ELECTROANALYTICAL STUDIES ON SOME ION SELECTIVE MEMBRANES ELECTRODES

Ph.D. THESIS

by

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A THESIS

Submitted in partial fulfilment of the
requirements for the award of the degree
of
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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled, **"ELECTROANALYTICAL STUDIES ON SOME ION SELECTIVE MEMBRANES ELECTRODES"** in partial fulfilment of the requirements for the award of the Degree of Doctor of Philosophy and submitted in the Department of Chemistry of the Indian Institute of Technology Roorkee, Roorkee is an authentic record of my own work carried out during a period from July, 2010 to February, 2014 under the supervision of **Dr. V. K. Gupta**, Professor and **Dr. A. K. Jain**, Emeritus Professors, Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other Institute.

(ARVIND KUMAR BHARTI)

This is to certify that the above statement made by the candidate is correct to the best of our knowledge.

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Supervisor

(V. K. Gupta)
Supervisor

Date:

The Ph.D. Viva-Voce Examination of **Mr. Arvind Kumar Bharti**, Research Scholar, has been held on ………..................

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ABSTRACT

Detection of environmental pollutants both organic and inorganic has been a major challenge to analytical chemists. In recent years many instrumental techniques *viz.*, Electro-thermal atomization-Atomic absorption spectroscopy (ETA-AAS), Inductively coupled plasma-Atomic emission spectrometry (ICP-AES), Neutron activation analysis, Ion chromatography, High performance liquid chromatography [HPLC], Flame photometry and Cyclic voltametry have been used for the quantitative analysis of pollutants. All these listed techniques are sophisticated, time consuming and costly and require huge infrastructure and expert handling. On the other hand Ion-selective electrodes (ISEs) provide an analytical procedure that is simple, convinces and fast. Analysis by Ion-selective electrode can be carried out in field and is also adaptable to online monitoring another major advantage of analysis by ISEs i.e. requires minimum chemical manipulation of sample and is applicable to turbid as well coloured solution.

Ion-selective electrodes are extensively used for determining concentration of various ions in bloods, biological fluids, eatables, drugs etc. One of the important applications of ion-selective electrodes is the monitoring of toxic metals in effluents and natural waters. Some of the established applications of ISEs are determination of F^- in drinking water, Ca^{2+} in dairy products, determination of promethium in spiked water sample and K^+ in fruit juices etc. They are also used to determine clinically important ions *viz.*, Na^+, K^+, Li^+ and Ca^{2+} in body fluids. They have also been used to determine metals in soils, fertilizers and plant products.

A survey of literature reveals that a number of Ion-selective electrodes have been developed for various metals and anions. However the availability of Ion-selective electrode for metal such as molybdenum, promethium, fluoride and mercury is rather limited. These are some reported electrode for these metals but they exhibits certain limitation such as short

working range, poor selectivity and higher response times. Thus improved Ion-selective electrode for these metals are requested attempts in this direction we initiated by us. To develop good ion-selective electrodes ionophores having high affinity for a particular ionic species is required. Different types of material such as solid electrolytes in other multivalent metals, ion exchange, macrocyclic, calixarene and Schiff base have been used for this purpose. We have used some Schiff base, calixarene and macrocycle to develop ion-selective membrane electrodes for molybdenum, promethium, fluoride and mercury. The result of this investigation is incorporated in the present thesis divided into six chapters which are discussed briefly here.

First chapter presents a **"***General Introduction***"** which describes the background of the research work, the problem statement and objectives of the present study. The chapter also summarized a review of good ion-selective electrodes for alkali metal ion, alkaline earth metal ion, rare earth metal ion, transition metal and anions.

Second Chapter presents; **"***Theory and Methodology of Ion Selective Membranes Electrodes*" This chapter describes the classification of ion-selective electrodes, theory of membrane potentials and parameters of ion-selective electrodes, the terms selectivity used in the study of ion selective electrode. The selectivity of an ion selective membrane is a measure of the selectivity of an electrode for the primary ion in the presence of interfering species. The degree of selectivity of the electrode is given by Eisenman-Nicolsky equation

$$E = E^0 \pm \frac{2.303RT}{z_A F}\log\left[a_A + \sum_{B \neq A}^{B} K_{A,B}^{Pot}(a_B)^{z_A/z_B} \right]$$

For determination of Selectivity coefficient three methods are used.

1. Separate Solution method
2. Mixed solution method

3. Fixed Interference Method

Third Chapter; this chapter reveal a *"Promethium ion-selective sensor based on the comparative study of two Schiff base ligands as neutral ionophores"* have been developed and effect of various plasticizers have been studied**.** Two Schiff base ligands (3,5:12.14:21,23-tribenzo-8,9:17,18:26,27-tricyclohexyl-1,6,10,15,19,24-hexaazo-[27]-1,6,10,15,19,24-triene (X_1) and 15,17,32,34-tetramethyl-3,29-dioxa-11,12,16,20,21,35-hexaazapentacyclo[29.3.1. 114,18.04,9.023,28]hexatriaconta 1(35),4,6,8,10,14(36),15,17,21,23,25,27,31,33-tetradecaene-13,19-dione (X_2)) as neutral ionophores and effect of various plasticizers: 2-nitrophenyl-octylether (*o*-NPOE), dibutyl phosphonate (DBP), dioctylphthalate (DOP), tri-(2-ethylhexyl) phosphate (TEHP), dibutyl butylphosphonate (DBBP), 1-chloronaphthalene (1-CN) and anion excluders: potassium tetrakis(p-chloropheny1) borate (KTpClPB), sodium tetraphenylborate (NaTPB) and oleic acid (OA) have been studied. The membrane with a composition of ionophore (X_1/X_2):KTpClPB:PVC:*o*-NPOE (w/w, %) in the ratio of 5:5:30:60 exhibited best performance. The best responsive membrane sensors (8 and 21) exhibited working concentration range of $4.5 \times 10^{-7} - 1.0 \times 10^{-2}$ mol L^{-1} and $3.5 \times 10^{-6} - 1.0 \times 10^{-2}$ mol L^{-1} with a detection limits of 3.2×10^{-7} mol L^{-1} and 2.3×10^{-6} mol L^{-1} and Nernstian slopes of 20.0 ± 0.5, 19.5 ± 0.5mV decade^{-1} of activity, respectively. The sensor no. 8 works satisfactorily in partially non-aqueous media up to 10% (v/v) content of methanol, ethanol and acetonitrile. Analytical application of the proposed sensor has been demonstrated in determination of promethium(III) ions in spiked water samples and the electrode could be used successful in water sample.

The **fourth Chapter**; *"A comparative study on PVC based sensors in determination of the Molybdenum***"**, deals with Ion-selective electrode based on macrocyclic for selective determination of molybdenum. Three macrocyclic 4,8-diaza-3,3,10,10-tetramethyl-1,2-

dithiacyclodecane(S_1), 5,8-diaza-3,3,10,10-tetramethyl-1,2-dithiacyclodecane-*N,N*”-diacetic acid (S_2) and *N,N”*-bis(2,2-dimethyl-2-mercaptoethyl)ethylenediamine-*N,N*-diacetic acid (S_3) when prepared and preliminary studies shows that macrocyclic neutral ionophores shows high affinity of molybdenum. These three membranes are used to develope molybdenum selective membrane electrode. A number of membrane prepared of three macrocyclic separately, number of PVC base three membrane prepared and investigated, the result have shown the sensor using as three ionophore perform best. The performance of electrodes adding the different plasticizer, It was found that ortho nitro phenyl octylether (*o*-NPOE) is the best plasticizer and potassium tetrakis(p-chlorophenyl) borate (KTpClPB) best cationic additives. The membrane having composition (w/w, mg%); 5.0(S):30.0(PVC):5.0 (KTpClPB):60.0(*o*-NPOE), performed best in respect of different performance characteristic. It exhibits a wide working concentration range $2.3 \times 10^{-7} – 1.0 \times 10^{-2}$ mol L^{-1} with a detection limit of 1.2×10^{-7} mol L^{-1} and slope of 11.2 decades^{-1} of activity. The sensor was found to be sufficient effective for the Molybdenum and it can be used to determine the concentration in different sample. The electrodes have a shelf life time of 2-5 months and dynamic response time of 11s.

The **fifth chapter**; *“A comparative study of fluoride selective PVC based electrochemical sensors”*: this chapter reports PVC based membrane electrodes based on four ionophore M_1–M_4 (Ionophore $\mathbf{M_1}$, meso-octamethylcalix[4]pyrrole. Ionophores $\mathbf{M_2}$, [7H,23H-34,39-etheno-6,43;24,30 dimethenotribenzo [o,v,g] [1,4,7,11,34] trioxadiazacyclo heptatriacontine-7,23-dione,8,9,10,11,13,14,16,17,19,20,21,22,31,32,33,40,41,42-octadeca hydro-44,45,46,47-tetrahydroxy-32,41-bis(methylene). Ionophore $\mathbf{M_3}$, is 7H,23H-34,39-etheno-6,43;24,30-dimethenotribenzo[o,v,g] [1,4,7,11,34] trioxadiazacycloheptatriacontine-7,23-boropyrene,8,9,10,11,13,14,16,17,19,20,21,22,31,32,33,40,41,42-octadecahydro- 44, 45, 46,47-tetrahydroxy-32,41-bis(methylene) and ionophore $\mathbf{M_4}$; dinitrophenyl functionalized tris-

(amide)) which have been synthesized and characterized by IR, ^1H NMR, spectroscopic investigations indicate good affinity of these ligands for fluoride anion. Different polyvinyl chloride (PVC) based membranes of ligands have been synthesized using different cationic excluders; CTAB, TDMAC, HTAB, ToMACI and plasticizers; DBBP, DBP, *o*-NPOE, CN, DOP, TEHB and investigated as F^- -selective sensors. The best performance is observed by the sensor with a membrane of composition (%, w/w) M_1:PVC:*o*-NPOE:CTAB 3.5:30.0:63.0:3.5. The sensor generates linear potential response over a wide working concentration range of 2.5×10^{-7} to 1.0×10^{-2} mol L^{-1} with Nernstian slope (59.8 mV $decade^{-1}$ of activity) over a pH range of 2.5–6.5 with a fast response time of ∼11 s. It shows good selectivity for fluoride anion (F^-) in preference to many anions. The sensor exhibits a shelf life of two and half months and could be successfully used for the comparative determination of fluoride contents in various samples. The proposed method is faster, cheaper and more accurate in comparison to already used methods.

The final and **Sixth chapter** “*Mercury selective potentiometric sensor based on low rim functionalized thiacalix[4]-arene as a cationic receptor*”: this is the last chapter it report the result of potentiometric sensor of mercury prepared by calixarene. PVC membrane of these calixarene where prepared and studied as a mercury selective electrodes. It was found that this membrane shows potential responses to mercury, the effect of plasticizer and performances of membrane electrodes also studies. This describes a novel potentiometric mercury(II) sensor based on the use of cation receptor 5,11,17,23-tetra-tert-butyl-25,27-dihydroxy-26,28-bis(O-methylglycylcarbonylmethoxy)thiacalix[4]-arene in poly(vinyl chlorid -e) (PVC) matrix for detection of Hg^{2+} has been developed. The sensor exhibits best performance with a membrane composition of PVC:*o*-NPOE:Ionophore:NaTPB of 60:120:5:10 (%, w/w). The sensor selectively used for determination of mercury ions is in the

concentration range $5.0 \times 10^{-8} - 1.0 \times 10^{-2}$ mol L^{-1} with a lower detection range of the order 1.0×10^{-8} mol L^{-1} and a Nernstian compliance of (29.5) within pH range 6.0 to 7.5 and fast response time of 10 s. it can also be worked satisfactory. Selectivity coefficient of the electrode shows the high affinity to Hg^{+2} over a number of metal ions. Influence of the membrane composition and possible interference of other ions have also been investigated on the response properties of the sensor, fast and stable response, good reproducibility and long-term stability of the sensor are demonstrated. It has been observed that the developed sensor satisfactorily works in partially non-aqueous media up to 10% (v/v) content of methanol and acetonitrile and could be used for a period of 2.5 months. Selectivity coefficients determined with fixed interference method (FIM) and match potential method (MPM) indicate high selectivity towards mercury(II) ions. The proposed electrode shows fairly good discrimination of mercury from other cations. The developed mercury ion-selective electrode can be successfully employed as an indicator electrode in potentiometric titration with EDTA.

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With profound gratitude, love and devotion, I dedicate this Ph.D. Thesis to my parent and Mama-Mami Ji.

Place: Roorkee

Dated: (ARVIND KUMAR BHARTI)

LIST OF PUBLICATIONS

1. Gupta, Vinod K., Jain, Rajeev, Hamdan, A. J., Agarwal, Shilpi and **Bharti, Arvind K.**, "A Novel ion selective sensor for promethium determination" *Anal. Chim. Acta,* **681,** 27 (2010).

2. Gupta, Vinod K., Jain, A. K., Pal, Manoj K., Agarwal, Shilpi, and **Bharti, Arvind K.**, "A Comparative study on PVC based sensors in determination of molybdenum", *Anal. Methods,* **3,** 334 (2011).

3. Gupta, Vinod K., Jain, Ajay K., Pal, Manoj K., and **Bharti, Arvind K.**, "Comparative study of fluoride selective PVC based electrochemical sensors", *Electrochim. Acta***, 80,** 316 (2012).

4. Gupta, Vinod K., Sethi, B., Sharma, R. A., Agarwal, Shilpi, and **Bharti, Arvind** "Mercury selective potentiometric sensor based on low rim functionalized thiacalix[4] -arene as a cationic receptor", *J. Mol. Liq.*, **177,** 114 (2013).

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Chapter 1

General Introduction

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Mercury selective potentiometric sensor based on low rim functionalized thiacalix[4]-arene as a cationic receptor

1.1. Introduction

Some important products of modern day industry which have improved the quality of life are pharmaceuticals and drugs, alloys and steels, cements, paints, polymers, textiles, glasses and ceramics, fungicides and insecticides etc. The development of these products has been possible to a great extent due to availability of variety of analytical methods which are used to analyse raw materials and products. To achieve this aim, researches have been trying to improve analytical procedures and make to available some fast procedures which are reliable, convenient, selective and sensitive [1-7].

The modern day industry have not only improved the quality of life but also affected adversely by polluting the environment. To monitor different pollutants in water, air and soils, sensitive and selective methods are needed. Of many pollutants that are present in the environment, heavy metals present in water samples are important pollutants with high toxicity and therefore should be monitored on regular basis.

A number of highly sophisticated instrumental techniques such as high performance liquid chromatography (HPLC) [8-17], reversed-phase high performance liquid chromatography (RP-HPLC) [18-24], gas chromatography-mass spectrometry (GC-MS) [25-32], liquid chromatography-mass spectrometry (LC-MS) [33-39], inductively coupled plasma-atomic emission spectrometry (ICP-AES)**,** electro thermal atomic absorption spectrometry (ETAAS), inductively coupled plasma-mass spectrometry (ICP-MS) [40-43] and many more have become available for determining the concentration of toxic heavy metals in aqueous solutions [44-52]. No doubt these techniques provide accurate and sensitive response in determination of element of interest but they require large infrastructure back up and adequate expertise for operations. Thus, the utility to analyse large number of samples become limited particularly on field and that is why analytical chemists have been trying for sometime to develop faster, convenient and easy to operate systems, which can be used to analyse to large number of samples both on the field, as well as in the laboratories. Such analytical systems have now become available which require minimum chemical manipulation of the sample and provide rapid, accurate, low-cost, on-field determination are the most preferred choice of analytical chemists. Ion-selective electrodes can also be used to analyse coloured and turbid solutions. In view of these advantages ion-selective electrodes have been widely used to monitor heavy metal in many environmental samples.

The technique is often non-destructive, adaptable to small sample volume with possible application in real-time analysis. As a result, a number of good commercially available ISEs have been developed which are now convenient tools for analysis. These ion-selective electrodes have been widely used for the quantification of many metals ion in biological fluids, food product, soil, fertilizers, medical samples, effluents and waste water and some of the established applications of ISEs are such as determination of F^- in drinking water, Ca^{+2} in dairy products and K^+ in fruits juice. In biomedical laboratories, ISEs are employed to determine clinically important ion (Na^+, K^+, Li^+ and Ca^{+2}) in body fluids.

However, it has been proved that ISEs are most advantageous in analysis of metallic and organic molecules still new methodologies are required for the best utilization in different research field, ion-pair method; a new methodology in application of ISEs in pharmaceutical, medical and environment is recently updated. In view of many advantages of ISEs, the research as the area is vigorous and ever-expanding one aimed to develop better electrodes with high sensitivity and selectivity.

1.2. Historical review of ion-selective electrodes

The ion-selective electrodes (ISEs) are one of the most important and frequently used electrochemical potentiometric sensors have been using in various purposes such as in laboratory analysis as well as in industry, process control, environmental monitoring, physiological measurements etc. They can deliver real time and on-line information in the presense of various specific ions in the mixture of samples. Ion-selective electrodes (ISEs) consists of a semipermeable membrane and generate electric potential on a membrane, solid or liquid, when placed between two solutions of different concentrations of an appropriate electrolytes and responds selectively to a particular ion in presences of other ions. The origine of electrode potential arises a membrane dates back to 1791, when Galvani observed bioelectric phenomenon while dissecting a frog. Later, in 1848 Bios proposed that living cell membrane have properties similar to an electrode of galvanic cell. However, the scientific basis to this phenomenon was given in 1890 when W. Ostwald proposed that the semi-permeability of the membrane was the main cause of potential generation [53]. Discovery of the glass electrode for hydrogen ion by Cramer in 1906 stimulated the making of chemical measurements with physiochemical instrumentation. Efforts in this direction were initiated by Kolthoff and Sanders [54] in 1937 who made first silver halides disc electrodes. In the early 1960s, E. Pungor [55] published his work on Ag-I based electrodes which were used for the determination of the activitiy of Ag^+ and I^- ions. Many workers continued researching towards the preparation of various ion-selective electrodes. However, active and widespread interest in research in the field of ISEs was generated in recent time with the discovery of a fluoride ion selective electrode based on the crystal of lanthanum fluoride in 1966 by Frant and Ross [56]. This electrode is considered as the second best electrode after glass electrode. As a result of renewed interest, different materials have been used in preparing membranes for developing electrodes for various ions. The efforts of different researches in the field of ion-selective electrodes have resulted in the availability of a number of liquid and solid state membrane electrodes for many cationic and ionic species.

Concepts from medicines and physiology improved the impotence in the development of ISEs. In 1970, Higuchi *et al.,* [57] introduced a liquid membrane electrode which responds both to organic and inorganic ions. In 2001, Buck *et al.*, developed most successful liquid membrane sensor using ionophore, which was found to be highly successful class of ISEs [58]. In 1970, Moody *et al*., explained most important procedures for compounding, drying, casting and mounting of PVC membranes [59]. Subsequently, PVC based ion-selective membranes have attracted much attention and have been used in the fabrication of electrochemical sensors for the determination of various cations, anion and drugs.

1.3. Literature survey

In view of the rapid industrialization and urbanization improve the importence of ISEs to analytical chemists. In recent years, the field of ion-selective electrodes is perhaps one of the most eminent examples for interdisciplinary research in analytical chemistry. A number of ISEs for analytical purpose have been reported in the literature. The reported work has been summarized in a number of books [60-69], reviews [70-81] and some important papers [82-86]. Periodic reviews in “Analytical Chemistry” [87-93] cover all the recent advances in this field. It is difficult to survey large number of publications in this area we present here literature only on some important and relevant electrodes dealing with alkali and alkaline earth and heavy metal ions and anions.

1.3.1. Alkali metal ion-selective electrodes

The determination of alkali metals ion, especially for Li^+, Na^+ and K^+ is of importance as they are commonly found in biological fluids, environments, medical and clinical samples. In the early development of ISEs for these ions, inorganic ion-exchangers were used as the electroactive materials for preparing the membrane phase but the developed electrodes exhibited poor selectivity for Li^+. A lithium ion-selective electrode is the the most investigated type due to its prophylactic and therapeutic action in various affective disorders. In eighties and nineties, the materials used for preparing the membranes of ISEs for alkali metal ions were generally neutral carrier of different types. Gadzekpo and co-worker [94,95] have reported a review, which summarizes different type of Li^+ -selective sensors, gives their applications and highlights the problem encountered in the determination of Lithium in serum and other biological fluids. Fiedler *et al.*, [96] introduced the first Lithium ion-selective electrodes based on *N,N'*-diheptyl-*N,N'*-5,5-tetramethyl-3,7-dioxanonanediamide. Electrode working range is 1.0 mol L^{-1} to 0.01 mol L^{-1} and it show high selectivity over sodium, potassium, magnesium and calcium. In 1981, Zhulov *et al.,* [97] developed an important Lithium ion-selective sensor using *N,N,N',N'*-tetraisobutylcyclohexaneo-1,2-dicarboxamide as electroactive material along with PVC as supporting matrix. This sensor showed working concentration range of 1.0×10^{-5}-1.0×10^{-1} mol L^{-1} and was highly selective for Li^+ ion. Some important neutral carrier molecules like, *N,N'*-dicyclohexyl-*N',N'*-diisobutyl-cis-cyclohexanedicarbonylamide [98], 6,6-dibenzyl-1,4,8,11-tetraoxacyclotetradecane [99], 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone [100], 14-crown-4 derivatives [101] and 1,10-phenanthroline derivative [102] were synthesized and explored as Li^+ -selective sensors and applied for the quantification of Lithium ion in different real samples. In 2005, Gupta *et al.,* [103] used a carbosiloxane dendrimer as ionophore in the construction of Lithium selective sensor. It reported with wide working concentration range of 2.5×10^{-5} - 1.0×10^{-1} mol L^{-1}, with a slope of 52.0 mV $decade^{-1}$ of activity and was used for the determination Lithium ion in blood serum.

A major interest for Na^+ analysis with ISEs comes from clinical chemistry. Most of the reported Na^+ ISEs developed by using neutral carriers as ionophores. The sensors prepared by Wu *et al.,* [104] based on triglycollic bisdiamides in PVC matrix performed well and showed good selectivity for Na^+ over other alkali and alkaline earth metals and could be used for the determination of sodium in water with high magnesium content. The sensors based on the membranes of crown ethers such as bis[(3n+l)-crown-n]ether derivatives [105], dibenzo-16-crown-5 derivatives [106], 16-crown-5-derivatives [107], bis (12-crown-4)methylmalonates [108], benzyloxymethyl-l1-crown-3 [109] and azoxycrown compounds with sulphur atoms in long side chains [110] were also found to be Na^+ -selective. Calixarenes have also been extensively used as carriers for the fabrication of sodium selective sensors. Prominent among these are the sensors developed by symmetrical, unsymmetrical and bridged *p*-tert-butylcalix[4]arylacetate [111], calix[4]arene derivatives [112] and triestermonoacid derivative of p-tert-butylcalix[4]arene [113]. All these sensors show high selectivity for Na^+ as calix[4]arene compounds exhibit an optimum cavity size for complexation with Na^+ and have been used for Na^+ determination in biological fluids. Recently, Kimura *et al.,* [114] designed several sol-gel derived membrane based Na^+ -selective sensors which contains bis(crownether) and valinomycin, as well as calix[4]arene ester and amide derivatives electroactive materials, while Kim *et al.,* [115] tried lipophilic trimesters of caix[4]arene and calix[4]quinine to develop Na^+ -selective sensors. These membranes showed good sensitivity, selectivity and low response time.

Most of the ISEs have been developed for K^+ in view of its importance in clinical chemistry because changes in K^+ concentration in human serum bring along the risk of acute cardiac arrhythmia. The first successful and commercially Potassium ion selective electrode was developed by Fiedler and Ruzika [116] by using valinomycin, a neutral carrier. Since then many workers [117-120] have developed valinomycin based ISEs for Potassium ion. Momma *et al.*, prepared a solid-state electrode using double layered film made of polypyrrole/polyanion composite and plasticized PVC while Heng and Hall developed glycidyl methacrylate, methylmethacrylate and n-butylacrylate polymers based membranes containing valinomycin. Most of them polymeric membrane showed Nernstian or Near-Nernstian responses over the potassium ion concentration range of 1.0×10^{-5}- 1.0×10^{-1} mol L^{-1} but suffer interference from Na^+ ion. A number of K^+ -selective sensors based on crown ethers *viz.,* cis and trans bis(crown ethers) [121], bis(15-crown-5) [122], 4'-picrylamino-5'-nitrobenzo-18-crown-6 [123] and 4-acryloyl amidobenzo-15-crown-5 and 4-acryloylamidobenzo-18-crown-6 [124] have been prepared. All these sensors show high selectivity for K^+ over other alkali and alkaline earth metals and have been used for determining potassium in biological fluids. Yan *et al.* [125] used calix[6]arene hexaester for the preparation of membranes and investigated its applicability to determine K^+ in human serum. Recently, Katsu *et al.*, [126] reported K^+ -selective sensor based on macrocyclic metacyclophanes analogous to calixarenes which showed linear response down to 7.0×10^{-6} mol L^{-1} of K^+ but suffer serious interference from Na^+. Bobacka *et al.*, [127,128] introduced solid state potassium ion-selective electrodes using carbon nanotubes as ion to electron transducer in polymer membranes.

The development of ISEs for Rb^+ has received relatively less attention than Cs^+ mainly because of their conspicuous absence in biological systems. However, still some sensors have been reported. Cosgrove *et al.*, [129] reported a valinomycin based sensor selective for Rb^+ and used it to determine rubidium in yeast cells. Gupta and co-workers [130] used epoxy resin based membranes of rubidium tungustoarsenate to develop Rb^+ -selective sensor. The sensors prepared were not highly selective but could be used for its determination by potentiometric titration procedure. A solid membrane electrode for the determination of Rb^+ -selectively in the concentration range $4 \times 10^{-5} – 1.0 \times 10^{-1}$ mol L^{-1} was reported by Shrivastava and co-workers [131]. Another Rb^+ -selective sensor was developed by Saleh *et al.,* [132] using indanopyrazalo [l,5-a] pyrimidines as electroactive material which showed Nernstian response in the narrow concentration range of 1.0×10^{-4} - 1.0×10^{-1} mol L^{-1}. Yang *et al.,* [133] used decylidene bis (4-benzo-15-crown-5) ether to develop Rb^+ -selective sensor. It exhibited a near Nernstian response in the concentration range of 5.0×10^{-5} - 1.0×10^{-1} mol L^{-1} with detection limit down to 20 μM. Hyun *et al.*, [134] explored binaphthyl based crown ethers derivatives as ionophores in the preparation of Rb^+ -selective polymeric membrane electrodes which worked in the linear concentration range 1.0×10^{-5} - 1.0×10^{-1} mol L^{-1}.

Caesium has also received much attention during the last two decades and various ionophores were reported for the development of Cs^+ -selective electrodes. PVC based membrane of cis-bis(crown ether) and 15-crown-5-phosphotungstic acid precipitates were found to be sufficiently Cs^+ -selective [135,136]. The electrode showed good selectivity for Cs^+ over other alkali, alkaline earth and some transition metals. Chen and Feng [137] used cesium tetraphenylborate incorporated in PVC for preparing Cs^+ -selective electrode, which showed linear response down to 30 μM but shows serious interference to K^+ and Rb^+. Another electrode was developed by Borosoum *et al.*, using 14- and 15-crown formazans which showed good selectivity for Cs^+ over a number of ions. Wang *et al.*, [138] found 15-crown-5-phosphotungustic acid precipitate selective for Cs^+. It showed Nernstian response in the concentration range of 1×10^{-4} - 1×10^{-1} mol L^{-1}. Several crown ether derivatives *viz.*, 14 and 15-crown formazans [139] and calix[4]crown ether-ester [140] showed good selectivity for Cs^+ over a number of ions. Cs^+ -selective electrodes based on several calixarenes *viz.*, calix[6]arene tetraester derivatives [141], bridged biscalix[4]arenes [142], 1,3-bisbridged cofacial-calix[6]crowns [143], Crown bridged thiacalix[4]arenes [144], have also been reported. Shamsipur *et al.*, [145] reported a 16-membered macrocylic diamide as a Cs^+-selective ionophore while Ganjali and co-workers [146] used a cavitand as Cs^+ -selective ionophore. Saleh *et al.*, [147] developed a Cs^+ -selective sensor using cephalexin antibiotic drug as ionophore. Later on in 2004, Arida *et al.*, developed Cs-Molybdophosphate based graphite electrode for the selective determination of Cs^+ ion [148]. Recently, a Cs^+ -selective electrode, having longest lifetime of nine months, based on 5-(4'-nitrophenylazo)25,27-bis(2-propyloxy)26,28-dihydroxycalix[4]arene has been reported by Ramanjaneyulu and co-workers [149] while Sadeghi *et al.*, [150] fabricated a Cs^+ -selective polymeric membrane coated graphite electrode based on 4',4''(5') di-tert-butyl di-benzo-18-crown-6.

1.3.2. Alkaline earth metal ions-selective electrode

The development of ISEs for alkaline earth metal has been of deep interest due to their occurrences in biological samples as well as in industrial wastes. A large number of electrodes for these ions have been reported. A brief review on IESs for these metals is given in the following paragraphs. Among alkaline earth metal ions, beryllium has received less attention in spite of its wide industrial uses. This may be due to high charge density on Be^{2+} leading to its excessive hydration, as a result of which the hydrated Be^{2+} is poorly sensed by ionophores. Fleet and Rechnitz [151] used phosphate ester ionophores to prepare Be^{2+} -selective sensors. Ganjali *et al.*, employed 2,4-dinitrophenyl hydrazine-benzo-9-crown-3 [152], naphtho-9-crown-3 [153], 2,3,5,6,8,9-hexahydro-1,4,7,10-benzotetraoxa-cyclo-dodecine-12-carbaldehyde-12-(2,4-dinitrophenyl)hydrazine [154] and 4-Nitrobenzo-9-crown-3-ether [155] to develop Be^{2+} -selective sensors. The sensor [155] showed Nernstian response to Be^{2+} and worked in the working concentration range of 1.0×10^{-10} - 1.0×10^{-4} mol L^{-1} with a limit of detection 3.5×10^{-11} mol L^{-1} (≈350 pg/L). Shamsipur *et al.*, [156] developed graphite coated Be^{2+} -selective sensors based on a macrocyclic diamide, 15-diaza-3,4;12,13-dibenzo-5,8,11-trioxabicyclo [13,2,2] heptadecane-2,14-dione and compared its characteristics with polymeric membrane electrode. In 2012, Gupta *et al.*, [157] constructed a PVC based Be^{2+} ion-selective electrode along with dibenzo (perhydrotriazino)aza-14-crown-4 ethers as electroactive material. It was reported with wide working concentration range 7.6×10^{-6} to 1.0×10^{-1} mol L^{-1}. Near Nernstian slope 30.7 mV per $decade^{-1}$ of activity and low response time 15 s over wide pH range 3.0 – 9.0 along with good reproducibility.

In case of Magnesium, very few ISEs were reported. The major challenge in the design of Mg^{2+} ionophores lies in the discrimination of Ca^{2+}. A Mg^{2+} -selective sensor was prepared by Saleh *et al.*, [158] using phenylene bis(ditolyl phosphineoxide) in PVC matrix which showed high selectivity for Mg^{2+} over Ca^{2+} in the concentration range of 6.0×10^{-5}- 1.0×10^{-1} mol L^{-1}. Further, Mg(II) oxinate [159] and 1-(*N*, *N*-dicyclohexylcarbamoyl)-2-(*N*, *N*-dioctadecylcarbamoyl) ethyl phosphonic acid monomethyl ester [160] were also used as ionophores for magnesium selective sensors. These sensors exhibited linear potential response towards Mg^{2+} ions with reasonably good selectivity. Gupta *et al.*, reported magnesium selective sensors based on benzo-15-crown-5 [161] having a working range of 1.0×10^{-5} - 1.0×10^{-1} mol L^{-1} and magnesium tetrazaporphyrin complex [162]. Both the sensors exhibited excellent selectivity for Mg^{2+} over other cations in the concentration range of 9.4×10^{-6} - 1.0×10^{-1} mol L^{-1} Nernstian slope. Agarwal *et al.*, [163] fabricated a heterogeneous membrane sensor by using zirconium(IV) selenomolybdate gel for the selective determination of Mg^{2+} ion.

Development of a convenient method for the determination of calcium ions has been an area of extensive research because of its widespread occurrence in biological and environmental systems. Initial attempts to develop a calcium selective sensor were not successful. In late sixties, Ross [164] developed a liquid membrane electrode for calcium ion using calcium-di-(n-decyl) phosphate in di-(n-octylphenyl)phosphonate having good response time and poor selectivity. Further, the useful Ca^{2+} -selective sensors were developed by Thomas and coworkers [165] by incorporating Ca-bis(2,6-dinitro-4[l,l,3,3-tetramethyl(butyl)]phenoxide and Ca-bis (di[l,l,3,3-tetramethylbutylphenyl)]) phosphate in PVC. Later on, various organophosphates, such as di(2-ethylhexyl) phosphate [166], Ca-di-(n-octylphenyl) phosphate [167], Ca-bis-(4-octylphenyl) phosphate [168] and polyaniline functionalized with bis[4-(l,1,3,3-tetramethyl butyl) phenyl]phosphate [169] were employed as electroactive material for Ca^{2+} -selective sensors. Some of these sensors respond to Ca^{2+} over a wide concentration range (down to 10^{-9} mol L^{-1}) with a fast response time but the selectivity of these sensors was not good. Kumar *et al.*, [170] developed Ca^{2+} ion-selective electrode by using dibenzo-18-crown-6 as ionophore. In 2007, Singh *et al.*, [171] developed highly -selective Ca^{2+} sensor with furildioxime as ionophore. While Jain *et al.*, [172] reported p-isopropyl calix[6]arene based sensor for the selective determination of calcium.

Barium is important metal and present in environmental samples. In view of its importance, it is important to determine its concentration in various drugs and minerals. Earlier, Ba^{2+} -selective electrode have been prepared by using non-ionic Antrarox CO-880 and its barium complex [173] was used to construct Ba^{2+} -selective sensors. Gupta *et al.*, [174] used dibenzo-24-crown-8 to develop a highly selective sensor for Ba^{2+} which exhibited linear response in the range of 14 µM - 0.1 M. Saleh [175] reported a Ba^{2+} -selective sensor using neutral bidentate organo phosphorous compounds. Singh *et al.*, [176] reported 2,3,4-pyridine-1,3,5,7,12-pentaazacyclopentadeca-3-ene as a Ba^{2+} -selective ionophore. Othman *et al.*, [177] used complex ion associate of barium(II)-Rose Bengal as an ionophore for preparing Ba^{2+} -selective PVC membrane sensor which exhibited fast linear potential response for Ba^{2+} ions over the concentration range 5×10^{-5} to 1.0×10^{-1} mol L^{-1} with a Nernstian slope of 28.5 ± 0.4 mV $decade^{-1}$ of activity. Recently, Zamani *et al.*, [178] constructed a Ba^{2+}-selective sensor based on 2,3-Diphenylquinoxaline-4', 4''-dioxytriethylene glycol and 3-deoxy--erythro-hexos-2-ulose bis(thiosemicarbazone) which showed high selectivity for Ba^{2+} over 1.0×10^{-6} to 1.0×10^{-2} mol L^{-1} with a lower detection limit of 5.6×10^{-7} mol L^{-1}.

Strontium is an important alkaline earth metal that is used in pyrotechnics device such as firework and signal flares, in refining of Zinc, in production of glasses for colored television sets and added to tin and lead alloys for increasing hardness and durability [179]. The first Sr^{2+} -selective sensor was developed by Baumann [180] using strontium complex of nonylphenoxypoly(ethyleneoxy)ethanol as electroactive material but it exhibited higher selectivity for Ba^{2+} over Sr^{2+}. Qian *et al.*, [181] reported a Sr^{2+}-selective sensor based on tetracyclohexyl-2,6-pyridine-bis(methyleneoxyacetamide) as ionophore which showed strong interference to Pb^{2+} and Ag^{+} ions. The sensor based on the membrane of dibenzo-30-crown-10 [182] was also found to be Sr^{2+} -selective. Gupta *et al.*, [183] used 5,11,17,23,29, 35-hexakis(1,1,3,3-tetramethylbutyl)-37,38,39,40,41,42-hexakis(carboxymethoxy)calyx[6] arene to prepare Sr^{2+} -selective sensor. Potentiometric membrane sensor based on 6-(4-nitrophenyl)-2-phenyl-4,4-dipropyl-3,5-diaza-bicyclo [3,1,0] hex-2-ene was developed by Zanjanchi *et al.*, [184] for trace level detection of Sr^{2+} ions. Zamani and co-workers [185] used 2, 3-Diphenylquinoxaline-4',4''-dioxytriethylene glycol as a suitable ionophore for preparing Sr^{2+} -selective sensor which exhibited a linear working concentration range of 1.0×10^{-6} - 1.0×10^{-2} mol L^{-1} and a detection limit of 6.7×10^{-7} mol L^{-1} with a Nernstian slope of 29.9 mV decade^{-1} of activity $a_{Sr}{}^{2+}$. Guo *et al.*, [186] explored 1-benzothiazol-3-benzoyl-thiocarbamide as neutral carrier for the fabrication of fast response Sr^{2+} -selective polymeric membrane sensor which exhibits Nernstian response to Sr^{2+} over 4.0×10^{-7} to 1.0×10^{-1} mol L^{-1} with a detection limit of 2.5×10^{-7} mol L^{-1} and a slope of 30.1 ± 0.1 mV decade^{-1} of $a_{Sr}{}^{2+}$.

1.3.3. Transition metals ions-selective electrodes

The determination of transition metals in mineral, soil, pharmaceutical, clinical, environmental and other samples is important in view of their toxicity above certain concentration level. As such, efforts have been made by many researchers in the field of ISEs to develop selective sensors for heavy metals, which may permit quick and reliable quantification. As a result of extensive investigations, a large number of sensors have been reported for the estimation of a number of transition metals. Here, a brief review of recently developed ISEs for various transitions elements *viz*., Cr^{3+}, Ni^{2+}, Ag^{+}, Zn^{2+}, Mn^{2+}, Fe^{3+}, V^{3+}, Hg^{2+}, Co^{2+}, Pb^{2+} etc. has been presented.

Chromium is highly toxic and has been used in many industries such as chrome plating, pigment manufacturing, refractory industries, wood treatment, leather tanning making steel and other alloys. A number of potentiometric sensors based on a variety of ionophores have been reported in past three decades. Masuda *et al.,* [187] reported the first Cr(III) coated wire ion selective electrode based on Aliquat $336S^{+}$-$Cr(SCN)_4^{-}$ ion pair, and the electrode displayed Nernstian slope (58.0 mV decade^{-1}) over a concentration range of 10^{-5} - 10^{-2} mol L^{-1}. Several chromium -selective electrodes based on asymmetrical Schiff base [188], 5-amino-1-phenyl-1H-pyrazole-4-carboxamide [189], crown ether[190] and several other neutral carriers *viz.*, glyoxal bis(2-hydroxyanil) [191], 2,3,8,9-tetraphenyl-1,4,7,10-tetraazacyclododeca-1,3,7,9-tetraene [192], 1,3-diamino-2-hydroxypropane-*N*, *N*,*N'*,*N'*-tetraacetic acid [193], 4-amino-3-hydrazino-6-methyl-1,2,4-triazin-5-one [194] were explored as Cr^{3+}-selective sensors. Recently, Schiff bases [195,196] have also been reported as highly -selective ionophores for chromium ion determinations.

Pungor and coworkers reported the first nickel-selective electrode based on Ni-dimethylglyoxime complex [197]. Recently, a number of ionophores *viz.*, 5,7,12,14-

tetramethyl dibenzotetraazaannulene [198], dibenzo-18-crown-6 [199], Schiff base [200, 201] have been reported for selective determination of nickel in various samples.

Silver is a precious metal ion and widely used in jewellery, tableware, hollow ware and coinage. It is also used in photography, electrical and electronic components, electroplating, catalysis, clinical treatment, mirrors etc. A number of ion-selective electrodes have been developed for Ag^+ ions. Lai and coworkers [202] reported the first neutral carrier Ag^+ -selective electrode based on dithiacrown ether. Since then, a number of Ag^+ ISEs involving mainly calixarene derivatives [203-206], crown ethers [207,208], Schiff bases [209,210] and sulphur donor neutral and macrocyclic ligands [211,212] have been reported.

Amongst heavy metal ions, the determination of mercury is probably most important to analysts in view of its acute toxicity. Hg^{2+} -selective sensor based on 1-(2-aminoaryl)-4,4,6-trimethyl-1,4,5,6-tetrahydro-6-hydroxy pyrimidine-2-thiol [213] and 2-amino-6-purinethiol and 5-amino-1,3,4-thiadiazole-2-thiol [214] as a chelating ionophores exhibited better performance characteristics. Saleh *et al.*, [215] developed a highly selective ethylenediamine bisthiophene carboxaldehyde based Hg^{2+} sensor which showed Nernstian response with a low detection limit of 7.0×10^{-8} mol L^{-1}. Recently, Hosseini *et al.*, [216] reported a Hg^{2+} -selective electrode using calix[4]arene derivative as an ionophore. It exhibited wide working concentration range of 1.0×10^{-6} to 1.0×10^{-1} mol L^{-1} and lower detection limit of 4.0×10^{-7} mol L^{-1} with a Nernstian response.

Manganese is essential micronutrient for various organisms but is toxic at higher concentration level. There has been little work done on manganese -selective sensors. Lal and coworkers explored cation exchange resin (Dowex 50WX-4) for the fabrication of Mn(II) -selective sensor [217]. The sensor worked in the concentration range of 1.0×10^{-5} - 1.0×10^{-1} mol L^{-1} with long response time. A Schiff base was used by Gupta *et al.*, [218] exhibited response to Mn^{2+} over the concentration range of 1.25×10^{-5} to 1.0×10^{-1} mol L^{-1}. A recently reported Mn^{2+} -selective electrode, based on *N*-(2-picolinamidoethyl)-picolinamide, showed high response to Mn^{2+} over the concentration range of 1.0×10^{-5} to 1.0×10^{-1} mol L^{-1} with Nernstian slope of 29.3 ± 0.5 mV $decade^{-1}$ of $a_{Mn}{}^{2+}$ and detection limit of 8.0×10^{-6} mol L^{-1}.

There are only few reports of Fe^{3+}-selective sensors in the literature. Mashhadizadeh *et al.,* [219] explored 2-[(2-hydroxy-1-propenyl-buta-1, 3-dienylimino)-methyl]-4-*p*-tolyazophenol as ionophore for the fabrication of Fe^{3+} -selective sensor but this sensor showed super-nernstain response. Recently Ekmekci *et al.,* [220] reported Fe^{3+} -selective sensor based on benzo-18-crown-6 crown ether as an ionophore. Zamani *et al.*, explored *N*-(2-hydroxyethyl)ethylenediamine-*N,N',N''*-triacetic acid [221], 5-amino-3-methyl-1-phenyl-1H-pyrazole-4-carboxamide [222] and di-tert-butylazodicarboxylate [223]. These sensors showed very low detection limits.

A number of Zn^{2+}-selective sensors based on different ionophores have been reported in the past few decades. Gupta *et al.*, [224] used 4-tert-butylcalix[4]arene to prepare Zn^{2+} -selective sensors worked over the concentration range of 9.8×10^{-6} to 1.0×10^{-1} mol L^{-1} with a near nernstian slope of 28.0 ± 1.0 mV $decade^{-1}$ of $a_{Zn}{}^{2+}$ and low detection limit of 5.0×10^{-7} mol L^{-1}. Singh *et al.*, [225] explored tripodal chelating ligand based Zn^{2+} -selective sensor which exhibited good selectivity to Zn^{2+} ions over a wide concentration range; 1.4×10^{-7} to 1.0×10^{-1} mol L^{-1} with a low limit of detection of 9.5×10^{-8} mol L^{-1}. Zn^{2+}-selective potentiometric sensor based on 3-hydroxy-2-naphthoic hydrazide [226] exhibited a Nernstian response over a concentration range of 1.8×10^{-7} - 3.6×10^{-1} mol L^{-1}, with a detection limit of 1.1×10^{-7} mol L^{-1}. Singh *et al.,* [227] introduced electrochemical sensors based on pendant armed macrocyclic ligand for the determination of Zn^{2+} ions. World wide toxicity of lead has made its monitoring desirable for the analysts.

A PVC membrane Pb^{2+} -selective electrode was prepared with 1,10-dibenzyl-1,10-diaza-18-crown-6 as ionophores [228]. This electrode had fast Nernstian response for Pb^{2+} over the working concentaration range of 5.0×10^{-5} to 1.0×10^{-2} mol L^{-1} and showed long shelf life of more than ten months. Bhat *et al.*, [229] constructed a coated wire lead ion-selective electrode using 5,11,17,23,29,35-hexa-tert-butyl-37,38,39,40,41,42-hexahydroxy calix[6]arene. This electrode exhibited linear Nernstian response over the concentration range of 1×10^{-6} to 1×10^{-1} mol L^{-1} with a slope of 30 ± 1 mV $decade^{-1}$ of a_{Pb}^{2+} and with a detection limit of 6×10^{-7} mol L^{-1}. Gupta *et al.*, [230] used *N,N'*-dibenzyl-1,4,10,13-tetraoxa-7,16-diaza cyclo-octadecane as an ionophore for preparing Pb^{2+} -selective sensor which exhibits a Nernstian response for Pb^{2+} over a wide concentration range of 8.2×10^{-6} to 1.0×10^{-1} mol L^{-1} with a slope of 30.0 ± 0.1 mV $decade^{-1}$ of a_{Pb}^{2+}. Wilson *et al.*, [231] reported PVC membrane ion-selective electrodes for Pb(II) ion based on 1,3-bis(*N'*-benzoylthioureido) benzene and 1,3-bis(*N'*-furoylthioureido)benzene. Both of these electrodes exhibited fast Nernstian response over a wide working concentration range.

Ganjali *et al.*, [232] developed Co^{2+} -selective sensor by incorporating newly synthesized oxime derivative in PVC matrix. The sensor exhibited a linear potential response to log a_{Co}^{2+} in the concentration range of 1.0×10^{-6} - 1.0×10^{-1} mol L^{-1} with a high response time of 25 s. A bridge modified 4-tert-butylthiacalix[4]arene(I) was employed by Jain *et al.*, [233] as electroactive material in the preparation of cobalt - selective sensor which performed linearly in the working concentrion range of 5.3×10^{-6} to 1.0×10^{-1} mol L^{-1} with near-Nernstian slope of 30.0 mV $decade^{-1}$ of a_{Co}^{2+} and a detection limit of ≈ 0.3 ppm. Kumar *et al.*, [234] used p-(4-n-butylphenylazo)calix[4]arene as an electroactive material for the fabrication of a new Co^{2+} -selective sensor which exhibited a fast linear response with the detection limit of 4.0 × 10^{-6} mol L^{-1}. Recently, Schiff's base has been explored successfully for the determination of vanadyl ions by Ganjali and coworkers [235].

1.3.4. Sensors for rare earth metal ions

Rare-Earths also called as lanthanides are an important group of 15 trivalent metals. They usually have magnetic, catalytic and fiber optics, superconductor, colored glasses, refinery industry and nuclear technology properties therefore, they are widely used in industry. The Rare-Earths element are distributed in low concentration throughout the earth's crust and are considered slightly toxic; however, their intraperitoneal administration affects metabolic processes. Therefore, industrial sources of lanthanides are potentially hazardous to human health and therefore there is a growing demand for determination of these metal ions. Considerable efforts have been made by researchers to develop selective sensors for rare-earths [236]. A detailed literature on promethium-selective sensors is presented in the subsequent Chapters of this thesis; while a brief review on ISEs for other rare-earths are given in the following paragraphs.

The determination of lanthanum ion has become necessary because of the increasing interest in coordination chemistry and bioinorganic, as well as in the increased industrial use of lanthanum compound and their enhanced discharge, toxic properties and adverse effect. There are only a few report on La(III) ion-selective electrodes till date. Pan *et al.*, [237] described a solid state La(III) ion-selective electrode. Amarchand *et al.*, [238] reported a PVC membrane and coated graphite electrode based on bis(2-mercaptoanil)-diacetyl but the above reported electrodes possessed narrow working concentration range and suffered serious interferences from various cations including Cu(II), Ni(II) and Ce(III). In addition to these, PVC based La(III) -selective electrodes based on other neutral carrier *viz.*, 4-methyl-2-hydrzinobenzothiazole [239], Gupta *et al.*, [240] fabricated a La(III) chemical sensor based on the monoaza-12-crown-4 in PVC matrix while Ganjali *et al.*, [241] explored the use of gliclazide in the preparation of PVC based La(III) -selective sensor and used it for determination of La(III) in binary mixture, in addition to these, PVC based La(III) -selective electrodes based on other neutral carrier *viz., N-S* Schiff's base bis(thiophenal)phenylene-1,3-diamine [242], 2,2'-dithiopyridine [243], rubeanic acid [244] have been reported.

Cerium is the mostly found in the rare earth elements. They are mostly used in commercial. These used as catalysts, additive to fuel to reduce emission and used as fluorescent lamp, glass and enamel to change their color and also considerable efforts have been made by researchers to develop selective sensor for Ce(III). Akhond *et al.*, utilized 2-aminobenzothiazole [245] in PVC matrix as a suitable ionophore for preparing Ce^{3+} -selective sensor. An addition to the family of Ce^{3+} sensors was made by Saleh *et al.*, by utilizing [4-(4-nitrobenzyl)-1-phenyl-3,5-pyrazolidinedion] [246] as electroactive material while Zamani *et al.*, utilized *N*-[(2-hydroxyphenyl)methylidene]-2-furohydrazide [247] for developing cerium ion sensor. Abedi *et al.*, [248] used 2, 5-Dioxo-4-imidazolidinyl as an excellent sensing material in the preparation of a PVC membrane for a Ce(III) -selective sensor. The developed sensor exhibited a wide linear response with a slope of 19.6 ± 0.3 mV decade^{-1} of $a_{Ce}{}^{3+}$ over the working concentration range of 1.0×10^{-6} to 1.0×10^{-1} mol L^{-1} and detection limit is 5.7×10^{-7} mol L^{-1}.

Neodymium has several important applications in the field of motors, loudspeakers and numerous appliances. Neodymium is also used in Nd : YAG lasers to generate 1.064 micrometer light. This is the most significant solid state laser. Neodymium is a key component of an alloys used to make high-power light weight magnet for electric motors of hybrid cars, and also use in wind turbines. In 2004, Agarwal and co-workers reported Nd(III) -selective sensor using inorganic ion exchange resin [249] but this sensor showed long response time. Norouzi *et al.,* Explored *N*-(2-furylmethylene)pyridine-2,6-diamine for determination of Nd(III) ion [250] while in recent year singh *et al.*, reported Nd(III) -selective sensor incorporating lariat ether as an ionophore [251].

In 1996, Chowdhury and co-worker [252] reported the first Sm^{+3} -selective sensor, they used bis(thiaalkylxanthato)alkanes as an ion carrier, Ganjali *et al.,* [253] fabricated Sm^{+3} -selective sensor using glipizid as an ionophore. Later on, Mittal and co-workers reported samarium(III) -selective sensors based on tin(IV) boratophosphate [254] and zirconium(IV) boratophosphate [255] but these sensor showed super Nernstian slope. In addition to these, Sm^{3+}-selective coated graphite electrode reported by Ganjali *et al*., [256] showed very high selectivity to Sm^{3+}. 3-{[2-oxo-1(2H)-acenaphthylenyliden]amino}-2-thioxo-1,3-thiazolidin-4-one [257] and 2-[(E)-1-(1H-pyrrol-2-yl)methylidene]-1-hydrazine carbothioamide [258] have also been reported as a suitable ionophores for the preparation of Sm^{3+} -selective sensor. 2-Ethoxy-1-ethoxycarbonyl-1, 2-dihydroquinoline [259] was used as a suitable neutral ionophore for the preparation of a highly selective Sm^{3+} membrane sensor. This sensor exhibited a Nernstian response over a wide concentration range of 1.0×10^{-6} to 1.0×10^{-2} mol L^{-1} with detection limit of 5.0×10^{-7} mol L^{-1}.

There have been few reports on Gd^{3+} -selective sensor. Ganjali *et al.*, [260] explored ionophore for determination of Gd^{3+} ion while Zamani co-worker [261] used 6-methyl-4-{[1-(2thienyl)methylidene]amino}3-thioxo-3, 4-dihydro-1,2,4-tri-azine-5-(2H) -one as an ionophore for the fabrication of Gd^{3+} -selective sensor. Ganjali *et al.*, [262] used a *N*-(2-pyridyl)-N'-(4-nitrophenyl)thiourea ($PyTu4NO_2$) as an excellent neutral ion carrier for Gd^{3+} ion -selective sensor. Singh *et al.,* [263] developed gadolinium -selective coated graphite electrode based on 2,6-bis-[1-{*N*-cyanopropyl,*N*-(2-methyl pridyl)}aminoethyl] pyridine as an ionophore for determination of Gd(III) ions in waste water and rock sample. Recently Gupta and co-worker [264] reported a novel gadolinium ion-selective membrane electrode based on 2-(4-phenyl-1,3-thiazol-2-yliminomethyl) phenol which is based on synthesized neutral carrier. The gadolinium sensor exhibits a Nernstian slope of 19.5 ± 0.5 mV decade^{-1} of Gd(III) activity over a wide concentration range of 9.38×10^{-7} to 1.0×10^{-2} mol L^{-1} with pH range of 3.5 – 8.5.

Terbium is used to dope in alkali earth metal halide for making solid state devices. It is also used in alloys and in the production of electronic devices. A number of terbium -selective sensors have been reported in literature. Ganjali and coworkers [265] reported a Tb(III) -selective electrode based on bis-pyrrolidene Schiff's base. Gupta *et al.*, [266] used S-2-benzothiazolyl-2-amino-α-(methoxyimino)-4-thiazolethiol acetate as neutral ionophore for preparing terbium -selective sensor. Recently, Zamani *et al.* [267] developed terbium (III) -selective sensor based on hematophorphyrin. Zamani *et al.* explored 4-amino-3-{2-[4-amono-6-methyl-5-oxo-4,5-diidro-1,2,4-triazin-3-(2H)-yliden]hydrazono}–6-methyl-3, 4-dihydro-1,2,4-triazin-5(2H)-one [268] as an ionophore for determination of terbium ions but the electrode showed poor performance in terms of concentration range and selectivity. Gupta *et al.*, [269] developed terbium -selective sensor based on *N*-(2-hydroxyphenyl)-3-(2-hydroxyphenylhydroxyphenylimino)-*N*-phenylbutanamidine was developed.

Ion-selective sensors for some other rare-earth metal ions *viz.*, for Pm^{3+} (III) [270], Yb^{3+} [271,272], Dy^{3+} [273-275], Eu^{3+} [276,277], Ho^{3+} [278,279], Tm^{3+} [280,281], UO_2^{2+} [282-284], Pr^{3+} [285,286], Lu^{3+} [287] and Er^{3+} [288] *etc.*, have also been reported. All these sensors exhibited good selectivity for the primary ion over a sufficiently wide working concentration range and have a low response time.

1.3.5. Sensors for anions

In the last decade, intensive research has been directed towards the preparation of a variety of selective receptors for anions. It is reported that the most successful and important ion selective sensor was developed by Frant and Ross based on the crystal of LaF_3. One other F^--selective sensor is developed by Newman *et al.*, [289] incorporating CaF_2 or LaF_3 or mixture. The sensor exhibited working concentration range of 10 µM - 10 mM and detection limit 0.6 µM. Nakamura *et al.,* [290] prepared membranes of phthalocyanine cobalt(III) for developing F^- sensors and used them for fluoride determination in non-aqueous medium and pharmaceuticals. Jose *et al.* [291] reported flouride ion selective sensor based on urea and thiourea derivatives which exhibited good selectivity for flouride ion over other halide ions. The other PVC based ion selective sensors prepared by incorporating different ionophores *viz*., triphenyl lead chloride [292], salen-Mn(II)complex [293] and tetrakis(4-*N,N*-dimethylaminobenzene)porphyrin manganese (III) acetate (MnTDAc) which responded selectively to I^- ions. The sensor based on MnTDAc [294] worked well over the working concentration range of 7.5×10^{-6} -1.0×10^{-2} mol L^{-1} with a slope of 59.4 mV decade^{-1} of activity. First time Havas *et al.,* [295] and Weiss *et al.,* [296] prepared bromide ion-selective membrane electrode. Later on Zhu *et al.,* [297] developed a bromide selective sensor based on benzalkonium as an ionophore. Masadome *et al.,* [298] prepared Br^- ion selective sensor which exhibited a linear concentration range of 1.0×10^{-3} to 1.0×10^{-2} mol L^{-1}. Ganjali *et al.,* [299] prepared a bromide liquid membrane sensor which worked in the concentration range of 1.0×10^{-5} to 1.0×10^{-1} mol L^{-1} and other sensor based on a iron(III) -salen carrier [300] exhibited detection limit of 6.0×10^{-5} mol L^{-1}. Shamsipur *et al.*, [301] prepared a bromide selective polymeric membrane sensor based on xanthenium bromide salt which worked in linear range of 1.0×10^{-5} to 3.0×10^{-2} mol L^{-1} and an another by using mercury(II) complex [302] which showed Nernstian response in the concentration range of 1.0×10^{-5} to 3.0×10^{-2} mol L^{-1}.

Carbonate compounds are used extensively in the manufacturing of glass, paper, rayon, soaps and detergents for dyeing processes in textile industries. Carbonate is only slightly toxic, but large doses are corrosive to the gastro intestinal tract where symptoms may include severe abdominal pain, vomiting, collapse and diarrhea. In view of its widespread occurrence, the accurate and rapid determination of carbonate is important. Herman and Rechnitz [303] reported first carbonate selective membrane sensor based on the tri-fluoroacetyl-*p*-butylbenzene derivatives. Later on, Scott *et al.*, [304] employed an anion binding complex such as mercuric EDTA in the buffer solution to decrease salicylate interference of the carbonate responsive membrane. The change of cationic site (e.g. tridodecylmethylammoniumchloride (TDDMACl) concentrations) in the trifluoro aceto-phenone (TFA) based membranes was examined by Sokalski *et al.,* [305] to improve their carbonate selectivity. Asymmetric membrane technology was utilized to prevent salicylate from responding to carbonate sensitive membranes in serum carbon dioxide measurements [306]. There are many attempts were also made to increase the selectivity of sensors by incorporating acceptor substituents into phenyl ring of trifluroacetic acid in para-position [307,308]. There is increasing the acidity of the trifluoroacetyl group, which is responsible for carbonate sensing. The interferences from high concentrations of chloride and salicylate still hinder wider application of carbonate sensors. Recently, Lee *et al.,* [309] used urea-functionalized calix[4]arenes as carriers for carbonate selective sensor. The sensor exhibited a linear response over a small concentration range (5.0×10^{-4} to 1.0×10^{-1} mol L^{-1}) with a slope of 29.2 mV decade^{-1} of activity.

The high concentration of nitrate is toxic for some aquatic life and is cause of fish death in marine water. It can inhibit growth, impair the immune system and cause stress in some aquatic species. Thus, it is necessary to determine concentration of nitrate in marine and environmental sample. Hutchins and Bachas [310] reported NO_3^- -selective sensor based on electrochemically modified polypyrrole. It was highly selective for nitrate ion over lipophilic salicylate or perchlorate ions. Some recently developed membrane sensors based on lipophilic derivative of iodocobalt(III)salen [311], (2-hydroxyanil)acetylacetone lead(II) [312], tris(2-aminoethyl)amine [313] and bis(2-hydroxyacetophenone) ethylenediimine vanadyl(IV) [314] showed good selectivity for NO_3^-. Schwarz *et al.*, [315] prepared NO_3^- -selective sensor using tridodecylmethyl ammonium nitrate as electroactive material and applied it for in-situ determination of NO_3^- in ground water and drinking water.

Sulphate is important in both the chemical and biological system. There are some sulphate selective sensors reported in the literature. Li *et al.,* [316] developed a sulphate selective sensor based on a derivative of imidazole as neutral carrier which showed strong interference to bromide and nitrate ions. Morigi *et al.,* [317] prepared another sulphate selective sensor based on hydrotalcites, which showed improved selectivity for sulphate over a number of anions. Recently, Ganjali *et al.,* used zinc-phthalocyanine [318], pyrylium perchlorate [319] and Schiff base complex of Zn (II) [320] to develop SO_4^{2-} -selective sensors. These sensors were used as an indicator electrode in the potentiometric titration of SO_4^{2-} with Ba^{2+}.

Thiocyanate selective sensors based on nickel and iron phthalocyanines were described by Amini *et al*,. [321]. These sensors demonstrated near Nernstian response over a wide linear concentration range of 5.0×10^{-7} to 1.0×10^{-1} mol L^{-1} of SCN^- and were also applied for the determination of SCN^- in urine samples. Another SCN^- -selective sensor was prepared by Poursberi *et al.,* [322] using copper-1,8-dimethyl-1,3,6,8,10,13-azacyclotetradecane complex as electroactive material. The sensor responded over to thiocyanate in linear range from 7.0×10^{-6} to 1.0×10^{-1} mol L^{-1} and was used in potentiometric determination of thiocyanate in saliva and urine samples. Hassan *et al.,* [323] reported thiocyanate selective sensors based on imidepyridine derivatives. The sensors were used for direct potentiometric measurements of thiocyanate ions over the concentration range of 0.2-580 μg mol L^{-1} and for monitoring sequential titration of some metal ions (e.g. Ag^+, Tl^+, Cu^{2+} and Pb^{2+}) in binary and ternary mixtures. Recently, Erden *et al.,* reported thiocyanate selective sensor based on 4-*tert*-butyl-tetra cyanomethoxycalix[4] arene which exhibited a linear response over the concentration range of 3.0×10^{-5} to 1.0×10^{-1} mol L^{-1} of SCN^- with a slope of 52.0 mV $decade^{-1}$ of activity [324]. Application of the sensor to the potentiometric titration of thiocyanate ion with silver nitrate has also been reported.

Phosphorus, a key nutrient in plant and microorganisms is involved in several biological and environmental processes. Thus, the determination of phosphate is important and many phosphate -selective potentiometric sensors have been developed using a variety of electroactive materials. Glazier and Arnold [325] reported dihydrogen phosphate selective sensors based on dibenzyltin dichloride. A study by Chaniotakis *et al.*, [326] led to the development of a phosphate -selective sensor based on a multidentate-tin (IV) carrier incorporated into liquid polymeric membrane. Liu *et al.*, [327] prepared a monohydrogen phosphate selective sensor by using bis(tribenzyl)tin oxide which showed Nernstian response in the concentration range of 5.0×10^{-6} - 1.0×10^{-1} mol L^{-1}. Sasaki *et al.,* [328] developed phosphate selective sensor based on organotin compounds. Recently, Gupta *et al.,* [329] reported monohydrogen phosphate selective sensor based on hexakis (carbamoyl -methoxy)calix[6] arene which worked in the concentration range of 1.7×10^{-5} to 1.0×10^{-1} mol L^{-1} and showed interference to ClO_4^- ion. Many other compounds *viz.,* cobalt phthalocyanine [330], polyamine [331], uranyl salophene [332], vanadyl salophene [333], guanidinium [334] and thiourea [335] have also been used as phosphate selective ionophores. Despite high selectivity for phosphate, the membranes containing these ionophores exhibited in many cases strongly sub-Nernstian response or very short functional life time (a few days) due to the degradation of ionophore molecules.

Salicylate-selective sensor based on lutetium(III)porphyrin was prepared by Messick *et al.,* [336]. Further, salicylate selective sensors based on complexes of Sn(IV) with 8-hydroxyquinoline and tetrakis(tert-butyl)phthalocyanine was developed by Blikova *et al.,* [337] and used to determine acetylsalicylic acid in medical preparations. A ClO_4^- selective sensors based on mercury(II) complexes of calix[4]arene derivatives was developed by Wroblewski *et al.,* [338]. This sensor showed linear response in the working concentration range of 1.0×10^{-5}-1.0×10^{-2} mol L^{-1} ClO_4^- with a slope of 56.5 mV $decade^{-1}$ of activity, but shows interference to iodide ion. Polyazacyclo alkanes were used by Lizondo-Sabater *et al.,* [339] to prepare ClO_4^- ion-selective electrode while Mazloum *et al.,* [340] reported ClO_4^- -selective membrane sensor based on a new complex of uranil and applied it for the determination of ClO_4^- in urine and water. Arsenite selective sensor was prepared by Gupta *et al.,* [341] using cobalt(III) *p*-tertramethoxyporphyrin as electroactive material which showed linear potential response in the working concentration range of 7.9×10^{-5} - 1.0×10^{-1} mol L^{-1} AsO_2^- with a slope of 28.8 mV $decade^{-1}$ activity. The sensor worked satisfactorily in non-aqueous medium and showed good selectivity for arsenite over a large number of anions.

1.3.6. Miscellaneous sensors

Ion-selective electrodes for organic ions, surfactants, biomolecules and gases have also been reported. Ueda [342] made use of p-1,1,3,3-tetramethylbutylcalyx[6]arene-hexaacetic acid hexaethyl easter embedded in PVC matrix to develop electrode for methylamine. The electrode shows a near Nernstian response in the concentration range of 1.0×10^{-5} - 1.0×10^{-2} mol L^{-1} with a slope of 58.5 mV $decade^{-1}$ of activity. Zhang and Yu [343] worked on the synthesis and membrane transport characteristic of macrocyclic polyether composed of 1,10-phenanthroline as carriers for primary amines. Mohammad *et al.,* [344] developed histamine selective electrodes using iron(III) and manganese(II) porphyrins and applied them to determine histamine in synthetic serum samples. Recently, Varga *et al.,* [345] describe a novel method for the preparation of anionic surfactant-selective electrode. Besides these, other ISEs have been developed for gases and organic species. Arnold *et al.,* [346] worked on the determination of glucose in a synthetic biological matrix. Stefan and co-workers [347] constructed potentiometric, enantio-selective membrane electrodes for the assessment of l-proline. Kumar *et al*., [348] developed a conductimetric immunosensor based on poly(3,4-ethylenedioxythiophene). A nicotine-selective sensor [349] has been prepared by adding silicotungstic acid and di (2-ethylhexyl) phthalate in PVC matrix which showed Nernstian response in the range $1\times 10^{-6} – 1.0 \times 10^{-4}$ mol L^{-1} nicotine. In addition to organic species, a number of gas sensors for NH_3, CO_2, SO_2, NOx, H_2S and O_2 have been reported [350]. The NH_3 gas sensors have been used in the analysis of fresh water, effluents and sewage, CO_2 sensor for blood analysis, SO_2 sensor for food and beverages and NOx for the measurement of nitrite in soil extracts and water samples. Electrochemical immunosensors were developed by Guilbault *et al*., [351] for the detection of 19-nortestosterone and methyltestosterone in bovine urine. Guilard and co-workers [352] designed a colorimetric sensor based on a 1,8-diaminoanthraquinone signaling subunit which exhibited efficient binding for lead ion in water and can be detected by naked-eye. Glennon *et al.,* [353] synthesized and electropolymerized *N*-acetyltyramine with a negatively charged sulfobutylether-*β*-cyclodextrin on a boron-doped diamond (BDD) electrode for dopamine detection.

1.4. The Problem

An overview of literature has revealed that intensive research has been done on ion-selective electrodes for the determination of alkali, alkaline earth, heavy metals and some anions. A large number of ISEs are reported for every single ion, however, for most of the ions, even the best sensor so far developed is not the final word and can always be improved in some respects with the availability of newer selective materials. Further, literature survey shows that the most of the sensors reported for molybdenum, promethium, fluoride and mercury metal ions are not of very high selectivity and generally show high response time and limited working concentration range. As the determination of these ions is important, attempts have been made to develop ISEs for these metal ions which show improved performance compared to the existing ones.

Therefore the research in the field of ISEs has been directed mainly in two directions (i) To develop more selective and sensitive sensor for many metals, anions for whom electrodes are not very high quality are available. (ii) To develop electrode systems for ionic species for whom ISEs have not been reported.

The main requirement for developing ion selective electrode is to use a material in the membrane phase which can act as good ionophore. It may allow transport of some ionic species selectivily. The major problem in the development of good ion-selective electrode is non availability of selective ionophores. Different types of materials such as insoluble salts of multi valent metals, solid electrolytes inorganic and organic exchangers, schiff bases, macrocycles and calixarenes have been used. A some newly synthesized schiff base and calixarene have been found to show strong affinity to some selective ionic species. We have therefore, uses them to develop ISEs for promethium (Pm^{3+}), molybdenum (Mo(V)), fluoride (F^-) and mercury (Hg^{2+}).

Survey of literature shows that only few ion selective electrodes reported for the promethium. In view of its toxic nature and its application in various fields, it is important to have analytical systems for quick determination of promethium in various samples. We have therefore used a schiff bases *viz.*, 3,5:12.14:21,23-tribenzo-8,9:17,18:26,27-tricyclohexyl-1,6,10,15,19,24-hexaazo-[27]-1,6,10,15,19,24-triene **(X_1)** and 15,17,32,34-tetramethyl-3,29-dioxa-11,12,16,20,21,35-hexaazapentacyclo[29.3.1.114,18.04,9.023,28]-

hexatriaconta 1(35),4,6,8,10,14 (36),15,17,21,23,25,27,31,33-tetradecaene-13, 19-dione **(X_2)** showing good affinity for Pm^{3+} as a ionophores for developing Pm^{3+} selective electrodes.

New schiff bases *viz.*, 4,8-diaza-3,3,10,10-tetramethyl-1,2-dithiacyclodecane **(S_1),** 5,8-diaza-3,3,10,10-tetramethyl-1,2-dithiacyclodecane-*N,N''*-diacetic acid **(S_2)** and *N,N''*-bis(2,2-dimethyl-2-mercaptoethyl)-ethylenediamine-*N,N"*-diacetic acid **(S_3)** showing good affinity for molybdenum have been used for preparing membranes as molybdenum selective electrodes.

polyether compounds *viz.*, 6H,22H,30H,41H-trinaphtho[2,3-m:2',3'-t;2',3''a] [1,4,7,11,15,19,22,26,11,30]heptaoxadiazacyclotritriaccontine-6,22-dione,7,8,9,10,12,13, 15,16,18,19,20,21,31,32,42,43-hexadecahydro-31,42-bis(methylene) **(M_1),** 7H, 23H-34,39etheno-6,43;24,30-dimethenotribenzo[o,v,g] [1,4,7,11,34]trioxadiazacyclohepta-triacontine-7,23-dione,8,9,10,11,13,14,16,17,19,20,21,22,31,32,33,40,41,42-octadecahydro 44,45,46,47-tetrahydroxy-32,41-bis(methylene.) **(M_2),** 7H,23H-34,39-etheno-6,43;24,30-dimethenotribenzo[o,v,g][1,4,7,11,34]trioxadiazacycloheptatriacontine-7,23-boropyrene,8, 9,10,11,13,14,16,17,19,20,21,22,31,32,33,40,41,42-octadecahydro-44,45,46,47-tetrahydroxy-32,41-bis(methyene) **(M_3)** and Dinitrophenyl functionalized tris-(amide) **(M_4)** have been found to exhibit high affinity for fluoride and have therefore been used to prepare PVC based electrode for F^-.

Finally, a new reported calixarene *viz.*, 5,11,17,23-tetra-tert-butyl-25,27-dihydroxy-26,28-bis(O-methyl glycylcarbonylmethoxy) thiacalix[4]-arene has been found to exhibit strong affinity towards Hg^{2+} and has, therefore been used as ionophore to prepare PVC based Hg^{2+} selective electrode. The results of above investigation are incorporated in chapter three to sixth of this thesis.

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2.1. Theory

In an ion selective electrode, a semipermeable membrane separates two solutions of different concentration of an appropriate electrolyte and the electric potential developed across the membrane is observed under zero current condition; i.e., when there is no transport of charge at any point in the system. The generation of membrane potential generally depends upon the ratio of activity of diffusible ions present on the two sides of membrane. Thus, the membrane potential can be used to determine activity/concentration of an ion by a proper membrane setup [1]. The theory of ion-selective electrodes and methodology adopted in such determinations is briefly discussed here.

A semipermeable cation-exchange membrane when placed between two solutions having different concentration of an electrolyte AY allows the diffusion of A^+ from higher to lower concentration side as membrane is more permeable to these ions and hinders partially or totally the diffusion of other ion Y^-. As a result, an electrical double layer is formed across the membrane and electrical potential gradient thereby generated. This potential is called membrane potential (E_m) and is the sum of Donnan and diffusion potential. Since potential developed across a membrane depends upon the activity of a particular charged species, it can be used to determine the activity of that species in any solution. Membrane potential E_m is given by the following expression [2]:

$$E_m = \frac{2.303RT}{Z_A F}\left[\log\frac{(a_A)_2}{(a_A)_1} - (z_Y - z_A)\int_1^2 t_Y^- d\log a^{\pm}\right] \qquad (1)$$

Where z_A and z_Y are the charges on the ion A and Y, respectively, t_y^- is the transport number of Y, $a^{\pm}$ is the mean activity of electrolyte and $(a_A)_1$ and $(a_A)_2$ denote the activities of A^+ in solutions 1 and 2, respectively.

First term on the right hand side of the equation (1) indicates the thermodynamic limiting value of the concentration potential, i.e. Donnan potential while the second term indicates the diffusion potential caused by co-ion flux in the membrane. However, if the membrane is treated to be ideally permselective ($t_y^-=0$), then equation (1) shows the Nernst equation form.

$$E_m = \pm \frac{2.303RT}{Z_A F} \log \frac{(a_A)_2}{(a_A)_1} \qquad (2)$$

Thus the equation (2) represents ideally permselective membrane's Donnan potential. The +ve sign will be for cation selective and –ve for anion selective membranes. The term can be considered as it gives thermodynamic limiting value of the concentration potential.

The following cell set up is generally used for the measurement of membrane potential using saturated calomel electrodes (SCE) or other reference electrodes.

External Reference Electrode (SCE)	External or Test Solution of AY	Membrane	Internal Solution of AY	Internal reference electrode (SCE)

2 1

$E_{L(2)}$ $E_{L(1)}$

Generally, compartment 1 contains reference or internal solution whose concentration is kept constant and the calomel electrode which dipped in it is called as internal reference electrode. The membrane part of these components i.e., internal reference electrode and internal solution is known as membrane electrode or membrane sensor. The saturated calomel electrode dipped in external solution, which is usually referred to as test solution or sample, is known as external reference electrode.

The electromotive force (emf) across this cell is the sum of all individual potential contributions. Many of these are sample-independent and the measured emf can usually be described by the following expression

$$E_{cell} = E_{cal} + E_{L(2)} + E_m + E_{L(1)} - E_{cal} \qquad (3)$$

Where E_{cal}, E_L and E_m are the saturated calomel electrode potential, liquid junction potential and membrane potential, respectively. From equations (2) and (3):

$$E_{cell} = E_{cal} - E_{cal} + E_{L(1)} + E_{L(2)} \pm \frac{2.303RT}{Z_A F} \log \frac{(a_A)_2}{(a_A)_1}$$

$$E_{cell} = [E_{L(1)} + E_{L(2)} - \frac{2.303RT}{Z_A F} \log (a_A)_1\ ] + \frac{2.303RT}{Z_A F} \log (a_A)_2 \qquad (4)$$

(For cation exchange membrane)

The values of $E_{L(1)}$ and $E_{L(2)}$ are small and generally remain constant. Also the term $\frac{2.303RT}{Z_A F} \log (a_A)_1$ remains constant if the concentration of internal solution is not changed. Therefore, in a given experimental setup, all the terms in parenthesis of equation (4) are constant and can be substituted by a constant E'_0. The value of E'_0 would change only when experimental conditions are changed. The equation (4) is reduced to well-known Nernst equation

$$E_{cell} = E'_0 + \frac{2.303RT}{Z_A F} \log (a_A)_2 \qquad (5)$$

Thus, the equation (5) indicates that the cell potential is directly proportional to the concentration or activity of the sample ions in aqueous solution under investigation. Attempts are generally not made to determine the membrane potential by subtracting external SCE potential. The whole electrochemical cell as described above is taken as a sensor and the value of E_{cell} gives activity of the ion of interest. If for a developed membrane sensor, the slope of the plot between E_{cell} and $\log(a_A)_2$ comes out to be equal to theoretical slope i.e., $\frac{0.0591}{Z_A}$, then the membrane is said to be ideal as it has responded according to Nernst equation (5) [3 - 5]. The slope of such a membrane is called Nernstian slope.

2.2. Classification of ion-selective electrode

The research on ion-selective electrodes (ISEs) has also been long dated but the continuous effort has been proved that it can use in different application or in improving the reported works. Recently the use of ISEs in biological research has shown a remarkable evidence to put up a new step toward a new application. The initial era saw an intensive search for novel electrode materials and new construction; this has given way subsequently to more introspective studies on ion selective and electrode mechanism. The rapid expansion of activity in the field of ISEs makes them highly desirable to have an idea of their categories as well for their practical applications.

According to IUPAC recommendations [6], ion-selective electrodes are classified in the following categories according to the physical state of the substances forming the electrode membrane, or possibly according to the nature of the substances affecting the ion exchange in the membrane.

2.2.1. Primary ion selective electrodes

2.2.2. Sensitized or Compound (multiple layer membrane) ion selective electrodes

2.2.3. Metal contact or solid-state ion selective electrodes.

2.2.1. Primary ion selective electrodes

These electrodes develop potential due to some ionic species. They have been further divided into two classes based on the preparation of their membrane.

2.2.1.1. Solid membrane electrodes

These are the electrodes in which the physical state of the membrane is solid. Depending on the composition of the membrane, these are further sub-divided into the following three categories.

a. *Glass electrodes*

These electrodes have membrane made of glass of various compositions. The operation of a glass electrode depends on an ion exchange process which involves migration of cations from one interstitial site to other. The first glass membrane H^+ ion-selective electrode has the composition as Na_2O (22%), SiO_2 (72%) and CaO (6%).

b. *Homogenous solid state electrodes*

These are the electrodes in which the membrane is prepared either from a single compound or from a homogenous mixture of two or more electroactive compounds in the form of a pellet or disc under high pressure. The electrodes prepared in this category are mainly made of silver halides, silver sulphides and lanthanum fluoride membranes and are used for the determination of halides, sulphide and silver ion. One of the most successful ISEs belonging to this category is LaF_3 based F^- ion-selective electrode.

c. *Heterogeneous solid state electrodes*

Heterogeneous electrodes include those where the sensing membrane is prepared by dispersing the active material in a chemically inert binder such as poly(vinyl chloride), silicone rubber, epoxy resins and paraffin. The binder and the electroactive compound are thoroughly mixed and a membrane is prepared. The inert binder not only provides a good adhesion matrix for the sensor particles but also makes the membrane flexible and crack resistant to prevent leakage of internal solution. It is important to mention that the binder should be compatible with the active material and should not swell in the sample solution.

2.2.1.2. Liquid membrane electrodes

The membrane of these electrodes consists of an organic liquid, immiscible with water, in which an electroactive material/ionophore has been dissolved. Normally those electroactive materials are chosen which show high exchange capacity for a particular ion and poor for all others. The solvent of the liquid membrane must be immiscible in water, have low vapour pressure, high viscosity and low dielectric constant to allow considerable association of the ions in the membranes.

2.2.2. Sensitized or Compound (multiple layer membrane) electrodes

These are usually the modified form of primary electrodes and are used to determine the concentration of gases and organic molecules rather than ions. In these electrodes, an ISE is combined with a specific chemical reaction or a separation step. They constitute a very important group because of their inherent selectivity as two membranes with their own characteristics are used to generate the response. This group of electrodes is further divided into the following two sub-headings.

2.2.2.1. Gas sensing electrodes

In gas sensing electrodes, a conventional ISE is coated with a thin film of reagent solution. A gas permeable membrane is interposed between this electrochemical cell and the sample under test. The gas to be determined diffuses through the separation layer until equilibrium is established in the internal electrolyte film. The dissolved gas and the reagent of the internal electrolyte constitute a buffering system. The activity of the buffered ion is determined by the ion-selective electrode.

2.2.2.2. Enzyme substrate electrodes

In these electrodes, the membrane is coated with a material containing an enzyme (between the solution and the glass electrode) which produces species by undergoing the reaction of an organic or inorganic substance (substrate). The produced species are responsible for the sensitivity of the electrode. Alternatively, the electrode is assayed by covering with a layer of substrate that which reacts with the enzyme, inhibitor or co-factor.

For example, a membrane containing immobilized urease, catalytically decomposes ambient urea to ammonium ions, which are sensed with a cation-selective glass membrane electrode.

2.2.3. Metal contact or Solid-state ion-selective electrodes

The solid solvent membrane composed of an electroactive compound is immobilized on the surface of a conducting solid. There is no inner electrolyte solution in these electrodes and the inner reference electrode is replaced by an electronic conductor, e.g., a bromide sensor film of AgBr is reversibly contacted with Ag, or an anion sensor based on cation radical salts is contacted with Pt. This configuration contrasts with normal membrane electrodes in which electrolyte solutions (inner filling solution and outer test solution) are in contact with opposite membrane sites. These electrodes offer the advantage of low detection limit, extended linear working range and high selectivity.

2.3. Term used in ISEs

Before further discussion on the performance of ion-selective electrodes, some of the terms used need to be defined. IUPAC compendium of nomenclature [7,8] is helpful in sorting out the terms.

2.3.1. Membrane

Membrane is a phase, finite in space, which separates two other phases and exhibits resistance to the permeation of different species [9]. Ion selective electrodes generally employ homogeneous/heterogeneous membranes of chemical compounds. The capability to differentiate between various permeating species is the principal characteristics of a membrane used in electrochemical sensors. This differentiation leads to the formation of an electrical double layer, which is the source of electric potential. The potential developed is basically due to two processes:

(i) Different mobilities of the ions through the membrane resulting in the generation of diffusion potential

(ii) Donnan or phase boundary potential arising from non-transport of one or more kind of ions. The potential developed is a function of activity ratios of the exchangeable ions on the two sides of the membrane.

Therefore, it can be used to determine the activity of an unknown solution. For the satisfactory performance of the membrane, the diffusion potential should be absent or be minimal. The membrane plays a critical role in the performance of the sensor in a particular environment. A successful membrane needs to be generally hydrophobic, have ion-exchange properties and contain a lipophilic ionophore that provides selectivity to the sensor. The lack of ion-exchange properties would lead to substantial uptake of sample cations as well as anions into the membrane, leading to effective breakdown of so-called perm selective behaviour. In some instances membrane materials are susceptible to *in vivo* oxidative cleavage and hydrolysis. This would cause deterioration of the membrane and in the long term would render the sensor inoperative.

2.3.2. Membrane Components

In general, the polymeric membrane used in ISEs consists of four components: Electroactive material (ionophore), lipophilic additive, plasticizer and the polymer matrix. The detailed description is described in subsequent sections.

i. Electroactive Material (Ionophore)

Ionophore or ion carrier is the key components of polymeric membrane ion-selective electrodes that govern the ion selectivity and sensitivity, due to the sensitive behaviour of the ISE in molecular-level is the binding between the ionophore and target ion. Ideally, it should be form reversible and relatively strong complex with target ion in presence of other ions. Various substances *viz.*, inorganic and organic ion exchanger, solid electrolyte, salts of multivalent atoms, metal chelates, polyaza and polythia macrocycles, crown ethers, cryptands and calixarenes; which have been used as ion carriers for the preparation of ISEs.

To be used as suitable ion carrier; the electroactive material should be physically compatible with the matrix, have a low solubility product, must exhibit some electrical conductivity, have balance between the free energies of ion-ionophore interaction and high conformational flexibility in order to guarantee rapid ion exchange at the membrane sample interface. To keep the concentration on ionophore constant in the membrane, the ionophore must retain within the membrane; thus, along with the binding centre it should contain numerous lipophilic groups to enhance its lipophilicity. Depending upon the nature of ionophore, ISEs can be classified into three different classes:

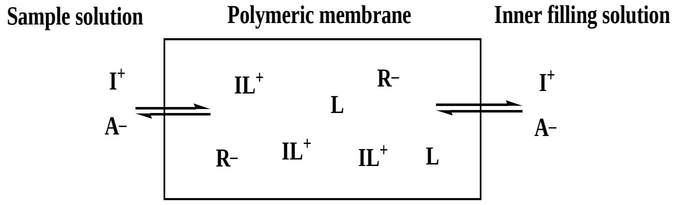
(i) Neutral carrier based ion-selective electrodes

(ii) Charged carrier based ion-selective electrodes

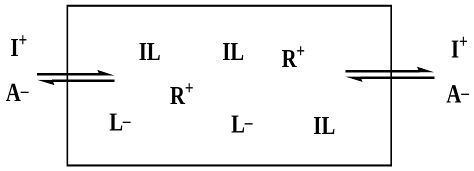
(iii) Ion exchanger based ion-selective electrodes.

Schematic representation of the equilibria between sample, ion-selective membrane, and inner filling solution for three important classes of solvent polymeric ion-selective membranes is shown in Figure 2.1 which shows formation of ion-ionophore complex in the membrane phase [10].

Neutral carrier based ion-selective electrode



Charged carrier based ion-selective electrode



Ion exchanger based ion-selective electrode

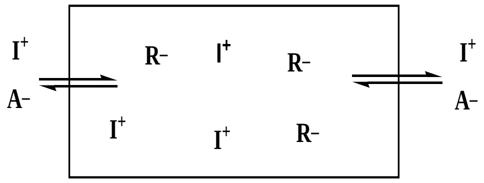


Figure 2.1: Representation of equilibria between sample membrane and inner filling solution: Top: electrically neutral carrier (L) and lipophilic cation exchanger (R-); center: charged carrier (L-) and anion exchanger (R+); and bottom: cation exchanger (R-).

ii. *Polymeric (Inert) Matrix*

The matrix used provides an inert base that imparts physical-mechanical stability and elasticity to the membrane. As it was mentioned above, polymer membrane gives a unique opportunity to electrode to obtain a selective towards particular ions by doping membrane with certain ionophore. Polymer matrix should be chemically inert, hydrophobic, flexible, non-porous; stable and crack resistant. Moreover, it should not swell in sample solutions. Polymers as homogenous membrane matrices first came in use with charged carriers. Poly(vinyl chloride) (PVC) [11], Silicon rubber [12], some methacrylates [13], polyurethanes [14] and polystyrene [15] have been demonstrated as polymer matrices meeting this requirement. However, the most commonly used polymer is PVC due to simplicity of membrane preparation. Although, different binders are in the used in the fabrication of solid state heterogeneous membrane electrodes, PVC has been found to be widely used, because of its relatively good mechanical properties, low cost, inertness and easy of plasticization and membrane prepare.

It also offers good resilience to mechanical and pressure damage as well as the electroactive materials is highly compatible with the matrix resulting in their reduced leaching from the membrane and the electrode life is increased to a substantial extent. Moody *et al.,* [16] discussed a detailed comparative study of PVC with other polymeric materials and their influence on the performance characteristics of Ca^{2+}-selective electrode was determined. Buck *et al.,* [17,18] discussed the properties of PVC and found that the presence of dissociated fixed exchange sites contributes to the electrode response and selectivity. Further, Mikhelson also reviewed the advantages and disadvantages associated with the PVC matrix [19]. The incorporation of neutral carrier in a PVC matrix has provided an economical way of simplifying ISE construction.

iii. Solvent mediator or Plasticizer

Plasticizers are the high molecular weight compounds which are used in polymeric membranes to enhance its flexibility, softness and provide mobility of membrane materials throughout the membrane phase. A good plasticizer should exhibit high lipophilicity, low tendency to exudates from the polymer matrix, improves capacity to dissolve the membrane components, low vapor pressure and dielectric constant and viscosity should be adequate [20]. Insufficient plasticizer lipophilicity causes its leaching from the membrane and, which is especially undesired for *in-vivo* measurements, for microelectrodes and sensors working under flow conditions. Extension of plasticizer alkyl chains may be a partial solution, as it may lead to incompatibility of plasticizer with membrane components. The membrane polarity, which may give a selectivity modifying influence because of the improved solvation of high valence ions by more polar media, depends also on the nature of membrane plasticizer.

It is well documented that the addition of plasticizers, significantly improve the working ability along with the improvement in the stability, shelf life and detection limit of the sensor. Being a dominating component of PVC membranes, plasticizer behaves as a membrane solvent, influence selectivity of membrane through both extraction of ions into organic phase and influencing their complexation with the ionophore [21,22].

In order to obtain a homogeneous organic phase, plasticizer must be compatible with the polymer and other membrane constituents have to be soluble in it. The main classes of plasticizers for polymeric ISEs are defined by now comprise lipophilic esters and ethers [23]. Polymeric membranes usually comprise of a matrix containing *ca.* 33 % (w/w) of PVC and 65 % of (w/w) plasticizer. A number of organic solvents such as phthalates, dioctylsebacate, 2-nitrophelyl octyl ether, acetophenone and benzyl acetate have been suitably and efficiently used as plasticizer to enhance the performance of ISEs.

iv. Lipophilic Additive or Lipophilic Ionic Sites

The prerequisite for obtaining a theoretical response with ISE membranes is their perm-selectivity, which means that no significant amount of counter ions may enter the membrane phase. Lipophilic ionic additive is a salt of non-exchangeable lipophilic anion/cation and an exchangeable counter ion. Their main function is to render the ion selective membrane permselective by reducing interference due to foreign ions, to optimize sensing selectivity (by defining the ratio of complexed to uncomplexed ionophore concentration in the membrane) and to reduce the bulk membrane impedance [24,25]. Besides, the presence of lipophilic additive in ion selective membrane not only diminishes the ohmic resistance but also increase the sensitivity of membrane electrodes. These additives may also catalyze the exchange kinetics at the sample-membrane interface [26, 27]. Thus, the concentration of additive relative to the ionophore has an important selectivity modifying characteristic due to the influence of the involved equilibrium. Lipophilic ion exchangers traditionally used for polymeric membrane preparation are the anionic tetraphenylborate derivatives *viz.*, Sodium tetrakis-[3,5-bis(1,1,1,3,3,3-hexafluoro-2-methoxy-2-propyl)-phenyl]borate trihydrate (NaHFPB), Sodium tetraphenyl borate (NaTPB) and potassium tetrakis p-(chloro phenyl)borate (KTpClPB) and the cationic tetraalkylammonium salts *viz.*, tridodecyl methylammonium chloride (TDDMACl), hexadecyl trimethylammonium bromide (HTAB) and Tributylammonium chloride (TBAC). The charges on both lipophilic ions are localized on a single (boron or nitrogen) atom, but the steric inaccessibility of the charged center, due to bulky substituents, may inhibit ion-pair formation in the membrane and provide, when necessary, non-specific interactions between ionic sites and sample ions.

2.3.3. Combination electrode or Cell assembly

It is an electrochemical apparatus that incorporates an ion-selective electrode and a reference electrode in a single assembly, thereby avoiding the need for a separate reference electrode. A simple format of the assembly is represented schematically in Figure 2.2.

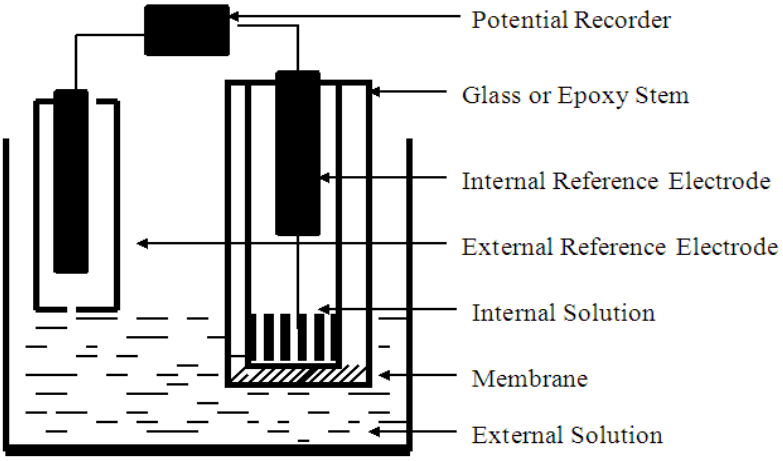


Figure 2.2: Schematic representation of membrane electrode cell assembly.

2.3.4. Calibration curve

The cell potential of the assembly is changed when the activity of the solution of primary ion is altered. According to recommendation of IUPAC a calibration plot is a plot of the cell potential (ISE potential minus external reference electrode potential) of a given ISE versus the logarithm of the ionic activity or concentration of primary ion. It determines the performance characteristics of the ion selective electrode and is used in the determination of primary ion concentration. For a primary ion A, the logarithm of its activity (log a_A) is usually plotted along the abscissa of the graph and the cell potential is plotted along the ordinate. A Typical calibration curve ordinarily is shown in Figure 2.3.

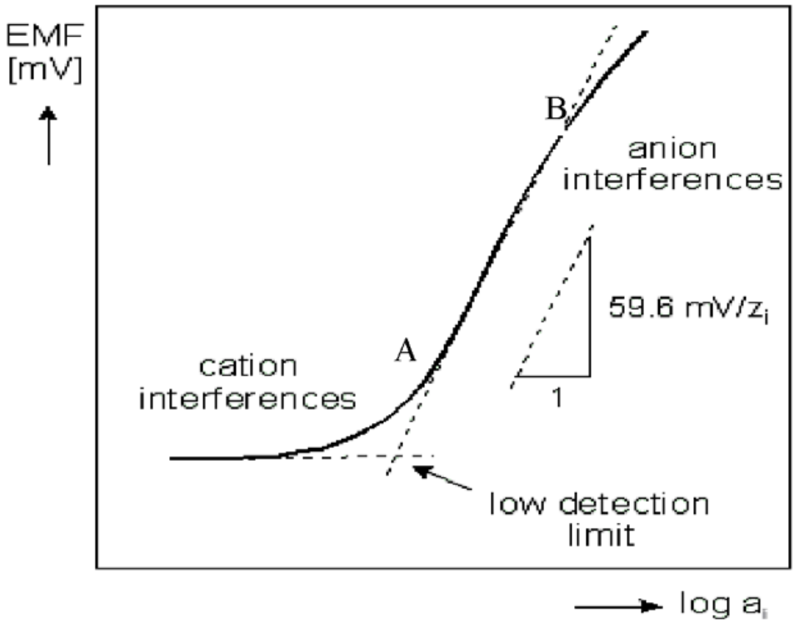


Figure 2.3: Calibration curve of an ion-selective electrode.

2.3.5. Limit of detection

According to the IUPAC recommendation of 1976, detection limit can be defined as the minimum concentration that can be determined for the primary ion. It is obtained from the point of intersection of two extrapolated linear segments of the calibration curve as shown in Figure 2.3. The potential response of ISEs becomes stable below the detection limit. This Nernstian limit is the more important criterion of electrode performance as it specifies the lower limit of the most useful range of the electrode.

2.3.6. Measuring range/Linear range/Working concentration range

The measuring range of ISEs is normally defined as the activity range over which the potential response of the cell is linear. In this range the electrode responds according to the Nernst equation. A maximum range will be achieved if the interfering ion is not complexed at all by the carrier. A typical linear range of the calibration curve of the ISE shown in Figure 2.3 is considered to be its linear part between A and B.

2.3.7. Slope of the electrode

Slope is normally defined as the gradient of the linear portion of the calibration curve. According to Nernst equation (5)

$$E_{cell} = E'_0 + \frac{2.303RT}{Z_A F}\log(a_A)$$

If the slope is equal to 2.303 RT/ z_AF, the slope is normally called Nernstian slope. If the slope of an ISE Nernstian, it is said that the electrode behaviour is ideal. The theoretical values of the slope is 59.1 mV decade^{-1} of activity at 298 K for monovalent ion, 29.5 mV decade^{-1} of activity for divalent ion and 19.7 mV decade^{-1} of activity for trivalent ion.

2.3.8. Response time

The first Recommendations by IUPAC [28] defined the practical response time as “the length of time which elapses between the instant at which an ion-selective electrode and reference electrode are brought into contact with a sample solution and the first instant at which the potential of the cell becomes equal to its steady state value within 1 mV”. In the ‘Recommendations for Publishing Manuscripts’ on Ion-Selective Electrodes issued shortly after, the response time was measured as “the first instant at which the potential of the cell has reached 90 % of the final value”. The corresponding symbol is t_{90}. However, a more recent version of recommendations with the same title reverted to t^* as the preferred expression of response speed. Finally, In 1994 Recommendations for Nomenclature of Ion-Selective Electrodes [1] adopted a still different criterion.

According to it, the response time is the time elapses between the instant at which an ion-selective electrode and a reference electrode are brought into contact with a sample solution and the first instant at which emf/time slope (ΔE/Δt) becomes equal to a limiting value on the basis of the experimental conditions and/or requirements concerning the accuracy.

The IUPAC recommendations outline two experimental procedures for measuring the response time. According to first method so called dipping method, the electrode is instantaneously immersed into a solution of known activity of the target ion; simultaneously the response time is recorded. The response time determined by this method is called as static response time. In second method response time is recorded by varying standard test solutions with different target ion concentrations. The measurement sequence is from lower to higher concentration [29]. To evaluate the reversibility of the electrodes, a similar procedure in the opposite direction can also be adopted.

2.3.9. Lifetime of ion-selective electrode

The lifetime of an ion-selective electrode may be defined as the time interval between the conditioning of the membrane and the moment when at least one parameter of the functionality characteristics of the device changes detrimentally. The working shelf life of an ISEs can vary from a few days to a few months. After this time the slope and detection limit of the sensor get changed significantly. It will depend on the nature of the samples analyzed and the lipophilicity of the ingredients of ion selective membrane. The continuous loss of plasticizer, ionophore or ionic site from the polymeric film into the sample due to an increasing period of exposure finally results in a breakdown of the ion measuring capacity of the system and hence, a primary reason for limited lifetime of ion selective electrodes [30].

2.3.10. Drift

This is the slow, non-random change with time in the potential (emf) of an ion-selective electrode assembly maintained in a solution of constant composition and temperature. The drift in potentials is measured by a linear curve fitting of the data collected in a given period of time.

2.4. Potentiometric selectivity of ISE membrane

Selectivity is the most important characteristic of the ISEs membrane, describing its specificity towards the primary ion in the presence of interfering ions. The ion for which the sensor is designed is called primary ion and all other ions are referred to as interfering ions or foreign ions or secondary ions. In fact, no ISEs responds exclusively to primary ion i.e., specific to it. However, in practice it is more selective to primary ions than to interfering ions. Therefore, it is a necessary parameter to determine as it indicates the commercial potential of any sensor. The degree of selectivity of the sensor for primary ions A, with respect to interfering ion B, is expressed in terms of potentiometric selectivity coefficient ($K^{Pot}_{A,B}$) which is defined by the semi-empirical Nicolsky-Eisenman equation (6).

$$E = E^{\circ} \pm \frac{2.303RT}{z_A F} \log \left[a_A + \sum K^{Pot}_{A,B}\, a_B^{z_A/z_B} \right] \quad (6)$$

Where z_A, z_B, a_A and a_B are the charges and activity of ions A and B, respectively. It is apparent from equation (6) that a value of $K^{Pot}_{A,B}$ =1 at Z_A=Z_B indicates equal response to both A and B. Similarly, the value of $K^{Pot}_{A,B}$ < 1 indicates that the sensor responds more to A in comparison to B i.e., the sensor is selective to A over B. Smaller is the value of selectivity coefficient better is the selectivity. On the other hand, $K^{Pot}_{A,B}$ > 1 indicates that the sensor's response is more towards B rather than A and in such a case it is said that the ion B causes considerable interference. When the charges $z_A \neq z_B$, the values of selectivity coefficient $K^{Pot}_{A,B} \cong 1$ does not indicate equal response to primary and interfering ions as per equation (6), but now it depends on the values of z_A and z_B. For different values of z_A and z_B, $K^{Pot}_{A,B}$ values showing equal response to both A and B have been computed from equation (6) at an activity of 1.0×10^{-2} mol L^{-1} of B and are summarized in Table 2.1.

The $K^{Pot}_{A,B}$ values indicating equal response for both ions A and B not only depend on z_A and z_B but also on the concentration of interfering ions at an activity of 1.0×10^{-3} mol L^{-1} of B, selectivity coefficient values change drastically as seen from Table 2.2.

Table 2.1: Selectivity coefficient values ($K^{Pot}_{A,B}$) indicating equal response of the sensor to both primary (A) and interfering ion (B) at an activity of 1.0×10^{-2} mol L^{-1} of B.

Charge on primary ion (A), z_A	Charge on interfering ion (B), z_B	$K^{Pot}_{A,B}$ Values
1	1	1.00
1	2	0.10
1	3	0.05
2	1	100
2	2	1.00
2	3	0.20
3	1	10^4
3	2	10.00
3	3	1.00

Table 2.2: Selectivity coefficient values showing equal response for primary (A) and interfering ion (B) at an activity of 1.0 × 10^{-3} M of B.

Charge on primary ion (A), z_A	Charge on interfering ion (B), z_B	$K_{A,B}^{Pot}$ Values
1	1	1.00
1	2	0.03
1	3	0.01
2	1	10^3
2	2	1.00
2	3	0.10

Thus, it is seen from Table 2.1 and 2.2 that the discussion of the selectivity of the sensors is rather difficult. At an activity of 1.0×10^{-2} mol L^{-1}, with $z_A=z_B=1$, $K_{A,B}^{Pot}>1$ indicate interference but with $z_A=2$ and $z_B=1$, $K_{A,B}^{Pot}>1$, does not indicate any serious interference. The interference becomes serious when $K_{A,B}^{Pot}>100$. As a matter of fact, with $z_A=2$ and $z_B=1$, a value of $K_{A,B}^{Pot}$ upto 100 means that sensor is more selective to A compared to B. Similar problem also exists when $z_A=1$, $z_B=2$ or $z_A=2$, $z_B=3$ etc. In order to make it easy to appreciate the relative selectivity of the sensor when large number of ions of different charges are involved, it would be better to have only a single value of $K_{A,B}^{Pot}$ that indicates equal response to A and B irrespective of their charges. Viteri and Diamond [31] have proposed a modification in the Nicolsky equation. They neglected the power term from the equation (6) and reported the data. The selectivity coefficient data reported in this way (i.e., by neglecting the power term, $z_{A/}$ z_B) comes out to be on a scale for which $K_{A,B}^{Pot}$ = 1 indicates equal response for both A and B irrespective of their charges. It is important to emphasize that selectivity coefficient values signify the selectivity only at the conditions of determination but in actual practice the interference caused depends on the relative concentration of the primary and interfering ions and other experimental conditions. Though the selectivity coefficient may not reflect exactly the interference level but still it is a very important parameter to estimate the likely performance of a sensor. However, it has been seen that the deviation between the expected performance of a sensor on the basis of selectivity coefficient and the experimental performance is not large. Therefore, it is necessary to evaluate the performance of a sensor in the presence of other ions by determining selectivity coefficient. A number of methods have been described to determine selectivity coefficient [32-34] and are grouped into the following categories.

2.4.1. Separate solution method (SSM)

2.4.2. Mixed solution method (MSM)

2.4.3. Matched potential method (MPM)

2.4.1. Separate solution method (SSM)

In SSM method, the potential of the cell containing test solution of primary ion A of activity a_A is first determined. The emf of this cell E_A is related to the activity of primary ion by the equation (7).

$$E_A = E^0 + \frac{2.303RT}{z_A F}\log a_A \tag{7}$$

Next, the emf of a separate cell containing test solution of interfering ion B of activity a_B is determined. Its emf E_B is related to activity a_B by the equation

$$E_B = E^0 + \frac{2.303RT}{z_A F}\log \mathrm{K}^{Pot}_{A,B}(a_B)^{z_A/z_B} \qquad (8)$$

From equations (7) and (8)

$$\log \mathrm{K}^{Pot}_{A,B} = \frac{E_B - E_A}{2.303RT/z_A F} + \log\frac{a_A}{(a_B)^{z_A/z_B}} \qquad (9)$$

When $E_A = E_B$

$$\mathrm{K}^{Pot}_{A,B} = \frac{a_A}{(a_B)^{z_A/z_B}} \qquad (10)$$

The separate solution method, although simple to perform, is not normally used for the determination of $\mathrm{K}^{Pot}_{A,B}$ values, because it does not represent the actual conditions under which the ion selective electrode is used [35].

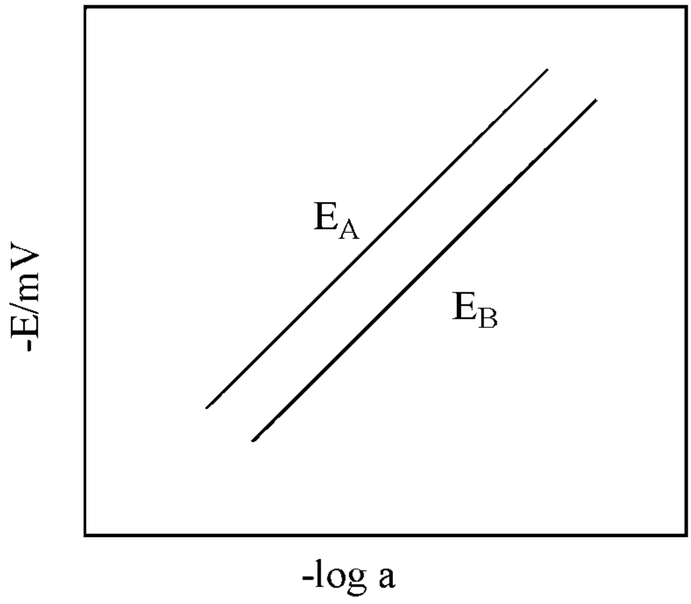


Figure 2.3: Potential *vs*. log a_A plot illustrating the determination of selectivity coefficient

by Separate solution method (activity of B=a_B).

2.4.2. Mixed solution method (MSM)

This method involves measurement of the sensor potential in a range of solutions containing both A and B. Since in real conditions, analyte ion (primary ion) is present together with many other foreign ions (interfering ions). Thus, this method is preferred over separate solution method. There are two procedures for determining selectivity coefficients using MSM.

Procedure I (Fixed Primary Method)

In this method, the potential of the cell containing test solution of primary ion (A) of activity a_A is first determined. The emf of this cell E_A is related to the primary ion by the equation (7). Then, the potential of the cell containing mixed solution of primary ion of activity a_A and interfering ion of activity a_B is determined. The emf of this cell E_{AB} is given by equation

$$E_{AB} = E^\circ + \frac{2.303RT}{z_A F}\log\left[a_A + \mathrm{K}_{A,B}^{Pot}(a_B)^{z_A/z_B}\right] \qquad (11)$$

From equations (7) and (11)

$$\mathrm{K}_{A,B}^{Pot} = \frac{a_A}{(a_B)^{z_A/z_B}}\left[\left(\frac{E_{A,B} - E_A}{10^{2.303RT/z_A F}}\right) - 1\right] \qquad (12)$$

Thus, knowing E_A and E_{AB} selectivity coefficient values can be calculated.

Procedure II (Fixed Interference Method)

In this procedure, the potential of the cell is measured for a number of solutions containing interfering ion of constant activity a_B but varying values of activity of primary ion a_A. The plot of potential so obtained against activity a_A is shown in Fig. 2.4.

This plot generally has three distinct regions. In the first region PQ, the linear response of the sensor indicates that it is responding only to primary ion, A, with no interference caused by B in this concentration range. In the second region QR, deviation from linearity is caused because now the sensor is also responding to the activity of B as the concentration of primary ion decreases. So in this region (QR), the response of the sensor is mixed and is due to both the ions A and B.

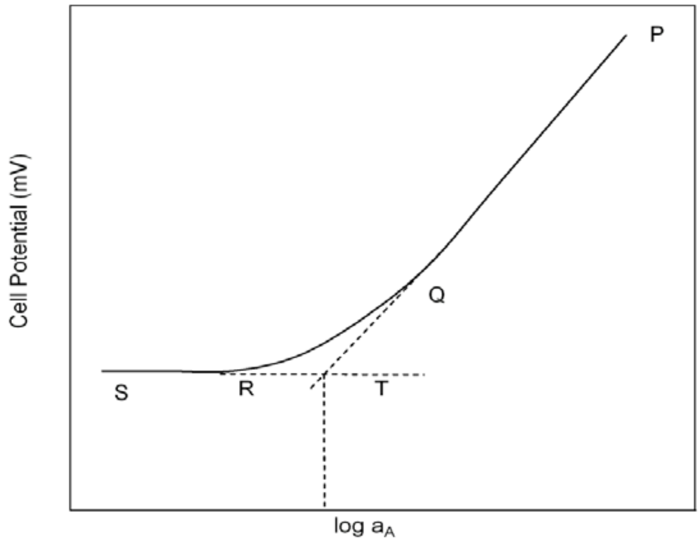


Figure 2.4: Potential *vs.* ($\log_{10} a_A$) plot illustrating the determination of selectivity coefficient by Fixed interference method.

The third region RS of the plot is linear and the potential is constant. Constancy in the potential indicates that the sensor is now only responding to interfering ion B with no contribution arising due to primary ion A. This generally occurs at lower activity of A. As the activity of B is constant and A is not affecting the potential in this concentration range, the potential of the sensor remains constant. The linear portion PQ and RS are then extrapolated and meet at the intersection point T. The potential corresponding to point T can be generated by constant activity of B or by the activity of A. Thus, for point T, E_A is equal to E_B (E_A is generated by A of activity a_A and E_B by B of activity a_B). Under this condition of E_A=E_B, the $K_{A,B}$ can be calculated by the following equation (10) already derived under separate solution method.

$$K_{A,B}^{Pot} = \frac{a_A}{(a_B)^{z_A/z_B}}$$

This procedure of mixed solution method is known as Fixed Interference Method (FIM) and is the most widely used procedure as per IUPAC recommendation for determining selectivity coefficients [36,37]. The reason is that the conditions prevailing at the membrane-solution interface are similar to those which are prevalent while analyzing the sample.

2.4.3. Matched potential method (MPM)

The Matched Potential Method (MPM), which is independent of the Nicolsky-Eisenman equation, was proposed by Gadzekpo and Christian [38] to overcome the difficulties in obtaining accurate selectivity coefficients when ions of unequal charge are involved. In this method, the selectivity coefficient K_{AB}^{Pot} is given by the following expression:

$$K_{A,B}^{Pot} = \frac{a'_A - a_A}{a_B} = \frac{\Delta a_A}{a_B} \qquad (13)$$

and is determined by measuring the change in potential upon increasing by a definite amount the primary ion activity from an initial value of a_A to a'_A and a_B represents the activity of interfering ion added to same reference solution of activity a_A which brings about same potential change. The potential response curve obtained in the matched potential method is shown in Figure 2.5.

This method provides practically realistic values of $K_{A,B}^{Pot}$. The characteristics of Matched potential method are that the charge number on primary and interfering ions is not taken into consideration and Nernstian responses are assumed neither to the primary nor interfering ions. These characteristics lead to the following advantages: (i) the power term problem for ions of unequal charge disappears, and (ii) the method is applicable even to non-Nernstian interfering ions.

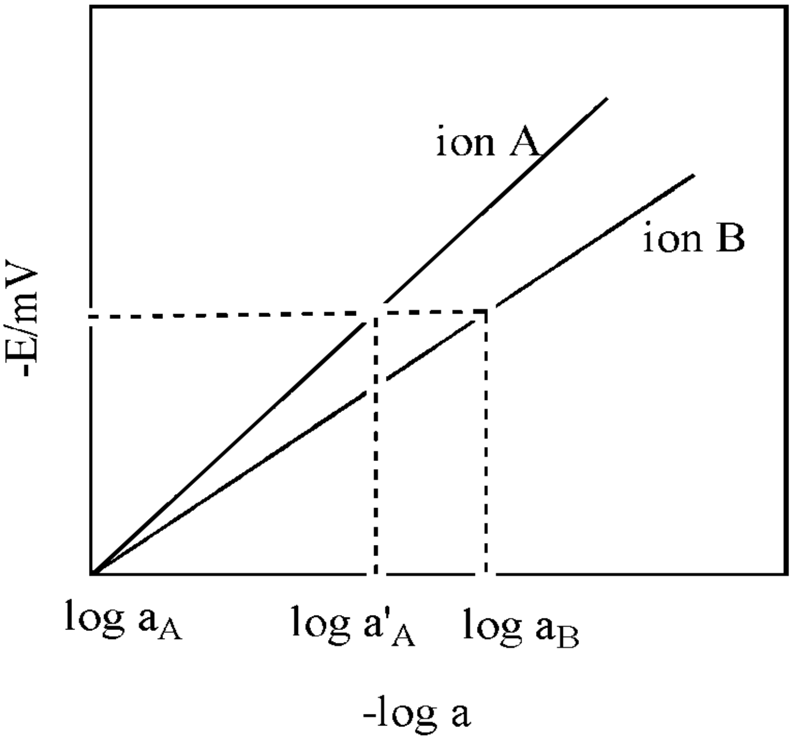


Figure 2.5: Potential *vs.* log a_A plot illustrating the determination of selectivity coefficient by Matched potential method (activity of B = a_B).

However, as this method is independent of the Nicolsky-Eisenman equation or its modified forms, and it is therefore difficult to correlate the values of $K_{A,B}^{Pot}$ obtained by this method with any particular phenomena such as ion exchange [39].

It is seen from the above paragraphs that the selectivity of ion selective electrode depends on the experimental conditions, usually the concentration of ions and the method of determination. It is for this reason, $K_{A,B}^{Pot}$ is not called selectivity constant but selectivity coefficient. Further, different methods give different values of selectivity coefficient as the conditions prevailing at the membrane-solution interface are not same [40-42]. In this thesis, the selectivity coefficient values have been determined using Fixed Interference and Matched Potential methods and the values have been worked out from the experimental data using equations (10) and (13).

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3.1. Introduction

Promethium is a highly radioactive lanthanide and a synthetic rare earth metal. Promethium-145 is the most common radioactive isotope with a half life time of 17.7 years. Promethium is a normal by product of the nuclear fission of uranium-238 and the radioactive decay of europium-151. It can also be synthesized by bombarding the more common lanthanide metal neodymium with neutron radiation, or by ion-exchange technology. Promethium (III) trichloride mixed with zinc sulphide was used as a major luminous paint for watches. This mixture is still occasionally used for some luminous paint applications. It is used in nuclear battery [1] in which cells convert the beta emissions into electric current. It has possible future applications in portable X-ray sources, and as auxiliary heat or power sources for space probes and satellites. High performance liquid chromatography [2] and liquid scintillation counting techniques [3] are limited methods for the determination of promethium in real samples. Therefore, a need was felt for the development of a rapid and sensitive method for the determination of promethium. The Schiff base compounds have recently attracted attention in the field of ion selective sensors due to presence of different donor atoms, cavity size, and ligand geometry to guest ions, significant selectivity, stability and sensitivity for specific ion. Thus, Schiff bases have been used as ionophores in PVC based sensors for determining the rare earth metals such as Gd^{3+} [4], Tb^{3+} [5], Ce^{3+} [6], Nd^{3+} [7], Ce^{3+} [8], La^{3+} [9]. Recently our group has developed a number of sensors for various ions [10–23]. In view of simplicity, wide range of applications of ion sensors, we explored two new Schiff bases: X_1 and X_2 as neutral ionophores in PVC based membranes for fabrication of Pm (III) selective sensors. The proposed sensor has excellent features like selectivity, sensitivity and response time.

3.2. Experimental

3.2.1. Reagents and materials

o-Nitrophenyloctylether (*o*-NPOE), dioctylphthalate (DOP), oleic acid (OA) and (1R, 2R)-1, 2-diaminocyclohexane were taken from Sigma Aldrich. Potassium tetrakis (p chloropheny1) borate (KTpClPB), Cetryltrimethylammonium-bromide (CTAB) and isophthalaldehyde were purchased from Fluka. Sodiumtetraphenylborate (NaTPB), di-n-butylphthalate (DBP), dibutylbutylphosphonate (DBBP), sodium salt of ethylenediaminetetraacetic acid (Na_2EDTA), high molecular weight polyvinyl chloride (PVC) and tetrahydrofuran (THF) were received from Merck. Chloronaphthalene (CN) and tri-(2- ethylhexyl) phosphate (TEHP) received from S.D. Fine. Promethium trichloride was taken from KFO, Japan Co. Ltd., and used as received without further purification. All the metal salt solutions of different concentration were prepared by diluting standard solution (0.1 mol L^{-1}) using millipore water.

3.2.2. Instrumentation

All potentiometric measurements were made with a pH/mVdigital potentiometer (model 5652 A, ECIL, India) using proposed sensor in conjunction with a double junction calomel reference electrode. UV/Vis absorption spectra were recorded using the double-beam in time spectrophotometer (Perkin-Elmer model Lambda 25, USA) and the temperature of the cell holder was maintained at 25 ± 0.1°C. Elemental analysis was performed by a CHN-O Rapid Heraeus elemental analyser (Hanau, Germany). IR spectra were found on a Perkin–Elmer model 843 (USA), the ^{1}H NMR spectra were obtained using BRUKER ADVANCE DPX 300MHz apparatus (Germany).

3.2.3. Procedures

3.2.3.1. Preparation of electrode

The membrane electrodes were prepared as explained by Craggs*et al.*, [24] and Poly(vinyl chloride) was taken as the innert matrix. The membrane were prepared by varing the amount of PVC, plasticizers (*o*-NPOE, DBBP, TEHP, CN, DBP and DOP), anionic excluders (KTpClPB, NaTPB and OA) and ionophores (X_1 and X_2) in 5 mL of THF. The solution was stirring with a glass rod to attain a homogenious solution. The stirring was continued by slowly evoparation until the volution of solution was reduced to 1 mL. The obtained homogenious solution was poured in an acrylic ring placed on a glass plate by avoiding the air bubles. The solution was evoparated for over night at room temperature. The membrane was separated from the glass plate, cut and glued to one of the glass ring by using Araldite.

3.2.3.2. Equilibration of membrane electrodes and potential measurements

The electrodes were equilibrated in a standard solution of 1.0×10^{-2} mol L^{-1} $PmCl_3$ [25]. The potential were taken by changing the test solution concentration of Pm^{3+} ion from 5.0×10^{-9} to 1.0×10^{-2} mol L^{-1} and by keeping constant internal solution i.e., 0.1 mol L^{-1} of Pm^{3+} ion and 5.0×10^{-1} mol L^{-1} of Na_2EDTA at 4.0 pH. Na_2EDTA was used to reduce zero-current ion fluxes from the membrane into the sample as reported in literature. The potentials were collected by the using following cell assembly.

SCE | test solution || PVC membrane || 0.1 mol L^{-1} internal solution | SCE

The activity of Pm^{3+} ion was calculated by using modified Debye-Huckel equation [24]. The activity was used only in the determination of selectivity coefficients whereas in all other experiment simply concentration was used.

3.2.3.3. Synthesis of macrocyclic Schiff base: X_1

To a solution of (1R,2R)-1, 2-diaminocyclohexane (1.14 g,10 mmol) in dichloromethane (10 mL), a solution of isophthalaldehyde (1.34 g, 10 mmol) in dichloromethane (15 mL) was added drop wise at 0 °C [26]. The mixture was stirred at room temperature for 2–3 h, the solvent evaporated and the crude product crystallized from benzenehexane or from ethyl acetate. Macrocycle, X_1 crystallized in several crops with a total yield of ca. 1.9 g, (ca. 90%). Mp 276–283°C; ^{1}H NMR ($CDCl_3$), δ, 1.50 (m, 2H), 1.76 (m, 4H), 1.85 (m, 2H), 3.42 (m, 2H), 7.28 (t, J = 7.7 Hz, 1H), 7.60 (broad s, 2H), 7.95 (s, 1H), 8.20 (s, 2H); ^{13}C NMR (CD_3OD), δ, 25.5 (CH_2), 33.9 (CH_2), 75.7 (CH=N), 128.9 (CH_{Ar}), 130.2 (CH_{Ar}), 131.9 (broad, CH_{Ar}), 137.6 (C_{Ar}), 163.2 (CH=N); IR ν 1647cm^{-1}; m/z calcd. for $C_{42}H_{48}N_6$ 636.3940, Fig. 3.1.

3.2.3.4. Synthesis of macrocycle: *15,17,32 34-tetramethyl-3 29-dioxa-11,12,16,20, 21, 35 hexaazapentacyclo[29.3.1.114,18.04,9.023,28] hexatriaconta-1(35),4,6,8,10,14(36),15, 17,21,23,25 27,31,33-tetradecaene-13,19-dione (X_2)*

The macrocyclic Schiff base's X_2 was synthesized by the reported method [27] (Fig. 3.2) 2,6-Dimethyl-3,5-pyridine dicarboxhydrazide (0.279 g, 1.25m mol) [28] and 2,6-Bis(2 formyl-phenoxymethyl)pyridine (0.347 g, 1mmol) [29] were separately dissolved in ethanol (50 mL). The dissolved solutions were added to a boiling solution of ethanol (300 mL) and acetic acid (1 mL) upto 2 h. The mixture was kept for refluxing for 3h, the solution was allowed to cool at room temperature and precipitate was obtained. Further the precipitate was purified by recrystallization with the mixture of DMF and water in 1:5 ratios. Yield: 65%. Mp. 340 ºC (decomp). IR (KBr), cm^{-1}:3150 (N-H), 1680 (C=O), 1640 (C=N). ^{1}H NMR: δ, 2.60 (6H, s, CH_3), 5.25 (4H, s, CH_2O), 6.90–8.00 (12H, m, Ar), 8.10 (2H, s, CH=N), 11.90 (2H, s, NH). Anal.Calcd.for $C_{30}H_{26}N_6O_4$: C, 67.41; H, 4.90; N, 15.72. Found: C, 68.03; H, 4.95; N, 15.77.

3.3. Results and discussion

3.3.1. Determination of formation constant

Inorder to understand the relation between analyte ion and ionophores, the formation constants were determined by using the potentiometric method i.e., sandwich membrane method [30]. In this technique the membrane electrode was prepared by fusing two polymeric membranes, among those one containing the ionophore. The electrode was separated with equimolar concentration on both sides and it membrane potentials were measured. As advised by the Mi and Bakker the stability constants were calculated with the following equation [31].

$$\beta_{IL_n} = \left(L_T - \frac{nR_T}{Z_I} \right)^{-n} \exp\left(\frac{E_M z_I F}{RT} \right) \qquad (2)$$

Where L_T is the total concentration of ionophore in the membrane segment, R_T is the concentration of lipophilic ionic site additives, n is the ion-ionophore complex stoichiometry and R, T and F are the gas constant, the absolute temperature and the Faraday constant, respectively and an ion carries a charge of Z_I^-. The determined values were tabulate in Table 3.1 in terms of ($\log\beta_{\mathrm{IIn}}$). It was from the table that Pm^{3+} ion is showing high value of stability constant (7.45 ± 0.3 for X_1 and 6.23 ± 0.3) as compared to rest of all cations, which clearly indicating the higher affinity of ligands towards Pm^{3+} ion.

3.3.2. Investigation of membrane composition

In order to attain the best membrane composition in the fabrication of Pm^{3+} ion-selective electrode, different membrane electrodes were fabricated by varying the concentration of membrane ingradients and its potentiometric details were shown in Table 3.2. In this trail, firstly we have prepared the dummy membrane electrodes without ionophores (electrode nos. 1 and 14) and found to be exhibited long time as and no/little response towards Pm^{3+} ion as expected. Later on by changing the PVC ratio that 30% of PVC was found to be given good results for both the ionophores (X_1 and X_2) i.e., electrode no 2 and 15. But the results still giving very poor in terms of low working range $4.5 \times 10^{-3} – 1.0 \times 10^{-2}$ mol L^{-1} (for electrode 2), $7.6 \times 10^{-4} – 1.0 \times 10^{-2}$ mol L^{-1} (for electrode 15) with a sub-Nernstian slopes of 17.0 ± 0.5 (for electrode 2) and 17.5 ± 0.5mVdecade$–^{1}$ of activity(for electrode 2). It is well known that the sensitivity and selectivity of membrane based ion selective electrode mainly dependent on membrane ingradients and nature of plasticizers and anionic excluders [32,33]. Thus the polymeric membrane electrodes were fabricated with varing ratios of different plasticizers (i.e., Tri-(2-ethylhaexyl)phosphate (TEHP), dibutyl butyl phosphonate (DBBP), di-butylphalate (DBP), o-nitrophenyloctyl ether (*o*-NPOE), 1-chloronapthalene (CN) and di-octylpthalate (DOP)). The obtained values were tabulate in Table 3.2. It was seen from table that the plasticizer *o*-NPOE giving best performance compared to rest of the plasticizers. The role in the best performance of the plasticizer *o*-NPOE in the determination of Pm^{3+} ion might be due to the high dielectric constant ($\varepsilon = 24$). Thus the electrode with *o*-NPOE show good results in terms of wide working concentration range of $4.5 \times 10^{-7} – 1.0 \times 10^{-2}$ mol L^{-1} (based on X_1, electrode no. 8) and $3.5 \times 10^{-6} – 1.0 \times 10^{-2}$ mol L^{-1} (based on X_2, electrode no. 21) with slope of 20.0 ± 0.5 mV decade^{-1} of activity (for X_1) and 19.5 ± 0.5 mV decade^{-1} of activity (for X_2). Further to improve Pm^{3+} ion selective electrodes by changing amount of anionic excluders with different anionic excluders (Sodiumtetraphenylborate (NaTPB), potasiumtetrakis(p-chlorophenyl)borate (KTpClPB) and oleic acid (OA)) and found that KTpClPB in 5.0 % (w/w) was given good potentiometric characteristic. Finally, it was cleared that electrode no. 8 and 21 based on X_1 and X_2 are good in terms of all the potentiometric characteristics such as lower detection limit and wide working concentration with near Nernstian slope.

3.3.3. Potentiometric Selectivity

Selectivity is the one of the most important perameter of ion-slective electrode and it is measured in terms of selectivity coefficient. Selectivity is the response of the electrode towards primary ion in presence of other ion. The selectivity of the reported successful electrodes (electrode no. 8 and 21) were calculated by FIM method (34–51). In this method the concentration of interfering ion was kept constant 1.0×10^{-3} mol L^{-1} and the membrane potential were measured by varying the concentration of Pm^{3+} ion. The selectivity coefficients were calculated by using following equation:

$$K_{A,B}^{Pot} = \frac{a_A}{(a_B)^{z_A/z_B}} \qquad (2)$$

Where Z_A and Z_B are the charges of the ions A and B, and a_A and a_B are the activity of ions A and B. The calculated selectivity coefficient values were shown in Table 3.4, the obtained values were smaller that 1.0, which indicated high selectivity of electrodes towards Pm^{3+} ion.

3.3.4. Response time and life time of proposed sensor

Response time also an important parameter of ion-selectivity electrode. It is the time required to get a steady potential. The calculated values of response time was given in Table 3.2, it was seen that the membrane electrode having plasticizer *o*-NPOE was found to be good i.e., low response time 10 s for electrode 8 and 14 s for electrode no. 21 based on X_1 and X_2 respectively. When the electrodes were not in use, the electrodes are stored in 0.1 mol L^{-1} solution of Pm^{3+} ion.

3.3.5. Effect of pH change and non-aqueous solvent

The effect pH on the performance of the electrodes (electrode no. 8 and 21) were studied in the pH range of 2.0–8.5 for 1.0×10^{-3} mol L^{-1} and 1.0×10^{-4} mol L^{-1} Pm^{3+} ion solutions. To neglect the effect of hydroxyl ions (OH^-) beyond pH=7, equimolar concentration of Na_2EDTA was added to each solution. The pH of the solution was adjested by using 1 M HCl/NaOH. At each pH of the solution the potentials were collected and graph was drawn between pH to potentials (Fig. 3.5). The potentials remained constant between the pH 4.0–7.5 for sensor no. 8 and pH 4.0–6.5 for sensor no. 21, thus this pH range was the working pH range for the electrode. The potential decreases at higher pH (>8.0) due to formation of Pm^{3+} hydroxyl complexes in the solution result in the limited availability of free $Pm^{3+.}$ At lower pH values, the potentials increase mainly because of interference of H^+, indicating that the membrane sensor responded to H^+ ion. Since sensor no. 8 exhibited best response characteristics, all further studies are carried out with it only. The potentiometric performance of the best electrode no. 8 was examined in non-aqueous media such as methanol-water, ethanol-water and acetonitrile-water and the results were tabulated in Table 3.5, it was cleared that the 10 % of the nonaqueous medium is acceptable for this electrode, because in this region constant values of slope and working concentration range was observed.

3.3.6. Analytical application

The proposed electrode was successfully applied for the selective determination of Pm^{3+} ion in spiked water samples. The sample solutions were prepared by using tap water from Roorkee city with the addition of 16, 100 and 500 $\mu g\ L^{-1}$ Pm^{3+} ion. The potentials were collected at the pH 5.0 and obtained values were shown in Table 3.6. It was found that the proposed electrode was showing recovery 99.9–100.

3.4. Conclusion

The membrane sensor no. 8 based on Schiff base (X_1) of composition: 5:5:30:60 (ionophore: KTpClPB: PVC: *o*-NPOE) showed best characteristics in comparison to X_2

based sensors. The sensor no. 8 showed working range of $4.5 \times 10^{-7} - 1.0 \times 10^{-2}$ mol L^{-1}, with a Nernstian slope of 20.0 ± 0.5 mV decade^{-1} of activity. The electrode showing independent potentials in the pH range of 4.0 – 7.5 and shown good results in the anion aqueous solution upto 10%. The electrode was successfully applied for the selective determination of Pm^{3+} ion in spiked water samples.

Tables:

Table 3.1: Formation constant of Schiff bases-metal complexes.

Metal Ion	Formation Constant (log β_{IL_n})		Metal Ion	Formation Constant (log β_{IL_n})	
	Schiff base (X_1)	Schiff base (X_2)		Schiff base (X_1)	Schiff base (X_2)
Tb^{3+}	3.78 ± 0.4	3.50 ± 0.6	Nd^{3+}	5.22 ± 0.4	5.14 ± 0.3
Pm^{3+}	7.45 ± 0.3	6.23 ± 0.3	Pr^{3+}	4.32 ± 0.5	4.26 ± 0.4
Lu^{3+}	2.83 ± 0.5	2.76 ± 0.6	Ho^{3+}	3.48 ± 0.7	3.42 ± 0.3
Er^{3+}	3.33 ± 0.5	3.28 ± 0.6	Tm^{3+}	3.22 ± 0.4	3.18 ± 0.5
Yb^{3+}	3.01 ± 0.4	2.91 ± 0.5	Cr^{3+}	3.25 ± 0.5	3.21 ± 0.3
Sm^{3+}	5.18 ± 0.4	5.11 ± 0.5	Pb^{2+}	1.18 ± 0.4	1.26 ± 0.6
Eu^{3+}	4.28 ± 0.4	4.22 ± 0.5	Ca^{2+}	1.31 ± 0.5	1.33 ± 0.6
Ce^{3+}	3.86 ± 0.3	3.81 ± 0.4	Mg^{2+}	1.44 ± 0.7	1.53 ± 0.4
Dy^{3+}	3.61 ± 0.5	3.58 ± 0.6	Li^{+}	1.12 ± 0.5	1.23 ± 0.3
Gd^{3+}	3.78 ± 0.6	3.72 ± 0.5	Na^{+}	1.35 ± 0.4	1.38 ± 0.5
La^{3+}	2.25 ± 0.3	2.13 ± 0.4			

Table 3.2: Optimization of PVC–membrane sensors based on ligands (X_1 and X_2) and performance characteristics as promethium (III) selective sensors.

S. No.	Composition of membrane sensors (%w/w)				Working Range (M)	Slope* ± 0.5	Response Time (s)
	X	PVC	Additives	Plasticizer			
1	0.0, X_1	30.0	5.0, KTpClPB	66.0	-	-	23
2	13.0,X_1	73.0	14.0, KTpClPB	0.0	4.3×10^{-3} -1.0×10^{-2}	17.0	25
3	5.0, X_1	30.0	5.0, KTpClPB	60.0, DBP	5.4×10^{-6} -1.0×10^{-2}	18.5	17
4	5.0, X_1	30.0	5.0, KTpClPB	60.0, DBBP	7.3×10^{-5} -1.0×10^{-2}	15.8	21
5	5.0, X_1	30.0	5.0, KTpClPB	60.0, TEHP	6.9×10^{-5} -1.0×10^{-2}	16.4	20
6	5.0, X_1	30.0	5.0, KTpClPB	60.0, CN	2.5×10^{-5} -1.0×10^{-2}	18.2	16
7	5.0, X_1	30.0	5.0, KTpClPB	60.0, DOP	4.5×10^{-5} -1.0×10^{-2}	17.7	14
8	5.0, X_1	30.0	5.0, KTpClPB	60.0, *o*-NPOE	4.5×10^{-7} -1.0×10^{-2}	20.0	10
9	6.0, X_1	30.0	5.0, KTpClPB	59.0, *o*-NPOE	7.5×10^{-7} -1.0×10^{-2}	19.5	11
10	7.0, X_1	73.0	5.0, KTpClPB	58.0, *o*-NPOE	8.2×10^{-7} -1.0×10^{-2}	19.3	12
11	4.0, X_1	30.0	5.0, KTpClPB	61.0 *o*-NPOE	6.5×10^{-6} -1.0×10^{-2}	18.6	12
12	3.0, X_1	30.0	5.0, KTpClPB	62.0, *o*-NPOE	8.5×10^{-6} -1.0×10^{-2}	18.3	11
13	5.0, X_1	35.0	5.0, KTpClPB	55.0, *o*-NPOE	9.5×10^{-7} -1.0×10^{-2}	18.8	12
14	00.0, X_2	30.0	5.0, KTpClPB	66.0	-	-	24
15	13.0, X_2	73.0	14.0, KTpClPB	00.0	7.6×10^{-4} -1.0×10^{-2}	17.5	14
16	5.0, X_2	30.0	5.0, KTpClPB	60.0, DBP	5.4×10^{-5} -1.0×10^{-2}	18.8	15
17	5.0, X_2	30.0	5.0, KTpClPB	60.0, DBBP	9.6×10^{-5} -1.0×10^{-2}	18.4	15
18	5.0, X_2	30.0	5.0, KTpClPB	60.0, TEHP	8.7×10^{-5} -1.0×10^{-2}	18.6	14
19	5.0, X_2	30.0	5.0, KTpClPB	60.0, CN	6.5×10^{-5} -1.0×10^{-2}	18.7	12
20	5.0, X_2	30.0	5.0, KTpClPB	60.0, DOP	7.7×10^{-5} -1.0×10^{-2}	19.0	13
21	5.0, X_2	30.0	5.0, KTpClPB	60.0, *o*-NPOE	3.5×10^{-6} -1.0×10^{-2}	19.5	14
22	6.0, X_2	30.0	5.0, KTpClPB	60.0, *o*-NPOE	5.1×10^{-6} -1.0×10^{-2}	19.2	15
23	7.0, X_2	30.0	5.0, KTpClPB	58.0, *o*-NPOE	6.5×10^{-6} -1.0×10^{-2}	18.6	17
24	4.0, X_2	30.0	5.0, KTpClPB	61.0, *o*-NPOE	7.5×10^{-5} -1.0×10^{-2}	18.6	16
25	3.0, X_2	30.0	5.0, KTpClPB	62.0, *o*-NPOE	8.6×10^{-5} -1.0×10^{-2}	19.4	15

26	5.0, X_2	35.0	5.0, KTpClPB	55.0, *o*-NPOE	9.1×10^{-6} -1.0×10^{-2}	18.9	18

*Triplicate measurement.

Table 3.3. The Effect of anionic additives on the performance of Pm (III) Selective sensors.

**Membrane sensor composition	**Anionic additive	Working concentration range (M)	Detection limit ± 0.5(M)	*Slope ± 0.5
X_1 : PVC : *o*-NPOE (w/w%) 5.0 : 30.0 : 60.0	-	5.6×10^{-5} to 1.0×10^{-2}	4.6×10^{-5}	16.0
	KTpClPB	4.5×10^{-7} to 1.0×10^{-2}	3.2×10^{-7}	20.0
	NaTPB	7.5×10^{-7} to 1.0×10^{-2}	6.5×10^{-7}	19.7
	OA	3.4×10^{-6} to 1.0×10^{-2}	2.8×10^{-6}	18.9
X_2 : PVC : *o*-NPOE (w/w%) 5.0: 30.0 : 60.0	-	4.4×10^{-3} to 1.0×10^{-2}	3.7×10^{-3}	16.5
	KTpClPB	3.5×10^{-6} to 1.0×10^{-2}	2.3×10^{-6}	19.5
	NaTPB	6.3×10^{-6} to 1.0×10^{-2}	5.8×10^{-6}	19.4
	OA	4.3×10^{-6} to 1.0×10^{-2}	3.7×10^{-5}	18.4

*mV decade^{-1} of activity.

**Anionic additives are added at 5.0% (w/w) of membrane composition.

Table 3.4: Selectivity coefficient values observed for best responsive membrane sensors (8 and 21).

Interfering ion (B)	*Selectivity coefficients($-logK_{Pm3+,B}^{Pot}$)	
	Sensor No.8	Sensor No. 21
Lu^{3+}	3.87	3.93
Er^{3+}	2.82	2.84
Sm^{3+}	1.48	1.53
Yb^{3+}	3.43	3.47
Eu^{3+}	1.70	1.76
Ce^{3+}	2.15	2.21
Gd^{3+}	2.33	2.36
Tb^{3+}	2.43	2.48
Dy^{3+}	2.53	2.58
La^{3+}	4.10	4.18
Nd^{3+}	1.45	1.50
Pr^{3+}	1.66	1.68
Ho^{3+}	2.63	2.67
Tm^{3+}	3.11	3.21
Cr^{3+}	3.03	3.12
Al^{3+}	3.55	3.65
Pb^{2+}	4.26	4.22
Ca^{2+}	4.27	4.21
Mg^{2+}	4.34	4.31
Na^{+}	4.23	4.14
Li^{+}	4.31	4.28

*Fixed Interference Method.

Table 3.5: The performance of the membrane sensor no. 8 in partially non-aqueous medium.

Non–aqueous content (%v/v)	Working concentration range (M)	Slope (mV decade^{-1} of activity)
0	4.5×10^{-7} - 1.0×10^{-2}	20.0 ± 0.5
Methanol		
5	4.5×10^{-7} - 1.0×10^{-2}	20.0 ± 0.5
10	4.5×10^{-7} - 1.0×10^{-2}	20.0 ± 0.5
15	6.6×10^{-7} - 1.0×10^{-2}	19.3 ± 0.5
Ethanol		
5	4.5×10^{-7} - 1.0×10^{-2}	20.0 ± 0.5
10	4.5×10^{-7} - 1.0×10^{-2}	20.0 ± 0.5
15	7.4×10^{-7} - 1.0×10^{-2}	19.4 ± 0.5
Acetonitrile		
5	4.5×10^{-7} - 1.0×10^{-2}	20.0 ± 0.5
10	4.5×10^{-7} - 1.0×10^{-2}	20.0 ± 0.5
15	8.3×10^{-7} - 1.0×10^{-2}	19.2 ± 0.5

Table 3.6: Results of detection of promethium in water after spiking in different amounts.

Promethium added(μg L^{-1})	Found by proposed sensor (μg L^{-1})	[a]Recovery ± SD (%)	t-test(P = 0.05; $t_{theoritical}$ = 2.21)
16	16.05	100.0 ± 0.2	$t_{experimental = 2.21}$
100	101.05	99.90 ± 0.1	$t_{experimental = 2.19}$
500	502.0	100.0 ± 0.1	$t_{experimental = 2.18}$

[a] Triplicate measurement.

Figures:

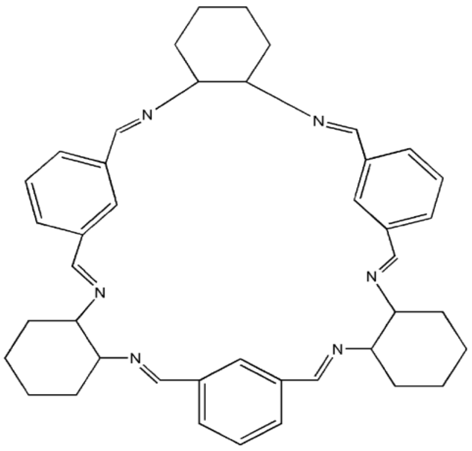

Figure 3.1: Structure of Schiff base **X$_1$** (3,5:12.14:21,23-tribenzo-8,9:17,18:26,27-tricyclohexyl-1,6,10,15,19,24-hexaazo-[27]- 1,6,10,15,19,24-triene).

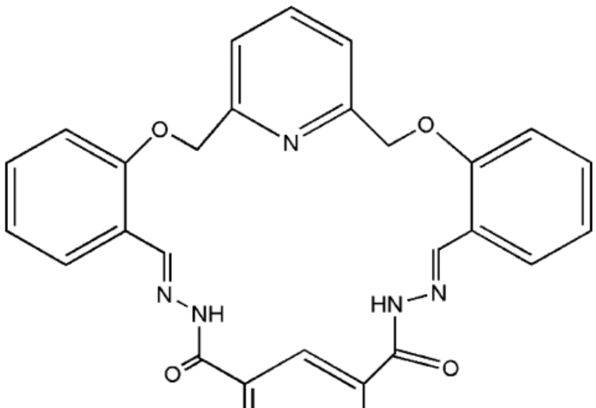

Figure 3.2: Structure of Schiff base X$_{2,}$ (15,17,32,34-tetramethyl-3,29-dioxa-11,12,16,20,21,35-hexaazapentacyclo[29.3.1.114,18.04,9.023,28]-hexatriaconta 1(35),4,6,8,10, 14(36),15,17,21,23, 25, 27,31,33-tetradecaene-13,19-dione).

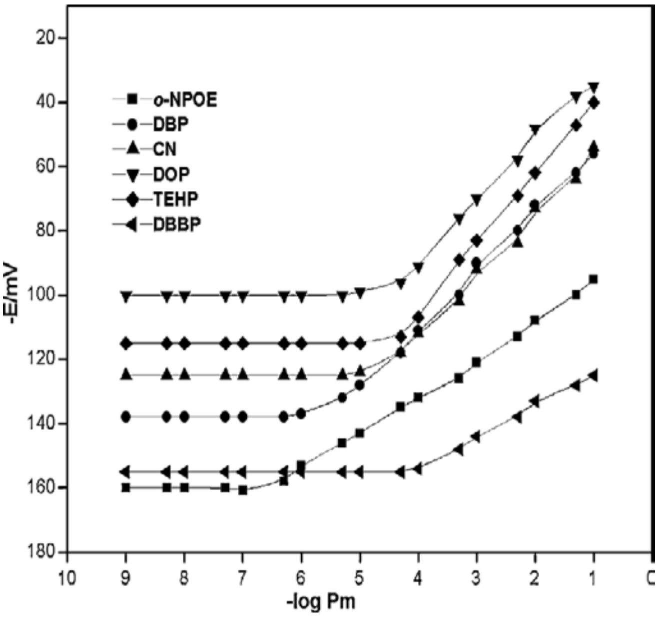

Figure 3.3: Effect of plasticizer: *o*-NPOE, DBBP, DOP, DBP, CN and TEHP on the performance of sensor no. 8.

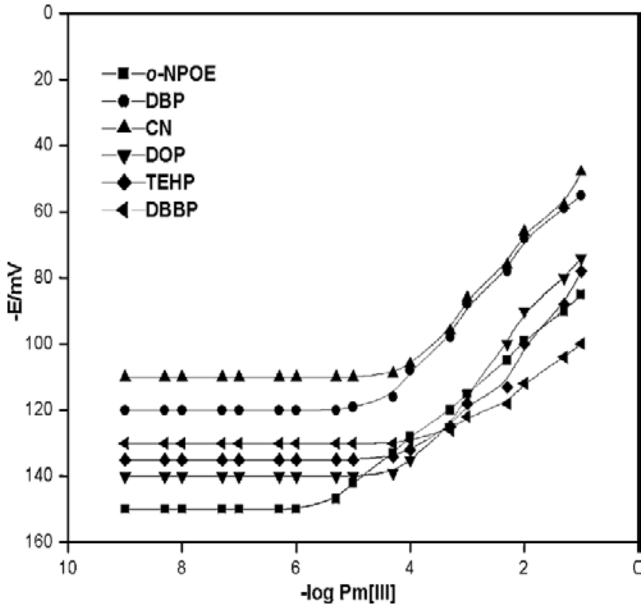

Figure 3.4: Effect of plasticizer: *o*-NPOE, DBBP, DOP, DBP, CN and TEHP on the performance of sensor no. 21.

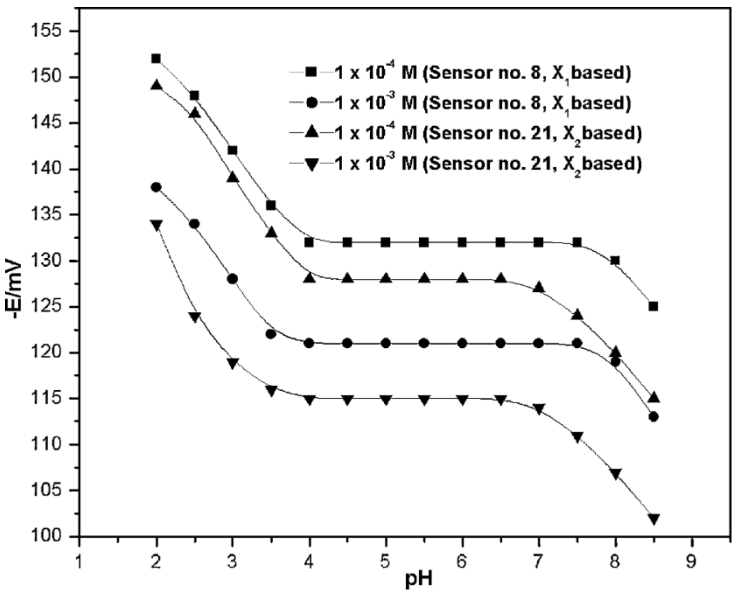

Figure 3.5: Effect of pH on the performance of sensor number 8 and 21.

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4.1. Introduction

Molybdenum is a component of many enzymes responsible for the initial stages of nitrogen, carbon and sulfur metabolism of plants, animals and man participates in a large number of enzymatic reactions [1,2]. There is an absolute dependence by plants on Mo as it plays a vital role in the earth nitrogen cycle where it is involved both in nitrate reduction and nitrogen fixation. Although molybdenum is essential for animals it shows evidence of toxicity at high levels. Molybdenum intoxication depends on its speciation and is also influenced by the uptake of other elements such as S(VI), W(V), Cu, Pb and Zn. In humans, a deficiency of Mo in the diet may lead to some health defects. Diets with a low Mo content (20 μg kg^{-1}) adversely affect growth and may lead to neurological disorders and even early death [3]. Molybdenum also seems to play a positive role in the prevention of tooth decay [4]. On the other hand, excess doses of Mo can be detrimental, persons having a diet rich in Mo being susceptible to gout, uricemia and xanthinuria and often suffer from an inflammation of extremities due to excess uric acid deposition [5,6]. The practice of supplementing human diets with trace elements has stimulated studies of Mo as an essential nutrient. Several studies using diets providing between 1 and 14 μg of Mo per kg body weight per day report that an optimal diet should provide about 2 μg Mo per kg body weight per day. This result is comparable with a daily intake of 128 μg Mo per kg proposed for a mixed diet composite [7]. The Mo requirement for infants is closely reflected in the Mo content of breast milk (5–63 ng g^{-1}) with the level depending on the time after parturition [8–10]. The level of Mo in plants depends on the soil content and soil conditions [11]. As Mo is taken up by plants in the form of the MoO_4^{2-} anion, plants grown on acidic soil accumulate very little Mo. The reported values of Mo in plants vary from 0.1 μg g^{-1} to several μg g^{-1} depending on the material analyzed and the Mo content of animal tissues do not differ significantly from these values. Early reported values for bovine liver were in the range 2.7–4.9 μg g^{-1} while the more recently reported values are 2.3–3.9 μg g^{-1} for bovine [12–15] and 0.23 μg g^{-1} for canine liver [16]. The results reported for the urinary Mo concentration of normal healthy human subjects vary between 33 and 113 μg l^{-1}, the early values of 33 μg g^{-1} from a normal subject and 57 μg g^{-1} from subjects living in a molybdenoferrous area. The above data are difficult to compare as there are other factors to be taken into consideration and the ratio Mo:creatinine would be more useful. Nevertheless the disparities may not be significant and probably depend on individual biochemical factors. Wandt and Pougnet [17] determined the Mo content in urinari calculi as 2.2 μg g^{-1}. The Mo contents reported for human milk are low. However, although most of the values reported (5–25 ng g^{-1} and 8–22 ng g^{-1}) are in a quite good agreement with each other. Molybdenum has also been determined in human lung tissue the values being 71 ng g^{-1} [18] and 8–740 ng g^{-1}, nail 0.15–5 μg g^{-1} and 0.2 μg g^{-1}[19–21], brain 16–29 ng g^{-1} [22].

In spite of utilization of some good techniques in determination of Mo such as; electrothermal atomization atomic absorption spectrometry (ETA AAS) [23,24], inductively coupled plasma emission spectrometry (ICP AES) [25–28], neutron activation analysis (NAA) [29] etc. All these listed techniques are sophisticated, time consuming and very costly. The ion-selective electrodes are found to be low cost and portable tool, which can be used for the multible measurements with low chemical maniplication. Thus, the researchers are very interested to develop various ISEs. Our group has been active in developing highly selective sensors for a number of cations and anions [30–41]. The present work illustrates the construction of novel polymeric membrane electrode by using 5,8-diazo-3,3,10,10-tetramethyl-1,2-dithiacyclodeca-4,8diene (S) as ionophore for the selective and sensitive determination of molybdenum ion.

4.2. Experimental

4.2.1. Reagents

Oleic acid (OA), *o*-nitrophenyl octyl ether (*o*-NPOE), dioctylphthalate (DOP), Sodium cyanoborohydride ($NaCNBH_3$), bromoacetic acid, ammonia, $(NH_4)_6Mo_7O_{24}.4H_2O$ and methyl trioctyl ammonium chloride (MTOAC) are taken from Sigma Aldrich. CH_3OH and CF_3COOH were from Sisco research Lab (Mumbai, Maharashtra, India). Sodium tetraphenylborate (NaTPB), dibutyl(butyl) phosphonate (DBBP) and high molecular weight polyvinyl chloride (PVC) from Merck. Chloronaphthalene (CN) and tri-n-butylphosphate (TBP) received from S.D. Fine chemicals. Potassium tetrakis(4-chlorophenyl borate) (KTpClPB) was received from Fluka. A 0.56 mol L^{-1} fresh solution of ascorbic acid was used for the reduction of Mo(VI) to Mo(V). Ammonium thiocyanate (5.0 mol L^{-1}) was used for the formation of the thiocyanate complex. The acidity of the solution was maintained by using 10.0 mol L^{-1} of HCl. A 0.5 mol L^{-1} solution of MTOAC was used for increasing the colour intensity of molybdenum complex. A 15×10^{-3} mol L^{-1} solution of *N*-phenylbenzimidoyl thiourea in 1-pentanol was used for the extraction of the molybdenum complex that was synthesized by condensation of *N*-phenylbenzimidoyl chloride with thiourea in an equimolar ratio as described in literature [29].

4.2.2. Synthesis of ionophores

All the synthesized ligands are derivatives of the cyclic Schiff base; 5,8-diazo-3,3,10,10-tetramethyl-1,2-dithiacyclodeca-4,8-diene (S) as previously synthesized and reported [42,43].

(A) Synthesis of 4,8-diaza-3,3,10,10-tetramethyl-1,2-dithiacyclodecane (S_1)

4.6 g (0.02 mol) of the Schiff base S was taken in 120 mL of MeOH, to this 0.42g of the sodium cyanoborohydride ($NaCNBH_3$) was added during the period of 15 minutes at pH 6.6. The reaction mixture was stirred for 3 h and acidified with HCl. The solvent was evoparated off, to the residue 40 mL of water and ammonium hydroxide was added until the pH of the solution was reached to 9.5. Further the compound was extracted with diethyl ether and dried with anhydrous sodium sulphate. ^{1}H NMR showed it to be pure diamine; the yield is nearly quantitative. ^{1}H NMR ($CDCl_3$): 1.25 and 1.37 (s, 12H), 2.16 (s, 2H), 2.55 and 2.61, 2.97 and 3.03 (2d, 4H), 2.02 (s, 4H). The dihydrochloride salt was prepared by the addition of concentrated HCl and crystallization from its ethanol–H_2O solution; the yield was 5.7 g (93%), Anal. Calcd for $C_{10}H_{22}N_2S_2$: C, 51.28; H, 9.40; N, 11.97; S, 27.35. Found: C, 51.25; H, 9.37; N, 11.96; S, 27.34; Fig. 4.1.

(B) Synthesis of 5,8-diaza-3,3,10,10-tetramethyl-1,2-dithiacyclodecane- *N,N'*-diacetic acid (S_2)

2.95 g of compound S_1 (0.0126 mol) was taken in 95 mL of absolute ethanol, to this 16 mL of ice cold water containing 3.85 g (0.0277 mol) of bromoacetic acid was added. The reaction mixture was cooled on ice-water bath and pH of the solution was adjusted to 12 by the addition of 1.11 g (0.0277 mol) NaOH. The pH of the reaction mixture was kept between 11.2-11.5 and heated to 40–42 ^{0}C for 6-7 h. The volume of the solution was reduced to 30 mL by the evoparation of ethanol. To the reaction mixture diethylether was added and the aqueous layer was separated and acidified to pH 2.5 using 6 M HCl. The solution was cooled to 5 ^{0}C for 3 h, the product thus obtained was filtered and dried with phosphorous pentoxide at 5 mm of Hg for 18 h. The product obtained amounted to 2.2 g. Another 0.04 g of product was obtained from the filtrate. The total yield was 61%. ^{1}H NMR (D_2O-DCl, pH = 0.3): 1.24 and 1.36 (s, 12H), 3.36 (s, 4H), 3.18 and

3.26, 3.39 and 3.47 (2d, 4H), 3.88 (s, 4H). Anal. Calcd for $C_{14}H_{26}N_2O_4S_2$.1/3H2O: C, 47.17; H, 7.48; N, 7.86. Found: C, 47.12; H, 7.60; N, 7.85, Fig. 4.1.

(C) Synthesis of *N,N'*-bis(2,2-dimethyl-2-mercaptoethyl)-ethylenediamine-*N,N'*-diacetic acid (S_3)

To a solution of 0.5 g of Na metal in 40 mL of liquid NH_3, 0.7 g (0.002 mol) of S_2 was added portion wise with continuous stirring and the stirring was continued for 30 min. to the reaction mixture NH_4Cl and liquid NH_3 to quench the reaction and by using vacuum evaporation at 10 mm Hg at 25.0 ^oC, liquid NH_3 was removed. The pH of the solution was lowed to 2.5 with the addition of HCl and the reaction mixture was kept at 5.0 ^oC for 20 h. White precipitate was obtained, it was separated by filteration and washed with ice cold water. Further the precipitate was dried by using P_2O_5 at room temperature for 16 h. The pure product amounted to 0.45 g (yield 64%). ^1H NMR (D_2O-NaOD): 1.30 (s, 12H), 2.73 (s, 4H), 2.83 (s, 4H), 3.26 (s, 4H). ^{13}C NMR (D_2O-NaOD): 33.0 (methyl), 42.6 (ethylene), 54.9 (CH_2 of ethyl), 60.5 ($HSCMe_2$), 71.6 (CH_2COO^-), 180.3 (COO^-). Anal. Calcd for $C_{14}H_{28}N_2O_4S_2$: C, 47.70; H, 8.01; N, 7.95. Found: C, 47.46; H, 8.19; N, 7.87, Fig. 4.1.

4.2.3. Preparation of membrane

As described in the section 3.2.3.1, different polymeric membrane electrodes were constructed by dissolving the different amounts of the membrane ingradients such as Schiff bases (S_1, S_2 and S_3), anion excluder (KTpClPB, NaTPB and OA), plasticizer (DOP, TBP, CN, DBBP and *o*-NPOE) and PVC in 4 mL of THF. The obtained membranes were glued to one end of the pyrex glass tube with the help of Araldite [44].

4.2.4. Equlibriation and Potential measurement of membrane electrodes

The prepare polymeric membrane electrodes were equlibriated for 2 days in 0.05 M Bis-Tris-HCl (background electrode), then in 1.0×10^{-2} mol L^{-1} of Mo(V) ion solution + 1.0×10^{-2} mol L^{-1} of sodium citrate (the pH was kept at < 6.5 with the help of HNO_3) for 3–4 h. Further the electrodes were stored in 0.05 M Bis-Tris-HCl. The potential response was collected by changing concentration of test solution from 1.0×10^{-9} to 1.0×10^{-2} mol L^{-1} of Mo(V) ion solution. The experiments were carried out at 25 ± 0.1 ^{0}C using a saturated calomel electrode (SCE) as a reference electrode and pH was kept at 4.3 (0.05 M Bis–Tris–HCl). The cell assembly was prepared shown below:

Hg/Hg_2Cl_2 | KCl (satd.) | test solution || PVC membrane || 0.01M Mo(V) + 0.01 sodium citrate| Hg/Hg_2Cl_2 | KCl (satd.) (1)

4.3. Results and discussion

4.3.1. Effect of internal solution

It is well known that the internal solution mainly effect the performance of the polymeric membrane electrode. Thus the effect of internal solution on the potentiometric properties such working concentration, slope and low detection limit was examined by varing the concentration of internal solution (i.e., solution of Mo(V) ion) from 1.0×10^{-2} - 1.0×10^{-4} mol L^{-1}. It was cleared that the concentration of internal solution 1.0×10^{-2} mol L^{-1} is found to be better. Thus, for the the further studies 1.0×10^{-2} mol L^{-1} of Mo(V) ion solution was used as internal solution.

4.3.2. Determination of stability constants

Stability constants (formation constant) is the one of the most important parameter, that which gives the fundamental idea of the relation between ion and ionophore (S_1, S_2 and S_3). It is helpful to know the selectivity of the ionophore towads ion. As explained in section 3.3.1., the stability constants were measured by sandwich membrane method [45]. The sandwich membrane elctrodes were prepared with the ionophores (S_1, S_2 and S_3). The membrane potentials E_M were collected for the prepared electrodes and the stability constants were calculated in terms of (log β_{ILn}). The obtained results were tabulated in Table 4.1, it is cleared from the table that the stability constant values for the Mo(V) ion (i.e., 5.19 ± 0.23 for S_1, 5.47 ± 0.23 for S_2 and 7.57 ± 0.25 for S_3) are very high as compared with rest of the ions. Which is clearly indicating the high affinity of ionophores towads Mo(V) ion.

4.3.3. Potentiometric response of membrane electrodes with different metal ions

The potentiometric response of the membrane electrodes were examined by preparing different membrane eletrodes using ionophore (S_1, S_2 and S_3) (Fig. 4.2 - 4.4). It has been observed that membrane sensors based on S_3 ligand had the best selectivity for Mo(V) ion. Furthermore the response of best responsive Mo(V) selective sensor was studied with different Mo^{n+} (different valency state of Mo) salt solutions and it was again reported that the sensor is only selective for Mo(V), Fig. 4.5.

4.3.4. Optimization of membrane composition

In order to achieve a best membrane electrode i.e., the electrode with wide working concentration range, lower detection limit along with near Nernstian slope, different electrodes were fabricated by varing the membrane composition (ionophore, plasticizers, anionic excluders and PVC) in different amount ratio. The calculated potentiometric details are shown in Table 4.2.

4.3.4.1. Effect of plasticizers and amount of ionophore

Plasticizer plays an important role in the polymeric membrane electrode, it improve the sensitivity and selectivity of the electrode. Thus different electrodes were prepared by using different plasticizers i.e., DOP, *o*-NPOE, TEHP, CN and DBP and its potentiometric studies were calculated. It is from the Table 4.2., the electrode with plasticizer *o*-NPOE is showing good results. The best results of the electrode with with plasticizer *o*-NPOE is might be due to higher dielectric constant i.e., *o*-NPOE ($\varepsilon = 24$) as compared to rest DBP ($\varepsilon = 6.4$), CN ($\varepsilon = 5$), DOP ($\varepsilon = 5$) and TEHP ($\varepsilon = 4.8$). Finally on comparison of all the electrodes prepared by using ionophore (S_1, S_2 and S_3), the electrode (electrode no. 7) based on S_3 having composition S_3:PVC:KTpClPB:*o*-NPOE ≡ 5:30:60:5 (%w/w, mg), is showing good performance characteristics such as lower detection limit (2.2×10^{-7} mol L^{-1}) with wide working concentration range (1.0×10^{-2} - 3.3×10^{-7} mol L^{-1}) and near Nernstian slope 29.6 mV/decade of activity. Similarly the effect of amount of ionophore was also examined and found that the membrane having ionophore (5 % w/w, mg) is showing good results.

4.3.4.2. Effect of anionic additives

Anionic excluders also cause for the sensitivity and selectivity of ion-selective electrode, mainly it reduces the resistance of the membrane. Thus the membrane electodes were prepared by without additive and exchanging additive with NaTPB and OA in place of KTpClPB of electrode no. 7, 17 and 27. The obtained potentiometric results were shown in Table 4.3, and it was cleared that the electrode having 5 % of KTpClPB as additive is showing good performance results as compared to rest. The best results of KTpClPB, may be due to the charge compensating of counter ion in the membrane.

4.3.5. Selectivity of the membrane electrode

It is most important property of the the ion-selective electrode, which tells influence of the secondary ions on the electrode in presene primary ion. The selectivity of the proposed electrodes no. 7, 17 and 27 were determined using both MPM [46] and FIM [47] methods.

In the matched potential method, the concentration of the primary ion was changed from $a_{Mo^{5+}}$ to $a'_{Mo^{5+}}$ and fixed concentration of the interfering ion (secondary ion) a_B was added to the reference solution. The selectivity coefficient was calculated by using following expression:

$$K^{Pot}_{Mo^{5+},B} = \frac{a'_{Mo5+} - a_{Mo5+}}{a_B} \qquad (3)$$

Where, a_{Mo5+} and a'_{Mo5+} were taken as 1.0×10^{-3} mol L^{-1} and 3.0×10^{-3} mol L^{-1} of Mo(V) and a_B, experimentally obtained.

As discussed in section 3.3.3, the selectivity coefficient values were calculated at a constant concentration of secondary ion (interfering ion) (1.0×10^{-2} mol L^{-1}). Thus the calculated selectivity coefficient values of electrodes no. 7, 17 and 27 were shown in Table 4.4. It is found from table that the electrode no. 7, 17 and 27 show more affinity towards Mo(V) ion compared to rest of metal ion. On comparision of electrodes 7, 17 and 27, the electrode 7 is showing high selectivity for Mo(V) ions.

4.3.6. Effect of pH and non-aqueous on the proposed electrode

The pH effect on the proposed membrane electrode no. 7 was examined in range of 2-9 at 1.0×10^{-3} M and 1.0×10^{-4} M Mo(V) ion solution. The different pH solution were prepared using buffer Tris-HCl. The potentiometric change thus obtained is cleared that the electrode having internal solution without sodium citrate has given very low pH range i.e., 2.4-3.2, where as on the addition of sodium citrate the pH range was increased 3.5-6.4

(Fig. 4.6). The increase in the pH range of the electrode with the addition of sodium citrate is due to the inhibitory property of precipitation of Mo(V) ion by sodium citrate [48–52]. The non-aqueous effect of sensor no. 7 was also examined and the potentiometric details thus obtained are tabulated in Table 4.5. The table illustrates that sensor no. 7 can tolerate 15% v/v of non-aqueous content.

4.3.7. Dynamic response and life time studies

As discussed in section 3.3.4, the dynamic response time of the electrodes with and without plasticizers were measured and shown in Table 4.2. The proposed electrode no. 7 was found to be shown the low dynamic response time 11 s (Fig. 4.7). The life time of the proposed sensor was also examined by immersing the electrode in 0.1 mol L^{-1} of Mo(V) solution. The potentiometric details were calculated for each 2 day up to 80 days. Thus obtained details (Table 4.6) clearly indicated that the electrode can be successfully applied for 75 days, after this the electrode is losing Nernstian behavior.

4.3.8. Analytical applications in determination of molybdenum in biological samples by proposed method with comparative analysis of spectrophotometric method and ETAAS

The proposed electrode was successfully applied for the selective determination of molybdenum ion in various natural samples followed by extraction.

4.3.8.1. Preparation of molybdenum standard solution for extraction process

A fresh standard solution of molybdenum, 1000 μg mL^{-1} was prepared by dissolving appropriate amounts of $(NH_4)_6Mo_7O_{24}.4H_2O$ in 1 L double distilled water. The working standard solutions were prepared by an appropriate dilution of the stock solution.

A 0.56 M fresh solution of ascorbic acid was used for the reduction of metal. Ammonium thiocyanate (5.0 M) was used for the formation of the thiocyanate complex. The acidity of the solution was maintained by using 10.0 M of HCl. A 0.5 M solution of methyl trioctyl ammonium chloride (MTOAC) was used for increasing the colour intensity of molybdenum complex. A 15×10^{-3} M solution of *N*-phenylbenzimidoyl thiourea in 1-pentanol was used for the extraction of the molybdenum complex that was synthesized by condensation of *N*-phenylbenzimidoyl chloride with thiourea in an equimolar ratio as described in literature [29].

4.3.8.2. Sample collection and pretreatment for sample preparations

All the samples (water bodies, soils, root nodules and urine samples) were collected from nearby to the city; Roorkee (India). The urine samples were collected from Institute Hospital (IIT Roorkee, India). All samples were collected in 100 mL polyethylene bottles.

4.3.8.2.1. Soil and root nodule sample preparations

The root nodules of leguminous plants were washed with distilled water in order to remove soil matter and dried in an oven for 24 h at 100 ^{0}C.

A 1.0 g of soil or root nodule samples were ground to 100 mesh size and placed in a 100 mL Teflon beaker. To this, 4 mL of 70% perchloric acid ($HClO_4$) and 10 mL 40% hydrofluoric acid (HF) were added. The sample was made wet with acids by swirling and kept on a hot plate. The dried mass was dissolved in 50 mL of 1.0 M hydrochloric acid (HCl), filtered and 1 mL of sample solution was used for the determination of molybdenum.

4.3.8.2.2. Water body sample preparations

A 100 mL aliquot of filtered water sample was evaporated nearly to dryness after adding a mixture of 5 mL of concentrated H_2SO_4 and 10 mL of concentrated HNO_3, and then cooled to room temperature. The residue was heated further with 10 mL of distilled water in order to dissolve the salts. The resulting solution was filtered with Whatman filter paper into 25 mL volumetric flask and made up to the mark with distilled water. Then, 1 mL of sample solution obtained was used for the analysis of molybdenum.

4.3.8.2.3. *Urine sample preparations*

Urine samples were collected in cleaned polyethylene bottle from age group of 23–50 people and stored in refrigerator until analysis. A 100 mL aliquot of urine sample was treated with 5 mL of sulfuric acid and 10 mL of nitric acid, and then heated nearly to dryness. The residue obtained was dissolved in 10 mL of deionized water and filtered with Whatman filter paper. A 1.0 mL sample solution was used for the analysis of molybdenum.

4.3.8.3. *Procedure for liquid–liquid extraction*

An aliquot of the sample solution containing 200–10,000 ng of Mo(VI) was transferred into a 100 mL separatory funnel, 2 mL ascorbic acid solution was added to reduce Mo(VI) to Mo(V), followed by addition of 3 mL 10 M HCl, 1 mL of ammonium thiocyanate and MTOAC. The aqueous phase was diluted to 10 mL with distilled water maintaining the temperature at 22 ± 2 ^{0}C. Then, the colored complex was extracted with 5 mL 1-pentanol (5.0×10^{-3} M) containing N-phenylbenzimidoyl thiourea (PBITU) for 5 min. All extracts after drying over anhydrous sodium sulphate (≈ 2.0 g) were transferred to a 10 mL volumetric flask and filled to the mark with 1-pentanol. The absorbance of the solution was measured at 470 nm by using the reagent blank as reference.

The concentration of molybdenum found in different types of water, soil and root nodule are given in Table 4.7 and Table 4.8. The results obtained from soils and root nodules by the proposed method are found to be in excellent agreement with those obtained by ETAAS and spectrophotometry at the optimized conditions. In addition, the present method was further extended for the determination of molybdenum in urine samples. The concentration of molybdenum in urine samples is given in Table 4.9.

4.4. Conclusion

The three different ionophores; 4,8-diaza-3,3,10,10-tetramethyl-1,2-dithiacyclo decane (S_1), 5,8-diaza-3,3,10,10-tetramethyl-1,2-dithiacyclodecane-*N,N'*-diacetic acid (S_2) and *N,N'*-bis(2,2-dimethyl-2-mercaptoethyl)ethylenediamine-*N,N'*-diacetic acid (S_3) have been synthesized and used as electro active materials in the fabrication of PVC based membrane electrode. Different polymeric membrane electrode with varing the membrane composition and ratio of the membrane ingradients such as ionophores, plasticizers, anionic excluders and its potentiometric results were compared. It was found that the electrode no. 7 based on S_3 with having membrane composition S_3:PVC:KTpClPB:*o*-NPOE ≡ 5:30:60: 5 (w/w%, mg) is showing best results in terms of wide working concentration range of $2.3 \times 10^{-7} – 1.0 \times 10^{-2}$ mol L^{-1}, low detection limit of 1.2×10^{-7} mol L^{-1} and high selectivity towards Mo(V) ion. The electrode can be used in partially in non-aqueous media up to 15%. Futher the proposed electrode (electrode no. 7) can be successfully used to quantify the Mo(V) ion in environmental samples such as root nodules, water, soils and urine samples. Thus the obtained results were compared with ETAAS and spectrophotometric method.

Tables:

Table 4.1: The formation constants of ligands (S) with some selected metals.

Cations	S_3	S_2	S_1
	Formation constant ($\log\beta_{ILn}$)^a ± SD	Formation constant ($\log\beta_{ILn}$)^a ± SD	Formation constant ($\log\beta_{ILn}$)^a ± SD
Na^+	0.51 ± 0.05	0.42 ± 0.03	0.39 ± 0.04
K^+	0.54 ± 0.03	0.48 ± 0.02	0.45 ± 0.03
Ag^+	1.20 ± 0.08	1.10 ± 0.03	1.03 ± 0.05
Cu^{2+}	2.21 ± 0.19	2.11 ± 0.13	1.91 ± 0.12
Pb^{2+}	2.58 ± 0.15	2.51± 0.10	2.49 ± 0.09
Cd^{2+}	2.55 ± 0.13	2.49 ± 0.12	2.40 ± 0.09
Zn^{2+}	2.10 ± 0.16	2.04 ± 0.11	1.94 ± 0.09
Co^{2+}	2.11 ± 0.12	2.06 ± 0.12	1.96 ± 0.11
Cr^{3+}	3.40 ± 0.21	3.38 ± 0.19	3.19 ± 0.17
Ce^{3+}	3.21 ± 0.25	3.19 ± 0.25	3.09 ± 0.22
In^{3+}	3.71 ± 0.19	3.69 ± 0.18	3.59 ± 0.16
Mo^{5+}	7.57 ± 0.25	5.47 ± 0.23	5.19 ± 0.23
Al^{3+}	3.61 ± 0.25	3.59 ± 0.21	3.51 ± 0.22
Tl^{3+}	3.56 ± 0.25	3.50 ± 0.25	3.48 ± 0.22

^{a} Mean value ± standard deviation (three measurements), measured at pH = 4.3.

Table 4.2: Optimization of membrane composition (w/w%).

Sensor No.	Composition of membrane sensors (w/w%)				Working Range (M)	^{a}Slope ± 0.5	Response Time (s)
	Ionophore	PVC	Additive	Plasticizer			
1	0.0, S_3	30.0	4.0, KTpClPB	66.0	-	-	22
2	13.0, S_3	73.0	14.0, KTpClPB	0.0	8.3×10^{-4} -1.0×10^{-2}	10.0	17
3	5.0, S_3	30.0	5.0, KTpClPB	60.0, DBP	2.5×10^{-6} -1.0×10^{-2}	11.3	12
4	5.0, S_3	30.0	5.0, KTpClPB	60.0, TEHP	5.5×10^{-5} -1.0×10^{-2}	10.6	13
5	5.0, S_3	30.0	5.0, KTpClPB	60.0, CN	5.3×10^{-5} -1.0×10^{-2}	10.4	13
6	5.0, S_3	30.0	5.0, KTpClPB	60.0, DOP	4.9×10^{-5} -1.0×10^{-2}	10.8	11
7	**5.0, S_3**	**30.0**	**5.0, KTpClPB**	**60.0, *o*-NPOE**	**3.3×10^{-7} -1.0×10^{-2}**	**11.7**	**11**
8	5.0, S_3	35.0	5.0, KTpClPB	55.0, *o*-NPOE	4.5×10^{-7} -1.0×10^{-2}	11.5	11
9	5.0, S_3	40.0	5.0, KTpClPB	50.0, *o*-NPOE	4.8×10^{-7} -1.0×10^{-2}	11.4	12
10	4.0, S_2	30.0	6.0, KTpClPB	60.0, *o*-NPOE	3.3×10^{-6} -1.0×10^{-2}	10.8	13
11	0.0, S_2	30.0	4.0, KTpClPB	66.0	_	_	24
12	13.0, S_2	73.0	14.0, KTpClPB	0.0	7.4×10^{-4} -1.0×10^{-2}	10.1	16
13	05.0, S_2	30.0	5.0, KTpClPB	60.0, DBP	2.4×10^{-5} -1.0×10^{-2}	11.2	11
14	05.0, S_2	30.0	5.0, KTpClPB	60.0, TEHP	5.9×10^{-5} -1.0×10^{-2}	10.5	13
15	05.0, S_2	30.0	5.0, KTpClPB	60.0, CN	5.5×10^{-5} -1.0×10^{-2}	10.4	13
16	05.0, S_2	30.0	5.0, KTpClPB	60.0, DOP	5.1×10^{-5} -1.0×10^{-2}	10.6	12
17	**05.0, S_2**	**30.0**	**5.0, KTpClPB**	**60.0, *o*-NPOE**	**3.5×10^{-6} -1.0×10^{-2}**	**11.5**	**11**

18	05.0, S_2	35.0	5.0, KTpClPB	55.0, *o*-NPOE	5.1×10^{-6} -1.0×10^{-2}	11.4	11
19	05.0, S_2	40.0	5.0, KTpClPB	50.0, *o*-NPOE	5.6×10^{-6} -1.0×10^{-2}	11.3	12
20	4.0, S_2	30.0	6.0, KTpClPB	60.0, *o*-NPOE	4.1×10^{-6} -1.0×10^{-2}	10.7	14
21	0.0, S_1	30.0	4.0, KTpClPB	66.0	_	_	22
22	13.0, S_1	73.0	14.0, KTpClPB	0.0	8.1×10^{-4} -1.0×10^{-2}	10.0	17
23	5.0, S_1	30.0	5.0, KTpClPB	60.0, DBP	2.4×10^{-5} -1.0×10^{-2}	11.0	13
24	5.0, S_1	30.0	5.0, KTpClPB	60.0, TEHP	6.2×10^{-5} -1.0×10^{-2}	10.3	15
25	5.0, S_1	30.0	5.0, KTpClPB	60.0, CN	5.7×10^{-5} -1.0×10^{-2}	10.5	14
26	5.0, S_1	30.0	5.0, KTpClPB	60.0, DOP	5.3×10^{-6} -1.0×10^{-2}	10.8	13
27	**5.0, S_1**	**30.0**	**5.0, KTpClPB**	**60.0, *o*-NPOE**	**5.5×10^{-6} -1.0×10^{-2}**	**11.3**	**12**
28	5.0, S_1	35.0	5.0, KTpClPB	55.0, *o*-NPOE	6.4×10^{-6} -1.0×10^{-2}	11.2	12
29	5.0, S_1	40.0	5.0, KTpClPB	50.0, *o*-NPOE	6.7×10^{-6} -1.0×10^{-2}	11.0	12
30	4.0, S_1	30.0	6.0, KTpClPB	60.0, *o*-NPOE	6.0×10^{-6} -1.0×10^{-2}	10.8	13

[a] mV/decade of activity.

Table 4.3: The Effect of anionic additives on the performance of Mo(V) Selective Sensors.

composition of Membrane sensor	Anionic additives	Working concentration range (M)	Detection limit ± 0.5 (M)	^{a}Slope ± 0.5
(Sensor no. 7) 5.0(S_3) : 30.0 (PVC) : 60.0 (*o*-NPOE) (w/w%)	_	4.5×10^{-4} to 1.0×10^{-2}	3.8×10^{-4}	10.3
	KTpClPB	2.3×10^{-7} to 1.0×10^{-2}	1.2×10^{-7}	11.7
	NaTPB	3.5×10^{-7} to 1.0×10^{-2}	2.5×10^{-7}	11.6
	OA	5.5×10^{-7} to 1.0×10^{-2}	4.4×10^{-7}	11.3
(Sensor no. 17) 5.0(S_2) : 30.0 (PVC) : 60.0 (*o*-NPOE) (w/w%)	_	4.8×10^{-4} to 1.0×10^{-2}	4.2×10^{-4}	10.3
	KTpClPB	2.5×10^{-6} to 1.0×10^{-2}	1.5×10^{-6}	11.5
	NaTPB	3.4×10^{-6} to 1.0×10^{-2}	3.0×10^{-6}	11.4
	OA	4.4×10^{-6} to 1.0×10^{-2}	4.0×10^{-6}	11.3
(Sensor no. 27) 5.0(S_1) : 30.0 (PVC) : 60.0 (*o*-NPOE) (w/w%)	_	5.8×10^{-4} to 1.0×10^{-2}	5.4×10^{-4}	10.0
	KTpClPB	5.4×10^{-6} to 1.0×10^{-2}	5.0×10^{-6}	11.3
	NaTPB	5.6×10^{-6} to 1.0×10^{-2}	5.2×10^{-6}	11.2
	OA	6.3×10^{-6} to 1.0×10^{-2}	5.9×10^{-6}	11.0

^{a}mV decade^{-1} of activity.

Table 4.4: Selectivity coefficient ($log^{Pot}_{Mo^{5+},B}$) values observed for best Mo(V) selective sensors (no. 7, 17 and 27) as calculated by fixed interference method (FIM) as well as matched potential method (MPM).

Interfering ion (B)	Selectivity coefficients (no. 7)		Selectivity coefficients (no. 17)		Selectivity coefficients (no. 27)	
	FIM[a]	MPM[b]	FIM[a]	MPM[b]	FIM[a]	MPM[b]
Na^+	-3.79 ± 0.4	-3.53 ± 0.2	-3.87 ± 0.3	-3.62 ± 0.2	-3.95 ± 0.2	-3.82 ± 0.4
K^+	-3.34 ± 0.3	-3.31 ± 0.3	-3.37 ± 0.4	-3.35 ± 0.4	-3.42 ± 0.3	-3.39 ± 0.4
Cu^{2+}	-3.27 ± 0.4	-3.25 ± 0.5	-3.37 ± 0.4	-3.35 ± 0.5	-3.43 ± 0.3	-3.39 ± 0.4
Pb^{2+}	-3.17 ± 0.2	-3.13 ± 0.3	-3.26 ± 0.3	-3.21 ± 0.2	-3.34 ± 0.4	-3.29 ± 0.3
Cd^{2+}	-3.15 ± 0.3	-3.17 ± 0.6	-3.25 ± 0.5	-3.21 ± 0.4	-3.33 ± 0.5	-3.30 ± 0.4
Zn^{2+}	-3.25 ± 0.5	-3.23 ± 0.5	-3.34 ± 0.4	-3.33 ± 0.3	-3.42 ± 0.3	-3.38 ± 0.2
Co^{2+}	-3.10 ± 0.5	-3.17 ± 0.6	-3.20 ± 0.5	-3.16 ± 0.5	-3.29 ± 0.4	-3.32 ± 0.5
Cr^{3+}	-2.26 ± 0.3	-2.27 ± 0.4	-2.35 ± 0.3	-2.31 ± 0.5	-2.42 ± 0.3	-2.37 ± 0.4
Ce^{3+}	-2.33 ± 0.2	-2.30 ± 0.5	-2.44 ± 0.3	-2.40 ± 0.4	-2.48 ± 0.2	-2.44 ± 0.4
Al^{3+}	-1.72 ± 0.3	-1.71 ± 0.3	-1.81 ± 0.4	-1.79 ± 0.2	-1.92 ± 0.3	-1.87 ± 0.4
Fe^{3+}	-2.26 ± 0.2	-2.23 ± 0.4	-2.34 ± 0.3	-2.30 ± 0.2	-2.43 ± 0.4	-2.39 ± 0.3
Tl^{3+}	-1.69 ± 0.3	-1.67 ± 0.5	-1.75 ± 0.5	-1.71 ± 0.3	-1.82 ± 0.3	-1.79 ± 0.5
Au^{3+}	-1.89 ± 0.4	-1.90 ± 0.2	-1.92 ± 0.4	-1.88 ± 0.4	-1.98 ± 0.5	-2.00 ± 0.4

[a] Fixed interference method. [b] Matched potential method

Table 4.5: The performance of best selective sensor (no. 7) in non-aqueous content.

Non–aqueous content (v/v%)	Working concentration range (M)	Slope (mV decade^{-1} of activity)
0	2.3×10^{-7} to 1.0×10^{-2}	11.7 ± 0.4
	Methanol	
5	2.3×10^{-7} - 1.0×10^{-2}	11.7 ± 0.3
10	2.3×10^{-7} - 1.0×10^{-2}	11.7 ± 0.2
15	2.6×10^{-7} - 1.0×10^{-2}	11.8 ± 0.5
20	5.5×10^{-7} - 1.0×10^{-2}	13.1 ± 0.3
	Ethanol	
5	2.3×10^{-7} - 1.0×10^{-2}	11.7 ± 0.3
10	2.5×10^{-7} - 1.0×10^{-2}	11.9 ± 0.3
15	2.5×10^{-7} - 1.0×10^{-2}	11.9 ± 0.5
20	6.3×10^{-7} - 1.0×10^{-2}	13.0 ± 0.5
	Acetonitrile	
5	2.3×10^{-7} - 1.0×10^{-2}	11.0 ± 0.4
10	2.3×10^{-7} - 1.0×10^{-2}	11.7 ± 0.2
15	2.4×10^{-7} - 1.0×10^{-2}	11.6 ± 0.4
20	6.1×10^{-7} - 1.0×10^{-2}	13.2 ± 0.2

Table 4.6: Effect of soaking time on the potential response of the molybdenum selective sensor no. 7.

Soaking Time (Electrode 7)	Slope(±0.2mV $decade^{-1}$)^{a}	Working concentration range (M)	Detection Limit
2 Days	30.0	2.3×10^{-7} - 1.0×10^{-2}	1.2×10^{-7}
7 Days	30.0	2.3×10^{-7} - 1.0×10^{-2}	1.2×10^{-7}
20 Days	29.7	2.3×10^{-7} - 1.0×10^{-2}	1.2×10^{-7}
45 Days	29.5	3.3×10^{-7} - 1.0×10^{-2}	1.4×10^{-7}
60 Days	29.0	3.5×10^{-7} - 1.0×10^{-2}	1.5×10^{-7}
75Days	28.6	3.4×10^{-7} - 1.0×10^{-2}	1.6×10^{-7}
80 Days	24.0	2.3×10^{-6} - 1.0×10^{-2}	1.2×10^{-6}

[a] ±standard deviation (three measurements).

Table 4.7: Analytical application of proposed sensor no.7 in determination of molybdenum in different natural water body preparation with comparative analysis of UV/Vis and ETAAS.

Water Sample[a]	Mo by UV/Vis		Mo by ETAAS		Proposed sensor No. 7	
	ng mL^{-1}	R.S.D. (n=5), ±%	ng mL^{-1}	R.S.D. (n=5), ±%	ng mL^{-1}	R.S.D. (n=5), ±%
River	24.8	1.4	25.2	2.5	24.7	1.5
Pond	62.2	1.3	63.1	2.4	61.9	1.4
Muncipal	200.3	1.5	202.1	2.9	200.0	1.4
Industrial	350.5	1.5	347.8	3.2	350.2	1.3
Rain	30.7	1.4	29.9	2.8	30.5	1.5
Well	20.4	1.5	21.3	3.9	20.1	1.5

[a] 1 mL volume of water sample used for analysis.

Table 4.8: Analytical application of proposed sensor no. 7 in determination of molybdenum in soil and roots nodule preparation with comparative analysis of UV/Vis and ETAAS.

Water Sample[a]	Mo by UV/Vis		Mo by ETAAS		Proposed sensor No. 7	
	ng mL^{-1}	R.S.D. (n=5),±%	ng mL^{-1}	R.S.D. (n=5),±%	ng mL^{-1}	R.S.D. (n=5),±%
Soil Sample						
Agriculture	150.5	1.4	151.2	2.8	150.2	1.5
Industrial	250.6	1.3	249.4	2.3	249.9	1.5
Forest	200.2	1.4	201.0	2.5	200.0	1.3
Residential	60.5	1.5	59.2	3.8	60.4	1.4
Root nodules						
Soyabean	55.0	1.6	53.8	2.2	55.2	1.4
Peanut	15.5	1.4	16.5	3.9	15.4	1.3
Black gram	21.6	1.3	22.3	3.0	21.2	1.2
Green gram	25.0	1.7	25.8	2.3	25.2	1.4

[a] 1 mL volume of water sample used for analysis.

Table 4.9: Analytical application of proposed sensor no. 7 in determination of molybdenum in urine sample with comparative analysis of ETAAS.

Sample	^{a}Molybdenum (ngmL^{-1})			
	Proposed sensor no. 7	R. S. D (n=3), ±%	ETAAS	R.S.D (n=3), ±%
1	31.2	1.2	31.3	1.5
2	15.3	1.4	15.5	1.8
3	23.3	1.2	23.6	1.6
4	22.2	1.5	22.5	2.0
5	20.5	1.3	20.8	1.5
6	32.4	1.2	32.6	1.6

Figures:

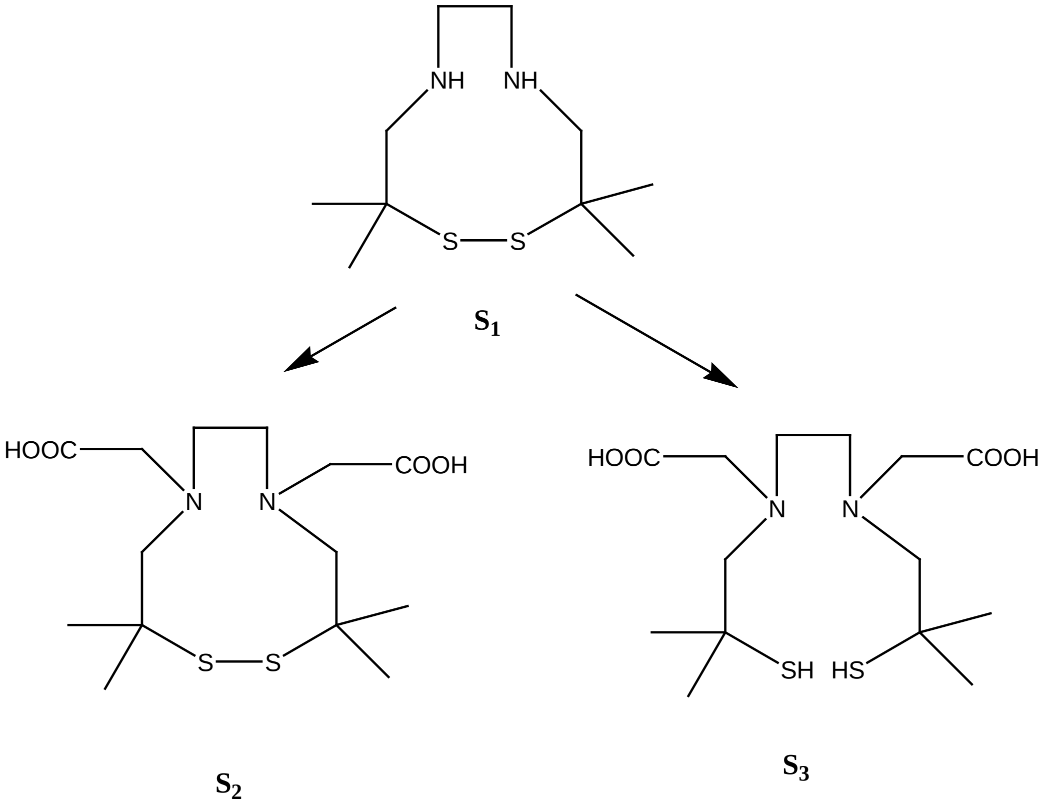

Figure 4.1: Structure of ionophores; S_1, S_2 and S_3.

4,8-diaza-3,3,10,10-tetramethyl-1,2-dithiacyclo decane **(S_1),**

5,8-diaza-3,3,10,10-tetramethyl-1,2-dithiacyclodecane-*N,N'*-diacetic acid **(S_2)**

and *N,N'*-bis(2,2-dimethyl-2-mercaptoethyl)ethylenediamine-*N,N'*-diacetic acid **(S_3)**

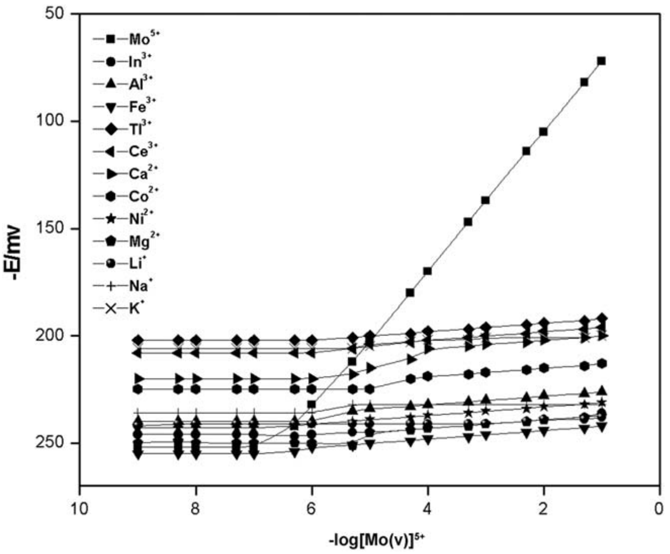

Figure 4.2: Response study of different membrane sensors based on ligand (S_3) with different metal ions.

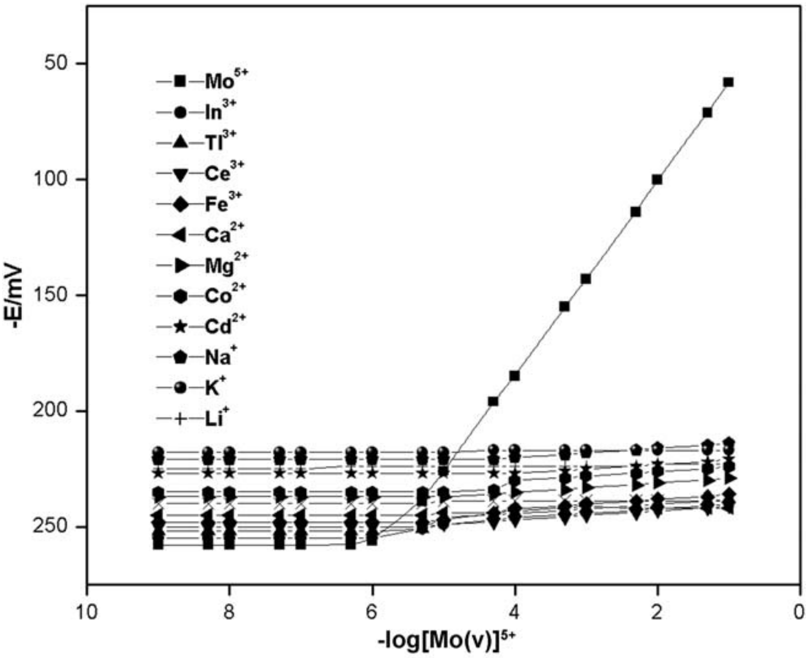

Figure 4.3: Response study of different membrane sensors based on ligand (S_2) with different metal ions.

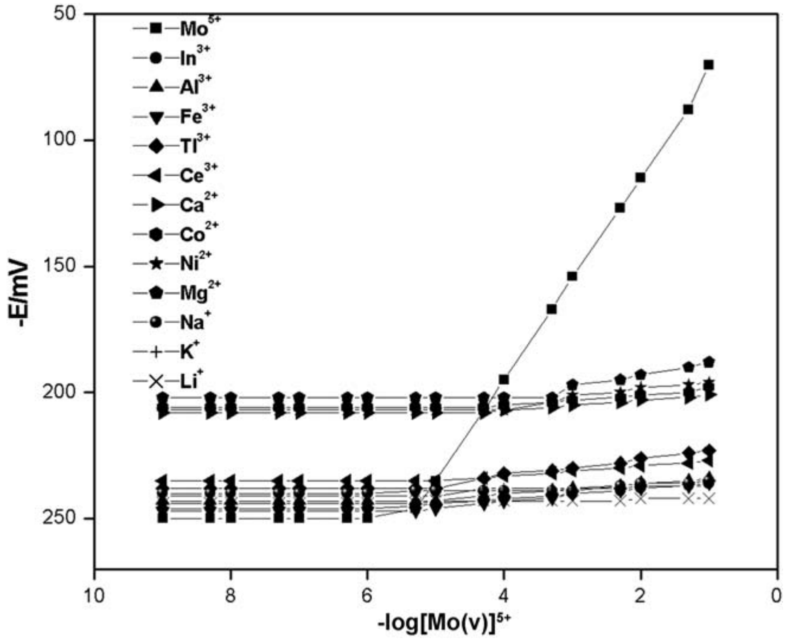

Figure 4.4: Response study of different membrane sensors based on ligand (S_1) with different metal ions.

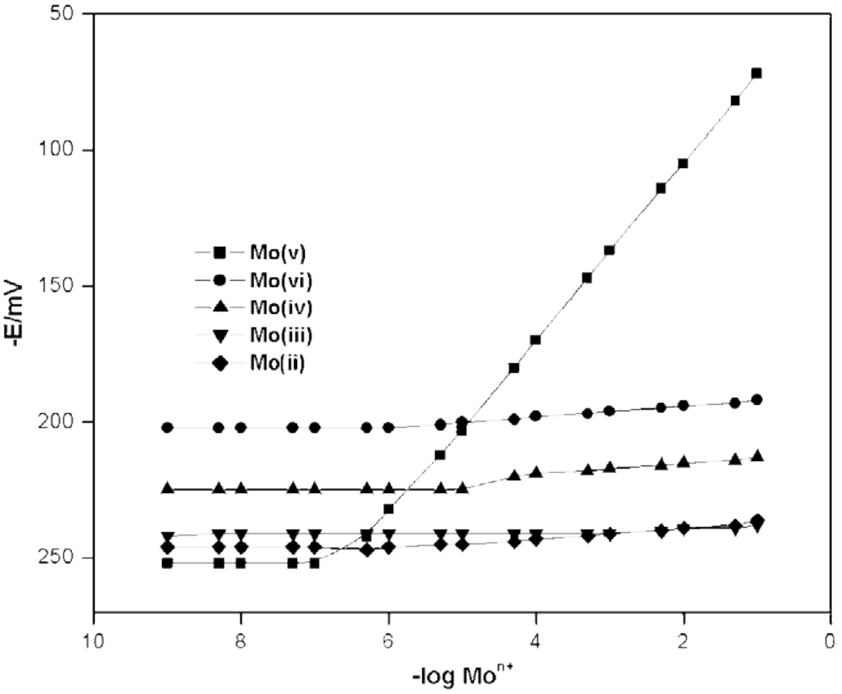

Figure 4.5: Response study of different membrane sensors based on ligand (S_3) with different Mo^{n+} ions.

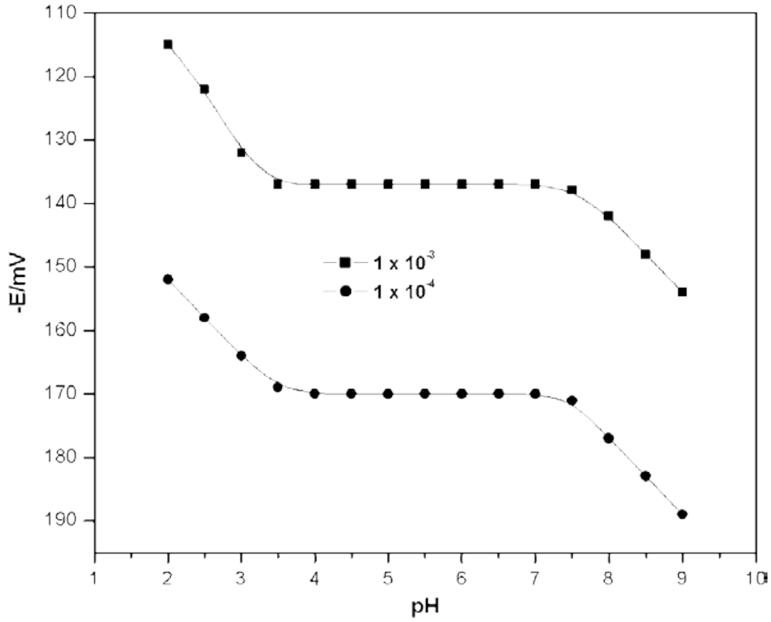

Figure 4.6: Effect of pH on the performance of sensor no. 7 based on ligand (S_3).

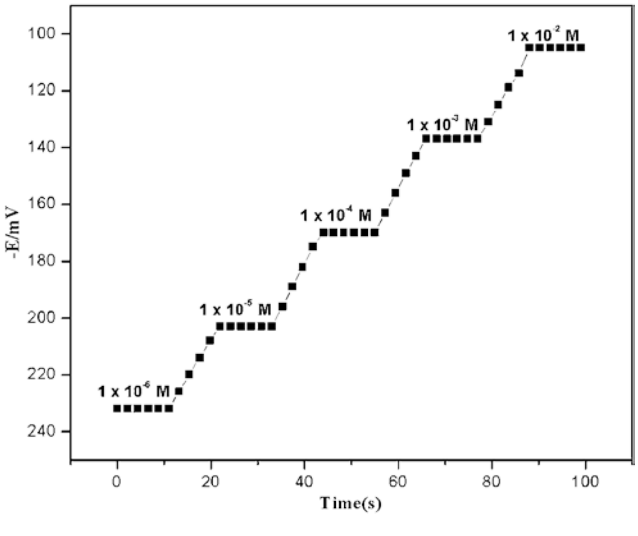

Figure 4.7: Dynamic response study of best responsive membrane sensor no. 7 based on ligand (S_3).

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Chapter 5

5.1. Introduction

Fluoride occurs in all water bodies in small quantity and its content depends on the origin of water sample [1]. It has been found it varies from 0.01 ppm (fresh water) to 1.5 ppm (sea water) [2]. Fluorine being highly reactive, a large number of its compounds both of metals and nonmetals are prepared which find diverse application in domestic and industrial process. Fluorine containing compounds range from potent toxins such as sarin [3] to life saving pharmaceuticals such as efavirenz [4], and from inert materials such as calcium fluoride to the highly reactive sulfur tetrafluoride. The range of fluorine containing compounds is considerable as fluorine is capable of forming compounds with all the elements except helium and neon [5,6].

The applications of fluoride and its compounds are many *viz.*, synthesis of organic and inorganic compounds, enzyme inhibition, nuclear fuel reprocessing, coating of non-sticky fry pans as a PTFE, polymers (Teflon), drugs and fluoridation of drinking water, etc. As a result of its varied applications, the fluoride gets access to the human body causing harm after a certain level of deposition. At higher concentrations, soluble fluoride salts are toxic. Referring to a common salt of fluoride, NaF, the lethal dose is estimated at 1–10 g for adults [7]. A lethal dose is approximately 28 mg/kg of body mass [8]. When the fluoride is ingested via food contamination, it initially acts locally on the intestinal mucosa, where it forms hydrofluoric acid in the stomach. Thereafter it binds with the calcium and interferes with the activity of various enzymes. Some of the chronic toxicities of fluoride ingestion above the lethal limit are dental fluorosis, skeletal fluorosis, and rheumatoid arthritis [9]. Due to large applications of fluoride containing inorganic and organic compounds, a number of natural water bodies are contaminated with fluoride. Thus, the determination of F^{-} ion is very important for the living species. There are number of techniques are available for the determination of fluoride in different samples are atomic absorption spectroscopy (AAS) [10,11], flow–injection [12], gas chromatography (GC) [13], high resolution nuclear magnetic resonance (NMR) spectrometry [14], capillary zone electrophoresis (CZE) [15], radioanalysis [16], colorimetric [17], fluorometric [18], and ion-selective electrode (ISE) [19]. The last decade has seen a rise in the study of ion-selective electrode techniques [20–63] for such purposes. The current research is focussed on the ion-selective electrode for the quantitative determination of fluoride content in different natural samples. However there has been some work already done on fluoride selective sensors. Still many improvements are also necessary for better application ranges. Considering this fact, we have used meso-octamethylcalix[4]pyrrole, tripodal amide receptor and macrocyclic neutral complexes of boron as ionophores in comparative analysis of PVC based membrane sensors in the determination of fluoride in different natural samples with improved working range and detection limit.

5.2. Experimental

5.2.1. Reagents and materials

Pyrrole, acetone and poly(vinyl chloride) (PVC) (Aldrich, Wisconsin, USA), *o*-nitrophenyl octyl ether (*o*-NPOE), CH_2Cl_2, Amberlyst^{TM}-15 (catalyst), dioctylphthalate (DOP), AcOEt, $CHCl_3$, isobutenyl binaphthyl di(acid chloride), n-methyl-2-pyrrolidone (NMP), 4,7,10-trioxatridecane-1,13-diamine and 1-pyrene-boronic acid Fluka (Ronkonkoma, NY), tri-(2-ethylhexyl)phosphate (TEHP) (BDH, Poole, England), 1-chloronapthalene (1-CN), dibutyl(butyl) phosphonate (DBBP), dibutylphthalate (DBP), cetyl trimethyl ammonium bromide (CTAB) from (Mobile Alabama, USA), tridodecylmethyl ammonium chloride (TDMAC), hexadecyltrimethyl ammonium bromide (HTAB), tri-octylmethyl ammonium tris(2-aminoethyl)amine, 3,5-dinitrobenzoyl chloride, triethylamine, chloride (ToMACl), triethylammine $(Et)_3N$, TBAF (tetrabutyl ammonium fluoride) and THF (sisco research Lab, Mumbai, India) products and used as received.

5.2.2. Synthesis of ionophores

5.2.2.1. Synthesis of meso-octamethylcalix[4]pyrrole (M_1)

The ionophore was synthesized as reported [64] with improved yield. 0.5 mL of pyrrole (7.2 mmol) and 0.52 mL of acetone (7.2 mmol) were taken in 5 mL of dichloromethane. To this dry amberlyst™-15 (10% w/w) was added and stirred for 8 hr at ambient temperature. Further progress of the reaction was monitored by thin layer chromatography (TLC). Once the reaction was completed, the catalyst was filtered out and washed with dichloromethane. The obtained filtrate was concentrated by using rotaevoparator and purified with column chromatography using petroleum ether-chloroform (9:1,v/v) as eluent on neutral alumina. Yield; 83%, mp; 296 ^{o}C. The elemental analysis of $C_{28}H_{36}N_4$ shown the results; calc; C; 62.4, H; 14.5, N; 15.4 and found C; 62.7, H; 9.6, N; 15.3, that is consistent to the empirical formula of ionophore.

^{1}H NMR spectra (298 K, δ = ppm); 7.01 (4H, br s, NH), 5.89 (8H, d, *J*=2.5 Hz, *β*-pyrrole), 1.50 (24 H, s). In the ^{1}H NMR spectrum of M_1 a sharp singlet at δ 1 5 0 is assigned to the eight bridge methyl groups, a doublet at δ 5.89 (*J* = 2.5 Hz) to the eight pyrrole ring β-protons and a broad peak at δ 7.01 was assigned to the four N-H protons. The ratio of the integrated peak areas are 6:2:1, in agreement with the empirical formula; $C_{28}H_{36}N_4$. (Fig. 5.1). *I.R (KBr)*; A strong N-H stretching peak appeared at 3450 cm^{-1} in the IR spectra of M_1 in both $CHCl_3$ solution and KBr pellets.

5.2.3. Synthesis of Polyether compounds (M_2 and M_3)

Polyether compounds (M_2 and M_3) were synthesized as pre-reported method [65] from the synthesized precursors; A.

5.2.3.1. Synthesis of precursor; A

6H,22H,30H,41H-trinaphtho[2,3-m:2’,3’-t;2’,3’’a] [1,4,7,15,19,22,26,11,30]hepta -diazacyclotritriaccontine-6,22-dione-7,8,9,10,12,13,15,16,18,19,20,21,31,32,42,43-hexa-decahydro-31,42-bis(methylene)

A solution of diamine derivative (4,7,10-trioxatridecane-1,13-diamine,1 mmol) containing $(Et)_3N$ (200 mg, 2 mmol) in 20 mL dry tetrahydrofuran (THF) was prepared in a flask and was cooled by ice-water bath, then isobutenyl binaphthyl di(acid chloride) (0.677 g, 1 mmol), also in 20 mL THF, was added dropwise to the solution over period of about 20 min and stirring was continued for overnight at room temperature. THF was evaporated off under reduced pressure and water was added into the residue to give a solid. The solid was filtered off, washed several times with water and dried.

Purification was performed by column chromatography with mixed AcOEt and $CHCl_3$ as the eluent. Polyether compound (A) was obtained (Fig. 5.2) as the main products in moderate to good Yield; 36% , Pale yellow solid, ^1H NMR ($CDCl_3$, 500 MHz) d 1.61–1.64 (–CH_2–, 4H, m), 3.30–3.39 (O–CH_2–, 12H, m), 4.76 (=C–CH_2–O, 2H, s), 4.82 (=C–CH_2–O, 2H, s), 5.38 (CH_2=C, 2H, s), 5.50 (CH_2=C, 2H, s), 7.06 (Ar–H, 2H, s), 7.16 (Ar–H, 2H, s), 7.24–7.27 (Ar–H, 4H, m), 7.33–7.36 (Ar–H, 2H, m), 7.49 (Ar–H, 2H, d, 8 Hz), 7.54–7.57 (Ar–H, 2H, m), 7.74 (Ar–H, 2H, d, 8 Hz), 8.02 (NH, 2H, broad), 8.54(Ar–H, 2H, s); TOF–MS: m/z 839.5 $(M^+ H)^+$.

5.2.3.2. Synthesis of M_2

7H,23H-34,39-etheno-6,43;24,30-dimethenotribenzo[o,v,g][1,4,7,11,34] trioxadi-azacycloheptatriacontine-7,23-dione,8,9,10,11,13,14,16,17,19,20,21,22,31,32,33,40,41,42-octadecahydro-44,45,46,47-tetrahydroxy-32,41-bis (methylene.)

Polyether a (100 mg) were dissolved in NMP (5 mL) and the solution was heated at 160 °C for some time different with the ring-size under argon atmosphere. After removal of NMP under reduced pressure, the residue was subjected to column chromatography on silica gel using mixed solvents of AcOEt and $CHCl_3$ as an eluent. The target macrocycles M_2 were obtained as the main product in more than 90% yields (Fig. 5.3).

^1H NMR ($CDCl_3$, 500 MHz) d 1.77–1.81 (–CH_2–, 4H,m), 3.43–3.53 (O–CH_2–, 12H, m), 3.56–3.58 (CONH–CH_2–, 4H, m), 3.85 (=C–CH_2– O, 2H, s), 3.93 (=C–CH_2–O, 2H, s), 4.92 (CH_2=C, 2H, s), 4.93 (CH_2=C, 2H, s), 6.15 (Ar–OH, 2H, s) , 7.00–7.02 (Ar–H, 2H, m), 7.14–7.17 (Ar–H, 2H, m), 7.29 (NH, 2H, broad), 7.31– 7.33 (Ar–H, 2H, m), 7.52 (Ar–H, 2H, d, 8 Hz), 7.57–7.59 (Ar–H, 2H,m), 7.64 (Ar–H, 2H, s), 7.71 (Ar–H, 2H, d, 8 Hz), 12.12 (Ar–OH, 2H, s); TOF–MS: m/z 837.4 $(M - H)^-$

5.2.3.3. Synthesis of M_3

7H,23H-34,39-etheno-6,43;24,30-dimethenotribenzo[o,v,g] [1,4,7,11,34] trioxa-diazacycloheptatriacontine-7,23-boropyrene-8,9,10,11,13,14,16,17,19,20,21,22,31,32,33, 40,41,42-octadecahydro-44,45,46,47-tetrahydroxy-32,41-bis (methylene).

A mixture of the equivalent amount of macrocycle (M_2) and 1-pyrene-boronic acid was dissolved in dry $CHCl_3$ in the presence of molecular sieve 4A, and the solution was continued to reflux overnight. After removal of the molecular sieve 4A by filtration and $CHCl_3$ by evaporation under vacuum, the residue was washed several times by cool methanol to give pure boron complex M_3 in excellent yields (Fig. 5.4).

Green powder, ^1H NMR ($CDCl_3$, 500 MHz) d 1.63-1.64 (–CH_2–, 4H, m), 3.24–3.27 (CONH–CH_2–, 4H, m), 3.30–3.33 (O–CH_2–, 4H, m), 3.48–3.49 (O–CH_2–, 8H, m), 4.03 (=C–CH_2–O, 2H, s), 4.05 (=C–CH_2–O, 2H, s), 5.09 (CH_2=C, 2H, s), 5.14 (CH_2=C, 2H, s), 7.02 (NH, 2H, broad), 7.15–7.17 (Ar–H, 2H, m), 7.20–7.23 (Ar–H, 2H,m), 7.52–7.53 (Ar–

H, 4H, m), 7.92 (Ar–H, 2H, d, 8.5 Hz), 7.96–7.97 (Ar–H, 2H, m), 8.07–8.16 (Py–H, 3H, m), 8.17 (Ar–H, 2H, s), 8.18–8.32 (Py–H, 4H, m), 8.44 (Py–H, 1H, d, 7.5 Hz), 8.98 (Py–H, 1H, d, 7.5 Hz), 12.04 (Ar–OH, 2H, s); TOF–MS: m/z 1033.8 $(M–H)^{-}$.

5.2.3.4. Synthesis of M_4: Dinitrophenyl functionalized tris-(amide)

Tripodal amide-based receptor [M_4] was synthesized by the reaction of tris(2-aminoethyl)amine with three equivalent of 3,5-dinitrobenzoyl chloride in the presence of triethylamine in dry chloroform at room temperature [66]. After stirring overnight, the reaction mixture was filtered and the precipitate was washed with water and methanol to remove the triethylammonium chloride and dried under vacuum to yield the light brown solid (Yield = 68%). The ionophore (Fig. 5.5) M_4 has been characterized by NMR, FT-IR, and ESI-MS.

M_4 m.p. = 252 ^{o}C; ^{1}H NMR (400 MHz, DMSO-*d6*) δ 2.79 (s, 6H, $-NCH_2$), 3.43 (s, 6H, $-OCH_2$), 8.88 (s,3H, ArH_{para},), 8.91 (s, 6H, ArH_{ortho}), 9.12 (s, 3H, -NH); ^{13}C NMR (100 MHz, DMSO-*d6*): δ 45.73 (×3C, $-NCH_2$), 53.08 (×3C, $-OCH_2$), 120.58 (×3C, ArH), 127.35 (×3C, ArH), 137.06 (×3C, ArH), 148.01 (×3C, ArH), 162.20 (×3C, C=O); ESI-mass: 729.15 [M+1]; FT-IR (υ cm^{-1}): 1670 (C=O), 3428 (N-H).

5.2.4. Preparation of PVC membrane electrodes

The PVC based membrane electrodes were fabricated [67] as explained in section 3.2.3.1., by dissolving appropriate amounts of membrane ingradients such as PVC as inert matrix, ionophores (M_1–M_4), cationic excluders (HTAB, TDMAC, CTAB and ToMACl) and plasticizers (DOP, CN, *o*-NPOE, DBBP, DBP, TEHB) in 5 mL of THF. It is known that the sensitivity and selectivity membrane electrodes mainly depend on the composition and ratio of membrane ingradients [68–71]. Thus, different membrane electrodes were fabricated with different membrane ingredients and ratio. The membranes having only

PVC as membrane ingredient (dummy membranes) have also been prepared to observe the presence of any background potentials due to binding of material. The potentials were not generated in the absence of the electroactive material ionophore in the membrane.

5.2.5. Equilibration of membranes and potential measurements

The prepared membranes were equilibrated for two days in 0.01 M TBAF (tetrabutyl ammonium fluoride) solution. The potentials were measured with a digital potentiometer (model 5652 A, ECIL, India) by varying the concentration of F^- in the test solution in the range 1.0×10^{-2} - 1.0×10^{-9} mol L^{-1} using a buffer solution Tris–HCl (pH 4.0). The cell assembly set up was as follows by using saturated calomel electrodes (SCE) as reference electrodes.

SCE | test solution || PVC membrane || 0.01M F^-(TBA salt)| SCE (Internal)

The activities of metal ions were calculated from the modified form of the Debye–Huckel equation [72].

5.3. Result and discussion

5.3.1 Effect of internal solution

The concentration effect of internal solution was on the F^- ion-selective membrane electrodes based on M_1-M_4 was examined by potentiometric technique in the range of 1.0×10^{-1} to 1.0×10^{-4} mol L^{-1}. It was observed that concentration of internal solution 1.0×10^{-2} mol L^{-1} was showing good results and this concentrated solution was treated as internal solution.

5.3.2. Optimization of membrane composition

In order to achieve a best polymeric membrane electrode for the selective determination of F^-, various membrane electrodes were prepared with different composition of membrane ingradients in different ratio. The potentiometric characteristic were calculated according to the IUPAC recommendations [73,74] and the results were shown in Table 5.1 to 5.3.

5.3.2.1. Effect of addition of plasticizer

Plasticizer plays an important role in the preparation of PVC based ion-selective electrode, It enhances the sensitivity and selectivity [75,76]. Once the membrane sensors based on different ligands (M_1–M_4) were synthesized and as their responses were checked against different concentration of F^- ion. Thus different membrane electrodes were prepared with the addition of different plasticizers having a different dielectric constants (ε) i.e., CN ($\varepsilon = 5$), *o*-NPOE ($\varepsilon = 24$), DBP ($\varepsilon = 6.4$), DOP ($\varepsilon = 5$), DBBP ($\varepsilon = 4.6$), TEHP ($\varepsilon = 4.8$) and PVC ($\varepsilon = 3.9$). The results of the effect of plasticizer on F^- membrane sensors based on different ligands are shown in Table 5.1. It is clear from the table that *o*-NPOE is a more effective plasticizer than that of others in preparing the F^- ISEs, may be due to its high dielectric constant providing the higher charge distribution in the membrane phase, which in turn increases the F^- ion-selectivity for proposed ionophores. The rest of the plasticizers other than *o*-NPOE have less dielectric constant and lead to smaller binding constants. It is cleared from the results that the plasticizers influence the mobility of ionophore and dielectric constant of complex [77,78].

5.3.2.2. Effect of addition of anionic additives

In order to reduce the resistance in the membrane, it is necessary to add the anionic additives. It could be helpful for improving the electrode performance. Thus membrane electrodes with different anionic excluders were prepared and its potentiometric characteristics were calculated and results were tabulated Table 5.2. It was cleared that the additive CTAB having 3.5 w/w % was found to be shown good results. It may be interpreted on the assumption that CTAB is a straight chain cationic surfactant incorporated in the membrane phase giving membrane uniform structure and making bromide ion available for exchange, thus acting as best anionic additive.

5.3.3. Response of the membrane sensors based on different ligands (M_1 to M_4)

The response studies of membrane sensors based on different ligands (M_1–M_4) was studied and it was found that the selectivity and sensitivity of membrane sensors were in order of $M_1 > M_4 > M_3 > M_2$ respective ligands. The high sensitivity and selectivity of M_1 based sensor can be easily understood as it has four HN of pyrrole which participates in H-bonding with F^- more suitably in comparison to others (M_2–M_4). Also the presences of octa-methyl groups, attached to the ring are advantageous for H-bonding with less steric hindrance [79]. Whereas M_3 (macrocyclic boron complex) is found to have average selectivity for F^- owing to its plural hydrogen bonding sites (hydroxy and amide groups), lewis acid site (neutral boron atom) and signaling subunit (pyrene fluorophore) [80] but due to stearic hindrance it is less sensitive and selective in comparison to M_1. The sensitivity and selectivity of M_2 is found to be less in comparison to all (M_1, M_3 and M_4) because of the absence of lewis acid site (neutral boron atom) with respect to M_3 and presence of some more steric hindrance with respect to M_1 and M_4. The good response against M_4 was reported because it is sterically more favorable for H-bonding with TBA-F. The best responsive characteristics of different ligand (M_1- M_4) based membranes are shown in Fig. 5.6 and Table 5.3.

5.3.4. Spectroscopic study on anion recognition property of different synthesized Inophores (M_1 to M_4)

We studied the UV/Vis spectroscopic study of H-bonding receptors (M_1–M_4) with different anions. The absorption spectra of H-bonding receptor M_1 was recorded in MeOH (3×10^{-5} mol/L). In the absence of anion, the receptor M_1 is characterized by a peak at 218 nm while on addition of TBA-F the absorption maxima is shifted to longer wavelength (Fig. 5.7) and absorption maxima of TBA-F is found to be higher in comparison to other anions. Similarly we studied the UV/Vis spectroscopic study for ionophore M_4 and it was found that receptor M_4, in the absence of any anionic guest, shows no characteristic absorption in the visible spectrum when recorded in any aprotic solvents. The UV/Vis study suggests that M_4 can selectively detect fluoride ions colorimetrically even in the presence of other competitive anions like Cl^-, Br^-, I^-, AcO^-, $NO3^-$ and SCN^- (Fig. 5.8). Upon gradual addition of standard F^- solution (10 mM) to a solution of M_4 (10 mM) in DMSO, a new absorption bands appears at λ_{max} = 388 nm. The absorption study of M_2 and M_3 was carried out in EtOH solution at 3.5×10^{-5} mol L^{-1} and 3×10^{-5} mol L^{-1} respectively. The absorption maxima's (λ_{max}) reported at 333 nm and 340 nm respectively after addition of TBA salts different anions (Figs. 5.9 and 5.10).

5.3.5. Determination of formation constant

In order to know the effinity between the ion-ionophore, the formation constants were calculated. In this communication formation constants were calculated by sandwich membrane method [81] as described in section 3.3.1. The formation constants were evaluated in terms of (log β_{ILn}) and shown in Table 5.4. It was found from the table 5.4, that all the ionophores are showing high binding constant values with F^- ion as compared to rest of the anions.

5.3.6. Determination of selectivity of membrane sensors for different anionic species

Selectivity coefficient values of the best responsive membrane sensors (8, 16 and 32) based on different ligands (M_1–M_3) was evaluated by using fixed interference method (FIM) [82] for different anionic species (B^{n-}). It is pertinent to mention here that selectivity coefficients determined by MPM method are sensitive function of concentration of the interfering ion while these do not depend upon concentration substantially when determined by FIM method therefore we used FIM method in order to avoid concentration dependence. As we described in section 3.3.3, we calculated the selectivity coefficient values at constant activity of interfering ion at 1.0×10^{-2} mol L^{-1} by maintain pH at 6.5 (Tris–HCl buffer).

The determined selectivity coefficient values for membrane sensor (16,24 and 8) are compiled in Table 5.5 and found that the polymeric membrane electrode no. 16 (based on M_1) showing best selectivity for F^- ion over most of the anions.

5.3.7. pH and non-aqueous effect.

The pH profile is one of the most important required parameter of an ion-selective electrode. Thus the pH effect was examined for the electrodes (16, 24, 8 and 32), at concentration 1.0×10^{-2} mol L^{-1} of F^- ion. The potentials were observed in the pH range 1.5-9.0 and a graph was ploted between potential vs pH (Fig. 5.11). From the figure it was cleared the the potentials were found to be constant from 2.5 - 6.5 and this range was taken as the working concentration range. Further, the effect of non-aqueous solutions such as water-ethanol, water-methanol and water acetonitrile was examined for electrode no. 16. Thus, from the obtained potentiometric characteristics (Table 5.6), it was cleared that the electrode is successfully working under 20% of non-aqueous solution. After the 20 % of the non-aqueous solution, the working concentration values are reducing gradually, so 20 % of non-aqueous solution is acceptable for the proposed electrode.

5.3.8. Stoichiometric Study of Ligand M_1

The stoichiometry of interaction between fluoride anion (F^-) and M_1 was studied by using Job's method [83]. The concentration of M_1 and TBAF was taken to be 2.0 × 10^{-3} M. Nine ethanolic solutions were prepared containing M_1 and TBAF in various molar ratios so that the final volume always amounted to 10 mL with the addition of buffer solution Tris–HCl (pH 4.0). The extraction was performed using 10 mL of acetone and the absorbance was measured at 223 nm. The plot reaches maximum value at a mole fraction $X_{max} = 0.5$ (Fig. 5.12), which indicates the 1:1 molar ratio interaction.

5.3.9. Dynamic response and life time

The dynamic response time and life time are also important parameters of the ion-selectivity electrode. The dynamic response time of the proposed electrode (electrode no. 16) was taken from the potential by changing 10 fold concentration of the test solution in the range 1.0 × 10^{-6} to 1.0 × 10^{-2} mol L^{-1}. The graph was drawn between potential vs time (Fig. 5.13) and found that the proposed electrode (electrode no. 16) is showing high response time i.e., 11 s. The electrode is showing good shelf life time of two and half months without any significant changes in the potentiometric properties. When the electrode is not in use, it is better to store in 1.0 × 10^{-2} mol L^{-1} solution of tetrabutyl ammonium fluoride (TBAF).

5.4. Analytical applications

5.4.1. Analytical application in determination of fluoride content in tea leaves

The sensor no. 16 analytically utilized in determination of fluoride contents in different Indian based tea samples.

5.4.1.1. Preparation of sample

One hundred grams of tea specimens was equally divided into four parts. A 10 g sample was taken randomly from each part, mixed evenly, and kept dried at 60 °C in a desiccator for 4 h. Then the sample was spread on a 10 cm × 10 cm square, and approximately 3 g was taken from five separate areas of the sample and mixed thoroughly. From this a 2.0 g accurately weighed sample was used for the experiment. Three triplicate samples were collected by the above-mentioned procedure. Each experimental sample was added to 200 mL of de-ionized water (100 °C) and kept on a water bath (100 °C) for 10 min, cooled to room temperature, filtered, and the filtrate brought back to 200 mL with de-ionized water.

5.4.1.2. Determination of F^- contents by electrode

According to the fluoride determination method [84] introduced by the US Environment Protection Agency (USEPA, 2005), 10 mL prepared tea infusion sample was combined with 10 mL TIASB buffer, brought to 50 mL with de-ionized water and mixed evenly. After stabilization, the electrical potential was recorded using the F^- selective electrode and reference electrode.

5.4.1.3. Sample preparation for spectrophotometric method

Fluoride standard solution 0, 1.00, 2.00, 4.00, 6.00, 8.00 mL were, respectively, poured into six flasks, added with de-ionized water to 10 mL, and then added with 10 mL mixed coloration solution, diluted to the scale with de-ion water, shaking evenly, put aside for an hour. Light absorption was measured at 620 nm wavelength, in contrast with pure water. Reagent vacancy of light absorption was deducted (zero content). The graph of light absorption was drawn to show the fluoride content and standard curve was obtained. According to the calculation C = KA, the relevant coefficient was 0.999.

5.4.1.4. Determination of F^- by spectrophotometric method

Ten milliters of experimental tea infusion was put into a flask, brought to 50 mL with de-ionized water, from which 10 mL solution was taken out and put into 10 mL flask, added with coloration solution 10 mL, quantified to 25 mL with de-ionized water, mixed evenly and put aside for 1 h. In contrast with pure water, light absorption was determined. Fluoride content was calculated with light absorption on the standard curve. The analysis data from both the methods are compiled in Table 5.7 The proposed method is faster, cheaper, and more accurate in comparison to already used methods.

Tables:

Table 5.1: Optimization of membranes composition based on different ligands (M_1 to M_4).

Sen. No.	Composition of membrane sensors (%w/w)				Working Range (M)	*Slope ± 0.5	Response Time (s)
	Ionophore	PVC	Additives	Plasticizer			
1	0.0, M_3	30.0	4.0, CTAB	66.0	-	-	20
2	13.0, M_3	73.0	14.0, CTAB	0.0	4.6×10^{-3} -1.0×10^{-2}	-56.0	25
3	3.5, M_3	30.0	3.5 , CTAB	63.0, DBP	4.6×10^{-5} -1.0×10^{-2}	-57.6	18
4	3.5, M_3	30.0	3.5, CTAB	63.0, DBBP	3.5×10^{-4} -1.0×10^{-2}	-56.8	21
5	3.5, M_3	30.0	3.5, CTAB	63.0, TEHP	2.9×10^{-4} -1.0×10^{-2}	-57.0	19
6	3.5, M_3	30.0	3.5, CTAB	63.0, CN	5.8×10^{-4} -1.0×10^{-2}	-58.0	17
7	3.5, M_3	30.0	3.5, CTAB	63.0, DOP	5.5×10^{-4} -1.0×10^{-2}	-57.8	15
8	**3.5**, M_3	**30.0**	**3.5**, CTAB	**63.0, *o*-NPOE**	**2.6×10^{-6} -1.0×10^{-2}**	**-59.5**	**11**
9	0.0, M_1	30.0	4.0, CTAB	66.0	-	-	25
10	13.0, M_1	73.0	14.0, CTAB	0.0	7.5×10^{-4} -1.0×10^{-2}	-57.8	14
11	3.5, M_1	30.0	3.5, CTAB	63.0, DBP	3.6×10^{-6} -1.0×10^{-2}	-59.2	18
12	3.5, M_1	30.0	3.5, CTAB	63.0, DBBP	5.6×10^{-5} -1.0×10^{-2}	-58.5	15
13	3.5, M_1	30.0	3.5, CTAB	63.0, TEHP	4.5×10^{-5} -1.0×10^{-2}	-58.7	13
14	3.5, M_1	30.0	3.5, CTAB	63.0, CN	4.8×10^{-6} -1.0×10^{-2}	-58.8	11
15	3.5, M_1	30.0	3.5, CTAB	63.0, DOP	4.6×10^{-6} -1.0×10^{-2}	-58.5	12
16	**3.5**, M_1	**30.0**	3.5, CTAB	**63.0, *o*-NPOE**	**2.5×10^{-7} -1.0×10^{-2}**	**-59.8**	**11**
17	0.0, M_4	30.0	4.0, CTAB	66.0	-	-	24
18	13.0, M_4	73.0	14.0, CTAB	0.0	9.2×10^{-4} -1.0×10^{-2}	-56.5	15
19	3.5, M_4	30.0	3.5, CTAB	63.0, DBP	4.6×10^{-6} -1.0×10^{-2}	-59.1	18
20	3.5, M_4	30.0	3.5, CTAB	63.0, DBBP	7.2×10^{-5} -1.0×10^{-2}	-58.5	19

21	3.5, M$_4$	30.0	3.5, CTAB	63.0, TEHP	6.3×10^{-5} -1.0×10^{-2}	-58.6	17
22	3.5, M$_4$	30.0	3.5, CTAB	63.0, CN	5.7×10^{-6} -1.0×10^{-2}	-57.5	16
23	3.5, M$_4$	30.0	3.5, CTAB	63.0, DOP	5.5×10^{-6} -1.0×10^{-2}	-58.4	13
24	**3.5**, M$_4$	**30.0**	3.5, CTAB	**63.0, *o*-NPOE**	**5.5×10^{-7} -1.0×10^{-2}**	**-59.6**	**13**
25	0.0, M$_2$	30.0	4.0, CTAB	66.0	-	-	20
26	13.0, M$_2$	73.0	14.0, CTAB	0.0	8.2×10^{-4} -1.0×10^{-2}	57.2	17
27	3.5, M$_2$	30.0	3.5 (CTAB)	63.0, DBP	7.2×10^{-6} -1.0×10^{-2}	-59.4	16
28	3.5, M$_2$	30.0	3.5 (CTAB)	63.0, DBBP	8.2×10^{-5} -1.0×10^{-2}	-58.7	16
29	3.5, M$_2$	30.0	3.5 (CTAB)	63.0, TEHP	7.5×10^{-5} -1.0×10^{-2}	-58.4	15
30	3.5, M$_2$	30.0	3.5 (CTAB)	63.0, CN	6.2×10^{-6} -1.0×10^{-2}	-59.2	18
31	3.5, M$_2$	30.0	3.5 (CTAB)	63.0, DOP	6.0×10^{-6} -1.0×10^{-2}	-59.0	17
32	**3.5**, M$_2$	**30.0**	**3.5 (CTAB)**	**63.0, *o*-NPOE**	**4.4×10^{-6} -1.0×10^{-2}**	**-59.5**	**17**

* Triplicate measurement.

Table 5.2: Effect of different cationic additives on the performance of best optimized membrane sensors based on ligands (M_1 to M_4).

Membrane sensor composition	**Anionic additives	Working concentration range (M)	Detection limit ± 0.5 (M)	*Slope ± 0.5
M_1 : PVC : *o*-NPOE (w/w%) 3.5 : 30.0 : 63.0	-	4.5×10^{-4} to 1.0×10^{-2}	3.8×10^{-5}	-57.0
	CTAB	2.5×10^{-7} to 1.0×10^{-2}	1.3×10^{-7}	-59.8
	HTAB	4.3×10^{-7} to 1.0×10^{-2}	3.2×10^{-7}	-59.5
	TDMAC	3.8×10^{-7} to 1.0×10^{-2}	2.5×10^{-7}	-59.6
	ToMACl	3.5×10^{-7} to 1.0×10^{-2}	2.4×10^{-7}	-59.6
M_3 : PVC : *o*-NPOE (w/w%) 3.5 : 30.0 : 63.0	-	4.3×10^{-4} to 1.0×10^{-2}	3.5×10^{-4}	-57.5
	CTAB	2.6×10^{-6} to 1.0×10^{-2}	1.6×10^{-6}	-59.5
	HTAB	5.6×10^{-6} to 1.0×10^{-2}	4.3×10^{-6}	-59.3
	TDMAC	4.8×10^{-6} to 1.0×10^{-2}	3.7×10^{-6}	-59.3
	ToMACl	4.6×10^{-6} to 1.0×10^{-1}	3.4×10^{-6}	-59.5
M_4 : PVC : *o*-NPOE (w/w%) 3.5 : 30.0 : 63.0	-	5.6×10^{-4} to 1.0×10^{-2}	4.2×10^{-4}	-57.3
	CTAB	5.5×10^{-7} to 1.0×10^{-2}	4.4×10^{-7}	-59.6
	HTAB	8.3×10^{-7} to 1.0×10^{-2}	7.2×10^{-7}	-59.4
	TDMAC	7.8×10^{-7} to 1.0×10^{-2}	6.3×10^{-7}	-59.5
	ToMACl	6.7×10^{-7} to 1.0×10^{-2}	5.6×10^{-7}	-59.5
M_2 : PVC : *o*-NPOE (w/w%) 3.5 : 30.0 : 63.0	-	4.4×10^{-4} to 1.0×10^{-2}	4.2×10^{-4}	-57.3
	CTAB	4.4×10^{-6} to 1.0×10^{-2}	3.3×10^{-6}	-59.5
	HTAB	8.4×10^{-6} to 1.0×10^{-2}	7.5×10^{-6}	-59.4
	TDMAC	7.7×10^{-6} to 1.0×10^{-2}	6.6×10^{-6}	-59.5
	ToMACl	6.3×10^{-6} to 1.0×10^{-2}	5.8×10^{-6}	-59.5

*Triplicate measurement.

**Cationic additives added at 3.5 (%w/w of membrane composition).

Table 5.3: Comparative results of best performing fluoride selective sensors.

Sensor No.	Working Range (M)	Detection Limit (M) ± 0.5	*Slope ± 0.5	Response Time (S)
16	2.5×10^{-7} -1.0×10^{-2}	1.3×10^{-7}	-59.8	11
24	5.5×10^{-7} -1.0×10^{-2}	4.4×10^{-7}	-59.6	13
8	2.6×10^{-6} -1.0×10^{-2}	1.6×10^{-6}	-59.3	11
32	4.4×10^{-6} -1.0×10^{-2}	3.3×10^{-6}	-59.5	17

Table 5.4: Binding constant measurement for M_1, M_2, M_3 & M_4 ligands with different anions.

Anion	M_1	M_3	M_4	M_2
	Formation constant (log β_{ILn})* ± SD	Formation constant (log β_{Iln})* ± SD	Formation constant (log β_{Iln})* ± SD	Formation constant (log β_{Iln})* ± SD
SCN^-	4.15 ± 0.05	2.88 ± 0.06	3.97 ± 0.03	2.66 ± 0.08
Cl^-	5.05 ± 0.03	4.18 ± 0.05	4.89 ± 0.04	3.89 ± 0.05
F^-	6.78 ± 0.05	5.45 ± 0.08	6.23 ± 0.05	5.39 ± 0.07
$H_2PO_4^-$	4.96 ± 0.06	3.65 ± 0.06	4.42 ± 0.03	3.60 ± 0.04
Br^-	4.76 ± 0.19	3.54 ± 0.21	4.51 ± 0.22	3.49 ± 0.06
HSO_4^-	4.58 ± 0.15	3.44 ± 0.06	4.44 ± 0.11	3.38 ± 0.03
I^-	4.43 ± 0.13	3.32 ± 0.11	4.31 ± 0.08	3.29 ± 0.07
CH_3COO^-	4.30 ± 0.16	3.28 ± 0.20	4.11 ± 0.22	3.25 ± 0.06
N_3^-	4.05 ± 0.12	2.76 ± 0.21	3.85 ± 0.11	2.68 ± 0.05
NO_2^-	3.89 ± 0.21	2.66 ± 0.09	3.71 ± 0.11	2.59 ± 0.06
NO_3^-	3.78 ± 0.25	2.56 ± 0.16	3.65 ± 0.09	2.50 ± 0.04
$HCOO^-$	3.62 ± 0.21	2.43 ± 0.15	3.54 ± 0.05	2.39 ± 0.07
Citrate ion	3.54 ± 0.16	2.38 ± 0.05	3.41 ± 0.16	2.31 ± 0.05
SO_4^{2-}	3.38 ± 0.10	2.11 ± 0.06	3.13 ± 0.06	2.03 ± 0.05
CO_3^{2-}	3.08 ± 0.15	2.03 ± 0.08	3.03 ± 0.08	1.98 ± 0.04
$C_2O_4^{2-}$	2.86 ± 0.07	1.96 ± 0.05	2.86 ± 0.04	1.88 ± 0.06

*Mean value ± standard deviation (three measurements).

Table 5.5: Selectivity coefficient values measured for different anionic species by Fixed Interference Method (Sensor no. 16, 8, 24 & 32)**.

Interfering ion (B)	$-logK^{Pot}_{F^-,\ B}$ (no.16) FIM*	$-logK^{Pot}_{F^-,\ B}$ (no.24) FIM*	$-logK^{Pot}_{F^-,\ B}$ (no.8) FIM*	$-logK^{Pot}_{F^-,\ B}$ (no.32) FIM*
Cl^-	1.32	2.23	2.44	2.48
Br^-	1.52	1.46	1.51	1.56
I^-	1.76	1.53	1.62	1.67
CH_3COO^-	1.86	2.37	2.42	2.39
HSO_4^-	1.68	1.62	1.71	1.68
SO_4^{2-}	3.13	4.05	4.26	4.11
$H_2PO_4^-$	1.38	2.31	2.38	2.29
NO_2^-	2.12	3.08	3.16	3.06
CO_3^{2-}	3.45	4.16	4.23	4.18
NO_3^-	2.22	3.15	3.25	3.18
SCN^-	1.95	2.85	2.87	2.80
$C_2O_4^{2-}$	3.76	4.23	4.28	4.21
Citrate	2.53	3.32	3.38	3.30
$HCOO^-$	2.45	3.22	3.32	3.29
N_3^-	2.04	2.95	3.06	2.99

* Fixed Interference Method.

** Measured at pH; 6.5.

Table 5.6: The performance of best F^- selective sensor (no. 16) in non-aqueous content.

Non–aqueous content (%v/v)	Working concentration range (M)	Slope (± 0.5 mV decade^{-1} of activity)
0	2.5×10^{-7} to 1.0×10^{-2}	-59.8
Methanol		
10	2.5×10^{-7} - 1.0×10^{-2}	-59.8
20	2.6×10^{-7} - 1.0×10^{-2}	-59.8
25	6.8×10^{-7} - 1.0×10^{-2}	-59.6
30	2.6×10^{-6} - 1.0×10^{-2}	-59.4
35	4.4×10^{-6} - 1.0×10^{-2}	-59.4
Ethanol		
10	2.5×10^{-7} - 1.0×10^{-2}	-59.8
20	2.5×10^{-7} - 1.0×10^{-2}	-59.8
25	7.5×10^{-7} - 1.0×10^{-2}	-59.7
30	3.2×10^{-6} - 1.0×10^{-2}	-59.6
35	5.2×10^{-6} - 1.0×10^{-2}	-59.5
Acetonitrile		
10	2.5×10^{-7} - 1.0×10^{-2}	-59.8
20	2.5×10^{-7} - 1.0×10^{-2}	-59.8
25	8.5×10^{-7} - 1.0×10^{-2}	-59.6
30	5.1×10^{-6} - 1.0×10^{-2}	-59.5
35	7.1×10^{-6} - 1.0×10^{-2}	-59.5

Table 5.7: Comparative analysis of different Tea samples of Indian origin.

Sample Brand Name	Fluoride in Tea Infusion (mg/mL)		
	[a]Sensor no. 16	[b]UV/Vis.	Mean
Tata Tea	1.54 ± 0.04	1.51 ± 0.05	1.53
Tajmahal Tea	1.43 ± 0.03	1.44 ± 0.04	1.44
Kesri Tea	1.66 ± 0.05	1.61 ± 0.03	1.64
Upper Assam	1.71 ± 0.04	1.69 ± 0.04	1.70
Pataka Tea	1.88 ± 0.04	1.87 ± 0.02	1.88
Duccan Tea	1.48 ± 0.05	1.44 ± 0.03	1.46
Lipton Tea	1.63 ± 0.02	1.64 ± 0.04	1.64

[a] Significantly different ($p < 0.05$).

[b] Significantly different ($p < 0.05$).

Figures:

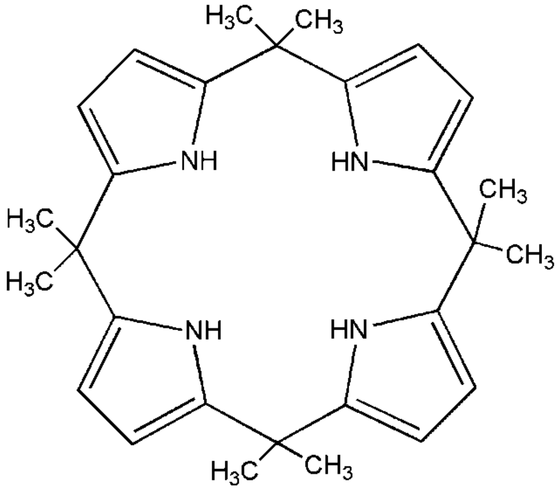

Figure 5.1: Ionophore M_1, meso-octamethylcalix[4]pyrrole.

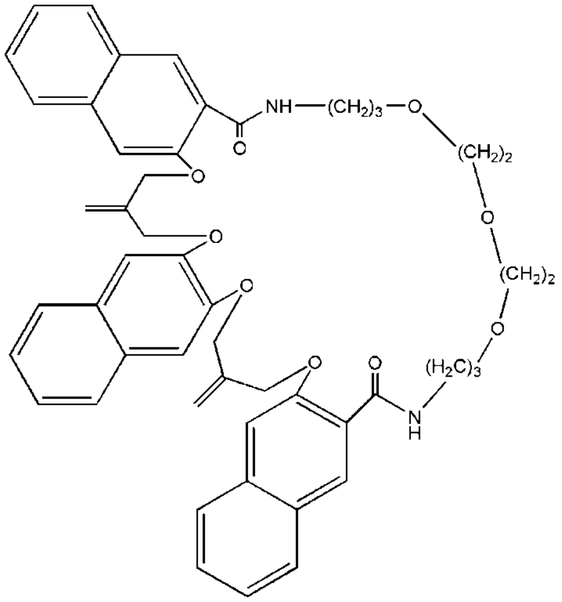

Figure 5.2: Figure of intermediate A, 6H,22H,30H,41H-trinaphtho[2,3-m:2’,3’-t;2’,3”*a*] [1,4,7,11,15,19,22,26,30] heptaoxadiazacyclotritriaccontine-6,22-dione-7,8,9, 10,12,13,15,16,18,19,20,21,31,32,42,43-hexadecahydro-31,42-bis(methylene).

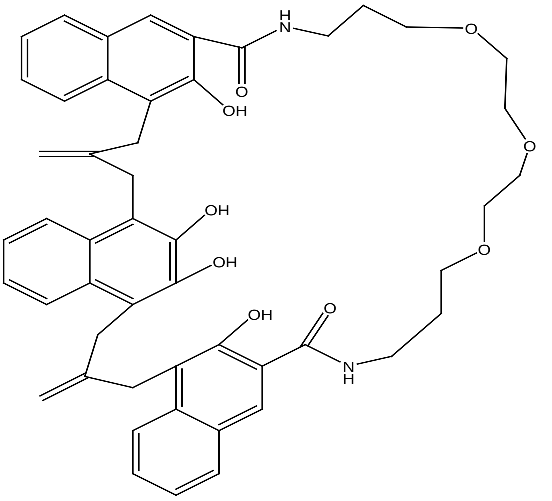

Figure 5.3: Figure of ionophore M_2, [7H,23H-34,39-etheno-6,43;24,30-dimethenotribenzo[o,v,g] [1,4,7,11,34] trioxadiazacycloheptatriacontine-7,23-dione-8,9,10,11,13,14,16,17,19,20,21,22,31,32,33,40,41,42-octadecahydro-44, 45,46,47-tetrahydroxy-32,41-bis (methylene).

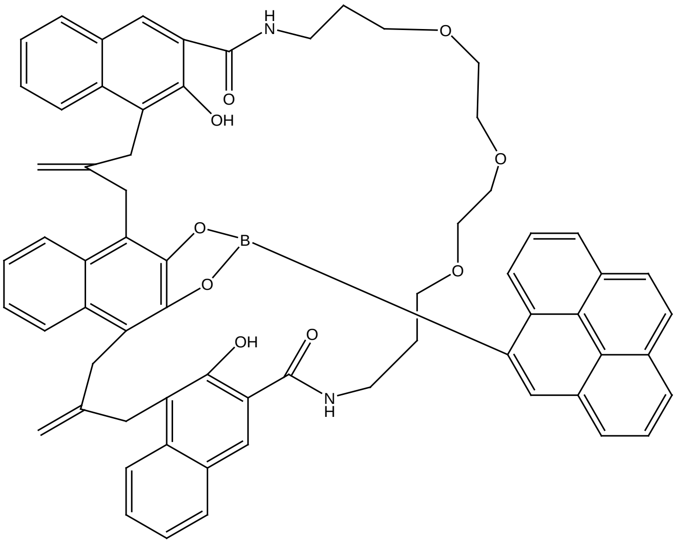

Figure 5.4: Figure of ionophore M_3, 7H,23H-34,39-etheno-6,43;24,30-dimethenotribenzo[o,v,g] [1,4,7,11,34] trioxadiazacycloheptatriacontine-7,23-boropyrene-8,9,10,11,13,14,16,17,19,20,21,22,31,32,33,40,41,42-octadeca-hydro-44,45,46,47-tetrahydroxy-32,41-bis(methylene).

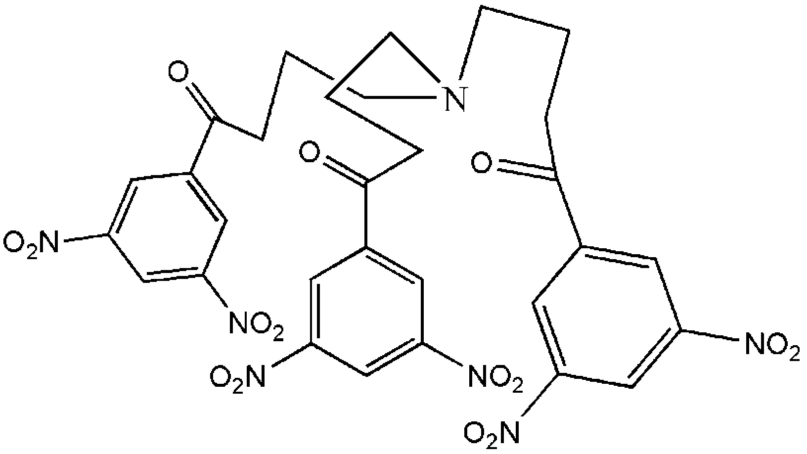

Figure 5.5: Figure of ionophore M_4, dinitrophenyl functionalized tris-(amide).

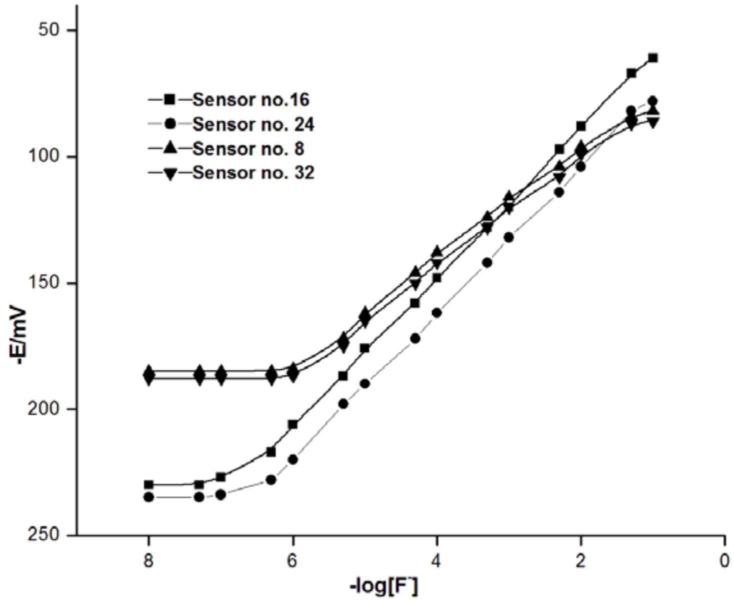

Figure 5.6: The potentiometric response study of optimized PVC membranes of different used ionophores (M_1–M_4). at working pH (2.5–6.5).

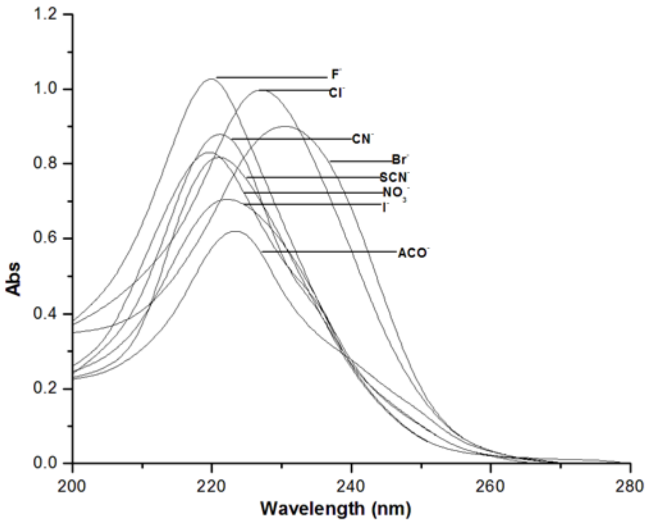

Figure 5.7: UV/Vis spectroscopic study of H-bonding ionophore (M_1) with different anions. At working pH (2.5–6.5), recorded in MeOH (3×10^{-5} mol L^{-1}). After shifting to longer wavelength.

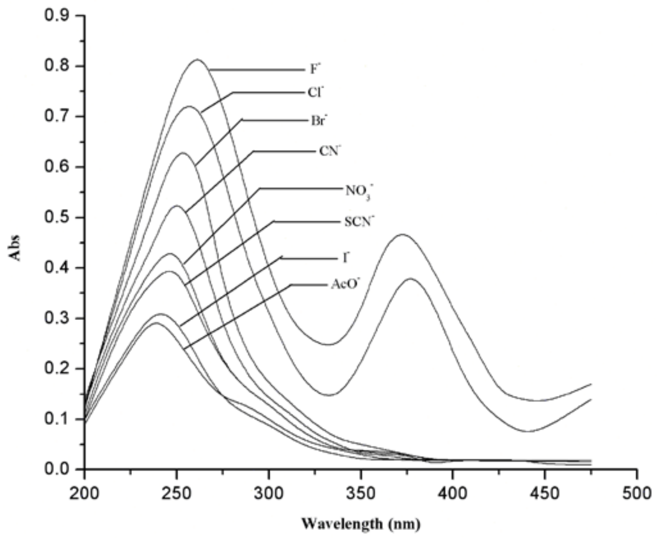

Figure 5.8: UV/Vis spectroscopic study of H-bonding ionophore (M_2) with different anions. At working pH (2.5–6.5), recorded in DMSO (3.5×10^{-5} mol L^{-1}). After shifting to longer wavelength.

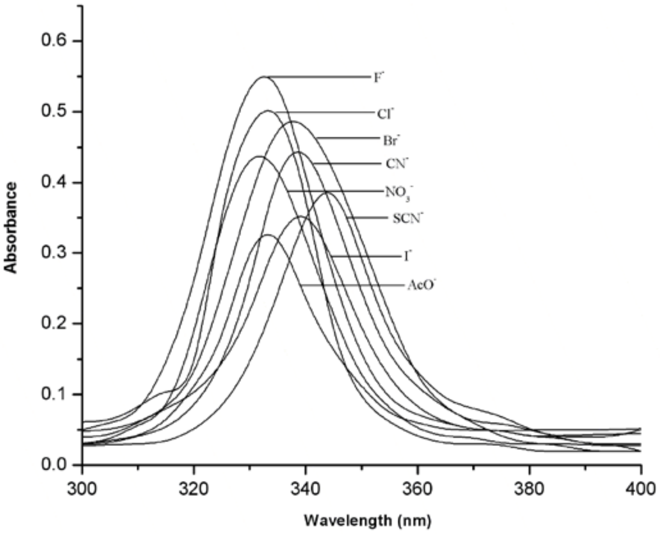

Figure 5.9: UV/Vis spectroscopic study of H-bonding ionophore (M_4) with different anions. At working pH (2.5–6.5), recorded in MeOH (3×10^{-5} mol L^{-1}). After shifting to longer wavelength (333 nm).

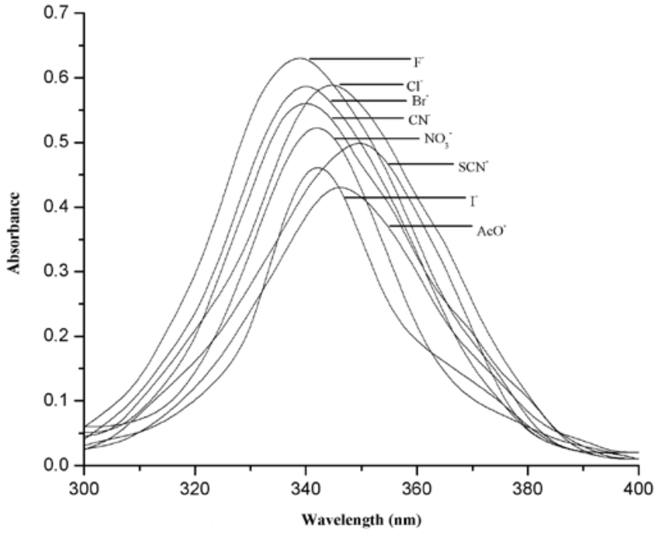

Figure 5.10: UV/Vis spectroscopic study of H-bonding ionophore (M_3) with different anions. At working pH (2.5–6.5), recorded in MeOH (3×10^{-5} mol L^{-1}). After shifting to longer wavelength (340 nm).

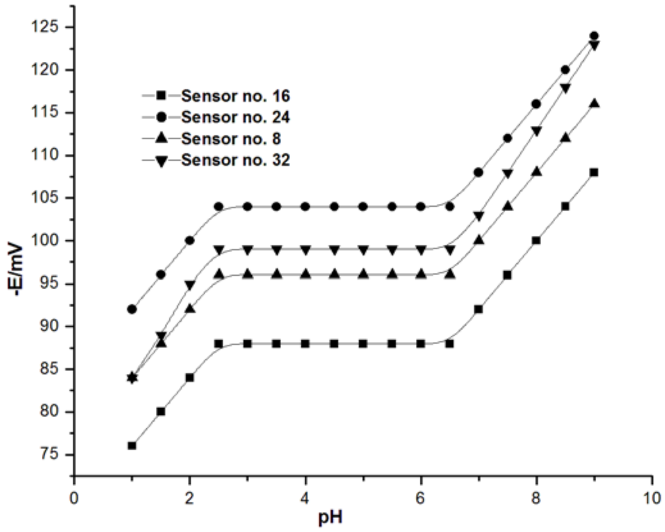

Figure 5.11: Effect of pH on the performance of optimized PVC membrane sensors (16.24, 8 and 32). At fixed concentration of TBAF (1.0×10^{-2} mol L^{-1}).

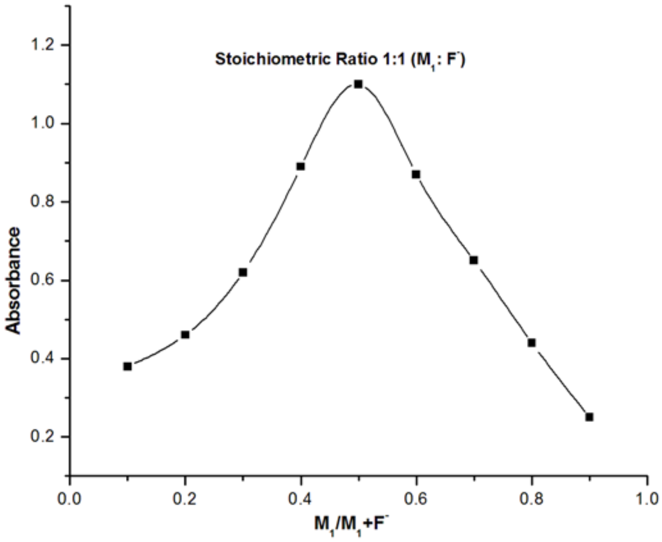

Figure 5.12: Stoichiometric study of ionophore M_1 with F^- (2.0×10^{-3} mol L^{-1}). Absorbance was measured at 223 nm, pH (4.0), Tris–HCl buffer.

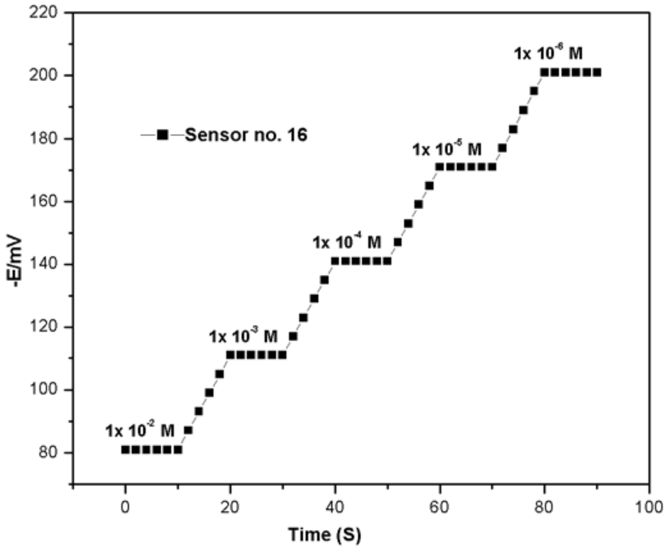

Figure 5.13: Dynamic response time study of best responsive PVC membrane sensor no.16. Recorded at concentration range; 1.0 × 10^{-6} to 1.0 × 10^{-2} mol L^{-1}, pH (4.0), Tris–HCl buffer.

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6.1. Introduction

Mercury is an extremely rare element in earth crust but it has been widespread in environment as a result of disposal of industrial and agricultural wastage [1,2]. Its concentration is continuously increasing in environment due to its extensive industrial applications. Mercury is used in lamps, batteries, thermameters, dental amalgams, explosives, electrolytic manufacture of chlorine and sodium hydroxide, catalysts, fungicides, herbicides, disinfectants, pigments and in pharmaceuticals. According to Environmental Protection Agency (EPA) mercury is a highly toxic because of its accumulative and persistent character in the environment and biota [3]. The tendency of mercury to accumulate in the food chain has resulted in many outbreaks of its toxicity. Its chronic exposure leads to an insidious form of toxicity that is manifested by neurological effects which is referred as the asthenic vegetative syndrome. The syndrome is characterized by tremor, psychological depression, irritability, insomnia, emotional instability, vasomotor disturbances and autism [4].

Thus, mercury is an environmentally and toxicologically important element. Its toxicity from environmental pollution and occupational exposure continues to be an area of concern through out the world. Thus, the need for its determination has generated increasing interest in the development of ion-selective electrodes for measurement of this analyte. In past years, a diverse range of mercury selective sensors has been developed [5-24] using PVC membrane and coated wire electrode. But these are suffering with the poor detection limit, narrow working concentration range and low pH range.

Calixarenes are well known for their relationship between design and selective complexation of metal ions because the size of their cavity is large enough to accumulate metal cation and they also have a sufficient number of donor atoms for coordination.

Therefore, the calixarenes are used as an ionophore for selective determination of metal ions in electrochemical sensors [25]. In the last decade the calixarenes are recognized to form stable complexes with metals and act as an ion carriers in the PVC membrane. Mostly calixarenes form 1:1 metal complexes with all metals. The cavity control of host-guest complexation and inflection of lipophilicity in calixarenes and their derivatives shows a remarkable sensitivity, selectivity and stability for specific ion. Therefore, these have been mostly used for selective determination of cations such as Hg^{2+} [13,20], Sr^{2+} [26], Ag^{+} [27,28], and Na^{+} [29,31]. The present work focuses on the use of 5,11,17,23-tetratertbutyl-25,27-dihydroxy-26,28-bis(*o*-methyl glycylcarbonylmethoxy) thiacalix [4]-arene as electroactive material for the fabrication of mercury selective electrode. It has been verified that these hosts adopt a pinched cone conformation in the solid as well as in the solution state. An investigation of hydrogen bonding in the solid state indicates a rather unusual involvement of bridging sulfur atoms in intramolecular hydrogen bonding interactions. Due to the complexity of hydrogen bonding interactions in the disubstituted molecule, an unusual crossover of the two tethered strandswere noticed. These structural features make the ionophore selective towards cations. Also, the UV/Vis and ^{1}H NMR spectroscopic studies of this compound carried out by Sreeja *et al.*, [32] prefigure that receptor 5,11,17,23-tetratert-butyl-25,27-dihydroxy-26,28-bis(*o*-methylglycylcarbonyl-methoxy) thiacalix [4]-arene selectively binds with Hg^{2+} ion. Thus it was thought worthwhile to explore the newly synthesized cation receptor as potential material for preparing membranes, which may show selective potential response to mercury(II) ion.

6.2. Experimental

6.2.1. Reagents

Sodiumtetraphenylborate (NaTPB), 2-nitrophenyloctyl ether (*o*-NPOE), 1-chloro-naphthalene (1-CN), and tri-n-butyl phosphates (TBP) were taken from High Media Laboratories (Mumbai), dibutyl phthalate (DBP), dioctyl phthalate (DOP) and EDTA were obtained from SD-Fine Chem Limited (Mumbai, India), AR-grade tetrahydrofuran (THF), methanol and acetonitrile (MECN) were obtained from Ranbaxy (New Delhi, India).

6.2.2. Synthesis of ionophore

The ionophore 5,11,17,23-tetra-tert-butyl-25,27-dihydroxy-26,28-bis(*o*-methyl glycylcarbonylmethoxy)thiacalix-[4]-arene (Fig. 6.1) was synthesized [32] by taking a solution of amino acid methyl ester hydrochloride (86 mg, 0.618 m mol) in dichloromethane (20 mL) at 0°C, triethylamine (0.2 mL, 0.93 m mol) was added and stirred for 30 min. Then the acid chloride of thiacalix[4]-arene di-acetic acid (135 mg, 0.155 m mol) in dry CH_2Cl_2 was syringed out at once. The reaction mixture was then washed with NaOH (1.0 M), hydrochloric acid, brine and column chromatography using 100% distilled ethyl acetate as eluent. A white powdery material was obtained. Anal. Calc. For [$C_{50}H_{62}N_2O_{10}$ S_4]: C, 61.32, H, 6.38, N, 2.86, O, 16.34, S, 13.10%. Found: C, 60.80, H, 6.32, N, 3.40, O, 16.50, S, 12.5%. IR(cm^{-1}): 3360 (broad) (N-H, O-H), 1740 (C=O), 1650 (C=O, amide I) 1525 (C=O II).

6.2.3. Preparation of PVC membranes

As described in the section 3.2.3.1., ionophore (5,11,17,23-tetra-tert-butyl-25,27-dihydroxy-26,28-bis(O-methyl glycylcarbonylmethoxy)thiacalix[4]-arene) was dissolved in 5 mL of THF along with anion excluder (NaTPB), plasticizers 1-CN, DOP, DBP, TBP and *o*-NPOE and poly(vinyl chloride) by varying the membrane composition. The mixture was shaken vigorously with a glass rod and the THF was allowed to evaporate up to 1 mL and then transfered gently (so that bubbles are not formed) into polyacrylate rings which were placed on a smooth glass plate. After the evaporation of THF, a transparent, bubblesles membrane of ~0.5 mm thickness was formed and it was removed carefully from the glass plate. The membrane way cut to size according to Pyrex glass and glued to one end using araldite. The membrane was optimized so that best performance characteristics were obtained. The quality of the membrane was controlled by taking the same composition and casting membranes slowly and carefully.

6.2.4. Apparatus and potential measurement

The ^1H NMR spectra of cation receptor was recorded on a Bruker AC 500 MHz spectrophotometer and elemental analysis was performed with a Vario ELIII instrument. The prepared PVC membranes were equilibrated for 24 h in 1.0×10^{-3} mol L^{-1} Hg^{2+} solution. The potential measurements were carried out at room temperature (25 ± 0.1°C) with a digital potentiometer instrument (model 5652 A, ECIL, India) according to following cell assembly, using saturated calomel electrodes (SCE) as a reference electrode in experiment.

Internal References Electrode SCE | Internal Solution || PVC membrane || Test Solution | Externel References Electrode (SCE) (Internal)

The cell potentials were measured by changing the concentration of Hg^{2+} in the test solution in the range 1.0×10^{-10} to 1.0×10^{-2} mol L^{-1}.

6.3. Results and discussion

6.3.1. The effect of membrane composition on potential response of membrane

The performances of the sensor such as selectivity and accuracy depend on the nature of the ionophore or receptor, composition of membrane and the nature of the plasticizer. It is reported that the best commonly used composition for preparation of PVC membrane was ionophore or receptor 1–7%, PVC 25–34%, plasticizer 60–80% and other lipophilic additive 0.02–2%. The potential of sensors having different membrane composition were measured as a function of mercury ion free concentration and their potential response plots shown in Fig. 6.2. By using the potentiometric plots working concentration range, the slope and the response time of sensor have been evaluated and given in Table 6.1 along with the response for each sensor. It is seen from Table 6.1 that the response of the membrane (sensor no. 1) without plasticizer is poor in terms of short concentration range, high response time, non Nernstian slope and poor detection limit. Thus it is necessary to improve the performance of the membranes. It is documented that the addition of plasticizer and lipophilic additive [33,34] improves the performences of membrane electrode it was found from Table 6.1 that the addition of plasticizers (1-CN, DOP, DBP, TBP and *o*-NPOE) improves the performance of the membranes in terms of near Nernstian slope, wider linear working concentration range, better detection limit and smaller response time. Further it is seen from Table 6.1 that out of the five plasticizers investigated *o*-NPOE improves the performance best. The best optimized membrane concentration was found to be PVC:*o*-NPOE:ionophores:NaTPB of 60:120:5:10 (%, w/w) and was thus chosen for further studies.

6.3.2. Calibration curve

The response of the proposed potentiometric sensor was measured and shown in Table 6.1 and Fig. 6.3. It was from the table that the sensor no. 5 shows a linear concentration range $5.0 \times 10^{-8} - 1.0 \times 10^{-2}$ mol L^{-1} with low detection limit 1.0×10^{-8} mol L^{-1} and near Nernstian slope 29.5 mV decade^{-1} of activity.

6.3.3. Response time and lifetime of proposed sensor

The response time for all the sensors is given in Table 6.1 [35–45]. It is seen from table 6.1 that the sensor that have membrane with plasticizers (1-CN, DOP, DBP, TBP and *o*-NPOE) show low response time. The respose time of sensor no. 5 with the plasticizer *o*-NPOE is found to be response time, 10 s.

Among all the sensors, the life time of the membrane sensors comprising *o*-NPOE was maximum and found to be 2.5 months for sensor no. 5. During this life time no significant drift in potential was noticed. The electrodes were stored in 0.1M Hg^{2+} solution when not in use. As the sensor no. 5 gave the best performance in terms of wide activity range, Nernstian slope, low response time and long life time, all further studies were carried out only on this sensor.

6.3.4. Effect of pH change and non-aqueous solvent

The effect of pH on the potentiometric response of the proposed electrode (Sensor 5) was examined in the range of 5.0-8.5 for solutions having the concentrations 1.0×10^{-3} mol L^{-1} and 1.0×10^{-4} mol L^{-1} of Hg^{2+} solutions [46–58].The pH of the solutions was changed by the addition of hydrochloric acid or sodium hydroxide. The results are shown in Fig. 6.4, its shows that the potentials remained constant for sensor no. 5 at pH range 6.0 to 7.5 at this range, a gradual change in potential was observed. Therefore, this pH range 6.0 to 7.5 was taken as the working pH range of the sensor. The effect of non aqueous media for sensor no. 5 was also examined with partially non-aqueous media using acetonitrile–water mixture and methanol–water and the obtained results are presented in Table 6.2. It shows that at 10 % non-aqueous content the values of slope and working concentration range remain constant. Thus, it is found that up to 10% of non-aqueous content is acceptable for the sensor.

6.3.5. Response time and lifetime of proposed sensor

It was established that the plasticizer *o*-NPOE improves the response time to the maximum extent of sensor due to its polarity. As expected the sensor no. 5 shows 10 s response times with plasticizer *o*-NPOE. The lifetime of the proposed membrane sensors was also calculated and found to be 2.5 months for sensor no. 5. When electrode is not use then it should be keep into 0.1 M Hg^{2+} ion solution.

6.3.6 Potentiometric selectivity of sensor

Selectivity is one of the required parameter of ion selective electrode, and expressed in terms of selectivity coefficient. In the present study the selectivity was measured by using fixed interference method (FIM) [59]. In the FIM, the selectivity coefficients were determined from potential measurements on solutions containing a fixed concentration of interfering ion (1.0×10^{-2} mole L^{-1}) and different amounts of Hg^{2+} ions [60–64]. The caliculated value of selectivity coefficient is given in Table No. 6.3. A value of 1.0 shows identical response to primary and interfering ions. According to table that the selectivity coefficient values are much smaller than 1.0 indicating that they exhibit sufficient selectivity towards Hg^{2+} over all the interfering ions studied.

6.3.7. Analytical application

The proposed electrode was tested as an indicator electrode in the potentiometric titration of Hg^{2+} ion with EDTA [65–72]. A 10 mL (1.0×10^{-3} mol L^{-1}) solution was titrated with 1.0×10^{-2} mol L^{-1} of EDTA solution (Fig. 6.5). The sharp break point in the potentiometric titration of Hg^{2+} against EDTA corresponds to Hg-EDTA stoichiometry.

6.4. Conclusion

The studies on membrane of 5,11,17,23-tetra-tert-butyl-25,27-dihydroxy-26,28-bis(o-methyl glycylcarbonylmethoxy) thiacalix [4]-arene have shown that they act as Hg^{2+} selective sensor. The electrode (Sensor no. 5) having a membrane composition (mg, %) 10:8:120:250 (Ionophore:NaTBP:PVC:*o*-NPOE) gave the best performance with a nernstian slope of 29.5 mV decade^{-1} of activity, low response time of 10 s and better selectivity for mercury(II) ion. The sensor was found to perform satisfactorily over the pH range 6.0 to 7.5 and even in the presence of 10% non aqueous content. The proposed sensors show fairly good discrimination for mercury(II) ions from other cations. The developed mercury ion-selective electrode can be successfully employed as an indicator electrode in potentiometric titration with EDTA.

Tables:

Table 6.1: Optimization of membrane compositions and their potentiometric response as in Hg^{2+} ion-selective sensors.

Sen. No.	Composition of membrane sensors (amount in mg)				Working concentration Range (M)	*Slope ± 0.5	Response Time (s)	Life-time (in Days)
	Iono-phore	**PVC**	Additives	Plasticizer				
1	5	60	5, NaTPB	0.0	5.0×10^{-3} -1.0×10^{-2}	15.2	45	25
2	5	60	5, NaTPB	120.0, CN	5.0×10^{-6} -1.0×10^{-2}	25.2	30	28
3	5	60	10, NaTPB	120.0, CN	1.0×10^{-5} -1.0×10^{-2}	26.5	34	40
4	5	60	5, NaTPB	120.0, *o*-NPOE	3.2×10^{-7} -1.0×10^{-2}	31.5	25	50
5	5	60	10, NaTPB	120.0, *o*-NPOE	5.0×10^{-8} -1.0×10^{-2}	29.5	10	75
6	5	60	5, NaTPB	120.0, TBP	1.0×10^{-7} -1.0×10^{-2}	32.0	20	55
7	5	60	10, NaTPB	120.0, TBP	4.0×10^{-5} -1.0×10^{-2}	28.2	20	43
8	5	60	5, NaTPB	120.0, DBP	1.2×10^{-6} -1.0×10^{-2}	29.0	25	48
9	5	60	10, NaTPB	120.0, DBP	2.2×10^{-5} -1.0×10^{-2}	30.1	30	56
10	5	60	5, NaTPB	120.0, DOP	2.2×10^{-6} -1.0×10^{-2}	35.3	30	60
11	5	60	10, NaTPB	120.0, DOP	4.0×10^{-7} -1.0×10^{-2}	39.7	35	45

Table 6.2: Performance of the membrane sensor no. 5 in partially non-aqueous medium.

Non-aqueous content (%v/V)	Working concentration range (M)	Slope (mV $decade^{-1}$)
0	$5.0 \times 10^{-8} – 1.0 \times 10^{-2}$	29.5 ± 0.5
Methanol		
5	$5.0 \times 10^{-8} – 1.0 \times 10^{-2}$	29.5 ± 0.5
10	$5.0 \times 10^{-8} – 1.0 \times 10^{-2}$	29.5 ± 0.5
15	$2.0 \times 10^{-6} – 1.0 \times 10^{-2}$	29.5 ± 0.5
Acetonitrile		
5	$5.0 \times 10^{-8} – 1.0 \times 10^{-2}$	29.5 ± 0.5
10	$5.0 \times 10^{-8} – 1.0 \times 10^{-2}$	29.5 ± 0.5
15	$4.0 \times 10^{-5} – 1.0 \times 10^{-2}$	29.5 ± 0.5

Table 6.3: Selectivity coefficient values (-log $K_{\mathrm{Hg}}{}^{2+}$, B^{Pot}) for Hg^{2+} selective sensor by 'fixed interferences methods'.

Interfering Ions	Selectivity Coefficient [-log $K_{\mathrm{Hg}}{}^{2+}$,B^{Pot}]^{a}
Na^+	4.9
Li^+	4.2
K^+	3.4
Mg^{2+}	4.7
Ag^+	2.9
Ba^{2+}	4.2
Sr^{2+}	4.2
Ni^{2+}	3.5
Cr^{3+}	5.3
Cu^{2+}	3.0
Zn^{2+}	4.3
Co^{2+}	5.1
La^{3+}	5.4
Ce^{3+}	4.9
Ca^{2+}	4.6
Cd^{2+}	3.3

[a] n=5, RSD % <1.2.

Figures:

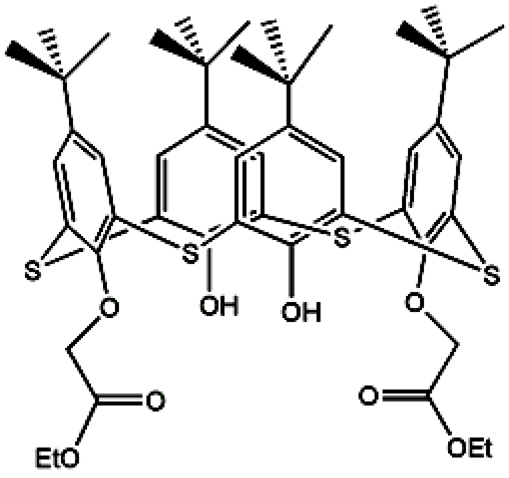

Figure 6.1: Structure of 5,11,17,23-tetra-tert-butyl-25,27-dihydroxy-26,28-bis(O-methylglycylcarbonylmethoxy) thiacalix [4]-arene.

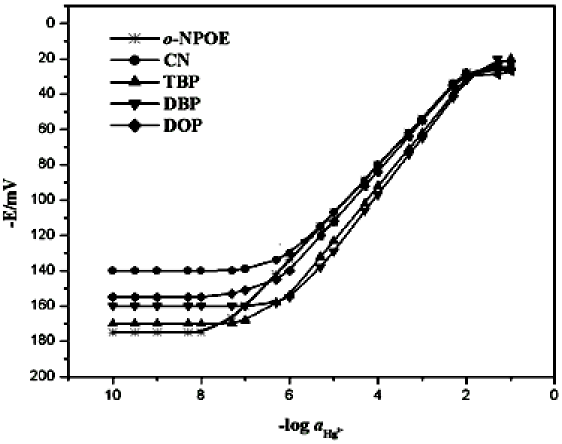

Figure 6.2: Variation of membrane potential with activity of promethium ions of PVC based membranes of without plasticizer, with plasticizers, *o*-NPOE, DBP, DOP, CN and TBP.

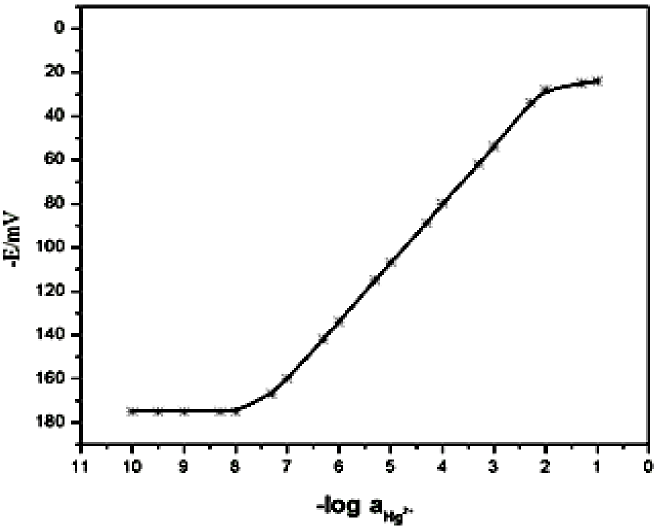

Figure 6.3: Calibration plot of mercury-selective sensor [best optimized membrane composition: PVC:*o*-NPOE:ionophore:NaTPB of 60:120:5:10 (%, w/w)].

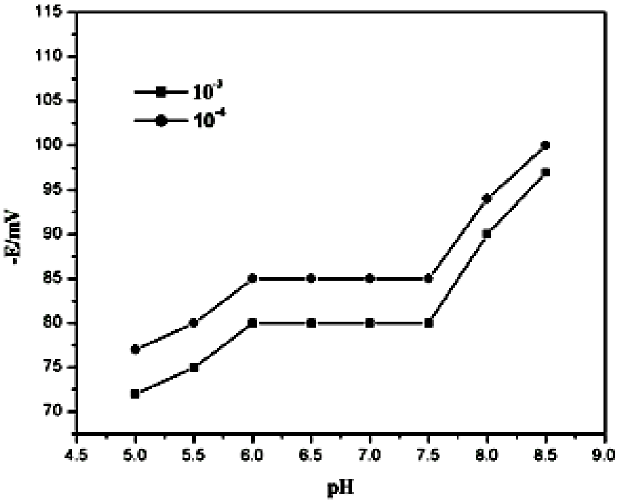

Figure 6.4: Effect of pH on potential response of the mercury selective sensor.

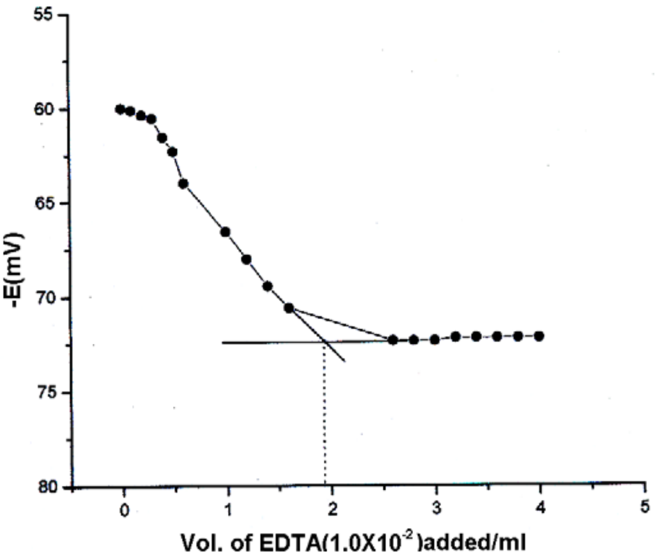

Figure 6.5 : Potentiometric titration plot of 1.0×10^{-3} mol L^{-1} Hg^{2+} solution (20 ml) with EDTA (1.0×10^{-2} mol L^{-1}) using the developed sensor as an indicator electrode.

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