Fabrication of Potentiometric Sensors for the Determination of Lanthanide Ions

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By

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Certificate

Certified that the present work entitled ***"Fabrication of Potentiometric Sensors for the Determination of Lanthanide Ions"****, submitted by Mrs. Beena S is an authentic record of research work carried out by her under my supervision at the Department of Applied Chemistry in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry of the Cochin University of Science and Technology and has not been included in any other thesis submitted previously for the award of any other degree.*

K. Girish Kumar
(Supervising Guide)

Declaration

I hereby declare that the present work entitled **"Fabrication of Potentiometric Sensors for the Determination of Lanthanide Ions"** is based on the original work done by me under the guidance of Dr. K. Girish Kumar, Professor, 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 other degree.

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Preface

Ion-Selective Electrodes are part of a group of relatively simple and inexpensive electro analytical tools which are commonly referred to as potentiometric chemical sensors since selective chemistry take place at 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. Ion selective electrodes allow the specific and quantitative determination of an almost unimaginable number of substances, ranging from simple inorganic ions through amino acids to complex organic molecules. The wide range of applications, low material requirements and simplicity of analytical procedure have not only brought ion-selective electrodes in to the lime light of analytical chemistry, but have promoted their use as tools for physiologists, medical researchers, biologists, geologists, environmental protection specialists, etc.

This thesis presents the synthesis and characterization of six ionophores, fabrication of ten potentiometric sensors based on these ionophores for the determination of lanthanide ions such as La^{3+}, Nd^{3+}, Pr^{3+}, Sm^{3+} and Gd^{3+} and their analytical application. The thesis is divided into eight chapters. A brief outline of the chapters is given below.

Chapter 1 presents a general introduction on the various electroanalytical techniques and their application. The chapter gives an idea of the different types of chemical sensors and discusses in detail about electrochemical sensors. It also gives a brief review of the important potentiometric sensors developed for different lanthanide ions.

Chapter 2 describes in detail the synthesis and characterization of all ionophores. The general method of preparation of the different types of sensors and conductometric study are also discussed. This chapter also deals with the preparation of solutions of metal salts, buffer solutions and binary mixtures along with the details of the instruments used for the investigations.

Chapter 3 details about the response characteristics of two types of sensors based on N^1,N^2-bis(naphthalene-1-yl)methylene(hexa-1,6-diamine) (NAH) as ionophore for the determination of lanthanum. The developed sensors were employed as indicator electrode in the potentiometric titration of lanthanum against EDTA and in the determination of lanthanum from binary mixtures.

Chapter 4 deals with fabrication of PVC membrane and CMCPE sensor for samarium. The sensors incorporate N^1,N^3-bis(3-nitrobenzylidene)propane-1,3-diamine(MBP) as electroactive materials. The response characteristics of developed sensors and the analytical application of the sensors as indicator electrode in the potentiometric titration of samarium (III) against EDTA and in the determination of samarium (III) from binary mixtures are also discussed in this chapter. A comparison with already reported sensors is also included in this chapter.

Chapter 5 discuss the response characteristics of the two sensors based on 1,4-bis (4-hydroxy-3-methoxybezylidene)thiosemicarbazide (HBTS) and N^1, N^2-bis(4-hydroxy-3-methoxybezylidene)butane-1,4-diamine (HMB) for praseodymium. The optimization of membrane composition, analytical applications of the newly developed sensors and a comparison of these new sensors with already reported similar sensors are the other points of discussion in this chapter.

Chapter 6 details on the response characteristics of the sensors developed for neodymium. The fabrication of carbon paste and PVC membrane sensors based on the ionophore N^1,N^2-bis(salicylidine)butane-1,4-diamine (SAB) and application of these sensors as indicator in the potentiometric titration of neodymium with EDTA are included in this chapter. The determination of neodymium present in its binary mixtures using these novel sensors is also discussed in this chapter along with a comparative study of the sensors with those already reported.

Chapter 7 deals with the fabrication of PVC membrane and CMCPE type sensor based on 2-[(2-mercaptophenylimine) methyl] phenol for gadolinium (III). The analytical application of these sensors as indicator electrode in the potentiometric titration of gadolinium (III) with EDTA and in the determination of gadolinium (III) form its binary mixtures are also discussed in this chapter along with a comparative study of the sensors with those already reported.

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.

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Contents

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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. The principal objective of the analytical chemistry is to obtain as much chemical information and of as high quality as possible from objects and systems by using as little material, time and human resources as possible and with minimal costs and risks[1]. There is an escalating need and desire for us to monitor all aspects of our environment in real time and this has been brought about by our increasing concerns with pollution, our health and safety. There is also a desire to determine contaminants and analytes at lower and lower levels and one could say that the aim of all modern analytical chemistry is to lower the detection limits and to improve the accuracy and precision at those limits[2]. Thus analytical chemistry is directly concerned with solving the analytical problems derived from chemical information needs in a variety of economic and social areas including industry, the environment, food science and technology, pharmaceutical analysis and clinical analysis. A qualitative analysis in analytical chemistry yields information about the identity of atomic or molecular species or the functional groups in the sample. Where as a quantitative analysis provides numerical information as to the relative amount of one or more of these components [3]. The quantitative execution of chemical reactions is the basis of traditional or classical methods of chemical analysis: gravimetry and titrimetry.

The need for trace level analysis led to the development of chromatographic methods, spectrophotometric methods and electroanalysis. Chromatography is mainly a separation technique. Ion chromatography is a technique used to separate and concentrate rare earths and transuranic ions. Gas chromatography which involves the separation of a mixture into its constituents by passing a moving gas phase over a stationary sorbent is also used in the determination of cations[4]. Spectrophotometry specifically refers to the use of a spectrophotometer[5]. Quantitative applications of absorption/emission spectroscopy depend on the use of Beer's law, which relates absorbance to concentration. A number of techniques have evolved based on absorption/emission spectroscopy from simple spectrophotometric methods involving the use of a spectrophotometer, flame emission spectroscopy (FES), atomic absorption spectroscopy (AAS), atomic fluorescence spectroscopy (AFS) to the highly precise inductively coupled plasma atomic emission spectroscopy (ICP AES).

Electroanalysis is another analytical technique used for the trace level analysis and can be defined as the application of electrochemistry to solve real life analytical problems[6]. Electroanalytical chemistry encompasses a group of quantitative and qualitative analytical methods based on the electrical properties of a solution of the analyte when it is made a part of an electrochemical cell. These techniques are capable of producing low detection limit and a wealth of characterization information describing electrochemically accessible systems[7]. Electroanalytical measurements have a number of important benefits such as[8].

1. selectivity and specificity
2. selectivity results from the choice of electrode material
3. high sensitivity and low detection limit
4. results can be furnished in real time or close to real time
5. portable sensors with dedicated instrumentation can be fabricated for use outside the laboratory
6. miniaturized sensors for application in cases where other probes may not be usable

The principal criterion of an electroanalytical technique is that the species which is desired to be measured should react directly (or indirectly through coupled reaction) at, or be adsorbed onto the electrode. Electroanalytical measurements can only be carried out in situations in which the medium between the two electrodes making up the electrical circuit be sufficiently conducting[7]. Thus, electroanalysis is complementary to other forms of analysis.

In comparison with other analytical techniques, electroanalytical methods have certain advantages such as the ability to distinguish the oxidation state of the element, provides rapid answer without digestion, as to the labile fraction of a given element in a particular oxidation state and the experiment can be performed on-site in the field. In cases where existing analytical techniques cannot be applied as they require complex and large equipment, electroanalysis provides a ready solution[6].

1.1. Types of Electroanalysis

There are essentially four types of electro analytical measurements that can be performed:

1. Conductometry,
2. Potentiometry,
3. Amperometry
4. Voltammetry.

1.1.1. Conductometry

In conductometry concentration of the species is obtained through measurement of solution resistance and therefore not species selective. It is useful in situations where it is necessary to ascertain whether the total ion concentration is below a certain permissible maximum level or for use as an on-line detector after separation of a mixture of ions by ion chromatography.

1.1.2. Potentiometry

This technique makes use of measurement of equilibrium potential of working electrode with reference to a standard electrode using high-impedance voltmeter under zero current condition. By the careful choice of the working electrode, ion selective electrodes, selective species determination can be achieved with minimal interference from other ions. Detection limits of the order of 100 nanomoles per liter of the total concentration of the ion present in a particular oxidation state, although down to 10 picomolar differences in concentration can be measured.

1.1.3. Amperometry

In this technique, a fixed potential is applied to the working electrode, which causes the oxidation or reduction of the species to be determined and produces current. If this potential is conveniently chosen, then the magnitude of the current is directly proportional to concentration. Detection limit in the micro molar region can be obtained.

1.1.4. Voltammetry

In voltammetry a varying potential is applied at the surface of an electrode and measures the resulting current with a three electrode system. This method can reveal the reduction potential of an analyte and its electrochemical reactivity. This method in practical terms is nondestructive since only a very small amount of the analyte is consumed at the two-dimensional surface of the working and auxiliary electrodes[9]. Several species that react at different applied potentials can be determined almost simultaneously in the same experiment without the need for prior separation. Very low detection limits of down to the picomolar level can be reached using state-of-the-art instrumentation and preconcentration of the analyte on the electrode surface.

An overview of analytical chemistry development demonstrates that electrochemical sensors represent the most rapidly growing class of chemical sensors. Electrochemical sensors and detectors are very attractive for on-site monitoring of analyte in the sample matrix. They are inherently sensitive and selective towards electroactive species, fast and accurate, compact, portable and cost effective. Such devices hold a leading position among sensors presently available and have found a vast range of important applications in the fields of clinical, industrial, environmental and agricultural analysis[10-11].

1.2. Chemical Sensor

A chemical sensor is a device that transforms chemical information, ranging from the concentration of a specific sample component to total composition analysis, into an analytically useful signal[12]. The chemical information, mentioned above, may originate from a chemical reaction of the analyte or from a physical property of the system investigated. There are two parts to a chemical sensor-a region where the selective chemistry takes place and then a 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, the production of heat, or a change in oscillator frequency of a crystal. The transducer responds to this signal and translates the magnitude of the signal into a measure of the amount of analyte. Depending on the type of transducer used, chemical sensors are classified in to the following groups

1.2.1. Electrochemical sensor

Electrochemical devices transform the effect of the electrochemical interaction between the analyte and the electrode into a useful signal. Such effects may be stimulated electrically or may result in a spontaneous interaction at the zero-current condition. These include potentiometric sensors (Ion selective electrode-ISE, Ion selective field effective transistor-ISFETs), voltammetric and amperometric sensors including solid electrolyte gas sensor.

1.2.2. Optical sensors

In optical sensors there is a spectroscopic measurement associated with the chemical reaction. Optical sensors are often referred to as optodes and use of optical fibers is a common feature. Absorbance, reflectance and luminescence measurements are used in the different types of optical sensors.

1.2.3. Mass sensitive sensor

This type of sensor makes use of the piezoelectric effect and include devices such as the surface acoustic wave sensor and are particularly useful as gas sensors. They rely on a change in mass on the surface of an oscillating crystal which shifts the frequency of oscillation. The extent of the frequency shift is a measure of the amount of material adsorbed on the surface.

1.2.4. Heat sensitive sensors

These are often called calorimetric sensors in which the heat of a chemical reaction involving the analyte is monitored with a transducer such as a thermistor or a platinum thermometer.

Compared to optical, mass and thermal sensors, electrochemical sensors are especially attractive because of their remarkable detectability, experimental simplicity and low cost[11].

1.3. Potentiometric Sensor

In potentiometric sensors, the analytical information is obtained by converting the recognition process into a potential signal, which is proportional (in a logarithmic fashion) to the concentration (activity) of species generated or consumed in the recognition event. An ion-selective membrane is the key component of all potentiometric ion sensors[13]. It establishes the preference with which the sensor responds to the analyte in the presence of various interfering ions from the sample. If ions can penetrate the boundary between two phases, then an electrochemical equilibrium will be reached, in which different potentials in the two phases are formed. If only one type of an ion can be exchanged between the two phases, then the potential difference formed between the phases is governed only by the activities of this target ion in these phases. When the membrane separates two solutions of different ionic activities (a_1 and a_2) and provided the membrane is only permeable to this single type of ion, the potential difference (E) across the membrane is described by the Nernst equation:

$$E = \text{constant} + RT/nF \times \ln(a_2/a_1)$$

If the activity of the target ion in phase 1 is kept constant, the unknown activity in phase 2 ($a_1 = a_x$) is related to (E) by:

$$E = \text{constant} + RT/nF \times \ln(a_x/a_1) = \text{const} + S \times \log(a_x)$$

where S=59.16/n [mV] at 298 K and n is the charge of the analyte. The potential difference can be measured between two identical reference electrodes placed in the two phases. In practice the potential difference i.e. the electromotive force is measured between an ion selective electrode and a reference electrode, placed in the sample solution. The potential measurements are made at zero current condition.

The glass electrodes[14-18] for pH measurements were the first developed potentiometric sensors that has been known since 1930s. The membrane in a pH electrode is the sodium silicate glass made by fusing a mixture of Al_2O_3, Na_2O and SiO_2. Increasing the Al_2O_3 content in the glass results in an increasing response to other monovalent cations. In 1937, Kolthoff and Sanders[19] made the first silver halide disc electrodes. In the early 1960s, Pungor[19] published his first paper on AgI-based electrodes and filed a patent on heterogeneous selective membranes with his co-workers, which were the basis for the first commercial solid-state ISEs. Concepts from medicine and physiology also spurred the development of ISEs. In 1964, Cyril Moore and Berton C. Pressman observed that neutral macrocyclic antibiotics induce ion permeation in mitochondria, leading to the development of neutral carrier electrodes. Wilhelm Simon, an eminent organic chemist at ETH in Zurich (Switzerland), used extracts of poisonous mushrooms containing the dipsipetide valinomycin dissolved in a liquid ion-exchanger membrane. Although the response was slow, an electrode that measured K^+ in the presence of a 5000-fold excess of the Na^+ was soon developed and patented. His studies on the structure selectivity relationships of many synthetic ionophores, plasticizers, and additives allowed him to fabricate novel ISEs[20]. In 1966, Frant and Ross[21] were reported the first potentiometric sensor for fluoride based on single crystal electrode. This pioneering work lead to the emergence of a new breed of potentiometric chemical sensors. Ross and Frant teamed up and formed the Orion Research Inc. and both of them considered as the founding father of ion selective electrodes.

The liquid membrane sensor[22] was first introduced in 1967 which provided the means for the direct determination of calcium ions. A major break through occurred in 1970 when a polymer film with sensing properties was produced by immobilizing the electroactive component into poly (vinyl chloride) [23]. Ruzicka et al[24] were the first to introduce liquid state electrode based on carbon in 1970. In 1971, Henry Freiser[25] introduced first coated wire electrode and it received considerable attention because of it dispensed with the inner reference solution. 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 polymerization[19, 26-27]. An enzyme ISE for amygdalin has also been proposed[28]. The development of sensors using spectral grade graphite powder, nujol oil and metal salts of low solubility in a plastic body was described by Mesaric and Dahmen[29] in 1973. In1980, Heimen et al[30] described the first use of a polymer film chemically modified carbon paste electrode (CMCPE).

Various on-line monitoring systems can benefit from the inherent specificity, wide scope, dynamic behavior and simplicity of potentiometric sensors[31]. They have become widely used as detectors in high speed automated flow analyzers, such as air-segmented [32-33] and flow-injection systems[34]. In addition, the coupling of modern ion chromatography with potentiometric detection has been used with significant success[34-35]. Miniaturization of ISE has also permitted their use as on-column detectors for capillary electrophoresis[36].

Rodwedder et al[37] and Fatibello and co-workers[38-41] have shown the use of coated graphite epoxy ion selective electrodes for the determinaton of cations using ion-pair formation with tricaprylylmethylammonium cation in a PVC matrix. Using a similar system with incorporation of saccharinate anion and toluidine, Rover et al[42] have described the construction of a tubular ion selective electrode useful for determination of saccharin. A more sensitive system for saccharin determination has been described by Alfaya et al[43] using a thin film of silsesquioxane 3-n-propylpyridinium chloride polymer coated on a graphite rod. The successful use of thin film electrodes modified, by nickel(II) hexacyanoferrate, for potassium determination has been described by Stradiotto and co-workers[44].

Potentiometric sensors are simple to use, easily automated for rapid sampling, with low interferences from the matrix and can be applied to small volumes. These advantages make potentiometric sensors an ideal choice for both clinical and industrial measurements where speed, simplicity and accuracy are essential. Thus research in the field of potentiometric sensors attains considerable attention and a number of sensors have been reported for metal ions such as alkali, alkaline earth, transition, lanthanides, etc; for anions such as perchlorate ion, Cl^- etc; for pharmaceutical compounds such as acetylsalicylic acid, mebendazole, diclofenac etc[45-57].

There are three basic types of potentiometric devices: ion- selective electrodes (IES), coated wire electrodes (CWES) and field effect transistors (FETS).

1.3.1. Ion-selective electrodes

Ion-selective electrodes are part of a group of relatively simple and inexpensive electroanalytical tools which are commonly referred to as potentiometric chemical sensors since selective chemistry take place at 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.

Ion selective electrodes allow the specific and quantitative determination of an almost unimaginable number of substances, ranging from simple inorganic ions through amino acids to complex organic molecules. The wide range of applications, low material requirements and simplicity of analytical procedure have not only brought ion-selective electrodes in to the lime light of analytical chemistry, but have promoted their use as tools for physiologists, medical researchers, biologists, geologists, environmental protection specialists, etc[58].

1.3.2. Coated-wire electrodes

Coated-wire electrodes (CWEs) were first introduced in the mid of 1970's by Freiser.[25, 59] In the classical CWE design, a conductor is directly coated with an appropriate ion-selective polymer membrane (usually poly(vinyl chloride, poly(vinylbenzyl chloride) or poly(acrylic acid)) to form an electrode system that is sensitive to electrolyte concentrations. The CWE response[25, 59 -60] is similar to that of classical ISE, with regard to detectability and range of concentration. The great advantage is that the design eliminates the need for an internal reference electrode, resulting in benefits during miniaturization, for example. This is particularly useful for the *in vitro* and *in vivo* biomedical and clinical monitoring of different kind of analytes.

1.3.3. Ion-selective field effect transistors (ISFET)

Ion-selective field effect transistors (ISFET) work as an extension of CWE. ISFET incorporate the ion-sensing membrane directly on the gate area of a field effect transistor (FET). The FET is a solid–state device that exhibits highimput impedance and low-output impedance and therefore is capable of monitoring charge buildup on the ion-sensing membrane. The construction is based on the technology used to fabricate microelectronic chips[61-63] and the great contribution is that it is possible to prepare small multisensor systems with multiple gates, for sensing several ions simultaneously, while their small size permits the *in vivo* determination of analytes.

1.4. Classification

Based on the physical state of the substance forming the electrode membrane, potentiometric sensors are classified into

1.4.1. Ion selective electrodes with solid membranes

The membrane can either be 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.

1.4.2. Ion selective electrodes with liquid membranes

In this case the electrode membrane is represented by a water immiscible liquid, in which a dissolved substance capable of exchanging the ion in the solution for which the electrode is selective. This substance is either an associate of this ion with an oppositely charged ion, soluble in the membrane or it is a complex of the ion for which the electrode is selective

According to the type of membrane used, potentiometric sensors are again classified into

1.4.3. Glass membrane

These are selective for ions such as H^+, Na^+, and NH_4^+. The glass electrode for pH measurements were the first potentiometric sensor developed based on glass membrane and has been known from 1930s. The membrane in a pH electrode is essentially a sodium silicate glass made by fusing a mixture of Al_2O_3, Na_2O and SiO_2.

1.4.4. Sparingly soluble inorganic salt membranes

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

1.4.5. Liquid membrane sensor

In these, an ion-selective complexing agent or ion exchanger is immobilized in a plastic matrix such as poly(vinylchloride).

1.4.6. Gel –immobilized and chemically bonded enzyme membranes

These membranes use the highly specific reactions catalysed by enzymes. The enzyme is incorporated into a matrix or bonded onto a solid substrate surface. These are the first examples of biosensors as they make use of biochemical process.

1.5. Ion recognition elements

The most significant component of the sensor is the ionophore or ion carrier which enables the sensor to respond to a particular ion selectively in the presence of other ions. The ionophores can be of an ion exchanger or a neutral macro cyclic compound having molecule-sized dimensions and containing cavities or semi-cavities, Schiff's bases, crown ethers etc.

1.6. Performance Factors

1. Working concentration range and detection limit

The linear range of the electrode is defined as that part of the calibration curve through which a linear regression would demonstrate that the data points do not deviate from linearity by more than 2 mV. According to the IUPAC recommendation[64], the detection limit of an ISE is calculated using the cross-section of the two extrapolated linear parts of the calibration curve.

2. Effect of PH

The pH plays a very important role in the response of the potentiometric sensors. It can influence the formation of protonated and unprotonated species of the same substance, it can favor the redox processes at the electrode or the electrode can become pH selective under certain conditions[65].

3. Response time

The dynamic response time is an essential parameter for a sensor[66]. The response time of an electrode is evaluated by measuring the average time required to achieve a potential within ±1 mV of the final steady-state potential, upon successive measurement of the potential of the respective ion, each having a ten-fold difference in concentration[67-68].

4. Selectivity

Selectivity is the most important characteristics of the sensors. It describes the sensors specificity towards target ion in the presence of other ions.

5. Life time

The life time of the 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 the detection limit of the sensor will decrease and increase, respectively. The reason for the limited lifetime of the carrier-based sensors may be due to the loss of plasticizer, carrier or ionic site from the polymeric film, as a result of leaching into the sample.

1.6.1. Application

The applicability of the sensors for continuous real time monitoring of certain analytes in the environment or in the online and offline process in the industry is of great importance. In addition to pollution applications, farming, gardening, veterinary and mining are all areas where sensors are needed for environmental monitoring.

1.7. A Brief Review on Important Potentiometric Sensors for Lanthanides

As part of the investigations, potentiometric sensors have been developed for the following lanthanides-La^{3+} Sm^{3+} Pr^{3+}, Nd^{3+} and Gd^{3+} A brief review of potentiometric sensors for these metal ions are presented blow.

1.7.1. Lanthanum

A variety of potential ion carriers have been used in the construction of sensors for lanthanum. Ito and Goto[69] tested the response of the lanthanum sensor impregnated with 1-phenyl-3-methyl-4-octadecanoyl-5-pyrazolone. Shamsipur et al[70] developed lanthanum selective sensor using 13,5-trithiacyclohexane as electroactive element.

5,14-N,N'-hydroxyphenyl-4,15-dioxo-1,5,14,18-tetraaza hexacosane was made use of as ion carrier for La^{3+} by Khalil[71]. Liquid membrane sensor[72] was reported with monoazo-12-crown-4 by Gupta et al. The sensor responded to lanthanum in the concentration range 3.16×10^{-5} to 1.0×10^{-1}, but working PH range was only 3-7. Mittal et al[73] explored the use of dicyclohexano derivative of 18-crown ethers as ionophore for lanthanum. Ganjali et al[74] reported a PVC membrane sensor and coated graphite electrode for La^{3+} based on bis(2-mercaptpanil)diacetyl. The sensors showed linear response to lanthanum, but are susceptible to interference from Na^{+} and Cr^{3+}. Akhond et al[75] suggested the use of 2,2'-dithiodipyridine as electroactive element in the fabrication of La^{3+} selective sensor. Singh et al[76] studied the response characteristics of membrane sensor based on hexaaza macrocycle, 8,16-dimethyl- 6,14-diphenyl-2,3,4,10,11,12-dipyridine-1,3,5,9, 11,13-hexaazacyclohexadeca-3,5,8,11,13,16-hexaene as membrane carrier which showed linear response to lanthanum in the range 1.0×10^{-1} - 7.94×10^{-7} M and have good working pH range. 1,10-diaza-4,7,13,16-tetraoxacyclo octadecane-N,N'-diacetic acid was explored as an ion carrier in the construction PVC membrane sensor by Suyanta et al[77]. Even though sensor was selective to lanthanum, other rare earth ions were found to be interfering with its working. PVC membrane sensors incorporating gliclazide, bis (thiophenal) phenylen-1,3-diamine, bis(2-methylbenzaldehyde)butane-2,3-dihydrazon, 4-methyl-2-hydrazinobenzo thiazole,3-hydroxy-N'-(pyridine-2-ylmethylene)-2-naphtho hydrazide, N-(2-pyridyl)-N'-(2-methoxyphenyl) -thiourea, octadentates Schiff's base, and (1-[9{2-[2-2-hydroxy-1-naphtyl)-3-(2-{[(E)-1-(2-hydroxy-1naphtyl)methylidine)amino}ethyl)-1-imidazolidyl} imino)methyl]-2-naphthol) as ionophores were fabricated by Ganjali et al[78-85]. Among them sensor based (1-[9{2-[2-2-hydroxy-1-naphtyl)-3-(2-

{[(E)-1-(2-hydroxy-1-naphtyl)methylidine)amino}ethyl)-1-imidazolidyl} imino) methyl]-2-naphthol) exhibited good detection limit of 4.5×10^{-10} M, but analytical application sensor was not reported.

1.7.2. Samarium

Chowdhury et al[86] reported the first samarium selective sensor impregnated with bis(thiaalkylxanthato)alkanes, but sensor showed interferences in the presence of Cu^{2+} and Fe^{2+}. A liquid PVC membrane sensor was reported by Ganjali et al[87]where the glipizid was used as the ionophore to detect Sm^{3+}. Shamsipur et al[88] fabricated a PVC membrane and coated graphite sensor for samarium based on 4,5,6,7-tetrathiocino[1,2-b:3,4-b]diimidazolyl-1,3,8,10-tetraethyl-2,9-dithione. Coated graphite sensor was found to have better concentration range and detection limit compared to the PVC membrane sensor, but the working pH range was only 4 - 6.5. Mittal et al[89] fabricated samarium selective sensor incorporated with Tin (IV) boratophosphate but the sensor gave a super Nernstian slope. Mittal and Sharma[90] studied the response characteristics of sensor fabricated with Zirconiun(IV)boratophosphate as ionophore which had good life time of 6 months. The use of Spiro[oxirane-pyrazolidinedione] derivative as ionophore for samarium was reported by Saleh et al[91] and the sensor was applied in the determination of acetylsalicylate and carbonate in some drugs. Zamani et al investigated the response characteristics of membrane sensor impregnated with 3-{[2-oxo-1(2*H*)-acenaphthylenyliden] amino}-2-thioxo-1,3-thiazolidin-4-one to Sm^{3+} ions[92]. The first asymmetric potentiometric Sm (III) micro-sensor was reported by Ganjali et al[93]. 2-((2-thioxothiazolidin-4- one) methyl) phenol was employed as ionophore and sensor showed linear response in the range of 1.0×10^{-9} to1.0×10^{-4} M with slope of 18.27.

1.7.3. Neodymium

There are only a limited number of reports on the design of highly selective electrodes for neodymium based on different non cyclic and macrocyclic ionophores. Shamsipur et al[94] reported the construction of a neodymium sensor based on 5-Pyridino-2,8-dithia[9](2,9)-1,10-phenanthrolinephane. The sensor exhibited linear response in the concentration range 1.0×10^{-6} to 1.0×10^{-2} with a fast response time and was applied to the recovery of Nd^{3+} ion from tap water samples. The working pH range of the sensor was found to be very low. P. Norouzi et al[95] developed a membrane sensor based on *N*-(2-Furylmethylene) pyridine-2,6-diamine which showed nenstian response to neodymium ions in the concentration range 1.0×10^{-5} to 1.0×10^{-2} M. The sensor was applied to direct monitoring of Nd^{3+} in various binary mixtures. 2-{[(6-aminopyridin-2-yl)imino]methyl}-phenol based sensor was developed by Ganjali et al[96] which showed Nernstain response to Nd^{3+}. Behmadi et al[97] demonstrated the use of benzylbis (thiosemicarbazone) in the determination of Nd^{3+} over the concentration range 1.0×10^{-2} and 1×10^{-6} M. The sensor was employed for the monitoring of Nd^{3+} from soil and sediment samples. Sensors based on two neutral ionophores, N,N′-bis((1-H-pyrrol-2-yl)methylene) cyclohexane-1,2-diamine and 3,3′-(cyclohexane-1,2-diylbis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene) bis(5-hydroxymethyl)pyridine-2-ol) are described for quantification of neodymium (III) by Gupta et al[98]. Sensor based on 3,3′-(cyclohexane-1,2-diylbis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)bis(5-hydroxymethyl) pyridine-2-ol) showed enhanced selectivity for Nd^{3+}.

1.7.4 Praseodymium

Only four reports have been published in literature for praseodymium. Ganjali et al produced a novel PVC membrane sensor for praseodymium based on hydrazide derivative[99]. Zamania and coworkers[100-101] reported the use of N, N-bis(α-methylsalicylidene) diethylenetriamine and N^1,N^2bis-(2-oxo-1,2-diphenylethylidene) ethane dihydrazide as electroactive components for the determination of Pr^{3+} ions. Both the sensors shoed linear response in the concentration range 1.0×10^{-6} to 1.0×10^{-2} M. The sensor based on N, N-bis (α-methyl salicylidene)diethylenetriamine was applied for the determination of Pr^{3+} from soil and sediments while with N^1,N^2bis-(2-oxo-1,2-diphenylethylidene)ethanedihydrazide based sensor used for the recovery of praseodymium from different water samples and the determination of fluoride ions in mouthwash samples. Gupta et al[102] developed two PVC membrane sensor by incorporating 1,3-diphenylpropane-1,3-diylidenebis(azan-1-ylidene) diphenol and N,N'-bis(pyridoxylideneiminato)ethylene as ion recognition element. Sensor based on N, N'-bis (pyridoxylideneiminato)ethylene exhibited enhanced selectivity for praseodymium.

1.7.5 Gadolinium

Ganjali and coworkers[103-105] reported three sensors for the determination of gadolinium based on different ionophores such as omeprazole, (2-[{3-[(2-sulfanylphenyl)imino)-1-methylbutylidene} amino] phenyl hydrosulfide and bis(thiophenal)pyridine-2,6-diamine. Among them sensor based on bis(thiophenal)pyridine-2,6-diamine showed enhanced response in the concentration range 1.0×10^{-6} to 1.0×10^{-1} M. Zamania et al[106] fabricated membrane sensor based on 6-methyl-4-{[1-(2-

thienyl)methylidene]amino}3-thioxo-3,4-dihydro-1,2,4-triazin-5-(2H)-one and was applied to the determination of concentration of Gd (III) ions in soil and sediment samples. Faridbod et al[107] developed a PVC membrane, sensor based on N-(2-pyridyl)-N'-(4-nitrophenyl) thiourea. The sensor showed linear response in the concentration range 1.0×10^{-8} to 1.0×10^{-3} M, but with a sub Nernstian slopes. Sharma et al[108] studied the response characteristics of sensor fabricated with Zirconium (IV)tungstophosphate (inorganic ion exchanger) as the ionophore which had a good working pH range of 4 – 10, but the slope was found to be super Nernstian of 30 mv/decade.

1.8. Scope of the Present Work

In many fields such as earth science, biology, environment and electronics, the knowledge about elemental distributions and chemical speciation is important[109]. The determination of metal levels especially the toxic ones both in the environment and in biological materials are increasingly demanded by the society. Among the different methods available for the trace level determination of metal ions, electroanalytical techniques, especially electrochemical sensors holds a leading position as they have reached the commercial stage and which have found a vast range of important applications in the fields of clinical, industrial, environmental and agricultural analyses. In continuation to our works in the area of low level monitoring of metal ions[49, 110-113], the present work focused on the fabrication of potentiometric sensors for the determination of lanthanides such as La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+} and Gd^{3+}. It is to be noted in this context, that only a very few sensors are developed so far for the determination of lanthanide ions. This fact enhances the importance of the present work. Total of ten sensors have been fabricated for these metal ions and that includes PVC membrane and CMCPE type sensors. Response characteristics such as working concentration range, slope, detection limit, pH range and selectivity were studied in case of all the sensors. The developed sensors have been applied for the determination of metal ions in real samples and also applied as an indicator electrode in the potentiometric titrations. It is hoped that all the ten sensors developed can be used for the determination of the respective metal ion with high accuracy and precision.

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Chapter 2

MATERIALS AND METHODS

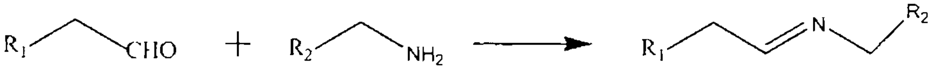
This chapter describes in detail the synthesis and characterization of all ionophores. The general method of preparation of the different types of sensors and conductometric study are also discussed. This chapter also deals with the preparation of solutions of metal salts, buffer solutions and binary mixtures along with the details of the instruments used for the investigations.

2.1. Reagents

Reagent grade sodium tetraphenyl borate (NaTBP), plasticizers such as bis(2-ethyl hexyl) phthalate (BEP), bis(2-ethyl hexyl) sebacate (BES), bis(2-ethyl hexyl) adipate (BEA), di-n-butyl sebacate (DBS), di-n-butyl phthalate (DBP), 3-hydroxy-3-methoxy benzaldehyde, 1-amino-2-hydroxy naphthyl sulphonic acid, 1,3-diaminopropane and 1,4-diamino butane were obtained from Lancaster, UK. High molecular weight PVC and di-n-butyl sebacate (DBS) were purchased from Merck, Germany and were used as received. Lanthanide salts were obtained from IRE LTD, India. Salicylaldehyde, thiosemicarbazide, tri-n-butyl phosphate (TBP), paraffin oil (heavy), tetrahydrofuran (THF) and all other solvents were collected from local vendors. High purity graphite powder was procured from Sigma Aldrich Corporation, USA.

2.2 Synthesis and Characterization of Ionophore

All the ionophores used for the sensor fabrication are Schiff's bases and were synthesized by the condensation of an aldehyde with a primary amine. The general scheme of the reaction is depicted below



They have been characterized by elemental analysis and spectroscopic techniques such as IR and NMR.

2.2.1. N^1,N^2-bis(naphthalene-1-yl)methylene(hexa-1,6-diamine) (NAH)

The ionophore N^1,N^2-bis(naphthalene-1-yl)methylene(hexa-1,6-diamine) (NAH) was synthesized by refluxing a mixture of 1-naphthaldehyde (0.2mol) and 1,6-diaminohexane (0.1mol) in 20 mL methanol for 3 hrs. The solvent was evaporated to 10 mL and resulting solution was cooled at room temperature. Pale yellow crystals were obtained which was then recrystalized from methanol.

The structure of the product was confirmed by IR, NMR and elemental analysis and is depicted in the chapter 3 as figure 3.1.

CHN analysis

Found (%): C- 84.90, H- 7.47, N-7.15

Calcd (%): C- 85.67, H- 7.19, N- 7.14

Spectroscopic analysis

IR (KBr)υ_{max}/cm: 1634(C=N, s), 1619, 3045, 2929, 1004, 801, 469, 550, 646, 727, 619, 944, 961, 1234, 1336, 1361, 1463.

^{1}HNMR (DMSO-D_6): 7.8-7.72 (2H, m, Ar-H), 7.5 (2H, t, Ar-H), 7.6 (4H, m, Ar-H), 7.3 (4H, d, Ar-H), 7.9 (2H, d, Ar-H), 8.7 (2H, s, CH=N), 3.6 (4H, t, N-CH_2), 1.7(4H, m, CH_2), 1.24 (4H, m, CH_2)

2.2.2. N^1,N^2-bis(salicylidine)butane-1,4-diamine (SAB)

The Schiff's base N^1,N^2-bis(salicylidine)butane-1,4-diamine(SAB) was prepared by refluxing (0.02mol) salicylaldehyde and (0.01mol) butane-1,4-diamine in 20 mL methanol for 3hrs.The yellow flakes that separated out was filtered and recrystallized from dichloromethane. The formation of the ionophore was confirmed by elemental analysis and spectroscopic techniques. The structure of the ionophore is depicted as figure 6.1 in chapter 6.

CHN analysis

Found (%): C - 72.44, H - 6.30, N - 9.25

Calcd (%): C - 72.95, H - 6.80, N - 9.45

Spectroscopic analysis

IR (KBr, cm^{-1}): 1604 (CH=N, S), 1581, 1528, 3565, 2885, 1352, 1490, 1282, 1223, 1047, 942,893,744,750, 659.

^{1}HNMR (DMSO-D_6): 8.5 (2H, s, CH=N), 7.49 (2H, d, Ar-H), 7.3 (2H, t, Ar-H), 6.9 (2H, m, Ar-H), 6.7(2H, m,Ar-H), 3.5 (4H, t, N-CH_2), 11.29 (2H, s, OH), 1.7 (4H, m, CH_2)

2.2.3 1,4-bis(4-hydroxy-3-methoxybezylidene)thiosemicarbazide (HBTS)

The ionophore, 1,4-bis(4-hydroxy-3-methoxybezylidene) thiosemi carbazide was synthesized by refluxing a mixture of 4-hydroxy-3-methoxy bezaldehyde (0.02 mol) and thiosemicarbazide (0.01 mol) in ethanol (20 mL) for 3 hrs. Precipitate obtained was filtered, washed, dried and then recrystallized from methanol. The ionophore was characterized by elemental analysis and spectroscopic techniques and the structure is depicted in chapter 5 as figure 5.1

CHN analysis

Found: C - 57.38, H - 5.17, N - 11.39, S-8.72

Calcd: C - 56.81, H - 4.77, N - 11.69, S-8.92

Spectroscopic analysis

IR (KBr) υ_{max}/cm: 1583 (C=N, s), 3564, 2983, 1880, 1505, 1455, 1371, 1027, 944, 852, 838,778.

^{1}HNMR (DMSO-D_6): 6.84 (2H, m, Ar-H), 2.3 (1H, s, N-H), 7.03 (2H, m, Ar-H), 7.1 (2H, s, Ar-H)) 8.12 (2H, s, CH=N), 3.81 (6H, s, OCH3), 11.2 (2H, s, OH)

2.2.4. N^1,N^2-bis(4-hydroxy-3-methoxybezylidene)butane-1,4-diamine (HMB)

The synthesis of the ionophore N^1,N^2-bis(4-hydroxy-3-methoxybezylidene) butane-1,4-diamine (HMB) was achieved by refluxing 4-hydroxy-3-methoxybenzaldehyde (0.02 mol) and 1,4-diamino butane (0.01 mol) in 30 mL ethanol for 4 hrs. The yellow precipitate was filtered, dried and recrystallised from the same solvent. The structure of the product was confirmed by elemental analysis, IR and NMR and is given in chapter 5 as figure 5.2.

CHN analysis

Found: C - 67.58, H - 7.68, N - 7.19

Calcd: C- 67.72, H - 7.58, N - 7.52

Spectroscopic analysis

IR (KBr, cm1): 1585 (CH=N, S), 3565, 2865, 1592, 1515, 1470, 1335, 1239, 1028, 942, 871, 621.

^{1}HNMR (DMSO-D$_6$): 8.15 (2H, s, CH=N), 3.7 (6H, s, OCH$_3$), 1.6 (4H, m, CH$_2$), 7.03(2H, d, Ar-H), 6.8 (2H, m, Ar-H), 7.09 (2H, s, Ar-H), 11.2 (2H, s, OH), 3.6 (4H, t, N-CH$_2$), 1.7 (4H, m, CH$_2$)

2.2.5 N^1, N^2- bis(3-nitrobenzylidene)propane-1,3-diamine (MBP)

The ionophore, N^1, N^2-bis(3-nitrobenzylidene)propane-1,3-diamine was synthesized by refluxing a mixture of 3-nitrobenzaldehyde (0.02 mol) and 1, 3-diaminopropane (0.01mol) in methanol (20 mL) for 3hrs. The reaction mixture was cooled to room temperature. Pale yellow crystals were obtained which was then filtered, washed, dried and recrystallized from methanol. The structure of the product was confirmed by elemental analysis, IR and NMR and is given in chapter 4 as figure 4.1.

CHN analysis

Found: C-60.12, H-4.54 and N- 16.38

Calcd: C-59.99, H-4.74 and N-16.46

IR (KBr, cm^{-1}): 1647 (C=N, s), 1536 ($ArNO_2$), 1353 ($ArNO_2$), 1466, 1059, 742, 2863, 3085

^{1}HNMR ($CDCl_3$): 8.57 (2H, s, Ar-H), 8.09 (2H, m, Ar-H), 7.6 (2H, m, Ar-H), 8.47 (2H, s, CH=N), 3.81 (4H, t, NCH_2), 2.16 (2H, m, CH_2), 8.2 (2H, d, Ar-H).

2.2.6. 2-((Z)-(2-mercaptophenylimine)methyl)phenol (MPM)

The ionophore, MPM was synthesized by refluxing a mixture of salicylaldehyde (0.001mol) and thiophenol (0.001mol) in ethanol (20 mL) for 3hrs.The reaction mixture was cooled to room temperature. Pale yellow crystals were obtained which was then filtered, washed, dried and recrystallized from the same solvent. The formation of the ionophore was confirmed by elemental analysis and spectroscopic techniques. The structure of the product is depicted as figure 7.1 in chapter 7.

CHN analysis

Found: C-68.36, H-4.74, N-6.46, S-13.63

Calcd: C-68.09, H-4.84, N-6.11, S-13.98

IR (KBr, cm^{-1}): 1630 (C=N, s), 3442, 1489, 1311, 1218, 973, 822, 734, 509.

^{1}HNMR ($CDCl_3$): 7.1 (3H, t, Ar-H), 5.2 (1H, s, Ar-OH), 7.45 (1H, d, Ar-H), 8.39 (1H, s, CH=N), 6.7 (1H, d, Ar-H), 6.8 (1H, t, Ar-H), 7.24 (1H, d, Ar-H), 6.9 4 (1H, t, Ar-H), 3.1 (1H, s, SH)

2.3. Preparation of the Metal Salt Solution

The stock solution (1.0×10^{-1} M) 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 Lanthanum chloride solution

About 9.284 g of lanthanum chloride was accurately weighed and transferred in to a 250 mL standard flask. The solution was then made up to the mark with distilled water and standardized using EDTA method.[4]

2.3.2. Neodymium chloride solution

8.967 g of neodymium chloride was accurately weighed and transferred to 250 mL standard flask. 2 mL (1N) HCl was added to dissolve the salt and made up to the mark with distilled water. It was then standardized using EDTA method[4].

2.3.3. Praseodymium solution

11.5g of praseodymium nitrate was accurately weighed and quantitatively transferred to a 250 mL standard flask followed by dilution with distilled water to the mark. Standardization of the stock solution was done according to EDTA method[4].

2.3.4 Samarium chloride solution

6.42g of samarium chloride was weighed and transferred to 250 mLstandard flask and diluted with distilled water up to the mark. Solution was then standardized by EDTA method[4].

2.3.5 Gadolinium chloride solution

9.29g of gadolinium chloride was weighed and transferred to 250 mL standard flask. 2 mL (1N) HCl was added to dissolve the salt and was then diluted with distilled water up to the mark. The solution was then standardized by EDTA method[4].

2.4. Preparation of Buffer Solutions

Buffers were used to maintain pH of the test solution and also during EDTA titrations. They were freshly prepared according to Robinson Table [114].

2.4.1 pH 5.0

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

2.4.2 pH 7

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

2.5 Preparation of Real Samples

The analytical applicability of the developed sensor was tested for the determination of metal ions from their binary mixtures.

2.5.1 Binary mixtures of Lanthanum

La-Pr, La-Nd, La-Pb and La-Ca combinations were selected for the study. Concentrations of both the components in each combination were made as 5.0 $\times 10^{-4}$ M. 0.0186 g $LaCl_3$, 0.0218 g praseodymium nitrate, 0.0179 g neodymium chloride, 0.0139 g lead chloride and 0.0055 g calcium chloride were accurately weighed and La-Pr, La-Nd, La-Pb and La-Ca binary mixtures were prepared by dissolving their respective salts in 100 mL standard flask. The solutions were made up to the mark with distilled water. pH of the mixtures were maintained at 5.

2.5.2 Binary mixtures of Neodymium

Nd-Pr, Nd-La and Nd-Pb combinations were selected for the study. Concentrations of both the components in each combination were made 5.0 $\times 10^{-4}$ M. For that 0.0179 g neodymium chloride, 0.0218 g of praseodymium nitrate, 0.0139 g lead chloride and 0.0186 g lanthanum chloride were accurately weighed and Nd-La, Nd-Pr and Nd-Pb binary mixtures were prepared by dissolving their respective salts in 100 mL standard flask. The solutions were made up to the mark with distilled water. pH of the mixtures were maintained at 7.

2.5.3. Binary mixtures of praseodymium

In this case Pr-La, Pr-Nd and Pr-Ca combinations were selected. Concentrations of both the components in each combination were made 5.0 $\times 10^{-3}$ M. For that 0.2175 g of praseodymium nitrate, 0.1856 g lanthanum chloride, 0.1793 g neodymium chloride and 0.0555 g calcium chloride were accurately weighed and Pr-La, Pr-Nd and Pr-Ca combinations were prepared by dissolving their respective salts in 100 mL standard flask. The mixtures were made up with distilled water. pH of the mixtures were maintained at 7.

2.5.4 Binary mixtures of samarium

Sm-Nd, Sm-Gd, Sm-Ca and Sm-Pb combinations were selected. Concentration of both the components in each combination were made 5.0 $\times 10^{-4}$ M. 0.0128 g samarium chloride, 0.0179 g neodymium chloride, 0.0186 g gadolinium chloride, 0.0055 g calcium chloride and 0.0139 g lead chloride were accurately weighed and Sm-Nd, Sm-Gd, Sm-Ca and Sm-Pb combinations were prepared by dissolving their respective salts in a 100 mL standard flask. The solutions were made up to the mark. pH of the mixtures were maintained at 7.

2.5.5 Binary mixtures of gadolinium

Gd-La, Gd-Pb and Gd-Pr combinations were selected for the study. Concentrations of both the components in each combination were made 5.0×10^{-4} M. 0.0186 g gadolinium chloride, 0.0186 g lanthanum chloride, 0.0139 g lead chloride and 0.0218 g of praseodymium nitrate were accurately weighed and Gd-La, Gd-Pb and Gd-Pr combinations were prepared by dissolving their respective salts in a 100 mL standard flasks. The solutions were made up to the mark. pH of the mixtures were maintained at 7.

2.6. Conductometric Study

Conductometric studies were carried out to investigate the extent of complexation of ionophores towards different metal ions. Complexation of each selected ionophore with a number of metal ions such as Sm^{3+}, La^{3+}, Gd^{3+}, Nd^{3+}, $Pr^{3+}$and Pb^{2+} were investigated conductometrially in acetonitrile solution (1.0×10^{-4} M of cation solution and 1.0×10^{-2} M of ligand) at 25± 1 ^{0}C. 20 mL of each ion solution was titrated with 1.0×10^{-2} M of respective ionophore solution in order to find out the stability of resulting complexes. The resulting molar conductance versus [M^{n+}/ L] mole ratio showed the formation of 1:1 complexes between ionophores and metal ions.

Formation constant of the complexes, K_f, of each ionophore towards different metal ions were evaluated by computer fitting of the molar conductance / molar ratio data with appropriate equations. [115-120]

2.7. Preparation of the Sensor Membrane

The most important component in a sensor is the electroactive ingredient or ionophore, which is responsible for the ion recognition. There are two different types of sensors that have been studied.

2.7.1. PVC membrane sensor

PVC membrane sensor is a liquid membrane sensor where immobilization of the ionophore in to the polyvinyl chloride is achieved to produce a thin film. Ionophore, PVC and plasticizer were taken in percentage weight. The percentage weight of these components in PVC membranes were approximately 1-7, 30-33, 60-69 for ionophore, PVC and plasticizer respectively. In the case of metal ion sensors, ionic additives or anionic excluders (sodium tetraphenyl borate or oleic acid) were added to prevent the interference from the sample anions. Its composition varies from 2-5% (w/w). All the components were taken in the specified ratio and dissolved in THF. The solution was poured into a glass ring stuck on to a glass plate and left for evaporation of THF. Small disc shaped membranes were cut out and glued to one end of a hollow Pyrex glass tube using Teflon tape. The tube was filled with the metal salt solution (internal solution) and the membrane was conditioned by dipping the electrode in 1.0×10^{-1} M metal salt solution. Figure 2.1 represents the stages involvedin the fabrication of a PVC membrane sensor.

2.7.2. Chemically modified carbon paste electrode (CMCPE)

Graphite and the ionophore (in varying %w/w ratios) were mixed thoroughly using a motor and piestle to give a homogeneous mixture. To this, acetone was added and this mixture was left overnight for the acetone to evaporate completely. It was made a paste by using binders. This paste was then packed to one end of the Teflon holder in which electrical contact was made with a copper rod through the centre of the electrode. Appropriate packing and a smooth surface was achieved by pressing the surface of the sensor against a filter paper. The sensor was conditioned in a 1.0×10^{-1} M solution of metal salt solution. Figure 2.2 represents the stages involved in the fabrication of a chemically modified carbon paste sensor.

2.8. EMF Measurements and Calibration

All measurements were performed by using a Metrohm 781 ion meter at 25±1°C. The cell assembly for potentiometric measurements can be represented as follows

PVC membrane sensor

Ag, AgCl| KCl || test solution |membrane | internal solution (1.0×10^{-1} M $SmCl_3$) || KCl | AgCl, Ag.

CMCPE

Ag, AgCl| KCl || test solution |CPE

The performance of the developed sensors were investigated by measuring potentials in the metal salt solution in the concentration range 1.0×10^{-1} - 1.0×10^{-7} M. The solutions were stirred and the stable potentials readings were taken.

2.9. Instrumentation

The CHN analysis were done on a CHN analyser, Elementar vario ELIII and FTIR were recorded on a ThemoNicolet Avartar370 spectrometer using KBr Pellet in the range 4000-400cm^{-1} at Sophisticated Test and Instrumentation Centre (STIC), Kerala. Proton NMR was taken in Bucker 300 MHz instrument using DMSO as solvent at NIIST, Trivandrum. Conductometric studies were carried out on a digital conductivity meter and all potentiometric measurements were done using Metrom pH meter.

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

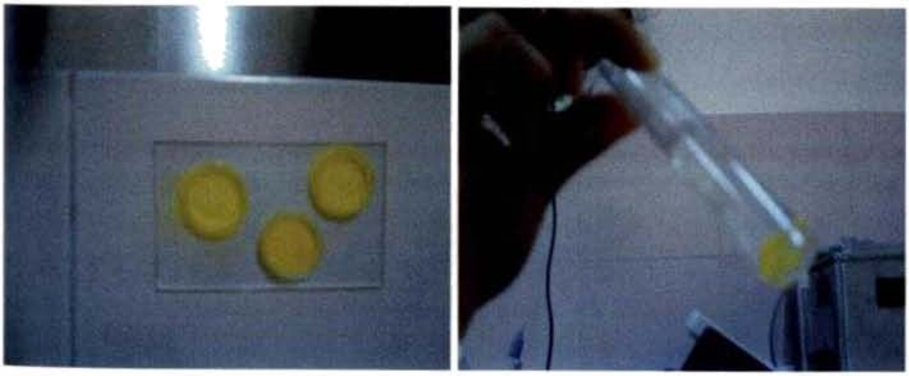


Figure 2.2 Stages involved in the fabrication of chemically modified carbon paste sensor

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Chapter 3

SENSOR FOR LANTHANUM

This chapter details about the response characteristics of two types of sensors based on Schiff's base as ionophore for the determination of lanthanum. The developed sensors exhibited good response over the concentration range of 1.0×10^{-6} to 1.0×10^{-1} M and fast response time. This sensor was used as indicator electrode in the potentiometric titration of lanthanum against EDTA and in the determination of lanthanum from binary mixtures.

Lanthanum is a rare earth element and its oxide compounds are widely used in industry. This includes the use of lanthanum in the preparation of glass fibers for optical purposes, in gasoline cracking compounds and in iron and steel industry to remove sulphur, carbon and electronegative elements from iron and steel[79, 121]. Lanthanum carbonate is used medically as a phosphate binder for the treatment of hyperphosphatima and lanthanum chloride manifests antitumor properties[122]. Inspite of all these uses, it is to be noted that lanthanum salts exhibits moderate toxicity.

Conventional methods employed for the determination of lanthanide ions are spectrophotometry[123], titrimetry[124], AES[125], isotopic dilution mass spectrometry[126] and neutron activation analysis[127]. But these methods required multiple sample preparation and also infrastructure backup[4] and hence are not convenient for analysis.

This chapter describes the fabrication of two types of sensor based on Schiff's base as ionophore for lanthanum.

3.1. Ionophore

The synthesis and characterization of the ionophore, N^1,N^2-bis (naphthalene-1-yl)methylene(hexa-1,6-diamine) (NAH) has been discussed in the section 2.2.1 of chapter 2 and structure is given as figure 3.1.

3.2. Fabrication of Lanthanum Selective Sensor

3.2.1. Potential response of the NAH based sensors

In order to check the suitability of NAH as potential ionophore, PVC membrane electrodes and chemically modified graphite electrodes were prepared for a wide variety of cations. General methods for the fabrication of these two types of electrodes are discussed in section 2.7 of chapter 2. In the preliminary step, PVC membranes having the composition of NAH (2%), PVC (32%), plasticizer (58%) and oleic acid (8%) were prepared. Similarly, graphite electrodes with graphite and ionophore in the ratio 95:5 were also prepared. The potential responses of various electrodes were obtained separately for each metal ion and are depicted as figure 3.2 and 3.3. It was found that, both the developed sensors demonstrated most sensitive response to lanthanum(III) which may be attributed to the selective complexation behavior of the ionophore to La^{3+} over other metal ions, as well as the rapid ion exchange kinetics of the resulting complex formed at the membrane sample interface.

Conductometic studies were also carried out to understand the selective complexation of the ionophore towards lanthanum ions. The complexations of NAH with different metal ions were studied conductometrically in acetonitrile solution at 25 ± 1 °C and results are summarized in Table 3.1. It was observed that the formation constant of the La^{3+}- NAH complex is more than that of the other metal ions studied. Since the conductometric results were also supportive to the selection of NAH as ionophore for lanthanum, lanthanum selective sensors have been fabricated using NAH as electroactive material.

3.2.2. Fabrication of the sensor membrane

The PVC membrane sensor was fabricated from a solution of NAH, (ionophore), PVC, plasticizer and additive in THF, following the general methods as discussed in section 2.7.1 of chapter 2. The sensor tube was filled with an internal solution of 1.0×10^{-1} M lanthanum chloride and conditioned by soaking in 1.0×10^{-1} M lanthanum chloride solution. The composition ratio of ionophore, PVC, plasticizer and additives in the membrane were also varied so as to obtain an optimized membrane composition. The optimized composition which resulted in a best Nernstian response and working concentration range was found to be 3:32:57:8 (ionophore: PVC: plasticizer: additive) (w/w %).

For the fabrication of CMCPE type of sensor, the ionophore and graphite were made in to a paste using a binder and this paste was packed into the Teflon holder as detailed in section 2.7.2 chapter 2. The best composition ratio for CMCPE type of sensor was found to be 90:10 (graphite: ionophore).Tri-n-butyl phosphate was found to be the suitable binder.

3.2.3. Equilibration of membranes and potential measurements

The two type of sensors were equilibrated by soaking in 1.0×10^{-1} M $LaCl_3$ solution .The equilibration time was 2 days for PVC membrane type sensor and 1 day for CMCPE type sensor. The potential measurements were carried out at 25 ± 1 °C on Metrohm 781 ion meter (pH maintained at 5 by adding buffer) in the concentration range 1.0×10^{-6} to 1.0×10^{-1} M $LaCl_3$ solution. The cell assembly for the two types of sensors can be represented as follows,

PVC membrane sensor

Ag, AgCl | KCl || test solution |membrane | internal solution (1.0×10^{-1} M $LaCl_3$) || KCl | AgCl, Ag

CMCPE sensor

Ag, AgCl | KCl || test solution | CMCPE

The performance of the sensors were investigated by measuring their potentials in $LaCl_3$ solution prepared in the concentration range

1.0×10^{-6} to 1.0×10^{-1} M. The solutions were stirred and the stable potential reading was taken.

3.2.4. Optimization of membrane composition

The sensitivity, linear dynamic range and selectivity of the membrane sensor depend on the nature and amount of carrier, plasticizer and lipophilic additives.[128-137] Hence, the optimizations of membrane composition are very important. A set of 10 sensors were fabricated with varying composition of membrane ingredients and are presented in the Table 3.2. Initially the effects of sensors, N_1-N_4, with different plasticizers were studied. Among the different plasticizers studied, the sensor, N_4, with DBP as the plasticizer resulted in best Nernstian response. This may be due to the plasticizer influence on the dielectric constant of the membrane phase, the mobility of the ionophore molecules and the state of the ligands.[138-142] The amount of ionophore has got influence on the concentration range and slope of the sensor. The optimum amount of ionophore was found to be 3% and further increase in the ionophore results in an increase in the slope. The presence of lipophilic additives improves the response behavior, selectivity and sensitivity of the PVC membrane sensors.[143-156] The effect of additives such as oleic acid and NaTBP on the response characteristics of the developed sensors were investigated and are compiled in Table 3.2. The response of the sensor, N_9, with NaTBP as anion excluder was found to be slow with super Nernstian slope in the concentration range 1.0×10^{-5} to 1.0×10^{-1} M $LaCl_3$ solution. But the sensor, N_6, with oleic acid as additive gave a Nernstian slope of 21.0 mV/decade in the range 1.0×10^{-6} to 1.0×10^{-1} M. The optimum amount of oleic acid was found to be 8% and further increase in the oleic acid percentage has no significant influence on the sensor response. The PVC membrane sensor, N_6, having a composition of 3% ionophore, 32% PVC, 57% DBP and 8% oleic acid exhibited best performance. Further studies were carried out with this sensor.

SEM analysis was conducted inorder to study the surface morphology of the optimized membrane. SEM is a strong and reliable tool for studying in detail the influence of surface morphology of the membranes and the reproducibility of the preparation conditions. The extend of homogeneity of a membrane surface is clearly visible in the SEM image. A homogenous membrane is found to exhibit good response characteristics such as high sensitivity and long shelf life. The SEM image obtained in the case of N_6 is found to be homogeneous and this accounts for the long life time and good response characteristics of the membrane sensor.

Carbon paste sensor based on NAH was also fabricated for Lanthanum. A set of seven CMCPE type sensors were developed by varying sensor metrics components and results are consolidated in the Table 3.3. Among the different binders tested tri-n-butyl phosphate was found to be the most suitable one. It was observed that the sensor, Nb_6, containing 10 % of modifier showed Nernstian response. However, increasing the ionophore content from 10% to 15% led to a super Nernstian slope which could probably be due to the decrease in conduction of the sensor material. Thus the sensor, Nb_6, with the composition ratio 90:10 (graphite: ionophore) was used for further studies.

3.2.5. Calibration curve and statistical data

Figure 3.5 and 3.6 represents the calibration graph for the sensors N_6 (PVC membrane sensor) and Nb_6 (CMCPE). Both the sensors showed linear response over the concentration range 1.0×10^{-6} to 1.0×10^{-1} M. The slope of the calibration graph was found to be 21.0 mV/decade and 21.4 mV/decade for the sensors N_6 and Nb_6 respectively. The limit of detection as determined from the intersection of the two extrapolated segments of the calibration graphs was found to be 1.0×10^{-6} M for the sensors N_6 and Nb_6.

3.2.6. Dynamic response time

Dynamic response time is an important factor for any ion selective sensor. The practical response time was recorded by changing the La^{3+} concentration in the range 1.0×10^{-6} to 1.0×10^{-1} M. The sensors, N_6 and Nb_6, reached their equilibrium potential in a very short time and were found to be 35s and 10s respectively. The practical reversibility of the sensors N_6 and Nb_6 were evaluated by taking measurements for La^{3+} in the sequence of high-to-low concentration and vice versa. The responses of the sensors remained unchanged regardless of the change in concentration of the metal salt solution.

3.2.7. Effect of pH

The pH dependence on the EMF of the sensors N_6 and Nb_6 were studied over the pH range 2 - 11 at 1.0×10^{-3} M $LaCl_3$. The pH was adjusted by adding Buffer. The results are depicted in figure 3.7 and figure 3.8 for the sensor N_6 and Nb_6 respectively. It was found that potential remains constant in the pH range 4.1 to 8.5 and 4.4 to 7.5 for the sensors N_6 and Nb_6 respectively. The observed potential drift at the higher values of pH could be due to the formation of some hydroxyl complex of La(III) in the solution and at the lower pH due to the response of the sensors to hydrogen ions.

3.2.8. Selectivity coefficients

The influence of the interfering ions on the response behavior of the sensor is usually described in terms of selectivity coefficient. The potentiometric selectivity coefficients of the sensors N_6 and Nb_6 were evaluated by Fixed interference method (FIM) [157-159] at 10^{-2} M concentration of interfering ions using the equation given below.

$$K^{pot}_{A,B} = a_A / a_B^{\ z_A/z_B}$$

Where a_A is the activity of the primary ion A (La^{3+}) at the lower detection limit in the presence of interfering ion B, a_B , the activity of the interfering ion B and z_A and z_B are their respective charges. The selectivity coefficients so obtained are compiled in Table 3.4. The sensors N_6 and Nb_6 showed good selectivity for lanthanum in the presence of ions Na^+, K^+, Mg^{2+}, Pb^{2+}, Ag^+, Ca^{2+}, Pr^{3+} and Sm^{3+}. However the selectivity coefficient value of gadolinium ion shows slight interference at higher concentration.

3.2.9. Shelf Life

The potential measurements were recorded every day over a period of time to determine the shelf life of the sensors. The operative life time for the sensors N_6 and Nb_6 was found to be 7 weeks and 5 weeks respectively. The sensors were all immersed in 1.0×10^{-1} M $LaCl_3$ solution when not in use. The surface of CMCPE type sensor could be renewed by squeezing off some paste, polishing the new surface against a filter paper and equilibrating the sensor in the metal salt solution for 1 day.

3.2.10. Analytical applications

The sensors N_6 and Nb_6 were successfully applied for the direct monitoring of La(III) in binary mixtures and the results are summarized in Table 3.5. It is observed that the recovery of La(III) ions are quantitative in all cases and the sensors can be used for the determination of La(III) in real samples having different analytical matrixes.

The developed sensors have been successfully applied as an indicator electrode in the titration of La(III) with EDTA at pH 5.The titration curves for the sensors, N_6 and Nb_6, are shown in figure 3.9 and 3.10 respectively. The shape of the curves obtained were similar to the standard sigmoid curve and showed sharp break point that corresponds to 1:1 stoichiometry of EDTA complex. This break point is taken as the end point of the titration.

3.2.11. Comparative study among the sensors N_6 and $Nb_6$and to some of the reported sensors.

The two sensors N_6 and Nb_6 are found to have very good response characteristics. The response characteristics of both the sensors are consolidated in the Table 3.6. Among the two sensors, N_6 is slightly better in terms of slope, pH range and shelf life time. But the life time of the sensor Nb_6 is only 5 weeks. However the surface could be renewed by cutting off a little of the paste, polishing it on a smooth surface and reconditioning it on 1.0×10^{-1} M $LaCl_3$ solution. Table 3.7 represents the comparative study of characteristics of the developed sensors of La^{3+} to some of the reported sensors. The sensors showed better working concentration range[70, 72, 74, 75, 77] and convenient pH[70,72] in comparison to the other La (III) selective sensors reported in the literature.

Figure 3.1 Structure of NAH

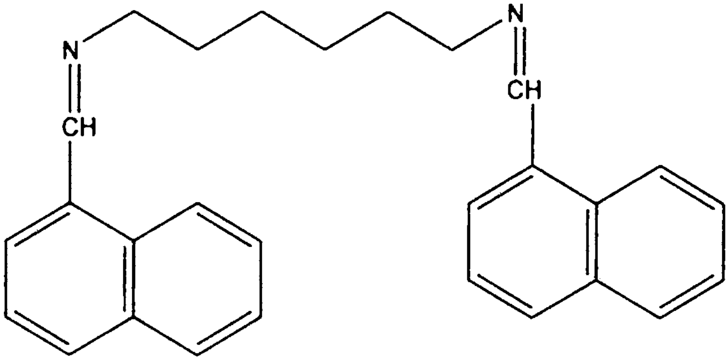

Figure 3.2 Potential response of various PVC membrane ion selective electrodes based on NAH

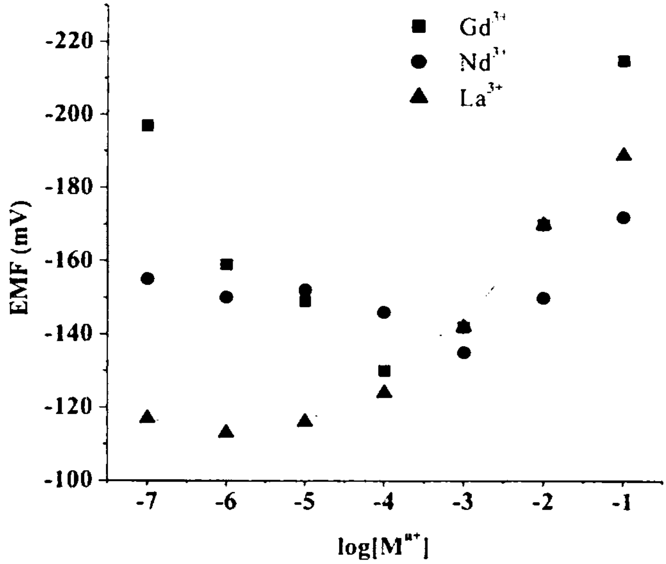

Figure 3.3 Potential response of various CMCPE ion selective electrodes based on NAH

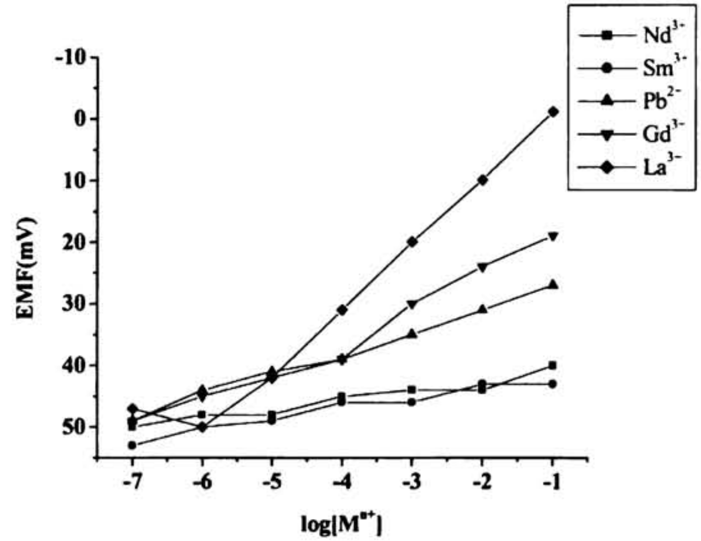

Figure 3.4 SEM image of the polymeric membrane of N_6 sensor

Figure 3.5 Calibration graph for La(III) selective PVC membrane sensor based on NAH (N_6)

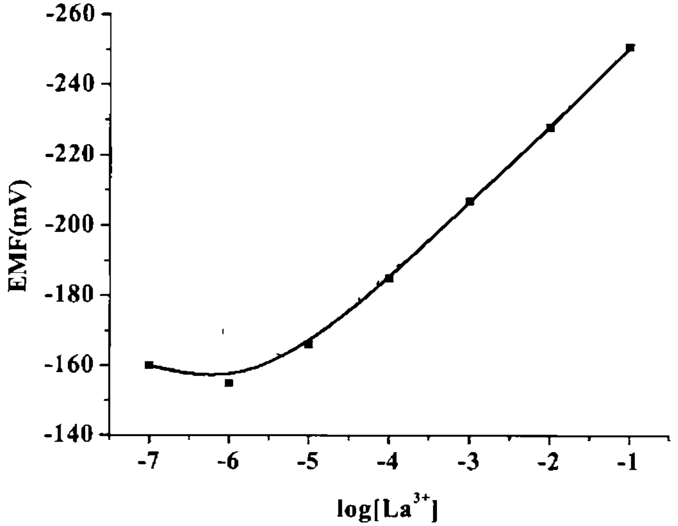

Figure 3.6 Calibration graph for La (III) selective CMCPE sensor based on NAH (Nb_6)

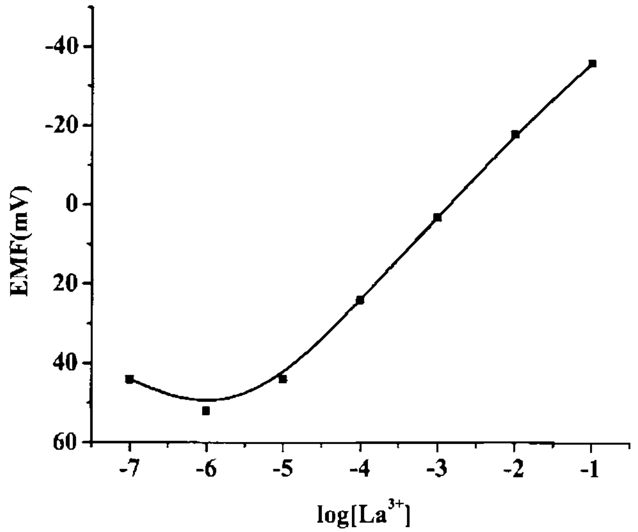

Figure 3.7 The effect of pH of test solution (1.0×10^{-3} M $LaCl_3$) on the response of La (III) membrane sensor N_6

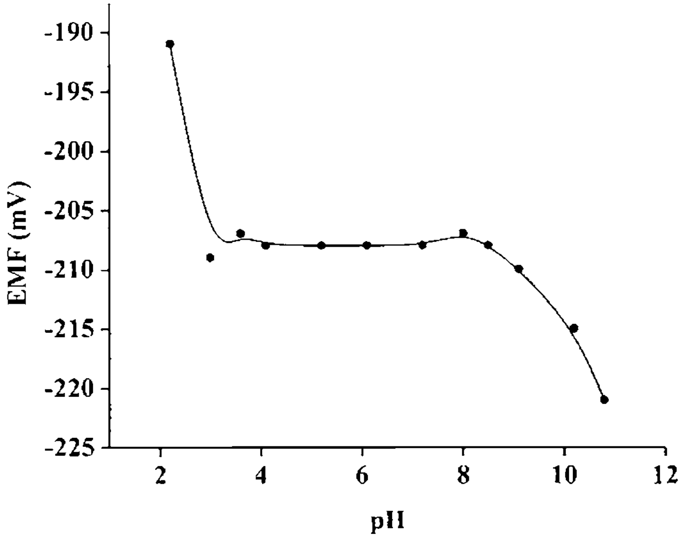

Figure 3.8 The effect of pH of test solution (1.0×10^{-3} M $LaCl_3$) on the response of La (III) sensor Nb_6

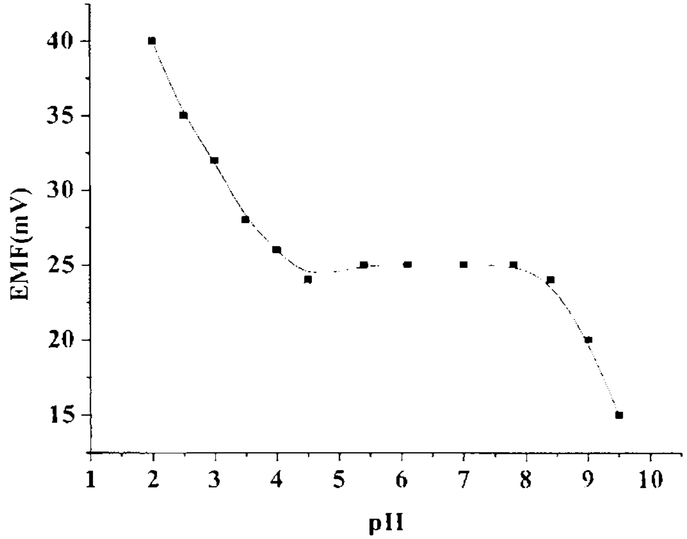

Figure 3.9 Potentiometric titration curve of 25 mL of 1.0 × 10^{-4} M $LaCl_3$ with 1 × 10^{-2} M EDTA for the membrane sensor N_6

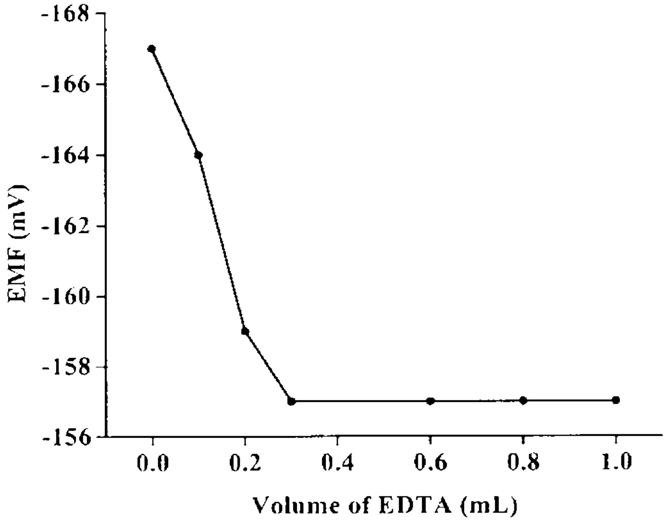

Figure 3.10 Potentiometric titration curve of 20 mL of 1.0 × 10^{-3} M $LaCl_3$ with 1.0 × 10^{-2} M EDTA for the CMCPE sensor Nb_6

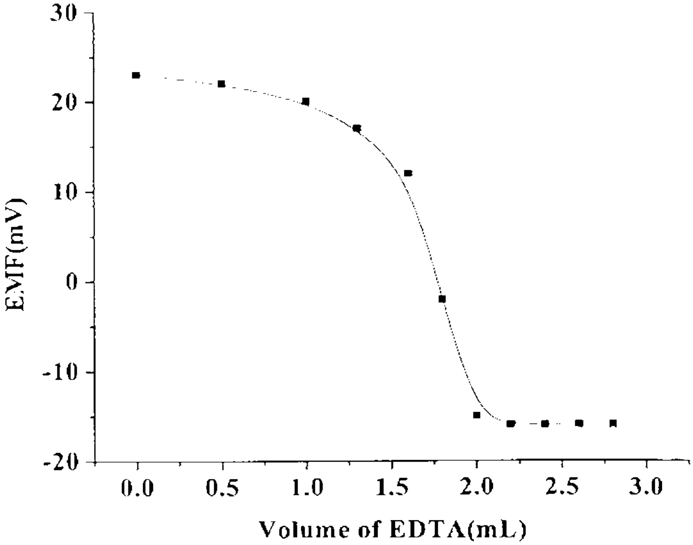

Table 3.1 The formation constants of NAH-M^{n+} complexes

Metal ion	Log K_f
La^{3+}	4.67
Gd^{3+}	2.34
Nd^{3+}	1.69
Pr^{3+}	2.04
Pb^{2+}	2.13

Table 3.2 Optimization of membrane composition

Sensor no.	Composition (%)				Slope (mV/ decade)	Concentration range (M)
	Ionophore	PVC	Plasticizer	Additives Oleicacid/ NaTBP		
N_1	2	32	BES, 58	8	32.0	10^{-4} to 10^{-1}
N_2	2	32	DBS, 58	8	36.3	10^{-4} to 10^{-1}
N_3	2	32	BEP, 58	8	38.1	10^{-4} to 10^{-1}
N_4	2	32	DBP, 58	8	24.6	10^{-4} to 10^{-1}
N_5	2.5	32	DBP, 57.5	8	22.9	10^{-6} to 10^{-1}
N_6	**3**	**32**	**DBP, 57**	**8**	**21.0**	**10^{-6} to 10^{-1}**
N_7	4	32	DBP, 56	8	28.2	10^{-5} to 10^{-1}
N_8	3	30	DBP, 59	8	29.2	10^{-5} to 10^{-1}
N_9	3	32	DBP, 57	8*	32.5	10^{-5} to 10^{-1}
N_{10}	3	32	DBP, 55	10	25.8	10^{-6} to 10^{-1}

* NaTBP

Table 3.3 Optimization of the composition of CMCPE type of sensor

Sensor no.	Ionophore % (w/w)	Graphite % (w/w)	Binders	Concentration range (M)	Slope (mV/decade)
Nb_1	5	95	TBP	10^{-6} to 10^{-1}	11.9
Nb_2	5	95	Paraffin	10^{-5} to 10^{-1}	10.3
Nb_3	5	95	DBP	10^{-6} to 10^{-1}	8.3
Nb_4	5	95	DBS	10^{-5} to 10^{-1}	7.5
Nb_5	7	93	TBP	10^{-6} to 10^{-1}	15.9
Nb_6	**10**	**90**	**TBP**	**10^{-6} to 10^{-1}**	**21.4**
Nb_7	15	85	TBP	10^{-6} to 10^{-1}	30.8

Table 3.4 Selectivity coefficients for N_6 and Nb_6 sensors using fixed interference methods of interfering ions.

Interfering ions (10^{-2} M)	K_{sel}	
	N_6	Nb_6
Na^+	6.53×10^{-2}	4.23×10^{-2}
K^+	6.12×10^{-2}	6.42×10^{-2}
Mg^{2+}	3.28×10^{-2}	3.92×10^{-2}
Pb^{2+}	3.57×10^{-2}	3.15×10^{-2}
Ag^+	6.24×10^{-2}	6.89×10^{-2}
Ca^{2+}	3.09×10^{-2}	3.34×10^{-2}
Gd^{3+}	7.43×10^{-1}	7.56×10^{-1}
Nd^{3+}	3.18×10^{-2}	3.23×10^{-2}
Pr^{3+}	3.22×10^{-2}	3.13×10^{-2}
Sm^{3+}	3.51×10^{-2}	3.67×10^{-2}

Table 3.5 Determination of Lanthanum in binary mixtures.

La^{3+} taken(M)	Added cation (M)	La^{3+} found(M)*	
		N_6	Nb_6
5.0×10^{-4}	Pb^{2+}, 5.0×10^{-4}	4.9×10^{-4}	5.0×10^{-4}
5.0×10^{-4}	Nd^{3+}, 5.0×10^{-4}	5.2×10^{-4}	5.1×10^{-4}
5.0×10^{-4}	Ca^{2+}, 5.0×10^{-4}	4.9×10^{-4}	4.8×10^{-4}
5.0×10^{-4}	Pr^{3+}, 5.0×10^{-4}	5.1×10^{-4}	5.1×10^{-4}

* Average of six replicates

Table 3.6 Response characteristics of the sensors N_6 and Nb_6

Parameter	Response characteristics	
	N_6	Nb_6
Working concentration range(M)	1.0×10^{-6} to 1.0×10^{-1}	1.0×10^{-6} to 1.0×10^{-1}
Slope(mV/decade)	21.0	21.4
Detection limit(M)	1.0×10^{-6}	1.0×10^{-6}
Response time	35s	10s
pH	4.1 to 8.5	4.4 to 7.5
Shelf life	7weeks	5weeks

Table 3.7 Comparison of characteristics of the developed sensors with some reported sensors

No.	Working concentration range	pH	Slope	Response time(s)	Ref.No.
1	8.1×10^{-5} to 5×10^{-2}	5-8	Nernstian	10	[70]
2	3.16×10^{-5} to 1×10^{-1}	3-7	20.5±1	15	[72]
3	1×10^{-6} to 1×10^{-1}	4-8.0	19.7	15	[74]
4	1×10^{-5} to 1×10^{-1}	4.0-8.0	19.7	15	[74]
5	7.1×10^{-6} to 2.2×10^{-2}	3.3-8	20.0±1	15	[75]
6	1×10^{-5} to 1×10^{-1}	3-9.0	19.5	27	[77]
7	4.0×10^{-4} to1.0×10^{-9}	3.5-8.5	19.5±0.3	25	[85]
8	$\mathbf{1.0\times10^{-6}}$ **to** $\mathbf{1.0\times 10^{-1}}$	**4.1-8.5**	**21.0**	**35**	**[N_6]**
9	$\mathbf{1.0\times10^{-6}}$ **to** $\mathbf{1.0\times 10^{-1}}$	**4.4-7.5**	**21.4**	**10**	**[Nb_6]**

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Chapter 4

SENSOR FOR SAMARIUM

This chapter describes the fabrication of PVC membrane and CMCP sensors based on Schiff's base as ionophore for samarium. The response characteristics of developed sensors and the analytical application of the sensors as indicator electrode in the potentiometric titration of samarium (III) against EDTA and in the determination of samarium (III) from binary mixtures are also discussed in this chapter. A comparison with already reported sensors is also included in this chapter.

Samarium is an important member of the rare earth family of elements and is known to constitute strong magnetic material. Along with other rare earth, it is used for carbon-arc lighting for the motion picture industry. $SmCO_5$ has been used in making permanent magnet material with the highest resistance to demagnetize of any known material. Samarium oxide has been used in optical glass to absorb the infrared radiation. Samarium doped with calcium fluoride crystals is used for the making of optical lasers [160]. The vapors or dusts of these elements are very toxic when inhaled [161]. The trace determination of rare earth is considered necessary due to the growing interest in bio-organic and inorganic chemistry and also owing to the various industrial applications of these species and also their toxic and other adverse effects.

The available methods for the trace determination of rare earth metal ions in solution include spectrophotometry[162], ICP-AES[163], X-ray fluorescence[164], isotopic dilution mass spectrometry[165] and neutron activation analysis[166-167]. These are either time consuming, involving multiple analysis or too expensive.

This chapter deals with fabrication of PVC membrane sensor and CMCPE type sensor based on MBP for samarium (III) and their analytical applications.

4.1. Ionophore

The synthesis and characterization of N^1,N^2-bis(3-nitrobenzy lidene) propane-1,3-diamine has been discussed in section 2.2.5 of chapter 2 and structure is given as figure 4.1.

4.2. Fabrication of Samarium Selective Sensor

4.2.1. Potential response of the MBP based sensors

Initially MBP was used as a potential ion carrier to prepare PVC membrane and CMCPE type sensors for a wide variety of metal ions and the potential response of the two types of sensors are shown in figure 4.2 and 4.3. It was found that the sensors show a Nernstian response to samarium ions. This may be attributed to the selective complexation behavior of the ionophore to Sm^{3+} over the other metal ions, as well as the rapid ion exchange kinetics of the resulting complex at the membrane sample interface.

In order to understand the selective complexation of MBP with samarium ions, the complexation of MBP with samarium and some other metal ions were studied conductometrically at 25 ± 1°C as discussed in section 2.6 of chapter 2 and results are consolidated in Table 4.1. Since the formation constant of the Sm^{3+}- MBP complex is more than that of the other metal ions studied, MBP was used as a suitable selective ionophore in the construction of samarium selective sensors.

4.2.2. Sensor membrane fabrication

The general method of fabrication of PVC membrane sensors and CMCPE type of sensors has been discussed under section 2.7 in Chapter 2. The PVC membranes prepared from a solution of MBP, PVC, plasticizer and additive were cut to size and glued to one end of the pyrex glass tube with Teflon tape. The tube was filled with 1.0×10^{-1} M samarium chloride solution as internal solution and conditioned by soaking in 1.0×10^{-1} M samarium chloride solution. To find out optimized membrane composition, membranes having varying composition of MBP, PVC, plasticizer and additive were fabricated and their response was also noted. The optimized composition which resulted in a best Nernstian response and working concentration range was found to be 4: 32: 61: 3 (MBP: PVC: DBS: NaTBP) (w/w %).

The CMCPE type of sensors was fabricated by packing the paste made from ionophore, graphite and binders into the Teflon holder as described in section 2.7.2 of chapter 2. The best composition ratio for CMCPE type of sensor was found to be 80:20 (graphite: MBP) (w/w %).

4.2.3. Equilibration of membranes and potential measurements

The optimum equilibration time for the PVC membrane sensor and CMCP sensor, in presence of 1.0×10^{-1} M $SmCl_3$ solution, was found to be 2 days and 1 day respectively. Afterwards the sensors generated stable and reproducible potential when placed in contact with samarium ion solution. All the potential measurements were made relative to Ag/AgCl reference electrode on Metrohm 781 ion meter at 25 ± 1 °C (pH maintained at 7 by adding buffer) in the concentration range 1.0×10^{-6} to 1.0×10^{-1} M $SmCl_3$ solution. The cell assembly for the two types of sensors can be represented as follows

PVC membrane sensor

Ag, AgCl| KCl || test solution |membrane | internal solution (1.0×10^{-1} M $SmCl_3$) || KCl | AgCl, Ag

CMCP Sensor

Ag, AgCl| KCl || test solution |CMCPE

4.2.4. Optimization of membrane composition

Optimization of membrane composition is a very important step in the sensor fabrication as nature and amount of carrier, plasticizer and lipophilic additives significantly influence the sensitivity, linearity and selectivity of the sensor. Thus, different aspects of the preparation of Sm^{3+} selective membrane based on MBP are optimized and the results are summarized in the Table 4.2. Since the nature of plasticizer influences the dielectric constant of the membrane phase, the mobility of the ionophore molecules and the state of the ligand, it is expected to play a key role in determining the selectivity, working concentration range and response time of the membrane electrode[168, 139-143]. Among the different plasticizers studied, the membrane sensor, M_1, based on DBS resulted in a best Nernstian slope. The presence of lipophilic anion sites in a cation selective membrane electrode not only improves the response behavior and selectivity of the sensor, but also enhances the sensitivity of the membrane[169, 144-157]. From the data given in Table 4.2, it is found that the slope of the sensor, M_6, is improved from 17.2 mV/decade to Nernstian value of 18.9 mV/decade when the percentage of additive changes from 2 to 3 and further increase in the additive results in an increase in the slope to super Nernstian value. The amount of the ionophore was also found to affect the sensitivity of the sensor. 4% was found to be the optimum amount of ionophore and further addition of ionophore resulted in some decrease in the response of the sensor. This may be due to some inhomogeneities and possible saturation of the membrane.

SEM image was taken inorder to understand the homogeneity of the optimized membrane. This technique allows the study of the membrane surface characteristics, such as morphological homogeneity and chemical composition. Homogeneity of the membrane may affect the response characteristics of the sensor. The SEM image of the membrane of M_7 is shown in Figure 4.4. The image obtained shows a homogenous membrane with the absence of solid particles or cumulus.

A set of nine CMCPE type sensors were developed by varying sensor composition and results are consolidated in the Table 4.3. The sensors with tri-n-butyl phosphate as binder gave better response than the sensors with other binders. It was found that the sensor Mb_8 with the composition ratio 80: 20 (graphite: ionophore) was the best in terms of response time, working concentration range and the Nernstian slope. On increasing the ionophore content, the system deviated from Nernstian slope which could be due to the decrease in conductance of the sensor material. Hence, the sensor Mb_8 was used for further studies.

4.2.5. Calibration curve and statistical data

Calibration graph which is the plot of EMF versus log [Sm^{3+}] for the sensors M_7 and Mb_8 are shown as figure 4.5 and figure 4.6. The sensors M_7 and Mb_8 showed linear response over the concentration range of 1.0×10^{-6} to 1.0×10^{-1} M and 1.0×10^{-5} to 1.0×10^{-1} M, respectively. The slope calculated from the calibration graphs was found to be 18.9 and 18.6 for M_7 and Mb_8 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 1.0×10^{-6} M and 1.0×10^{-5} M.

4.2.6. Dynamic response time

The practical response time was recorded by changing the Sm^{3+} concentration in the range 1.0×10^{-5} to 1.0×10^{-1} M. The sensors reached to the equilibrium potential in a very short time in whole concentration range. The response time was found to be 15 and 10 seconds for M_7 and Mb_8 respectively. The practical reversibility of the sensors M_7 and Mb_8 were evaluated by taking measurements in the sequence of high-to-low concentration of the analyte and vice versa. The sensing behavior of the sensors remained unchanged when potentials were recorded either from low to high concentrations or vice versa.

4.2.7. Effect of pH

The pH response profile for the sensors was tested by using a 1.0×10^{-3} M samarium chloride solution over the pH range 2.0 to 10 and are shown as figure 4.7 and figure 4.8.The pH of the solutions were adjusted using suitable buffer solution. It was observed that the sensor response is hardly affected by change in pH in the range 2.5 to 7.8 and 3 to 7.5 for M_7 and Mb_8 respectively. The change in potential at lower pH may be due to the response of the sensor to hydrogen ions and at higher pH could be due to the formation of some hydroxyl complex of Sm (III) in solution.

4.2.8. Selectivity

One of the most important characteristics of any membrane sensor is its relative response for the primary ion over other ions present in solution, usually expressed in terms of potentiometric selectivity coefficients. Potentiometric selectivity coefficients of samarium membrane sensor were evaluated by fixed interference method (FIM) as described in chapter 3. The resulting selectivity coefficient values are given in Table 4.4. The data shows that, the electrodes have reasonably good selectivity for samarium in presence of other ions tested.

4.2.9. Shelf Life

The stability or shelf life of all the PVC membrane and CMCPE sensor was tested over a period of 7 weeks. The life time of the sensorsM_7 and Mb_8 was found to be 6 weeks and 5 weeks respectively. During this period, the sensor showed no significant deviation on the optimized response characteristics. The response of the carbon paste sensor can be restored by squeezing out a small amount of the paste, scrapping off the excess and polishing the new surface against a filter paper. The sensor was stored in 1.0×10^{-1} M samarium (III) chloride solution when not in use.

4.2.10. Analytical applications

The developed samarium sensors were found to work well under laboratory conditions. Both the sensors were successfully applied for the direct monitoring of samarium ions in various binary mixtures and the results are presented in Table 4.5. It is observed that the recovery of Sm(III) ions is quantitative in all cases and the sensors can be used for the determination of Sm (III) in real samples having different analytical matrixes.

The developed sensors have been successfully applied as an indicator electrode in the titration of Sm(III) with EDTA at pH 7.The titration curves for the sensors are shown in the figure 4.9 and 4.10 respectively. A very good inflection point which corresponds to 1:1 stoichiometry of EDTA complex was observed from the titration curve.

Hence, the amount of Sm(III) in solution can be accurately determined with the developed sensors.

4.2.11. Comparative study among the sensors M_7 and Mb_8 and to some of the reported sensors.

Both the sensors are found to have very good response characteristics. Table 4.6 consolidates the response characteristics of the sensors M_7 and Mb_8. Working concentration range, pH and life time are better for PVC membrane sensor, but response time was found to be good for CMCPE. The Table 4.7 gives a comparative study of response characteristics of the newly developed sensors with some of the already reported sensors. It is obvious that the proposed sensors are superior in terms of slope, pH range and response time[87, 89-93] when compared with most of the reported sensors.

Figure 4.1 Structure of MBP

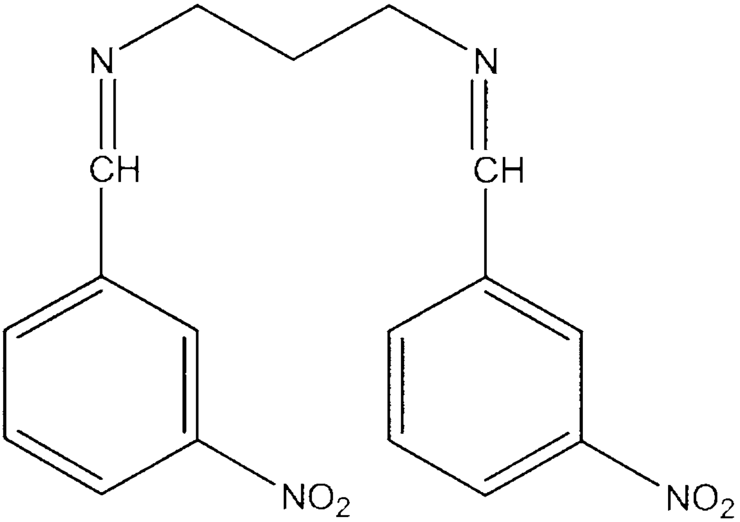

Figure 4.2 Potential response of various PVC membrane ion selective electrodes based on MBP

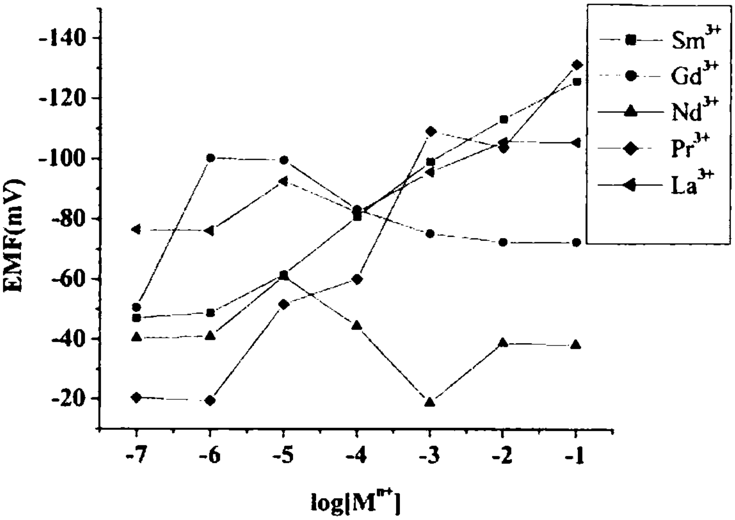

Figure 4.3 Potential response of various CMCPE electrodes based on MBP

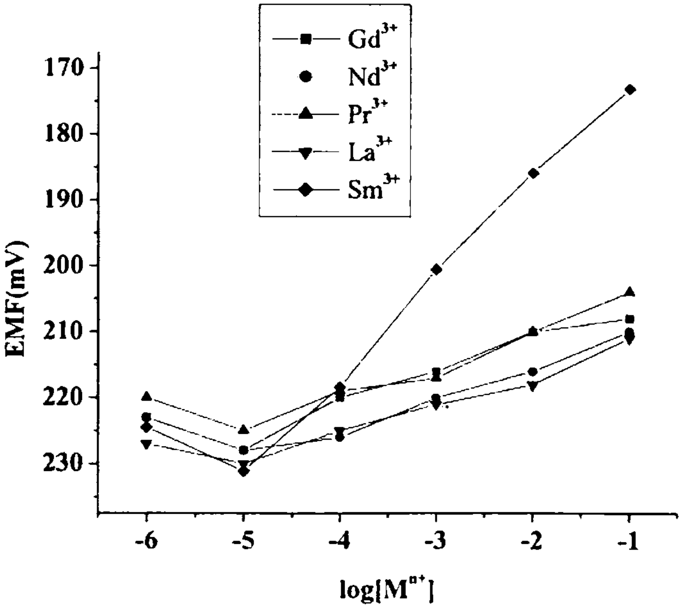

Figure 4.4 SEM image of the polymeric membrane of M_7 sensor

Figure 4.5 Calibration graph for Sm(III) selective PVC membrane sensor based on MBP (M_7)

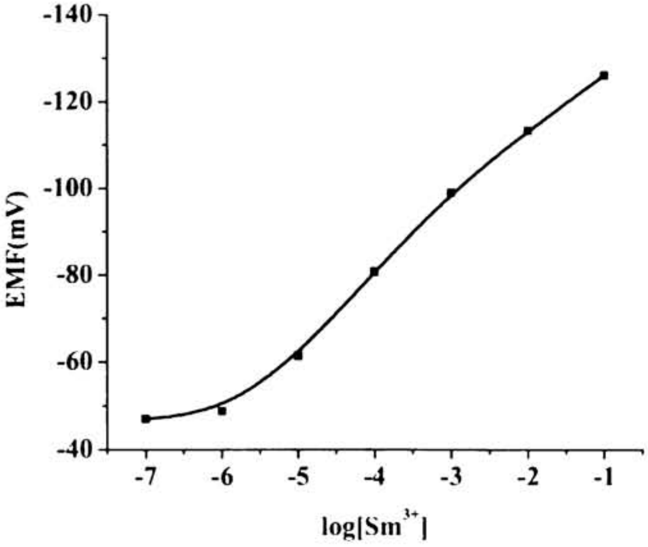

Figure 4.6 Calibration graph for Sm(III) selective CMCP sensor based on MBP (Mb_8)

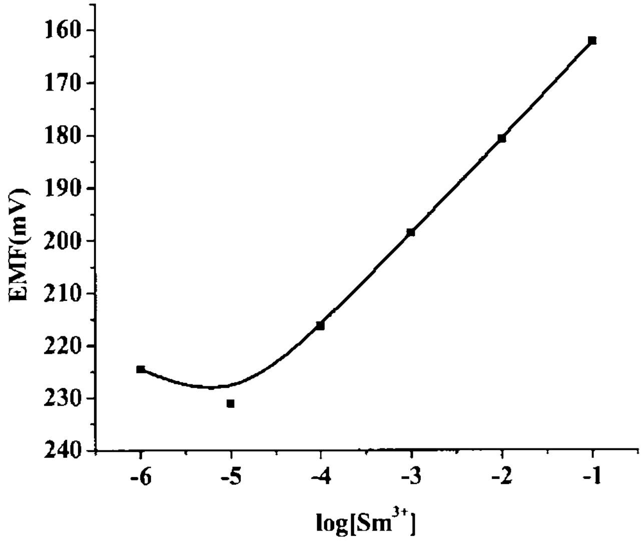

Figure 4.7 The effect of pH of test solution (1.0 × 10^{-3} M $SmCl_3$) on the response of PVC membrane sensor M_7

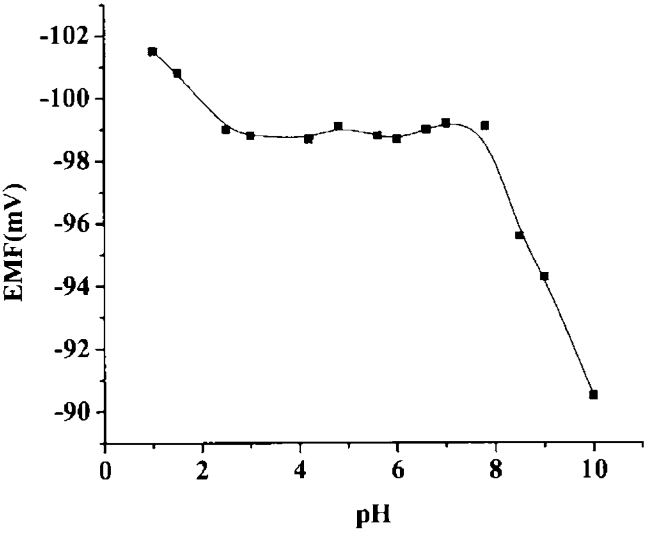

Figure 4.8 The effect of pH of test solution (1.0×10^{-3} M $SmCl_3$) on the response of CMCP sensor Mb_8

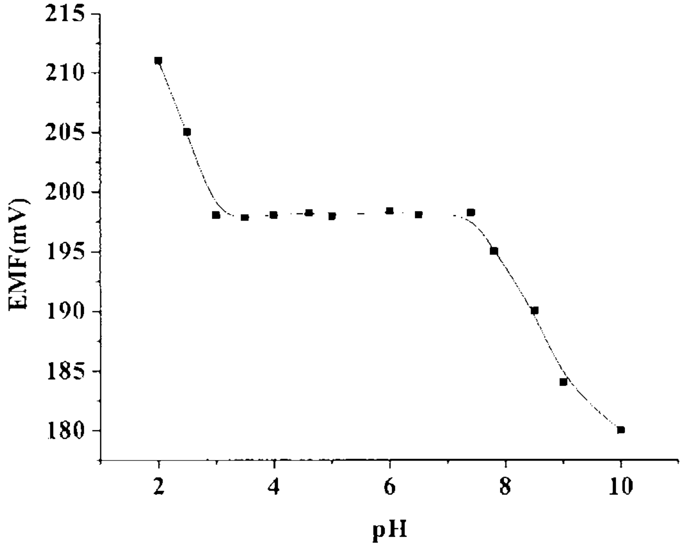

Figure 4.9 Potentiometric titration curve of 20 mL of 1.0×10^{-3} M $smCl_3$ with 1.0×10^{-2} M EDTA for the membrane sensor M_7

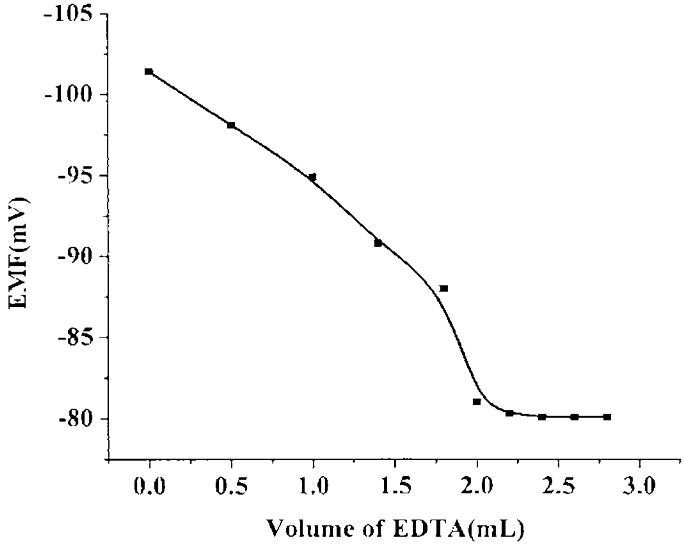

Figure 4.10 Potentiometric titration curve of 20 mL of 1.0×10^{-3} M $SmCl_3$ with 1.0×10^{-2} M EDTA for the membrane sensor Mb_8.

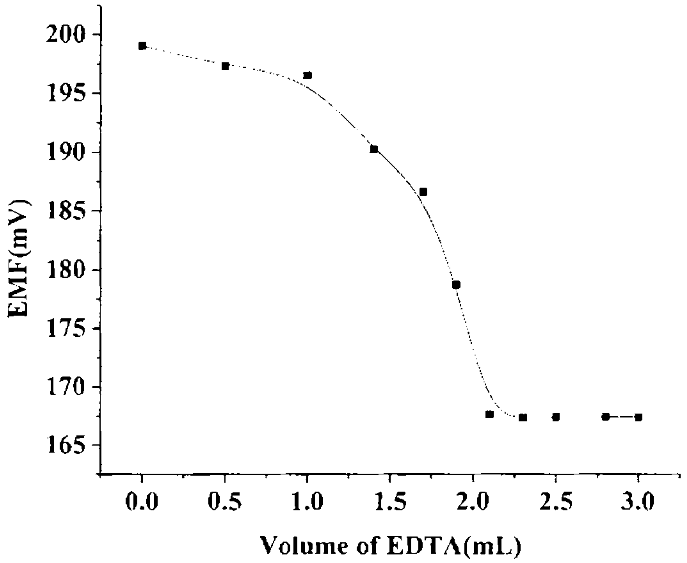

Table 4.1 Formation constants of MBP-M^{n+} complexes

Metal ion	Log K_f
Sm^{3+}	3.95
Gd^{3+}	2.12
Nd^{3+}	2.11
Pr^{3+}	2.21
La^{3+}	1.94

Table 4.2 Optimization of membrane composition.

Sensor no.	Composition (%)				Slope (mV/ decade)	Concentration range (M)
	Ionophore	PVC	Plasticizer	Additives NaTBP		
M_1	3	32	DBS, 62	3	16.5	10^{-6} to10^{-2}
M_2	3	32	BEA, 62	3	15.4	10^{-5} to 10^{-2}
M_3	3	32	DBP, 62	3	14.2	10^{-5} to 10^{-2}
M_4	3	32	BES, 62	3	10.5	10^{-4} to 10^{-1}
M_5	3	32	BEP, 62	3	10.2	$10^{-4}$to 10^{-1}
M_6	4	32	DBS, 62	2	17.2	10^{-5} to 10^{-1}
M_7	**4**	**32**	**DBS, 61**	**3**	**18.9**	**10^{-6} to 10^{-1}**
M_8	5	32	DBS, 60	3	10.3	10^{-5} to 10^{-1}
M_9	4	32	DBS, 59	5	29.6	10^{-5} to 10^{-1}

Table 4.3 Optimization of the composition of CMCPE type of sensor

Sensor no.	Ionophore % (w/w)	Graphite % (w/w)	Binders	Concentration range (M)	Slope (mV/decade)
Mb_1	10	90	DBS	10^{-4} to 10^{-1}	6.7
Mb_2	10	90	Paraffin	10^{-4} to 10^{-1}	8.2
Mb_3	10	90	DBP	10^{-5} to 10^{-1}	6.3
Mb_4	10	90	BEP	10^{-5} to 10^{-1}	5.4
Mb_5	10	90	TBP	10^{-5} to 10^{-1}	10.6
Mb_6	15	85	TBP	10^{-5} to 10^{-1}	15.2
Mb_7	17	83	TBP	10^{-5} to 10^{-1}	16.6
Mb_8	**20**	**80**	**TBP**	**10^{-5} to 10^{-1}**	**18.6**
Mb_9	23	77	TBP	10^{-5} to 10^{-1}	26.3

Table 4.4 Selectivity coefficients for M_7 and Mb_8sensors using fixed interference methods of interfering ions

Interfering Ions	K_{sel}	
	M_7	Mb_8
Na^+	5.54×10^{-2}	6.98×10^{-2}
K^+	6.73×10^{-2}	5.78×10^{-2}
Mg^{2+}	2.67×10^{-2}	2.75×10^{-2}
Pb^{2+}	2.12×10^{-2}	2.05×10^{-2}
Ag^+	5.68×10^{-2}	4.65×10^{-2}
Ca^{2+}	2.57×10^{-2}	2.48×10^{-2}
Gd^{3+}	3.23×10^{-2}	3.28×10^{-2}
Nd^{3+}	4.52×10^{-2}	4.48×10^{-2}
La^{3+}	2.35×10^{-3}	2.58×10^{-3}
Pr^{3+}	4.56×10^{-2}	4.68×10^{-2}

Table 4. 5 Determination of samarium in binary mixtures.

Sm^{3+}(M) taken	Added cation (M)	Samarium found(M)*	
		M_7	Mb_8
5.0×10^{-4}	Gd^{3+} (5.0×10^{-4})	4.8×10^{-4}	4.9×10^{-4}
5.0×10^{-4}	Nd^{3+} (5.0×10^{-4})	5.2×10^{-4}	5.1×10^{-4}
5.0×10^{-4}	Ca^{2+} (5.0×10^{-4})	4.9×10^{-4}	5.2×10^{-4}
5.0×10^{-4}	Pb^{2+} (5.0×10^{-4})	5.3×10^{-4}	4.9×10^{-4}

*Average of six replicates

Table 4.6 Response characteristics of the sensors M_7 and Mb_8

Parameter	Response characteristics	
	M_7	Mb_8
Working concentration range(M)	1.0×10^{-6} to1.0 × 10^{-1}	1.0×10^{-5} to 1.0 × 10^{-1}
Slope(mV/decade)	18.9	18.6
Detection limit(M)	1.0×10^{-6}	1.0×10^{-5}
Response time	15s	10s
pH	2.5-7.8	3- 7.5
Shelf life	6 weeks	5 weeks

Table 4.7 Comparison of response characteristics of proposed sensor with other Sm^{3+} sensor reported in literature.

Sensor no.	Working conc. range (M)	pH	Response time(s)	Slope (mV/decade)	Reference
1	1×10^{-6} to 1×10^{-1}	4-8	10	19.8	[87]
2	1×10^{-5} to 1×10^{-1}	4-10	15	40	[89]
3	1×10^{-5}to1×10^{-1}	6-10	15	20.2	[90]
4	1×10^{-6} to 1×10^{-1}	4-8.2	5	19.3±0.2	[91]
5	1×10^{-6}to1×10^{-1}	3.5-7.5	10	19.3±0.6	[92]
6	1×10^{-9} to 1×10^{-4}	3-8	25	18.27±0.3	[93]
7	**1.0×10^{-6} to 1.0×10^{-1}**	**2.5 -7.8**	**15**	**18.9**	**[M_7]**
8	**1.0×10^{-5} to 1.0×10^{-1}**	**3.0 -7.5**	**10**	**18.6**	**[Mb_8]**

* * *

Chapter 5

SENSOR FOR PRASEODYMIUM

This chapter discusses the response characteristics of the two sensors based on two different ionophores for praseodymium. The optimization of membrane composition, analytical applications of the newly developed sensors and a comparison of these new sensors with already reported similar sensors are the other points of discussion in this chapter.

Praseodymium is one of the rare earth elements used for the production of high strength metal alloys for aircraft engines, carbon lights for motion picture industry and didymium glass to make certain types of welders and glass blower's goggles.

It also finds application in house hold equipments such as color televisions, fluorescent lamps, energy-saving lamp and glasses. The vapors or dusts of praseodymium are very toxic when inhaled. This can cause lung embolisms, especially during long-term exposure[170]. The presence of praseodymium has an adverse effect on cell membrane, reproductive system and nervous systems of aquatic life. Thus the determination of praseodymium in different samples is of special interest.

The methods usually employed for the determination of lanthanides are spectrophotometry[163], ICP-AES[164], isotope dilution mass spectrometry[171], neutron activation analysis[172] and X-ray fluorescence spectrometry[173]. These methods require multiple sample preparation and expensive instruments. This chapter presents the results of two sensors based on two different ionophores that have been fabricated for the determination of praseodymium.

5.1. Ionophore

The synthesis and characterization of the ionophores 1,4-bis(4-hydroxy-3-methoxybezylidene)thiosemicarbazide(HBTS) and N^1,N^2-bis(4-hydroxy-3-methoxybezylidene)butane-1,4-diamine (HMB) have been discussed in chapter 2 and structures are given as figure 5.1 and 5.2.

5.2. Fabrication of Praseodymium Selective Membrane

5.2.1. Potential response of the HBTS and HMB based sensors

In preliminary investigations, HBTS was used as ionophore in the fabrication of PVC membranes and HMB as ionophore in CMCP electrodes for a number of metal ions. Figure 5.3 and figure 5.4 represents the potential response of the membrane electrodes based on HBTS and CMCP electrodes based on HMB. Among the different metal ions tested, praseodymium ions demonstrated most sensitive response towards both ionophores. Therefore these ionophores were selected as suitable sensor material for praseodymium.

The complexation of HBTS and HMB with praseodymium ion and other metal ions were investigated conductometrically at 25 ± 1 °C in order to get an idea about the stability and selectivity of the resulting complex and results are summarized in the Table 5.1. It was observed that the formation constant of the Pr^{3+}- HBTS and Pr^{3+}-HMB complexes are more than that of the other metal ions studied. Hence, HBTS and HMB were selected as suitable ionophore for the construction of praseodymium selective sensors.

5.2.2. Sensor membrane fabrication

HBTS was selected as ionophore for the fabrication of PVC membrane sensors. The membrane electrodes were fabricated from a plasticized PVC solution containing HBTS and additives as discussed in chapter 2 and were equilibrated by dipping in 1.0×10^{-1} M praseodymium nitrate solution. The composition ratio of ionophore, PVC, plasticizer and additives in the membrane were also varied so as to obtain an optimized membrane composition. The optimized composition which resulted in a best Nernstian response and working concentration range was found to be 2: 31: 62: 5 (ionophore: PVC: plasticizer: NaTBP) (w/w %).

Carbon paste sensors possess the advantage that it requires no internal filling solution. Its fabrication is reliable, fast, easy and simple. Chemically modified carbon paste sensors based on HMB as ionophore were fabricated as detailed in chapter 2. Five different binders were tried to find out the most suitable one that would give best slope, wide concentration range and fairly good detection limit. The graphite ionophore paste in suitable binder was packed to the open end of a Teflon holder in which electrical contact was made with a copper rod through the centre of the holder. The electrode was conditioned by soaking in 1.0×10^{-1} M praseodymium nitrate solution. One of the merits of this type of sensor is that the working surface can be renewed by rubbing the surface on a filter paper. The sensor having the composition 88: 12 (graphite: ionophore) resulted in a best Nernstian response and DBS was found to be the suitable binder.

5.2.3. Equilibration of membranes and potential measurements

Equilibration time of the sensors, H_8 and Hb_7, was also optimized so that it generated a stable and reproducible potential. The optimum equilibration time in presence of 1.0×10^{-1} M $Pr(NO_3)_3$ solution was 2 days for PVC membrane type sensor and 1 day for CMCPE type sensor. The potential measurements were carried out at 25 ± 1 °C on Metrohm 781 ion meter (pH maintained at 7 by adding buffer). All the measurements were carried out using the following cell assembly:

PVC membrane sensor

Ag, AgCl | KCl || test solution | membrane | internal solution(1.0×10^{-1} M $Pr(NO_3)_3$) || KCl | AgCl, Ag

CMCPE sensor

Ag, AgCl | KCl || test solution | CMCPE

The performance of the sensors was investigated by measuring their potentials in $Pr(NO_3)_3$ solutions prepared in the concentration range 1.0×10^{-6} to 1.0×10^{-1} M. The solutions were stirred and the stable potential reading was taken.

5.2.4. Optimization of membrane composition

The response characteristics of the PVC based membrane sensor are influenced by the nature and amount of ionophore, additive and plasticizer. The effect of these parameters on the response characteristics of the membrane sensor was studied to arrive at an optimum composition and results are shown in Table 5.2. Plasticizers are additives that increase the plasticity or fluidity of the material, to which they are added. The presence of plasticizer in the PVC membrane enhances the mobilities of their constituents. The amount and nature of a plasticizer may affect the response characteristics of the sensor such as sensitivity and response time. Among the different plasticizers studied, DBP was found to be the most effective plasticizing agent in the preparation of the PVC membrane. The amount of the ionophore is one of the most important parameters which influence the response of the sensor. The influence of variation in ionophore percentage on the membrane response was studied. From the Table 5.2, it is obvious that the concentration range and slope of the sensor was improved significantly by varying the percentage of ionophore from 1-2 and further increase in the ionophore results in an increase in the slope. 2% was found to be the optimum concentration of ionophore. The presence of lipophilic additives improves the potentiometric behavior of certain cation selective electrode by reducing the ohmic resistance and improving the response behavior and selectivity. The influence of lipophilic additives such as NaTBP and oleic acid on the response behavior of the membrane sensor was also tested and results are compiled in the Table 5.2. From the data given in the Table 5.2, it is obvious that the membrane sensor, H_5, with NaTBP as additive shows better response for praseodymium in the concentration range 1.0×10^{-5}-1.0×10^{-1} than the sensor with oleic acid as additive. Moreover, the behavior of the sensors towards more Nernstian approach was observed on increasing the additive from 4-5% (sensor H_8). The optimized membrane composition of ionophore, PVC, plasticizer and additives are in the ratio 2: 31: 62: 5 %.

In order to investigate the surface morphology of developed membrane, SEM image was taken. The SEM image of the membrane of H_8 is shown in the Figure 5.5. A homogenous membrane is found to exhibit good response characteristics such as high sensitivity and long shelf life. As it is obvious from the figure that the membrane is not much homogenous and this can be attributed to the short shelf life of the sensor H_8.

HMB was also employed as ionophore for the fabrication of carbon paste sensor for praseodymium. The response of the carbon paste sensor too depends on the composition of the sensor matrix. Table 5.3 consolidates the results obtained while investigating the effect of composition of matrix on the sensor response characteristics. The optimized amount of ionophore was found to be 12 %. A higher quantity of ionophore gave a sub Nernstian behavior which may be attributed to the saturation of the sensor matrix. Another important factor which influences the sensor response is the plasticizer. Five different binders were employed for the fabrication of carbon paste sensor to study the effect of binders on the response of the sensor and results are compiled in the Table 5.3. DBS was found to be the suitable binder. The sensor, Hb_7, with optimized composition 12:88 (ionophore: graphite) gave a slope of 18.0mV/decade in the concentration range 1.0×10^{-5} to 1.0×10^{-1} M praseodymium nitrate solution.

5.2.5. Calibration curve and statistical data

The working concentration range, slope and detection limit of PVC membrane and CMCPE sensors are consolidated in the Table 5.6. The calibration graph for the sensors H_8 and Hb_7 are shown in the figure 5.6 and 5.7. Both the sensors showed linearity in the concentration range 1.0×10^{-5} to 1.0×10^{-1} M. The slope of the calibration graph was found to be 20.3 mV/decade and 18.0 mV/decade for the sensors H_8 and Hb_7 respectively. The limit of detection was calculated from the intersection of the two extrapolated linear portions of the calibration curve and was found to be 1.0×10^{-5} M and 8.9×10^{-6} M for the sensors H_8 and Hb_7 respectively.

5.2.6. Dynamic response time

The response time of an electrode is evaluated by measuring the average time required to achieve a potential within ±1 mV of the final steady-state potential, upon successive measurement of the potential of the respective ion, each having a ten-fold difference in concentration.

The practical response time was recorded by changing the Pr^{3+} concentration in the range 1.0×10^{-5} to 1.0×10^{-1} M. The sensors, H_8 and Hb_7, reached their equilibrium potential in a very short time and were found to be 15s and 10s respectively. This is probably due to the very fast exchange kinetics of complexation-decomplexation of the Pr^{3+} with HBTS and HMB on the test solution-membrane interface. The practical reversibility of the sensors H_8 and Hb_7 were evaluated by taking measurements for Pr^{3+} solutions with a 10-fold difference in concentration in the sequence high-to-low concentration and vice versa. The sensing behavior of the membrane remained unchanged when potentials were recorded either from low to high concentrations or vice versa.

5.2.7. Effect of pH

The effect of pH on the response of the newly developed sensors, H_8 and Hb_7 were studied over the pH range 2 - 11 at 1.0×10^{-3} M $Pr(NO_3)_3$. The pH adjustments were carried out by adding suitable buffer solution. The results are shown in figure 5.8 and figure 5.9 for the sensor H_8 and Hb_7 respectively. It is obvious from the figures that potential remains constant despite the pH change in the range of 3.7 to 8.8 and 3.6 to 8.6 for the sensors H_8 and Hb_7 respectively. Beyond this pH range, drastic drift in potential is observed. Therefore, these intervals can be chosen as the working pH range for the sensors. The variation above the pH range may be due to the formation of some hydroxyl complex of Pr(III) in the solution and at the lower pH due to the response of the sensors to hydrogen ions.

5.2.8. Selectivity coefficients

Selectivity, which describes an ion-selective electrode's specificity toward the target ion in the presence of interfering ions, is the most important characteristic of these devices. The potentiometric selectivity coefficients of the Pr(III) sensor were evaluated by fixed interference method (FIM) at 10^{-2} M concentration of interfering ions. The experimental conditions employed and the resulting values obtained are given in Table 5.4. The data shows that, the sensors H_8 and Hb_7 are significantly selective to praseodymium over all other interfering ions studied except Sm(III). The selectivity coefficient value of samarium ion shows slight interference.

5.2.9. Shelf Life

The potential measurements were recorded every day over a period of time to determine the shelf life of the sensors. The operative life time for the sensors H_8 and Hb_7 was found to be 2 weeks and 5 weeks respectively. The sensors were all immersed in 1.0×10^{-1}M $Pr(NO_3)_3$ solutions when not in use. The surface of CMCPE type sensor could be renewed as explained in the previous chapters for CMCPE sensors.

5.2.10. Analytical applications

The sensors H_8 and Hb_7 were successfully applied for the direct monitoring of Pr(III) in binary mixtures and the results are summarized in Table 5.5. It was observed that the recoveries of Pr(III) ions are quantitative in all cases and the sensors can be used for the determination of Pr(III) in real samples having different analytical matrixes.

The developed sensors have been successfully applied as an indicator electrode in the titration of Pr(III) with EDTA at pH 7.The titration curves for the sensors, H_8 and Hb_7, are shown in the figure 5.10 and 5.11 respectively. The shape of the curves obtained were similar to the standard sigmoid curve and showed sharp break point that corresponds to 1:1 stoichiometry of EDTA complex. This break point is taken as the end point of the titration.

5.2.11. Comparative study among the sensors H_8 and Hb_7 and to some of the reported sensors.

The response characteristics of both type of sensors are consolidated in Table 5.6. The working concentration range and pH range are almost comparable in the case of both type of sensors. The response time and life time was found to be better in the case of carbon paste sensor.

Table 5.7 represents the comparative study of the characteristics of the developed sensors with some of the reported sensors. The sensors showed comparable working concentration range, pH and response time with respect to the other Pr(III) selective sensors reported in literature[99-101].

Fig. 5.1 Structure of HBTS

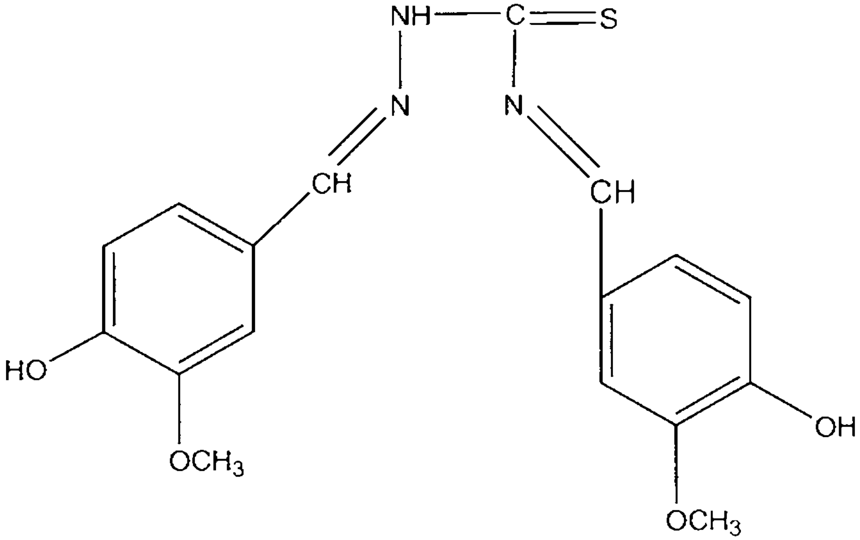

Fig. 5.2 Structure of HMB

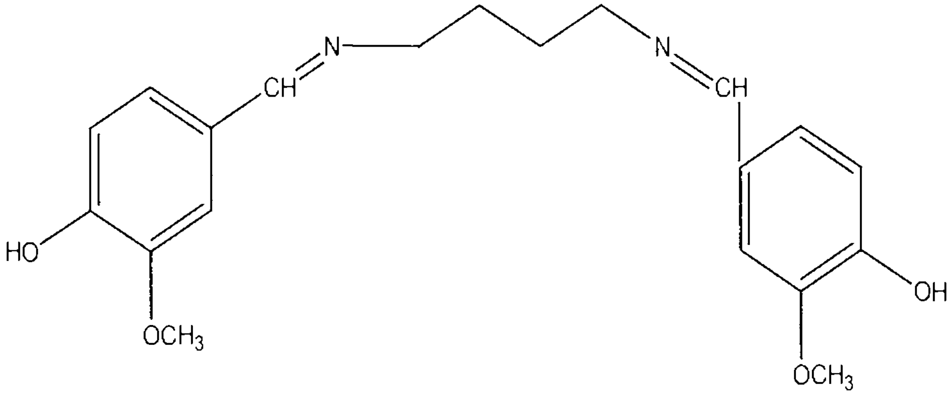

Fig.5.3 Potential response of various PVC membrane ion selective electrodes based on HBTS

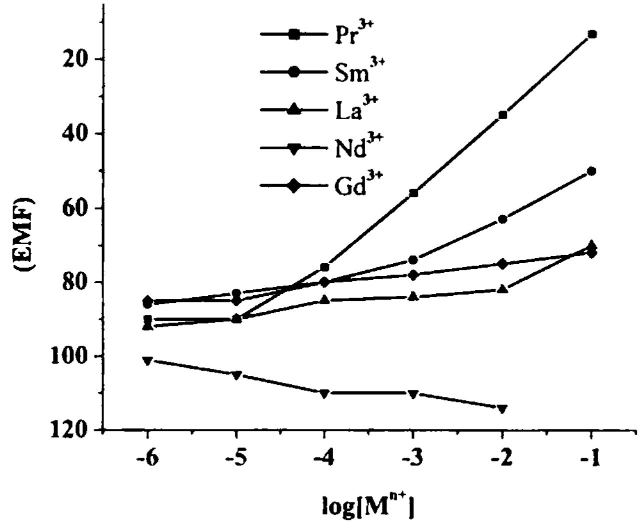

Fig.5.4 Potential response of various CMCPE ion selective electrodes based on HMB

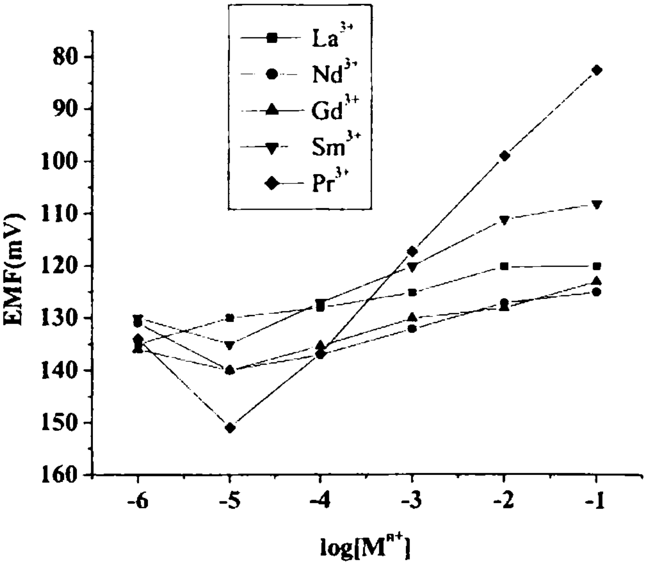

Fig.5.5 SEM image of the polymeric membrane of H_8 sensor

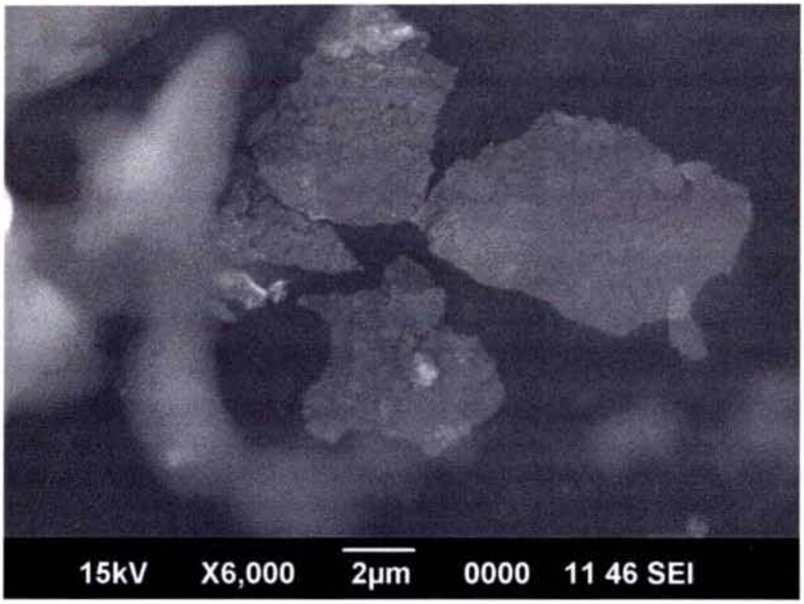

Fig. 5.6 Calibration graph for Pr(III) selective PVC membrane sensor based on HBTS (H_8)

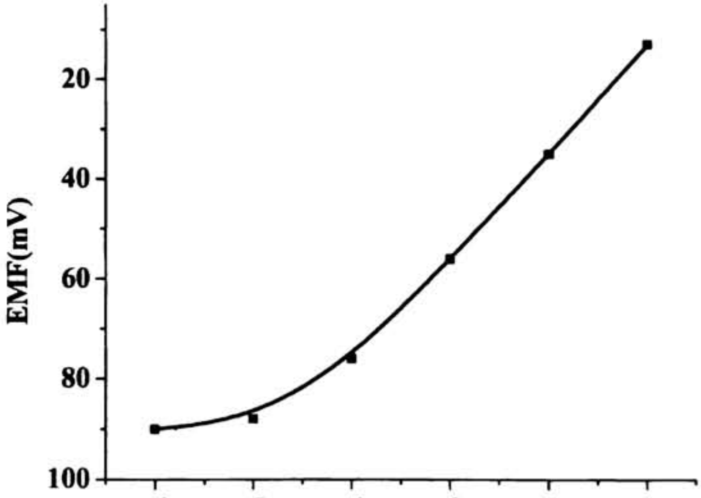

Fig. 5.7 Calibration graph for Pr(III) selective CMCPE sensor based on HMB (Hb_7)

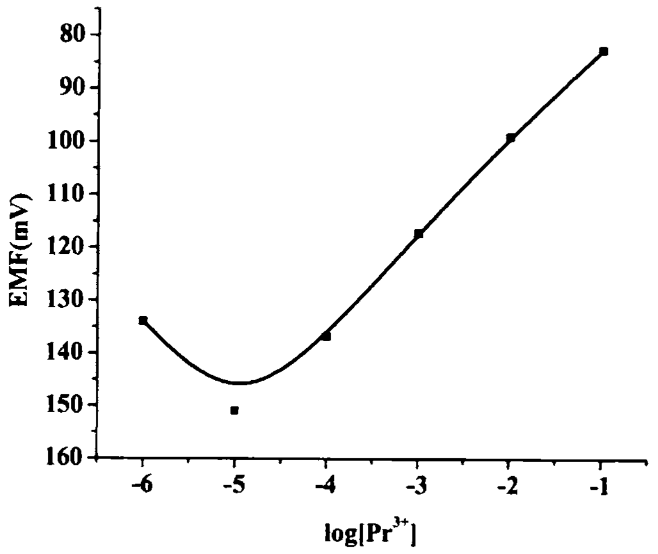

Fig. 5.8 The effect of pH of test solution (1.0×10^{-3} M $Pr(NO_3)_3$) on the response of Pr(III) membrane sensor H_8

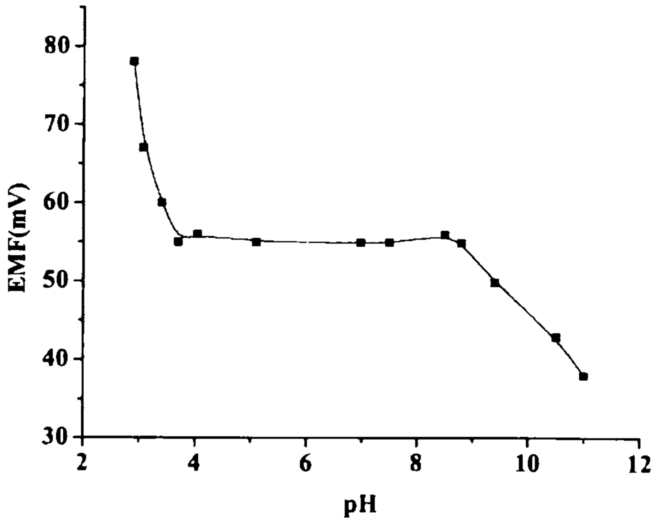

Fig. 5.9 The effect of pH of test solution (1.0×10^{-3} M $Pr(NO_3)_3$) on the response of Pr(III) sensor Hb_7

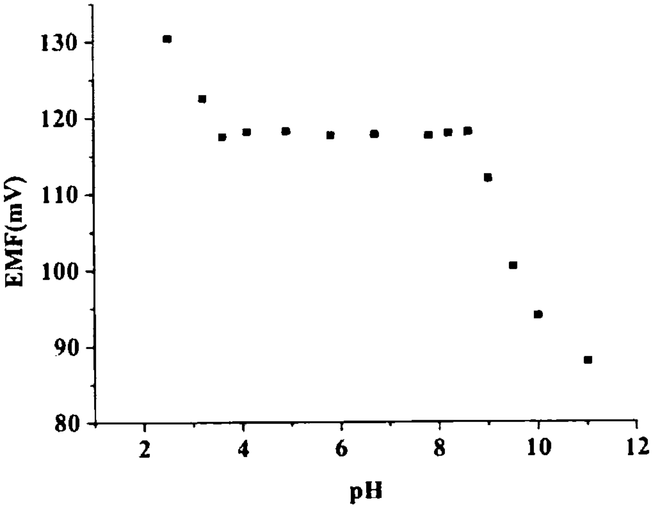

Fig 5.10 Potentiometric titration curve of 20 mL of 1.0×10^{-3} M $Pr(NO_3)_3$ with 1.0×10^{-2} M EDTA for the membrane sensor H_8

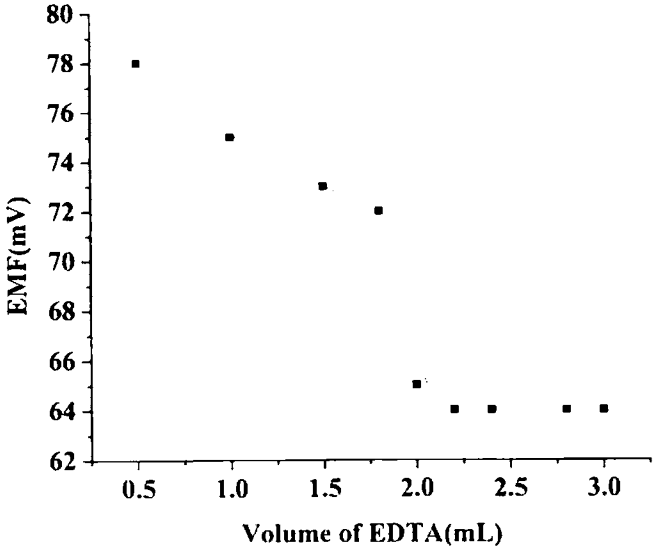

Fig5.11 Potentiometric titration curve of 25 mL of 1.0 × 10^{-3} M $Pr(NO_3)_3$ with 1.0 × 10^{-2} M EDTA for the CMCP sensor Hb_7

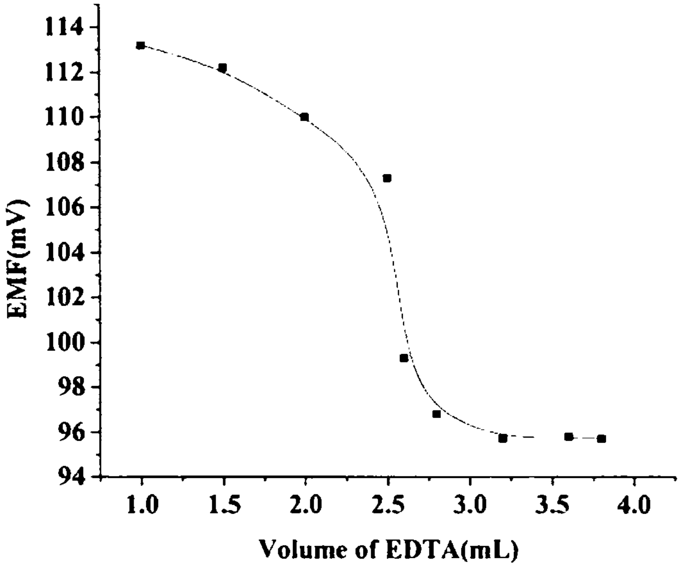

Table 5.1 Formation constants of HBTS-M^{n+} and HMB-M^{n+} complexes.

Metal ion	Log K_f	
	HBTS	HMB
Sm^{3+}	2.43	2.41
Pr^{3+}	4.17	4.23
Gd^{3+}	2.20	2.25
Nd^{3+}	1.95	2.10
La^{3+}	2.18	2.13
Pb^{2+}	2.25	2.18

Table 5.2 Optimization of membrane composition.

Sensor no.	Composition (%)				Slope (mV /decade)	Concentration range (M)
	Ionophore	PVC	Plasticizer	Additives Oleicacid/ NaTBP		
H_1	2	31	BES, 63	4	25.8	10^{-5} to10^{-1}
H_2	2	31	DBS, 63	4	44.3	10^{-4} to 10^{-1}
H_3	2	31	BEP, 63	4	11.7	10^{-4} to 10^{-1}
H_4	2	31	DMS, 63	4	22.8	10^{-4} to 10^{-1}
H_5	2	31	DBP, 63	4	21.7	10^{-5} to 10^{-1}
H_6	1	31	DBP, 64	4	18.3	10^{-4} to 10^{-1}
H_7	3	31	DBP, 62	4	28.2	10^{-5} to 10^{-1}
H_8	**2**	**31**	**DBP, 62**	**5**	**20.3**	**10^{-5} to 10^{-1}**
H_9	2	31	DBP, 63	4^*	37.4	10^{-4} to 10^{-1}

* Oleic acid

Table 5.3 Optimization of the composition of CMCPE type of sensor

Sensor No.	Ionophore %	Graphite %	Binders	Concentration range (M)	Slope (mV/decade)
Hb_1	10	90	TBP	10^{-4} to 10^{-1}	13.4
Hb_2	10	90	DBP	10^{-4} to 10^{-1}	13.1
Hb_3	10	90	BEP	10^{-4} to 10^{-1}	12.5
Hb_4	10	90	BEA	10^{-5} to 10^{-1}	11.1
Hb_5	10	90	DBS	10^{-5} to 10^{-1}	16.6
Hb_6	11	89	DBS	10^{-5} to 10^{-1}	17.7
Hb_7	**12**	**88**	**DBS**	**10^{-5} to 10^{-1}**	**18.0**
Hb_8	13	87	DBS	10^{-5} to 10^{-1}	17.6

Table 5.4 Selectivity coefficients of various interfering cations.

Interfering ions (10^{-2} M)	K_{sel}	
	H_8	Hb_7
Na^+	5.53×10^{-2}	5.64×10^{-2}
K^+	6.43×10^{-2}	6.53×10^{-2}
Mg^{2+}	2.24×10^{-2}	2.15×10^{-2}
Pb^{2+}	2.14×10^{-2}	2.25×10^{-2}
Ag^+	6.54×10^{-2}	5.46×10^{-2}
Ca^{2+}	2.13×10^{-2}	2.10×10^{-2}
Gd^{3+}	3.64×10^{-2}	3.43×10^{-2}
Nd^{3+}	2.98×10^{-2}	2.93×10^{-2}
La^{3+}	3.35×10^{-2}	3.23×10^{-2}
Sm^{3+}	2.51×10^{-1}	2.67×10^{-1}

Table 5.5 Determination of Praseodymium in binary mixtures.

Pr^{3+} taken(M)	Added cation (M)	Pr^{3+} found(M) *	
		H_8	Hb_7
5.0×10^{-3}	La^{3+} (5.0×10^{-3})	4.8×10^{-3}	4.9×10^{-3}
5.0×10^{-3}	Nd^{3+} (5.0×10^{-3})	5.2×10^{-3}	5.1×10^{-3}
5.0×10^{-3}	Ca^{2+} (5.0×10^{-3})	4.8×10^{-3}	4.8×10^{-3}

*Average of six replicates

Table 5.6 Response characteristics of the sensors H_8 and Hb_7

Parameter	Response characteristics	
	H_8	Hb_7
Working concentration range(M)	1.0×10^{-5} to 1.0×10^{-1}	1.0×10^{-5} to 1.0×10^{-1}
Slope(mV/decade)	20.3	18.0
Detection limit(M)	1.0×10^{-5}	8.9×10^{-6}
Response time	15s	10s
pH	3.7 to 8.8	3.6 to 8.6
Shelf life	2 weeks	5 weeks

Table 5.7 Comparison of response characteristics of proposed sensor with other Pr^{3+} sensor reported in literature.

Sens. No	Working conc. range (M)	pH	Response time(s)	Slope (mV/decade)	Reference
1	1×10^{-6} - 1×10^{-2}	2.8–8.7	10	19.6±0.4	[101]
2	1×10^{-6} - 1×10^{-2}	3.5 - 8	<20	21.1	[99]
3	1×10^{-6} - 1×10^{-2}	3 - 8.4	15	19.8	[100]
4	**1.0×10^{-5} – 1.0×10^{-1}**	**3.7 - 8.8**	**15**	**20.3**	**[H_8]**
5	**1.0×10^{-5} – 1.0×10^{-1}**	**3.6 - 8.6**	**10**	**18.0**	**[Hb_7]**

***** ❁ *****

Chapter 6

SENSOR FOR NEODYMIUM

This chapter explains the response characteristics of the sensors developed for neodymium. The fabrication of carbon paste and PVC membrane sensors based on the ionophore N^1,N^2-bis(salicylidine)butane-1,4-diamine (SAB) and application of these sensors as indicator in the potentiometric titration of neodymium with EDTA are included in this chapter. The determination of neodymium present in its binary mixtures using these novel sensors is also discussed in this chapter along with a comparative study of the sensors with those already reported.

Neodymium is the most abundant of the rare earths, after cerium and lanthanum. The most important application of neodymium is as the fundamental basis of neodymium-iron-boron (Nd_2-Fe-B) permanent magnets. It is used extensively in the automotive industry with many applications including starter motor, brake systems, seat adjusters and car stereo speakers. Yttrium-aluminum garnet (YAG) solid-state lasers utilize neodymium because it has optimal absorption and are used in various medical applications, drilling, welding, and material processing. Neodymium and other lanthanide oxides are widely used in the preparation of optical glasses, glass fibers for optical purposes, gasoline-cracking catalysts, polishing compounds and carbon arcs, and in the iron and steel industries to remove sulfur, carbon, and other electronegative elements from iron and steel[121]. Neodymium salts are used as catalysts in polymerization of 1, 3-butadiene and isoprene[174-175]. Moreover, in recent years, the monitoring and evaluation of rare earth elements in some biological materials has received increasing attention, from both nutritional and toxicological points of view[122.176]. The conventional methods for determination of Nd^{3+} ions are spectrophotometry[177], X-ray fluorescence[178] (AAS), neutron activation analysis[179], isotopic dilution method[180] and inductively coupled plasma atomic emission spectroscopy (ICP AES)[181]. But these methods require multiple sample preparation and also infrastructure backup and are not convenient.

This chapter detail about the fabrication of PVC membrane sensor and CMCP sensor for neodymium.

6.1. Ionophore

The synthesis and characterization of the ionophores N^1,N^2-bis (salicylidine)butane-1,4-diamine (SAB) has been discussed in section 2.2.2 of chapter 2 and structure is given as figure 6.1.

6.2. Fabrication of Neodymium Selective Membrane

6.2.1. Potential response of the SAB based sensors

To check suitability of SAB as ion carrier, PVC and CMCP electrodes were fabricated by incorporating SAB for a number of metal ions and potential responses are depicted in figure 6.2 and 6.3. It was found that the electrodes showed a Nernstian response to neodymium ions and this may be due to the fast exchange kinetics at the membrane sample interface.

Conductometic studies were also carried out to understand the selective complexation of the ionophore towards neodymium ions. The complexation of SAB with different metal ions was studied conductometrically in acetonitrile solution at 25 ± 1 °C and results are summarized in Table 6.1. It was observed that the formation constant of the Nd^{3+}- SAB complex is more than that of the other metal ions studied.

As the above two findings are favorable for the selection of SAB as ion carrier, neodymium selective sensors have been fabricated using SAB as ion recognition element.

6.2.2. Sensor membrane fabrication

The fabrication of the PVC membrane sensor was in accordance with the method discussed in section 2.7.1 of chapter 2. In order to arrive at optimized membrane composition, sensors having varying proportion of membrane components were fabricated and their potential responses were recorded. The optimized membrane composition that gave the best response in terms of slope, concentration range and response was found to be 3:32:62:3 (SAB: PVC: plasticizer: NaTBP) (w/w %).

Carbon paste obtained by mixing SAB, graphite and binders as detailed in chapter 2 was packed into the open end of Teflon holder in which electrical contact was made with a copper rod through the centre of the electrode holder. The electrode surface was polished using a filter paper to produce reproducible working surface. The finished electrode was conditioned by dipping it overnight in 1.0×10^{-1} M neodymium chloride solution. The optimized composition was found to be 90: 10 (graphite: SAB).

6.2.3. Equilibration of membranes and potential measurements

PVC membrane and carbon paste sensors were equilibrated for 1 day in 1.0×10^{-1} M neodymium chloride solution. The potentials were measured by varying the concentration of neodymium chloride in test solution in the range 1.0×10^{-6} to 1.0×10^{-1} M. The potential measurements were carried out at 25 ± 1°C on a Metrohm 781 ion meter. Ag/AgCl reference electrode was used in conjunction with the developed sensor. The cell assembly for potentiometric measurements can be represented as follows:

PVC membrane sensor

Ag, AgCl | KCl || test solution |membrane | internal solution (1.0×10^{-1} M $NdCl_3$) || KCl | AgCl, Ag

CMCPE sensor

Ag, AgCl | KCl || test solution | CMCPE

6.2.4. Optimization of membrane composition

The sensitivity, selectivity and linearity of the membrane sensors were greatly influenced by the nature of ionophore, membrane composition and nature of plasticizer. The performance characteristics of different membranes having ingredients of different proportions are summarized in Table 6.2. As expected, the amount of ionophore was found to affect the PVC membrane sensitivity. The calibration slope of the membrane sensor was found to be increased when ionophore percentage varied from 2-3% and further addition of the ionophore resulted in a decrease in determination range of the sensor, probably due to some inhomogeneity and possible saturation of the membrane. The nature of plasticizer influences the dielectric constant of the membrane phase and state of the ligand. Of the four plasticizer studied, DBS resulted in best slope (SA_3). The effect of both OA and NaTPB, as suitable lipophilic additives, on the response characteristics of the proposed PVC membrane was also investigated, and the results are also included in Table 6.2.The sensor, SA_3, with NaTBP as additive gave better slope than oleic aid. 3% NaTBP was found to be the optimum amount and further increment in the additive resulted in a super nernstian slope. Thus optimized membrane composition which resulted in best performance was found to be 3: 32: 62: 3 (SAB: PVC: DBS: NaTBP).

The surface structure of the membrane was studied using SEM image. The SEM image of the membrane SA_6 is presented in the Figure 6.4. This image gives an idea of the homogeneity of the membrane which is a main factor affecting the response characteristics of the sensor. It is clear from the figure that the surface of the optimized membrane is smooth and homogeneous.

A set of seven CMCPE type sensors were developed by varying sensor composition and results are consolidated in Table 6.3. Among the different binders tested di-n-butyl sebacate was found to be the most suitable one. It was found that the sensor Sb_6 with the composition ratio 90:10 (Graphite: ionophore) (w/w %) was the best in terms of response, time working concentration range and the Nernstian slope. Further increase in the ionophore percentage resulted in a super Nernstian slope (Sb_7).

6.2.5. Calibration curve and statistical data

Figure 6.5 and 6.6 represents the calibration graph for the sensors SA_6 (PVC membrane) and Sb_6 (CMCPE).Working concentration range for SA_6 and Sb_6 was found to be 1.0×10^{-6} to 1.0×10^{-2} M. Slope of the calibration graph for SA_6 and Sb_6 was 20.6 and 19.5 respectively. The detection limit, taken at the point of intersection of the extrapolated linear segment of the calibration curve, was found to be 8.7×10^{-7} M and 4.7×10^{-7} M.

6.2.6. Dynamic response time

The practical response time required for the Nd^{3+} sensor to reach a potential within ±1mV of the final equilibrium value was measured by changing the Nd^{3+} concentration in the range 1.0×10^{-6} to 1.0×10^{-2} M. The sensors, SA_6 and Sb_6, reached their equilibrium potential in a very short time and were found to be 15s and 10s respectively. The practical reversibility of the sensors SA_6 and Sb_6 were evaluated by taking measurements for Nd^{3+} in the sequence of high-to-low concentration and vice versa. The response of the sensors remained unchanged regardless of the change in concentration of the metal salt solution.

6.2.7. Effect of pH

The pH dependence of the membrane sensor (SA_6) and CMCPE type sensor (Sb_6) have been tested using 1.0 × 10^{-4} M $NdCl_3$ solution over the pH range from 2 to 11 and results are shown in the figure 6.7 and 6.8. It was found that potential remains constant in the pH range 3.0 to 7.5 and 3.5 to 7.5 for the sensors SA_6 and Sb_6 respectively. Beyond this pH, a drift in potential is observed which may be due to the formation of hydroxide of Nd^{3+} at higher pH and interference by hydrogen ion at lower pH.

6.2.8. Selectivity coefficients

Selectivity is perhaps the single most important characteristics of any sensor, which defines the nature of device and extent to which it may be employed in the determination of a particular ion in presence of other interfering ions. Potentiometric selectivity coefficient of the neodymium sensors were evaluated by fixed interference method at 10^{-2} M concentration of interfering ions. The selectivity coefficients so obtained are compiled in Table 6.4. The selectivity coefficients are on the order of 10^{-4} to 10^{-2}, which seems to indicate that these cations have negligible effect on the functionality of the neodymium sensors. The relatively good selectivity of the electrodes for neodymium ions arose from the stronger tendency of the carrier molecule for complexing with Nd^{3+} compared to other cations.

6.2.9. Shelf Life

The average life time or the shelf life of the developed sensors was studied. As already explained the working surface of the carbon paste electrode can be renewed. The potential measurements were recorded every day over a period of time to determine the shelf life of the sensors. The sensors were all kept in 1.0 × 10^{-1} M neodymium chloride solution when not in use to avoid drying and cracking. The life time of the sensors, SA_6 and Sb_6, were found to be 7 weeks and 5 weeks respectively.

6.2.10. Analytical applications

The utility of the sensors SA_6 and Sb_6 were investigated in the determination of neodymium ions in various binary mixtures and the results are presented in Table 6.5. It was observed that the recoveries of Nd(III) ions are quantitative in all cases and the sensors can be used for the determination of Nd (III) in real samples having different analytical matrixes.

The developed sensors have been successfully applied as an indicator electrode in the titration of Nd(III) with EDTA at pH 7. The titration curves for the sensors are shown in the figure 6.9 and 6.10 respectively. A very good inflection point which corresponds to 1:1 stoichiometry of EDTA complex was observed from the titration curve. Hence, the amount of Nd(III) in solution can be accurately determined with the developed sensors.

6.2.11. Comparative study among the sensors SA_6 and Sb_6 and to some of the reported sensors.

Both the sensors are found to have very good response characteristics. The response characteristics of both the sensors are consolidated in the Table 6.6. While the working concentration ranges are the same for both the electrodes, the shelf time of carbon paste electrode is less compared with the PVC electrode. Table 6.7 represents comparative study of characteristics of the proposed sensors with some of the reported sensors. The presently developed sensors are highly comparable with all the reported sensors[94-96].

Fig.6.1 Structure of SAB

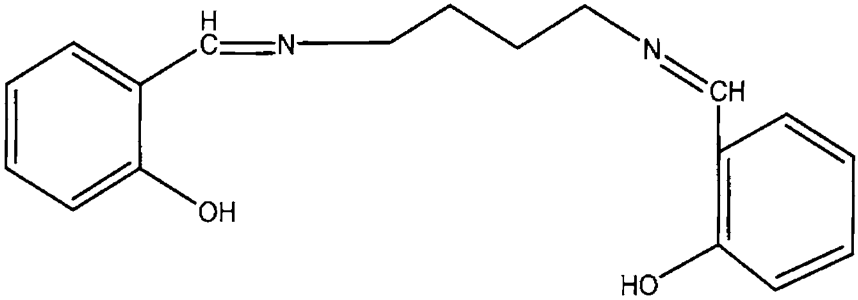

Fig.6.2 Potential response of various PVC membrane ion selective electrodes based on SAB

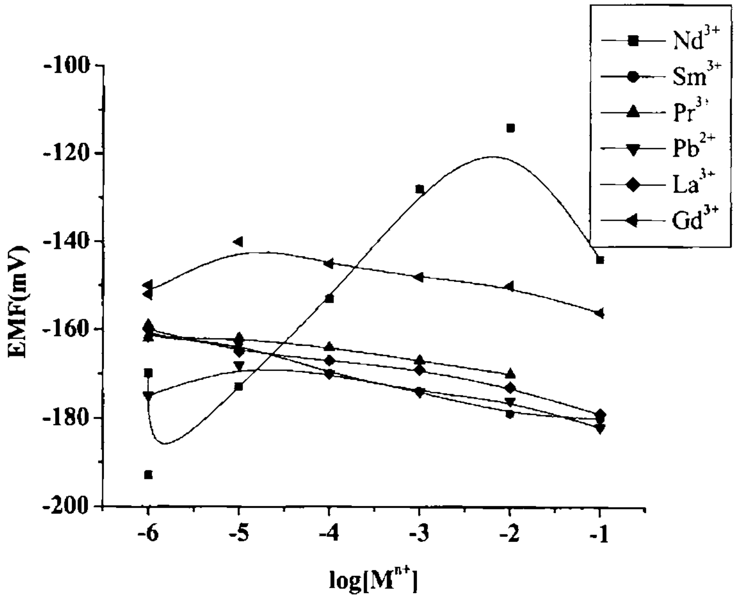

Fig. 6.3 Potential response of various CMCPE ion selective electrodes based on SAB

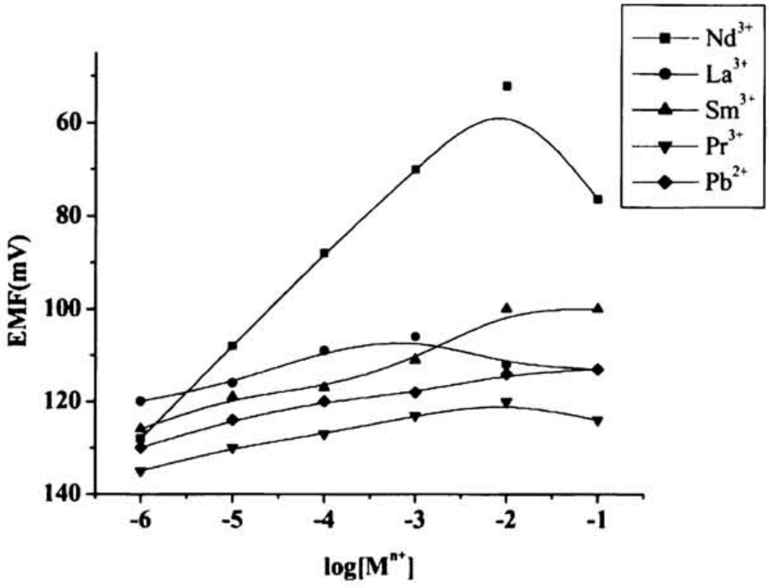

Fig. 6.4 SEM image of the polymeric membrane of SA_6 sensor

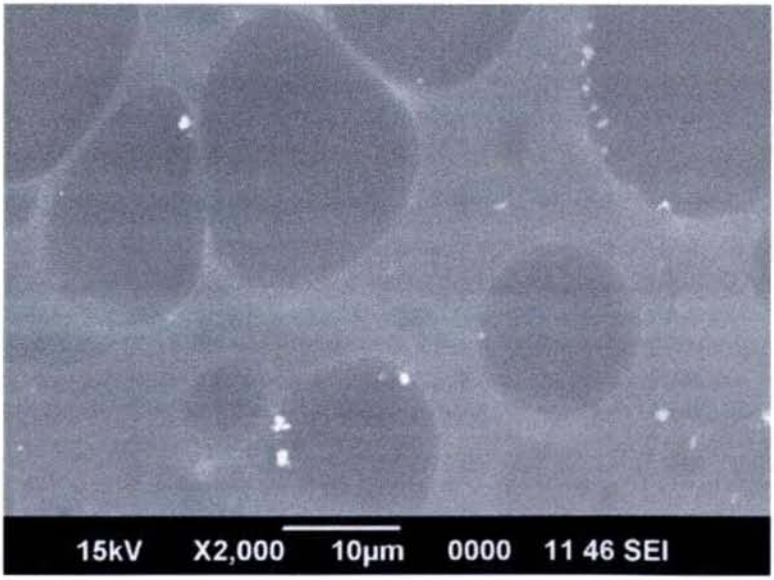

Fig. 6.5 Calibration graph for Nd(III) selective PVC membrane sensor based on SAB (SA_6)

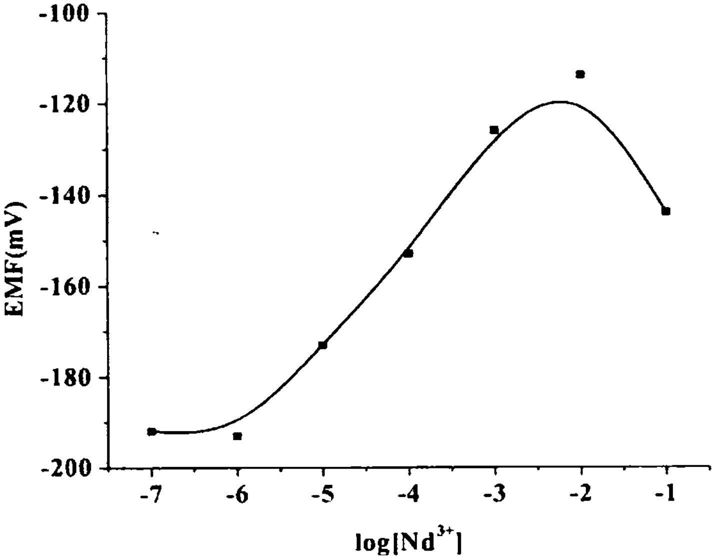

Fig. 6.6 Calibration graph for Nd(III) selective CMCPE sensor based on SAB (Sb_6)

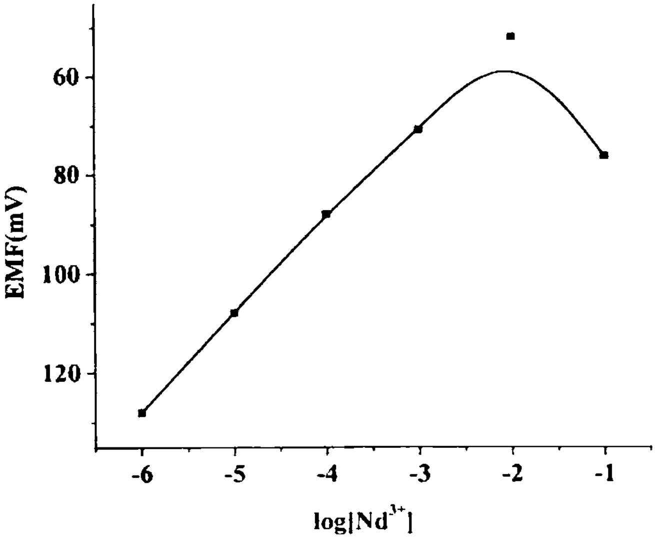

Fig.6.7 The effect of pH of test solution (1.0 × 10^{-4} M $NdCl_3$) on the response of Nd (III) membrane sensor SA_6

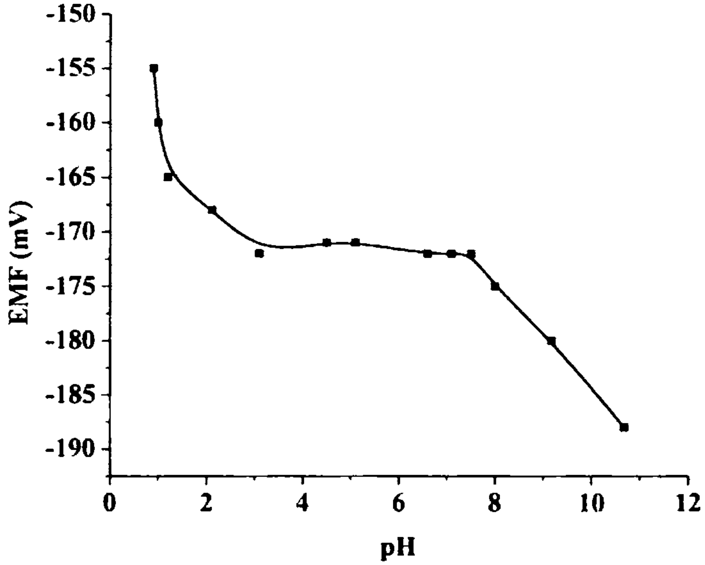

Fig. 6.8 The effect of pH of test solution (1.0 × 10^{-4} M $NdCl_3$) on the response of Nd(III) sensor Sb_6

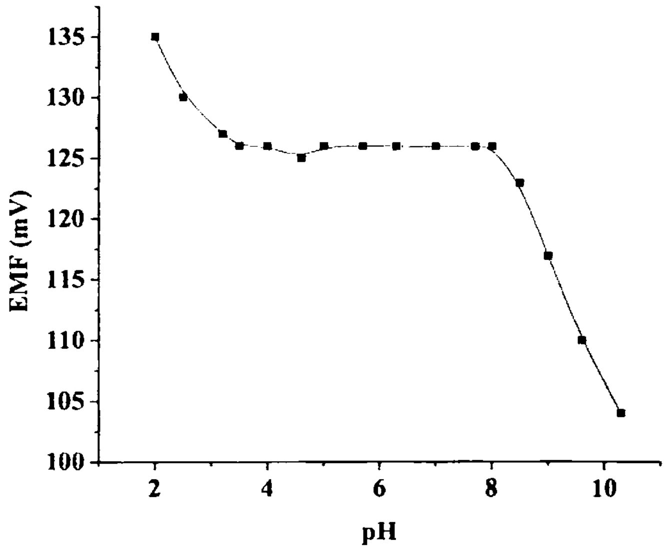

Fig. 6.9 Potentiometric titration curve of 25 mL of 1.0×10^{-3}M $NdCl_3$ with 1.0×10^{-2} M EDTA for the membrane sensor SA_6

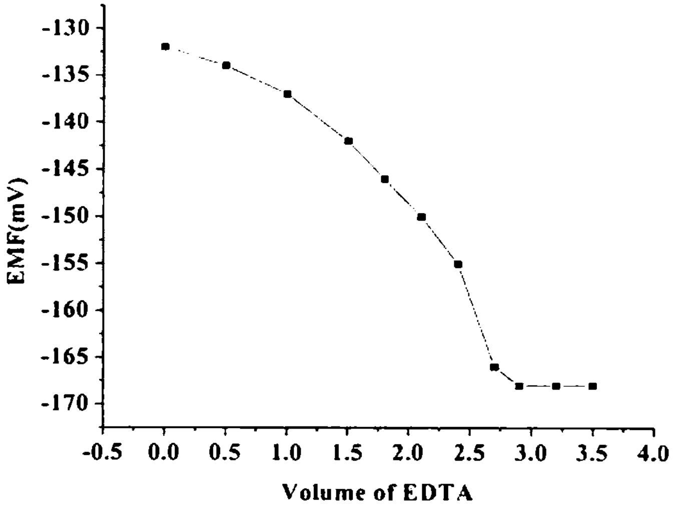

Fig. 6.10 Potentiometric titration curve of 25 mL of 1.0×10^{-3} M $NdCl_3$ with 1.0×10^{-2} M EDTA for the CMCPE sensor Sb_6

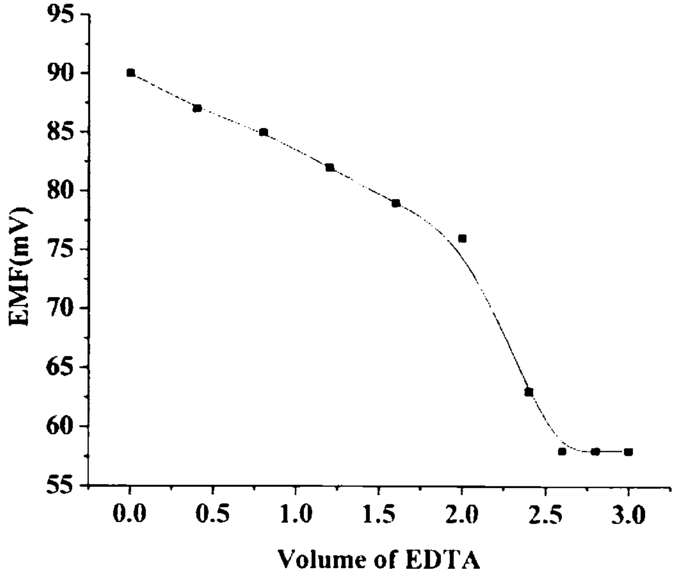

Table 6.1 The formation constants of SAB-M^{n+} complexes

Metal ion	**Log K_f**
Nd^{3+}	4.35
Gd^{3+}	2.12
Sm^{3+}	2.29
Pr^{3+}	2.15
Pb^{2+}	2.23

Table 6.2 Optimization of membrane composition.

Sensor no.	Composition (%)				Slope (mV/ decade)	Concentration range (M)
	Ionophore	PVC	Plasticizer	Additives NaTBP/ oleic acid		
SA_1	2	32	DBP, 63	3	13.3	10^{-6} to10^{-3}
SA_2	2	32	BEA, 63	3	10.9	10^{-5} to 10^{-2}
SA_3	2	32	DBS, 63	3	16.7	10^{-6} to 10^{-2}
SA_4	2	32	BEP, 63	3	12.5	10^{-6} to 10^{-4}
SA_5	2	32	DBS, 63	3*	10.9	$10^{-5}$to 10^{-2}
SA_6	**3**	**32**	**DBS, 62**	**3**	**20.6**	**10^{-6} to 10^{-2}**
SA_7	4	32	DBS, 61	3	21.3	10^{-4} to 10^{-1}
SA_8	3	32	DBS, 60	5	25.3	10^{-5} to 10^{-2}

*Oleic acid

Table 6.3 Optimization of the composition of CMCPE type of sensor

Sensor no.	Ionophore % (w/w)	Graphite % (w/w)	Binders	Concentration range (M)	Slope (mV/decade)
Sb_1	5	95	DBP	10^{-6} to 10^{-4}	10.9
Sb_2	5	95	BEA	10^{-5} to 10^{-2}	13.5
Sb_3	5	95	BEP	10^{-5} to 10^{-2}	8.9
Sb_4	5	95	BEP	10^{-5} to 10^{-2}	5.4
Sb_5	5	95	DBS	10^{-6} to 10^{-2}	16.5
Sb_6	**10**	**90**	**DBS**	**10^{-6} to 10^{-2}**	**19.5**
Sb_7	12	88	DBS	10^{-5} to 10^{-2}	28.2

Table 6.4 Selectivity coefficients for SA_6 and Sb_6 sensors using fixed interference methods of interfering ions

Interfering Ions	K_{sel}	
	SA_6	Sb_6
Na^+	7.16×10^{-2}	7.28×10^{-2}
K^+	7.53×10^{-2}	7.49×10^{-2}
Mg^{2+}	2.77×10^{-2}	2.45×10^{-2}
Pb^{2+}	2.23×10^{-2}	2.48×10^{-2}
Ag^+	5.78×10^{-2}	6.46×10^{-2}
Ca^{2+}	5.67×10^{-2}	4.36×10^{-3}
Gd^{3+}	9.68×10^{-3}	8.53×10^{-3}
Sm^{3+}	1.02×10^{-2}	2.48×10^{-2}
La^{3+}	6.55×10^{-3}	6.14×10^{-4}
Pr^{3+}	8.55×10^{-3}	9.54×10^{-4}

Table 6. 5 Determination of Neodymium in binary mixtures.

Nd^{3+}(M) taken	Added cation (M)	Nd^{3+} found(M)*	
		SA_6	Sb_6
5.0×10^{-4}	La^{3+} (5.0×10^{-4})	4.8×10^{-4}	4.9×10^{-4}
5.0×10^{-4}	Pr^{3+} (5.0×10^{-4})	5.1×10^{-4}	5.1×10^{-4}
5.0×10^{-4}	Pb^{2+} (5.0×10^{-4})	4.9×10^{-4}	4.8×10^{-4}

*Average of six replicates

Table 6.6 Response characteristics of the sensors SA_6 and Sb_6

Parameter	Response Characteristics	
	SA_6	Sb_6
Working concentration range(M)	1.0×10^{-6} to 1.0×10^{-2}	1.0×10^{-6} to 1.0×10^{-2}
Slope(mV/decade)	20.6	19.5
Detection limit(M)	8.7×10^{-7}	4.7×10^{-7}
Response time	15s	10s
pH	3.0-7.5	3.5- 8.0
Shelf life	7 weeks	5 weeks

Table6.7 Comparison of the response characteristics of the developed sensors with other reported neodymium sensors

Sens. No	Working conc. range (M)	pH	Response time(s)	Slope (mV/decade)	Reference
1	1×10^{-5} - 1×10^{-2}	3.5 – 8.5	<10s	19.6±0.3	[96]
2	1×10^{-5} - 1×10^{-2}	4.0 – 8.0	15s	19.6±0.3	[95]
2	1×10^{-6} - 1×10^{-2}	4.0 – 6.5	<5s	20.1	[94]
3	**1.0×10^{-6} – 1.0×10^{-2}**	**3.0 - 7.5**	**15s**	**20.6**	**$[SA_6]$**
4	**1.0×10^{-6} – 1.0×10^{-2}**	**3.5 - 8.0**	**10s**	**19.5**	**$[Sb_6]$**

* * *

Chapter 7

SENSOR FOR GADOLINIUM

This chapter deals with the fabrication of PVC membrane and CMCPE type sensor based on 2-[(2-mercaptophenylimine) methyl] phenol for gadolinium(III). The analytical application of these sensors as indicator electrode in the potentiometric titration of gadolinium(III) with EDTA and in the determination of gadolinium(III) form its binary mixtures are also discussed in this chapter along with a comparative study of the sensors with those already reported.

Gadolinium is a silvery white rare earth metal. It finds application in neutron therapy to target tumors, in neutron radiography, in shielding of nuclear reactors and as an efficient catalyst for decarboxylation of oxaloacetic acid, conversion of ortho to Para hydrogen and polymerization of ethylene. Because of its paramagnetic properties, solutions of organic gadolinium complexes and gadolinium compounds are the most popular intravenous MRI contrast agents in medical magnetic resonance imaging Although gadolinium agents have proved useful for patients with renal impairment, the use of certain gadolinium containing agents may lead to serious illness such as nephrogenic systemic fibrosis and nephrogenic fibroseny dermopathy in patients with severe renal failure requiring dialysis. Therefore the trace level determination of gadolinium in various samples is very important.

The available methods for the low-level determination of rare-earth ions in solution include spectrophotometry[182], ICP-AES[183], isotopic dilution mass spectrometry[184], neutron activation analysis[185] and X-ray fluorescence spectrometry[186]. These methods are either time consuming and involve multiple sample manipulations or expensive and are not convenient. This chapter discusses the fabrication of two types of sensors for the determination of gadolinium.

7.1. Ionophore

The synthesis and characterization of the ionophore 2-[(2-mercaptophenylimine)methyl]phenol (MPM) has been discussed in section 2.2.6 of chapter 2 and structure is given as figure 7.1.

7.2. Fabrication of Gadolinium Selective Membrane

7.2.1. Potential response of the MPM based sensors

As a preliminary step, PVC membrane and CMCP electrodes were fabricated using MPM as ion carrier for a number of metal ions and potential responses are shown in figure 7.2 and 7.3. Among the different tested cations, Gd^{3+} demonstrates the most sensitive response and seems to be suitably determined by these electrodes. Therefore, this ionophore was selected as a suitable sensor material for Gd^{3+}selective sensor.

To investigative the selective complexation of MPM towards gadolinium, complexation of MPM with different metal ions was studied conductometrically as discussed in section 2.6 of chapter 2 and results are consolidated in Table 7.1. As it is obvious, the formation constant of the Gd^{3+}- MPM complex is more than that of the other metal ions studied and hence MPM can be selected as suitable carrier for gadolinium (III).

7.2.2. Sensor membrane fabrication

The general method of fabrication of the PVC membrane and CMCPE type of sensors has been discussed in section 2.7 of Chapter 2.

For the fabrication of PVC membrane sensor, disc shaped membranes prepared from a solution of MPM, PVC, plasticizer and additive were cut out and stuck on to the open end of a Pyrex glass tube. The sensor tube was filled with an internal solution of 1.0×10^{-1} M $GdCl_3$ and conditioned by soaking in 1.0×10^{-1} M gadolinium chloride solution. The optimized composition which resulted in a best Nernstian response and working concentration range was found to be 5: 32: 60: 3 (MPM: PVC: DBP: NaTBP) (w/w %).

The CMCPE type of sensor was fabricated by packing the paste of ionophore and graphite in suitable binder into the open end of the Teflon holder and conditioned by soaking in1.0 × 10^{-1} M gadolinium chloride solution. The best composition ratio for CMCPE type of sensor was found to be 87:13 (graphite: MPM).

7.2.3. Equilibration of membranes and potential measurements

The optimum equilibration time for the PVC membrane and CMCP sensors, in presence of 1.0 × 10^{-1} M gadolinium chloride was found to be 2 days, after which it generated stable potentials in contact with gadolinium chloride solutions. All the potential measurements were carried out by means of Metrohm 781 ion meter at 25±1 °C and cell assembly used for the measurements can be represented as follows:

PVC membrane sensor

Ag, AgCl | KCl || test solution |membrane | internal solution (1.0 × 10^{-1} M $GdCl_3$) || KCl | AgCl, Ag

CMCPE sensor

Ag, AgCl | KCl || test solution | CMCPE

7.2.4. Optimization of membrane composition

The important features of the PVC membranes such as nature of plasticizer, nature and amount of ionophore, and especially, the nature and amount of the additives are significantly influence the sensitivity and selectivity of the sensors. Thus, the different aspects of the membrane preparation based on MPM for Gd^{3+} were optimized and the results are given in Table 7.2. From the results, it was found that among the four different plasticizers used, DBP (sensor MP_1) was the most effective solvent mediator in preparation of the PVC membrane. It is also known that the presence of lipophilic additives not only diminishes the ohmic resistance and enhances the sensitivity and selectivity of the membrane sensors, but also catalyze the exchange kinetics at the sample-membrane interface. The effect of nature and amount of additive on the response of the membrane sensor was investigated and results are compiled in the Table 7.2. The data given in the table shows that NaTBP is more suitable additive than oleic acid. Moreover, 3% was found to be the optimum amount of additive. The amount of the ionophore was also found to affect the sensitivity of the sensors. 5% was found to be the optimum amount of ionophore and further addition of ionophore content resulted in a diminished response from the sensors which may be due to the saturation of the membrane. The sensor, MP_7, with the composition ratio 5:32:60:3 (MPM:PVC:DBP:NaTBP) (%w/w) was found to give the best response characteristics.

The SEM image was taken inorder to investigate the surface morphology of the membrane of MP_7. Fiure 7.4 presents the SEM image of the PVC membrane of MP_7. The homogeneity of membranes may also affect the sensitivity and response characteristics of the sensors. A smooth and uniform membrane is obtained for MP_7.

The weight ratio of graphite, ionophore and nature of binders were varied to arrive at optimum composition for CMCP sensor and results are consolidated in Table 7.3. Sensor, PM_6, with a composition of 87:13 (graphite: MPM) gave best Nernstian response. TBP was found to be the suitable binder. Further increase in the ionophore percentage resulted in a sub Nernstian slope.

7.2.5. Calibration curve and statistical data

The calibration plot of the EMF versus log [Gd^{3+}] for the sensors MP_7 and PM_6 are shown as Figure 7.5 and 7.6. The sensors MP_7 and PM_6 showed linear response over the concentration range 1×10^{-6} to 1×10^{-2} with a slope of 19.9 and 19.4 mV/decade respectively. The detection limit was found to be 3.7×10^{-7} and 3.2×10^{-7}M respectively.

7.2.6. Dynamic response time

The response time of the sensors MP_7 and PM_6 was found to be 10s and 5s. The practical reversibility of the sensors MP_7 and PM_6 were evaluated by taking measurements in the sequence of high-to-low concentration and vice versa of the analyte. The sensing behavior of the sensors was remained unchanged when potentials were recorded either from low to high concentrations or vice versa.

7.2.7. Effect of pH

The performance of the sensors was also accessed at different pH values. For this purpose the potential response of the sensors was determined at 1.0×10^{-4} M in the pH range 2 to 10 and results are shown as Figure 7.7 and 7.8. pH was adjusted by adding suitable buffer solution. It is obvious from the figures that response of the sensors remains constant over the pH range.3.0 to 8.5 and 3.5 to 8.5 for MP_7 and PM_6 respectively. The increase in potential at lower pH may be ascribed to interference by hydrogen ions and decease in potential at higher pH may be due to the formation of some hydroxyl complex of the Gd(III).

7.2.8. Selectivity

The influence of interfering ions on the response behavior of the sensors is usually described in terms of selectivity coefficient. The selectivity coefficients were determined at 1.0 × 10^{-2} M concentration of foreign ions by using the fixed interference method. The selectivity coefficient values are consolidated in Table 7.4. It is evident from the selectivity coefficients data, that the sensor exhibits a high performance for gadolinium ion compared with other metal ions.

7.2.9. Shelf Life

The operative life time for the sensors MP_7 and PM_6 was found to be 8 weeks and 5 weeks respectively, during which it could be used without any measurable divergence. The sensors were all kept immersed in 1.0 × 10^{-1} M gadolinium chloride solution when not in use. The surface of CMCPE type sensor could be renewed by squeezing out a small amount of the paste, scrapping off the excess, polishing the new surface against a filter paper.

7.2.10. Analytical applications

The practical utility of the proposed sensors were tested by their use as an indicator electrode in the potentiometric titration of Gd(III) with EDTA at pH7 and resulting titration curve is shown as Figure 7.9 and 7.10 for MP_7 and PM_6 respectively. As it is obvious from the figures, the sensors can monitor the amount of gadolinium ions.

The developed sensors were also successfully applied to the direct determination of gadolinium ions in various binary mixtures and the results are presented in Table 7.5. It was observed that the recoveries of Gd(III) ions are quantitative in all cases and the sensors can be used for the determination of Gd (III) in real samples having different analytical matrixes.

7.2.11. Comparative study among the sensors MP_7 and PM_6 and to some of the reported sensors.

The response characteristics of the membrane sensor and CMCP sensor are consolidated in Table 7.6. The response time, working concentration range and pH are almost comparable in the case of both type of sensors, but life time was found to be greater in case of PVC membrane sensor.

Table7.7 compares the response characteristics of newly developed sensors with those of the previously reported sensors in literature. The sensors showed comparable working concentration range, pH and response time with respect to the other Gd(III) selective sensors reported in literature[103-105,107-108].

Figure 7.1 Structure of MPM

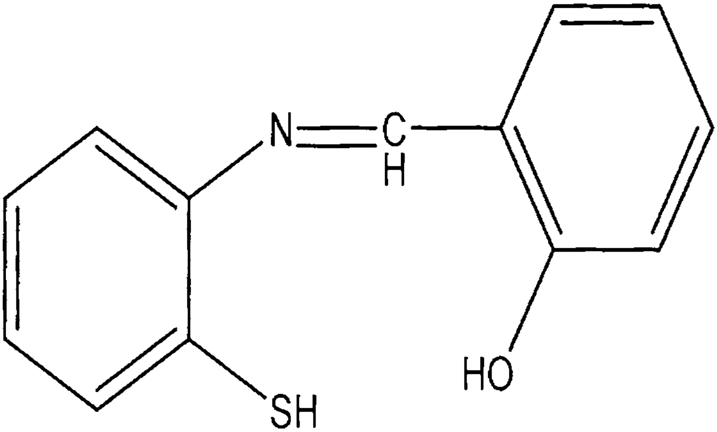

Figure 7.2 Potential response of various PVC membrane ion selective electrodes based on MPM

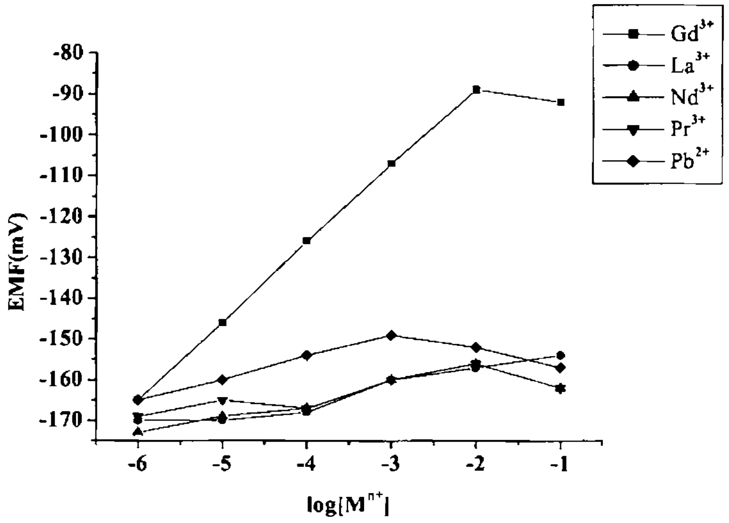

Figure 7.3 Potential response of various CMCPE ion selective electrodes based on MPM

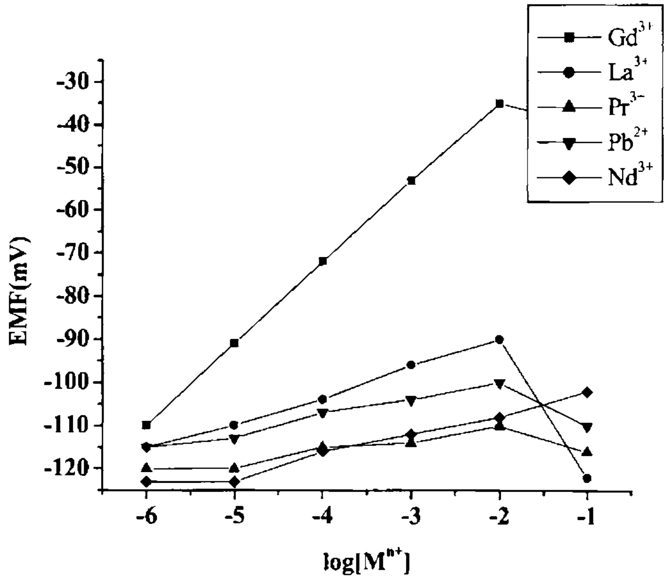

Figure 7.4 SEM image of the polymeric membrane of MP_7 sensor

Figure 7.5 Calibration graph for Gd(III) selective PVC membrane sensor based on MPM (MP_7)

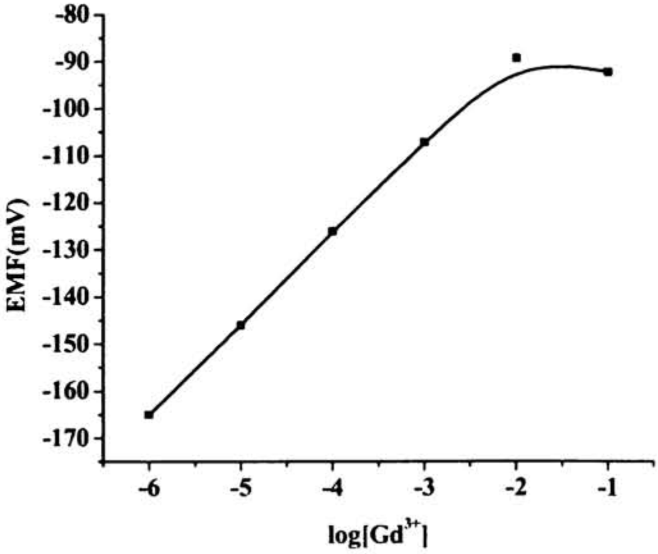

Figure 7.6 Calibration graph for Gd(III) selective CMCPE sensor based on MPM (PM$_6$)

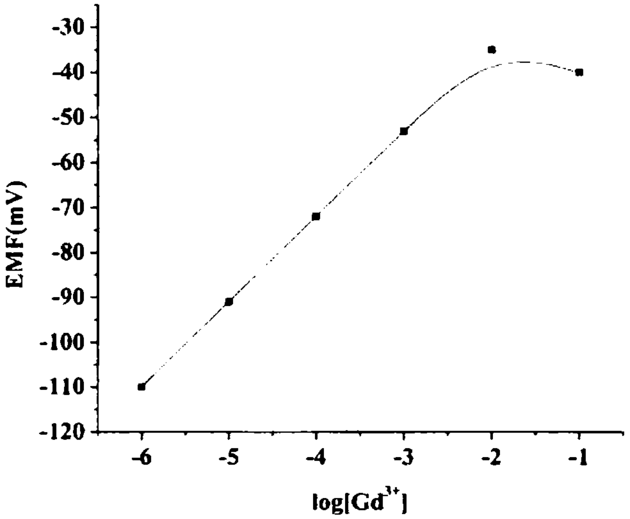

Figure 7.7 The effect of pH of test solution (1.0 × 10^{-4} M GdCl$_3$) on the response of Gd(III) membrane sensor MP$_7$

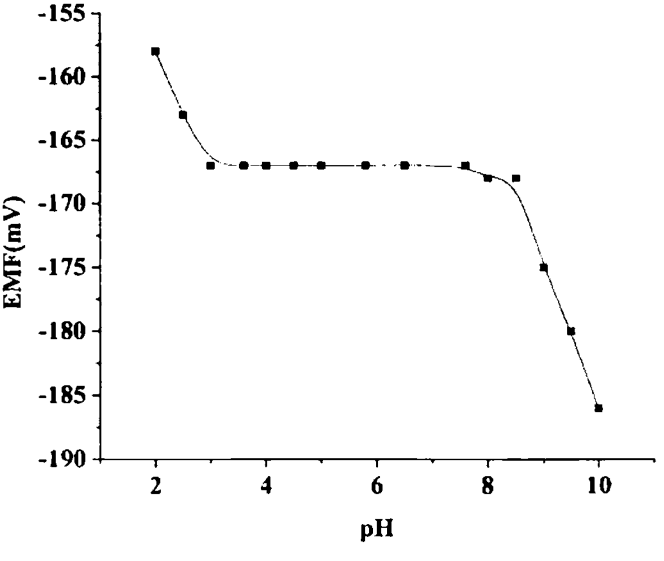

Figure 7.8 The effect of pH of test solution (1.0×10^{-4} M $GdCl_3$) on the response of Gd(III) sensor PM_6

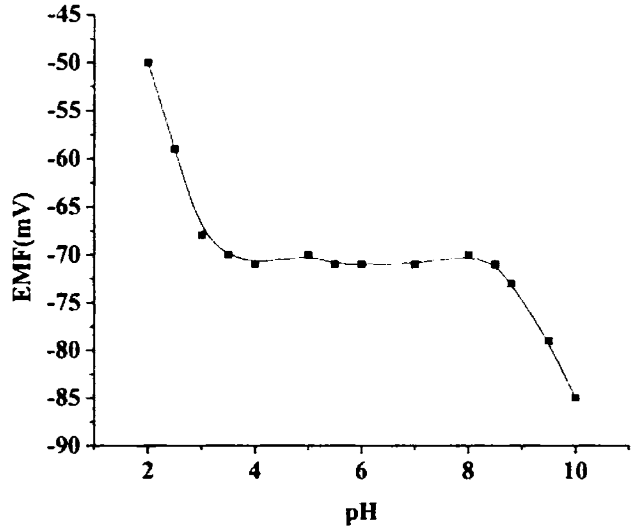

Fig. 7.9 Potentiometric titration curve of 25 mL of 1.0×10^{-3}M $GdCl_3$ with 1.0×10^{-2} M EDTA for the membrane sensor MP_7

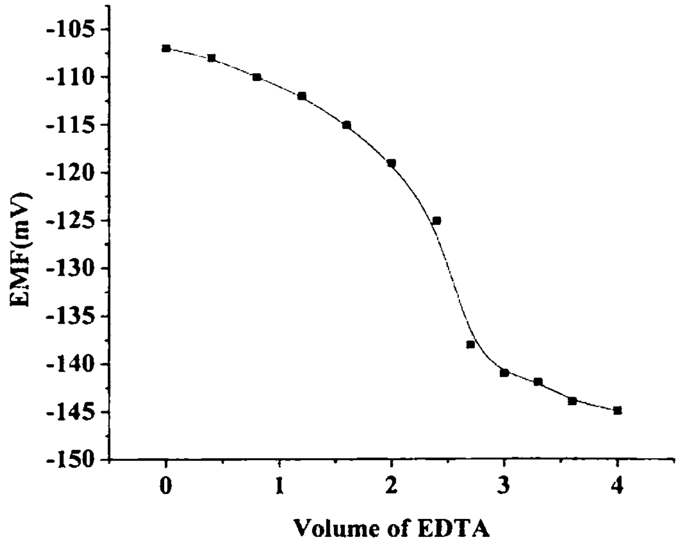

Fig. 7.10 Potentiometric titration curve of 25 mL of 1.0 × 10^{-3}M $GdCl_3$ with 1.0 × 10^{-2} M EDTA for the CMCPE sensor PM_6

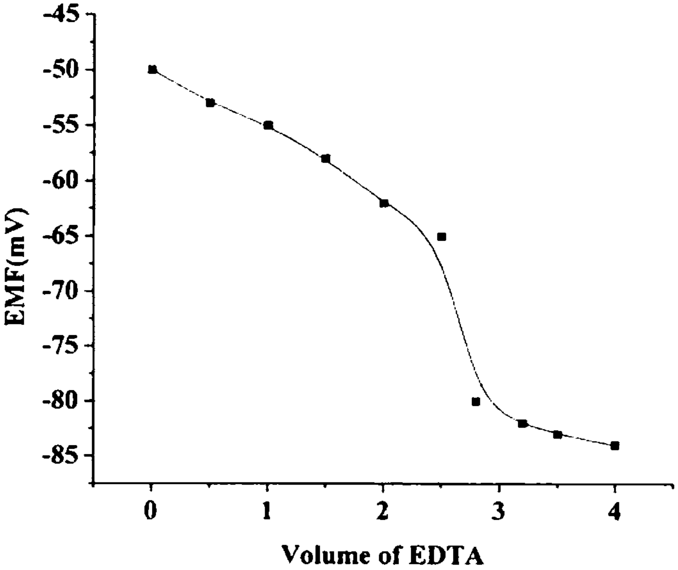

Table 7.1 The formation constants of MPM-M^{n+} complexes

Metal ion	Log K_f
Gd^{3+}	4.14
Sm^{3+}	2.28
Nd^{3+}	2.16
Pr^{3+}	2.24
Pb^{2+}	2.27

Table 7.2 Optimization of membrane composition.

Sensor no.	Composition (%)				Slope (mV/ decade)	Concentration range (M)
	Ionophore	PVC	Plasticizer	Additives NaTBP/oleic acid		
MP_1	3	32	DBP, 62	3	15.3	10^{-6} to10^{-2}
MP_2	3	32	BEA, 62	3	11.5	10^{-5} to 10^{-2}
MP_3	3	32	DBS, 62	3	10.5	10^{-5} to 10^{-2}
MP_4	3	32	BEP, 62	3	12.7	10^{-5} to 10^{-2}
MP_5	3	32	DBS, 62	3*	9.7	$10^{-5}$to 10^{-2}
MP_6	4	32	DBP, 61	3	17.3	10^{-6} to 10^{-2}
MP_7	**5**	**32**	**DBP, 60**	**3**	**19.9**	**10^{-6} to 10^{-2}**
MP_8	6	32	DBP, 59	3	16.8	$10^{-5}$to 10^{-2}

*Oleic acid

Table 7.3 Optimization of the composition of CMCPE type of sensor

Sensor no.	Ionophore % (w/w)	Graphite % (w/w)	Binders	Concentration range (M)	Slope (mV/decade)
PM_1	10	90	DBS	10^{-4} to 10^{-1}	15.9
PM_2	10	90	BEA	10^{-5} to 10^{-2}	16.1
PM_3	10	90	DBP	10^{-5} to 10^{-2}	15.4
PM_4	10	90	TBP	10^{-6} to 10^{-2}	16.5
PM_5	12	88	TBP	10^{-6} to 10^{-2}	17.6
PM_6	**13**	**87**	**TBP**	**10^{-6} to 10^{-2}**	**19.4**
PM_7	15	85	TBP	10^{-5} to 10^{-2}	16.8

Table 7.4 Selectivity coefficients for MP_7 and PM_6sensors using fixed interference methods of interfering ions

Interfering Ions	K_{sel}	
	MP_7	PM_6
Na^+	4.16×10^{-2}	4.38×10^{-2}
K^+	5.72×10^{-2}	6.69×10^{-2}
Mg^{2+}	5.46×10^{-2}	5.24×10^{-2}
Pb^{2+}	3.12×10^{-2}	3.23×10^{-2}
Ca^{2+}	4.48×10^{-2}	4.36×10^{-2}
Nd^{3+}	8.15×10^{-3}	8.34×10^{-3}
Sm^{3+}	2.16×10^{-2}	3.25×10^{-2}
La^{3+}	4.65×10^{-3}	3.14×10^{-3}
Pr^{3+}	7.56×10^{-3}	7.34×10^{-3}

Table 7. 5 Determination of Gadolinium in binary mixtures.

Gd^{3-}(M) taken	Added cation (M)	Gd^{3-} found(M)*	
		MP_7	PM6
5.0×10^{-4}	La^{3+} (5.0×10^{-4})	4.9×10^{-4}	4.9×10^{-4}
5.0×10^{-4}	Pr^{3+} (5.0×10^{-4})	5.1×10^{-4}	5.1×10^{-4}
5.0×10^{-4}	Pb^{2+} (5.0×10^{-4})	4.9×10^{-4}	4.8×10^{-4}

*Average of six replicates

Table 7.6 Response characteristics of the sensors MP_7 and PM_6

Parameter	Response Characteristics	
	MP_7	PM_6
Working concentration range(M)	1.0×10^{-6} to 1.0×10^{-2}	1.0×10^{-6} to1.0×10^{-2}
Slope(mV/decade)	19.9	19.4
Detection limit(M)	3.7×10^{-7}	3.2×10^{-7}
Response time	10s	5s
pH	3.0-8.5	3.5- 8.5
Shelf life	8 weeks	5 weeks

Table 7.7 Comparison of the response characteristics of the developed sensors with other reported gadolinium sensors

Sens. No	Working conc. range (M)	pH	Response time(s)	Slope (mV/decade)	Reference
1	1×10^{-5}- 1×10^{-1}	4.0 – 8.0	<10	19.8 ± 0.3	[104]
2	1×10^{-5} to 1×10^{-1}	3.0 -7.0	15	30	[108]
3	1×10^{-6} - 1×10^{-1}	3.5 – 8.0	<15	19.4	[105]
4	1×10^{-5} - 1×10^{-1}	4.0 -10.0	10	19.3	[103]
5	1×10^{-8} -1×10^{-3}	4.0 -9.0	15	17.4	[107]
6	**1.0×10^{-6} – 1.0×10^{-2}**	**3.0 - 8.5**	**10**	**19.9**	**[MP_7]**
7	**1.0×10^{-6} – 1.0×10^{-2}**	**3.5 - 8.5**	**5**	**19.4**	**[PM_6]**

* * *

Chapter 8

CONCLUSIONS

This chapter presents a brief summary of the important findings and results of the work. The main objective of the present work is also included in this chapter.

The main objectives of the present work include the following

- Synthesis of the ionophores
- Characterization of the synthesized ionophores by elemental analysis, infrared, and NMR spectroscopic methods
- Fabrication of different types of sensors
- Investigation of the response of the developed sensor to different cations
- Optimization of the membrane composition

- Study of the response characteristics of the developed sensor
- Analytical applications
- Comparison with other reported sensors

As part of the present investigations, a total of 10 sensors have been fabricated for lanthanide ions such as lanthanum, neodymium, praseodymium, samarium and gadolinium. These 10 sensors include PVC membrane and chemically modified carbon paste type sensors incorporating Schiff's base as electro active component. Systematic application studies have been carried out for all the developed sensors and the results revealed that the presently developed sensors are far superior than most of the sensor reported. The ten potentiometric sensors developed for the respective metal ions are

Lanthanum (III)	PVC membrane and CMCPE type sensors based on N^1,N^2-bis(naphthalene-1-yl)methylene(hexa-1, 6-diamine) (NAH)
Samarium (III)	PVC membrane and CMCPE type sensors based on N^1, N^3-bis(3- nitrobenzylidene)propane-1,3-diamine (MBP)
Praseodymium (III)	PVC membrane sensor based on 1,4 Bis (4-hydroxy-3-ethoxybezylidene)thiosemicarbazide (HBTS) and and CMCPE type sensors based on N^1,N^2-bis(4-hydroxy-3-ethoxybezylidene)butane-1,4-diamine (HMB)

Neodymium (III)	PVC membrane and CMCPE type sensors based onN^1,N^2-bis(salicylidine)butane-1,4-diamine (SAB)
Gadolinium (III)	PVC membrane and CMCPE type sensors based On 2-[(2-mercaptophenylimine)methyl]phenol (MPM)

The field of sensors is rapidly developing and efforts are being made to design sensors, which are cost effective, simple in operation, reliable, small instrumental arrangement and portable. Attempts are being made for the fabrication of sensors with disposable characteristics as it avoids electrode poisoning from repeated usage of the same sensor surface for successive analyses. The presently developed sensors will no doubt, form a basis for such development. It is hoped that the developed potentiometric sensors can find wide applications in the future analytical chemistry.

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REFERENCES

1. R. Kellner, J. M. Mermet, M. Otto, M. Vallarcel and H. M. Widmer, *Analytical Chemistry*, 2nd Edn, Wiley-VCH Verlay GmbH & Co. KGaA (2004).

2. R. W. Cattrall, *Chemical Sensors*, Oxford Chemistry Primers, New York (1997).

3. D. A. Skoog, D. M. West and F. J. Holler, *Fundamentals of Analytical Chemistry*, Saunders College Publishing, USA (1996).

4. J. Mendham, R. C. Denney, J. D. Barnes and M. Thomas, *Vogel's Textbook of Quantitative Chemical Analysis*, 6th Edn, Pearson Education Ltd, Singapore (2002).

5. D. Malinin and J. H. Yoe, *J. Chem. Edu.*, **38**, 129 (1961).

6. C. M. A. Brett and A. M. Oliveira Brett, *Electroanalysis*, Oxford University Press, Oxford (1998).

7. A. J. Bard and L. R. Faulkner, *Electrochemical Methods, Fundamentals and Applications*, Wiley, New York (1980).

8. C. M. A. Brett, *Pure Appl. Chem.*, **73**, 1969 (2001).

9. http//www. wikipedia.com

10. J. Wang, *Electrochemical Sensors for Environmental Monitoring: A Review of Recent Technology,* National Exposure Research Laboratory Office of Research and Development, U.S. Environmental Protection Agency.

11. N. R. Stradiotto, H. Yamanaka and M.V. B. Zanoni, *J. Braz. Chem. Soc.*, **14**, 159 (2003).

12. A. Hulanicki, S. Geab and F. Ingman, *Pure Appl. Chem.*, **63**, 1247 (1991).

13. W. Wroblewski, *Chemical Sensors Research Group*, Warsaw University of Technology, Poland (2005).

14. T. Kubata, S. Matsitani, M. Shiro and H. Koyama, *Chem. Commun.*, 1541 (1968).

15. J. V. Leyendekkers, *Anal. Chem.*, **43**, 1835 (1971).

16. G. Eisenman, *Glass Electrodes for Hydrogen and other Cations Principles and Practice*, Marcel Dekker, New York (1967).

17. G. Eisenman and C. W. Reilley, *Advances in Analytical Chemistry and Instrumentation,* Wiley, New York (1965).

18. M. Dole, *The Glass Electrode*, New York (1941).

19. R. Buck and E. Lindner, *Anal. Chem.*, **73**, 88A (2001).

20. D. Ammann, W. E. Morf, P. Anker, P. C. Meier, E. Pretsch and W. Simon, *Ion-Sel. Electrode Rev.*, **5**, 92 (1983).

21. M. S. Frant and J. W. Ross, *Science*, **154**, 1553 (1966).

22. J. Ross, *Science*, **156**, 1378 (1967).

23. G. J. Moody, R. B. Oke and J. D. R. Thomas, *Analyst*, **95**, 910 (1970).

24. J. Ruzicka and J. C. Tjell, *Anal. Chim. Acta*, **49**, 349 (1970).

25. H. Freiser, *Ion Selective Electrodes in Analytical Chemistry*, Plenum Press, New York (1980).

26. J. Havas and E. Pungor, *Proc. IMEKO Symposium on Electrochemical Sensors*, Veszprem, 79 (1968).

27. E. Pungor and T. Toth, *Analyst*, **95**, 625 (1970).

28. G. A. Rechnitz and R. A. Llenado, *Anal. Chem.*, **40**, 1779 (1970).

29. S. Mesaric and E. A. M. F. Dahmen, *Anal. Chim. Acta*, **64**, 431 (1973).

30. W. R. Heineman, H. J. Wieck and A. M. Yacynych, *Anal. Chem.*, **52**, 345 (1980).

31. T. E. Edmonds, *Chemical Sensors*, Chapman and Hall, New York (1988).

32. J. Wang, *Analytical Electrochemistry*, VCH, New York (1994).

33. K.Toth, E. Lindner, Z. Feher and E. Pungor, *Anal. Chim. Acta*, **179**, 359 (1986).

34. M. Trojanowich and W. Matuszewski, *Anal. Chim. Acta,* **138**, 71 (1982).

35. I. Isidak and A. Covington, *Electroanalysis*, **5**, 815 (1993).

36. A. Nann, I. Silvestri and W. Simon, *Anal. Chem.*, **65**, 1662 (1993).

37. J. J. R. Rohwedder, C. Pasquini, I. M. Raimundo, M. Conceição, B. S. M. Montenegro, A. N. Araujo and C. M. C. M. Couto, *J. Autom. Meth. Managem. Chem.*, **24**, 105 (2002).

62. R. G. Kelly and A. E. Owen, *J. Chem. Soc. Faraday Trans.*, **1**, 1195 (1986).

63. T. Gennett and W. C. Purdy, *Am. Lab.*, ***23***, 60 (1991).

64. F. Faridbod, M. R. Ganjali, R. Dinarvand and P. Norouzi, *Afr. J. Biotechnol.*, **6**, 2960 (2007).

65. R. I. Stefan and H. Y. Aboul Enein, *Electrochemical Sensors in Bioanalysis*, Marcel Dekker, New York (2001).

66. S. Matysik, F. M. Matysik, J. Mattusch and W. D. Einicke, *Electroanalysis*, **10**, 98 (1998).

67. G. G. Guilbault, R. A. Durst, M. S. Frant, H. Freiser, E. H. Hansen, T. S. Light, E. Pungor, G. Rechnitz, N. M. Rice, T. J. Rohm, W. Simon and J. D. R. Thomas, *Pure Appl. Chem.*, **48**, 127 (1976).

68. C. Macca, *Anal. Chim. Acta*, **512**, 183 (2004).

69. T. Ito and C. Goto, *J. Trace. Microprobe Tech.*, **19**, 601 (2001).

70. M. Shamsipur, M. Yousefi, M. Hosseini and M. R. Ganjali, *Anal. Chem.*, **74**, 5538 (2002).

71. S. Khalil, *Anal. Lett.*, **36**, 1335 (2003).

72. V. K. Gupta, S. Jain and S. Chandra, *Anal. Chim. Acta*, **486**, 199 (2003).

73. S. K. Mittal, S. K. A. Kumar and H. K. Sharma, *Talanta*, **62**, 801 (2004).

74. M. R. Ganjali, R. Kiani-Anbouhi, M. Shamsipur, T. Poursaberi, M. Salavati-Niasari, Z. Talebpour and M. Emami, *Electroanalysis*, **16**, 1002 (2004).

75. M. Akhond, M. B. Najafi and J. Tashkhourian, *Anal. Chim. Acta*, **531**, 179 (2005).

76. A. K. Singh, P. Saxena, S. Mehtab and B. Gupta, *Anal. Sci.*, **22**, 1339 (2006).

77. S. Suyanta, S. I. Rahayu, Buchari and I. Noviandri, *Jurnal Matemtika Dan Sains*, **11**, 32 (2006).

78. M. R. Ganjali, A. Daftari, M. Rezapour, T. Puorsaberi and S. Hahgoo, *Talanta*, **59**, 613 (2003).

79. M. R. Ganjali, M. Qomi, A. Daftari, P. Norouzi, M. Salavati-Nissari and M. Rabbani, *Sen. Actuators B*, **98**, 92 (2004).

80. M. R. Ganjali, P. Matloobi, M. Ghorbani, P. Norouzi and M. Salavati-Niasari, *Bull. Korean Chem. Soc.*, **26**, 38 (2005).

81. M. R. Ganjali, P. Norouzi, L. Shamsolahrari and A. Ahmadi, *Sens. Actuators B*, **114**, 713 (2006).

82. M. R. Ganjali, P. Norouzi, N. Nasrin Yousefian, F. Faridbod and M. Adib, *Bull. Korean Chem. Soc.*, 27, 1581 (2006).

83. M. R. Ganjali, P. Norouzi, T. Alizadeh, A. Tadjarodi and Y. Hanifehpour, *Electroanalysis*, **18**, 1091 (2006).

84. M. R. Ganjali, M. B. Gholivand, M. Rahimi-Nasrabadi, B. Maddah, M. Salavati-Niasari and F. Ahmadi, *Sens. Lett.*, **4**, 356 (2006).

85. M. R. Ganjali, H. Ganjali, B. Larijani and P. Norouzi, *Int. J. Electrochem. Sci.*, **4**, 914 (2009).

86. D. A. Chowdhury, T. Ogata, S. Kamata and K. Ohashi, *Anal. Chem.*, **68**, 366 (1996).

87. M. R. Ganjali, M. R. Pourjavid, M. Rezapour and S. Haghgoo, *Sens. Actuators B*, **89**, 21 (2003).

88. M. Shamsipur, M. Hosseini, K. Alizadeh, Z. Talebpour, M. F. Mousavi, M. R. Ganjali, M. Arca and V. Lippolis, *Anal. Chem.*, **75**, 5680 (2003).

89. S. K. Mittal, H. K. Sharma and A. S. K. Kumar, *Sensors*, **4**, 125 (2004).

90. S. K. Mittal and H. K. Sharma, *J. Anal. Chem.*, **60**, 1069 (2005).

91. M. B. Saleh, A. A. Abdel Gaber, M. M. R. Khalaf and A. M. Tawfeck, *Anal. Lett.*, **39**, 17 (2006).

92. H. A. Zamani, M. R. Ganjali and M. Adib, *J. Braz. Chem. Soc.*, **18**, 215 (2007).

93. M. R. Ganjali, Z. Memari, F. Faridbod and P. Norouzi, *Int. J. Electrochem. Sci.*, **3**, 1169 (2008).

94. M. Shamsipur, M. Hosseini, K. Alizadeh, M. F. Mousavi, A. Garau, V. Lippolis and A. Yari, *Anal. Chem.*, **77**, 276 (2005).

95. P. Norouzi, M. R. Ganjali, A. Ahmadalinezhad and M. Adib, *J. Braz. Chem. Soc.*, **17**, 1309 (2006).

96. M. R. Ganjali, A. Ahmadalinezhad, P. Norouzi and M. Adib, *J. Appl. Electrochem.*, **36**, 931 (2006).

97. H. Behmad, H. A. Zamani, M. R. Ganjali and P. Norouzi, *Electrochim. Acta*, **53**, 1870 (2007).

98. V. K. Gupta, R. N. Goyal and R. A. Sharma, *Anal. Chim. Acta*, **647**, 66 (2009).

99. M. R. Ganjali, F.S. Mirnaghi, P. Norouzi and M. Adib, *Sens. Actuators B*, **115**, 374 (2006).

100. H. A. Zamani, M. R. Ganjali, P. Norouzi and S. Meghdadi, *Anal. Lett.*, **41**, 902 (2008).

101. H. A. Zamani, M. Masrournia, S. Sahebnasagh and M. R. Ganjali, *Anal. Lett.*, **42**, 555 (2009).

102. V. K. Gupta, R. N. Goyal, M. K. Pal and R. A. Sharma, *Anal. Chim. Acta*, **653**, 161 (2009).

103. M. R. Ganjali, M. Tahami, M. Shamsipur, T. Poursaberi, S. Haghgoo and M. Hosseini, *Electroanalysis*, **15**, 1038 (2003).

104. M. R. Ganjali, M. Emami, M. Rezapour, M. Shamsipur, B. Maddah, M. Salavati-Niasari, M. Hosseini and Z. Talebpoui, *Anal. Chim. Acta*, **495**, 51 (2003).

105. M. R. Ganjali, M. Rezapour, P. Norouzi and M. Salavati-Niasari, *Electroanalysis*, **17**, 2032 (2005).

106. H. A. Zamani, G. Rajabzadeh, M. R. Ganjali and P. Norouzi, *Anal. Chim. Acta*, **598,** 51 (2007).

107. F. Faridbod, M. R. Ganjali, S. Labbafi and P. Norouzi, *Anal. Lett.*, **41**, 2972 (2008).

108. H. Sharma and N. Sharma, *E-J. Chem.*, **6,** 1139 (2009).

109. H. Haraguchi, *Bull. Chem. Soc. Jpn.*, **72**, 1163 (1999).

110. K. Girish Kumar and R. Muthuselvi, *Asian J. Chem.*, **131**, 337 (2001).

111. K. Girish Kumar and R. Muthuselvi, *Microchim. Acta*, **137**, 25 (2001).

112. K. Girish Kumar and R. Muthuselvi, *J. Anal. Chem.*, **61**, 28 (2006).

113. K. Girish Kumar, Remalakshmy Poduval, Pearl Augustine, Sareena John and Beena S, *Anal. Sci.*, **22**, 1333 (2006).

114. R. A. Robinson and R. H. Stokes, *Electrolyte solutions, the measurement and interpretation of conductance, chemical potential, and diffusion in solutions of simple electrolytes*, 2nd Edn, Butterworths, London (1968).

115. K. M. Tawarah and S. A. Mizyed, *J. Solution Chem.*, **18**, 387 (1989).

116. V. A. Nicely and J. I. Dye, *J. Chem. Edu.*, **48**, 443 (1971).

117. P. Debye and H. Huckle, *Phys. Z.*, **24**, 305 (1923).

118. Y. Takada, *Bull. Chem. Soc. Jpn.*, **56**, 3600 (1983).

119. M. R. Ganjali, P. Norouzi, A. Daftari, F. Faridbod and M. Salavati-Niasari, *Sens. Actuators B*, **120**, 673 (2007).

120. M. R. Ganjali, M. H. Zargazi and A. Mohajeri, *Pol. J. Chem.*, **75**,743 (2001).

121. R. E. Kirk and D. F. Othmer, *Encyclopedia of Chemical Technology*, Wiley, New York, **19**, 851 (1982).

122. W. Yongxing, W. Xiaorong and H. Zichum, *Bull. Enviorn. Contamin. Toxicol.*, **64**, 611 (2000).

123. A. Hrdlicka, J. Havei, C. Moreno and M. Valiente, *Anal. Sci.*, 7, 925 (1991).

124. A. Mazzucotelli, F. Depaz, E. Magi and B. Frache, *Anal.Sci.*, **8**, 189 (1992).

125. A. Masuda, N. Nakamura and T. Tanaka, *Geochim. Cosmochim. Acta*, **37**, 239 (1973).

126. W. B. Hess and H. P. Holcomb, *Anal. Chem.*, 37, 169 (1965).

127. S. F. Marsh, *Anal. Chem.*, **39**, 641 (1967).

128. A. R. Fakhari, M. R. Ganjali and M. Shamsipur, *Anal. Chem.*, **69**, 3693 (1997).

129. S. Amemiya, P. Buhlmann, Y. Umezawa, R. C. Jagessar and D. H. Burns, *Anal. Chem.*, **71**, 1049 (1999).

130. E. Ammann, P. Pretsch, W. Simon, E. Lindner, A. Bezegh and E. Pungor, *Anal. Chim. Acta*, **171**, 119 (1985).

131. R. Eugster, P. M. Gehrig, W. E. Morf, U. Spichiger and W. Simon, *Anal. Chem.*, **63**, 2285 (1991).

132. A. K. Jain, V. K. Gupta and J. R. Raisoni, *Sensors*, **4**, 115 (2004).

133. E. Bakker, P. Buhlmann, and E. Pretsch, *Electroanalysis*, **11**, 915 (1999).

134. Y. Tani and Y. Umezawa, *Sens. Lett.*, **3**, 99 (2005).

135. M. F. S. Teixeira, O. Fatibello-Filho and L. A. Ramos, *Quim. Nova*, **28**, 817 (2005).

136. A. K. Singh, R. Singh and P. Saxena, *Sensors*, 4, 187 (2004).

137. T. Rosatzin, E. Bakker, Y. Suzuki and W. Simon, *Anal. Chem. Acta*, **280**, 197 (1993).

138. E. Bakker, P. Bulhlmann and E. Pretsch, *Chem. Rev.*, **97**, 3083 (1997).

139. X. Yang, N. Kumar, H. Chi, D. D. Hibbert and P. N. W. Alexander, *Electroanalysis*, **9**, 549 (1997).

140. W. E. Morf, *The Principles of Ion-Selective Electrodes and Membrane Transport*; Elsevier, New York (1981).

141. Y. Masoda, Y. Zhang, C. Yan and B. Li, *Talanta*, ***46***, 203 (1998).

142. R. Eugster, T. Rrosazin, B. Rusterholz, B. Aebersold, U. Pedrazza, D. Ruegg, A. Schmid, U. F. Spichiger and W. Simon, *Anal. Chim. Acta*, **289**, 1 (1994).

143. M. R. Ganjali, P. Norouzi, F. Faridbod, A. Sepehrifard, M. Ghandi, and A. Moghimi, *Canadian J. Anal. Sci. Spec.*, **52**, 46 (2007).

144. M. Huster, P. M. Gehrig, W. E. Morf, and W. Simon, *Anal. Chem.*, **63**, 133 (1990).

145. S. Ameniya, P. Bühlmann, E. Pretsch, B. Rusterholz and Y. Umezawa, *Anal. Chem.*, **72**, 1618 (2000).

146. H. A. Zamani, M. R. Ganjali and M. J. Pooyamanesh, *J. Braz. Chem. Soc.*, **17**, 149 (2006).

147. O. Lindner, E. Graf, Z. Niegriesz, K. Toth, E. Purgor and R. P. Buck, *Anal. Chem.*, **60**, 295 (1988).

148. P. M. Gehrig, W. E. Morf, M. Welti, E. Pretsch and W. Simon, *Helv. Chim. Acta*, **73**, 203 (1990).

149. M. Shamsipur, M. Javanbakht, M. R. Ganjali, M. F. Mousavi, V. Lippolis and A. Garau, *Electroanalysis*, **14**, 1691 (2002).

150. D. Ammann, *Ion-selective microelectrodes: Principles, design and application*, Springer-Verlag, Berlin (1986).

151. E. Malinowska, *Analyst*, **115**, 1085 (1990).

152. Koryta, J. *Anal. Chim. Acta*, **233**, 1 (1990).

153. W. E. Morf, D. Ammann and W. Simon, *Chimia*, **28**, 65 (1974).

154. P. Buhlmann, S. Yajima, K. Tohda and Y. Umezawa, *Electrochim. Acta*, **40**, 3021 (1995).

155. P. Buhlmann, S. Yajima, K. Tohda, K. Umezawa, S. Nishizawa and Y. Umezawa, *Electroanalysis*, **7**, 811 (1995).

156. W. E. Morf, G. Kahr and W. Simon, *Anal. Lett.*, **7**, 9 (1974).

157. R. P. Buck and E. Lindner, *Pure. Appl. Chem.*, **66**, 2527 (1994).

158. Y. Umezawa, K. Umezawa and H. Sato, *Pure. Appl. Chem.*, **67**, 507 (1995).

159. E. Bakker, E. Pretsch and P. Buhlmann, *Anal. Chem.*, **72**, 1127 (2000).

160. http://www.webelements.com

161. http://www.en.wikipedia.org

162. M. Soylak and O. Turko lu, *Talanta*, **53**, 125 (2000).

163. S. S. Biswas. R. Kaimal, A. Sethumadhavan and P. S. Murty, *Anal. Lett.*, **24**, 1885 (1991).

164. L. C. Chandola, I. J. Machado and A. N. Mohile, *Michrochim. Acta*, **66**, 399 (1976).

165. Bing Li, Yali Sun and Ming Yin, *J. Anal. At. Spectrom.*, **14**, 1843 (1999).

166. T. Kawashima, M. Osawa, Y. Mochizuki and H. Hamaguchi, *Bull. Chem. Soc. Jpn.*, **34**, 705 (1961).

167. V. Cercasov and R. Heller, *J. Radioanal. Nucl. Chem.*, **60**, 453 (1980).

168. M. Shamsipur, M. Yousefi and M. R. Ganjali, *Anal. Chem.*, **72**, 239 (2000).

169. U. Schaller, E. Bakker, U. E. Spichiger and E. Pretsch, *Anal. Chem.*, **66**, 391 (1994).

170. http://www. lenntech.com

171. J. Wei, W. Naixing, Si Zhikun, L. Fuxiang, Wu Bo, M. Quanjie and Xu Xiuqin, *Analyst*, **126**, 1440 (2001).

172. G. Küppers and G. Erdtmann, *Fresenius' J. Anal. Chem.*, **307**, 369 (1981).

173. R. M. Dixit and S. S. Deshpande, *Fresenius' J. Anal. Chem.*, **292**, 375 (1978).

174. G. S. S. Rao, V. K. Upadhyay and R. C. Jain, *J. Appl. Polym. Sci.*, **71**, 595 (1999).

175. V. S. Bodrova, E. P. Piskareva, L. F. Shelokhneva and I. A. Poletaeva, *Polym. Sci. Ser. A*, **40**, 1741 (1998).

176. W. Chen, Y. Gu and G. Zhao, *Chim. Rare Earths*, **20**, 58 (1999).

177. I. M. Krasil'nikov, I. D. Skorova, .V. Sholomov, A. Konstantinov and A. P. Matyushin, *At. Energ.*, **48**, 146 (1980).

178. J. J. Labrecque, J. M. Beusen and R. E. V. Grieken, *X-Ray Spectrom.*, **15**, 13 (2005).

179. I. Roelandts, *Anal. Chem.*, **53**, 676 (1981).

180. E. S. Beary and P. J. Paulsen, *Anal. Chem.*, **66**, 431 (1994).

181. G. I. Ramendik, E. V. Fatyushina and A. I. Stepanov, *J. Anal. Chem.*, **58**, 152 (2003).

182. L. Lepine, R. Gilbert and G. Belanger, *Anal. Chem.*, **58**, 1152 (1986).

183. E. M. Frame and E. E. Uzgiris, *Analyst*, **123**, 675 (1998).

184. S. A. Chitambar and C. K. Mathews, *Fresenius' J. Anal. Chem.*, **274**, 9 (1975).

185. V. S. Rudenko and A. B. Medvedev, *At. Energ.*, **61**, 942 (1986).

186. R. Boniforti and R. Riccardi, *X-Ray Spectrom.*, **4**, 159 (2006).

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LIST OF PUBLICATIONS AND PRESENTATIONS

PUBLICATIONS

1. PVC Supported Liquid Membrane and Carbon Paste Potentiometric Sensors Incorporating a Mn(III)-Porphyrin for the Direct Determination of Undissociated Paracetamol, *Electroanalysis* **20**, 2009 (2008).
2. Electroactive Dipyrromethene - Cu(II) Monolayers Deposited onto Gold Electrodes for Voltammetric Determination of Paracetamol, *Electroanalysis,20,* 2317, (2008).
3. K. Girish Kumar, Sareena John, Pearl Augustine, Remalakshmy Poduval and Beena S., A novel mebendazole selective membrane sensor and its application to pharmaceutical analysis, Anal. Sci., **23**, 291(2007).
4. K. Girish Kumar, Remalakshmy Poduval, Pearl Augustine, Sareena John and Beena S., A PVC plasticized sensor for Ni (II) ion based on a simple ethylenediammine derivative, *Anal. Sci.*, 22, 1333 (2006).

PRESENTATIONS

1. **"Fabrication of Lanthanum sensor for water analysis"** Presented in an international conference on "The Challenges and Strategies for the sustainability of safe drinking water" (2006) held at Gandhigram Rural Institute, Tamil Nadu.
2. **"Fabrication of Highly Selective PVC membrane sensor for Praseodymium"** Presented in an international conference on

"Materials for the New the Millennium" (2007) held at Cochin university of Science and Technology, India.

3. "**A Novel Schiff base Modified Carbon Paste Sensor for Samarium**" Presented in a National conference on "Current Trends in Chemistry" (2008) held at Cochin university of Science and Technology, India.
4. **"A New PVC Membrane Sensor For Samarium"** Presented in an international conference on "Materials for the new millennium (2010) held at Cochin university of Science and Technology, India.
5. "**A new PVC membrane sensor for Neodymium (III) based on N^1, N^2-bis(salicylidine)butane-1,4-diamine**" Presented in a National conference on "Fifteenth National Convention of Electrochemists" held at VIT , Vellore, India.