of Tp_3 sensor is shown as Figure 3.4. The extent of homogeneity of the membrane surface is clear in the SEM image.

A set of eight carbon paste sensors were developed by varying the weight ratio of graphite to ionophore to arrive at an optimum composition for carbon paste sensor and the results are consolidated in the Table 3.2. A sensor without the ionophore Tc_1 was first prepared and it was observed that there was no response to lead ions. The sensors with paraffin oil as binder (pasting liquid) gave better response than the sensors with other binders. The main function of the binder is to link mechanically the graphite particles and the ionophore. Besides this main function, the binder as the second main moiety of carbon paste co-determines its properties[210]. It was found that the sensor (Tc_5) with graphite to ionophore ratio 85:15 was the best in terms of slope, working concentration range and response time. On increasing the ionophore content, the system deviated from Nernstian slope which may be due to the decrease in conductance of the sensor material. Hence this sensor (Tc_5) was used for further studies.

3.5.1 Working concentration range and slope

Calibration graph of the EMF (mV) versus pPb^{2+} for the sensors Tp_3 and Tc_5 are shown as Figure 3.5 and Figure 3.6. The working concentration range for the sensors Tp_3 and Tc_5 are found to be $5.0 \times 10^{-7} – 1.0 \times 10^{-1}$ M and $1.0 \times 10^{-7} – 1.0 \times 10^{-1}$ M respectively. The slope calculated from the calibration graph was found to be 29.5 (±0.5) mV $decade^{-1}$ and 28.9 (±0.8) mV $decade^{-1}$ for the sensors Tp_3 and Tc_5 respectively. The detection limit was calculated from the graph by the intersection of the two extrapolated linear segments of the calibration plot and was found to be 2.5×10^{-7} M and 1.9×10^{-7} M for the sensors Tp_3 and Tc_5 respectively.

3.5.2 Effect of concentration of internal filling solution

The influence of the concentration of the internal filling solution on the Pb^{2+} selective membrane sensor was studied. The concentration of the internal filling solution was changed from 1.0×10^{-1} M to 1.0×10^{-4} M and the calibration plot was obtained. It was found that variation of the concentration of the internal filling solution did not cause any significant difference in the potential. Hence a 1.0 × 10^{-1} M Pb^{2+} ion solution was fixed as the internal filling solution for the PVC membrane sensor. There is no need for an internal filling solution in the case of a carbon paste sensor which is its main advantage.

3.5.3 Response time and life time of the sensors

Response time is governed by the transport diffusion processes in the aqueous diffusion layer. It is the time required for the lead ion sensor to reach a potential within ±1 mV of final equilibrium value. Practical response time of the sensors Tp_3 and Tc_5 were obtained from Figure 3.7 and Figure 3.8 and was found to be 10 s and 22 s respectively. The life time of the sensors were investigated by measuring the potentials in standard solutions each day. The slope of the sensors was calculated each time. A Nernstian slope was obtained for a period of 4 months in the case of membrane sensor Tp_3 and 4 weeks for the carbon paste sensor Tc_5.

3.5.4 Effect of pH and non aqueous media

The influence of pH on the EMF response of the sensors Tp_3 and Tc_5 are studied for two fixed concentrations, 1.0 × 10^{-3} M and 1.0 × 10^{-4} M over a pH range of 2.0 – 9.0. The pH was adjusted by introducing small drops of nitric acid (0.05M) or sodium hydroxide (0.05M). The effects of pH on the sensors are shown as Figure 3.9 and Figure 3.10. It was found that the potential remained constant over a pH range of 2.8 – 7.0 and 3.0 – 7.0 for the sensors Tp_3 and Tc_5 respectively. The observed change in potentials at higher pH values may be due to the hydrolysis of Pb^{2+}, while at lower pH values H^+ ions start contributing to the charge transport process of the membrane, thereby causing interference.

The performance of the sensors Tp_3 and Tc_5 were also investigated in partially non-aqueous media using ethanol-water and methanol-water mixtures. The membrane worked satisfactorily in 25% of non-aqueous content in the case of PVC membrane sensor Tp_3 and 10% in the case of carbon paste sensor Tc_5. However, above the tolerance level slope and working concentration range was reduced and potentials show drift which may be attributed to leaching of the ligand into the sample solution. The results of performance of the sensors Tp_3 and Tc_5 in partially non- aqueous media are presented in Table 3.3 and Table 3.4 respectively.

3.5.5 Potentiometric selectivity

The response of any ion selective sensor to the primary ion in the presence of other ions present in the solution is expressed in terms of the potentiometric selectivity coefficient. It gives a basic source of information on the interferences in the ion selective response. The interference of various ions on the selectivity of the developed sensors has been examined by the Fixed Interference Method[174]. The selectivity coefficients were determined at 1.0×10^{-2} M concentration of foreign ions and the concentration of Pb^{2+} ions was varied. Selectivity coefficient values were calculated using equation (1).

The selectivity coefficient values are summarized in Table 3.5. A perusal of the selectivity coefficient values indicate that the sensors show very good selectivity to Pb^{2+} ions in presence of Cr^{3+}, $Mn^{2+,}$ $Co^{2+,}$ $Fe^{2+,}$ Cu^{2+}, Zn^{2+}, Sn^{2+}, Hg^{2+}, Ni^{2+}, Ba^{2+}, Na^{+}, K^{+} and Ag^{+} but only moderate selectivity in presence of Cd^{2+} ions.

3.6 Analytical applications

The applications of the developed sensors Tp_3 and Tc_5 were further investigated by using the sensors in the determination of lead in ‘Eveready battery waste’. The sample was prepared as discussed under section 2.5.3 in chapter 2. The results presented in Table 3.6 show that this method is comparable to the standard ICP – AES method.

The sensors Tp_3 and Tc_5 were successfully applied as an indicator electrode in conjuction with Hg | Hg_2Cl_2, KCl (sat.) in the potentiometric titration of lead (II) nitrate solution with EDTA. The titration curves for the sensors Tp_3 and Tc_5 are depicted in Figure 3.11 and Figure 3.12. The titration plots obtained were all of the standard sigmoid shape and the end point corresponds to 1:1 stoichiometry of Pb-EDTA complex.

3.7 Conclusion

Potentiometric sensors were developed for the selective determination of Pb^{2+} ions. The developed sensors include both PVC membrane sensor and a carbon paste sensor. The linear range obtained for the sensor Tp_3 was $5.0 \times 10^{-7} – 1.0 \times 10^{-1}$ M whereas in the case of Tc_5 was $1.0 \times 10^{-7} – 1.0 \times 10^{-1}$ M. The pH ranges of the sensors Tp_3 and Tc_5 were 2.8 – 7.0 and 3.0 – 7.0 respectively. The slope, response time and shelf life of the sensor Tp_3 was found to be far superior when compared to the sensor Tc_5. But the linear concentration range is better for Tc_5 compared to Tp_3. Moreover, the use of the newly developed sensors for the determination of Pb^{2+} ions in real samples with less cost, with accuracy and without the need for any special treatment of the samples is all advantageous over other reported techniques. The response characteristics of the two sensors Tp_3 and Tc_5 are consolidated in Table 3.7.

The two sensors Tp_3 and Tc_5 have very good response characteristics. Table 3.8 lists the comparative study of the response characteristics of the developed sensors with some of the reported sensors for lead. It can be seen that the developed sensors are superior in terms of working concentration range[212,213,216,217,88,98] pH range,[215,216,217,88,98] and Tp_3 is superior in terms of life time[211,212, 213,215,216,217,88].

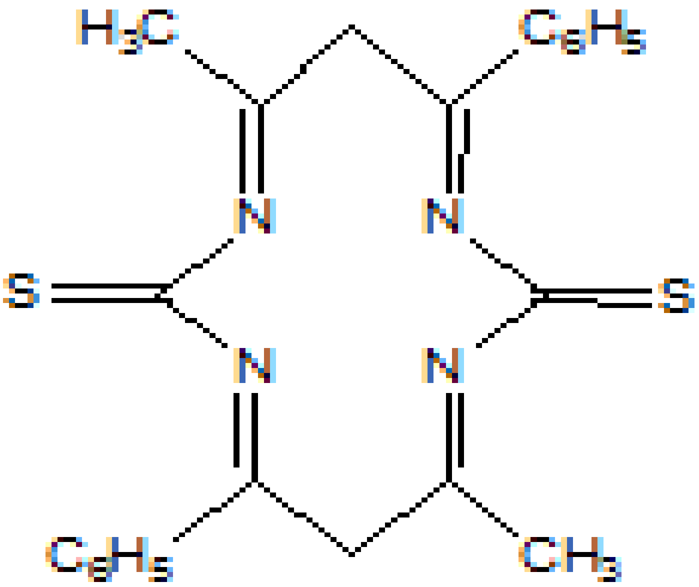


Figure 3.1 – Structure of the ionophore TDDDCT

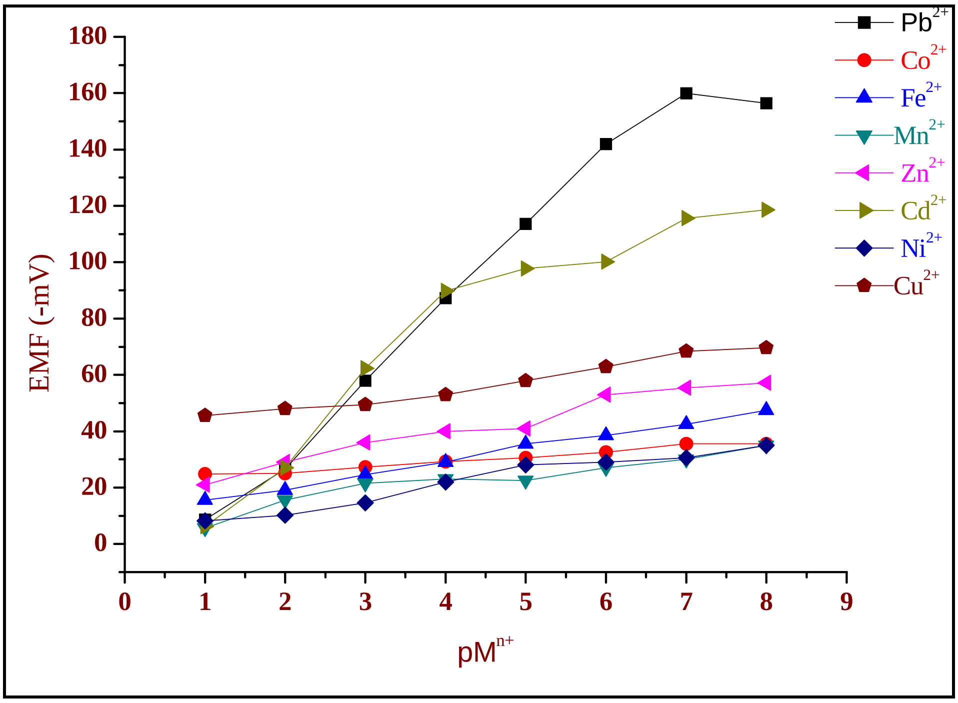


Figure 3.2 - Potential response of the PVC membrane sensor based on TDDDCT to different cations.

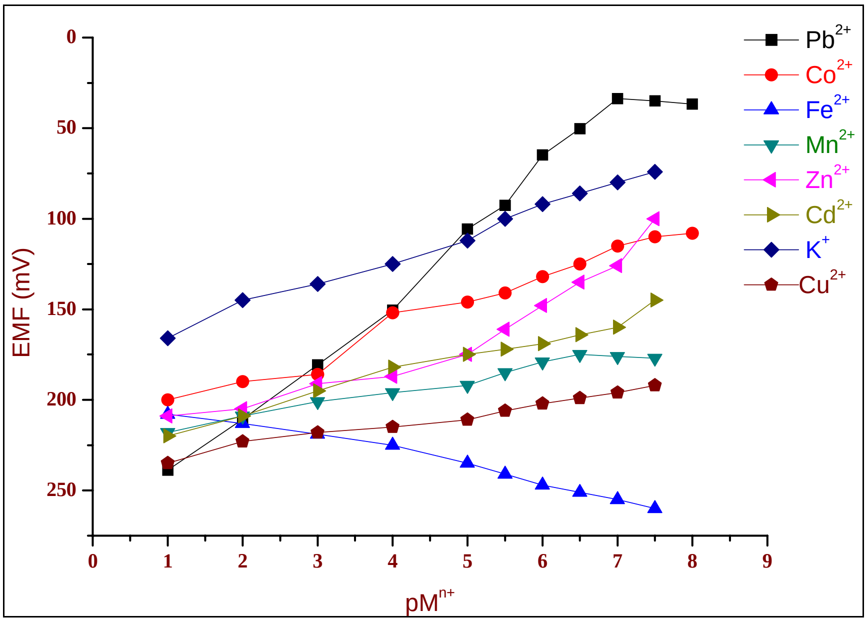


Figure 3.3 - Potential response of the carbon paste sensor based on TDDDCT to different cations.

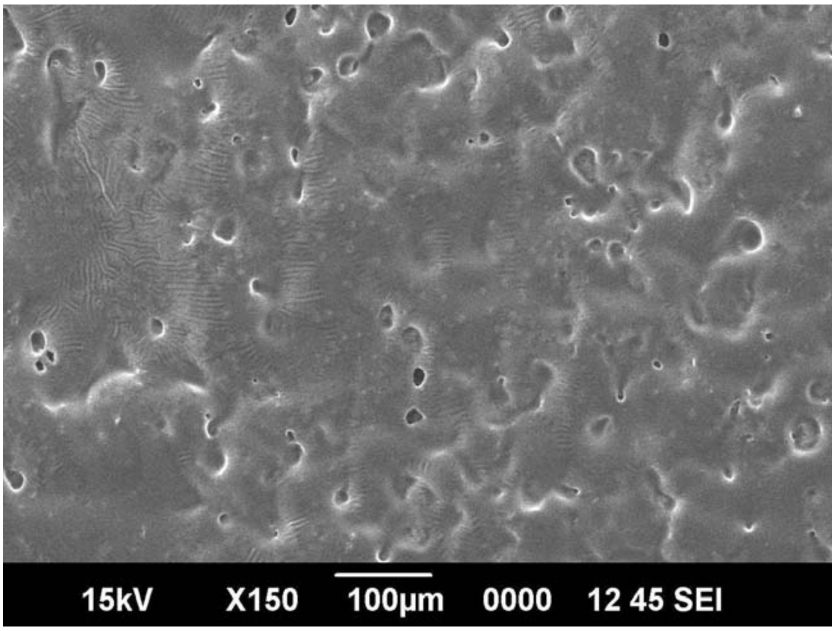


Figure 3.4 - SEM image of the PVC membrane sensor Tp_3 based on TDDDCT

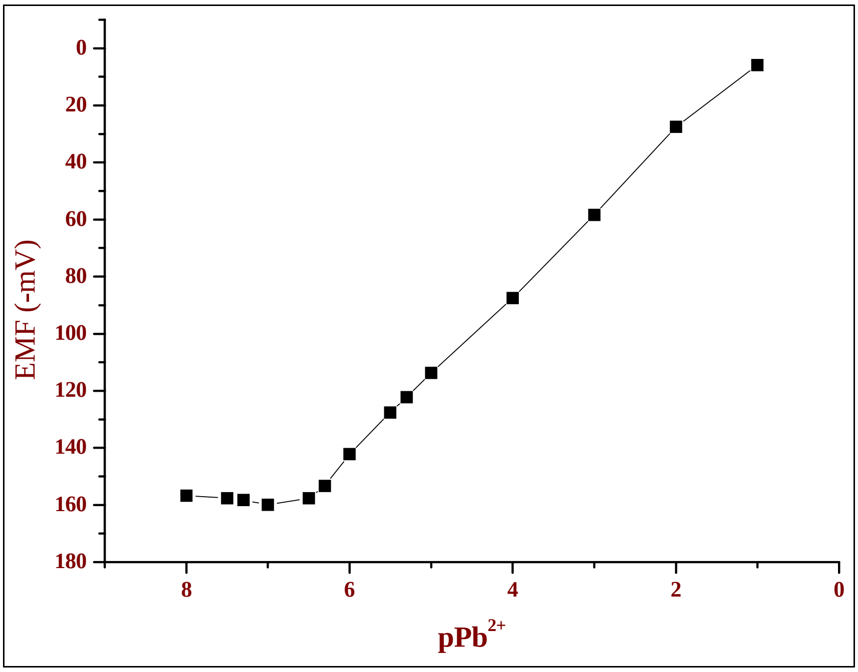


Figure 3.5 – Calibration graph of the PVC membrane sensor Tp_3 based on TDDDCT

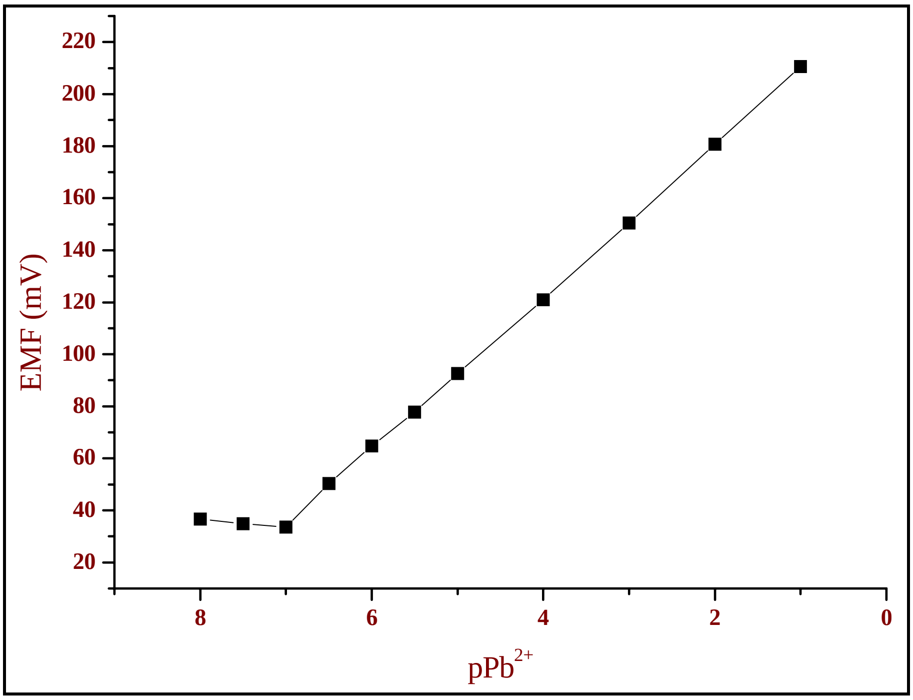


Figure 3.6 – Calibration graph of the carbon paste sensor Tc$_5$ based on TDDDCT

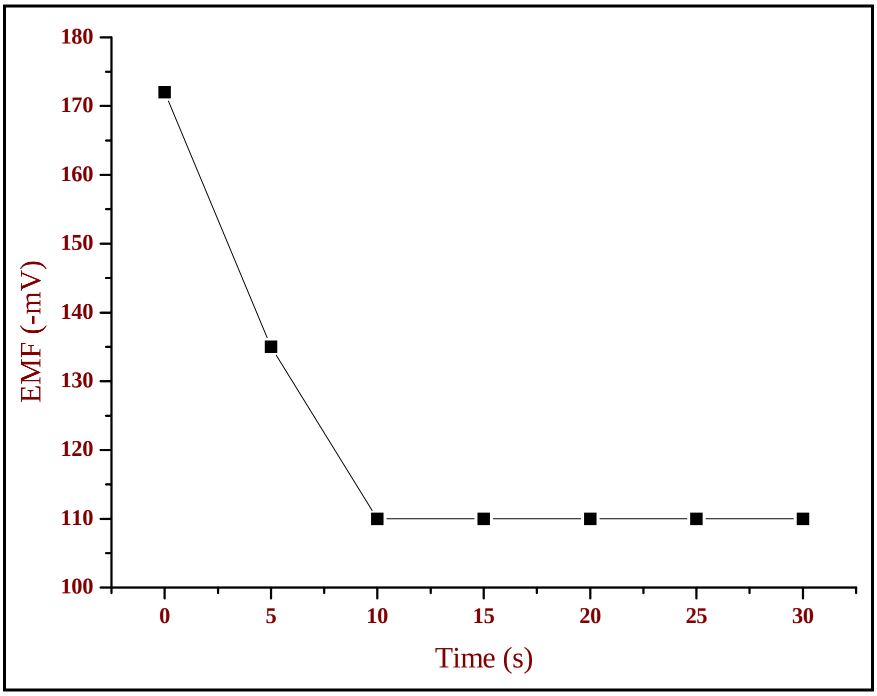


Figure 3.7 - Practical response time of the PVC membrane sensor Tp_3 based on TDDDCT

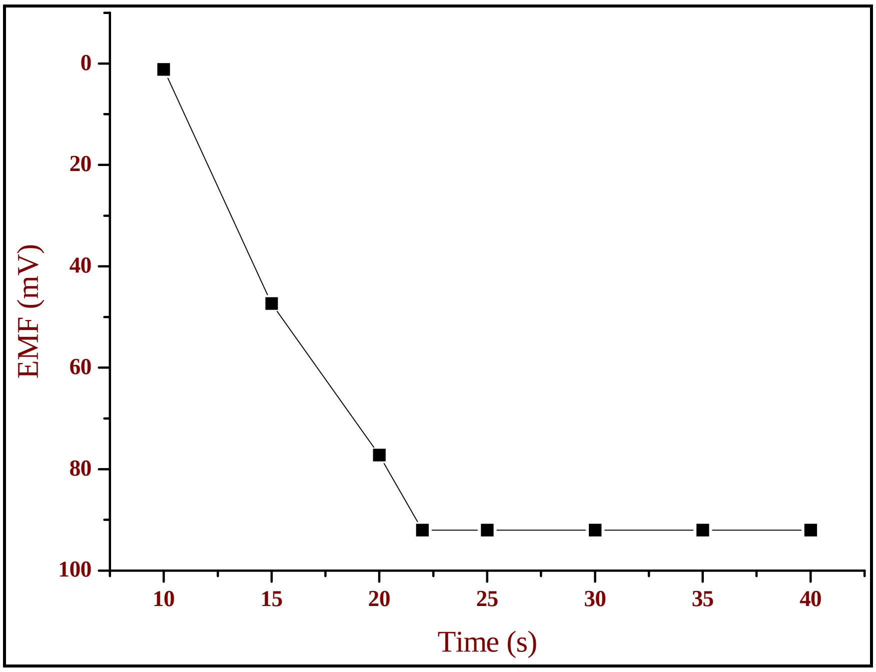


Figure 3.8 - Practical response time of the carbon paste sensor Tc_5 based on TDDDCT

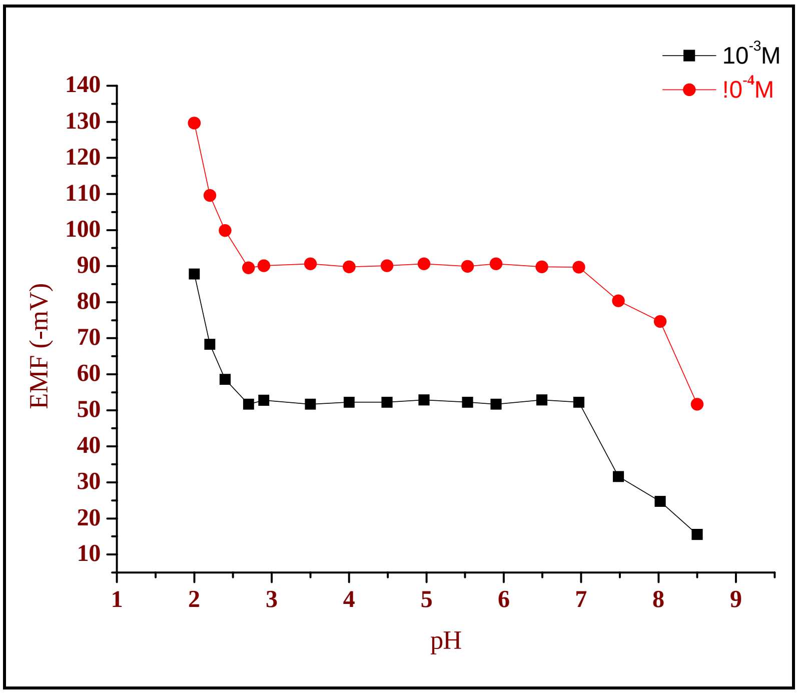


Figure 3.9 – Effect of pH on the cell potential of the PVC membrane sensor Tp_3 based on TDDDCT

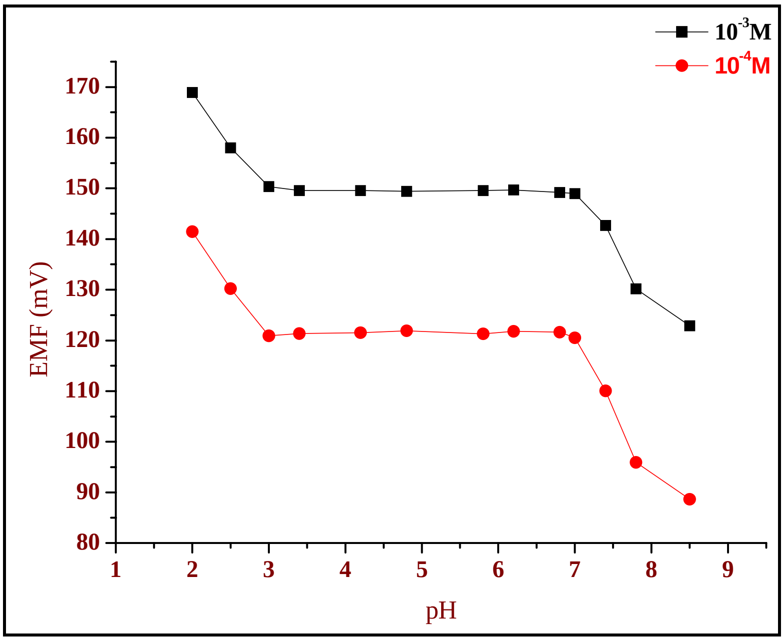


Figure 3.10 – Effect of pH on the cell potential of the carbon paste sensor Tc_5 based on TDDDCT

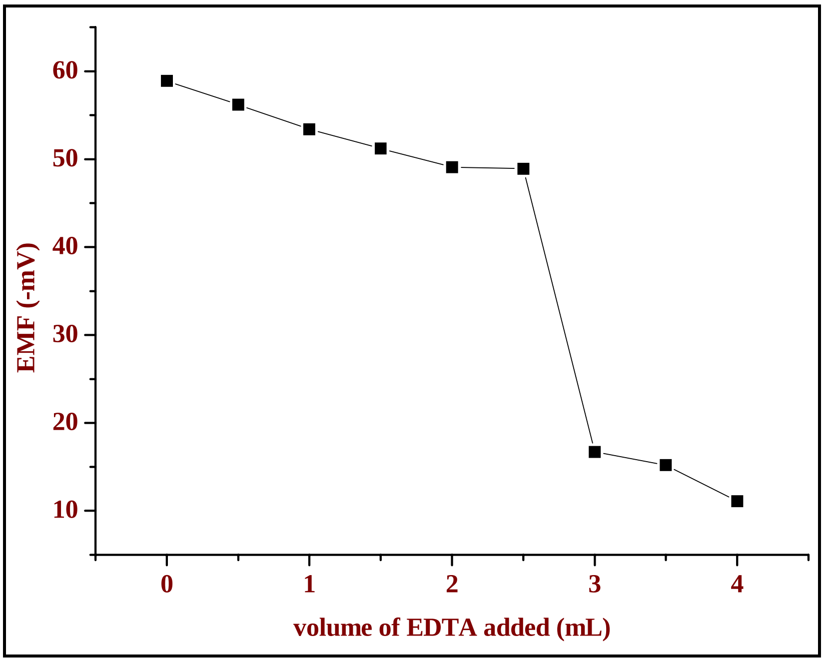


Figure 3.11 – Potentiometric titration curve of 25.0 mL of 1.0 × 10^{-3} M Pb^{2+} solution with 1.0 × 10^{-2} M EDTA using the PVC membrane sensor Tp_3 based on TDDDCT

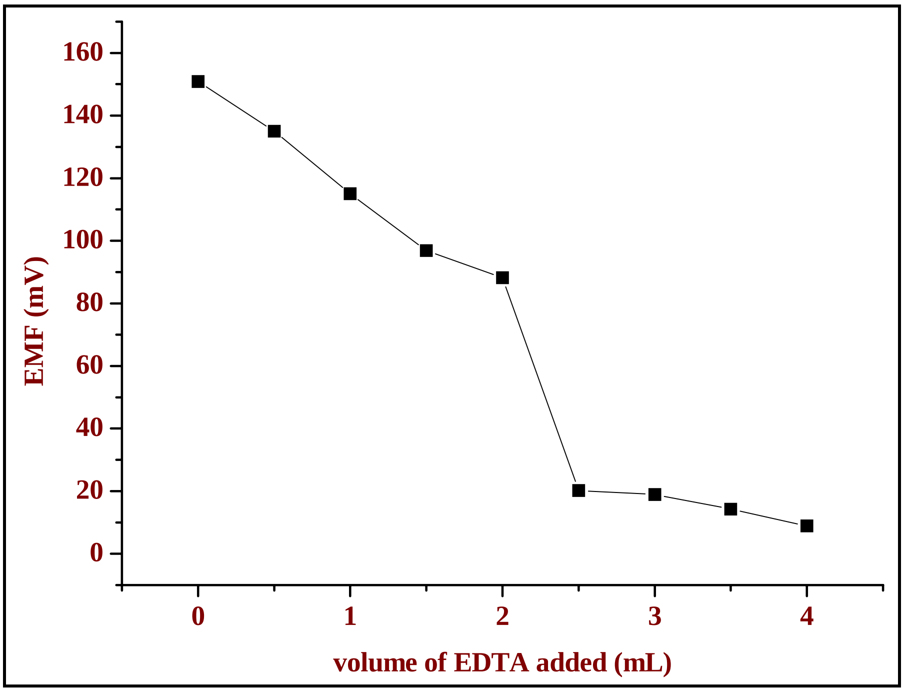


Figure 3.12 – Potentiometric titration curve of 25.0 mL of 1.0 × 10^{-3} M Pb^{2+} solution with 1.0 × 10^{-2} M EDTA using the sensor the carbon paste sensor Tc_5 based on TDDDCT

Table 3.1 – Optimization of composition of the PVC membrane based onTDDDCT

Sensor	Ionophore	PVC	Plasticizer	NaTPB	Working concentration range (M)	Slope mV decade^{-1}
Tp_{1}	3	94	0	3	$1.0\times10^{-4}-1.0\times10^{-2}$	19.5 ± 0.8
Tp_{2}	3	30	DOP, 64	3	$1.0\times10^{-6}-1.0\times10^{-2}$	30.7 ± 0.3
Tp_{3}	3	32	DOP, 62	3	$5.0\times10^{-7}-1.0\times10^{-2}$	29.5 ± 0.5
Tp_{4}	3	34	DOP, 60	3	$1.0\times10^{-6}-1.0\times10^{-2}$	27.6 ± 0.2
Tp_{5}	3	32	DMS, 62	3	$4.0\times10^{-6}-1.0\times10^{-2}$	21.3 ± 0.4
Tp_{6}	3	32	DBS, 62	3	$4.0\times10^{-4}-1.0\times10^{-2}$	22.4 ± 0.5
Tp_{7}	3	32	DOS, 62	3	$1.0\times10^{-6}-1.0\times10^{-2}$	25.2 ± 0.7
Tp_{8}	3	32	DOA, 62	3	$4.0\times10^{-5}-1.0\times10^{-2}$	17.8 ± 0.3
Tp_{9}	3	32	DBP, 62	3	$8.0\times10^{-5}-1.0\times10^{-2}$	19.5 ± 0.5
Tp_{10}	2	33	DOP, 62	3	$1.0\times10^{-6}-1.0\times10^{-2}$	26.8 ± 0.6
Tp_{11}	2	34	DOP, 62	2	$4.0\times10^{-6}-1.0\times10^{-2}$	25.9 ± 0.3
Tp_{12}	4	32	DOP, 62	2	$8.0\times10^{-5}-1.0\times10^{-2}$	22.4 ± 0.5

Table 3.2 Optimization of the composition of the carbon paste sensor based on TDDDCT

Sensor	Ionophore	Graphite	Working concentration range (M)	Slope mV decade^{-1}
Tc_{1}	0	100	–––––	2.2 ± 0.6
Tc_{2}	5	95	$1.0\times10^{-5}-1.0\times10^{-2}$	21.4 ± 0.7
Tc_{3}	10	90	$4.0\times10^{-6}-1.0\times10^{-1}$	24.6 ± 0.5
Tc_{4}	12	88	$2.0\times10^{-6}-1.0\times10^{-1}$	27.8 ± 0.8
Tc_{5}	15	85	$1.0\times10^{-7}-1.0\times10^{-1}$	28.9 ± 0.8
Tc_{6}	20	80	$8.0\times10^{-7}-1.0\times10^{-1}$	34.3 ± 0.3
Tc_{7}	25	75	$8.0\times10^{-6}-1.0\times10^{-2}$	34.9 ± 0.6
Tc_{8}	30	70	$1.0\times10^{-6}-1.0\times10^{-2}$	30.2 ± 0.5

Table 3.3 – Effect of partially non-aqueous medium on the slope of the PVC membrane sensor Tp_3

Non-aqueous content (%v/v)	Slope (mVdecade^{-1})	Working concentration Range (M)
0	29.5	$5.0 \times 10^{-7} - 1.0 \times 10^{-1}$
Ethanol		
10	29.5	$5.0 \times 10^{-7} - 1.0 \times 10^{-1}$
20	29.3	$6.5 \times 10^{-7} - 1.0 \times 10^{-1}$
25	28.9	$7.8 \times 10^{-7} - 1.0 \times 10^{-1}$
30	22.1	$8.2 \times 10^{-6} - 1.0 \times 10^{-2}$
Methanol		
10	29.2	$5.0 \times 10^{-7} - 1.0 \times 10^{-1}$
20	28.7	$6.7 \times 10^{-7} - 1.0 \times 10^{-1}$
25	28.6	$9.5 \times 10^{-7} - 1.0 \times 10^{-1}$
30	22.3	$8.5 \times 10^{-6} - 1.0 \times 10^{-1}$

Table 3.4 – Effect of partially non-aqueous medium on the slope of the carbon paste sensor Tc_5

Non-aqueous content (%v/v)	Slope (mVdecade^{-1})	Working concentration range(M)
0	29.5	$1.0 \times 10^{-7} - 1.0 \times 10^{-1}$
Ethanol		
10	28.7	$4.0 \times 10^{-7} - 1.0 \times 10^{-1}$
15	21.3	$6.0 \times 10^{-5} - 1.0 \times 10^{-2}$
Methanol		
10	29.3	$3.2 \times 10^{-7} - 1.0 \times 10^{-1}$
15	23.2	$9.2 \times 10^{-6} - 1.0 \times 10^{-2}$

Table 3.5 – Selectivity coefficients for the sensors Tp_3 and Tc_5 using Fixed Interference Method at 1.0×10^{-2} M concentration of interfering ion

Interfering ion (X)	Tp_3	Tc_5
Cr^{3+}	8.5×10^{-3}	3.7×10^{-3}
Co^{2+}	4.1×10^{-3}	3.1×10^{-3}
Fe^{2+}	9.9×10^{-4}	8.8×10^{-4}
Cu^{2+}	6.5×10^{-3}	6.9×10^{-3}
Zn^{2+}	2.4×10^{-3}	3.1×10^{-3}
Sn^{2+}	6.1×10^{-3}	2.9×10^{-3}
Hg^{2+}	1.7×10^{-2}	3.1×10^{-2}
Cd^{2+}	3.6×10^{-1}	7.9×10^{-1}
Na^{+}	8.1×10^{-4}	9.2×10^{-4}
K^{+}	9.3×10^{-4}	8.4×10^{-3}
Ag^{+}	7.6×10^{-2}	4.5×10^{-2}
Mn^{2+}	5.2×10^{-3}	7.1×10^{-3}
Ni^{2+}	2.1×10^{-3}	3.9×10^{-3}
Ba^{2+}	1.8×10^{-3}	3.3×10^{-3}

Table 3.6 – Determination of the Pb^{2+} content in 'Eveready battery' waste

Sample	Tp_3 ppm*	Tc_5 ppm*	ICP-AES ppm
Eveready battery waste	21.40 ± 0.03	21.44 ± 0.02	21.51

*RSDs based on three triplicates

Table 3.7 - Response characteristics of the sensors Tp_3 and Tc_5

Parameter	Response characteristics	
	Tp_3	**Tc_5**
Working concentration range (M)	$5.0 \times 10^{-7} – 1.0 \times 10^{-2}$	$3.0 \times 10^{-7} – 1.0 \times 10^{-2}$
Slope (mV decade^{-1})	29.5 ± 0.5	28.9 ± 0.8
Detection Limit (M)	2.5×10^{-7}	1.9×10^{-7}
Response time	10 s	22 s
pH range	2.8 – 7.0	3.0 – 7.0
Non aqueous tolerance limit	25%	10%
Shelf life	4 months	4 weeks

Table 3.8 A comparative study of the characteristics of the developed sensors for lead with some reported sensors

No	Working concentration range (M)	pH range	Life Time	Slope (mV decade^{-1})	Ref. No.
1	$1.0 \times 10^{-7} – 1.0 \times 10^{-2}$	3.5 – 7.5	6 months	29.1	115
2	$1.0 \times 10^{-9} – 1.0 \times 10^{-3}$	3.5 – 9.0	3 months	29.1	211
3	$2.6 \times 10^{-6} – 1.0 \times 10^{-1}$	4.5 – 7.5	NM*	28.2	212
4	$1.0 \times 10^{-5} – 1.0 \times 10^{-2}$	3.0 – 7.0	3 months	NM	213
5	$1.0 \times 10^{-8} – 1.0 \times 10^{-2}$	2.0 – 10.5	9 months	29.2	214
6	$2.2 \times 10^{-8} – 6.1 \times 10^{-4}$	6.0	NM*	29.1	215
7	$6.0 \times 10^{-7} – 1.0 \times 10^{-1}$	3.0 – 6.0	2 months	29.1	216
8	$4.0 \times 10^{-6} – 1.0 \times 10^{-2}$	4.5 – 7.0	2 weeks	27.5	217
9	1.4×10^{-6} - 1.0×10^{-1}	3.0 – 6.0	100 days	29.0	88
10	1.1×10^{-5} - 1.0×10^{-1}	2.1 – 4.0	6 months	30.0	98
11	$5.0 \times 10^{-7} – 1.0 \times 10^{-1}$	2.8 – 7.0	4 months	29.5	Tp_3
12	$1.0 \times 10^{-7} – 1.0 \times 10^{-1}$	3.0 – 7.0	4 weeks	28.9	Tc_5

*NM– not mentioned

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Chapter 4

SENSORS FOR MANGANESE

Contents

This chapter discusses in detail the fabrication of a PVC membrane sensor and a carbon paste sensor based on a calix[4]resorcinarene as ionophore. The response characteristics of the developed sensors are discussed in detail. The sensors worked well over a wide concentration range $1.0 \times 10^{-5} - 1.0 \times 10^{-1}$ *M and with a fast response time. The developed sensors were applied as an indicator electrode in the potentiometric titration of* Mn^{2+} *against EDTA.*

Manganese is a pinkish-gray, brittle and chemically active metal which is not magnetic. It is the twelveth most abundant element in the earth's crust and it is an essential trace element in the photosynthetic oxygen evolution in chloroplasts in plants. Human bodies contain about 10-20 mg of manganese most of which is located in the kidneys and liver and in human body manganese functions as an enzyme activator and as a component of metalloenzymes. Being a part of many biological enzymes, it is considered as an essential element. Neanderthals had used black manganese dioxide as a cosmetic fifty thousand years ago[218]. Manganese compounds have been used since ancient times for cave paintings.

Although manganese compounds are less toxic than those of other widespread metals such as nickel and copper, prolonged exposure to manganese dust and fumes may affect central nervous system. Symptoms of manganese poisoning are hallucinations, forgetfulness, lung embolism, bronchitis, headache and insomnia. A form of Parkinson’s disease type neurodegenaration called ‘Manganism’ has been linked to high exposure to manganese dusts amongst miners and smelters since the early 19th centuary[219]. EPA recommends 0.05 mg/L as the maximum allowable manganese concentration in drinking water.

The common methods adopted for the determination of manganese are AAS[220,221], ICP-MS[222], fluorometry[223] etc. But these techniques are costly and require pre-sample treatment and very skilled persons are required as a supervisor to handle the instrument.

Only a few reports on manganese sensors are found in literature[116-125]. Among this there is only one sensor reported for manganese, based on macrocyclic compound as electroactive substance. As part of the present investigations a calix[4]resorcinarene has been synthesized and used as the electroactive component in the fabrication of a PVC membrane sensor and a carbon paste sensor.

4.1 Synthesis of the Ionophore

The ionophore 2,8,14,20-tetrakis(naphthyl)calix[4]resorcinarene (TNCR) was synthesized by the solvent free method using a mixture of 1-naphthaldehyde and resorcinol along with a catalytic amount of p-toluenesulphonic acid[167]. The synthesis and characterisation of the ionophore TNCR has been discussed in detail under section 2.2.2 in chapter 2. The structure of the ionophore TNCR is shown as Figure 4.1.

4.2 Sensors based on TNCR

The ionophore TNCR has been used to fabricate two types of sensors, the carbon paste sensor and PVC membrane sensor. Initially the potential response of the sensors based on TNCR was studied for different cations. Figure 4.2 and Figure 4.3 depicts the response of the PVC membrane sensor and carbon paste sensor to different cations. It was found that the sensors were highly responsive to manganese ions with respect to other ions. This may be attributed to the rapid complexation and decomplexation of Mn^{2+} ions with TNCR at the membrane sample interface.

4.3 Fabrication of the Sensors

The PVC membrane sensor was prepared as discussed under section 2.6.1 and carbon paste sensor as discussed under section 2.6.2. of chapter 2. The best response was observed with dioctyl phthalate (DOP) as plasticizing agent and sodium tetraphenylborate (NaTPB) as anionic additive. The composition ratio that gave the best response in terms of slope, concentration range and response time was found to be 2 : 32 : 63 : 3 for TNCR : PVC : DOP : NaTPB (w/w%). The ionophore, PVC, plasticizer and anionic additive taken in specified percentage-weight ratios were dissolved in THF. The mixture was then poured into glass rings struck on to a glass plate. It was allowed to stand overnight for slow evaporation of the solvent and formation of the sensing membrane. Small disc shaped membranes formed were cut out and glued to one end of a hollow Pyrex glass tube. The electrode body was filled with 1.0×10^{-1} M manganese chloride solution and conditioned by dipping it in 1.0×10^{-1} M manganese chloride solution for 2 days.

Carbon paste sensor forms a very important class of chemical sensors. Its fabrication is comparatively easy. In the case of carbon paste sensor the graphite and ionophore was made into a paste in tributyl phosphate. The resulting paste was then packed to the open end of a Teflon holder. A copper rod through the centre of the electrode body provides the electrical contact. The composition ratio that gave the best response in terms of slope, concentration range and response time was found to be 90 : 10 (graphite : TNCR) (%w/w).

4.4 Potential measurement and calibration

A Metrohm 781 ion meter was used for potential measurements. All emf measurements were carried out at 25 ± 1^{o}C. A saturated calomel electrode was used as the external as well as the internal reference electrode. The electrochemical cell assembly may be represented as follows:

For PVC membrane sensor:

External reference electrode | test solution | PVC membrane based on TNCR | internal filling solution (0.1M Mn^{2+}) | internal reference electrode

For carbon paste sensor

Reference electrode | test solution | carbon paste electrode based on TNCR

Performance of the developed sensors were investigated by measuring the potential in Mn^{2+} solutions prepared in the concentration range $1.0 \times 10^{-8} – 1.0 \times 10^{-1}$ M. The solutions were stirred and the stable potential readings were taken. The performance of the membrane characteristics were tested by various operation parameters, such as selectivity, response time, life time, working concentration range of the electrode, the effect of pH of the analyte solution and the effect of membrane composition on the response of the sensor were investigated. These factors are discussed in detail in the next section.

4.5 Optimization studies of the two types of sensors

The Optimization of the membrane composition for the PVC membrane sensor is important as the amount of the ionophore, plasticizer/PVC ratio and nature of the additives and the membrane solvent (plasticizer) influence the sensitivity and selectivity of the sensors. Table 4.1 clearly shows how the slopes of the sensors vary on changing the composition of the membrane.

The dielectric constant of the plasticized poly(vinyl chloride) is an important factor to be considered in liquid membranes. In the ion - selective electrodes the dielectric constant of the PVC is a function of the nature of the plasticizer as well as its proportion in the polymeric matrix[224]. Since about 60 to 70% by weight of the membrane composition is due to the plasticizer it is generally expected that the values of the dielectric constants of the liquid membranes are similar to that of pure liquid plasticizer. The variation observed in the sensor response when different plasticizers are used, may be attributed to different carrier mechanisms[225].

The sensor fabricated without any plasticizer Tm_1, gave a sub Nernstian slope and on the addition of the plasticizer the response of the sensor improved. The six different plasticizers used were Dioctyl phthalate (DOP), Dioctyl adipate (DOA), Dibutyl phthalate (DBP), Dimethyl sebacate (DMS), Dioctyl sebacate (DOS), Dibutyl sebacate (DBS). The best response was found to be for the sensor fabricated using DOP.

The response of the sensor was also studied by varying the amount of the ionophore. The optimum amount of the ionophore has been found to be 2.0 (%w/w). The presence of lipophilic negatively charged additives (anionic excluders) improves the potentiometric behaviour of the PVC membrane sensor by reducing the ohmic resistance and improving the response, selectivity and sensitivity[226]. The membrane $Tm_{\mathbf{6}}$ with composition 2 : 32 : 63 : 3 for TNCR : PVC : DOP : NaTPB (w/w%) was used for further studies.

The SEM analysis was conducted to study the surface morphology of the developed membrane Tm_6. Figure 4.4 shows the SEM image of membrane Tm_6. The extend of homogeneity of the membrane surface is clear in the SEM image. A homogeneous membrane is found to exhibit good response characteristics such as high sensitivity and selectivity.

A set of nine carbon paste sensors were fabricated by varying the compositions of ionophore to graphite ratio and the results are consolidated in Table 4.2. It was observed that the sensor, Mc_1 with zero percentage of the ionophore showed negligible response. However by increasing the amount of the ionophore to about 10% there is a sharp increase in the response of the sensor. Further increase in the amount of ionophore led to an irregular pattern of the slope which may be due to the decrease in the conductance of the sensor material. The nature of the binder in the sensor matrix influences the response of the carbon paste sensor. The best response of the sensor was obtained when tributyl phosphate was used as the binder. The sensor Mc_6 with graphite to ionophore ratio 90 : 10 was used for further studies.

4.5.1 Working concentration range and slope

The plots of the EMF (mV) versus pMn^{2+} gave the calibration graph for the sensors Tm_6 and Mc_6 and are shown as Figure 4.5 and Figure 4.6. The working concentration range for both the sensors Tm_6 and Mc_6 are found to be 1.0×10^{-5} - 1.0×10^{-1} M. The slope calculated from the calibration graph was found to be 29.8 (± 0.4) mV $decade^{-1}$ and 30.0 (± 0.5) mV $decade^{-1}$ for the sensors Tm_6 and Mc_6 respectively. The detection limit was calculated from the graph by the intersection of the two extrapolated linear segments of the calibration plot and was found to be 5.1×10^{-6} M and 6.5×10^{-6} M for the sensors Tm_6 and Mc_6 respectively.

4.5.2 Effect of concentration of internal filling solution

The effect of concentration of the internal filling solution on the response characteristics of Mn^{2+} selective membrane sensor was critically investigated. To study this effect the concentration of the internal filling solution was changed from 1.0×10^{-1} M - 1.0×10^{-4} M. The calibration plot obtained was studied and found that the slopes remain unchanged. Hence the concentration of the internal filling solution has no effect on the response of the sensor. Hence a 1.0×10^{-1} M Mn^{2+} ion solution was fixed as the internal filling solution for the PVC membrane sensor. There is no need for an internal filling solution in the case of a carbon paste sensor which is one of the advantages of the carbon paste sensor.

4.5.3 Response time and life time of the sensors

The response time is the average time for the sensor to reach a potential within ±1 mV of its final equilibrium value. The practical response time of the sensor was calculated by measuring the time required to achieve 95% of the equilibrium potential by dipping the sensor in a series of Mn^{2+} ion solutions each having a tenfold difference in concentration. From the plot of EMF against time (Figure 4.7 and Figure 4.8), the practical response time for the sensors Tm_6 and Mc_6 were found to be 25 s and 30 s respectively. The life time of the sensors were investigated by measuring the potentials in standard solutions each day. The slope of the sensors was calculated each time. A Nernstian slope was obtained for a period of 4 months in the case of PVC membrane sensor Tm_6 and 3 weeks for the carbon paste sensor Mc_6.

4.5.4 Effect of pH and non aqueous media

The effect of pH of the test solution on the EMF response of the developed sensors was also investigated. The effect was studied for two different concentrations, 1.0×10^{-3} M and 1.0×10^{-4} M of Mn^{2+} solution. The pH was adjusted by introducing small drops of nitric acid (0.05M) or sodium hydroxide (0.05M). The potential remained constant in the pH range 3.2 – 7.0 for the PVC membrane sensor $Tm_{6.}$ The potential of the carbon paste sensor Mc_6 remained constant in the pH range 3.2 – 6.6. This has been illustrated in Figure 4.9 and Figure 4.10. Thus the useful pH range of the PVC membrane sensor Tm_6 is 3.2 – 7.0 and of the carbon paste sensor Mc_6 is 3.2 – 6.6. The observed drift in potential at higher pH may be due to the formation of some hydroxyl complexes of Mn^{2+} ion in solution and at lower pH may be due to the interference from H^+ ions.

The functioning of the sensors Tm_6 and Mc_6 in partially non-aqueous media was also investigated using ethanol-water and methanol-water mixtures. It was found that no significant change observed in the slope for the PVC membrane sensor Tm_6 up to 25% of non-aqueous content and for the carbon paste sensor Mc_6 up to 15% of non-aqueous content. The results obtained are compiled in Table 4.3 and 4.4. Above the tolerance level of the sensors Tm_6 and $Mc_{6,}$ the slope gets affected which may be due to leaching of the ligand into the sample solution.

4.5.5 Potentiometric selectivity

The selectivity is the most important characteristic of a sensor as it determines the extent of the utility of the sensor in real sample measurement. The potentiometric selectivity coefficients of the sensors Tm_6 and Mc_6 towards different cations were determined by the Fixed Interference Method[174,220]. The selectivity coefficient values were determined at 1.0×10^{-2} M concentration of foreign ions and at varying concentration of Mn^{2+} ions. The selectivity coefficients were calculated using equation (1).

The sensors Tm_6 and Mc_6 show good selectivity for Mn^{2+} ions in the presence of Cr^{3+}, Co^{2+}, Fe^{2+}, Cu^{2+}, Zn^{2+}, Sn^{2+}, Hg^{2+}, Pb^{2+}, Ni^{2+}, Ca^{2+}, Ba^{2+}, Cd^{2+} K^+, Ag^+ and Na^+. The selectivity coefficient values are consolidated in Table 4.5.

4.6 Analytical application

The utility of the sensors Tm_6 and Mc_6 were also investigated by applying them as an indicator electrode in conjuction with Hg | $Hg_2Cl_{2,}$ KCl (sat.) in the potentiometric titration of manganese (II) chloride solution with EDTA. The pH of the solution was adjusted at 6.0. The titration curves for the sensors Tm_6 and Mc_6 are depicted in Figure 4.11 and Figure 4.12. The titration plots obtained were not the standard sigmoid shape but the plots show a sharp break point that corresponds to 1:1 stoichiometry of Mn-EDTA complex. This break point is taken as the end point of the titration.

4.7 Conclusion

The two sensors Tm_6 and Mc_6 are found to have very good response characteristics. The PVC type membrane sensor, Tm_6 show better response characteristics in all respects and it has a shelf life of 4 months. The shelf life of the carbon paste sensor is only 3 weeks but the surface could be renewed by cutting off a little of the paste, polishing it on a smooth surface and reconditioning in 1.0×10^{-1} M manganese chloride solution. Table 4.6 consolidates the response characteristics of the sensors Tm_6 and Mc_6.

The comparison of the characteristics of the developed sensors with some of the reported sensors for manganese is summarized in Table 4.7. It can be seen that the developed sensors are superior in terms of working concentration range[121,125], slope[121,229], and pH range[121,229]. The sensor Tm_6 is superior in terms of life time[116, 121,227,228,229].

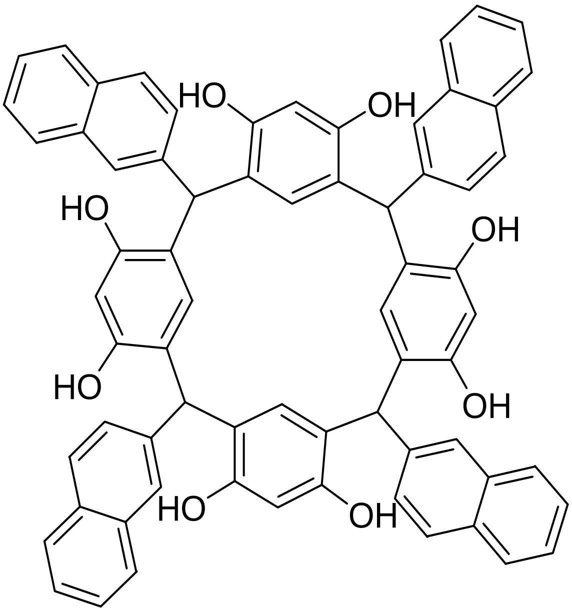

Figure 4.1 – Structure of the ionophore - TNCR

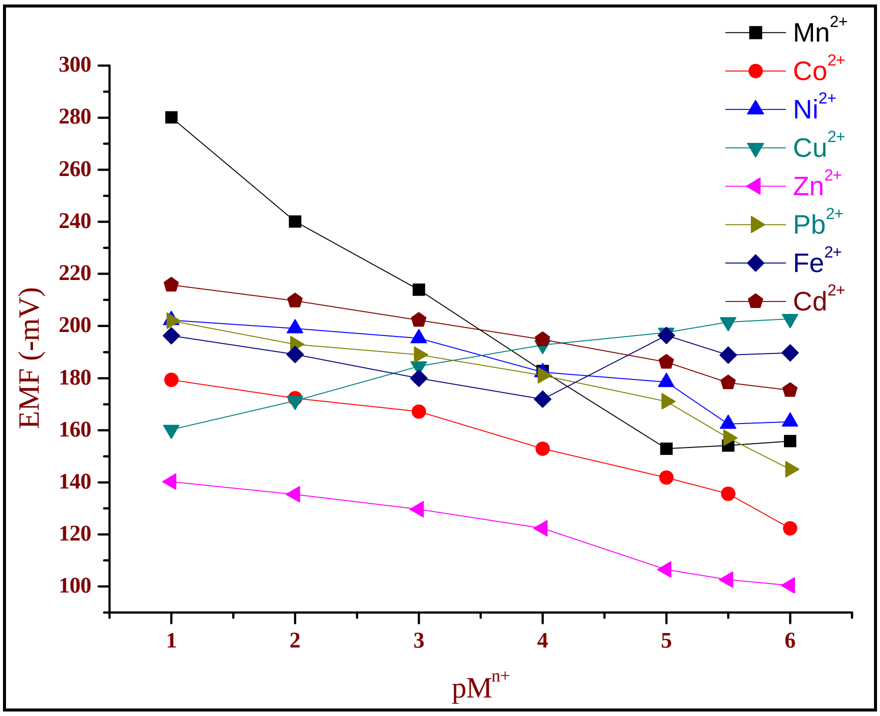

Figure 4.2 - Potential response of the PVC membrane sensor based on TNCR to different cations.

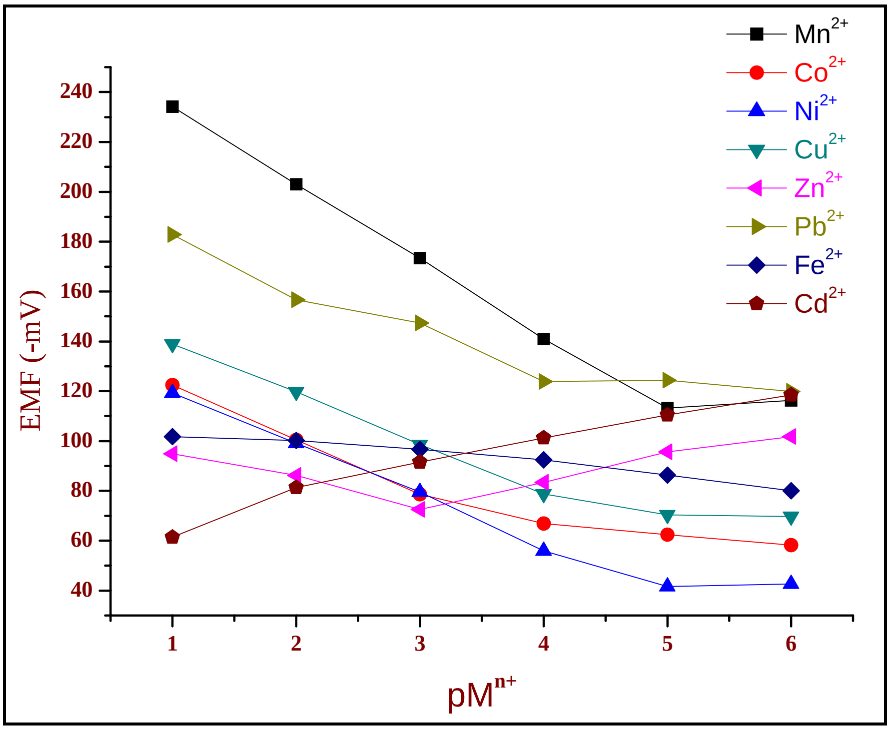

Figure 4.3 - Potential response of the carbon paste sensor based on TNCR to different cations.

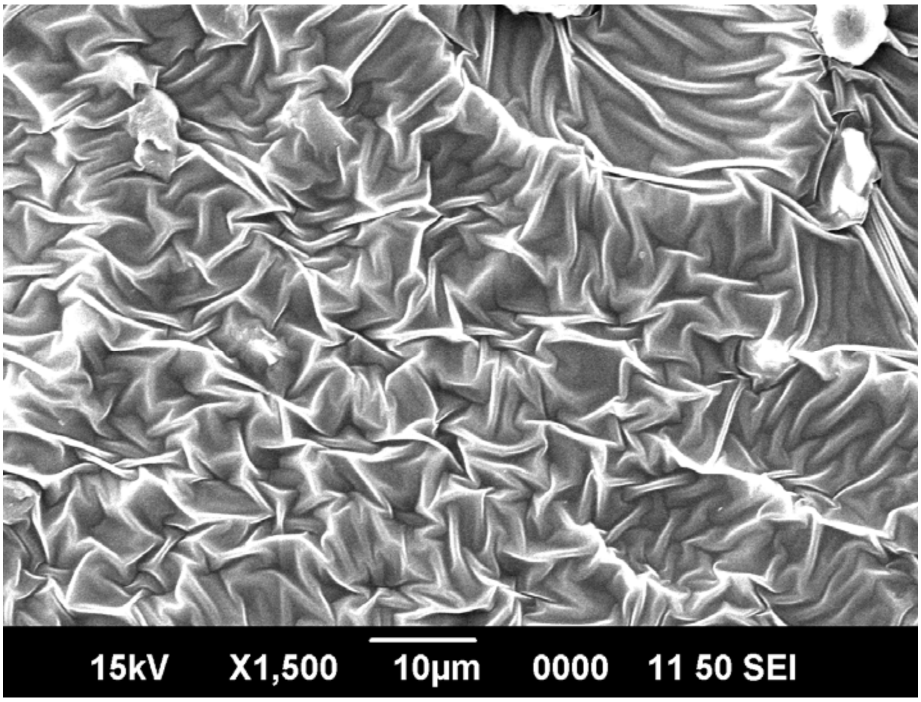

Figure 4.4 SEM image of the PVC membrane sensor Tm_6 based on TNCR

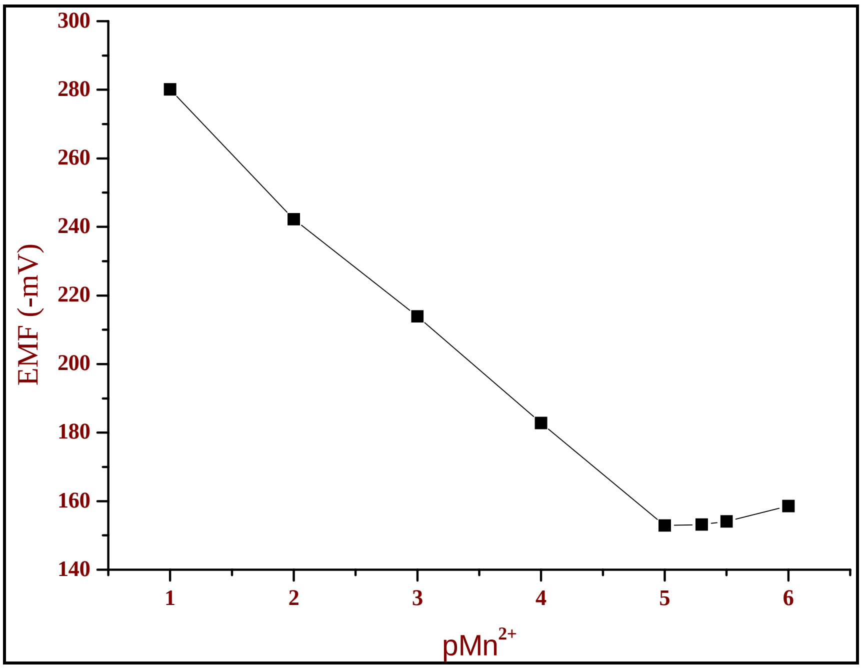

Figure 4.5 – Calibration graph of the PVC membrane sensor Tm_6 based on TNCR

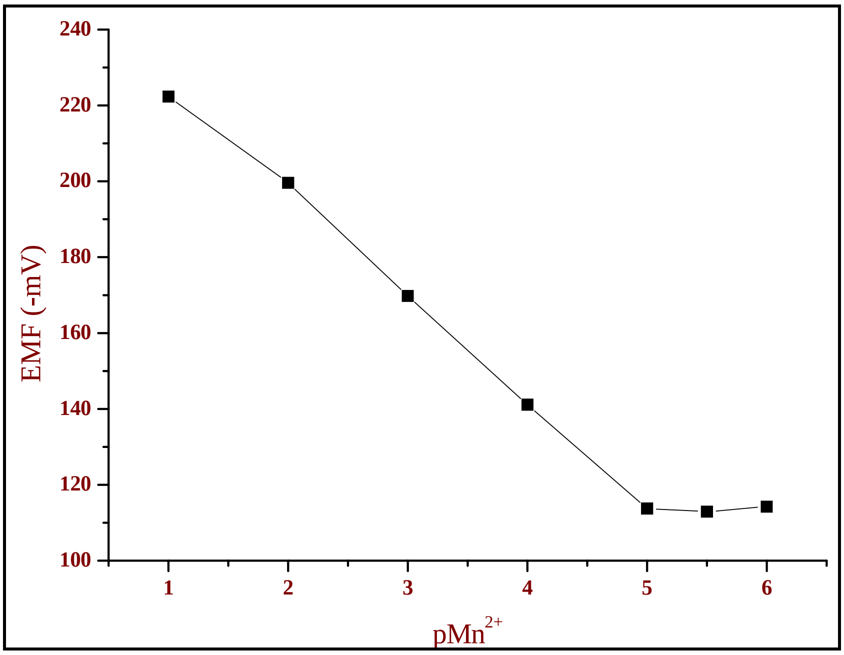

Figure 4.6 – Calibration graph of the carbon paste sensor Mc_6 based on TNCR

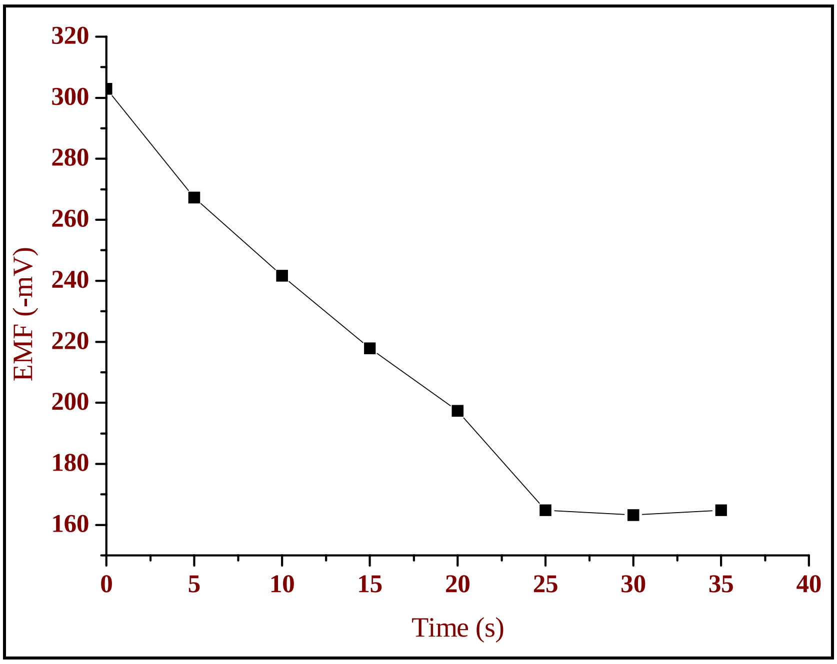

Figure 4.7 - Practical response time of the PVC membrane sensor Tm_6 based on TNCR

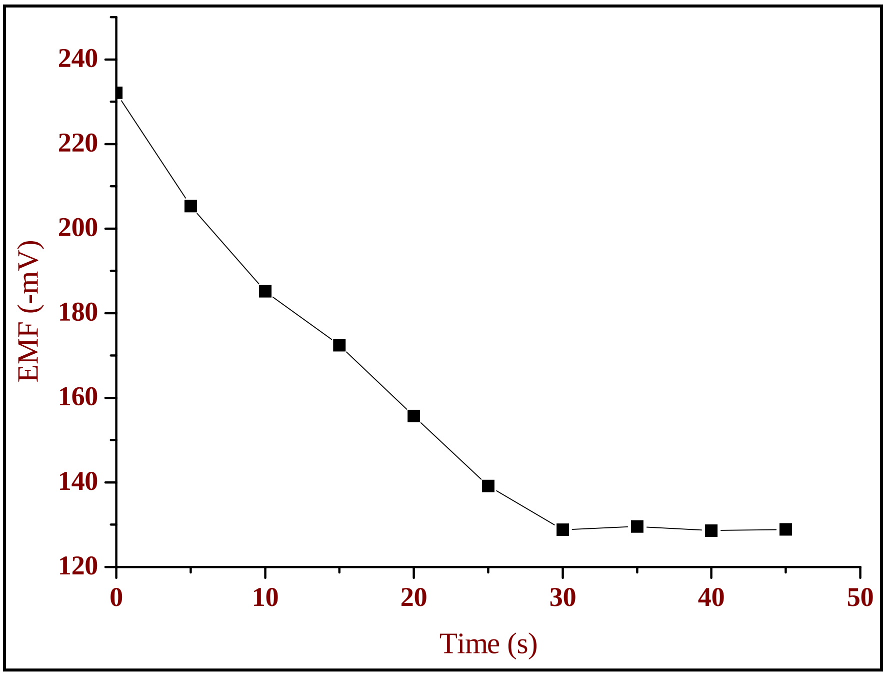

Figure 4.8 - Practical response time of the carbon paste sensor Mc_6 based on TNCR

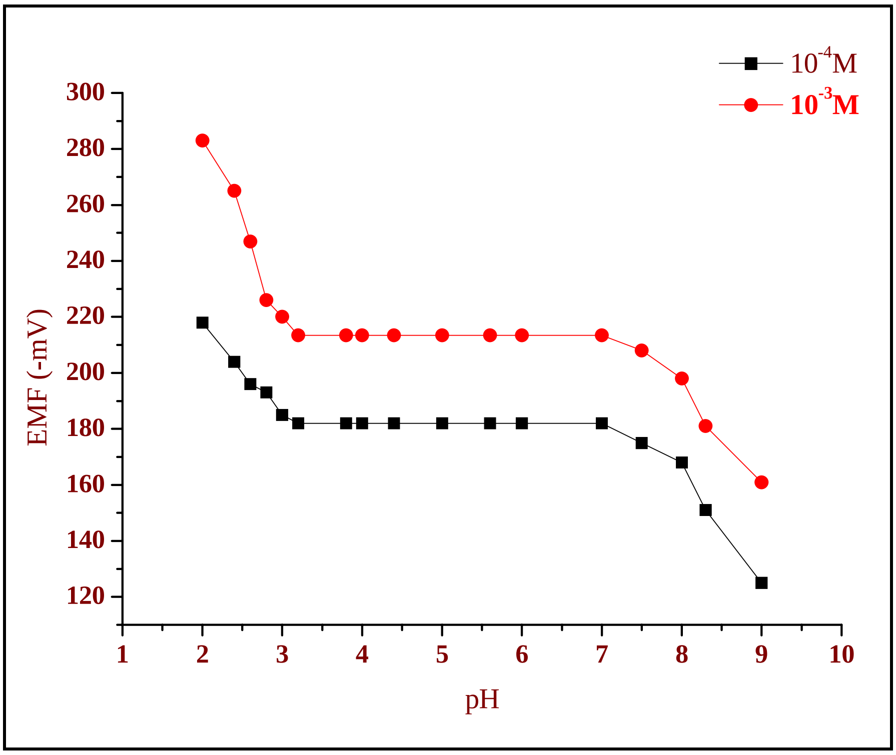

Figure 4.9 – Effect of pH on the cell potential of the PVC membrane sensor Tm_6 based on TNCR

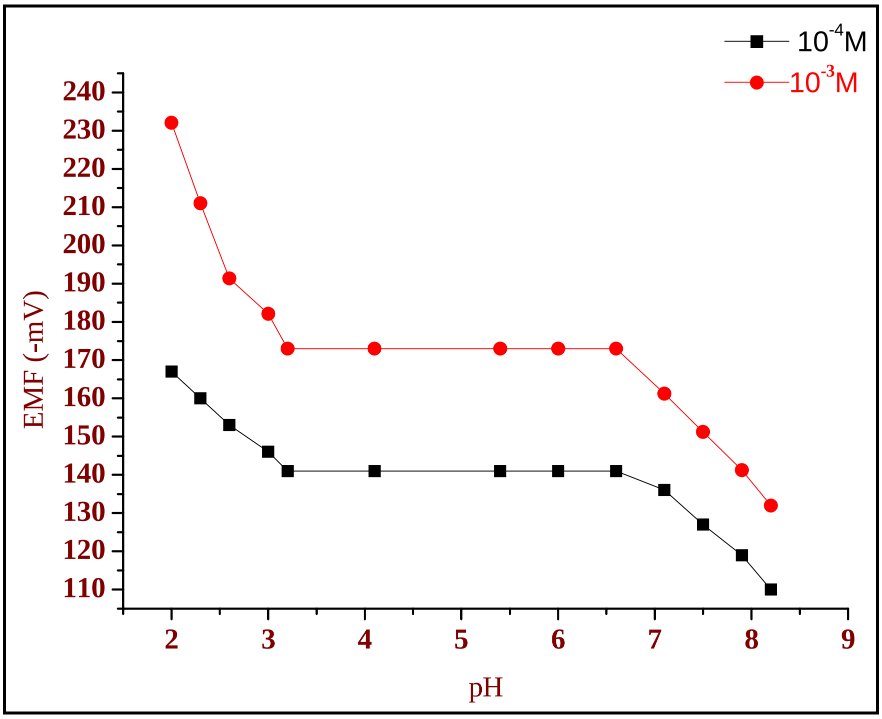

Figure 4.10 – Effect of pH on the cell potential of the carbon paste sensor Mc_6 based on TNCR

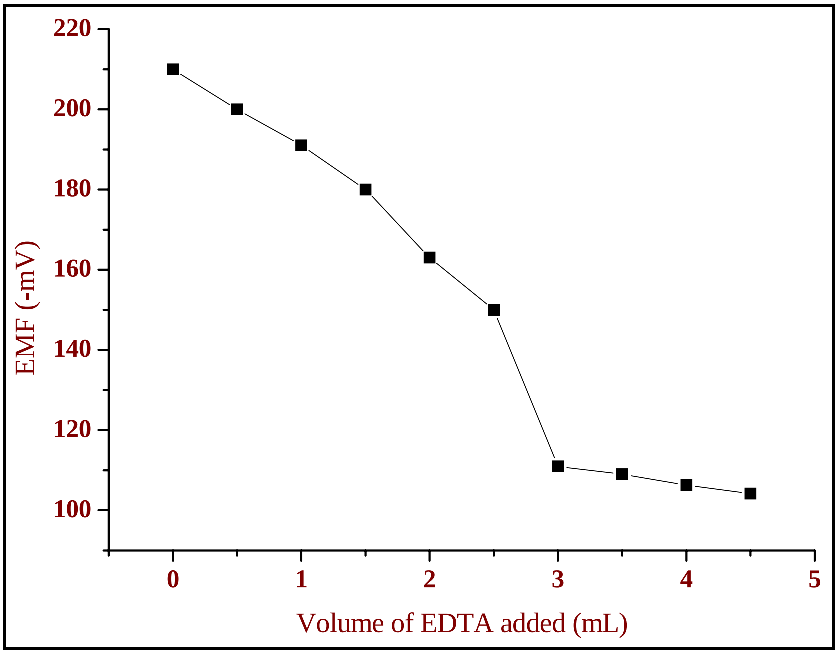

Figure 4.11 – Potentiometric titration curve of 25.0 mL of 1.0 × 10^{-3} M Mn^{2+} solution with 1.0 × 10^{-2} M EDTA using the PVC membrane sensor Tm_6 based on TNCR

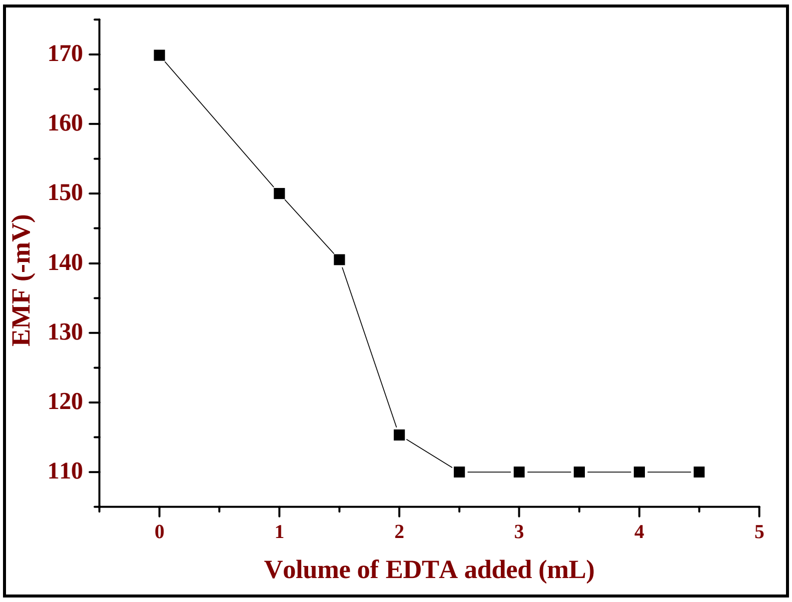

Figure 4.12 – Potentiometric titration curve of 25.0 mL of 5.0 × 10^{-3} M Mn^{2+} solution with 1.0 × 10^{-2} M EDTA using the carbon paste sensor Mc_6 based on TNCR

Table 4.1 – Optimization of the PVC membrane ingredients for the PVC membrane sensor based on TNCR

Sensor	**w/w % composition of each membrane**				**Working concentration range (M)**	**Slope (mV decade^{-1})**
	TNCR	**PVC**	**Plasticizer**	**NaTB**		
Tm$_1$	2.0	95	0	3	$1.0 \times 10^{-4} – 1.0 \times 10^{-1}$	19.2 ± 0.9
Tm$_2$	1.0	32	DOP, 64.0	3	$5.0 \times 10^{-4} – 1.0 \times 10^{-1}$	32.1 ± 0.6
Tm$_3$	1.2	32	DOP, 63.8	3	$1.0 \times 10^{-5} – 1.0 \times 10^{-1}$	32.1 ± 0.1
Tm$_4$	1.6	32	DOP, 63.4	3	$1.0 \times 10^{-4} – 1.0 \times 10^{-1}$	34.2 ± 0.6
Tm$_5$	1.8	32	DOP, 63.2	3	$8.0 \times 10^{-5} – 1.0 \times 10^{-1}$	33.5 ± 0.3
Tm$_6$	2.0	32	DOP, 63	3	$1.0 \times 10^{-5} – 1.0 \times 10^{-1}$	29.8 ± 0.4
Tm$_7$	3.0	32	DOP, 62.0	3	$1.0 \times 10^{-5} – 1.0 \times 10^{-1}$	32.1 ± 0.5
Tm$_8$	2.0	32	DOA, 63.0	3	$5.0 \times 10^{-1} – 1.0 \times 10^{-1}$	27.5 ± 0.4
Tm$_9$	2.0	32	DBP, 63.0	3	$5.0 \times 10^{-1} – 1.0 \times 10^{-1}$	31.9 ± 0.2
Tm$_{10}$	2.0	32	DMS, 63.0	3	$1.0 \times 10^{-4} – 1.0 \times 10^{-1}$	22.1 ± 0.9
Tm$_{11}$	2.0	32	DOS, 63.0	3	$1.0 \times 10^{-3} – 1.0 \times 10^{-1}$	25.9 ± 0.7
Tm$_{12}$	2.0	32	DBS, 63.0	3	$1.0 \times 10^{-3} – 1.0 \times 10^{-1}$	32.9 ± 0.8

Table 4.2 – Optimization of the ionophore composition for the carbon paste sensor based on TNCR

Sensor	**Ionophore**	**Graphite**	**Working Concentration range (M)**	**Slope (mV decade^{-1})**
Mc$_1$	0	100	– – – – –	3.5
Mc$_2$	2	98	$1.0 \times 10^{-3} – 1.0 \times 10^{-1}$	35.1 ± 0.2
Mc$_3$	4	96	$1.0 \times 10^{-4} – 1.0 \times 10^{-1}$	33.5 ± 0.5
Mc$_4$	6	94	$8.0 \times 10^{-5} – 1.0 \times 10^{-1}$	32.8 ± 0.4
Mc$_5$	8	92	$3.0 \times 10^{-5} – 1.0 \times 10^{-2}$	31.7 ± 0.1
Mc$_6$	10	90	$1.0 \times 10^{-5} – 1.0 \times 10^{-1}$	30.0 ± 0.5
Mc$_7$	12	88	$1.0 \times 10^{-5} – 1.0 \times 10^{-1}$	34.9 ± 0.3
Mc$_8$	15	85	$5.0 \times 10^{-4} – 1.0 \times 10^{-1}$	33.2 ± 0.2
Mc$_9$	20	80	$1.0 \times 10^{-3} – 1.0 \times 10^{-1}$	22.1 ± 0.6

Table 4.3 – Effect of partially non-aqueous medium on the slope and working concentration range of the PVC membrane sensor Tm_6

Non-aqueous content (%v/v)	Slope (mV decade^{-1})	Working concentration range (M)
0	29.8	$1.0 \times 10^{-5} – 1.0 \times 10^{-1}$
Ethanol		
10	29.6	$1.0 \times 10^{-5} – 1.0 \times 10^{-1}$
20	30.3	$2.6 \times 10^{-5} – 1.0 \times 10^{-1}$
25	28.2	$5.8 \times 10^{-5} – 1.0 \times 10^{-1}$
30	21.3	$1.0 \times 10^{-3} - 1.0 \times 10^{-1}$
Methanol		
10	29.3	$1.0 \times 10^{-5} – 1.0 \times 10^{-1}$
20	30.2	$3.4 \times 10^{-5} – 1.0 \times 10^{-1}$
25	28.3	$7.0 \times 10^{-5} – 1.0 \times 10^{-1}$
30	21.4	$1.0 \times 10^{-3} – 1.0 \times 10^{-1}$

Table 4.4 – Effect of partially non-aqueous medium on the slope and working concentration range of the carbon paste sensor Mc_6

Non-aqueous content (%v/v)	Slope (mVdecade^{-1})	Working concentration Range (M)
0	30.5	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$
Ethanol		
10	30.6	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$
15	30.3	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$
20	19.8	$3.2 \times 10^{-4} - 1.0 \times 10^{-1}$
Methanol		
10	30.9	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$
15	29.7	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$
20	20.5	$2.0 \times 10^{-4} - 1.0 \times 10^{-1}$

Table 4.5 - Selectivity coefficients for the sensors Tm_6 and Mc_6 using Fixed Interference Method at 1.0×10^{-2} M concentration of interfering ion

Interfering ion (X)	Tm_6	Mc_6
Cd^{2+}	8.6×10^{-4}	7.9×10^{-4}
Co^{2+}	4.1×10^{-3}	3.1×10^{-3}
Sn^{2+}	5.6×10^{-3}	6.9×10^{-3}
Cu^{2+}	7.5×10^{-3}	7.9×10^{-3}
Zn^{2+}	4.4×10^{-3}	4.6×10^{-3}
Pb^{2+}	6.2×10^{-3}	7.1×10^{-3}
Hg^{2+}	2.7×10^{-3}	3.1×10^{-3}
Fe^{2+}	6.9×10^{-4}	6.8×10^{-4}
Na^{+}	8.1×10^{-4}	9.2×10^{-4}
K^{+}	9.3×10^{-4}	8.4×10^{-3}
Ag^{+}	5.6×10^{-2}	4.9×10^{-2}
Ni^{2+}	2.1×10^{-1}	2.9×10^{-3}
Ca^{2+}	2.8×10^{-3}	3.1×10^{-3}
Cr^{3+}	6.5×10^{-3}	7.2×10^{-3}
Ba^{2+}	3.8×10^{-3}	3.3×10^{-3}

Table 4.6 - Response characteristics of the sensors Tm_6 and Mc_6

Parameter	Response characteristics	
	Tm_6	Mc_6
Working concentration range (M)	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$
Slope (mV decade^{-1})	29.8 ± 0.4	30.0 ± 0.5
Detection Limit (M)	5.1×10^{-6}	6.5×10^{-6} M
Response time	25 s	30 s
pH range	3.2 – 7.0	3.2 – 6.6
Non aqueous tolerance limit	25%	15%
Shelf life	4 months	3 weeks

Table 4.7 A comparative study of the characteristics of the developed sensors for manganese with some reported sensors

No	Working concentration range (M)	pH range	Life Time	Slope (mV decade^{-1})	Ref. No.
1	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$	4.0 - 8.0	3 months	29.6 ± 0.5	227
2	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$	4.0 - 9.0	2 months	29.3 ± 0.5	228
3	$1.2 \times 10^{-5} - 1.0 \times 10^{-1}$	3.0 - 8.0	4 months	28.5 ± 0.3	125
4	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$	NM	NM*	Non Nernstian	229
5	$5.0 \times 10^{-5} - 1.0 \times 10^{-3}$	4.0	2 weeks	Near Nernstian	121
6	$5.0 \times 10^{-6} - 1.0 \times 10^{-1}$	3.0 - 6.5	NM*	30.0 ± 0.3	116
7	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$	3.2 – 7.0	4 months	29.8 ± 0.4	Tm_6
8	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$	3.2 – 6.6	3 weeks	30.0 ± 0.5	Mc_6

*NM – not mentioned

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Chapter 5

SENSORS FOR NICKEL

Contents

This chapter describes the response characteristics of two types of sensors based on calix[4]resorcinarene for the determination of nickel ions. Various parameters that illustrate the response of the sensors were also investigated in detail. The analytical applications of the developed sensors have been illustrated in the form of potentiometric titration plots and also by the determination of nickel in real samples. A comparison of the developed sensors with some of the reported sensors has also done.

Pure nickel is a hard, silvery white metal which is ductile. Nickel compounds are widely used for nickel plating, to colour ceramics, to make rechargeable batteries, in stainless steel, alnico magnet, electric guitar strings, microphone capsules and as a catalyst. It is present in low concentration in red meat, cotton seed, hydrogenated vegetable oils, chocolates, soya beans, oatmeal, cornmeal, milk and milk products. Enzymes of some microorganisms and plants contain nickel as an active centre, which makes the metal an essential nutrient for them.

If nickel concentration exceeds the normal level, it may become a potential health hazard. Nickel toxicity can cause acute pneumonitis, dermatitis, asthma, cancer of lungs, adverse effects on blood and kidneys and disorders of central nervous system[230,231]. Due to the importance of nickel in biological system and industry and a narrow window of concentration between essentiality and toxicity, nickel monitoring has become quite essential. A number of analytical methods such as injection spectrophotometry, Atomic Absorption Spectrometry (AAS), ICP-AES, and flame photometry have been used for the trace level analysis of nickel. But these methods have some practical inconveniences as they need sample pre treatment and require infrastructure back up whereas ISEs provide a mean of determining ions most conveniently, economically and without any sample pre treatment.

This chapter describes the fabrication of two types of sensors - a PVC membrane sensor and a carbon paste sensor - using calix[4]resorcinarene as an ionophore.

5.1 Synthesis of the Ionophore

The ionophore used for the fabrication of sensors for nickel is 2,8,14,20-tetrakis(3,4-dimethoxyphenyl)calix[4]resorcinarene. It was synthesised by taking a 1:1 mixture of veratraldehyde and resorcinol along with a catalytic amount of p-toluene sulphonic acid and they were mixed together in a mortar and pestle and ground vigorously. The final product was washed with water and recrystallised from methanol. The synthesis and characterization of the ionophore, 2,8,14,20-tetrakis(3,4-dimethoxyphenyl)calix[4]resorcinarene (TDPCR) has been discussed in detail under section 2.2.3 in chapter 2. The structure of TDPCR is shown as Figure 5.1.

5.2 Sensors based on TDPCR

Two types of sensors - PVC membrane sensor and carbon paste sensor - were fabricated using TDPCR as ionophore. The potential responses of both the sensors towards different cations are shown as Figure 5.2 and Figure 5.3.

5.3 Fabrication of the Sensors

The fabrication of the PVC membrane sensor was in accordance with the procedure reported by Cragg and Moody[173]. The detailed procedure for the fabrication of the PVC membrane is discussed in section 2.6.1 in chapter 2. The sensing material ie; the ionophore, plasticizer, anion excluder and PVC are dissolved in 5-7 mL of THF. The resulting solution was then poured into small rings glued to a glass plate. The membrane formed after the slow evaporation of the solvent is cut out and glued to one end of a glass tube. The tube was filled with 1.0×10^{-1} M $(NiNO_3)_2$ solution and it was conditioned by soaking in 1.0×10^{-1} M $(NiNO_3)_2$ solution for 24 hours.

The selectivity and sensitivity of a sensor largely depends on the nature of the plasticizer and also on the ratio of the PVC, plasticizer and ionophore in the matrix. An appropriate selection of these constituents results in a highly selective and sensitive sensor that exhibits a stable and reproducible potential response[232]. So while fabricating PVC membrane sensor for nickel ions all these factors were considered and DOP was used as the plasticizer. The best membrane composition was found to be 31: 61: 2: 6 (PVC: DOP: NaTPB: TDPCR) (w/w%).

Carbon paste sensor forms an important class of chemical sensors and it possesses the advantage that it requires no internal filling solution.

The fabrication of these type of sensors is simple fast and easy. Carbon paste sensors have been successfully applied as potentiometric sensors for the determination of various species[233].

The ionophore and graphite in suitable proportion was mixed thoroughly. The mixture was made into a paste using a suitable binder. The resulting paste was packed into a Teflon holder. A copper rod through the centre of the electrode body provides the electrical contact. It was conditioned by soaking in 1.0×10^{-1} M $(NiNO_3)_2$ solution for 12 hours.

5.4 Potential measurement and calibration

A Metrohm 781 ion meter was used for potential measurements. All emf measurements were carried out at $25 \pm 1^{o}C$. A saturated calomel electrode was used as the external as well as the internal reference electrode. The electrochemical cell assembly may be represented as follows:

For PVC membrane sensor:

External reference electrode | test solution | PVC membrane based on TDPCR | internal filling solution (0.1M Ni^{2+}) | internal reference electrode

For carbon paste sensor

Reference electrode | test solution | carbon paste electrode based on TDPCR

Standard solutions of the analyte were prepared by serial dilution of the stock solution. The EMF of the cell was directly measured by the developed sensors using the previously mentioned cell assembly. Calibration graph was obtained by plotting EMF (mV) versus pNi^{2+}. The calibration graph was used for subsequent determination of unknown solutions.

The performance characteristics of the developed sensor are described in terms of its linear concentration range, detection limit, slope, response time and shelf life. These factors are discussed in detail in the next section.

5.5 Optimization studies of the two types of sensors

The response characteristic of a sensor is influenced by the type and properties of the PVC matrix used for the fabrication of the sensor. The PVC acts as a regular support matrix for the membrane. A plasticizer increases the flexibility, softness and workability of the membrane. It influences the sensitivity, selectivity and working concentration range of the sensor due to the variation in free energy of interaction of the electroactive ions and ionophore in polymer matrices. Addition of plasticizers improves sensitivity and selectivity of the PVC membrane and gives a better response[234]. Among the different plasticizers used DOP was found to be the most effective plasticizing agent while others gave a non Nernstian response. The properties of the polymer matrix depend on the amount of the ionophore and plasticizer used.

The amount of the ionophore is one of the parameters which influence the response characteristics of the sensor. The variation in the slope with change in the membrane composition is represented in Table 5.1. The optimum amount of the ionophore for the sensor based on TDPCR was found to be 6.0 (%w/w). A further increase in the amount of ionophore resulted in a diminished response, which may be attributed to the saturation of membrane.

The effect of anionic excluder was also studied as the incorporation of these lipophilic additives can significantly influence the response characteristics of the sensor developed. It was found that the best response is for the sensor having 2% of sodium tetraphenyl borate (NaTPB). The composition ratio that gave the best response in terms of working concentration range, response time and slope was found to be 6 : 31 : 61 : 2 for (TDPCR : PVC : DOP : NaTPB). The sensor Tn_5 with this composition was used for further studies.

The SEM image of the membrane of the sensor Tn_5 was taken in order to investigate the surface morphology and is shown as Figure 5.4. The SEM image shows that the membrane is homogeneous. SEM is a strong and reliable tool for studying in detail the surface morphology of the membranes and the reproducibility of the preparation conditions.

The response of the carbon paste sensor also depends on the composition of the sensor matrix. Table 5.2 illustrates the variation in the slope of the sensor with change in the ionophore to graphite ratio. A set of 9 different sensors were fabricated by varying the sensor matrix composition. The sensor Nc_1 without ionophore showed negligible response to nickel ions. It was found that the sensor Nc_6 with composition ratio 18 : 82 (TDPCR : graphite) was best in terms of response time, working concentration range and slope. On increasing the amount of the ionophore non linearity in the response of the sensor was observed which may be due to the decrease in the conductance of the sensing material. So the sensor Nc_6 was selected for further studies.

5.5.1 Working concentration range and slope

The calibration plot of the EMF (mV) versus pNi^{2+} for the sensors Tn_5 and Nc_6 are shown as Figure 5.5 and Figure 5.6 respectively. The working concentration range for the sensors Tn_5 and Nc_6 are found to be $8.0 \times 10^{-7} – 1.0 \times 10^{-1}$ M and $5.0 \times 10^{-6} – 1.0 \times 10^{-1}$ M respectively. The slope calculated from the calibration graph was found to be 28.5 (±0.5) mV $decade^{-1}$ and 29.8 (±0.8) mV $decade^{-1}$ for the sensors Tn_5 and Nc_6 respectively. The detection limit was calculated from the graph by the intersection of the two extrapolated linear segments of the calibration plot and was found to be 2.7×10^{-7} M and 2.9×10^{-6} M for the sensors Tn_5 and Nc_6 respectively.

5.5.2 Effect of concentration of internal filling solution

The influence of concentration of the internal filling solution on the response characteristics of the PVC membrane sensor Tn_5 was studied. The concentration of the internal filling solution was changed from 1.0×10^{-1} M - 1.0×10^{-4} M. The calibration plot was obtained in each case. It has been observed that there is no change in the response of the sensor Tn_5 when the concentration of the internal filling solution was changed. Hence the concentration of the internal filling solution was fixed at 1.0×10^{-1} M for all studies. For the carbon paste type sensors no internal filling solution is required.

5.5.3 Response time and life time of the sensors

The plot of the changes in EMF with respect to time for the sensors Tn_5 and Nc_6 are shown as Figure 5.7 and Figure 5.8 respectively. The practical response time for the sensors Tn_5 and Nc_6 was obtained from the plot and was found to be 10 s and 20 s respectively. The average life time or the shelf life of the developed sensors was studied. The working surface of the carbon paste electrode can be renewed. The potential measurements were recorded everyday over a period of time to determine the shelf life of the sensors. The slope was calculated and compared with the slope of the original calibration plot. The sensor Tn_5 showed a decrease in potential response after a period of 4 months and the sensor Nc_6 worked well without a decrease in potential for a period of 3 weeks. When not in use the sensors were kept in 1.0×10^{-1} M Ni^{2+} solution. After this period a decrease in the stability of the sensors was observed which may be due to the leaching of the ionophore from the sensing membrane.

5.5.4 Effect of pH and non aqueous media

The pH dependence on the EMF response of the developed sensors Tn_5 and Nc_6 was investigated for two different concentrations 1.0×10^{-3} M and 1.0×10^{-4} M of Ni^{2+} solution, over a pH range of 2.0 – 9.0. The pH was adjusted by introducing small drops of nitric acid (0.05M) or sodium hydroxide (0.05M). The results for the sensors Tn_5 and Nc_6 are shown as Figure 5.9 and Figure 5.10 respectively. Figure 5.9 reveals that the EMF is independent of pH in the range 4.5 – 8.3 for the sensor Tn_5 and Figure 5.10 show that for the sensor Nc_6 EMF is independent of pH in the range 4.6 – 8.0. Hence the working pH range for the sensor Tn_5 is 4.5 – 8.3 and for the sensor Nc_6 it is 4.6 – 8.0. The observed drift in the potential values may be related to the response of the membrane sensor to H^+ ions at low pH and to the formation of some Ni^{2+} hydroxyl complexes at higher pH values[235,236].

The working of the sensors Tn_5 and Nc_6 was also studied in partially non aqueous media using ethanol-water mixture and methanol-water mixture. The PVC membrane sensor Tn_5 worked satisfactorily in mixtures having 25% (v/v) non aqueous content whereas for the carbon paste sensor

Nc_6 the non aqueous tolerance limit is 15% (v/v). Above the tolerance level, the slopes get affected which may be due to the leaching of the ligand into the sample solution. The results obtained for the sensors Tn_5 and Nc_6 are compiled in Table 5.3 and 5.4 respectively.

5.5.5 Potentiometric selectivity

One of the most important characteristics of any ion selective sensor is its response to the primary ion in the presence of other ions in solution. This is expressed in terms of potentiometric selectivity coefficient. The potential response of the developed sensors Tn_5 and Nc_6 in presence of other ions was investigated by the Fixed Interference Method (FIM)[174,220]. In the determination of the selectivity coefficient values the concentration of the interfering ions was kept at 1.0×10^{-2} M and the selectivity coefficient values are calculated using equation (1).

The calculated selectivity coefficients are summarized in Table 5.5. The results reveal that sensors Tn_5 and Nc_6 show good selectivity for Ni^{2+} ions in the presence of Cr^{3+}, Mn^{2+}, Co^{2+}, Fe^{2+}, Cu^{2+}, Zn^{2+}, Sn^{2+}, Hg^{2+}, Pb^{2+}, Cd^{2+}, Na^+ and Ag^+.

5.6 Analytical applications

The developed sensors Tn_5 and Nc_6 were successfully applied for the determination of Ni^{2+} content in real samples like chocolate, vegetable oil (Dalda) and waste water samples from electroplating industries. The preparation of the real samples is discussed in detail in section 2.5 of chapter 2. The results of the analysis are presented in Table 5.6 and it shows that the method is comparable to the standard ICP-AES.

The developed sensors Tn_5 and Nc_6 were also used as an indicator electrode in conjuction with Hg | Hg_2Cl_2, KCl (sat.) in the potentiometric titration of Ni^{2+} solution with EDTA. The titration curve is shown as Figure 5.11 and Figure 5.12 for the sensors Tn_5 and Nc_6 respectively. The plots are not of sigmoid shape but the sharp break point corresponds to the stoichiometry of the Ni-EDTA complex.

5.7 Conclusion

Both Tn_5 and Nc_6 were found to have very good response characteristics. They revealed good selectivity over a wide variety of cations. Table 5.7 consolidates the response characteristics of the sensors Tn_5 and Nc_6. PVC membrane sensor Tn_5 is superior to carbon paste sensor Nc_6 in terms of working concentration range, detection limit, response time and in tolerance limit in non- aqeous content. The shelf life of carbon paste sensor is only 3 weeks but it had an advantage that the surface could be renewed by cutting off a little of the paste, polishing it on a smooth surface and reconditioning it in 1.0×10^{-1} M $(NiNO_3)_2$ solution.

Table 5.8 lists the comparative study of the characteristics of developed sensors with some of the reported sensors for Ni^{2+}. Sensors Tn_5 and Nc_6 are superior in terms of working concentration range[235,236,237,239,131,132,133,134], slope[238,132,133,137] and Tn_5 is superior in terms of life time[240,239,238,237,133,137] when compared with the performance of the above sensors.

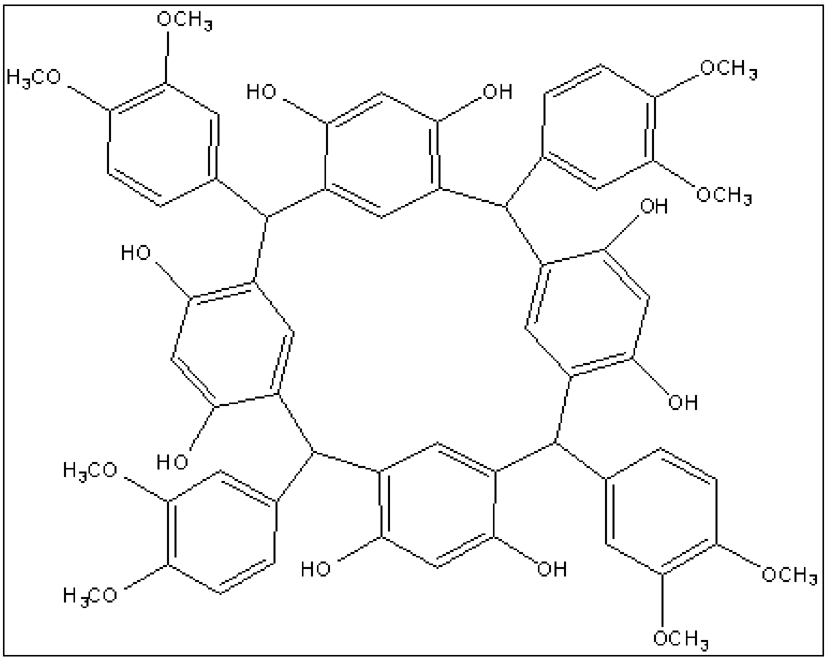

Figure 5.1 – Structure of the ionophore TDPCR

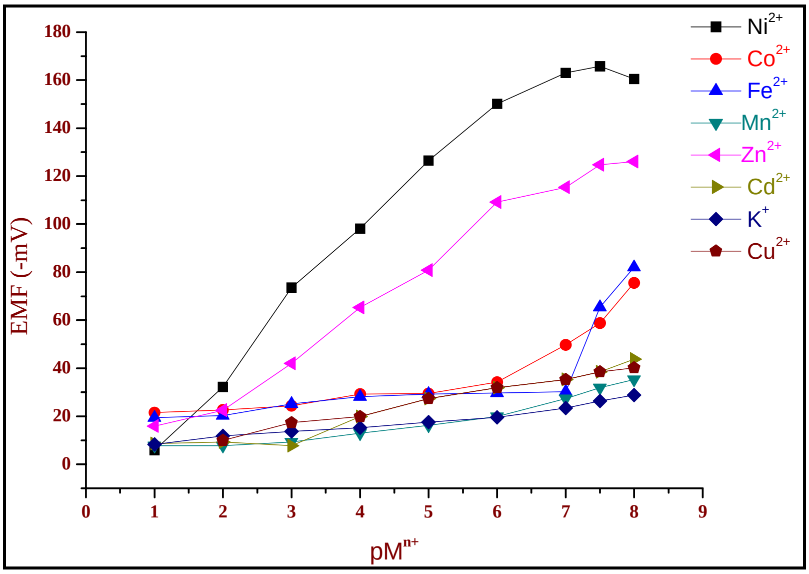

Figure 5.2 - Potential response of the PVC membrane sensor based on TDPCR to different cations.

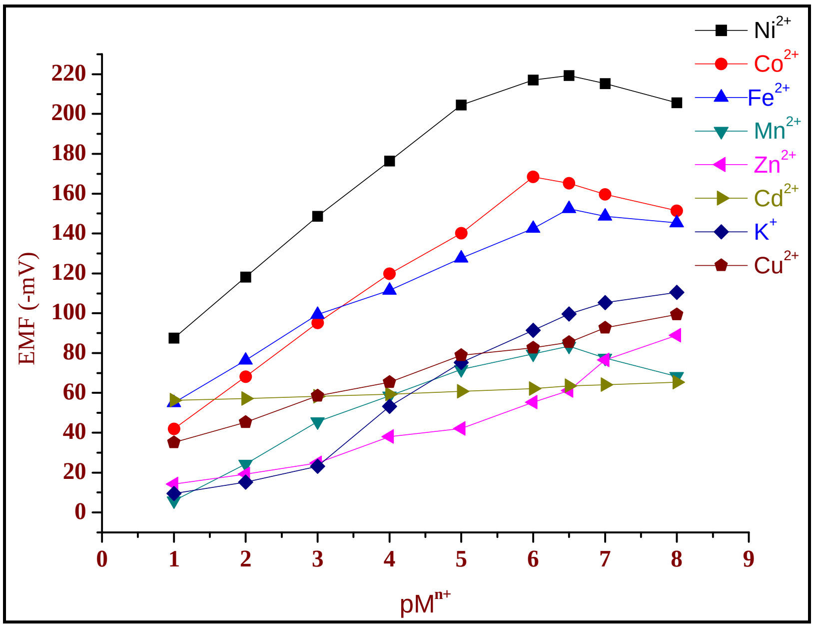

Figure 5.3 - Potential response of the carbon paste sensor based on TDPCR to different cations.

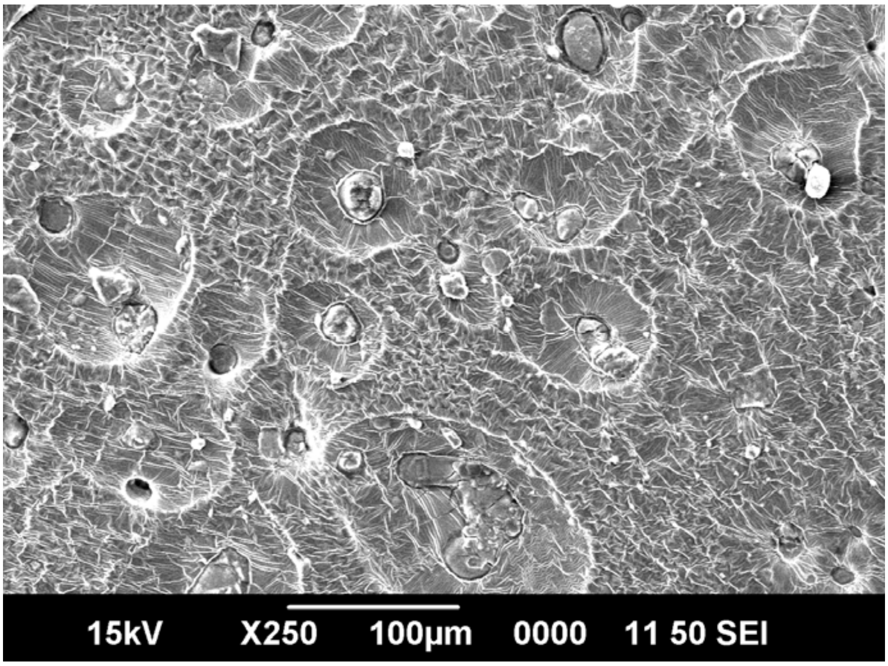

Figure 5.4 - SEM image of the polymeric membrane of the sensor Tn_5

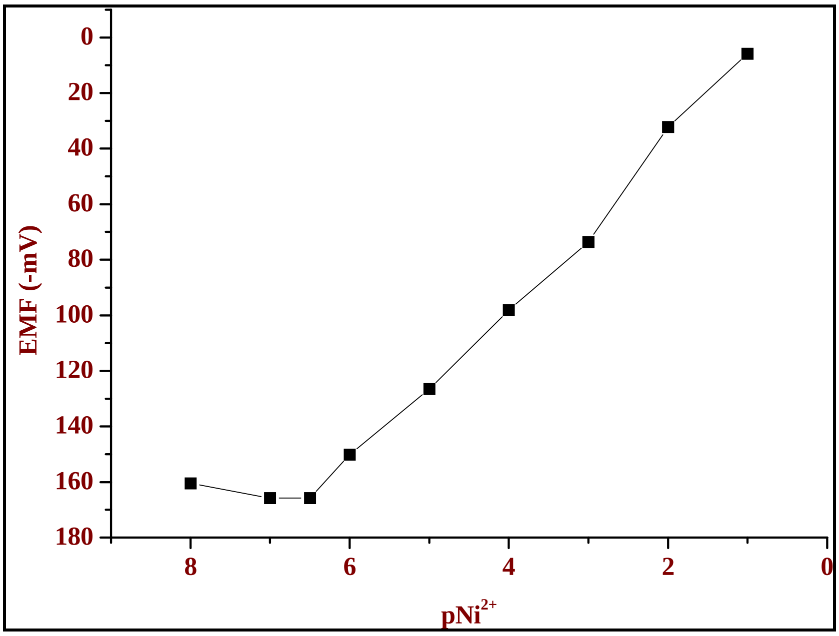

Figure 5.5 – Calibration graph of the PVC membrane sensor Tn_5 based on TDPCR

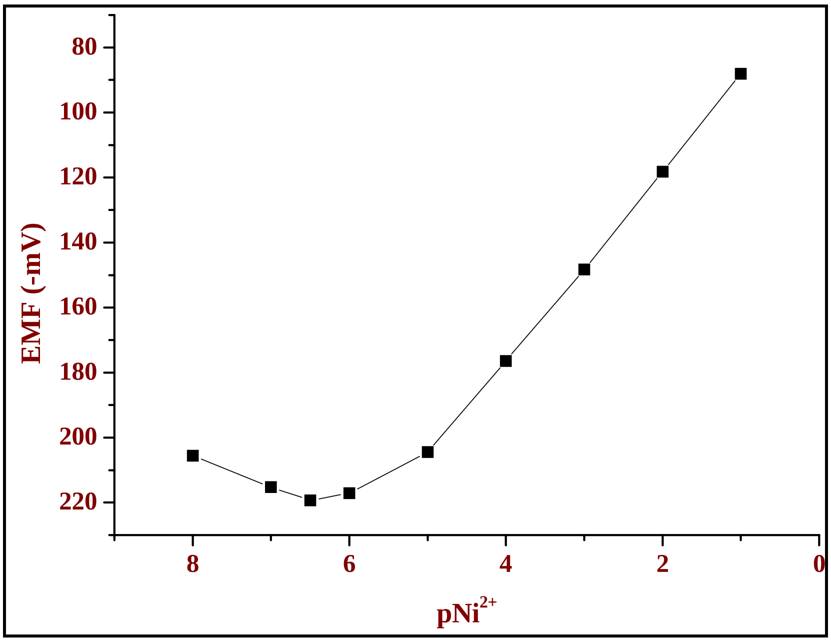

Figure 5.6 – Calibration graph of the carbon paste sensor Nc_6 based on TDPCR

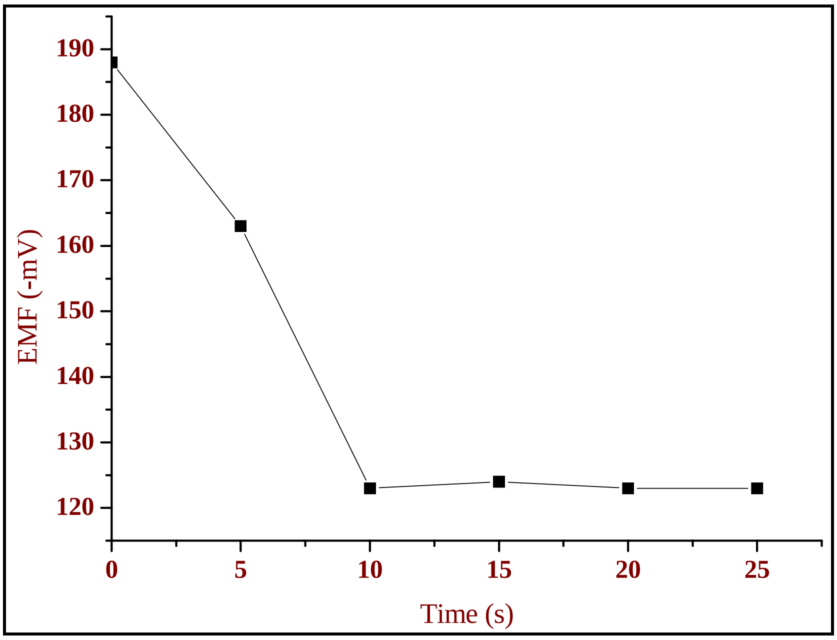

Figure 5.7 - Practical response time of the PVC membrane sensor Tn_5 based on TDPCR

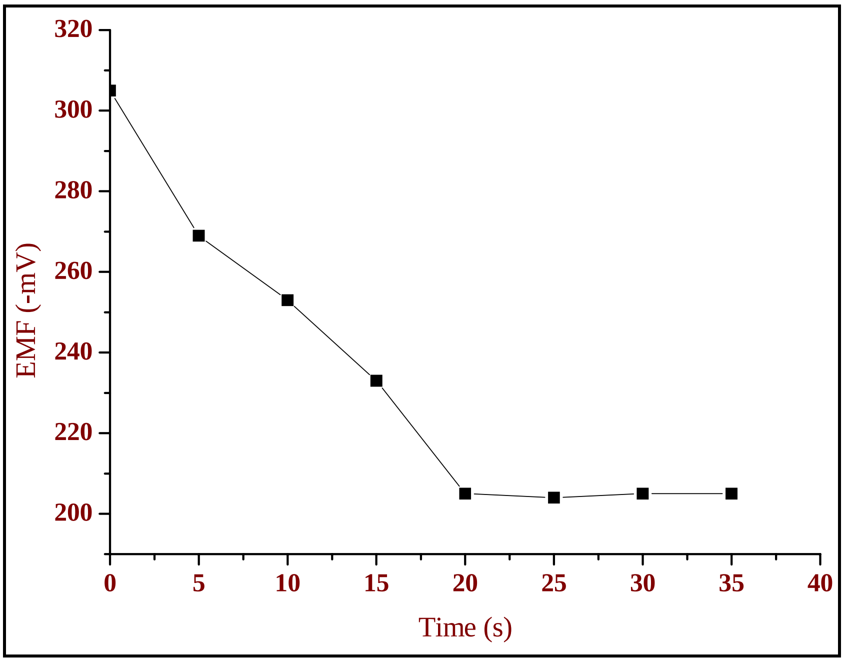

Figure 5.8 - Practical response time of the carbon paste sensor Nc_6 based on TDPCR

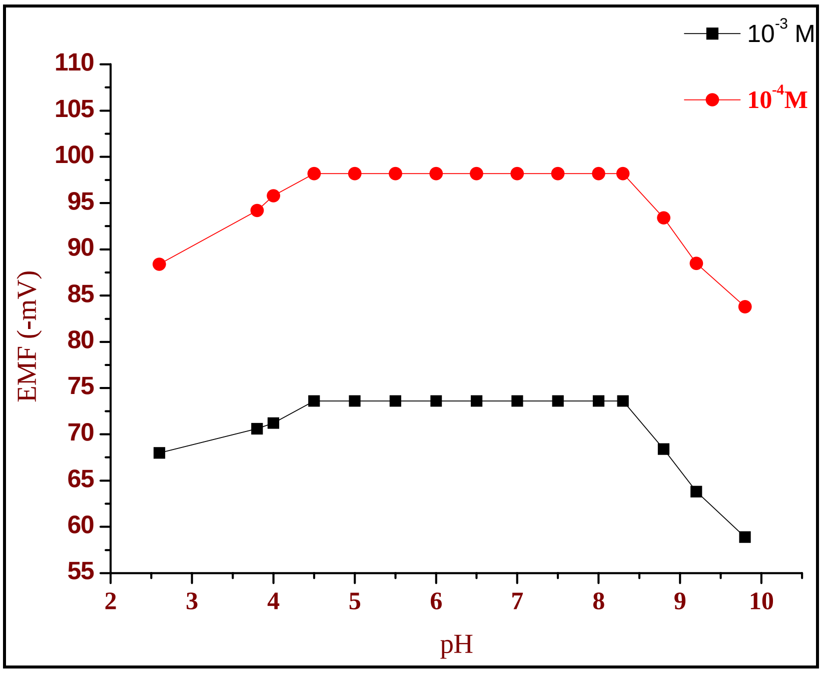

Figure 5.9 – Effect of pH on the cell potential of the PVC membrane sensor Tn_5 based on TDPCR

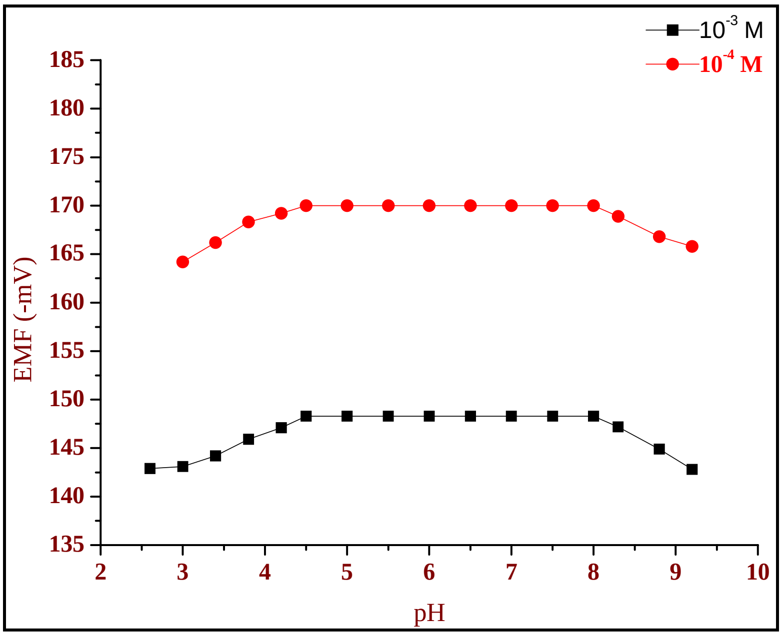

Figure 5.10 – Effect of pH on the cell potential of the carbon paste sensor Nc_6 based on TDPCR

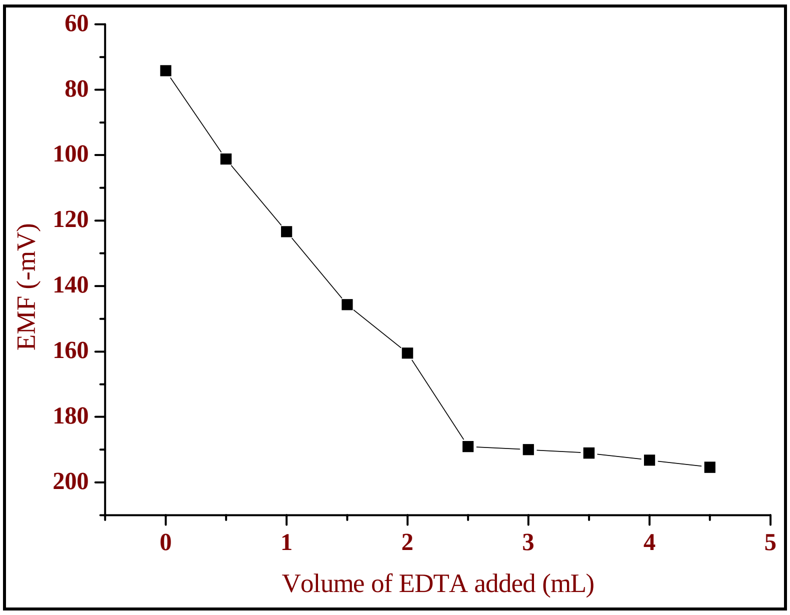

Figure 5.11 – Potentiometric titration curve of 25.0 mL of 1.0 × 10^{-3} M Ni^{2+} solution with 1.0 × 10^{-2} M EDTA using the sensor the PVC membrane sensor Tn_5 based on TDPCR

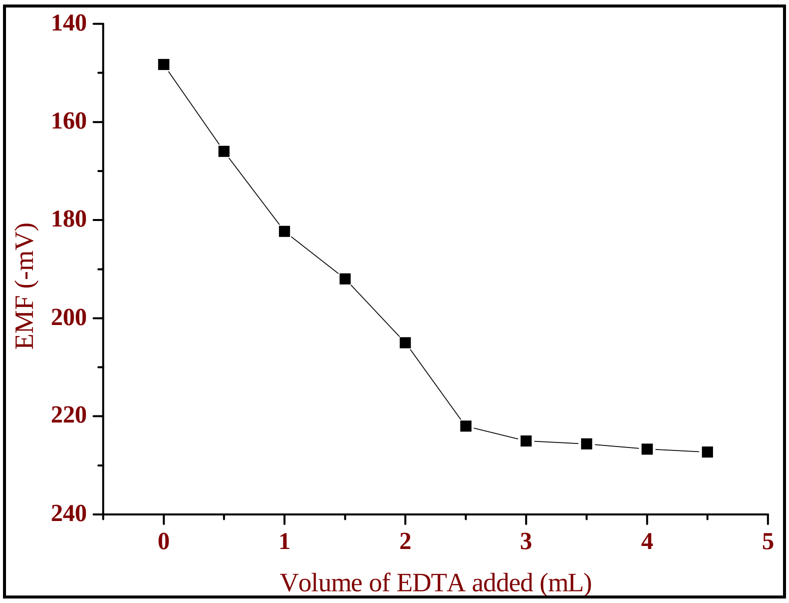

Figure 5.12 – Potentiometric titration curve of 25.0 mL of 1.0×10^{-3} M Ni^{2+} solution with 1.0×10^{-2} M EDTA using the carbon paste sensor Nc_6 based on TDPCR

Table 5.1 – Optimization of the PVC membrane ingredients for the PVC membrane sensor based on TDPCR

Sensor	TDPCR	PVC	Plasticizer	NaTPB	Working concentration range (M)	Slope (mV decade^{-1})
Tn$_1$	6	92	0	2	$1.0 \times 10^{-3} – 1.0 \times 10^{-1}$	8.2 ± 0.2
Tn$_2$	3	32	DOP,63	2	$4.0 \times 10^{-5} – 1.0 \times 10^{-1}$	19.3 ± 0.7
Tn$_3$	4	31	DOP,63	2	$1.0 \times 10^{-5} – 1.0 \times 10^{-1}$	21.5 ± 0.9
Tn$_4$	5	31	DOP,62	2	$1.0 \times 10^{-6} – 1.0 \times 10^{-1}$	24.0 ± 0.4
Tn$_5$	6	31	DOP,61	2	$8.0 \times 10^{-7} – 1.0 \times 10^{-1}$	28.5 ±0.5
Tn$_6$	6	31	DOA,61	2	$1.0 \times 10^{-5} – 1.0 \times 10^{-1}$	24.2 ± 0.6
Tn$_7$	6	31	DBS,61	2	$3.0 \times 10^{-5} – 1.0 \times 10^{-1}$	23.4 ± 0.4
Tn$_8$	6	31	DOS,61	2	$1.0 \times 10^{-5} – 1.0 \times 10^{-1}$	34.5 ± 0.3
Tn$_9$	6	31	DBP,61	2	$1.0 \times 10^{-4} – 1.0 \times 10^{-1}$	23.8 ± 0.5
Tn$_{10}$	6	31	DMS,61	2	$1.0 \times 10^{-4} – 1.0 \times 10^{-1}$	21.7 ± 0.4

Table 5.2 – Optimization of the ionophore composition for the carbon paste sensor based on TDPCR

Sensor	Ionophore	Graphite	Working Concentration range (M)	Slope (mV decade^{-1})
Nc$_1$	0	100	– – – –	4.8 ± 0.6
Nc$_2$	4	96	$3.0 \times 10^{-4} – 1.0 \times 10^{-1}$	24.1 ± 0.2
Nc$_3$	8	92	$8.0 \times 10^{-5} – 1.0 \times 10^{-2}$	24.8 ± 0.9
Nc$_4$	12	88	$4.0 \times 10^{-5} – 1.0 \times 10^{-2}$	25.4 ± 0.4
Nc$_5$	15	85	$1.0 \times 10^{-5} – 1.0 \times 10^{-1}$	27.6 ± 0.1
Nc$_6$	18	82	$5.0 \times 10^{-6} – 1.0 \times 10^{-1}$	29.8 ± 0.8
Nc$_7$	20	80	$5.0 \times 10^{-4} – 1.0 \times 10^{-1}$	31.5 ± 0.7
Nc$_8$	22	78	$1.0 \times 10^{-4} – 1.0 \times 10^{-1}$	32.6 ± 0.5
Nc$_9$	25	75	$3.0 \times 10^{-4} – 1.0 \times 10^{-1}$	22.9 ± 0.8

Table 5.3 – Effect of partially non-aqueous medium on the slopeand working concentration range of the PVC membrane sensor Tn_5

Non-aqueous content (%v/v)	**Slope (mVdecade^{-1})**	**Working concentration Range (M)**
0	28.5	$8.5 \times 10^{-7} – 1.0 \times 10^{-1}$
Ethanol		
10	28.9	$8.7 \times 10^{-7} – 1.0 \times 10^{-1}$
20	29.1	$8.6 \times 10^{-7} – 1.0 \times 10^{-1}$
25	28.1	$9.3 \times 10^{-7} – 1.0 \times 10^{-1}$
30	21.8	$6.7 \times 10^{-5} – 1.0 \times 10^{-1}$
Methanol		
10	29.3	$8.3 \times 10^{-7} – 1.0 \times 10^{-1}$
20	28.6	$9.2 \times 10^{-7} – 1.0 \times 10^{-1}$
25	28.8	$9.7 \times 10^{-7} – 1.0 \times 10^{-1}$
30	20.4	$7.6 \times 10^{-5} – 1.0 \times 10^{-1}$

Table 5.4 – Effect of partially non-aqueous medium on the slope and working concentration range of the carbon paste sensor Nc_6

Non-aqueous content (%v/v)	**Slope (mVdecade^{-1})**	**Working concentration Range (M)**
0	29.8	$1.0 \times 10^{-6} – 1.0 \times 10^{-1}$
Ethanol		
10	29.8	$1.0 \times 10^{-6} – 1.0 \times 10^{-1}$
15	29.5	$1.0 \times 10^{-6} – 1.0 \times 10^{-1}$
20	20.6	$8.7 \times 10^{-4} – 1.0 \times 10^{-1}$
Methanol		
10	29.9	$2.4 \times 10^{-6} – 1.0 \times 10^{-1}$
15	29.6	$8.7 \times 10^{-6} – 1.0 \times 10^{-1}$
20	20.8	$7.4 \times 10^{-4} – 1.0 \times 10^{-1}$

Table 5.5 - Selectivity coefficients for the sensors Tn_5 and Nc_6 using fixed interference method at 1.0 × 10^{-2} M concentration of interfering ion

Interfering ion (X)	Tn_5	Nc_6
Cr^{3+}	5.5 × 10^{-3}	4.9 × 10^{-3}
Mn^{2+}	9.2 × 10^{-2}	9.2 × 10^{-2}
Co^{2+}	8.4 × 10^{-3}	7.9 × 10^{-3}
Fe^{2+}	3.7 × 10^{-3}	2.9 × 10^{-3}
Cu^{2+}	5.4 × 10^{-3}	5.0 × 10^{-3}
Zn^{2+}	7.6 × 10^{-3}	7.8 × 10^{-3}
Sn^{2+}	3.4 × 10^{-3}	2.9 × 10^{-3}
Hg^{2+}	8.7 × 10^{-3}	8.2 × 10^{-3}
Pb^{2+}	2.9 × 10^{-3}	3.6 × 10^{-3}
Cd^{2+}	2.8 × 10^{-3}	3.6 × 10^{-3}
Na^{+}	6.7 × 10^{-4}	6.2 × 10^{-4}
Ag^{+}	3.7 × 10^{-3}	3.5 × 10^{-3}

Table 5.6 – Determination of the Ni^{2+} content in real samples using the sensors Tn_5 and Nc_6.

Sample	Sensor Tn_5 (ppm)*	Sensor Nc_6. (ppm)*	ICP – AES (ppm)
Chocolate	0.94 ± 0.02	0.91 ± 0.04	0.93
Vanaspathi	1.09 ± 0.06	1.04 ± 0.01	1.11
Effluent sample	2.81 ± 0.06	2.93 ± 0.03	2.83

*RSDs based on three replicates

Table 5.7 - Response characteristics of the sensors Tn_5 and Nc_6

Parameter	Response characteristics	
	Tn_5	**Nc_6**
Working concentration range (M)	$8.0\times 10^{-7} - 1.0 \times 10^{-1}$ M	$5.0 \times 10^{-6} - 1.0 \times 10^{-1}$ M
Slope (mV decade^{-1})	28.5 ± 0.5	29.8 ± 0.8
Detection Limit (M)	2.7×10^{-7} M	2.9×10^{-6} M
Response time	10 s	20 s
pH range	4.5 – 8.3	4.6 – 8.0
Non aqueous tolerance limit	25	15
Shelf life	4 months	3 weeks

Table.5.8 A comparative study of the characteristics of the developed sensors for nickel with some reported sensors

No.	Working concentration range (M)	pH range	Life time	Slope (mV decade^{-1})	Ref. No.
1	$5.0 \times 10^{-6} - 1.0 \times 10^{-1}$	3.2 – 7.9	4 months	29.5 ± 1.0	235
2	$5.0 \times 10^{-6} - 1.0 \times 10^{-1}$	3.6 – 7.4	4 months	29.9 ± 1.0	236
3	$5.0 \times 10^{-6} - 1.0 \times 10^{-2}$	3.5 – 7.5	1 month	29.7 ± 0.2	237
4	$1.0 \times 10^{-8} - 1.0 \times 10^{-2}$	2.0 – 9.0	1 month	Non Nernstian	238
5	$2.0 \times 10^{-6} - 5.5 \times 10^{-3}$	4.0 – 8.0	1.5 months	29.8 ± 0.3	239
6	$2.0 \times 10^{-7} - 1.0 \times 10^{-2}$	4.5 – 9.0	2 months	30.0 ± 1.0	240
7	$4.6 \times 10^{-7} - 1.0 \times 10^{-1}$	3.0 – 8.0	4 months	29.5 ± 0.3	128
8	$7.0 \times 10^{-6} - 1.0 \times 10^{-1}$	2.0 – 7.6	5 months	29.8 ± 0.2	131
9	$2.8 \times 10^{-6} - 1.0 \times 10^{-1}$	2.5 – 7.5	4 months	30.5 ± 0.4	132
10	$3.1 \times 10^{-6} - 1.0 \times 10^{-2}$	2.5 – 7.0	2 months	30.7 ± 0.2	133
11	$3.9 \times 10^{-6} - 1.0 \times 10^{-1}$	2.5 – 7.7	4 months	29.5 ± 0.2	134
12	$7.1 \times 10^{-7} - 1.2 \times 10^{-2}$	3.0 – 6.0	2 months	30.3 ± 0.7	137
13	$8.5 \times 10^{-7} - 1.0 \times 10^{-1}$	4.5 – 8.3	4 months	28.5 ± 0.5	Tn_5
14	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$	4.6 – 8.0	3 weeks	29.8 ± 0.8	Nc_6

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Chapter 6

SENSORS FOR COPPER

Contents

The fabrication of a PVC membrane sensor and a carbon paste sensor for copper are discussed in detail in this chapter. The different performance characteristics of the developed sensors including concentration range, slope, detection limit, response time, pH range and shelf life have been explained in detail. The electrode has a fast response time and showed high selectivity for copper over a number of interfering ions. The present study has covered the applicability of the newly developed sensors as an indicator electrode in the potentiometric titration of Cu^{2+} *ions against EDTA and also for the determination of* Cu^{2+} *ions in effluent samples.*

Copper is a reddish-coloured metal and occupies the same family of silver and gold in the periodic table. Copper possesses high electrical and thermal conductivity and resists corrosion. It is widely used in cooking utensils, as fertilizers, bactericides and fungicides. It is used for disease control in livestock and poultry. In industry it is used in electroplating, as an activator in froth floatation of sulphide ores, production of wood preservatives. Copper is an essential element for human beings as it is required for several enzyme systems and biological electron transport[241].

The Recommended Dietary Allowance[242] (RDA) for copper in normal healthy adults is 0.9 mg/day. Copper is an industrially important metal[243] and it is an essential metal for the normal functioning of the living system. But it is toxic at elevated levels and it is known to cause Wilson's disease, hypoglycaemia and dyslexia[244]. The toxicity is due to the aquo-complexed free copper ions rather than its organic or inorganic complexes[245]. In view of such toxic effects of copper, its monitoring is very important.

Several analytical methods have been used to determine copper which include spectrophotometry[246], fluorometry[247], atomic absorption spectrometry[248], inductively coupled plasma-optical emission spectroscopy (ICP-OES)[249] and chromatography[186]. The disadvantages of these methods are they require sample pre-treatment and infrastructure back up. Ion selective electrodes have several advantages such as ease of preparation, simple instrumentation and fast response time with very high selectivity. This chapter presents the fabrication of two types of sensors incorporating a porphyrin as ionophore for the determination of Cu^{2+} ions.

6.1 Synthesis of the Ionophore

Ionophore is the electroactive component of a sensor. In the development of sensors 5,10,15,20-tetrakis(3-methoxy-4-hydroxyphenyl)porphyrin (TMHPP) was used as the ionophore. Freshly distilled pyrrole, 3-methoxy-4-hydroxy benzaldehyde and boiling propionic acid was refluxed for 30 minutes and allowed to cool. The precipitated purple crystals were washed with methanol and purified by column chromatography. The detailed procedure for the synthesis of the ionophore and its characterisation are discussed in section 2.2.4 of chapter 2. The structure of the ionophore TMHPP is shown as Figure 6.1.

6.2 Sensors based on TMHPP

Both PVC membrane sensor and carbon paste sensor was fabricated using TMHPP as ionophore. The preliminary investigations involved the study of potential responses of the sensors to different cations. This is depicted in Figure 6.2 and Figure 6.3 which shows the response of the PVC membrane sensor and carbon paste sensor respectively. The high sensitivity of the sensors to copper ions may be due to the fast exchange kinetics at the membrane-sample interface.

6.3 Fabrication of the Sensors

The fabrication of the PVC membrane sensor is discussed in detail in section 2.6.1 of chapter 2 and carbon paste sensor in section 2.6.2 of chapter 2. The procedure reported by Cragg and Moody was used in the fabrication of the PVC membrane sensor[173].

The preliminary step in the fabrication of the PVC membrane sensor involves dissolving ionophore, plasticizer, anion excluder and PVC in a minimum quantity of THF. The resulting solution was then poured into glass rings struck on a glass plate. It was left overnight allowing the slow evaporation of the solvent. The membrane thus formed was glued to one end of a glass tube. The glass tube was then filled with 1.0×10^{-1} M cupric nitrate solution. The prepared sensor was left for conditioning for 24 hours by dipping in 1.0×10^{-1} M cupric nitrate solution. The composition ratio of the membrane that gave the best response in terms of slope, concentration range, response time and detection limit was found to be 31 : 64 : 2 : 3 (PVC : DMS : NaTPB : TMHPP) (w/w%). Here the plasticizer used was DMS.

The sensitivity and linearity of a carbon paste sensor depends on the amount of ionophore and nature of plasticizer used. Graphite powder and ionophore was mixed thoroughly. It was made in to a paste in paraffin oil and packed into the open end of the capillary tube. A copper rod through the centre of the electrode body provides the electrical contact. The sensor was conditioned by dipping in 1.0×10^{-1} M cupric nitrate solution for 12 hours. The best response was obtained for the sensor with composition ratio 90 : 10 (graphite : TMHPP) (%w/w).

6.4 Potential measurement and calibration

A Metrohm 781 ion meter was used for potential measurements. All EMF measurements were carried out at $25 \pm 1^{o}C$. A saturated calomel electrode was used in conjunction with the developed sensor. The cell assembly for potentiometric measurements may be represented as follows:

For PVC membrane sensor:

External reference electrode | test solution | PVC membrane based on TMHPP | internal filling solution (0.1M Cu^{2+}) | internal reference electrode

For carbon paste sensor

Reference electrode | test solution | carbon paste electrode based on TMHPP

A 1.0×10^{-1} M $Cu(NO_3)_2$ solution was prepared in a 100mL standard flask. The dilution series were prepared by serial dilution of the stock solution. Performance of the developed sensors were investigated by measuring the EMF of the cell in Cu^{2+} solutions prepared in the concentration range $1.0 \times 10^{-8} – 1.0 \times 10^{-1}$ M. The solutions were stirred and the stable potential reading was taken. The calibration graph was obtained by plotting EMF versus pCu^{2+}. The calibration graph was used for subsequent determination of unknown concentrations.

6.5 Optimization studies of the two types of sensors

The reliability of the sensor design is influenced by the matrix composition, electroactive material distribution in the membrane and the reliability of response characteristics[250]. Electroactive material has the primary role in the response characteristics of the sensor. The choice of the plasticizer as well as ionophore/plasticizer ratio has also been proved to be very important for the electrode response[232]. The matrix of the membrane is represented by the PVC and plasticizer which in turn form the medium for the electroactive material. Various ratios of ionophore, PVC and plasticizer were tried to prepare the membrane as the composition influences the response characteristics of the sensor through membrane equilibrium. The function of the plasticizer in the membrane is to improve the mobility of the ionophore in the membrane matrix. A membrane Ta_1 without plasticizer was first prepared but it was hard and fragile and it gave only a sub Nernstian slope. The addition of plasticizers improved the workability of the sensor. The electrode plasticized with DMS showed the optimal response characteristics towards copper ions. It was found that the sensor Ta_4 with DMS as plasticizer was found to give the best response in terms of slope and working concentration range. With too much plasticizer (DMS) the membrane was viscid and the mechanical intensity would decrease.

The incorporation of lipophilic additives can significantly influence the performance characteristics of membrane electrodes[251]. The presence of lipophilic anionic sites in cation selective membrane selective electrodes not only diminishes the ohmic resistance but also facilitates the process of ion extraction into the membrane and increases the response behaviour and selectivity of the electrode[252]. Table 6.1 shows the optimization of membrane composition of PVC membrane sensor based on TMHPP for Cu^{2+} ions. The sensor Ta_4 with composition 31 : 64 : 3 : 2 for PVC : DOP : TMHPP : NaTPB (w/w%) was used for further studies.

SEM analysis was conducted in order to study the surface morphology of the developed Ta_4 membrane. The extent of homogeneity of the membrane surface is clearly visible in the SEM image. A homogeneous membrane is found to exhibit good response characteristics such as high sensitivity and long shelf life. The SEM image of membrane is shown in Figure 6.4.

As in the case of optimization of membrane ingredients of a membrane sensor, the optimization of carbon paste composition was conducted by varying the amount of ionophore and graphite and suitably selecting the binder. The response characteristic of a carbon paste electrode is largely affected by the nature of binder used. The best response was obtained when paraffin oil was used as the binder. Without the ionophore the sensor showed a negligible response towards the analyte. The optimization of carbon paste composition of the sensor incorporating TMHPP is given in Table 6.2. The sensor Pc_3 with optimized composition in the ratio 10 : 90 (ionophore : graphite) showed best response in terms of working concentration range, slope and response time.

6.5.1 Working concentration range and slope

The calibration graph which is the plot of EMF versus pCu^{2+} for the sensors Ta_4 and Pc_3 is shown as Figure 6.5 and Figure 6.6 respectively, where Ta_4 denote PVC membrane sensor and Pc_3 denote carbon paste sensor. The working concentration range for both the sensors Ta_4 and Pc_3 was found to be $1.0 \times 10^{-6} – 1.0 \times 10^{-1}$ M. The slope calculated from the calibration graph was found to be 29.0 (± 0.4) mV decade^{-1} and 28.4 (± 0.7) mV decade^{-1} for the sensors Ta_4 and Pc_3 respectively. The detection limit was calculated from the graph by the intersection of the two extrapolated linear segments of the calibration plot and was found tobe 7.6×10^{-7} M for the PVC membrane sensor Ta_4 and 8.9×10^{-7} M for the carbon paste sensor Pc_3.

6.5.2 Effect of concentration of internal filling solution

The effect of concentration of internal filling solution on the potential response of the sensor was investigated. The concentration of the internal solution, $Cu(NO_3)_2$ was changed from 1.0×10^{-1} M to 1.0×10^{-4} M and the potential response of the electrode was measured. It was found that the variation of concentration of internal filling solution does not cause any significant difference on the potential response of the sensor. Hence a 1.0×10^{-1} M $Cu(NO_3)_2$ solution was fixed as the internal filling solution in all studies using the sensor. A carbon paste sensor requires no internal filling solution. This is one of the significant advantages of the carbon paste sensor.

6.5.3 Response time and life time of the sensors

For analytical applications, the response time of a membrane sensor is an important factor. The practical response time for the sensors Ta_4 and Pc_3 was obtained from Figure 6.7 and Figure 6.8 and was found to be 20s and 25s respectively. The life time of the copper sensors was studied by periodically recalibrating the potentiometric response to copper ions in the standard solutions. The operative life time for the sensors Ta_4 and Pc_3 was found to be 3 months and 4 weeks respectively. The sensors were all kept immersed in 1.0×10^{-1} M $Cu(NO_3)_2$ solution when not in use. And as explained in the previous chapters for carbon paste sensors, the surface could be renewed.

6.5.4 Effect of pH and non-aqueous media

The behaviour of the sensors Ta_4 and Pc_3 was studied over a pH range of 2.0 – 8.0 for two fixed concentrations 1.0×10^{-3} M and 1.0×10^{-4} M of Cu^{2+} solution. The pH was adjusted by introducing small drops of nitric acid (0.05M) or sodium hydroxide (0.05M). The results are shown as Figure 6.9 and Figure 6.10 for the sensors Ta_4 and Pc_3 respectively. The potential remained constant in the pH range 3.1 – 7.2 for the sensor Ta_4 and in the pH range 3.5 – 7.0 for the sensor Pc_3. However the observed changes below and above this pH range may be due to interference from H^+ ions and formation of some hydroxyl complexes of Cu^{2+} ion in solution, respectively.

The performance of the sensors Ta_4 and Pc_3 was also investigated in partially non-aqueous media using methanol-water and ethanol-water mixtures. The results obtained are compiled in Table 6.3 and 6.4 for the sensors Ta_4 and Pc_3 respectively. It was seen that no significant change occurs in the slope for the sensors up to 20% of non-aqueous content in the case of PVC membrane sensor Ta_4 and the tolerance level was 10% for carbon paste sensor Pc_3. However, above the tolerance level of the sensors Ta_4 and Pc_3, the slopes get affected which may be attributed to leaching of the ligand into the sample solution.

6.5.5 Potentiometric selectivity

The most important characteristic of a membrane sensor is its response for the primary ion in the presence of other ions. So the design and development of the sensor and the evaluation of degree of interference from other ions would be of great importance. The extent of interference of other ions or species on the response of the developed sensors Ta_4 and Pc_3 were studied by the Fixed Interference Method (FIM)[174,220]. The selectivity coefficients were determined at 1.0×10^{-2} M concentration of interfering ions and the concentration of Cu^{2+} ions was varied and calculated using equation (1).

The selectivity coefficient values are summarized in Table 6.8. The results clearly demonstrate that the sensors has shown very good selectivity for Cu^{2+} ions in presence of Cd^{2+}, Co^{2+}, Mn^{2+}, Mg^{2+}, Zn^{2+}, Sn^{2+}, Hg^{2+}, Pb^{2+}, Ni^{2+}, Ca^{2+}, Ba^{2+}, Na^+, K^+ and Ag^+ but only moderate selectivity in presence of Fe^{2+} ions.

6.6 Analytical applications

The developed sensors worked well Ta_4 and Pc_3 under laboratory conditions. They were successfully applied as an indicator electrode in the potentiometric titration of copper (ll) nitrate solution with EDTA at pH 5.0. The titration curves for the sensors Ta_4 and Pc_3 are shown as Figure 6.11 and Figure 6.12. The conventional sigmoid shaped plot is not obtained. But the end point corresponds to 1:1 stoichiometry of Cu-EDTA complex.

The applicability of the sensors Ta_4 and Pc_3 was further investigated in the determination of copper (ll) in waste water samples collected from electroplating unit. The preparation of the samples was done as explained in Section 2.5.3 in Chapter 2. The results obtained are presented in Table

6.6. The results obtained were in good agreement with those obtained from ICP-AES method.

6.7 Conclusion

A polymeric membrane sensor Ta_4 and a carbon paste sensor Pc_3 was developed based on TMHPP. The prepared sensors exhibited long life time, good stability, sensitivity and selectivity. The sensors can be used most conveniently, economically and without any sample pre-treatment. The PVC membrane sensor Ta_4 has better response characteristic than the carbon paste sensor $Pc_{3.}$ The life time of the sensor Ta_4 is much better than the sensor $Pc_{3.}$ But its surface can be renewed by cutting a little of the paste, polishing it on a smooth surface and reconditioning it by dipping it in 1.0×10^{-1} M copper (ll) nitrate solution. The response characteristic of the sensor is presented in Table 6.7.

A comparative data of the developed sensors along with some reported work in the literature is summarized in Table 6.8. It can be seen that the developed sensors are superior in terms of working concentration range[254,255,257,259,146] , pH range[254,259,146], and slope[144,146]. The sensor Ta_4 is superior in terms of life time[144,146,256,259].

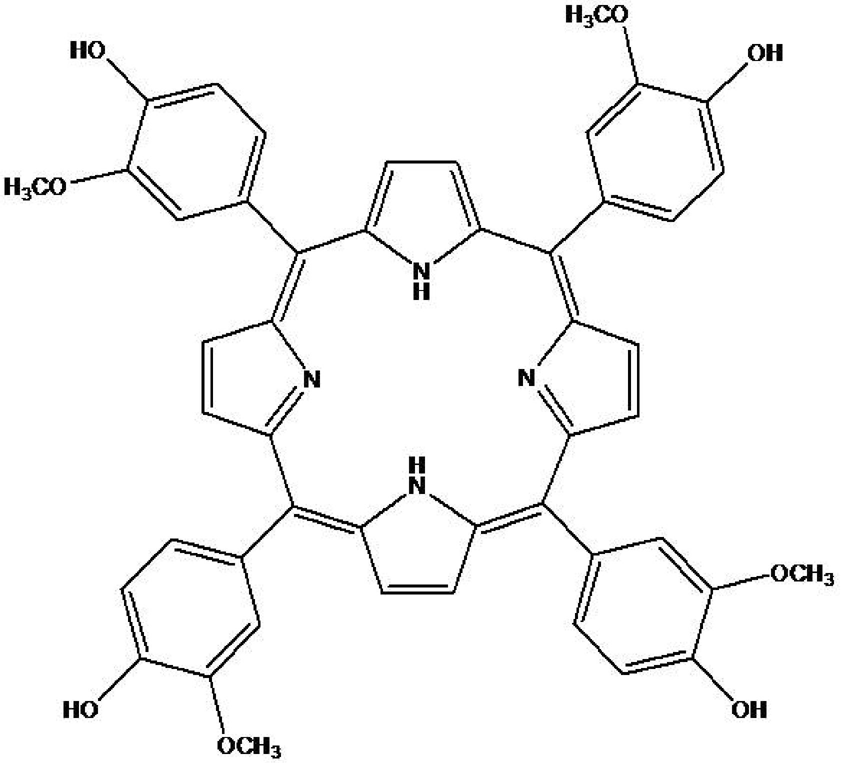

Figure 6.1 – Structure of the ionophore TMHPP

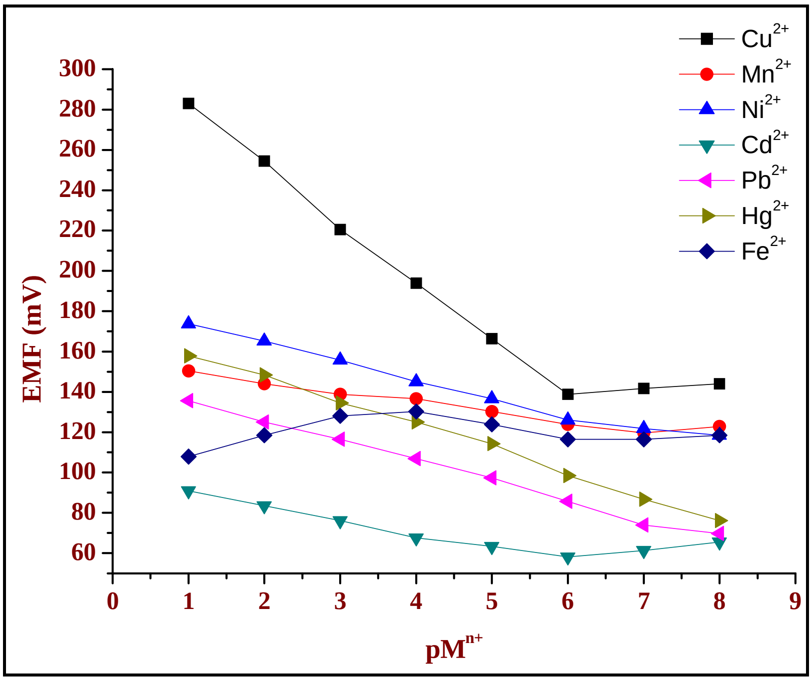

Figure 6.2 - Potential response of the PVC membrane sensor based on TMHPP to different cations.

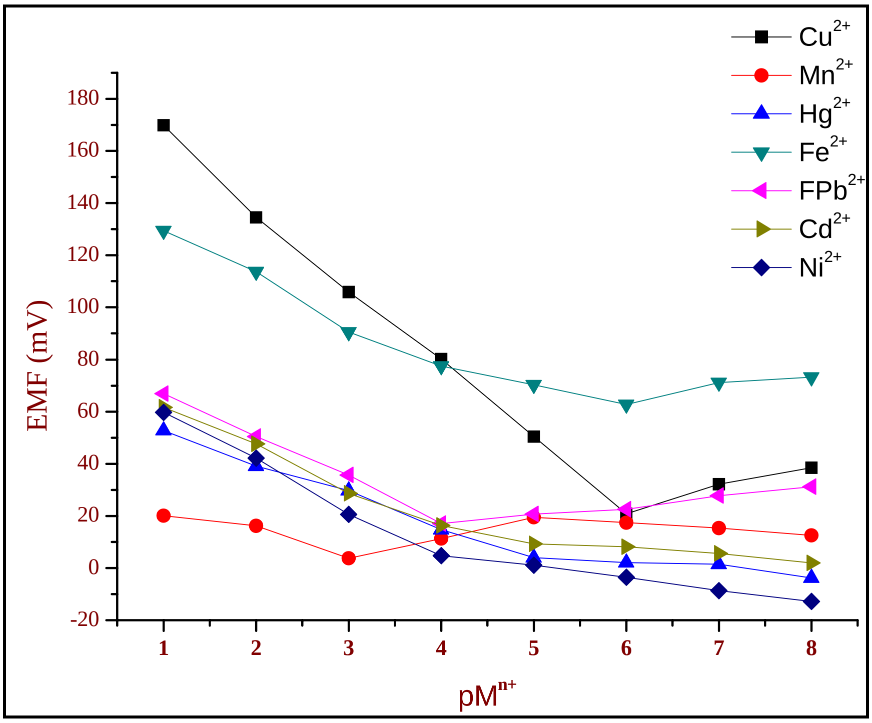

Figure 6.3 - Potential response of the carbon paste type sensor based on TMHPP to different cations.

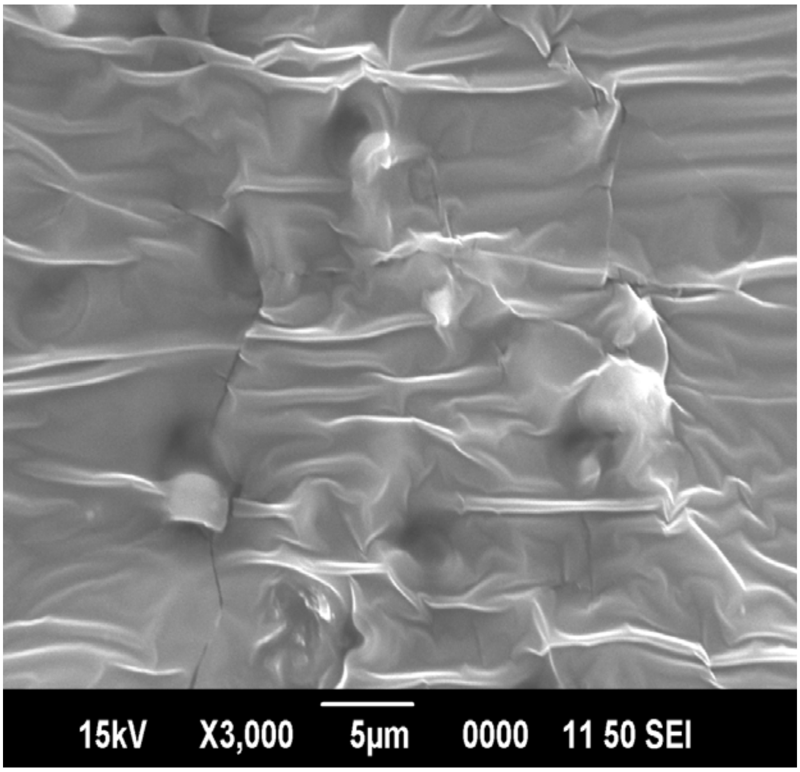

Figure 6.4 - SEM image of the PVC membrane type sensor Ta_4 based on TMHPP

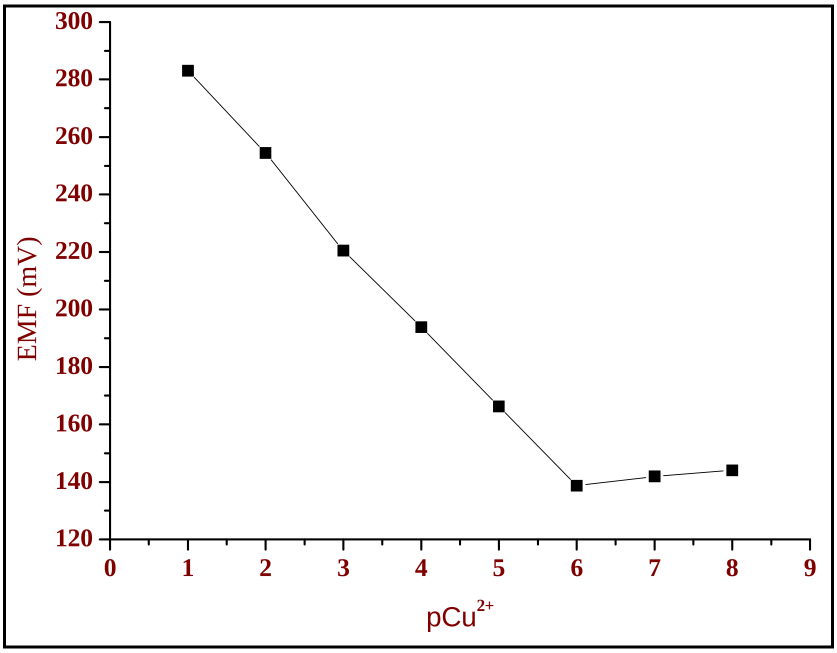

Figure 6.5 – Calibration graph of the PVC membrane sensor Ta_4 based on TMHPP

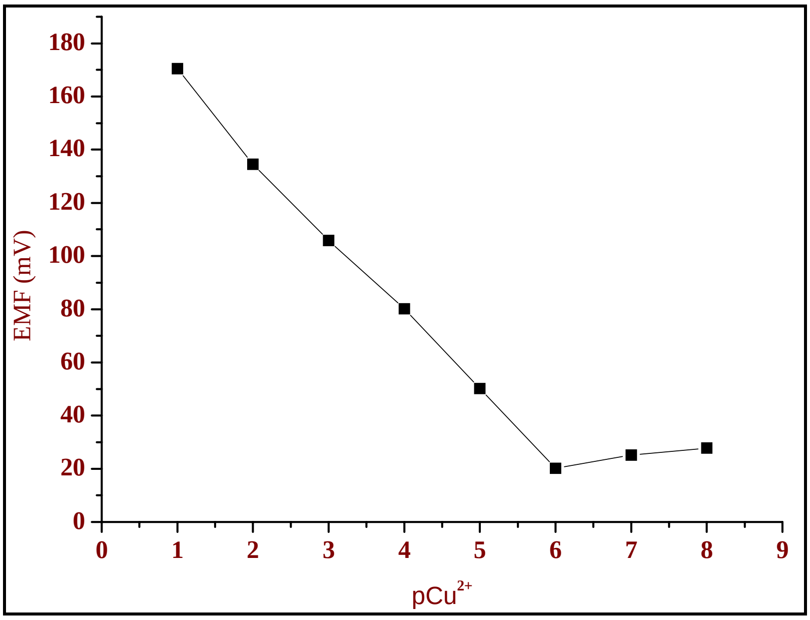

Figure 6.6 – Calibration graph of the carbon paste type sensor Pc_3 based on TMHPP

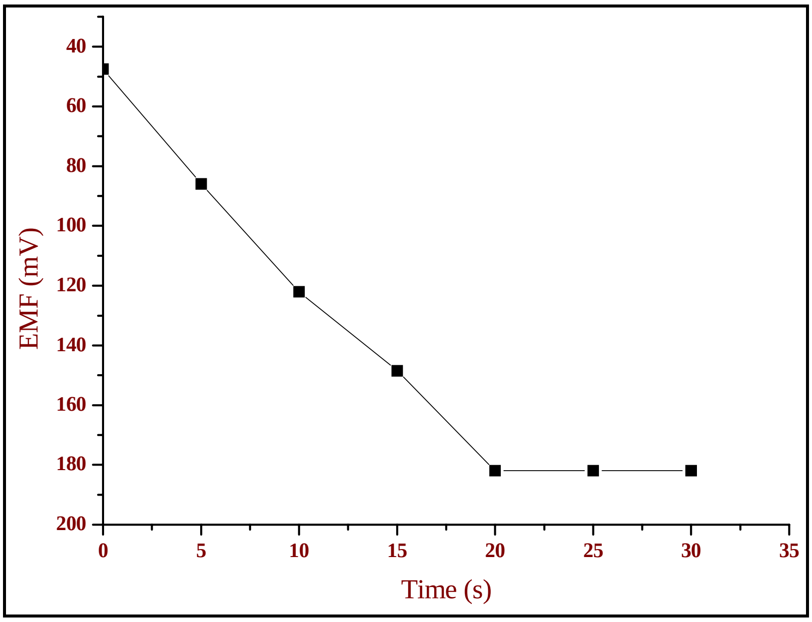

Figure 6.7 - Practical response time of the PVC membrane type sensor Ta_4 based on TMHPP

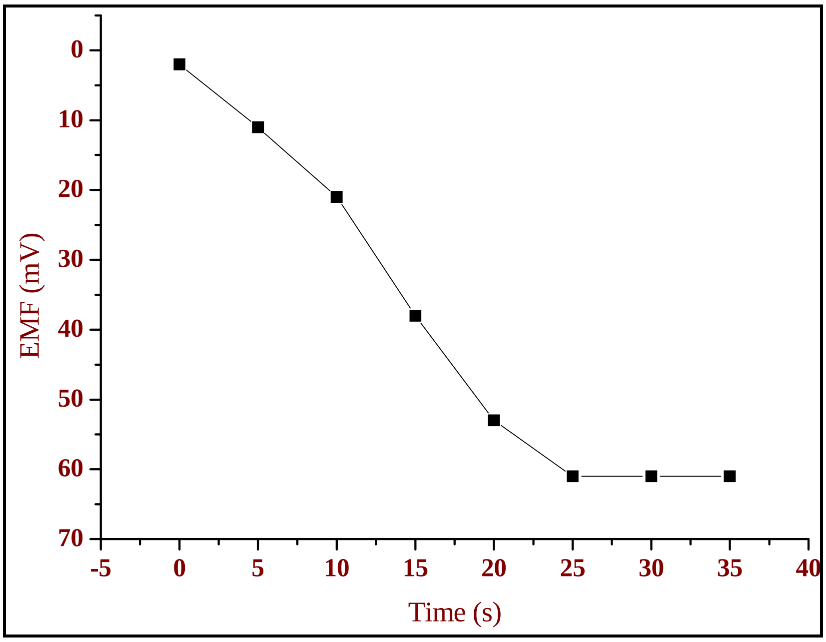

Figure 6.8 - Practical response time of the carbon paste type sensor Pc_3 based on TMHPP

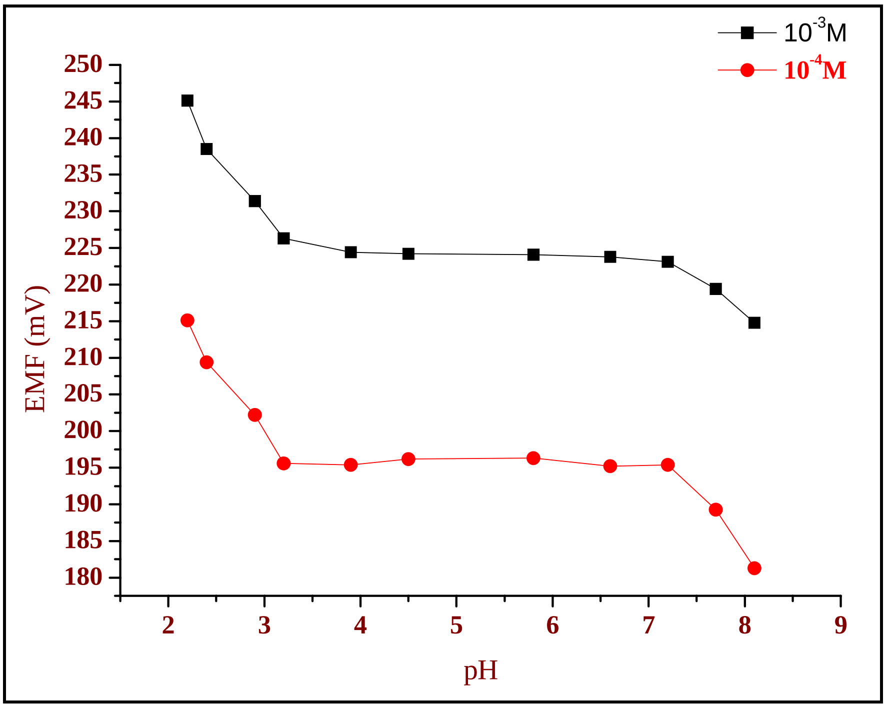

Figure 6.9 – Effect of pH on the cell potential of the PVC membrane sensor Ta_4 based on TMHPP

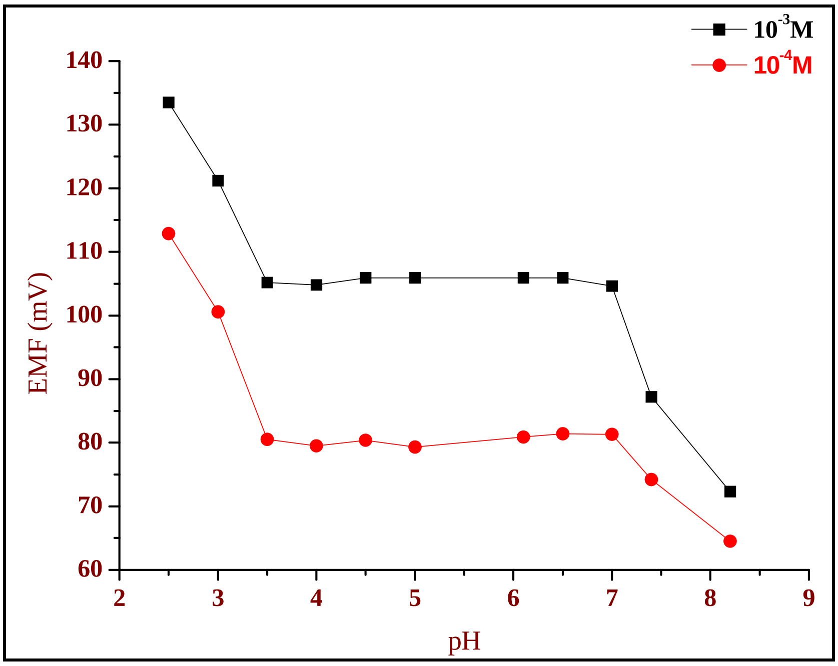

Figure 6.10 – Effect of pH on the cell potential of the carbon paste sensor Pc_3 based on TMHPP

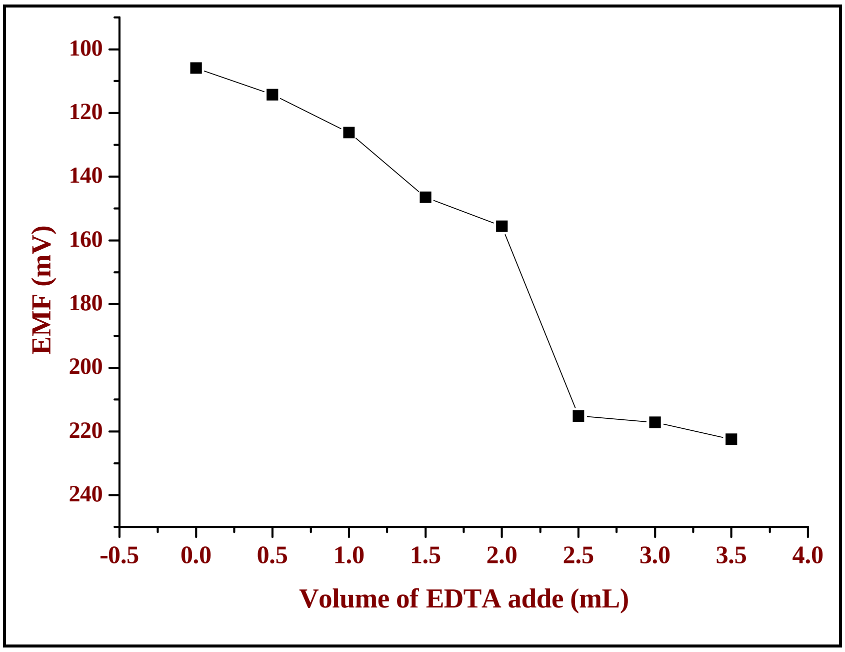

Figure 6.11 – Potentiometric titration curve of 25.0 mL of 1.0 × 10^{-3} M Cu^{2+} solution with 1.0 × 10^{-2} M EDTA using the sensor the PVC type membrane sensor Ta_4 based on TMHPP

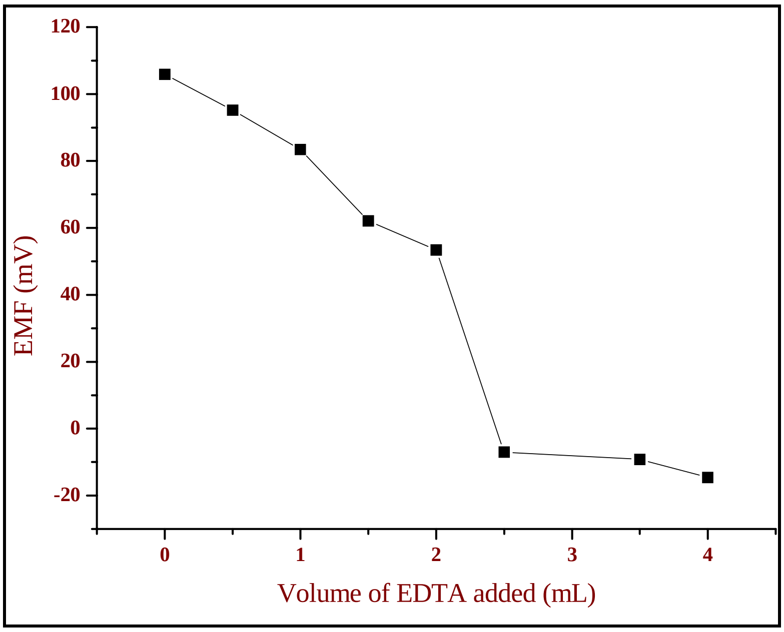

Figure 6.12 – Potentiometric titration curve of 25.0 mL of 1.0 × 10^{-3} M Cu^{2+} solution with 1.0 × 10^{-2} M EDTA using the carbon paste sensor Pc_3 based on TMHPP

Table 6.1 – Optimization of the PVC membrane ingredients for the PVC membrane sensor based on TMHPP

Sensor	TMHPP	PVC	Plasticizer	NaTPB	Working concentration range (M)	Slope (mV decade^{-1})
Ta_1	3	95	0	2	$1.0 \times 10^{-3} - 1.0 \times 10^{-1}$	21.2 ± 0.9
Ta_2	1	31	DMS,66	2	$4.0 \times 10^{-5} - 1.0 \times 10^{-1}$	24.9 ± 0.3
Ta_3	2	31	DMS,65	2	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$	27.5 ± 0.1
Ta_4	3	31	DMS,64	2	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$	29.0 ± 0.4
Ta_5	4	31	DMS,63	2	$8.0 \times 10^{-6} - 1.0 \times 10^{-1}$	32.4 ± 0.7
Ta_6	3	31	DOA,64	2	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$	34.1 ± 0.2
Ta_7	3	31	DBP,64	2	$3.0 \times 10^{-5} - 1.0 \times 10^{-1}$	22.9 ± 0.4
Ta_8	3	31	DOP,64	2	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$	24.5 ± 0.3
Ta9	3	31	DOS,64	2	$1.0 \times 10^{-4} - 1.0 \times 10^{-1}$	23.1 ± 0.2
Ta_{10}	3	31	DBS,64	2	$1.0 \times 10^{-4} - 1.0 \times 10^{-1}$	19.8 ± 0.1

Table 6.2 – Optimization of the ionophore composition for the carbon paste sensor based on TMHPP

Sensor	Ionophore	Graphite	Working concentration range (M)	Slope (mV decade^{-1})
Pc_1	0	100	- - - - -	2.2
Pc_2	5	95	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$	19.3± 0.3
Pc_3	10	90	$3.0 \times 10^{-6} - 1.0 \times 10^{-1}$	28.4 ± 0.7
Pc_4	15	85	$8.0 \times 10^{-6} - 1.0 \times 10^{-1}$	30.3± 0.3
Pc_5	20	80	$1.0 \times 10^{-5} - 1.0 \times 10^{-2}$	33.5± 0.1
Pc_6	25	75	$1.0 \times 10^{-4} - 1.0 \times 10^{-1}$	22.9± 0.7
Pc_7	30	70	$1.0 \times 10^{-4} - 1.0 \times 10^{-2}$	18.4± 0.5
Pc_8	35	65	$1.0 \times 10^{-4} - 1.0 \times 10^{-2}$	18.3± 0.2
Pc_9	40	60	$1.0 \times 10^{-4} - 1.0 \times 10^{-2}$	17.5± 0.4

Table 6.3 – Effect of partially non-aqueous medium on the slope and working concentration range of the PVC membrane sensor Ta_4

Non-aqueous content (%v/v)	Slope (mV decade^{-1})	Working concentration range (M)
0	29.0	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$
Ethanol		
10	29.0	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$
15	28.9	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$
20	28.9	$3.4 \times 10^{-6} - 1.0 \times 10^{-1}$
25	25.2	$1.0 \times 10^{-4} - 1.0 \times 10^{-1}$
Methanol		
10	28.9	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$
15	28.6	$3.2 \times 10^{-6} - 1.0 \times 10^{-1}$
20	28.4	$4.7 \times 10^{-6} - 1.0 \times 10^{-1}$
25	24.9	$2.0 \times 10^{-4} - 1.0 \times 10^{-1}$

Table 6.4 – Effect of partially non-aqueous medium on the slope and working concentration range of carbon paste sensor Pc_3

Non-aqueous content (%v/v)	Slope (mVdecade^{-1})	Working concentration Range (M)
0	28.4	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$
Ethanol		
5	28.5	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$
10	28.2	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$
15	25.9	$8.0 \times 10^{-5} - 1.0 \times 10^{-1}$
Methanol		
5	28.4	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$
10	28.3	$2.0 \times 10^{-6} - 1.0 \times 10^{-1}$
15	26.6	$7.0 \times 10^{-6} - 1.0 \times 10^{-1}$

Table 6.5 - Selectivity coefficients for the sensors Ta_4 and Pc_3 using Fixed Interference Method at 1.0×10^{-2} M concentration of interfering ion

Interfering ion (X)	Ta_4	Pc_3
Na^+	4.1×10^{-3}	4.2×10^{-3}
K^+	8.3×10^{-3}	8.4×10^{-3}
Ag^+	5.6×10^{-2}	5.9×10^{-2}
Mg^{2+}	7.8×10^{-3}	7.1×10^{-3}
Ca^{2+}	1.5×10^{-3}	1.1×10^{-3}
Zn^{2+}	1.4×10^{-3}	1.6×10^{-3}
Pb^{2+}	6.2×10^{-3}	6.1×10^{-3}
Hg^{2+}	2.7×10^{-3}	3.1×10^{-3}
Fe^{2+}	1.2×10^{-1}	1.8×10^{-1}
Co^{2+}	7.4×10^{-3}	7.1×10^{-3}
Ni^{2+}	3.1×10^{-2}	2.9×10^{-2}
Mn^{2+}	8.4×10^{-3}	6.2×10^{-3}
Cd^{2+}	3.7×10^{-3}	7.9×10^{-3}
Sn^{2+}	5.6×10^{-3}	4.9×10^{-3}
Ba^{2+}	5.8×10^{-3}	5.4×10^{-3}

Table 6.6 – Determination of copper content in water sample from electroplating unit

Sample	Sensor Ta_4 (ppm)*	Sensor Pc_3 (ppm)*	ICP-AES (ppm)
Effluent sample	6.81 ± 0.02	6.79±0.03	7.2

*RSDs based on three replicates

Table 6.7 - Response characteristics of the sensors Ta_4 and Pc_3

Parameter	Response characteristics	
	Ta_4	Pc_3
Working concentration range (M)	$1.0 \times 10^{-6} – 1.0 \times 10^{-1}$	$1.0 \times 10^{-6} – 1.0 \times 10^{-1}$
Slope (mV decade^{-1})	29.0 ± 0.4	28.4 ± 0.7
Detection Limit (M)	7.6×10^{-7}	8.9×10^{-7}
Response time	20 s	25 s
pH range	3.1 – 7.2	3.5 – 7.0
Non aqueous tolerance limit	20%	15%
Shelf life	3 months	4 weeks

Table 6.8 - A comparative study of the characteristics of the developed sensors for copper with some reported sensors

No.	Working concentration range (M)	pH range	Life Time	Slope (mV decade^{-1})	Ref. No.
1	$1.0\times 10^{-7} – 1.0 \times 10^{-1}$	2.7 – 6.2	10weeks	27.9 ± 0.8	144
2	$1.0\times 10^{-6} – 1.0 \times 10^{-1}$	3.5 – 7.0	3 months	29.0 ± 0.8	253
3	$5.0\times 10^{-6} – 5.0 \times 10^{-2}$	4.0 – 7.0	3 months	29.0 ± 0.1	254
4	$1.0\times 10^{-5} – 2.0 \times 10^{-1}$	2.5 – 5.5	3 months	29.4	255
5	$1.0\times 10^{-6} – 1.0 \times 10^{-1}$	3.0 – 6.8	NM*	29.2 ± 0.4	256
6	$5.0\times 10^{-6} – 1.0 \times 10^{-1}$	2.8 – 7.5	4 months	29.88	257
7	$1.0\times 10^{-6} – 1.0 \times 10^{-1}$	2.1 – 6.2	6 months	29.9	258
8	$8.1\times 10^{-6} – 1.0 \times 10^{-2}$	4.5 – 6.0	2 months	34.2 ± 0.4	146
9	$2.0\times 10^{-6} – 1.5 \times 10^{-2}$	5.5 – 6.5	NM*	29.5 ± 1.0	259
10	$2.0\times 10^{-7} – 1.0 \times 10^{-1}$	3.0 - 11	4 – 5months	29.5 ± 1.0	145
11	$1.0\times 10^{-6} – 1.0 \times 10^{-1}$	3.1 – 7.2	3 months	29.0 ± 0.4	Ta_4
12	$1.0\times 10^{-6} – 1.0 \times 10^{-1}$	3.5 – 7.0	3 weeks	28.4 ± 0.7	Pc_3

*NM – not mentioned

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Chapter 7

SENSOR FOR SALICYLATES

Contents

The fabrication, performance characteristics and applications of a PVC membrane sensor with high selectivity towards salicylate ions have been described in this chapter. The different electrochemical response characteristics of the developed sensor have been discussed in detail. In this sensor a manganese complex of porphyrin is incorporated as an electroactive material. The sensor worked well over a concentration range $1.0 \times 10^{-5} – 1.0 \times 10^{-1}$ *M with a fast response time. The sensor has been successfully applied for the determination of salicylate in different pharmaceutical preparations.*

Salicylates in the form of willow bark, were used as an analgesic during the time of Hippocrates[260] and their antipyretic effects have been recognized for more than 200 years[261]. Salicylate ion (Sal^-) is the main hydrolyzed product of tablet aspirin or aspirin-like substances, which are commonly used as effective analgesics. Salicylates can be quite toxic if taken in large doses. Level in plasma higher than 2.2 mmol L^{-1} of salicylates is regarded as being toxic for human beings[262].

The most widely used analytical method for the determination of salicylate is based on the Trinder reaction[263] in which salicylate reacts with ferric ions to form a coloured complex in acid solution. But this method lacks selectivity over many common anions. Several methods such as HPLC[264-266], fluorometric[267], phosphorimetric[268], luminescent[269] and biomimetic[270] methods have been reported for its determination. Most of these methods require sophisticated instrumentation and time consuming pre-treatment steps. Method using ion selective electrode is relatively simple and do not require expensive instrumentation.

This chapter deals with the fabrication and electrochemical studies of a PVC membrane sensor for salicylate ion based on TPMC.

7.1 Synthesis of the Ionophore

5,10,15,20-tetrakis (3-methoxy-4-hydroxyphenyl) porphyrinato manganese(III) chlorid**e (**TPMC) was used as ion carrier into plasticized PVC membrane. TPMC is prepared by refluxing TMHPP (synthesis of TMHPP is explained in detail in section 2.2.4 of chapter 2) and manganese acetate in glacial acetic acid for 72 hours. The residue is extracted into methanol and treated with conc. HCl to precipitate manganese complex of porphyrin. The detailed procedure for the synthesis and characterisation of the ionophore TPMC has been discussed in detail under section 2.2.5 of chapter 2. The structure of the ionophore TPMC is shown as Figure 7.1.

7.2 Sensor based on TPMC

A PVC membrane sensor was fabricated using TPMC as ionophore. The potential response of the sensor towards different anions is shown as Figure 7.2. The sensor revealed remarkable selectivity for salicylate ions relative to the most common inorganic and organic anions.

7.3 Fabrication of the Sensor

The detailed procedure for the fabrication of the PVC membrane sensor is discussed in section 2.6.1 of chapter 2. The PVC membrane sensor was fabricated according to the procedure reported by Cragg's and Moody[172]. The preliminary step involves dissolving the PVC in about 5-7 mL of THF followed by ionophore, plasticizer and lipophilic additives. The resulting solution was poured into glass strings struck on a glass plate. It was then covered with a filter paper and left to dry allowing the slow evaporation of the solvent. Small disc shaped membranes thus obtained were cut out and glued to one end of a glass tube. This was left to dry and the tube was filled with internal filling solution (0.1 M sodium salicylate and 0.1M NaCl). The prepared membrane sensor was finally conditioned by soaking in 0.1 M sodium salicylate solution for 2 days.

7.4 Potential measurement and calibration

A Metrohm 781 ion meter was used for potential measurements. All emf measurements were carried out at 25 ± 1^{o}C. A saturated calomel electrode was used in conjunction with the developed sensor. The cell assembly for potentiometric measurements may be represented as follows:

External reference electrode | test solution | PVC membrane based on TPMC | internal filling solution (0.1M sodium salicylate and 0.1 M sodium chloride) | Internal reference electrode.

The performance of the electrode was investigated by measuring its potential in salicylate solutions prepared in the concentration range 1.0×10^{-7} M - 1.0×10^{-1} M. All solutions were freshly prepared by dilution from the 1.0×10^{-1} M stock standard solution, with distilled water. The solutions were stirred and potential readings recorded when they became stable. The data were plotted as observed potential versus $pSal^-$.

7.5 Optimization studies of the PVC membrane sensor

The durability and mechanical strength of PVC membrane sensors can be improved by properly selecting the composition of the membrane during the design of the sensors[271]. The key component of any sensor is the ionophore which enables the sensor to respond selectively to a particular analyte. For the development of a truly anion selective electrode, a strong interaction between the ionophore and anion is required in order to complex anion in a selective fashion[272]. Metalloporphyrins as ionophore for anions show specific metal-ligand interaction. The central metal atom and the bulkiness of the side chains that surround the porphyrin rings control the selectivity of the ion selective electrodes[273]. The membrane without the ionophore displayed insignificant selectivity towards salicylate but in the presence of the ionophore the membrane showed remarkable selectivity for salicylate. An increase in the level of TPMC caused an increase in the slope of the calibration curve. A better response is obtained with 6% of ionophore. Further increase in the concentration of TPMC showed a decrease in the slope of the calibration curve.

The selectivity, sensitivity and linearity of a sensor depend significantly on the membrane composition and the nature of plasticizers used. The main purpose of the plasticizer is to lower the glass transition temperature of PVC and to produce homogeneous and flexible films with good mechanical stability. It acts as a fluidizer allowing homogeneous dissolution and diffusional mobility of the ionophore inside the membrane. Among five different plasticizers used, the electrode plasticized with DOP showed the optimal response characteristics towards salicylate. When the other four plasticizers were used, the electrode showed a relatively low slope, high detection limit and long response time.

The addition of lipophilic ionic additives to the membrane composition decreases the membrane resistance, co-ion interferences, improves detection limit and selectivity. In practice alkali salts of tetraphenylborate derivatives are used for cationic selective membranes and tetraalkylammonium salts for anionic selective membranes. The potentiometric response of the membrane was greatly improved in the presence of lipophilic cationic additive, MTOAC. It was found that the incorporation of NaTPB, as ionic additive had no significant effect on the response of the membrane but decreased the slope of the calibration graph. Thus several membranes of varying PVC / plasticizer / ionic additive / ionophore ratios were tested. Optimization of the membrane composition for the PVC membrane sensor is presented in Table 7.1. A membrane with the optimized ingredient composition 31 : 61 : 2 : 6 for PVC : DOP : MTOAC : TPMC (w/w%) showed the best potentiometric response for salicylate ions. The sensor Ts_4 with this composition was used for further studies.

The surface morphology of the developed membrane was analysed using SEM. This technique allows the study of membrane surface characteristics such as morphological homogeneity. The SEM image of the membrane of Ts_4 sensor is shown in Figure 7.3. The image obtained shows a homogenous membrane.

7.5.1 Working concentration range and slope

The potential response of the optimized salicylate selective electrode to varying concentrations of salicylate ions was examined. The calibration plot of the EMF (mV) versus $pSal^-$ for the sensor Ts_4 is shown as Figure 7.4. From the graph the working concentration range for the sensor Ts_4 is found to be $1.0 \times 10^{-5} – 1.0 \times 10^{-1}$ M. The slope calculated from the graph is 58.9 (±0.5) mV $decade^{-1}$. The practical limit of detection obtained from the intersection of two extrapolated segments of the calibration graph was about 8.9×10^{-6} M.

7.5.2 Effect of concentration of internal filling solution

The influence of the concentration of internal solution on the potential response of the salicylate selective electrode was studied with different concentration of inner reference solution of sodium salicylate from 1×10^{-1} - 1×10^{-4} M. The results showed that the concentration of internal solution does not cause any significant difference in the potential response of the electrode. So 1×10^{-1} M solution of sodium salicylate was taken as the internal solution in all studies using the sensor.

7.5.3 Response time and life time of the sensors

Response time is the average time required for the ion selective electrode to reach a potential within ±1 mV of final equilibrium value. From Figure 7.5, response time of the sensor Ts_4 was found to be 10s. The membrane electrode could be used for about 3 months without any measurable divergence. The life time of the sensor was tested for about 100 days. During this period the electrodes were daily used and found that after about 3 months there was a considerable change in its slope and detection limit. This may be due to the leaking of membrane ingredients from the membrane to the solution. Thus the prepared membrane electrode could be used for 3 months without substantial change in its performance characteristics.

7.5.4 Effect of pH on the potential response

The effect of pH of the test solution on the potential response of the electrode was tested by measuring the EMF of a cell that contained salicylate adjusted to the appropriate pH. The effect was studied for two fixed concentrations 1.0×10^{-3} M and 1.0×10^{-4} M over a pH range of 2.0 – 9.0. The effect of pH is shown as Figure 7.6. The electrode potential was found to be independent of pH in the range 4.5 – 8.5. The potential change at low pH values may be due to the protonation of salicylate ion and the behaviour at high values of pH can be explained in terms of the increased interference from hydroxide ions.

7.5.5 Potentiometric selectivity

Potentiometric selectivity coefficient was determined by the Fixed Interference Method (FIM)[174,220]. In fixed interference method the response of an ion selective electrode is measured in solutions of the primary ion, salicylate, and interfering anion. The selectivity coefficient for various anions was evaluated with a fixed concentration of interference (10^{-2} M) and varying amount of salicylate concentrations. Table 7.2 lists the potentiometric selectivity coefficient data of the sensor for several anions relative to salicylate. The selectivity coefficients clearly indicate that the electrode is selective to salicylate over a number of other anions. In this work interference studies were made for the ions F^-, Cl^-, Br^-, I^- ClO_4^-, SCN^-, CN^-, PO_4^{3-}, CH_3COO^- and SO_4^{2-}. According to the tabulated data in Table 7.2 the interfering effect of the ions is in the order $ClO_4^- > SCN^- > CN^- > I^- = CH_3COO^- > Br^- > Cl^- > F^- > SO_4^{2-} > PO_4^{3-}$. The table illustrates that the electrode is highly selective to salicylate ion with respect to other anions. This may be due to the weak interaction between other anions and the ionophore.

7.6 Analytical application

The developed electrode was used successfully for the determination of salicylate content of hydrolyzed pharmaceutical preparations. Aspirin tablets of three different companies were taken and treated according to the procedure described in section 2.5.4 in chapter 2. The salicylate content in the resulting solutions were determined by the developed method and spectrophotometric method. The results of analysis by both methods are illustrated in Table 7.3 and it is clear that values obtained by the presently developed method are in good agreement with those obtained by the spectrophotometric method.

7.7 Conclusion

A PVC membrane sensor based on TPMC was developed for salicylate ion. The sensor exhibited a Nernstian slope of 58.9 ± 0.5(mV decade^{-1}) and a linear concentration range of $1.0 \times 10^{-5} – 1.0 \times 10^{-1}$ M. The lower detection limit of the sensor was 8.9×10^{-6} and the working pH range of the sensor was 4.5 – 8.5. It has a shelf life of 3 months and a response time of 10 s. These sensors are very easy to prepare and can be used without significant interference from other anionic species present in the sample. The response characteristic of the sensor is shown in Table 7.4.

Table 7.5 lists the comparative analysis of the characteristics of the developed sensor with some of the reported sensors for salicylate ion. It can be seen that the developed sensor is superior in terms of pH range[153,274,276], life time[150,153,159,274,275,276] and slope[153,276].

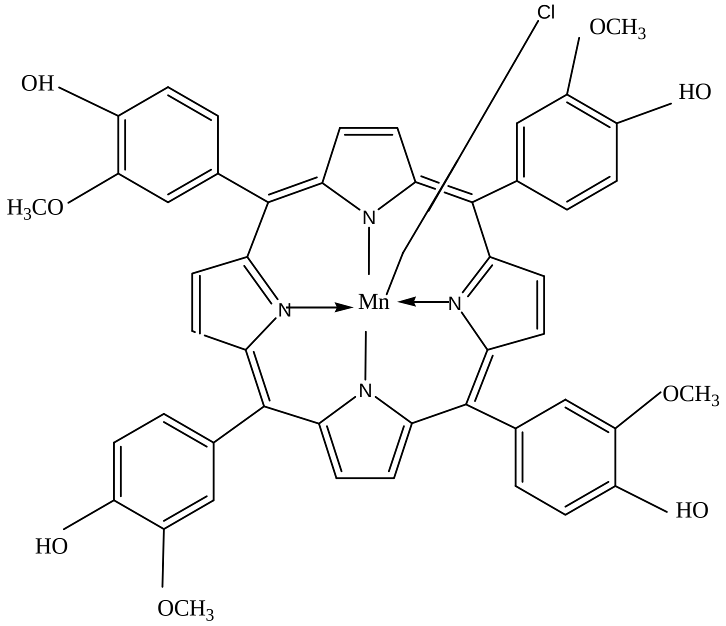

Figure 7.1 – Structure of the ionophore – TPMC

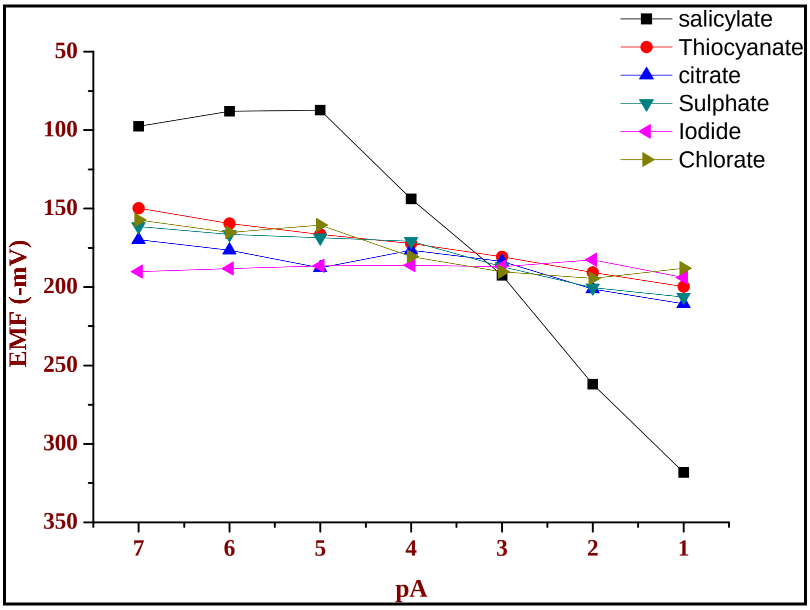

Figure 7.2 - Potential response of the developed sensor Ts_4 based on TPMC to different anions

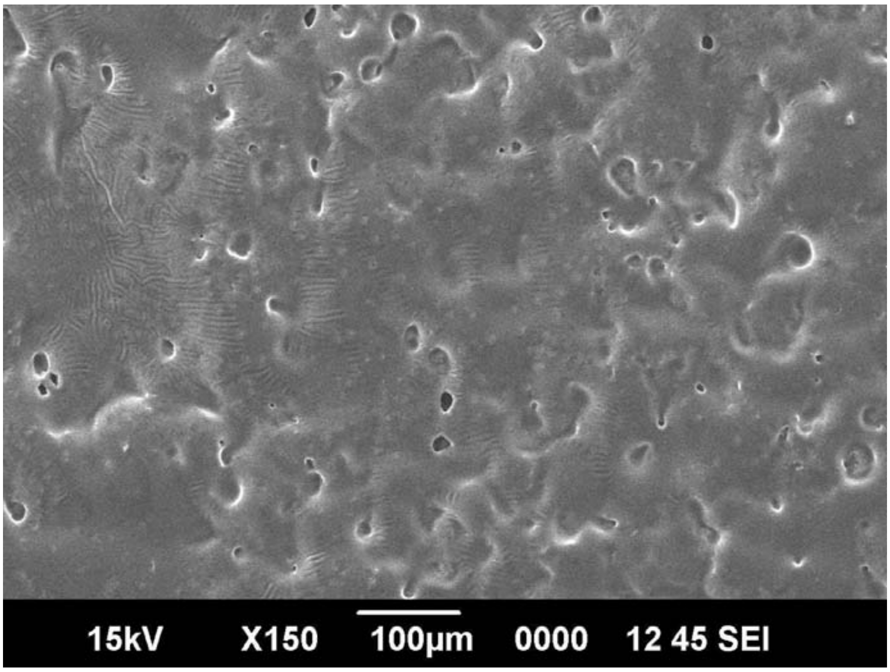

Figure 7.3 - SEM image of the polymeric membrane of the sensor Ts_4

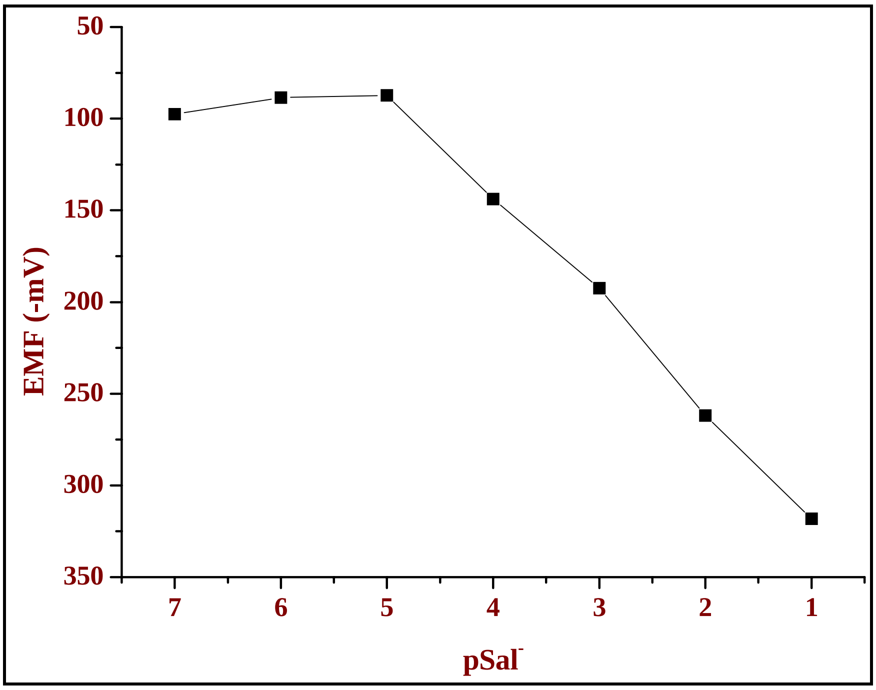

Figure 7.4 – Calibration graph of the PVC membrane sensor Ts_4 based on TPMC

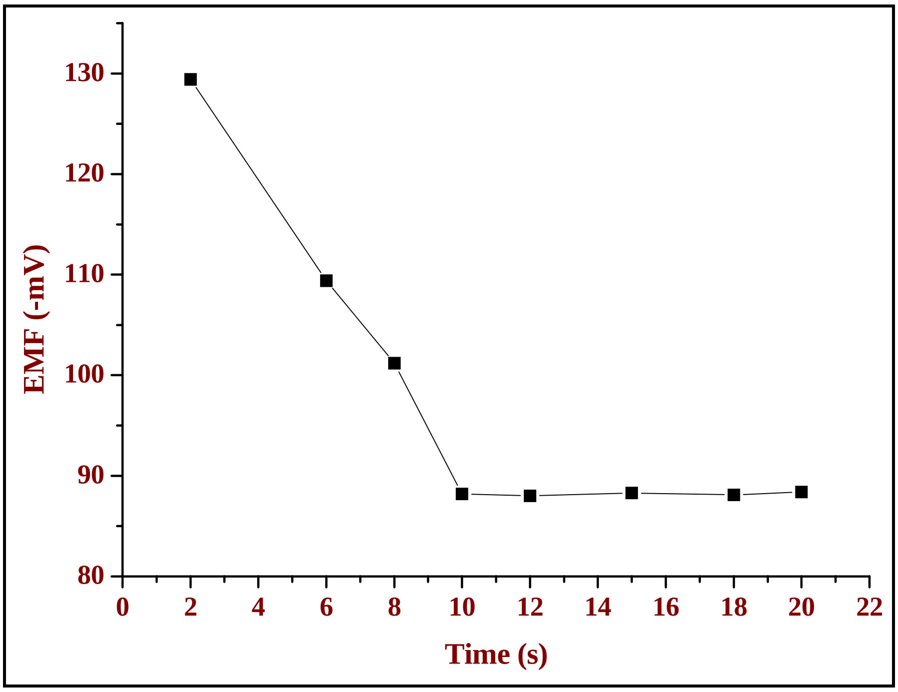

Figure 7.5 - Practical response time of the PVC membrane sensor Ts_4 based on TPMC

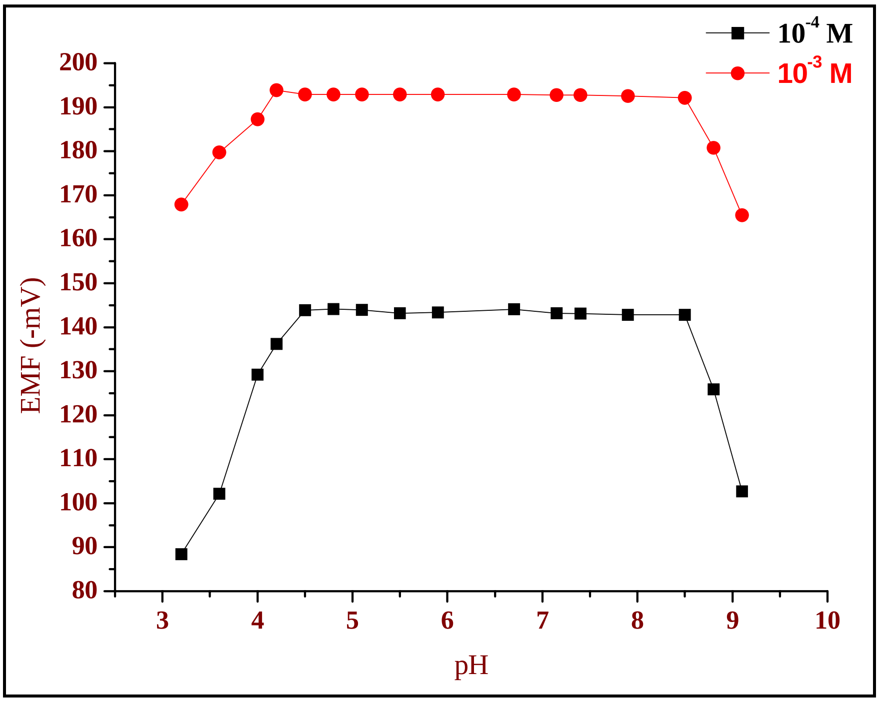

Figure 7.6 – Effect of pH on the cell potential of the PVC membrane sensor Ts_4 based on TPMC

Table 7.1 – Optimization of the membrane ingredients for the PVC membrane sensor based on TPMC

Sensor	**PVC**	**TPMC**	**Plasticizer**	**MTOAC**	**Working concentration range (M)**	**Slope (mV decade^{-1})**
Ts_1	92	6	0	2	$1.0 \times 10^{-4} - 1.0 \times 10^{-1}$	47.3 ± 0.5
Ts_2	33	3	DOP,62	2	$5.2 \times 10^{-5} - 1.0 \times 10^{-1}$	49.1 ± 0.7
Ts_3	30	5	DOP,63	2	$3.0 \times 10^{-5} - 1.0 \times 10^{-1}$	51.3 ± 0.3
Ts_4	31	6	DOP,61	2	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$	58.9 ± 0.5
Ts_5	30	7	DOP,61	2	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$	57.6 ± 0.2
Ts_6	31	6	DOA,61	2	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$	48.6 ± 0.8
Ts_7	31	6	DBS,61	2	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$	50.6 ± 0.3
Ts_8	31	6	DMS,61	2	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$	49.7 ± 0.1
Ts_9	31	6	DBP,61	2	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$	51.9 ± 0.9

Table 7.2 - Selectivity coefficients for the sensor Ts_4 using Fixed Interference Method at 1.0×10^{-2} M concentration of interfering ion.

Interfering ion (X)	Selectivity coefficients for the sensor Ts_4
F^-	5.2×10^{-5}
Cl^-	3.4×10^{-4}
Br^-	3.2×10^{-3}
I^-	5.8×10^{-3}
ClO_4^-	7.8×10^{-1}
SCN^-	8.4×10^{-2}
CN^-	7.5×10^{-3}
PO_4^{3-}	5.0×10^{-7}
CH_3COO^-	5.8×10^{-3}
SO_4^{2-}	8.3×10^{-7}

Table 7.3 - Determination of salicylate content in pharmaceutical preparations

Sample	Maker's specification (mg / tablet)	PVC membrane Sensor* (mg / tablet)	Spectrophotometric Method* (mg / tablet)
1	50	49	48
2	180	178	174
3	350	348	346

*Average of 6 replicates.

Table 7.4 - Response characteristics of the sensor Ts_4

Parameter	Response characteristics
Working concentration range (M)	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$
Slope (mV decade^{-1})	58.9 ± 0.5
Detection Limit (M)	8.9×10^{-6}
Response time	10 s
pH range	4.5 – 8.5
Shelf life	3 months

Table 7.5 - A comparative study of the characteristics of the developed sensor for salicylate with some reported sensors

No.	Working concentration range (M)	pH range	Life time	Slope (mV decade^{-1})	Ref. No
1	$5.0 \times 10^{-7} - 1.0 \times 10^{-1}$	5	2 months	55.0 ± 1.0	153
2	$7.0 \times 10^{-7} - 1.0 \times 10^{-1}$	6.0 – 9.5	2 months	59.5 ± 1.0	150
3	$2.5 \times 10^{-6} - 1.0 \times 10^{-1}$	5	2 months	61.0 ± 1.6	274
4	$1.0 \times 10^{-7} - 1.0 \times 10^{-1}$	5.5 – 10.5	2 months	59.0 ± 0.3	275
5	$1.0 \times 10^{-6} - 1.0 \times 10^{0}$	4.5 – 10.5	3 months	59.1 ± 1.0	157
6	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$	3.5 – 10.5	3 months	60.9 ± 1.0	158
7	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$	2.7 – 7.8	2 months	59.6 ± 1.0	159
8	$6.0 \times 10^{-6} - 1.0 \times 10^{-1}$	5.5	7 weeks	62.0 ± 1.2	276
9	$1.0 \times 10^{-7} - 1.0 \times 10^{-1}$	6.0 – 9.0	3 months	59.1	277
10	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$	4.5 – 8.5	3 months	58.9 ± 0.5	Ts_4

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CONCLUSION

A brief summary of the important findings of the work is discussed in this chapter. It also discusses an outline of the different stages involved in the work in brief.

As part of the present investigations a total of nine sensors have been developed which include PVC membrane sensors and carbon paste sensors. In each of the two types of the sensors, the main component was the electroactive substance or ionophore.

The main stages involved in the work are:

(1) Synthesis of the ionophores.

(2) Characterization of the synthesized ionophores by elemental analysis and spectroscopic methods.

(3) SEM analysis of the membranes prepared in the case of PVC membrane sensors.

(4) Fabrication of different types of sensors

(5) Investigation of the response of the developed sensors to different ions.

(6) Optimization of the membrane composition

(7) Study of the response characteristics of the developed sensors such as slope, linear range, detection limit, effect of concentration of the internal filling solution, effect of pH, shelf life, response time and selectivity.

(8) Analytical applications

(9) Comparison with other reported sensors

The nine sensors fabricated can be listed as follows

Pb^{2+} ions - PVC membrane type and carbon paste type sensors based on 1,3,7,9-tetraaza-2,8-dithia-4,10-dimethyl-6,12-diphenyl cyclododeca-4,6,10,12-tetraene.

Mn^{2+} ions - PVC membrane type and carbon paste type sensors based on 2,8,14,20-tetrakis(naphthyl)calix[4]resorcinarene.

Ni^{2+} ions - PVC membrane type and carbon paste type sensors based on 2,8,14,20-tetrakis(3,4-dimethoxyphenyl)calix[4]resorcinarene.

Cu^{2+} ions - PVC membrane type and carbon paste type sensors based on 5,10,15,20-tetrakis(3- methoxy-4-hydroxyphenyl)porphyrin.

Sal^- (Salicylate ion) - PVC membrane type sensor based on 5,10,15,20-tetrakis(3-methoxy-4-hydroxyphenyl)porphyrinato manganese(III) chloride.

The sensors developed are useful in the determination of lead (ll), manganese (ll), nickel (ll), copper (ll) and salicylate ion. The selectivity studies reveal that the developed sensors are highly selective to the respective ions in the presence of foreign ions. The developed sensors were also employed for the determination of the ions in real samples.

The development and application of ion selective electrodes (ISEs) continue to be exciting and expanding areas of analytical research. They provide accurate, rapid and low cost method of analysis. Also analysis by these methods is non destructive and adaptable to small sample volumes. Ion selective electrodes (ISEs) can be used to make direct or indirect measurements in complex samples without concern about sample colour or turbidity. All these advantages make ISE based techniques attractive to scientists in many disciplines. It is hoped that the developed potentiometric sensors can find wide applications in the future analytical chemistry.

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PAPERS PRESENTED

1. A Nickel (ll) selective Potentiometric sensor based on 3,4-dimethoxy calix[4]resorcinarene in PVC matrix. [International Conference on Materials for the Millennium Matcon 2010 held at CUSAT]
2. Development of a PVC membrane sensor for salicylate ions. [National Seminar on Current Trends in Chemistry CTric 2011 held at CUSAT]
3. Development of a PVC plasticized membrane sensor for Lead (ll) ions. [National Seminar on Current Trends in Chemistry CTric 2012 held at CUSAT]

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