SYNTHESIS AND ANALYTICAL APPLICATIONS OF POLYDENTATE MACROCYCLES AS CHEMICAL SENSORS

A THESIS

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled, **SYNTHESIS AND ANALYTICAL APPLICATIONS OF POLYDENTATE MACROCYCLES AS CHEMICAL SENSORS** 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, 2007 to July, 2011 under the supervision of Dr. A. K. Singh, Professor, 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.

Prerna

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

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Signature of External Examiner

ABSTRACT

Environmental pollution is a major global problem posing serious risk to man and animals. It is defined as the human alteration of chemical or physical characteristics of the environment to a degree that is harmful to living organisms. Rapid pace of urbanization, industrialization and indiscriminate use of chemicals such as pesticides and drugs have resulted in increased contamination and degradation of the environment leading to adverse health effects on living beings and problems associated with residues in food of animal origin. Recent emergences in environmental related toxicity in man and animals and detection of chemical residues in food products at an increasing frequency have underlined the impact of pollution on biotic component. The deleterious health effects may be observed in the form of overt clinical signs and higher morbidity and mortality or as subtle or subclinical effects. Heavy metal toxicity has posed a serious threat to mankind by its incorporation to the food chain resulting in the degradation of ecosystem. Some heavy metals are essential for most of the redox reactions which are fundamental for cellular functions. However, heavy metals become toxic when they are not metabolized by the body and get accumulated in tissues and organs which results in many nutritional deficiencies and can lead to neurological and autoimmune disorders, cancer and other debilitating chronic diseases. Thus, monitoring and evaluation of heavy metal ions in the environment have received increasing attention from both nutritional and toxicological point of view.

A number of analytical techniques such as atomic absorption spectroscopy, inductively coupled plasma atomic emission spectroscopy, inductively coupled plasma mass spectrometry, isotopic dilution, radiometric neutron activation analysis, fluorescence, chemiluminescence phosphorescence techniques, high performance liquid

chromatography, ion chromatography, voltammetry *etc*. are available for routine analysis of metal ions in environmental samples. Although, these methods provide accurate and reproducible results, but suffers from high capital cost, large scale infrastructure back up and requires adequate expertise which makes them unsuitable for online analysis and routine analysis of large number of environmental samples. Besides this, the use of these techniques can be problematic and erroneous in coloured and turbid solutions. Thus, there is vital need for the development of selective, portable and inexpensive diagnostic technique for the determination of various metal ions. Ion-selective electrodes (ISEs) have proved promising alternative which overcomes or minimizes the above drawbacks. ISEs find applications in a variety of fields like clinical, environmental, industrial, agricultural and process monitoring, as well as detectors in HPLC and capillary electrophoresis.

Ion-selective electrode consists of a semipermeable membrane that separates two different solutions of an appropriate electrolyte and responds selectively to a particular ion in presence of other ions. The membrane constitutes an active ion-exchanger ingredient generally called an ionophore or electroactive material. The design and function of synthetic ionophores is based on diverse parameters *viz* structure and cavity size of the ligand, stability and selectivity of its metal ion complex, its solubility and the ability to extract the metal ion into membrane phase. Macrocycles are a favoured class in this area as their complexes have high stability constant and sufficient conformation flexibility for rapid ion exchange. The strong and selective interaction of macrocycles with specific metal ions makes these ligands suitable candidate to be used as ionophores in the construction of ion-selective electrodes.

The field of ion-selective membrane research is a vigorous and ever expanding one. ISEs have been not only practical solutions to a great variety of analytical problems but also useful tools for probing host-guest chemistry. The aim of the present work is to synthesize new polydentate macrocyclic ligands and their complexes which are used as electroactive component in the preparation of membranes for determination of various metal ions. The performance of the Polymeric membrane electrode has also been compared with another electrode *i.e.* Coated graphite electrode having membrane of same ingredients. The electrode which shows better response characteristics in terms of Nernstian response, working concentration range, detection limit, response time and selectivity has been used for real sample analysis.

For the sake of convenience, simplicity and clarity, the work embodied in the thesis has been organized as follows:

The First Chapter of the thesis is on "***General Introduction***" and presents a review of all the literature on the previously reported sensors of alkaline, alkali earth, transition, rare earth metal ions and anions. The problem of present research activities have also been posed in the context of the cited work.

The Second Chapter on "***Theory and Methodology***" encompasses classification of ISEs, theory of membrane potential and various terms used in the description of ion selective electrodes. The description of the selectivity of sensor membrane and method of its determination has also been described.

The Third Chapter of the thesis "***Membranes of Macrocyclic ligands as cation selective sensor for transition metal ions***" deals with synthesis and characterization of polydentate macrocycles and pendant armed macrocyclic ligands and their analytical application in the preparation of cation-selective electrodes. Polymeric membrane electrode (PME) and coated graphite electrode (CGE) for nickel ion were prepared based on 2,9-(2-methoxyaniline)$_2$-4,11-Me$_2$-[14]-1,4,8,11-tetraene-1,5,8,12-N$_4$ (I) as a suitable neutral ionophore. In order to improve the performance characteristics of PVC based membranes, the addition of various plasticizers *viz.* *o*-nitrophenyloctylether (*o*-NPOE), dioctylphthalate (DOP), dibutylphthalate (DBP), 1-chloronaphthalene (CN) and tri-n-butylphosphate (TBP) and ionic additives sodium tetraphenylborate (NaTPB) was tested for optimization of membrane composition and their potential response was investigated. The best performance was obtained for the membrane sensor having a composition of I:PVC:TBP:NaTPB as 6:90:100:4 (w/w; mg). The electrodes exhibit Nernstian slopes for Ni^{2+} ions over wide concentration ranges of 4.6×10^{-7} to 1.0×10^{-1} mol L^{-1} for PME and 7.7×10^{-8} to 1.0×10^{-1} mol L^{-1} for CGE with limits of detection of 2.7×10^{-7} mol L^{-1} for PME and 3.7×10^{-8} mol L^{-1} for CGE. The response time for PME and CGE was found to be 10 s and 8 s respectively. The potentiometric response of both electrodes is independent of the pH of the test solution in the pH range 3.0-8.0. The proposed electrodes revealed a good selectivity over a wide variety of cations including alkali, alkaline earth, transition and heavy metal ions. Since CGE showed better results over PME, it was used as an indicator electrode in the potentiometric titration of nickel ion with EDTA and in direct determination of Ni^{2+} ion in different fruit juices and wine samples.

Poly(vinyl chloride) (PVC) based membranes of macrocycles 2,3,4:9,10,11-dipyridine-1,3,5,8,10,12-hexaazacyclotetradeca-2,9-diene [II(a)] and 2,3,4:9,10,11-di pyridine-1,5,8,12-tetramethylacrylate-1,3,5,8,10,12-hexaazacyclotetradeca-2,9-diene [II(b)] were prepared and investigated as Co^{2+} selective electrodes. The best performance was observed with the membranes having the composition II(b):PVC:TBP:NaTPB in the ratio of 6:39:53:2 (w/w; mg). The performance of the membrane based on II(b) was compared for PME and CGE. The PME exhibits detection limit of 4.7×10^{-8} mol L^{-1} with a Nernstian slope of 29.7 mV decade^{-1} of activity between pH 2.5-8.5 whereas CGE exhibits the detection limit of 6.8×10^{-9} mol L^{-1} with a Nernstian slope of 29.5 mV decade^{-1} of activity between pH 2.0-9.0. The response time for PME and CGE was found to be 11 s and 8 s respectively. The CGE has been found to work satisfactorily in partially non-aqueous media upto 35% (v/v) content of methanol, ethanol and 25% (v/v) content of acetonitrile and could be used for a period of 4 months. The CGE was successfully applied for the determination of Co^{2+} in real and pharmaceutical samples and as an indicator electrode in potentiometric titration of cobalt ion.

The construction and performance characteristics of polymeric membrane electrodes based on two newly synthesised macrocyclic ligands 6,7:14,15-Bzo_2-10,11-(4-methylbenzene)-[15]-6,8,12,14-tetraene-9,12-N_2-1,5-O_2 III(a) and 6,7:14,15-Bzo_2-10,11-(4-methylbenzene)-[15]-6,14-diene-9,12-dimethylacrylate-9,12-N_2-1,5-O_2 III(b) for quantification of Zn^{2+} ions were investigated and the best response was observed for the membrane having composition III(b):PVC:TBP:NaTPB in the ratio of 4:37:57:2 (w/w; mg). The response characteristics of PME based on III(b) was also compared with CGE. The electrode exhibits Nernstian slope for Zn^{2+} ions with limits of detection of 3.3×10^{-7} mol L^{-1} for PME and 7.9×10^{-8} mol L^{-1} for CGE with response time of 12 s and 10 s for PME and CGE respectively. Futhermore, the electrodes generated constant potentials in the pH range of 3.0-8.0 for PME and 2.5-9.0 for CGE. The practical utility of the CGE has been demonstrated by its usage as an indicator electrode in potentiometric titration of EDTA with Zn^{2+} ion solution. The high selectivity of CGE also permits their use in the determination of Zn^{2+} ions in water, biological, milk and tea samples.

The Fourth Chapter of the thesis ***"Membranes of Macrocyclic ligands as cation selective sensor for rare earth metal ions"*** includes the synthesis and characterization of macrocyclic ligands which act as electroactive component in the fabrication of polymeric membrane electrode and coated graphite electrode for the quantification of rare earth metal ions in real samples. The two macrocyclic pendant ligands 3,4,5:12,13,14-dipyridine-2,6,11,15-tetramethyl-1,7,10,16-tetramethylacrylate-1,4,7,10,13,16-hexaaza-cyclooctadeca-3,13-diene [IV(a)] and 3,4,5:12,13,14-dipyridine-2,6,11,15-tetramethyl-

1,7,10,16-tetra(2-cyanoethane)-1,4,7,10,13,16-hexa- azacyclooctadeca-3,13-diene [IV(b)] have been synthesized and explored as neutral ionophores for preparing poly(vinylchloride) (PVC) based membrane sensors selective to Tb^{3+} ions. The best performance was obtained for the membrane sensor having a composition of IV(a):PVC:1-CN:NaTPB in the ratio of 6:32:58:4 (w/w; mg). The comparison of response characteristics of PME based on IV(a) with CGE revealed the superiority of the latter. The electrodes exhibit Nernstian slope for Tb^{3+} ions with limits of detection of 3.4×10^{-8} mol L^{-1} for PME and 5.7×10^{-9} mol L^{-1} for CGE. The response time for PME and CGE was found to be 10 s and 8 s respectively. The potentiometric responses are independent of the pH of the test solution in the pH range 3.0-7.5 for PME and 2.0-8.5 for CGE. The CGE has found to work satisfactorily in partially non-aqueous media upto 30% (v/v) content of methanol, ethanol and 20% (v/v) content of acetonitrile and could be used for a period of 5 months. The CGE was used as indicator electrode in the potentiometric titration of Tb^{3+} ions with EDTA and in determination of fluoride ions in various samples. It can also be used in direct determination of Tb^{3+} ions in tap water and various binary mixtures with quantitative results.

The performance characteristics of PME and CGE based on two newly synthesized macrocyclic ligands 2,12-(2-methoxyaniline)$_2$-4,14-Me$_2$-[20]-1,4,11,14-tetraene-1,5,8,11,15,18-N$_6$ [V(a)] and 2,12-(2-methoxyaniline)$_2$-4,14-Me$_2$-8,18-dimethylacrylate-[20]-1,4,11,14-tetraene-1,5,8,11,15,18-N$_6$ [V(b)] have been investigated for the quantification of Yb^{3+} ions. The best performance was obtained for the membrane sensor having a composition of V(b):PVC:BA:NaTPB in the ratio of 5:40:52:3 (w/w; mg). The electrodes exhibit Nernstian slope for Yb^{3+} ions with limits of detection of 4.3×10^{-8} mol L^{-1} for PME and 5.8×10^{-9} mol L^{-1} for CGE. The response time for PME and CGE was found to be 10 s and 8 s respectively. The potentiometric responses are independent of the pH of the test solution in the pH range 3.0-8.0 for PME and 2.5-8.5 for CGE. The CGE has found to work satisfactorily in partially non-aqueous media upto 30% (v/v) content of methanol, ethanol and 20% (v/v) content of acetonitrile and could be used for a period of 5 months. As CGE showed better response characteristics than PME, it was therefore, used as indicator electrode in the potentiometric titration of Yb^{3+} ions with EDTA and in determination of fluoride ions in mouthwash samples. It can be used for determination of sulfite in red and white wine samples and also in determination of Yb^{3+} in various binary mixtures with quantitative results.

Plasticized membranes using 2,3,4:12,13,14-dipyridine-1,3,5,8,11,13,15,18-octaazacycloicosa-2,12-diene [VI(a)] and 2,3,4:12,13,14-dipyridine-1,5,8,11,15,18-hexamethylacrylate-1,3,5,8,11,13,15,18-octaazacycloicosa-2,12-diene [VI(b)] have been prepared and explored as Ce^{3+} ion selective sensor. Optimum performance was observed for the membrane sensor having a composition of VI(b):PVC:*o*-NPOE:KTpClPB in the ratio of 6:34:58:2 (w/w; mg). The electrodes exhibit Nernstian slope for Ce^{3+} ions with limits of detection of 8.3×10^{-8} mol L^{-1} for PME and 7.7×10^{-9} mol L^{-1} for CGE. The response time for PME and CGE was found to be 12 s and 10 s respectively. The potentiometric responses are independent of the pH of the test solution in the pH range 3.5-7.5 for PME and 2.5-8.5 for CGE. The CGE could be used for a period of 5 months. The practical utility of the CGE has been demonstrated by its usage as an indicator electrode in potentiometric titration of oxalate and fluoride ions with Ce^{3+} ion solution. The proposed electrode was also successfully applied to the determination of fluoride ions in mouthwash solution and oxalate ions in real samples.

The Fifth Chapter of the thesis "***Membranes of Macrocyclic complexes as anion selective sensor***" includes the synthesis and characterization of macrocyclic complexes which were incorporated as ionophore in the fabrication of PME and CGE for the quantification of anions in water and biological samples. The electrode characteristics and selectivities of PVC-based PME and CGE incorporating the newly synthesized zinc complex of 6,7:14,15-Bzo$_2$-10,11-(4-methylbenzene)-[15]-6,8,12,14-tetraene-9,12-N$_2$-1,5-O$_2$ [VII(a)] and zinc complex of 6,7:14,15-Bzo$_2$-10,11-(4-methylbenzene)-[15]-6,14-diene-9,12-dimethylacrylate-9,12-N$_2$-1,5-O$_2$ [VII(b)] for the determination of thiocyanate ions have been investigated and compared. The best response was observed with the membrane having composition VII(b):PVC:*o*-NPOE: HTAB in the ratio of 6:33:59:2 (w/w; mg). This electrode exhibited Nernstian slope for thiocyanate ions over working concentration range of 4.4×10^{-7} to 1.0×10^{-2} mol L^{-1} with detection limit of 2.2×10^{-7} mol L^{-1}. The performance of this electrode was compared with coated graphite electrode (CGE) which showed better response characteristics with respect to Nernstian slope (59.0 ± 0.2) mV decade^{-1} activity, wide concentration range of 8.9×10^{-8} to 1.0×10^{-2} mol L^{-1} and detection limit of 6.7×10^{-8} mol L^{-1}. The response time for CGE and PME was found to be 8 s and 10 s respectively. The proposed electrode (CGE) was successfully applied to direct determination of thiocyanate in biological and environmental samples and also as indicator electrode in potentiometric titration of SCN^- ion.

The newly synthesized zinc complexes of 6,7:13,14-Dibenzo-2,4,9,11-tetramethyl-1,5,8,12-tetraazacyclotetradecane-1,4,6,8,11,13-hexaene [VIII(a)] and 6,7:13,14-Dibenzo-2,4,9,11-tetramethyl-1,5,8,12-tetramethylacrylate-1,5,8,12-tetra-azacyclotetradecane-6,13-diene [VIII(b)] were explored as electroactive material in the preparation of PME and CGE and the best response was observed for the membrane having composition VIII(b):PVC:BA:HTAB in the ratio of 7:32:59:2 (w/w; mg). The response characteristics of PME based on the above mentioned membrane was also compared with CGE. The electrode exhibits Nernstian slope for perchlorate ions over wide concentration ranges *i.e.* 8.3×10^{-7} to 1.0×10^{-2} mol L^{-1} (with PME) and 1.0×10^{-7} to

1.0×10^{-2} mol L^{-1} (with CGE) and response time of 12 s and 9 s for PME and CGE respectively. Futhermore, the electrodes generated constant potentials in the pH range of 3.0-8.0 for PME and 2.5-9.0 for CGE. The high selectivity of CGE for perchlorate ions permits its use in the determination of perchlorate ions in water and human urine samples.

Thus, membranes of the electrodes prepared and studied are an important addition to the existing electrodes as they have shown some better performance characteristics over the existing ISEs.

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With profound gratitude, love and devotion, I dedicate this Thesis to my family.

Roorkee

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LIST OF PUBLICATIONS

1. A. K. Singh, **Prerna Singh**, Sameena Mehtab
   Polymeric membrane and coated graphite electrode based on newly synthesized macrocyclic ligand for trace level determination of nickel ion in fruit juices and wine samples
   Journal of Inclusion Phenomenon and Macrocyclic Chemistry, *63*, 87-95 (2009).

2. A. K. Singh, **Prerna Singh**, Shibdas Banerjee, Sameena Mehtab
   Development of Electrochemical sensors for nano scale Tb(III) ion determination based on pendant macrocyclic ligands
   Analytica Chimica Acta, *633*, 109–118 (2009).

3. A. K. Singh, **Prerna Singh**
   Nano-level monitoring of Yb(III) by fabrication of coated graphite electrode based on newly synthesized hexaazamacrocyclic ligand
   Analytica Chimica Acta, *643*, 74–82 (2009).

4. A. K. Singh, **Prerna Singh**, G. Bhattachargee
   Determination of Cobalt ions at nano level based on newly synthesized pendant armed macrocycle by polymeric membrane and coated graphite electrode
   Talanta, *80*, 685–693 (2009).

5. A. K. Singh, **Prerna Singh**
   Determination of Cerium ion by polymeric membrane and coated graphite electrode based on novel pendant armed macrocycle
   Analytica Chimica Acta, *675*, 170–180 (2010).

6. **Prerna Singh**, A. K. Singh, A. K. Jain
   Electrochemical sensors for determination of Zn^{2+} *ions based on pendant armed macrocyclic ligand*
   Electrochimica Acta, *56*, 5386-5395 (2011).

7. **Prerna Singh**, A. K. Singh

   Determination of thiocyanate ions at nano level in real samples using coated graphite electrode based on synthesised macrocyclic zinc(II) complex

   Analytical and Bioanalytical Chemistry, *400*, 2261-2269 (2011).

8. **Prerna Singh**, A. K. Singh

   Electrochemical Sensor for selective determination of perchlorate ions based on zinc complexes of macrocyclic ligands

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CONTENTS

Chapter 1

General Introduction

1.1 INTRODUCTION

In recent years, the recognition of generation of large quantities of toxicants and their by products due to the industrial and/or cultural activities and transport and their persistence in the environment and biological activities brings out the necessity and importance of their assessment of risk they poses to the ecosystems (*eg.* aquatic-environment-coastal waters, rivers, lakes and ground water) [1-4]. Indeed, understanding the impact of contaminants on the environment, including the organisms which live in it, is rather complicated.

The heightened concern for reduction of environmental pollution that has been occurring over the past 20-25 years has stimulated active continuing research and literature on toxicology of heavy metals. While the toxic effects of these substances is a widespread concern in the modern industrial context, Man has succeeded in poisoning himself with them repeatedly throughout recorded history. Virtually all metals can produce toxicity when ingested in sufficient quantities but there are several which are especially important because either they are so pervasive, or produce toxicity at such low concentrations. In general heavy metals produce toxicity by forming complexes or ligands with organic compounds. These modified biological molecules lose their ability to function properly, and results in malfunction or death of the affected cells. The most common group involved in ligand formation are oxygen, sulphur and nitrogen. When metals bind to these groups they may inactive important enzyme systems, or affect protein structure. The accumulation of various heavy and toxic elements in the environment has become a challenge to the environmentalists and analytical chemists alike as it poses a serious problem to human and animal health. Heavy metals and many anions constitute an important group of pollutants and their easy and quick determination even at very low concentration in environmental and biological samples is a necessity for assurance against acute intoxication or prolonged exposure that may lead to many diseases or death [5,6].

There are many techniques for determining the concentration of cations and anions in aqueous solutions *viz.* UV-Vis spectroscopy, atomic absorption spectroscopy, inductively coupled plasma atomic emission spectroscopy, inductively coupled plasma mass spectrometry, isotopic dilution, radiometric neutron activation analysis, fluorescence, chemiluminescence techniques, high performance liquid chromatography, ion chromatography and voltammetry. Although, these methods provide accurate and reproducible results, but suffers from high capital cost, large scale infrastructure back up and requires adequate expertise which makes them unsuitable for routine and online analysis. Besides this, the use of these techniques can be problematic and erroneous in coloured and turbid solutions. Thus, there is vital need for the development of selective, portable and inexpensive diagnostic technique for the determination of various metal ions. Ion Selective electrodes (ISEs) have comfortably taken a leading place among all electrochemical methods of analysis due to number of unquestionable advantages such as simplicity, low cost, quick response, wide working concentration range, and analytically relevant selectivity. ISEs can be employed in the analysis of samples in various fields including clinical, environmental, industrial and agricultural studies. A number of commercially available ISEs have been developed as convenient tools for analysis of cations and anions in food products, biological fluids, effluents, wastewater, soil, fertilizers etc [7,8].

Ion-selective electrode consists of a semipermeable membrane that separates two different solutions of an appropriate electrolyte and responds selectively to a particular ion in presence of other ions. The membrane constitutes an active ion-exchanger ingredient generally called an ionophore or electroactive material. Ionophore plays a key role in the sensitivity of an ion-selective electrode. The creation of cavities and cleft in the ionophore are complementary to the size and charge of a particular ion leading to selective interactions. One of the most important feature of ISEs is the selectivity towards a specific analyte, which is generally limited by the interaction of an ionophore within the membrane with other ions in solution. The ion-ionophore interactions based on their ion-exchange property or size-exclusion of the ionophore, determine the selectivity of an ion sensor and its proper functioning towards a specific ion. The design and function of synthetic ionophores is based on diverse parameters *viz.* structure and cavity size of the ligand, stability and selectivity of its metal ion complex, its solubility and the ability to extract the metal ion into membrane phase. Many intensive studies on the design and synthesis of highly selective ionophores as sensory molecules for ISEs have been reported and much interest has been focused on macrocyclic compounds. The field of coordination chemistry of macrocyclic compounds has undergone a spectacular growth due to the synthesis of a great number and variety of synthetic macrocycles that behave as coordinating ligands for metal ions. Macrocyclic compounds with a wide range of ring sizes have the ability to accommodate metal ions of suitable size and form inclusion complexes. The coordination chemistry of metals reveals that they possess very high affinity for macrocycles as these offer different types of donor atoms, ionic charges, coordination number and vivid geometry of resultant complex. The properties of macrocycles *viz.* high complexation capability or extraction selectivity for a particular metal ion, enough conformational rigidity for rapid ion exchange, high lipophilicity to remain in the membrane and moderate molecular weight to allow high mobility, make them suitable candidates as ionophores in the construction of ion-selective electrodes.

Research aimed at expanding the application of ISEs is still flourishing with the goal of improving their performance, reaching better understanding of their response mechanism and finding new chemical or physical configurations. Thorough evaluation of the response is essential to forecast the chances of success of novel ISEs that are proposed at constant rate in the current literature.

1.2 MACROCYCLIC LIGANDS

The field of macrocyclic chemistry has undergone an enormous expansion in recent years and the coordination chemistry of macrocyclic ligands has evolved into a fascinating area of current research interest. A macrocycle is defined as a cyclic compound having nine or more members (including all hetero atoms) along with three or more donor (ligating) atoms [9]. Several classes of macrocyclic ligands containing varying combination of aza (N), oxa (O) and sulfa (S) ligating atoms can be tailored to accommodate specific metal ions by the fine tuning of the ligand design features like macrocyclic ring size, nature of donor set, donor array, ligand conjugation, ligand substitution, ligand flexibility and nature of ligand backbone.

Macrocycles are important and powerful ligands ubiquitous in transition metal coordination chemistry for the following reasons:

(i) They mimic important biological ligands developed long ago by nature e.g. porphyrin prosthetic group of many metalloproteins.

(ii) They impart thermodynamic and kinetic stability to their metal complexes uncommon or nonexistent with ligands of less complex topology.

The complexes of transition metal ions with synthetic macrocyclic ligands are significant due to their resemblance with natural systems that lie at the centre of life *viz.* iron-porphyrin core in haemoglobin, the cobalt-corrin of vitamin B_{12} and the magnesium-hydroporphyrin in chlorophyll [10]. Due to complex nature of these molecules, specific role of a particular metal ion is not well understood, which is a real limitation on the pace of advancement of knowledge in the field of macrocyclic chemistry. Therefore, one has to resort to studies with simple compounds *e.g.* synthetic nitrogen donor macrocycles, which can be considered as models for their natural compounds [11-13] and help in further understanding of biological systems as well as the significant role of the particular metal ion. Apart from the above fact, the transition metal complexes of macrocyclic ligands play multifarious roles as antibiotic, antifungal, antibacterial, antitumour, anticancer, radiotherapeutic agents as well as therapeutic reagents for the treatment of metal toxicity, functional groups for chelating ion exchange materials, selective metal extractants in hydrometallurgy and to study host-guest interactions.

1.2.1 HISTORICAL BACKGROUND

The chemistry of macrocyclic ligands represents a large area of research ranging from chemistry to biochemistry [14]. In 1886, Baeyer synthesized the first macrocycle possessing subheterocyclic ring by acid catalyzed condensation of pyrrole with acetone [15] while the porphyrin was first obtained by H. Fischer in 1929 [16]. The synthesis of 1,4,8,11-teraazacyclotetradecane was first reported in 1936 [17], although cobalt [18] and nickel [19] complexes of this macrocycle were not prepared until the mid-1960s. Prior to the 1960s there were only a few scattered reports of "synthetic macrocycles". Linstead *et al.* [20,21] and Elvidge *et al.* [22] in a series of papers in 1950s reported the synthesis of a variety of tri- and tetradentate macrocyclic compounds some of which are related to porphyrins and phthalocyanins. Brown and French synthesized another class of macrocycles called tetraoxaquaterenes by acid catalyzed condensation of furan with a dialkyl ketone [23].

A variety of polyaza-, polythia- and azathia- macrocycles were prepared by 'template' procedures in the early 1960s. Curtis [24] described the reaction between tris-ethylenediaminenickel(II)perchlorate and acetone, and later [25] assigned macrocyclic structure to the product. Following these reports, the generality of the above type of reaction was demonstrated, and a new series of synthetic macrocycles were developed [26]. At approximately the same time Thompson and Busch [27] achieved the first deliberate synthesis of a new synthetic macrocyclic ligand by template method. A review article covering the synthesis of new synthetic macrocyclic complexes was published in 1964 [28] and attention was drawn on the relationship of many of these new compounds to naturally occurring biologically important species. After 1964, the field of coordination chemistry of macrocyclic compounds expanded rapidly.

The fact that macrocyclic compounds may behave as models for important natural products, provided stimulus for expansion, although the scope and variety of the compounds studied was limited. Karn and Busch reported Ni(II) complexes of a tetradentate macrocycle 2,12-dimethyl-3,7,11,17-tetraazabicyclo(11.3.1) heptdeca-1(17),2,11,13,15-pentaene [29]. A new series of macrocyclic compounds which have the ability to function as complexing agents was reported by Pedersen [30]. He synthesized a number of cyclic polyethers or "crown" compounds with a variety of ring sizes. These compounds have strong ability to coordinate to alkali and alkaline earth metal ions. Later, the first macropolycyclic complexing agents or cryptands were synthesized by Lehn and co-workers [31]. The cryptands originally synthesized were bicyclic species; however, species containing three and four macrocycles have also been reported.

The development of any area of chemistry is usually accompanied by the introduction of new terminology. Thus the term "template effect", which reflects the controlling influence of the metal ion in a particular synthesis, was introduced by Busch [32]. Two template effects; kinetic template effect and thermodynamic template effect, have been noted. The term "macrocyclic effect" was introduced by Cabbiness and Margerum in 1969 [33] to account for the greater thermodynamic stability of complexes containing macrocyclic ligands in comparison to those of non macrocyclic ligands of similar structure.

Considerable efforts in several research laboratories over the past few years have brought a new degree of sophistication to the study of macrocyclic metal complexes. The earlier work centered almost exclusively on development of new and novel methods for synthesis of a broad range of seemingly unrelated ligands and complexes. The synthesis of macrocycles was mainly based on d-block cations [34-38] but later it has been extended to s- and p-block cations as template devices to synthesize polydentate macrocycles [39-42]. Recent years have witnessed a growing interest towards macrocyclic complexes of lanthanides [43-45], because of their potential applications in biology, material science and chemical processes. A large number of reports [46-55] published till date cover the development in this area.

1.2.2 SYNTHESIS OF MACROCYCLIC COMPLEXES

Recognition of the importance of complexes containing macrocyclic ligands has led to a considerable effort being invested in developing reliable inexpensive synthetic routes for these compounds [56-58]. Syntheses of macrocycles falls into three categories: first; *in situ* synthesis, second; synthesis involving complexation reactions and third; synthesis involving modification of the macrocyclic ligand and/or the metal ion.

1.2.2.1 Template Method

The first category involves the synthesis of the macrocyclic ligand in the presence of a metal ion. Such *in situ* reactions have been widely used for the synthesis of many synthetic and "classical" macrocycles such as porphyrins, corrins etc. The presence of a metal ion in certain cyclization reactions has been shown to markedly increase the yield of a cyclic product. There is no doubt that the metal ion plays an important role in directing the steric course of the reaction. Lindoy and Busch have discussed this role in terms of coordination template effect. If the directive influence of the metal ion controls the steric course of a sequence of stepwise reaction, the kinetic template effect is considered to be operative. If the metal ion perturbs an existing equilibrium in the organic system by preferential coordination with one of the components, and by this coordination the required product is obtained as its metal complex, then the thermodynamic (or equilibrium) template effect is considered to be operative. Most *in situ* synthesis of macrocyclic ligands probably involves the kinetic template effect; however, it is not always possible to be definite about the role of the metal ion and to conclude which of the two effects is in operation in a specific synthesis. Polarization effect, kinetic lability, thermodynamic stability, and the stereochemistry of both metal ion and reactants are some of the important factors that relate to the course of a particular reaction.

There are both advantages and disadvantages of the *in situ* approach to macrocyclic synthesis. One advantage of this approach is that the yield of a particular macrocycle can be improved by the addition of a metal ion during the course of a reaction. The improved yield is usually attained by the elimination or substantial reduction of side reactions, such as, polymerization or reactions to produce non-macrocyclic products. Often a particular macrocycle can be obtained only in the presence of metal ion and isolated as its metal complex, the macrocycle itself being unstable in the absence of a metal ion. Another advantage of this approach is the possibility of selectivity. By employing a metal ion with certain steric requirements or preferences, a reaction may be controlled and thereby a particular macrocyclic product can be obtained at the expense of an undesired macrocyclic product. Although the steric requirements of a metal ion may be used in some cases, there may be a disadvantage in others; for example, they may preclude the formation of the desired macrocyclic product. Another potential disadvantage of the *in situ* approach is that the macrocyclic product is usually coordinated to the metal ion, and its removal from the metal ion is not always possible. Thus, *in situ* synthesis are less general and more metal-ion specific. In spite of these drawbacks and the possibility that the macrocyclic complex may be contaminated with the other metal-complex impurities, the *in situ* synthesis approach has gained widespread acceptance as a powerful technique for the synthesis of macrocyclic ligands.

1.2.2.2 Non-Template Method

The second category involves complexation reaction between a presynthesized macrocyclic ligand and the metal ion in solution; this technique is called the 'Non-Template' method. Advantages of this approach are that the macrocyclic ligand may be isolated and purified. The characterization of an organic ligand is often more easily accomplished than purification and characterization of a metal complex. The usual volatility, diamagnetism, and solubility of the ligand in less polar solvents makes spectroscopic techniques (*viz.* mass spectrometry and NMR spectroscopy) more amenable to the organic ligand than to the metal complex. Thus, after purification and characterization, the complexation reaction should be relatively free from side reactions, otherwise, it may lead to impurities in the desired product. Another advantage of this approach is that, changes in the macrocyclic ligand upon complexation can be readily detected if the physical properties of the ligand differ from those of the complex. One potential disadvantage of the complexation reaction approach is that, the synthesis of the organic macrocycle often results in low yield of the desired product. In attempt to increase the yield of the macrocycle and reduce side reactions such as, polymerizations, the final ring closure reaction in a stepwise synthesis, is often carried out under conditions of high dilution.

In spite of problems that may be encountered during the synthesis of macrocyclic ligands, the complexation reaction approach has been extensively employed for the synthesis of complexes containing synthetic macrocycles. Perhaps the greatest disadvantage of this approach to synthesis is the generality of the process. In principle, the number of complexes that may be synthesized from a ligand and a metal ion, is restricted only by the nature of the reactants. Admittedly this is a gross simplification of the process; however, this approach is considerably more general in nature than *in situ* process, which is more metal-ion specific and thus may be more limited in scope. Often the *in situ* and complexation approaches to synthesis are combined; the macrocyclic ligand is first synthesized by an *in situ* reaction, and then separated from the metal ion by a displacement process. Reactions between the free ligand and other metal ions may then be carried out in solution.

1.2.2.3 Coordinated-ligand Modification Method

The third approach to the synthesis of macrocyclic complexes involves the modification of the ligand and/or the metal ion in the macrocyclic complex. Several macrocyclic ligands have been chemically modified while remaining coordinated to a metal ion. Most macrocyclic complexes are kinetically inert to ligand substitution, and thus the metal ion plays an important role in these "coordinated-ligand" reactions. The most extensively studied reactions are those involving oxidative dehydrogenation. The products are often metal-ion specific, a dramatic demonstration of the importance of the metal ion in controlling the reactions of a coordinated ligand. Coordination of a macrocyclic ligand to a metal ion may change the acid-base properties of the ligand.

1.3 ION-SELECTIVE ELECTRODES

The ISEs are one of the most frequently used potentiometric sensors during laboratory analysis as well as in industry, process control, physiological measurements, and environmental monitoring. They can deliver real-time and on-line information on the presence of specific ions in complex samples.

1.3.1 HISTORICAL DEVELOPMENT

The history of ion-selective electrodes dates back to 1791, when Galvani observed bioelectric phenomenon while dissecting a frog. Later, in 1848, Brois proposed that living cell membranes have properties similar to an electrode of galvanic cell. However, the study of the potential difference across semi-permeable membranes by W. Ostwald in 1890 was another major contribution in this field. Cremer in 1906 discovered glass electrode selective for hydrogen ions. Initially the potential response was interpreted in terms of Donnan equilibrium but in 1930s, Nicolsky suggested that electrode response is dependent on the active sites of the glass capable of ion exchange and the concept enabled the selectivity coefficient of an electrode to be calculated.

In 1937, Kolthoff and Sanders [59] studied the potentialities of solid silver halide membrane based electrodes and initiated the use of materials other than glass in the construction of ISE. Ag-I based electrodes [60] were reported by Pungor and Hollos-Rokosinyi in 1961. They produced a membrane electrode by embedding silver iodide in paraffin, and demonstrated the selectivity of the electrode to iodide ions in the presence of chloride ions. Subsequently, Pungor and his coworkers developed a whole range of electrodes of good selectivity and giving Nernstian response; the electrodes all had heterogeneous membranes consisting of an active material supported in an inert matrix of silicone rubber. These electrodes were the first truly selective electrodes (non-glass) to be developed, which gave a response that is thermodynamically reversible with respect to the primary ion. The commercial development of ISEs began when Frant and Ross [61] developed calcium and fluoride electrodes. The fluoride selective electrode, based on lanthanum fluoride doped with europium fluoride, is the second best electrode developed after glass electrode.

Concepts from medicines and physiology also spurred the development of ISEs. In 1970, Higuchi *et al.* [62] introduced a liquid membrane electrode which responds both to organic and inorganic ions. The intuitive and systematic work of Buck and Linder group in designing new, highly selective ionophores made the ionophore-based liquid membrane sensors the most successful class among the ISEs [63]. The most important procedures for compounding, casting, drying and mounting PVC membranes were put forward by Moody and coworkers [64]. Therefore, the PVC based ion-selective membranes have attracted much attention and have been used in the construction of chemical sensors for a variety of cations and anions.

1.3.2 LITERATURE SURVEY

The importance of ISEs is being increasingly realized by analytical chemists in view of the rapid global expansion of industry and technology. A number of books [65-70], reviews [71-75] and some significant papers [76-80] have appeared in the recent past. Periodic reviews in "Analytical Chemistry" [81-84] cover publications in this field including theory, methodology, and applications of ISEs. The list is quite extensive and it is not possible to report the total bibliography on ISEs. Thus, only significant publications, which highlight various aspects of ISEs developed for different ions, are presented in the subsequent pages.

1.3.2.1 Sensors for Alkali Metal Ions

There has been appreciable interest in the development of ISEs for alkali metal ions as the determination of Li^+, Na^+, K^+ is important in biological fluids. In eighties and nineties, the materials used for preparing the membranes of ISEs for alkali metal ions were generally neutral carriers of different types. In 1981, Zhulov *et al.* developed an important Li^+-selective sensor using neutral carrier *N,N,N,'N'*-tetra-isobutylcyolohexaneo-1,2-dicarboxamide [85] with PVC as binder. This sensor showed working concentration range within 1.0×10^{-5} - 1.0×10^{-1} M and was selective for Li^+ over other alkali and alkaline earth metal ions. Gadzekpo and coworkers [86] have written a review, which summarizes different types of Li^+ selective sensors, gives their applications and highlights the problems encountered in the determination of lithium in serum and other biological fluids. Later on, some other neutral carriers, *N,N'*-dicyclohexyl-*N',N'*-diisobutyl-cis-cyclohexanedicarbonylamide [87], 6,6-dibenzyl-1,4,8,11-tetraoxacyclotetra decane [88], l-phenyl-3-methyl-4-benzoyl-5-pyrazolone [89] and carbosiloxane dendrimer [90] were also investigated as suitable ionophores to develop Li^+ selective sensors. Recently, Ibrahim *et al.* [91] synthesized diazapolyoxa macrocyclic ditosylates which were employed as neutral carriers in Li^+ selective electrodes. The electrodes exhibited nearly Nernstian responses with relatively high selectivity for lithium over other inorganic cations.

Most of the reported Na^+ selective sensors developed are based on neutral carriers. The sensors prepared by Wu *et al.* [92] based on triglycollic bisdiamides in PVC matrix performed well compared to earlier reported sensors. This sensor 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 [93], dibenzo-16-crown-5 [94], azo- and azoxycrown compounds with sulphur atoms in long side chains [95] and silacrown ether [96] 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 [97], calix[4]arene derivatives [98] and p-tert-butylcalix[4]arene ethyl ester [99]. 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. Kimura *et al.* [100] designed several sol-gel derived membranes selective to Na^+ which encapsulate valinomycin and bis(crownether) as electroactive materials. Adnan *et al.* reported a sodium ion selective PVC-coated graphite rod electrode based on 4-amino-benzo-15-crown-5 derivatives of fullerenes which exhibited Nernstian response with detection limit of 5×10^{-5} mol L^{-1} [101].

In 1973, Fiedler and Ruzika developed the first successful and commercially available sensor for potassium ion using valinomycin, as neutral carrier [102]. Since then many workers have developed valinomycin based ISEs for K^+. Heng and Hall [103] developed glycidyl methacrylate, methylmethacrylate and n-butylacrylate polymers based membranes containing valinomycin. All polymeric membranes gave Nernstian or near-Nernstian responses over the potassium ion concentration range of 1.0×10^{-5}-1.0×10^{-1} M but suffer interference from Na^+ ions. A number of K^+ selective sensors based on crown ethers *viz.*, 4',4"(5")-di-tert-butyldibenzo-18-crown-6-ether [104], benzo-15-crown-5 ether [105] and cis-,trans-bis (crown ethers) [106] 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 serum and biological fluids. Yan *et al.* [107] used calix[6]arene hexaester for the preparation of membranes and investigated its applicability to determine K^+ in human serum. Recently, Katsu *et al.* [108] reported K^+ selective sensor based on macrocyclic metacyclophanes analogous to calixarenes which showed linear response down to 7 μM of K^+ but suffer serious interference from Na^+.

The development of ISEs for Rb^+ has received relatively less attention mainly because of their conspicuous absence in biological systems. However, still some sensors have been reported. Jain and coworkers [109] 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. Cosgrove *et al.* [110] reported a valinomycin based sensor selective for Rb^+ and used it to determine rubidium in yeast cells. Another Rb^+ selective sensor was developed by Saleh *et al.* [111] using indanopyrazalo[1,5-a] pyrimidines as electroactive material which showed Nernstian response in the concentration range of 1.0×10^{-4}-1.0×10^{-1} M . Hyun and co-workers [112] incorporated binaphthyl-based crown ethers as an electroactive material in the fabrication of a Rb^+ selective sensor which exhibited Nernstain response over working concentration range of 1.0×10^{-5} - 1.0×10^{-1} M and good selectivity for Rb^+ over other cations.

Cesium has also received less attention and thus, less work on the development of Cs^+-selective electrode has been reported. Wang and Shih [113] found 15-crown-5-phosphotungustic acid precipitate selective for Cs^+. It showed Nernstian response in the concentration range of 10^{-4}-10^{-1} M. Four calix[4]arene dibenzocrown ether compounds were prepared by Kim and co-workers and evaluated as Cs^+-selective ligands in solvent polymeric membrane sensors [114]. These sensors showed linear response to Cs^+ ion in the concentration range of 1.0×10^{-6} to 1.0×10^{-1} M. Cs^+ selective sensors based on tetraesters of calix[4]arene and calix[4]crown ether-ester [115] have also been reported. Saleh *et al.*

developed Cs^+ selective sensor using cephalexin antibiotic [116]. A new Cesium ion selective graphite rod electrode based on Cs-Molybdophosphate as membrane carrier was prepared by Arida and co-workers [117]. This electrode exhibited a linear response with slope of 46.5 ± 1 mV/decade within the concentration range of 1.0×10^{-5}-1.0×10^{-1} mol L^{-1} Cs^+ ion. Peper *et al.* developed a Cs^+-selective electrode by doping ethylene glycol-functionalized cross-linked polystyrene microspheres (P-EG) into a plasticized poly(vinyl chloride) (PVC) matrix containing sodium tetrakis-[3,5-bis(trifluoromethyl)phenyl] borate (TFPB) as the ion exchanger [118].

1.3.2.2 Sensors for Alkaline Earth Metal Ions

Alkaline earth metal ions are also important ions to be determined as they are widely distributed in natural and biological samples as well as in industrial wastes. Considerable efforts have been made by researchers to develop selective sensors for alkaline earth metal ions.

Among alkaline earth metal ions, beryllium has received less attention inspite 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 [119] used phosphate ester ionophores to prepare Be^{2+} selective sensors. Ganjali *et al.* employed 2,3,5,6,8,9-hexahydro-1,4,7,10-benzotetraoxacyclododecine-12-carbaldehyde-12-(2,4-dinitrophenyl)hydrazine [120], 2,3,5,6,8,9-hexahydronaphto[2,3-b][1,4,7,10] tetraoxacyclododecine [121] and 4-nitrobenzo-9-crown-3-ether [122] to develop Be^{2+} selective sensors. Beiraghi *et al.* developed an optical sensor for selective determination of Be^{2+} ion by incorporation of 1,8-dihydroxyanthrone in a poly (vinyl chloride) membrane [123].

A Mg^{2+} selective sensor was prepared by Saleh [124] 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} M. Further, 1-(N,N-dicyclohexylcarbamoyl)-2-(N,N-dioctadecylcarbamoyl)ethyl phosphonic acid monomethyl ester [125] was also used as ionophore for magnesium-selective sensor. This sensor exhibited linear response towards Mg^{2+} ions with reasonably good selectivity. Zamani *et al.* [126] reported a Mg^{2+} selective sensor incorporating 4,5-Bis(benzoylthio)-1,3-dithiole-2-thione as an ionophore. This sensor exhibited a near-Nernstian response to Mg^{2+} ion in the concentration range of 1.0×10^{-5} to 1.0×10^{-1} M, with a slope of 29.2 mV $decade^{-1}$ of activity. Shoukry and co-workers developed a Mg^{2+} selective electrode by incorporating chlorophyll as an electroactive component. The sensor exhibited average slope of 31.2 mV $decade^{-1}$ of activity over a concentration range of 4.0×10^{-5}-2.8×10^{-2} M [127]. Recently, Zhu *et al.* proposed a novel Mg(II) selective ion-channel mimetic sensor based on a known Ca ionophore, ETH 5234 [128].

Calcium ions play striking role in many cellular processes as their specific interaction with biological and model membranes are essential for structure, dynamics and stability of membranes. In the late sixties, Ross [129] developed a liquid membrane sensor for calcium ions using calcium-di-(n-decyl) phosphate in di-(n-octylphenyl) phosphonate medium having good response time and poor selectivity. Thomas and coworkers [130] prepared an Ca^{2+} selective sensor 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. These sensors, showed good selectivity for Ca^{2+} ions over a large number of cations and working concentration range was 1.0×10^{-6} to 1.0×10^{-1} M. Later on, various organophosphates, such as Ca-di-(n-octylphenyl) phosphate [131] and polyaniline functionalized with bis[4-(1,1,3,3-

tetramethyl butyl) phenyl]phosphate [132] were employed as electroactive material for Ca^{2+} selective sensors. Some of these sensors respond to Ca^{2+} ions over a wide concentration range with a fast response time but the selectivity of these sensors was not good. Bis-di[4-(1,1,3,3-tetramethylbytyl)phenyl phosphoric acid] [133], ETH 1001 [134], tetronasin antibiotic [135], furildioxime [136] and p-isopropylcalix[6]arene [137] have also been explored as ionophores in the construction of ion-selective electrodes for Ca(II) ions.

Strontium is an important metal and is used in the production of glasses for colour television sets and added to tin and lead alloys for increasing hardness and durability. Thus, it is important to determine this metal in different samples. The first Sr^{2+} selective sensor was developed by Baumann [138] using strontium complex of nonylphenoxypoly(ethyleneoxy)ethanol as electroactive material but it exhibited higher selectivity for Ba^{2+} than Sr^{2+}. Gupta *et al.* used 4-tert-butylcalix[8]arene [139] and 5,11,17,23,29,35-hexakis(1,1,3,3-tetramethylbutyl)-37,38, 39, 40, 41, 42-hexakis (carboxy methoxy)calix[6]arene) [140] to prepare Sr^{2+} selective sensors. These sensors worked in the concentration range of 1.0×10^{-5} -1.0×10^{-1} M but suffered interference from Pb^{2+} and Na^{+} ions. Recently, various compounds *viz.* 2-[(2-mercaptophenylimino)methyl]phenol [141], 2,3-Diphenylquinoxaline-4',4''-dioxytriethylene glycol [142] and 1-benzothiazol-3-benzoyl-thiocarbamide [143] have been used as ionophores in the fabrication of Sr^{2+} ion selective electrode which showed wide working concentration range and good selectivity for Sr^{2+} ion.

Determination of barium is important as it is present in various drugs. Earlier, non-ionic Antrarox CO-880 and its barium complex [144] were used to construct Ba^{2+} selective sensors. The sensors were also assessed for measuring SO_4^{2-} ion by analyte substraction. Othman *et al.* [145] used complex ion associate of barium(II)-Rose Bengal as an electroactive material for preparing Ba^{2+} selective sensor which was applied for the analysis of barium ions in waste water samples and in lithophone pigment. The determination of sulphate in fresh and potable water samples by the proposed sensor was also described. Recent literature reveals that various ionophores have been proposed which shows high selectivity to Ba^{2+} ion [146-148].

1.3.2.3 Sensors for Transition Metal Ions

The analysis of transition metal ions in the environment, clinical, industrial and biological samples is still a challenging task due to both the low levels of metals in the samples and complexity of the matrices. The determination of transition metals in various samples is of considerable importance in view of their toxicity above certain concentration level. A lot of efforts have been made by many researchers in the field of ion-sensors 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 metal ions. In the following pages only a brief review on ISEs for Cu^{2+}, Cr^{3+} Ag^{+}, Hg^{2+}, etc. is given. A detailed literature survey on various ISEs for Ni^{2+}, Co^{2+} and Zn^{2+} is presented in the subsequent Chapters of the thesis.

Copper is an essential element in human body and plays an important role in various biological processes and has widespread occurrence in environment. Palanivel *et al.* explored CuS-Ag_2S mixture as an electroactive material to prepare copper selective sensor [149] but this sensor suffered interferences from Hg^{2+}, Hg^{+}, Ag^{+} and Fe^{3+}. Jain *et al.* explored some macrocycles 3,5,7,7,10,12,14-octamethyl-1,4,8,11-tetraazacyclo-tetradeca-4,11-diene diperchlorate, 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetrazacyclo-tetradeca-4,11-dienedipercholrate [150] and Schiff base chelate [151] for determination of copper. A comparative investigation on Cu^{2+} selective sensors was carried out by Gismera *et al.*

using thiohydrazone and thiosemicarbazone [152], dithiosalicylic and thiosalicylic acids [153] as chelating ionophores. These sensors exhibited interference due to Hg^{2+}, Cl^-, SO_4^{2-} ions. In addition to these, 2-[{(2-hydroxyphenyl)imino}methyl]-phenol and 2-[{(3-hydroxyphenyl)imino}methyl]-phenol [154], 1,2-bis(E-2-hydroxy benzylidene amino)anthracene-9,10-dione [155], 1-Phenyl-2-(2-hydroxyphenylhydrazo)butane-1,3-dione [156] and 2-((2-(2-(2-(2-hydroxy-5-methoxybenzylideneamino) phenyl)disufanyl)phenylimino) methyl)-4-methoxyphenol Schiff base [157] have been explored for determination of copper ions in recent years.

Among various heavy metals, the pollution by chromium ions is of considerable concern, as it is highly toxic and has been used in many industries such as chrome plating, pigment manufacturing, refractory industries, leather tanning, wood treatment, and making steel and other alloys. A number of potentiometric sensors based on a variety of ionophores have been reported in the past three decades. Masuda *et al.* [158] 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) over a concentration range of 10^{-5}-10^{-2} M. In 1989, Chattopadhyaya reported precipitate based chromium selective electrode utilizing chromium dithizonate as an ionophore [159]. Several chromium selective electrodes based on asymmetrical Schiff bases [160], 5-amino-1-phenyl-1H-pyrazole-4-carboxamide [161], 1-(2-(1H-imidazole-1-yl)-1-(4-methoxyphenyl) ethylidene)-2-phenyl hydrazine [162] and crown ether [163] have also been reported.

Quick determination of trace quantities of Ag^+ ion is of critical importance due to its multi-purpose nature and its widespread use in dentistry, electronic and photographic film production industry. Lai and coworkers [164] reported the first neutral carrier Ag^+-selective electrode based on dithiacrown ether. Since then a number of electrodes have been reported for Ag^+ ions and calixarene derivatives remain the most extensively used compounds in the construction of Ag^+-selective electrodes. Some of the calixarenes are 1,3-bis(2-benzothiazolyl)thioalkoxy-*p*-tert-butylcalix[4]arenes [165], selenium functionalized calix[4]arene [166] and thiacalix[4]arene conjugated with gold nanoparticles [167]. Due to the affinity of soft acid Ag^+ ions towards soft base sulphur atoms, a number of thia containing ionophores *viz.* sulphur containing podants [168], bis(thiothiazole)derivative [169], corrole derivatives [170] and tripodal broom molecules [171] have been reported as suitable ionophores for Ag^+-ISEs in recent years.

The determination of mercury is probably most important to analysts in view of its acute toxicity. Various materials such as mixture of AgI-Ag_2S [172], Hg(II)-chelates [173] and dithia crown ethers [174] have been tried as membrane material for preparing Hg^{2+} selective sensor. These attempts have not been very successful as the reported sensors [173] except AgI-Ag_2S [172] show high response time (5-8 minutes) and poor selectivity. Mahajan *et al.* used salicylaldehyde thiosemicarbazone as an ionophore for preparing Hg^{2+} sensor [175]. The sensor showed good potentiometric response for Hg^{2+} ions over a wide concentration range of 1.7×10^{-6} - 1.0×10^{-1} M with a Nernstian slope of 29.0 mV decade^{-1} of activity but suffer strong interference from Ag^+ ions. In addition to these, various ionophores have been explored for fabrication of mercury ion-selective electrodes in recent years [176-181].

Manganese is essential micronutrient for various organisms but is toxic at higher concentration level. It therefore becomes important to monitor manganese in environmental samples. There has been little work done on manganese selective sensors. Lal and coworkers explored cation exchange resin (Dowex 50WX-4) for fabrication of Mn(II) selective sensor [182]. The sensor worked in concentration range of 1.0×10^{-5} - 1.0×10^{-1} M with long response time. Agarwal and coworkers used

$[Mn(Py)_4](SCN)_2$ for determination of Mn^{2+} [183] but this sensor shows high response time and suffers interference from Co^{2+} and Pb^{2+} ions. Singh *et al.* explored a macrocycle *i.e.* 14,16-dimethyl-1,4,7,10,13-pentaazacyclohexadeca-13,16-diene for fabrication of Mn^{2+} selective sensor [184]. Although, this sensor worked well over a wide concentration range 1.2×10^{-5} - 1.0×10^{-1} M and shows fast response time but suffers interferences from Cu^{2+}, Zn^{2+}, Hg^{2+} and La^{3+} ions. Several compounds viz. *N,N'*-bis(2'-pyridine carboxamide)-1,2-ethane [185], bisethylenediimine [186] and 2,2′-bis(salicylideneamino) azobenzene [187] *etc.* have been employed as an electroactive material in the preparation of Mn(II) selective electrodes.

Iron is essential nutrient as it provides a fundamental structure to haemoglobin, myoglobin, haemeenzymes and many cofactors involved in enzyme activities. It is considered as being a moderately toxic element, but medical research studies have shown that the toxic doses of iron and its compounds can lead to serious problems, including depression, rapid and shallow respiration, coma, convulsions and cardiac arrest. Therefore, its determination is necessary in environmental and biological samples. There are only few reports of Fe(III) selective sensors in the literature. Pejcic and coworkers reported Fe(III) selective sensor based on chalcogenide glass system [188]. Ekmekci *et al.* [189] reported Fe(III) selective sensor based on benzo-18-crown-6 crown ether as an ionophore. In addition to these, various compounds [190-194] have been incorporated as an electroactive material in the fabrication of Fe(III) selective electrodes.

Relatively less work has been done on the development of Au^{3+} selective sensor as compared to other transition metal ions. Zhang and coworkers explored benzyldimethyloctadecylammoniumaurichloride [195] for the determination of gold in minerals. The electrode showed Nernstian response to $AuCl_4^-$ in the concentration range 0.35 μM to 7mM. Hassan *et al.* proposed Au(III) selective electrode based on nitron tetrachloroaurate(III) as an electroactive material which exhibited fast response time over the working concentration range of 1.0×10^{-5} - 1.0×10^{-1} M [196].

Among transition metal ions, vanadium has received less attention. Very few attempts have been reported for determination of vanadyl ions. PVC based membrane sensors using ion carriers such as 1,8-diaminonaphthlene [197], vanadyl phosphate [198] have been reported for the fabrication of vanadyl ions. Recently Schiff's base has been explored successfully for determination of vanadyl ions by Ganjali and coworkers [199].

1.3.2.4 Sensors for Rare Earth Metal Ions

The rare earth elements (REEs) are distributed in low concentration throughout the earth's crust and are considered slightly toxic. REEs are being increasingly used as an important component in lasers, phosphors, magnetic bubble memory films, refractive index lenses, fiber optics, superconductors, high-intensity lightning, coloured glasses, refining industry and nuclear technology. A detailed literature on Tb^{3+}, Yb^{3+} and Ce^{3+} selective sensors is presented in the subsequent Chapters of this thesis, while a brief review on ISEs for other rare-earths is given in the following paragraphs.

The determination of lanthanum ions has become necessary because of the increasing interest in bioinorganic and coordination chemistry, as well as in the increased industrial use of lanthanum compounds and their enhanced discharge, toxic properties and other adverse effects. There are only a few reports on La(III) ion-selective electrodes till date. Pan *et al.* [200] described a solid state La(III)-selective electrode. Amarchand *et al.* [201] 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 carriers *viz.* 4-methyl-2-hydrazinobenzothiazole [202], $Bzo_2Me_2Pyo_2$(16)-hexaeneN_6 [203], and benzo-15-crown-5 [204] have also been reported.

In 1996, Chowdhury and coworkers reported the first Sm^{3+} selective sensor, by using bis(thiaalkylxanthato)alkanes as an ion carrier [205]. Later on Mittal and coworkers reported samarium(III) selective sensors based on tin(IV) boratophosphate [206] and zirconium(IV) boratophosphate [207] but these sensors showed super Nernstian slope. In addition to these, Sm^{3+} selective sensor based on 2-((2-thioxothiazo-lidin-4-one)methyl)phenol [208], 2-ethoxy-1-ethoxycarbonyl-1,2-dihydroquinoline [209] and 2-[(E)-1-(1H-pyrrol-2-yl)methylidene]-1-hydrazinecarbothioamide [210] have also been reported.

There have been few reports on Gd^{3+} selective sensors. Zamani and coworkers used 6-methyl-4-{[1-(2thienyl)methylidene]amino}3-thioxo-3,4-dihydro-1,2,4-triazin -5-(2H) -one [211] as an ionophore for fabrication of Gd^{3+} selective sensor. Singh *et al.* explored 2,6-bis-[1-{*N*-cyanopropyl,*N*-(2-methylpridyl)}aminoethyl] pyridine as an ionophore for the determination of Gd(III) ions in waste water and rock samples [212].

In 2004, Agarwal and coworkers reported Nd(III) selective sensor using inorganic ion exchange resin [213] but this sensor showed long response time. Norouzi *et al.* explored N-(2-furylmethylene)pyridine-2,6-diamine for determination of Nd(III) ion [214] while in recent year Singh *et al.* reported Nd(III) selective sensor incorporating lariat ethers as an ionophore [215].

Ion selective sensors for some other rare-earth metal ions *viz.*, Dy^{3+} [216,217], Eu^{3+} [218], Ho^{3+} [219], Tm^{3+} [220], UO^{2+} [221,222], Pr^{3+} [223] *etc.*, have also been reported. All these sensors exhibited good selectivity for the ion of interest, sufficiently wide working concentration range and low response time.

1.3.2.5 Sensors for Anions

In recent years, intensive research has been directed towards the preparation of a variety of selective receptors for anions. The most successful and important anion selective sensor is for F^- anion which is based on the crystal of LaF_3. Another F^- selective sensor incorporating CaF_2 or LaF_3 or mixture of both has been reported by Newman *et al.* [224]. The sensor exhibited working concentration range of 10 μM - 10 mM and detection limit up to 0.6 μM F^-. Nakamura *et al.* [225] used membranes of phthalocyanine cobalt(III) for preparing F^- sensors and used them for fluoride estimation in non-aqueous medium and pharmaceuticals. In recent years, various ionophores *viz.* aluminum(III) porphyrins [226], complexes of Zr(IV) and Al(III) with 2,7,12,17-tetra-tert-butyl-5,10,15,20-tetraazaporphine [227] and Al(III)- and Zr(IV)-salophens [228] have been used in the preparation of F^--selective electrode. Similarly, attempts have also been made to prepare Cl^- selective sensor by using different ionophores such as lanthanide tris(b-diketonates) [229], 2,5-dihydroxy-p-benzoquinone [230] and polypyrrole-graphite-epoxy composite [231]. Havas *et al.* first time used bromide ion-selective membrane electrode [232] and Weiss *et al.* utilized bromide ionic electrodes in waters which were sensitive to poisoning by I^- and S^{2-} [233], later on Zhu *et al.* studied on the benzalkonium bromide ion-selective electrode [234]. PVC based membrane sensors incorporating different ionophores *viz.*, tetrakis(4-N,N-dimethylaminobenzene)porphyrinatomanganese(III) acetate (MnTDAc) [235], Cd chelates of schiff bases, N,N'-bis(salicylidene)-1,4-diaminobutane, (Cd-S1) and N,N'-bis(salicylidene)-3,4-diaminotoluene (Cd-S2) [236], 3-amino-5-mercapto-1,2,4-triazole cobalt(II) [237], meso-tetrakis(2-alkoxyphenyl)-porphyrin cobalt(II) [238], Bis-(o-phenylenediamine)Cu(II) [239] and poly(3-aminophenylboronic acid) [240] have been developed which responded selectively to I^- ions.

After halide determination, the next important ion determined is nitrate due to its presence in soils, ground waters and various other samples. Schwarz *et al.* [241] prepared NO_3^- selective sensor using tridodecylmethyl ammonium nitrate as an electroactive material and applied it for in-situ determination of NO_3^- in ground water and drinking water. Some recently developed membrane sensors based on tris(2-aminoethyl)amine [242], 1,8-bis(salicylaldiminato)-3,6-dioxaoctane Ni(II) complex [243] and bis-thiourea [244] showed good selectivity for NO_3^-.

Carbonate compounds are used extensively in the manufacturing of glass, paper, rayon, soaps, detergents and 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 reported first carbonate selective membrane sensors based on the tri-fluoroacetyl-*p*-butylbenzene derivatives [245]. However, the applicability of these sensors has often been limited because of interference caused by lipophilic anions such as salicylate, perchlorate, and thiocyanate. Later on, Scott *et al.* employed an anion-binding complexone such as mercuric EDTA in the buffer solution to decrease salicylate interference of the carbonate responsive membrane [246]. The change of cationic site (e.g. tridodecylmethylammonium chloride (TDDMACl) concentrations) in the trifluoroacetophenone (TFA) based membranes was examined by Sokalski *et al.* to improve their carbonate selectivity [247]. Asymmetric membrane technology was utilized to prevent salicylate from responding to carbonate sensitive membranes in serum carbon dioxide measurements [248]. Several attempts were also made to increase the selectivity of sensors by incorporating acceptor substituents into phenyl ring of TFA in para-position [249,250], thus increasing the acidity of the trifluoroacetyl-group, which is responsible for carbonate sensing. Nevertheless, the interferences from high concentrations of chloride and salicylate still hinder wider application of carbonate sensors.

A sulphate selective sensor based on a derivative of imidazole as neutral carrier was reported by Li *et al.* [251] which showed strong interference to bromide and nitrate ions. Hydrotalcites based sulphate selective sensor was reported by Morigi *et al.* [252] which showed improved selectivity for sulphate over a number of anions. Recently, Sathyapalan and co-workers [253] designed a sulphate ion selective electrode based on a hydroxyl Schiff base which showed remarkable selectivity to SO_4^{2-} ion.

A few other anion selective sensors have also been reported. Messick *et al.* [254] reported salicylate selective sensor based on lutetium(III)porphyrin. Blikova *et al.* [255] prepared salicylate selective sensors based on complexes of Sn(IV) with 8-hydroxyquinoline and tetrakis(tert-butyl)phthalocyanine and used them to determine acetylsalicylic acid in medical preparation. Recent literature reveals that various ionophores have been proposed which shows high selectivity to salicylate ion [256-259].

Arsenite selective sensor was prepared by Gupta *et al.* [260] using cobalt(III)*p*-tertrmethoxy porphyrin as an electroactive material which showed linear potential response in the concentration range of 7.9×10^{-5} - 1.0×10^{-1} M AsO_2^- with a slope of 28.8 mV decade^{-1} of activity. The sensor worked satisfactorily in non-aqueous medium and showed good selectivity for arsenite over a large number of anions.

1.3.2.6 Miscellaneous Sensors

Besides inorganic ions, efforts have also been made to develop sensors for gases and organic species. Ueda *et al.* [261] made use of p-1,1,3,3-tetramethylbutyl calix[6]arenehexaacetic acid hexaethyl ester embedded in PVC matrix to develop sensor for methylammonium ion. The sensor exhibited a near Nernstian response in the concentration range of $1.0 \times 10^{-5} - 1.0 \times 10^{-2}$ M with a slope of 58.5 mV decade^{-1} of activity. Mohammad *et al.* [262] developed histamine selective sensors using iron(III) and manganese(II) porphyrins and applied them to determine histamine in synthetic serum samples. Varga *et al.* [263] described a novel method for the preparation of anionic surfactant-selective sensors. The sensors thus developed showed Nernstian response, fast response time and good stability. Cocaine, caffeine, penicillin-G, diclofenac, atropine, viagra, and some chiral drugs selective sensors have been developed and applied for their estimation in pharmaceutical analysis [264-268]. A nicotine-selective sensor [269] has been prepared by adding silicotungstic acid and di-(2-ethylhexyl)phthalate in PVC matrix which showed Nernstian response in the range 1 μM - 0.1 mM 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 [270]. 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. Similarly, biosensors for a number of biomolecules have been prepared and some of them are commercially available [271-273].

1.4 THE PROBLEM

Polydentate macrocyclic ligands are cyclic molecules consisting of an organic framework interspersed with heteroatoms that are capable of interacting with a variety of species. They display unique and exciting chemistry as they can function as receptors for substrates of widely differing physical and chemical properties and can drastically alter these properties upon complexation. These ligands and complexes exhibit high kinetic and thermodynamic stability as compared to their non-cyclic counterparts along with the ability to stabilize unusual oxidation states. Nature prefers macrocyclic derivatives for carrying out extremely diverse fundamental biological functions *viz.* photosynthesis (chlorophyll), oxygen transport (haemoglobin), electron transport (cytochromes), modification of substrates (vitamin B_{12}) etc. Studies of the geometry around the metal center present in active sites and its electronic and magnetic behavior are highly cumbersome due to the fact that the metal ion is embedded in a biopolymer backbone. Hence, the synthesis and study of model systems (which are low molecular weight complexes that mimic either the structure or function of naturally occurring molecules) is important for an insight about the cooperative phenomena, electron transfer and magnetic interaction between metal centers which in turn leads to an enhanced understanding of the metal in biological system. The approach to developing model systems has been towards the construction of ligands and metal complexes that approximate the environment about certain metal ions of the active sites and to explore the full range of complex reactivity in these systems. This can be done by introducing the proper number and type of donor atoms, geometry, steric requirements etc into the ligands and there are almost infinite variety of modifications that can be incorporated into the ligands. This approach would contribute to the understanding of biochemistry as well as provide information in the basic area of metal ion chemistry. In view of the above-mentioned facts and for enhancement of our knowledge on macrocyclic chemistry, attempts have been made in the present study to synthesize and characterize polydentate macrocyclic ligands and their complexes. The synthesis and characterization of specific macrocyclic ligands and their complexes with different ring sizes and varying degree of unsaturation have been reported in experimental section of subsequent chapters of the thesis.

The most intriguing characteristic of the macrocyclic compounds is their ability to selectively bind certain cations in preference to others that may be present in solution. They are a class of compounds known for their remarkable selectivity for various transition and non- transition metal ions. Their use in separation of metal ions which are present in very low concentration from other concentrated metal ions is of particular interest. The determination of various metals up to very low levels has become important due to their deleterious effects on the environment and living organisms. The various conventional methods for the determination of metal ions like AES, photometry, titrimetry, AAS etc. are tedious, costly and time consuming. The development and use of potentiometric sensors or ion-selective electrodes for the determination of metals at low concentrations is a highly desirable proposition as these are rapid, versatile, economic and easy to operate devices. Macrocyclic ligands find useful application as membrane materials in the development of ion-selective electrodes that serve as a handy tool for quantitative analysis of a variety of ions and molecules. The survey of literature reveals that various kinds of macrocyclic ligands and complexes have been used as ionophores in the construction of ISEs for alkali, alkaline and heavy metal ions. The development of a large number of electrodes for a particular metal ion have been due to the efforts made by the researchers in the field to improve the working concentration range, selectivity, life time, response time and also extend the usability of these devices to real samples. However, for most of the ions, even the best electrodes so far developed is not the last word and can always be improved provided newer selective materials are available. Success of an ISE to a great extent depends on the selectivity of the electroactive component present in the membrane. The selectivity of the electroactive material is due to the high affinity that materials may show for some particular ion as a result of ion-exchange process, sorption process, complexation process or ion-pair formation. Different materials show affinity due to either of these processes.

In the present research work efforts were made to explore the possible use of some newly synthesized macrocycles as selective ionophores in developing ion-selective electrodes. The efforts were successful in the construction of cation selective electrode for selective determination of Ni^{2+}, Co^{2+}, Zn^{2+}, Tb^{3+}, Yb^{3+} and Ce^{3+} ions and the results are reported in Third and Fourth Chapter of the thesis. The newly synthesized macrocyclic complexes were also incorporated as an electroactive material (ionophore) in the fabrication of anion selective electrodes which respond selectively to SCN^- and ClO_4^- ions and results are discussed in Fifth Chapter of the thesis.

REFERENCES

1. Audry, S., Schafer, J., Blanc, G. and Jouanneau, J.M., "Fifty-year sedimentary record of heavy metal pollution (Cd, Zn, Cu, Pb) in the Lot River reservoirs (France)", *Environmental Pollution*, **132**, 413 (2004).
2. Rivett, M.O., Petts, J., Butler, B. and Martin, I., "Remediation of contaminated land and groundwater: experience in England and Wales", *Journal of Environmental Management*, **65**, 251 (2002).
3. Loska, K., Wiechula, D. and Korus, I., "Metals contamination of farming soils affected by industry", *Environmental International*, **30**, 159 (2004).
4. Kemp K., "Trend and sources for heavy metals in urban atmosphere", *Nuclear Instruments and Methods in Physics Research B*, **189**, 227 (2002).
5. Wu, H.B., McKay, C., Broussard, L.A., Hoffman, R.S., Kwory, T.C., Moyer, T.P., Otten, E.M., Welch, S.L. and Wax, P., "National Academy of Clinical Biochemistry Laboratory Medicine Practice Guidelines: Recommendation for the use of laboratory tests to support poisoned patients who present to the emergency department", *Clin. Chem.*, **49**, 357 (2003).
6. Nordberg, G., Jin, T., Leffler, P., Svensson, M., Zhou, T. and Nordberg, M., "Metallothioneins and diseases with special reference to cadmium poisoning", *Analusis*, **28**, 396 (2000).
7. Ganjali, M.R., Norouzi, P. and Rezapour M., "Potentiometric Ion-Selective Sensors", *Encyclopedia of Sensors*, **4**, (2006).
8. Egorov, V. V., Rakhman'ko, E.M. and Rat,ko A.A., "Anion-Selective Electrodes Liquid Membranes", *Encyclopedia of Sensors*, **1**, (2006).
9. Melson, G.A., "Coordination Chemistry of Macrocyclic Compound", Plenum, New York (1979).
10. Hughes, M.N., "The Inorganic Chemistry of Biological Processes", 2nd Ed., Wiley, New York (1981).
11. Williams, D.R., "The Metals of Life", Van Nostrand-Reinhold, London (1971).
12. Gould, R.F. (ed.), "Bioinorganic chemistry", Advances in Chemistry Series No. 100, American Chemical Society, Washington (1971).

13. Eichhorn, G.L. (ed.), "Inorganic Biochemistry", Elsevier, Amsterdam (1973).

14. Dolphin, D., "The Porphyrins (Biochemistry-part B)", New York, Academic Press, London (1979).

15. Baeyer, A., "Ueber ein condensations product von pyrrol mit aceton", *Ber. Dtsch. Chem. Ges.*, **19**, 2184 (1886).

16. Fischer, H. and Zeile, K., "Synthese des haematoporphyrins, protoporphyrins and haemins", *Liebigs Ann. Chem.*, **98**, 468 (1929).

17. Van Alphen, J., "Aliphatic polyamines", *Rec. Trav. Chim. Pays-Bas Belg.*, **55**, 835 (1936).

18. Bosnich, B., Poon, C.K. and Tobe, M.L., "Complexes of cobalt (III) with a cyclic tetradentate secondary amine", *Inorg. Chem.*, **4**, 1102 (1965).

19. Bosnich, B., Tobe, M.L. and Webb, G.A., "Complexes of nickel (II) with a cyclic tetradentate secondary amine", *Inorg. Chem.*, **4**, 1109 (1965).

20. Linstead, R.P. and Whalley, J., "Conjugated macrocycles. Part XXII. Tetraazaporphin and its metallic derivatives", *J. Chem. Soc.*, 4839 (1952).

21. Ficken, G.E. and Linstead, R.P., "Conjugated macrocycles. Part XXIII. Tetraazacyclohexenotetraazaporphin", *J. Chem. Soc.*, 4846 (1952).

22. Elvidge, J.A. and Linstead, R.P., "Conjugated macrocycles. Part XXIV. A new type of cross-conjugated macrocycle, related to the azaporphines", *J. Chem. Soc.*, 5008 (1952).

23. Brown, W.H. and French, W.N., "Condensation of furan with carbonyl compounds", *Can. J. Chem.*, **36**, 537 (1958).

24. Curtis, N.F., "Transition metal complexes with aliphatic Schiff bases. Part I. Nickel (II) complexes with n-isopropylidenethylenediamine Schiff bases", *J. Chem. Soc.*, 4409 (1960).

25. Curtis, N.F. and House, D.A., "Structure of some aliphatic Schiff base complexes of nickel (II) and copper (II)", *Chem. Ind.*, **42**, 1708 (1961).

26. Curtis, N.F., "Macrocyclic coordination compounds formed by condensation of metal amine complexes with aliphated carbonyl compounds", *Coord. Chem. Rev.*, **3**, 3 (1968).

27. Thompson, M.C. and Busch, D.H., "Reaction of coordinated ligands IX. Utilization of the template hypothesis to synthesize macrocyclic ligands *in situ*", *J. Am. Chem. Soc.*, **86**, 3651 (1964).

28. Busch, D.H., "The significance of complexes of macrocyclic ligands and their synthesis by ligand reactions", *Rec. Chem. Prog.*, **25**, 107 (1964).

29. Karn, J.L. and Busch, D.H., "Nickel(II) complexes of tetradentate macrocycle 2,12-dimethyl-3,7,11,17-tetraazabicyclo(11.3.1)heptadeca-1(17),2,11,13,15-pentaene", *Nature*, **211**, 160 (1966).

30. Pedersen, C.J., "Cyclic polyethers and their complexes with metal salts", *J. Am. Chem. Soc.*, **89**, 2495 (1967).

31. Dietrich, B., Lehn, J.M. and Sauvage, J.P., "Less cryptates", *Tetrahed. Lett.*, **10**, 2885 (1969).

32. Lindoy, L.F. and Busch, D.H., "Preparative Inorganic Reactions", Wiley-Interscience, New York (1971).

33. Cabbiness, D.K. and Margerum, D.W., "Macrocyclic effect on the stability of copper (II) tetraamine complexes", *J. Am. Chem. Soc.*, **91**, 6540 (1969).

34. Nelson, S.M., "Development in the synthesis and coordination chemistry of macrocyclic Schiff base ligands", *Pure Appl. Chem.*, **52**, 2461 (1980).

35. Drew, M.G.B., Rodgers, A., McCann, M. and Nelson, S.M., "Template synthesis of a bimetallic complex of a 30-membered decadentate macrocyclic ligand: The crystal and molecular structure of a lead (II) complex", *J. Chem. Soc., Chem. Commun.*, 415 (1978).

36. Fenton, D.E., "Tetraimine Schiff base macrocycles derived from heterocyclic dicarbonyls", *Pure Appl. Chem.*, **58**, 1437 (1986).

37. Miyokawa, K., Hirashima, H. and Masuda, I., "Synthesis and characterization of nickel (II) complexes with potentially pentadentate macrocyclic ligands having N_3O_2 donor set", *Polyhedron*, **4**, 1891 (1985).

38. Shakir, M., Mohamed, A.K., Varkey, S.P. and Nasman, O.S.M., "Synthesis and spectroscopic studies of bis(macrocyclic) dimetal(II) complexes based on 14-18 membered pentaaza units", *Synth. React. Inorg. Met. -Org. Chem.*, **28**, 135 (1998).

39. Fenton, D.E., Cook, D.H., Nowell, I.W. and Walker, P.E., "Alkaline earth metal complexes of pyridinyl containing Schiff base macrocycles: X-ray crystal and molecular structures of the calcium and strontium complexes", *J. Chem. Soc., Chem. Commun.*, 279 (1978).

40. Cook, D.H. and Fenton, D.E., "Alkaline-earth metal complexes of macrocyclic Schiff bases derived from furan-2,5-dicarbaldehyde", *J. Chem. Soc., Dalton Trans.*, 810 (1979).

41. Bansal, A. and Singh, R.V., "Template synthesis, spectroscopic studies and biological screening of macrocyclic complexes of lead(II)", *Ind. J. Chem., Sec. A*, **40**, 989 (2001).

42. Prasad, R.N. and Gupta, S., "Template synthesis of 2,11-dimethyl-3,12-diethyl/propyl/phenyl-1,4,10,13-tetraazacyclooctadeca-1,3,10,12-tetraene complexes of Mg(II), Ca(II), Sr(II) and Ba(II)", *J. Chil. Chem. Soc.*, **49**, 29 (2004).

43. Alexander, V., "Design and synthesis of macrocyclic ligands and their complexes of lanthanides and actinides", *Chem. Rev.*, **95**, 273 (1995).

44. James, S., Kumar, D.S. and Alexander, V., "Synthesis of lanthanide(III) complexes of 20-membered octaaza and hexaaza Schiff base macrocycles", *J. Chem. Soc., Dalton Trans.*, 1773 (1999).

45. Benetollo, F., Bombieri, G., Adeyga, A.M., Fonda, K.K., Gootes, W.A., Samaria, K.M. and Vallarino, L.A., "Lanthanide (III) complexes of six nitrogen donor macrocyclic ligands with benzyl-type peripheral substituents, and crystal structure of $[La(NO_3)_2(H_2O)(C_{36}H_{38}N_6)]$ $(NO_3)(H_2O)$", *Polyhedron,* **21**, 425 (2002).

46. Bhasin, C.P. and Panchal, D.G., "First approach towards some novel macrocyclic complexes having mixed ligands: Dialkyl dithiophosphate derivatives of some Ni(II) macrocyclic complexes having N2S2 potential donors in 14 to 20-membered rings, *Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry*, **35**, 213 (2005).

47. Byun, J.C., Lee, W.H. and Han, C.H., "Synthesis and characterization of the first tetraazadiphenol macrocyclic dinickel(II) complex containing μ(O,O')-

nitrito-nitro-aqua ligands", *Inorganic Chemistry Communications*, **9**, 563 (2006).

48. Tamayo, A., Casabo, J., Escriche, L., Gonzalez, P., Lodeiro, C., Rizzi, A.C., Brondino, C.D., Passeggi, M.C.G., Kivekaes, R. and Sillanpaeae, R., "Structural and EPR Studies on Single-Crystal and Polycrystalline Samples of Copper(II) and Cobalt(II) Complexes with N2S2-Based Macrocyclic Ligands", *Inorganic Chemistry*, **46**, 5665 (2007).

49. Ertul, S., Bayraki, M. and Beduk, A.D., "The syntheses and characterization of three novel macrocyclic polyether ligands and some of their alkaline metal complexes", *Iranian Journal of Chemistry & Chemical Engineering*, **27**, 24 (2008).

50. Patil, S.A., Kamble, U.V. and Badami, P.S., "Biologically active 22-membered N4 tetraaza macrocyclic triazoles: template synthesis and spectroscopic approach", *Pharma Chemica*, **1**, 210 (2009).

51. Choi, K.Y., Choi, B.S. and Lee, C.H., "Synthesis and Characterization of Nickel(II) Complex of 3,14-Dimethyl-2,6,13,17-Tetraazatricyclo[14,4,01.18,07.12]Docosane Containing Pyrazine-2-Carboxylate Ligand", *Journal of Chemical Crystallography*, **40**, 1035 (2010).

52. Khan, T.A., Naseem, S., Hajra, R. and Shakir, M., "Synthesis, Physicochemical, and Antimicrobial Screening Studies of Complexes of Co(II), Ni(II), Cu(II), and Zn(II) with 18-membered Schiff Base Octaazamacrocyclic Ligand", *Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry*, **40**, 861 (2010).

53. Khan, T.A., Ghani, S.S. and Naseem, S., "Interaction of Co(II), Ni(II), Cu(II), and Zn(II) with 12- and 14-membered macrocycles containing O2N2 donors", *Journal of Coordination Chemistry*, **63**, 4411 (2010).

54. Singh, D.P., Grover, V., Kumar, K. and Jain, K., "Synthesis and characterization of divalent metal complexes of the macrocyclic ligand derived from isatin and 1,2-diaminobenzene", *Journal of the Serbian Chemical Society*, **76**, 385 (2011).

55. Hazra, S., Mondal, S., Fleck, M., Sasmal, S., Carolina Sanudo, E. and Mohanta, S., "Syntheses, molecular and supramolecular structures,

electrochemistry and magnetic properties of two macrocyclic dinickel(II) complexes", *Polyhedron*, **30**, 1906 (2011).

56. Lindoy, L.F., "The Chemistry of Macrocyclic Ligand Complexes", Cambridge University Press, Cambridge (1989).
57. Dalley, N.K., "Synthetic Multidentate Macrocyclic Compounds", Izzat, R.M. and Christensen, J.J., Eds., Academic Press, New York (1978).
58. Yatsimirskii, K.B., Kolchinski, A.G., Pavlishchuk, V.V. and Talanova, G.G., "Synthesis of Macrocyclic Compounds", Naukova Dumka, Kiev (1987).
59. Kolthoff, I.M. and Sanders, H.L., "Electric potentials at crystal surfaces, and at silver halide surfaces", *J. Am. Chem. Soc.*, **59**, 416 (1937).
60. Pungor, E. and Hollos-Rokosinyi, E., "Use of membrane electrodes in the study of ion concentration", *Acta Chim. Acad. Sci. Hung.*, **27**, 63 (1961).
61. Frant M.S. and Ross, J.W., "Electrodes for sensing fluoride ion activity in solution", *Science*, **154**, 1553 (1966).
62. Higuchi, T., Illian, C.R. and Tossounian, J.L., "Plastic electrodes specific for organic ions", *Anal. Chem.*, **42**, 1674 (1970).
63. Buck, R.P. and Lindner, E., "Tracing the history of selective ion sensitive sensors", *Anal. Chem.*, **A 97**, 88 (2001).
64. Moody, G.J., Oke, R.B. and Thomas, J.D.R., "A calcium-selective electrode based on a liquid ion exchanger in poly(vinyl chloride) matrix", *Analyst*, **95**, 910 (1970).
65. Durst, R.A., "Ion-selective electrodes", Natl. Bur. Standards Spec. Publ., Washington (1969).
66. Moody, G.J. and Thomas, J.D.R., "Selective ion-sensitive electrodes", Merrow, Watford (1971).
67. Morf. W.E., "The principles of ion-selective electrodes and of membrane transport", Elsevier Scientific Publishing Co., New York (1981).
68. Florido, A., "Dynamic characteristics of ion-selective electrodes", CRC Press (1988).
69. Buck, R.P. and Lindner, E., "Recommendation for nomenclature of ion-selective electrode", *Pure Appl. Chem.*, **66**, 2527 (1994).

70. Cattrall, R.W., "Chemical sensors", Oxford University Press, Oxford (1997).

71. Pungor, E. and Toth, K., "Precipitate based ion-selective electrodes", *Pure Appl. Chem.*, **34**, 105 (1973).

72. Covington, A.K., "Ion-selective electrodes", *Crit. Rev. Anal. Chem.*, **3**, 355 (1974).

73. Coetzee, C.I., "Inorganic ion-exchangers as ion sensors", *Ion-selective Electrode Rev.*, **3**, 105 (1981).

74. Bakker, E., Buhlmann, P. and Pretsch, E., "Carrier-based ion-selective electrodes and bulk optodes. 1. General characteristics", *Chem. Rev.*, **97**, 3083 (1997).

75. Buhlmann, P., Pretsch, E. and Bakker, E., "Carrier-based ion-selective electrodes and bulk optodes. 2. Ionophores for potentiometric and optical sensors", *Chem. Rev.*, **98**, 1593 (1998).

76. Johnson, R.D. and Bachas, L.G., "Ionophore-based ion-selective potentiometric and optical sensors", *Anal. Bioanal. Chem.*, **376**, 328 (2003).

77. Wroblewski, W., Dybko, A., Malinowska, E. and Brzozka, Z., "Towards advanced chemical microsensors-an overview", *Talanta*, **63**, 39 (2004).

78. Pungor, E., "The theory of ion selective electrodes", *Anal. Sci.*, **14**, 249 (1998).

79. Bakker, E. and Pretsch, E., "Potentiometry at trace levels", *Trends in Anal. Chem.*, **20**, 11 (2001).

80. Sutter, J., Morf, W.E., De Rooij, N.F. and Pretsch, E., "Current response of ion-selective solvent polymeric membranes at controlled potential", *J. Electroanal. Chem.*, **571**, 27 (2004)

81. Mark, A.A. and Mark. E.M., "Ion-selective electrodes", *Anal. Chem.*, **52**, 20R (1980).

82. Janata, J. and Josowicz, M., "Chemical sensors", *Anal. Chem.*, **70**, 179R (1998).

83. Bakker, E. and Telting-Diaz, M., "Electrochemical sensors", *Anal. Chem.*, **74**, 2781 (2002).

84. Bakker, E. and Qin, Y., "Electrochemical sensors", *Anal. Chem.*, **78**, 3965 (2006).

85. Zhulov, A.F., Erne, D., Ammann, D., Guggi, M., Pretsch, E. and Simon, W.,

"Improved lithium ion-selective electrode based on a lipophilic diamide as neutral carrier", *Anal. Chim. Acta*, **131,** 117 (1981).

86. Gadzekpo, V.P.Y., Moody, G.J., Thomas, J.D.R. and Christian, G.D., "Lithium ion-selective electrodes", *Ion-Selective Electrode Rev.*, **8**, 173 (1986).

87. Zhong, J., Li, J., Liu, M., Bai, Y., Yang, X., Xiao, D. and Wang, K., "Lithium ion-selective PVC membrane electrode with neutral ionophore", *Huaxue Chuanganqi*, **20**, 12 (2000).

88. Mu, X. and Jain, C., "Lithium ion-selective electrode for clinical applications", *Sens. Actuat. B*, **73,** 425 (2001).

89. Dou, T., Liu, M. Shao, C. and Li, F., "Preparation of lithium ion-selective electrode based on ketone", *Huaxue Chuanganqi*, **19,** 36 (1999).

90. Gupta, V.K., Chandra, S., Agarwal, S. and Lang, H., "Lithium-selective potentiometric sensor based on a second generation carbosiloxane dendrimer", *Sens. Actuat. B*, **107**, 762 (2005).

91. Ibrahim, Y.A., Behbehani, H., John, E., Shuaib, N.M. and Shoukry, A.F., "Synthesis of azacrown sulfonamides via ring closing metathesis and their evaluation in lithium ion selective electrodes", *Arkivoc*, (x), 5 (2008).

92. Wu, G., Lu, C., Gao, S., Xue, X., Du, X., Tan, G., Xu, J., Yao, Z., Zhang, F. and Yan, Z., "Construction and application of PVC-membrane sodium ion-selective electrodes", *Fenxi Huaxue*, **11,** 515 (1983).

93. Lukyanenko, N.G., Titova, N.Y., Karpinchick, O.S., and Melnik, O.T., "Sodium selective electrodes based on PVC membranes containing bis [(3n+l)-crown-n] ether derivatives", *Anal. Chim. Acta*, **259**, 145 (1992).

94. Ohki, A., Lu, J.P., Hallman, J.L., Huang, X. and Bartsch, R.A., "Sodium ion-selective electrodes based on dibenzo-16-crown-5 compounds with pendent ester groups", *Anal. Chem.*, **67,** 2405 (1995).

95. Skwierawska, A., Biernat, J.F. and Bilewicz, R., "13-membered azo- and azoxycrown compounds with sulphur atom in long side chain", *Supramol. Chem.*, **12,** 213 (2000).

96. Chandra, S. and Heinrich, L., "A new sodium ion selective electrode based

on a novel silacrown ether", *Sens. Actuat. B*, **114**, 849 (2006).

97. Diamond, D., Svehla, G., Seward, E.M. and McKervey, M.A., "Sodium ion-selective electrode based on methyl *p*-tert-butylcalix[4]arylacetate as the ionophores", *Anal. Chim. Acta*, **204**, 223 (1988).

98. O'Connor, K.M., Cherry, M., Swehla, G., Harris, S.J. and McKervy, M.A., "Symmetrical, unsymmetrical and bridged calix[4]arene derivatives as neutral carrier ionophores in poly(vinyl chloride) membrane sodium selective electrodes", *Talanta,* **41**,1207 (1994).

99. Marques de Oliveira, I. A., Risco, D., Vocanson, F., Crespo, E., Teixidor, F., Zine, N., Bausells, J., Samitier, J. and Errachid, A., "Sodium ion sensitive microelectrode based on a p-tert-butylcalix[4]arene ethyl ester ", *Sens. Actuat. B*, **130**, 295 (2008).

100. Kimura, K., Yajima, S., Okamoto, K. and Yokoyama, M., "Supported sol-gel-derived membranes for neutral carrier-type ion-selective electrodes", *J. Mat. Chem.*, **10**, 1819, (2000).

101. Adnan, K., Devrim, Y., Hasan, N. and Burhanettin, C., "A new sodium ion selective PVC-coated graphite rod electrode based on 4-amino-benzo-15-crown-5 derivatives of fullerenes", *Reviews in Analytical Chemistry*, **26**, 219 (2007).

102. Fiedler, U. and Ruzika, J., "Electroneutral valinomycin based potassium selective electrode: High selectivity over alkali and alkaline earth metals", *Anal. Chim. Acta*, **67**, 179 (1973).

103. Heng, L.Y. and Hall, E.A.H., "Methacrylate-acrylate based polymers of low plasticizer content for potassium ion-selective membranes", *Anal. Chim. Acta*, **324**, 47 (1996).

104. Han, W.S., Lee, Y.H., Jung, K.J., Ly, S.Y., Hong, T.K. and Kim, M.H., "Potassium ion-selective polyaniline solid-contact electrodes based on 4',4''(5'')-di-tert-butyldibenzo-18-crown-6-ether ionophore", *J. Anal. Chem.*, **63**, 987 (2008).

105. Olcay, S., Erdal, P., Guler, E. and Guler, S., "Preparation and application of potassium ion-selective membrane electrode based on benzo-15-crown-5 ether", *Current Anal. Chem.*, **5**, 53 (2009).

106. Oh. K.C., Kang, B.C., Cho, Y.L., Jeong, K.S., Yoo, E.-A. and Paeng, K.J., "Potassium-selective PVC membrane electrodes based on newly synthesized cis and trans bis (crown ethers)", *Anal. Sci.*, **14,** 1009 (1998).

107. Yan, W.H., Lee, A., Daniel, W.M., Kwong, W.J., Tarn, W.L. and Wang, K., "Potassium ion-selective optodes based on calix[6]arene hexaester and application in human serum array", *Analyst*, **121**, 531 (1996).

108. Katsu, T., Yokoyama, Y., Ueda, K., Kohno, K. and Yamato, T., "Potassium-selective membrane electrodes based on macrocyclic metacyclophanes analogous to calixarenes", *Anal. Sci.*, **21**, 175 (2005).

109. Jain, A.K., Singh, R.P. and Agarwal, S., "Solid membranes of rubidium tungustoarsenate as a rubidium sensitive electrode", *Ind. J. Chem.*, **19**, 1029 (1980).

110. Cosgrove, R.F. and Beezer, A.E., "A rubidium ion-selective electrode for the assay of polyene antibiotics", *Anal. Chim. Acta*, **105**, 77 (1979).

111. Saleh, M.B., "Rubidium ion-selective electrodes based on indanopyrazalo [1,5-a] pyrimidines", *Analyst*, **119**, 2205 (1994).

112. Hyun, M.H., Piao, M.H., Cho, Y.J. and Shim, Y.B., "Ionophores in rubidium ion-selective membrane electrodes", *Electroanalysis*, **16**, 1785 (2004).

113. Wang, D. and Shih, J.S., "Caesium ion-selective electrode based on 15-crown-5 phosphotungstic acid precipitates", *Analyst*, **110**, 635 (1985).

114. Kim, J.S., Ohki, A, Ueki, R., Ishizuka, T., Shimotashiro, T. and Maeda, S., "Cesium-ion selective electrodes based on calix[4]arene dibenzocrown ethers", *Talanta*, **48**, 705 (1999).

115. Mahajan, R.K., Kumar, M., Sharma, V. and Kaur, I., "Cesium ion selective electrode based on calix[4]crown ether-ester", *Talanta*, **58**, 445 (2002).

116. Saleh, M.B., Hassan, S.S.M., Abdel Gaber, A.A. and Abdel Kream, N.A., "PVC membrane cesium ion-selective sensor based on cephalexin antibiotic", *Anal. Lett.*, **36**, 2367 (2003).

117. Arida, H.A.M., Aglan, R.F. and El-Reefy, H.A., "A New Cesium Ion Selective Graphite Rod Electrode Based on Cs-Molybdophosphate", *Anal. Lett.*, **37**, 21 (2004).

118. Peper, S., Gonczy, C. and Runde, W., "Cs^+-selective membrane electrodes based on ethylene glycol-functionalized polymeric microspheres", Talanta, 67, 713 (2005).

119. Fleet, B. and Rechnitz, G.A., "Fast flow studies of biological reactions with ion-selective membrane electrodes", *Anal. Chem.*, **42**, 690 (1970).

120. Ganjali, M.R., Ghorbani, M., Norouzi, P., Daftari, A., Faal-Rastegar, M. and Moghimi, A., "Nano levels detection of beryllium by a novel beryllium PVC-based membrane sensor based on 2,3,5,6,8,9-hexahydro-1,4,7,10-benzotetraoxacyclododecine-12-carbaldehyde-12-(2,4-dinitrophenyl)hydrazine", *Sens. Actuat. B*, **100**, 315 (2004).

121. Ganjali, M. R., Norouzi, P., Faridbod, F., Sepehrifard, A., Ghandi, M. and Moghimi, A., "Monitoring of beryllium(II) ions by using a novel beryllium(II) membrane sensor, based on 2,3,5,6,8,9-hexahydronaphto[2,3-b][1,4,7,10] tetraoxacyclo dodecine", *Canadian Journal of Analytical Sciences and Spectroscopy*, **52**, 46 (2007).

122. Ganjali, M. R.; Norouzi, P.; Dinarvand, R.; Faribod, F.; Moghimi, A., "Subnanomolar determination of a beryllium ion by a novel Be(II) microsensor based on 4-nitrobenzo-9-crown-3-ether", *Journal of Analytical Chemistry*, **63**, 684 (2008).

123. Beiraghi, A., Babaee, S. and Roshdi, M., "A selective optical sensor for beryllium determination based on incorporating of 1,8-dihydroxyanthrone in a poly (vinyl chloride) membrane", *Journal of Hazardous Materials*, **190**, 962 (2011).

124. Saleh, M.B., "Neutral-carrier based magnesium selective electrodes", *J. Electroanal. Chem.*, **373**, 89 (1994).

125. Amemiya, S., Buhlmann, P., Pretsch, E., Rusterholtz, B. and Umezawa, Y., "Cationic or anionic sites? Selectivity optimization of ion-selective electrodes based on charged ionophores", *Anal. Chem.*, **72**, 1618 (2000).

126. Zamani, H.A., Nezhadali, A. and Saghravanian, M., "Magnesium-PVC Membrane Sensor Based on 4,5-Bis(Benzoylthio)-1,3-Dithiole-2-Thione", *Anal. Lett.*, **41**, 2727, (2008).

127. Shoukry, A.F., Al-Waheb, D. and Al-Bashir, R., "Mg(II) ion-selective

electrode on chlorophyll as ion exchanger", *Analytical Chemistry: An Indian Journal*, 7, 153 (2008).

128. Zhu, J., Qin, Y. and Zhang, Y., "Magnesium-Selective Ion-Channel Mimetic Sensor with a Traditional Calcium Ionophore", *Analytical Chemistry*, **82**, 436 (2010).

129. Ross, J.W., "Liquid membrane calcium(II)-selective electrode based on calcium di-(n-decyl)phosphate in di(n-octylphenyl)phosphonate", *Science*, **156**, 1378 (1967).

130. Kamata, S., Moody, G.J. and Thomas, J.D.R., "A poly(vinyl chloride) matrix membrane calcium-selective electrode based on calcium-bis[2,6-dinitro-4(l,l,3,3-tetra methylbutyl) phenoxide]", *Anal. Chim. Acta*, **108**, 385 (1979).

131. Craggs, A., Moody, G.J. and Thomas, J.D.R., "Evaluation of calcium-selective electrodes based on di(n-alkylphenyl)phosphate sensors and their calibration with ion buffers", *Analyst*, **104**, 412 (1979).

132. Lindfors, T. and Ivaska, A., "Calcium-selective electrode based on polyaniline functionalized with bis[4-(l,l,3,3-tetramethylbutyl)pheny]phosphate", *Anal. Chim. Acta*, **437**, 171 (2001).

133. Lakshminaryanaiah, N., "Calcium ion selective membrane electrode", *J. Memb. Sci.*, **8**, 255 (1981).

134. Bedlechowicz, I., Sokalski, T., Lewenstam, A. and Maj-Zurawska, M., "Calcium ion-selective electrodes under galvanostatic current control", *Sens. Actuat. B*, **10**, 836 (2005).

135. Calvo, D., Bartroli, J. and del Valle, M., "EIS study of potentiometric membranes selective to Ca^{2+} employing the new ionophoric antibiotic tetronasin", *Electrochimica Acta*, **51**, 1569 (2006).

136. Singh, A.K. and Mehtab, S., "Calcium(II)-selective potentiometric sensor based on furildioxime as neutral carrier", *Sens. Actuat. B*, **123**, 429 (2007).

137. Jain, A.K., Raisoni, J. and Jain, S., "Calcium(II)-selective potentiometric sensor based on p-isopropylcalix[6]arene in PVC matrix", *Intern. J. Environ. Anal. Chem.*, **88**, 209 (2008).

138. Baumann, E.W., "Preparation and properties of strontium selective

electrode", *Anal. Chem.*, **47**, 959 (1975).

139. Gupta, V.K., Jain, A.K., Khurana, U. and Singh, L.P., "PVC-based neutral carrier and organic exchanger membranes as sensors for the determination of Ba^{2+} and Sr^{2+}", *Sens. Actut. B*, **55**, 201 (1999).

140. Gupta, V.K., Ludwig, R. and Agarwal, S., "Strontium(II) sensor based on a modified calix[6]arene in PVC matrix", *Anal. Sci.*, **21**, 293 (2005).

141. Zamani, H.A., Ganjali, M.R., Norouzi, P. and Adib, M., "Strontium PVC-membrane sensor based on 2-[(2 mercaptophenyli mino) methyl] phenol", *Materials Science & Engineering, C: Biomimetic and Supramolecular Systems*, **28**, 157 (2008).

142. Zamani, H.A., Masroumia, M., Mohamadzadeh, H., Ganjali, M.R., Rahimizadeh, M. and Ziaei, P., "2,3-Diphenylquinoxaline-4',4"-dioxytriethylene glycol as a sensing and selective material for construction of strontium-PVC membrane sensor ",*Materials Science & Engineering, C: Materials for Biological Applications*, **29**, 976 (2009).

143. Guo, J., Chai, Y., Yuan, R., Ma, Y. and Zou, Z., "A fast response strontium(II) selective polymeric membrane sensor based on 1-benzothiazol-3-benzoyl-thiocarbamide as neutral carrier", *Sensor Letters*, **8**, 596 (2010).

144. Moody, G.J., Thomas, J.D.R., Lima, J.L.F.C. and Machado, A.A.S.C., "Characterization of poly (vinyl chloride) barium ion-selective electrodes without an internal reference solution", *Analyst*, **113**, 1023 (1988).

145. Othman, A.M., El-Shahawi, M.S. and Abdel-Azeem, M., "A novel barium polymeric membrane sensor for selective determination of barium and sulphate ions based on the complex ion associate barium(II)-Rose Bengal as neutral ionophore", *Anal. Chim. Acta.*, **322**, 555 (2006).

146. Fadeeva, V.P., Vershinin, V.I. and Kuzmina, E.A., "Determination of sulfur in organic compounds using a barium-selective electrode", *Journal of Analytical Chemistry*, **63**, 775 (2008).

147. Ma, Y.H., Yuan, R., Chai, Y.Q. and Liu, X.L., "A highly selective polymeric membrane barium(II) electrode based on a macrocyclic tetrabasic ligand as neutral carrier", *Anal. Bioanal. Chem.*, **395**, 895 (2009).

148. Peshkova, M.A., Timofeeva, N.V., Grekovich, A.L., Korneev, S.M. and Mikhelson, K.N., "Novel Ionophores for Barium-Selective Electrodes: synthesis and Analytical Characterization", *Electroanalysis*, **22**, 2147 (2010).

149. Palanivel, A. and Riyazuddin, P., "Silver sulphide-copper sulphide coated graphite as an electrode for selective determination of Ag(I) and Cu(II)", *Ind. J. Chem.*, **23A**, 1051 (1984).

150. Jain, A.K., Gupta, V.K, Sahu, B.B. and Singh, L.P., "Copper(II) selective electrodes based on macrocyclic compounds", *Anal. Proc.*, **32**, 99 (1995).

151. Jain, A.K., Singh, R.K., Jain, S. and Raisoni, J., "Copper(II) ion selective electrode based on a newly synthesized Schiff-base chelate", *Transition metal chemistry*, **33**, 243 (2008).

152. Gismera, M.J., Mendiola, M.A., Procopio, J.R. and Sevilla, M.T., "Copper potentiometric sensors based on copper complexes containing thiohydrazone and thiosemicarbazone ligands", *Anal. Chim. Acta*, **385**, 143 (1999).

153. Gismera, M.J., Procopio, J.R., Sevilla, M.T. and Hernandez, L., "Copper(II) ion-selective electrodes based on dithiosalicylic and thiosalicylic acids", *Electroanalysis*, **15**, 126 (2003).

154. Singh, A.K., Jain, A.K., Singh, J. and Mehtab, S., "Development of an electrochemical sensor based on Schiff base for Cu(II) determination at nano level in river water and edible materials", *Int. J. Environmental Analytical Chemistry*, **89**, 1081 (2009).

155. Jeong, E., Lee, H.K., Ahmed, M.S., Seo, H. and Jeon, S., "Copper(II) selective PVC membrane electrodes based on schiff base 1,2-bis(E-2-hydroxybenzylideneamino)anthracene-9,10-dione complex as an ionophore", *Bull. Korean Chem. Soc.*, **31**, 401 (2010).

156. Kopylovich., M.N., Mahmudov, K.T. and Pombeiro, A.J.L., "Poly(vinyl) chloride membrane copper-selective electrode based on 1-phenyl-2-(2-hydroxy phenyl hydrazo)butane-1,3-dione", *Journal of Hazardous Materials*, **186**, 1154 (2011).

157. Shokrollahi, A., Abbaspour, A., Ghaedi, M., Haghighi, A.N., Kianfar, A.H.

and Ranjbar, M., "Construction of a new Cu^{2+} coated wire ion selective electrode based on 2-((2-(2-(2-(2-hydroxy-5-methoxy benzylidene amino)phenyl)disufanyl)phenylimino) methyl)-4-methoxyphenol Schiff base", *Talanta*, **84**, 34 (2011).

158. Masuda, Y., Ishida, E. and Hiraga, K., "Preparation and analytical application of simple coated-wire cobalt(II) and chromium(III) ion-selective electrode", *Nippon Kagaku Kaishi*, 1453 (1980).
159. Chattopadhyaya, M.C., "Precipitate-based selective ion sensitive membrane electrodes for tripositive chromium and cadmium", *J. Ind. Chem. Soc.*, **66**, 54 (1989).
160. Shamsipur, M., Soleymanpour, A., Akhond, M., Sharghi, H. and Sarvari, M.H., "Highly selective chromium(III) PVC-membrane electrodes based on some recently synthesized Schiffs bases", *Electroanalysis*, **17**, 776 (2005).
161. Zamani, H.A., Rajabzadeh, G., Masrornia, M., Dejbord., A., Ganjali, M.R. and Seifi, N., "Determination of Cr^{3+} ions in biological and environmental samples by a chromium (III) membrane sensor based on 5-amino-1-phenyl-1H-pyrazole-4-carboxamide", *Desalination*, **249**, 560 (2009).
162. Abbaspour, A., Refahi, M., Nezhad, A.K., Rad, N.S. and Behrouz, S., "Carbon composite–PVC based membrane coated platinum electrode for chromium determination", *Journal of Hazardous Materials*, **184**, 20 (2010).
163. Fekri, M.H., Khanmohammadi, H. and Darvishpour, M., "An electrochemical Cr(III)-Selective Sensor-Based on a Newly Synthesized Ligand and Optimization of Electrode With a Nano Particle, *Int. J. Electrochem. Sci.*, **6**, 1679 (2011).
164. Lai, M.T. and Shih, J.S., "Mercury(II) and silver(I) ion-selective electrodes based on dithia crown ethers", *Analyst*, **111**, 891 (1986).
165. Zeng, X., Weng, L., Chen, L., Leng, X., Zhang, Z. and He, X., "Improved silver ion-selective electrodes using novel 1,3-bis(2-benzothiazolyl)thioalkoxy-*p*-tert-butylcalix[4]arenes", *Tetrahedron Lett.*, **41**, 4917 (2000).
166. Di, X., He, X., Zeng, X. and Zou, B., "Study on silver ion selective electrode using selenium functionalized calix[4]arenes as ionophores", *Fenxi Huaxue*,

32, 430 (2004).

167. Jagerszki, G., Grun, A., Bitter, I., Toth, K. and Gyurcsanyi, R.E., "Ionophore–gold nanoparticle conjugates for Ag^+-selective sensors with nanomolar detection limit", Chem. Comm., 46, 607 (2009).

168. Chung, S., Wantae, K., Sung, B.P., Dae, Y.K. and Shim, S.L., "Silver (I)-selective membrane electrodes based on sulfur-containing podants", *Talanta*, **44**, 1291 (1997).

169. Badr, I.H.A., "A new neutral carrier for silver ions based on a bis(thiothiazole) derivative and its evaluation in membrane electrodes", *Microchim. Acta*, **149,** 87 (2005).

170. Zhang, X., Han, Z., Fang, Z., Shen, G. and Yu, R., "5,10,15-Tris(penta fluorophenyl)corrole as highly selective neutral carrier for a silver ion-sensitive electrode", *Anal. Chim. Acta*, **562**, 210 (2006).

171. Yamamoto, C., Seto, H., Ohto, K., Kawakita, H. and Harada, H., "Effect of π Electrons on the Detection of Silver Ions by Ion-selective Electrodes Containing Tripodal Broom Molecules as an Ionophore", Analytical Sciences, 27, 389 (2011).

172. Komljevic, J. and Radic, N., "Use of a multi-purpose solid state ion-selective electrode body and a silver iodide-based membrane hydophobized by PTFE for the determination of iodide and mercury (2+)", *Analyst*, **111**, 887 (1986).

173. Kopytin, A.V., Zhukov, A.F., Urusov, Y.I., Koytina L.A. and Gordiezkii, A.V., "Research and development of selective membrane electrodes. Communication 14. Determination of mercury(II) and thallium(III)", *Zh. Anal. Khim.*, **34**, 465 (1979).

174. Masuda, Y. and Schido, E., "Mercury(II) ion selective electrodes based on thia-crown ligands as neutral carriers", *Bunseki Kagaku*, **39**, 683 (1990).

175. Mahajan, R.K., Kaur, I., Lobana, T.S., "A mercury(II) ion-selective electrode based on neutral salicylaldehyde thiosemicarbazone", *Talanta*, **59**, 101 (2003).

176. Ensafi, A.A, Meghdadi, S. and Allafchian, A.R., "Highly Selective Potentiometric Membrane Sensor for Hg(II) Based on Bis(Benzoyl

Acetone) Diethylene Triamine", IEEE Sensors Journals, 8, 248 (2008).

177. Bakhtiarzadeh, F. and Ghani, S.A., "The Electropolymerization of 2,6-Diamino pyridine and Its Application as Mercury Ion Selective Electrode", *Electroanalysis*, **22**, 549 (2010).

178. Mahajan, R.K., Puri, R.K., Marwaha, A., Kaur, I. and Mahajan, M.P., "Highly selective potentiometric determination of mercury(II) ions using 1-furan-2-yl-4-(4-nitrophenyl)-2-phenyl-5H-imidazole-3-oxide based membrane electrodes", *Journal of Hazardous Materials*, **167**, 237 (2009).

179. Mohammad Kazem Rofouei, M.K., Mohammadi, M. and Gholivand, M.B., "Mercury(II) selective membrane electrode based on 1,3-bis(2-methoxy benzene)triazene", *Materials Science and Engineering C*, **29**, 2154 (2009).

180. Dalkıran, B., O¨ zel, A.D., Parlayan, S., Canel, E, Ocak, U and Kılıc, E., "A novel lariat crown compound as ionophore for construction of a mercury(II)-selective electrode", *Monatsh Chem*, **141**, 829 (2010).

181. Alizadeh, T., Ganjali, M.R. and Zare, M., "Application of an Hg^{2+} selective imprinted polymer as a new modifying agent for the preparation of a novel highly selective and sensitive electrochemical sensor for the determination of ultratrace mercury ions", *Anal. Chim. Acta*, **689**, 52 (2011).

182. Lal, U.S., Chattopadhyaya, M.C., Ghosh, K. and Dey, A.K., "Manganese(II) sensitive electrode using cation exchange resin membrane", *Indian Agriculturist*, 139 (1982).

183. Agarwal, V. and Chattopadhyaya, M.C., "A hetergenous precipitate based manganese(II)-coated wire ion-selective electrode", *Anal. Lett.*, **22**, 1451 (1989).

184. Singh, A.K. and Saxena, P., "Manganese(II)- selective PVC membrane electrode based on a pentaazamacrocyclic manganese complex", *Sens. Actuat. B*, **121**, 349 (2007).

185. Aghaie, M., Giahi, M. and Zawari, M., "Manganese(II) Ion-Selective Membrane Electrode Based on N-(2-picolinamido ethyl)-Picolinamide as Neutral Carrier", *Bull. Korean Chem. Soc.*, **31**, 2980 (2010).

186. Wang, X., Chai, Y. and Yuan, R., "Study on highly selective manganese electrode based on bisethylenediimine as a neutral carrier", *Huaxue Yanjiu*

Yu Yingyong, **20**, 1260 (2008).

187. Gholivand, M.B., Gorji, M. and Joshaghani, M., "Manganese(II)-ion-selective electrode based on 2,2′-bis(salicylideneamino)azobenzene incorporated in poly(vinyl chloride) matrix", *Collect. Czech. Chem. Commun.*, **74**, 1411 (2009).

188. Pejcic, B. and Marco, R.D., "Impedance measurements of a chalcogenide membrane iron(III) selective electrode in contact with aqueous electrolytes", *Electrochim. Acta*, **49**, 3525 (2004).

189. Ekmekci, G., Uzun, D., Somer, G. and Kalaycı, S., "A novel iron(III) selective membrane electrode based on benzo-18-crown-6 crown ether and its applications", *J. Membrane Sci.*, **288**, 36 (2007).

190. Zamani, H.A., Ganjali, M.R and Salavati-Niasari, M., "Fabrication of an iron(III)-selective PVC membrane sensor based on a bis-bidentate Schiff base ionophore", *Transition Met Chem*, **33**, 995 (2008).

191. Aghaie, M., Giahi, M., Aghaie, H., Arvand, M., Pournaghdy, M. and Yavari, F., "New Fe(II) Ion–selective electrode based on N-Phenylaza-15-Crown-5 as neutral carrier in PVC matrix", *Desalination*, **247**, 346 (2009).

192. Motlagh, M.G., Taher, M.A. and Ahmadi, A., "PVC membrane and coated graphite potentiometric sensors based on 1-phenyl-3-pyridin-2-yl-thiourea for selective determination of iron(III)", *Electrochimica Acta*, **55**, 6724 (2010).

193. Babakhanian, A., Gholivand, M.B., Mohammadi, M., Khodadadian, M., Shockravi, A., Abbaszadeh, M. and Ghanbary, A., "Fabrication of a novel iron(III)–PVC membrane sensor based on a new 1,1-(iminobis(methan-1-yl-1 yli dene)) dinaphthalen-2-ol synthetic ionophore for direct and indirect determination of free iron species in some biological and non-biological samples", *Journal of Hazardous Materials*, **177**, 159 (2010).

194. Masrournia, M., Zamani, H.A., Mirrashid, H.A.,Ganjali, M.R. and Faridbod, F., "Di-tert-butylazodicarboxylate based PVC membrane sensor for Fe(III) ion measurement in pharmaceutical formulation", *Materials Science and Engineering C*, **31**, 574 (2011).

195. Zhang, W., Du, Y., Zou, F., Hua, H., Ni, P., Tang, Q. and Zhou, J., "Preparation and application of the PVC membrane gold (III) ion-selective electrode based on benzyldimethyloctadecylammonium tetrachloroaurate", *Fenxi Huaxue*, **15**, 565 (1987).

196. Hassan, S.S.M., Elnemma, E.M. and Hamada, M.A., "Nitron tetrachloroaurate(III) electrodes with poly(vinyl chloride) and liquid membranes for the selective determination of gold", *Talanta*, **38**, 561 (1991).

197. Akbari, A., Mousavi, M.F., Shamsipur, M. and Rahmanifar, M.S., "A PVC-based 1,8-diaminonaphthalen electrode for selective determination of vanadyl ion", *Talanta*, **60**, 853 (2003).

198. Akbari, A., Mousavi, M.F., Shamsipur, M., Rahmanifar, M.S. and Barzegar, M., "A PVC-based vanadyl phosphate membrane potentiometric sensor for vanadyl Ions", *Anal. Lett.*, **37**, 203 (2004).

199. Ganjali, M.R., Norouzi, P., Faridbod, F., Riahi, S., Ravanshad, J., Tashkhourian, J., Salavati-Niasari, M. and Javaheri, M., "Determination of vanadyl ions by a new PVC membrane sensor based on N, N'-bis-(Salicylidene)-2,2-dimethylpropane-1,3-diamine", *IEEE Sens. J.*, **7**, 544 (2007).

200. Pan, E., Xuemei, Z. and Huang, Z., "Synthesis of saturated urushiol crown ether-rare earth complexes and study on lanthanum(III) ion selective electrode", *Yingyong Huaxue*, **11**, 20 (1994).

201. Amarchand, S., Menon, S.K. and Agarwal, Y.K., "Novel potentiometric PVC-membrane and coated graphite sensor for Lanthanum (III)", *Electroanalysis*, **12**, 522 (2000).

202. Ganjali, M.R., Akbar, V., Ghorbani, M., Norouzi, P. and Ahmadi, A., "PPb level monitoring of lanthanium by a novel PVC-membrane sensor based on 4-methyl-2-hydrazinobenzothiazole", *Anal. Chim. Acta*, **114**, 713 (2006).

203. Singh, A.K., Saxena, P., Mehtab, S. And Gupta, B., "A Selective Membrane Electrode for Lanthanum(III) Ion Based on a Hexaaza Macrocycle Derivative as Ionophore", *Analytical Sciences*, **22**, 1339 (2006).

204. Zavar, M.H.A., Heydari, S. Rounaghi, G.H. and Ashraf, N., "Graphite Disk Lanthanum(III)-Selective Electrode Based on Benzo-15-crown-5", *J. of the*

Electrochemical Soc., **158**, F142 (2011).

205. Chowdhury, D.A., Ogata, T.S., Kamata, K., Ohashi, K., "Samarium(III)-selective electrode using neutral bis(thiaalkylxanthato)alkanes", *Anal. Chem.*, **68**, 366 (1996).

206. Mittal, S.K., Sharma, H.K. and Kumar, A.S.K., "Samarium (III) selective membrane sensor based on tin(IV) boratophosphate", *Sensors*, **4**, 125 (2004).

207. Mittal, S.K. and Sharma, H.K., "A samarium(III) selective electrode based on zirconium(IV) boratophosphate", *J. Anal. Chem.*, **60**, 1069 (2005).

208. Ganjali, M.R., Memari, Z., Faridbod, F. And Norouzi, P., "Samarium Microsensor: An Asymetric Potentiometric Membrane Sensor", *Int. J. Electrochem. Sci.*, **3**, 1169 (2008).

209. Naddaf, E. and Zamani, H.A., "Samarium(III)-PVC-Membrane Sensor Based on Ethoxy-1-ethoxycarbonyl-1,2-dihydroquinoline", *Analytical letters*, **42**, 2838 (2009).

210. Zamani, H.A., "Determination of Fluoride Ions in Mouthwash Samples by a PVC Membrane Samarium(III) Sensor", *Analytical letters*, **42**, 615 (2009).

211. Zamani, H.A., Rajabzadeh, G., Ganjali, M.R. and Norouzi, P., "Determination of gadolinium(III) ions in soil and sediment samples by a novel gadolinium membrane sensor based on 6-methyl-4-{[1-(2-thienyl)methylidene]amino}3-thioxo-3,4-dihydro-1,2,4-triazin-5-(2H)-one", *Anal. Chim. Acta*, **598**, 51 (2007).

212. Singh, A.K., Jain, A.K. and Singh, J, "Novel coated graphite electrode for the selective determination of Gd(III) in rocks and waste water samples", *Electrochimica Acta*, **54**, 5640 (2009).

213. Agarwal, H. and Chandra, S., "Studies on PVC-based chelating inorganic ion exchange resin membrane sensor for neodymium(III) ion", *Indian J. Chem.*, **43**, 2361 (2004).

214. Norouzi, P., Ganjali, M.R., Ahmadalinezhad, A. and Adib, M., ".Novel neodymium(III) membrane sensor based on N-(2-furylmethylene)pyridine-2,6-diamine", *J. Brazil. Chem. Soc.*, **17**, 1309 (2006).

215. Singh, A.K., Singh, J. and Jain, A.K., "Highly Selective Nd(III) Sensors:

Novel Macrocyclic Compounds for Potentiometric Determination of Neodymium", *Electroanalysis*, **22**, 2443 (2010).

216. Ganjali, M.R., Ravanshad, J., Hosseini, M., Salavati-Niasari, M., Pourjavid, M.R. and Baezzat, M.R., "Novel Dy(III) sensor based on a new bis-pyrrolidene Schiff's base", *Electroanalysis*, **16**, 1771 (2004).
217. Ganjali, M.R., Dodangeh, M., Ghorbani, H., Norouzi, P. and Adib, M., "PPb level monitoring of Dy(III) ions by a highly sensitive and selective Dy(III) sensor based on a new asymmetrical Schiff's base", *Anal. Lett.*, **39**, 495 (2006).
218. Ganjali, M.R., Rahimi, M., Maddah, B., Moghimi, A. and Borhany, S., "An Eu(III) sensor based on *N*,*N*-diethyl-*N*-(4-hydroxy-6-methylpyridin-2-yl)guanidine", *Anal. Sci.*, **20**, 1427 (2004).
219. Ganjali, M.R., Rasoolipour, S., Rezapour, M., Norouzi, P., Amirnasr, M., Meghdadi, S., "A novel Ho(III) sensor based on N,N'-bis(2-pyridinecarboxamide)-1,2-benzene as a neutral ion carrier", *J. Brazil. Chem. Soc.*, **17**, 1211 (2006).
220. Ganjali, M.R., Rasoolipour, S., Rezapour, M., Norouzi, P. and Adib, M., "Synthesis of thiophene-2-carbaldehyde-(7-methyl-1,3-benzothiazol-2-yl)hydrazone and its application as an ionophore in the construction of a novel thulium(III) selective membrane sensor", *Electrochem. Commun.*, **7**, 989 (2005).
221. Hassan, S.S.M., Ali, M.M. and Amr, M.Y., "PVC membrane based potentiometric sensors for uranium determination", *Talanta*, **54**, 1153 (2001).
222. Jain, A.K., Gupta, V.K., Khurana, U. and Singh, L.P., "A new membrane sensor for UO^{22+} ions based on 2-hydroxyacetophenoneoxime-thiourea-trioxane resin", *Electroanalysis*, **9**, 857 (1997).
223. Ganjali, M.R., Mirnaghi, F.S., Norouzi, P. and Adib, M., "Novel Pr(III)-selective membrane sensor based on a new hydrazide derivative", *Sens. Actuat.B*, **115**, 374 (2006).
224. Newman, J.D., Pirzad, R., Cowell, D.C. and Dowman, A.A., "Development of a polycrystalline fluoride ion-selective electrode", *Analyst*, **114**, 1579 (1989).

225. Nakamura T., Tsukamoto, Y. and Izutsu, K., "Development and application of a fluoride-selective electrode based on a polymer modified with phthalocyanine cobalt(III) for use in non-aqueous solutions", *Bunseki Kagaku*, **39**, 689 (1990).

226. Mitchell-Koch, J.T., Pietrzak, M., Malinowska, E. and Meyerhoff, M.E., "Aluminum(III) porphyrins as ionophores for fluoride selective polymeric membrane electrodes", *Electroanalysis*, **18**, 551 (2006).

227. Gorski, L., Mroczkiewicz, M., Pietrzak, M. And Malinowska, E., "Complexes of tetra-tert-butyl-tetraazaporphine with Al(III) and Zr(IV) cations as fluoride selective ionophores", *Anal. Chim. Acta*, **633**, 181 (2009).

228. Gorski, L., Matusevich, A., Parzuchowski, P., Luciuk, I. and Malinowska, E., "Fluoride-selective polymeric membrane electrodes based on Zr(IV)- and Al(III)-salen ionophores of various structures", *Anal. Chim. Acta*, **665**, 39 (2010).

229. Mahajan, R.K., Kaur, I., Kaur, R., Uchida, S., Onimaru, A., Shinoda, S. and Tsukube, H., "Anion receptor functions of lanthanide tris(b-diketonate) complexes: Naked eye detection and ion-selective electrode determination of Cl^- anion", *Chem. Comm.*, 2238 (2003).

230. Mohanraja, M. and Sundaram, R., "Determination of chloride ion in industrial effluent by chlorine ion-selective potentiometric sensor", *Journal of Ecotoxicology & Environmental Monitoring*, **18**, 517 (2008).

231. Alvarez-Romero, G. A., Ramirez-Silva, M. T., Galan-Vidal, C. A., Paez-Hernandez, M. E. and Romero-Romo, M. A., "Development of a chloride ion-selective solid state sensor based on doped polypyrrole-graphite-epoxy composite", *Electroanalysis*, **22**, 1650 (2010).

232. Havas, J., Papp, E. and Pungor, E., "Determination of anions. II. Analytical uses of bromide and chloride ion-selective membrane electrodes", *Anal. Kem,* **74**, 292 (1968).

233. Weiss, D., Ustred. U.G. and Prague, C., "Utilization of bromide and chloride ionic electrodes for determining bromides in waters", *Chemicke Listy*, **65,** 305 (1971).

234. Zhu, S.M., Guo, L.P. and Dong, X.Z., "Study on the benzalkonium bromide ion-selective electrode", *Acta Pharmaceutica Sinica*, **22,** 314 (1987).

235. Khalil, M.R., Yamchi, R.H., Sharghi, H. and Shamsipur, M., "Tetrakis(4-N,N-dimethylaminobenzene)porphyrinato]manganese(III) acetate as a novel carrier for a selective iodide PVC membrane electrode", *Anal. Sci.*, **20**, 805 (2004).

236. Singh, A.K. and Mehtab, S., "Polymeric membrane sensors based on Cd(II) Schiff base complexes for selective iodide determination in environmental and medicinal samples", *Talanta*, **74**, 806 (2008).

237. Zhou, W., Chai, Y.Q., Yuan, R., Wu, X. and Guo, J.X., "Potentiometric iodide selectivity of polymer-membrane sensors based on Co(II) triazole derivative", *Electroanalysis*, **20**, 1434 (2008).

238. Liang, K.Z. and Mu, M.J., "Preparation and study of iodide ion selective electrode using a new coordination complex of cobalt(II) and meso-tetrakis(2-alkoxyphenyl)-porphyrin as neutral carriers", *Lihua Jianyan, Huaxue Fence*, **45**, 508 (2009).

239. Rawat, A., Chandra, S. and Sarkar, A., "Highly selective potentiometric iodide ion sensors based on Bis-(o-phenylenediamine)Cu(II) complex", *Sensor Letters*, **8**, 753 (2010).

240. Ciftci, H. and Tamer, U., "Electrochemical determination of iodide by poly(3-aminophenylboronic acid) film electrode at moderately low pH ranges", *Anal. Chim. Acta*, **687**, 137 (2011).

241. Schwarz, J., Kaden, H. and Pausch, G., "Development of miniaturized potentiometric nitrate- and ammonium selective electrodes for applications in water monitoring", *Fresenius' J. Anal. Chem.*, **367**, 396 (2000).

242. Ortuno, J.A., Exposito, R., Sanchez-Pedreno, C., Albero, M.I. and Espinosa, A., "A nitrate-selective electrode based on a tris(2-aminoethyl)amine triamide derivative receptor", *Anal. Chim. Acta*, **525**, 231 (2004).

243. Ardakani, M. M., Ardakani, M.H.M., Karimi, M.A., Azimi, M.S., Iranpoor, F. and Salavati-Niasari, M., "Potentiometric membrane electrode for determination of nitrate based on 1,8-bis(salicylaldiminato)-3,6-dioxaoctane Ni(II) complex", *Chemia Analityczna*, **53**, 17 (2008).

244. Rawat, A., Chandra, S. and Sarkar, A., "Nitrate selective polymeric membrane electrode based on bis-thiourea ligand as carrier", *Sensor Letters*, **7**, 1100 (2009).

245. Herman, H.B. and Rechnitz, G.A., "Carbonate ion-selective membrane electrode", *Science*, **184**, 1074 (1974).

246. Scott, W.J., Chapoteau, E. and Kumar, A., "Carbonate selective electrode based on heterogeneous membrane of trifluoroacetophenone derivative", *Clin. Chem.*, **32**, 137 (1986).

247. Sokalski, T., Paradowski, D., Ostaszewska, J., Maj-Zurawska, M., Meiczkowski, J., Lewenstam, A. and Hulanicki, A., "Observations on the behavior of some trifluoro acetophenone derivatives as neutral carriers for carbonate ion-selective electrodes", *Analyst*, **121**, 133 (1996).

248. Sakong, D.S., Cha, M.J., Shin, J.H., Cha, G.S., Ryu, M.S., Hower, R.W. and Brown, R.B., "Asymmetric membrane-based potentiometric solid-state ion sensors", *Sens. Actuat. B.*, **32**, 161 (1996).

249. Makarychev-Mikhailov, S., Goryacheva, O., Mortensen, J., Legin, A., Levitchev, S. and Vlasov, Y., "Carbonate sensors based on 4-Hexyltrifluoro acetophenone modified by acceptor substituents in phenyl ring", *Electroanalysis*, **15**, 1291 (2003).

250. Makarychev-Mikhailov, S., Legin, A., Mortensen, J., Levitchev, S. and Vlasov, Y., "Potentiometric and theoretical studies of the carbonate sensors based on 3-bromo-4-hexyl-5-nitrotrifluoroacetophenone", *Analyst*, **129**, 213 (2004).

251. Li, Z.Q., Liu, G.D., Duan, L.M., Shen, G.L. and Yu, R.Q., "Sulphate selective PVC membrane electrode based on a derivative of imidazole as a neutral carrier", *Anal. Chim. Acta*, **382**, 165 (1999).

252. Morigi, M., Scavetta, E., Berrettoni, M., Giorgetti, M. and Tonelli, D., "Sulfate-selective electrodes based on hydrotalcites", *Anal. Chim. Acta.*, **439**, 265 (2001).

253. Sathyapalan, A., Zhou, A., Kar, T., Zhou, F. and Su, H., "A novel approach for the design of a highly selective sulfate-ion-selective electrode", *Chemical Communications*, **3**, 325 (2009).

254. Messick, M.S., Krishnan, S.K., Hulvey, M.K. and Steinle E.D., "Development of anion selective polymer membrane electrodes based on lutetium(III) porphyrins", *Anal. Chim. Acta*, **559**, 223 (2005).

255. Blikova, Y.N., Lezerovich, N.N., Pasekova, N.A. and Shvedene, N.V., "Salicylate- selective electrodes based on complexes of tin(IV) with organic ligands", *Khimiya*, **41**, 259 (2000).

256. Mazloum A.M., Ebrahimi, P. and Mansournia, M.R., "The complex (2,3;6,7; 10, 11; 14, 15-tetraphenyl-4, 9, 13, 16-tetraoxo-1, 5, 8, 12-tetraazacyclohexa decane) copper (II) as a carrier for a salicylate-sensitive poly(vinylchloride) membrane electrode", *Russian Journal of Electrochemistry*, **44**, 1065 (2008).

257. Xu, W., Yuan, R. and Chai, Y., "Salicylate-selective potential response of an electrode based on a copper(II)-phthalocyanine derivative as an ionophore", *Chinese Journal of Chemistry*, **27**, 99 (2009).

258. Ardakani, M.M., Pourhakkak, P., Salavati-Niasari, M., Karimi, M.A. and Mashhadizadeh, M.H., "Highly selective and sensitive membrane salicylate electrode based on complex of (1,8-diamino-3,6-dioxaoctane) nickel(II)", *Journal of the Brazilian Chemical Society*, **22**, 30 (2011).

259. Sun, Z.Y., Xiang, Can, H., Feng, L.J. and Deng, Z.T., "New Schiff base dinuclear copper(II) complex as carriers for salicylate-selective electrode", *Fenxi Kexue Xuebao*, **26**, 697 (2010).

260. Gupta, V.K. and Agarwal, S., "PVC based 5,10,15,20-tetrakis (4-methoxyphenyl) porphyrinatocobalt(II) membrane potentiometric sensor for arsenite", *Talanta*, **65**, 730 (2005).

261. Ueda, K., Hioki, H., Kubo, M., Kodama, M., Takaishi, K., Yokosu, H. and Katsu, T., "Highly selective methylammonium-selective membrane electrode made by the modification of the upper rim of calix[6]arene derivatives", *Sens. Actuat. B*, **106**, 772 (2005).

262. Mohammad, K.A., Shahrokhian, S. and Tangestaninejad, S., "Porphyrin as carriers in poly(vinyl chloride) based membranes potentiometric sensors for histamine", *Analyst*, **124**, 1319 (1999).

263. Varga, I., Meszaros, R., Szakacs, Z. and Gilanyi, T., "Novel method for the preparation of anionic surfactant-selective electrodes", *Langmuir*, **21**, 6154

(2005).

264. Pizzariello, A., Jozef, S., Stred'ansky, M. and Miertus, S., "A biosensing method for the detection of caffeine in coffee", *J. Sci. Food Agric.*, **79**, 1136 (1999).

265. Santos, E.M.G., Araujo, A.N., Couto, C.M., Montenegro, M., Conceicao, B.S.M., Kejzlarova, A. and Solich, P., "Ion selective electrodes for penicillin-G based on Mn(III)TPP-Cl and their application in pharmaceutical formulations control by sequential injection analysis", *J. Pharm. Biomed. Anal.*, **37**, 185 (2005).

266. Bibire, N., Tantaru, G., Stan, M. and Apostu, M. "Liquid membrane selective electrode for atropine assay", *Farmacia*, **52**, 103 (2004).

267. Stefan, R.I., Staden, J.F.V. and Aboul-Enein, H.Y., "A new construction for a potentiometric, entioselective membrane electrode its utilization to the S-captoril assay", *Talanta*, **48**, 1139 (1999).

268. Stefan, R.I., Staden, J.F.V. and Aboul-Enein, H.Y., "Detection of S-enantiomers of cilazepril, pentopril and trandolapril using potentiometric, enantiometric membrane electrode", *Electroanalysis*, **11**, 192 (1999).

269. Kang, X.J. and Wang, C.Y., "New sensor for the determination of nicotine in tobacco products", *Electroanalysis*, **2**, 81 (1990).

270. Tamaki, J., "High sensitivity semiconductor gas sensors", *Sens. Lett.*, **3**, 89 (2005).

271. Benmakroha, Y., Christie, I., Desai, M. and Vadgama, P., "Poly(vinyl chloride), polysulfone and sulfonated polyether-ether sulfone composite membranes for glucose and H_2O_2 perm-selectivity in amperometric biosensors", *Analyst*, **121**, 521 (1996).

272. Stredansky, M., Pizzariello, A., Strdanska, S. and Miertus, S., "Determination of D- fructose in food stuffs by an improved amperometric biosensor based on a solid binding matrix", *Anal. Comm.*, **36**, 57 (1999).

273. Palmisano, F., De Benedetto, G.E. and Zambonin, C.Z., "Lactate amperometric biosensor based on an electrosynthesized bilayer film with covalently immobilized enzyme", *Analyst*, **122**, 365 (1997).

Chapter 2

Theory and Methodology

Ion-selective electrodes (ISEs) have continued to be one of the most important developments in analytical chemistry. They have been used very successfully from decades in various areas of chemical analysis. While the initial era saw an intensive search for novel electrode materials and new constructions, this has given a way subsequently to more introspective studies on ion-selectivity and electrode mechanism. The rapid expansion of activity in the field of ion-selective electrodes makes them highly desirable to have an idea of their categories as well as their practical applications.

2.1 CLASSIFICATION OF ION-SELECTIVE ELECTRODES

According to IUPAC [1] recommendations, in terms of the mode of operation, ion-selective electrodes are classified as primary, those respond to the species of interest directly, and sensitized, those response to some other species (not necessarily ionic) through the agency of a sensitizer.

2.1.1 Primary Electrodes

Primary electrodes are normally classified as follows:

2.1.1.1 Crystalline Membrane Electrodes

Membranes constructed by using crystalline material comes under this heading and can further be divided into two sub-headings:

a. Homogeneous membrane electrodes

In this type of electrodes, the membrane is made up of crystalline material prepared from either a single compound or a homogeneous mixture of compounds. The active component of these electrodes consists of a solid material like LaF_3, AgCl, Ag_2S or a mixture such as $Ag_2Se + Cu_2Se$ or $Ag_2S + AgI$.

b. Heterogeneous membrane electrodes

These are prepared by incorporating the powdered active crystals or mixture of active substances in an inert matrix such as poly(vinyl chloride) or silicone rubber on hydrophobized graphite. The flexible nature of the resulting membrane is advantageous as it resists breakage.

2.1.1.2 Non-crystalline membrane electrodes

In these electrodes, a support matrix, containing an ion exchanger (either cationic or anionic), a plasticizer solvent and possibly an uncharged, selectivity-enhancing species, forms the ion-selective membrane which is usually imposed between two aqueous solutions. The support used can be either porous (e.g. millipore filter, glass frit, etc.) or non-porous (e.g. glass or inert polymeric material such as PVC, yielding with the ion-exchanger and the solvent a 'solidified' homogeneous mixture). The response of the electrode is due to the presence of ion-exchange material in the membrane and the selectivity of the electrode is related to selective exchange behavior of the ion-exchanger. They may be rigid or non-rigid matrix electrodes:

a. Rigid matrix (self-supporting electrodes)

This category involves mainly synthetic cross linked polymers *viz.* polystyrene sulfonate, sulfonated poly(tetrafluoroethylene), amino-poly(vinyl chloride) or silicate glass electrodes. These are ion selective electrodes in which the sensing membrane is a thin polymer with fixed sites or a thin piece of glass. The chemical composition of the polymer or the glass determines the selectivity of the membrane.

These are mainly selective for hydrogen ion and monovalent (alkali metal cations) ions. These electrodes operate on the fact that when a glass membrane is immersed in a solution containing hydrogen ions, an ion-exchange mechanism with the fixed SiO^- groups in the glass membrane boundary region is initiated. The glass material is made up of a solid silicate matrix within which alkaline metal ions are mobile. When this glass membrane is brought in contact with an aqueous solution, its surface becomes hydrated to a depth of about 100 nm and the alkali metal cations from the glass matrix can be exchanged for other ions in solution, preferably H^+, creating a potential across the membrane that is a linear function of the pH of the solution.

b. Non-rigid matrix electrodes

They contain electrodes with mobile charged sites. This group of electrodes can further be divided into the following sub-headings based on the charge they bear:

(i) Positively charged mobile carrier electrodes

Positively charged hydrophobic cations (e.g., those of quaternary ammonium salts or salts of substitutionally inert transition metal complexes such as the derivatives of 1,10-phenanthroline) which, when dissolved in a suitable organic solvent and held in an inert support (e.g., poly(propylene carbonate) filter or PVC), provide membranes which are sensitive to changes in the activities of anions. These electrodes contain a liquid ion-exchanger, a substance that has the ability to enter into heterogeneous equilibrium with the ion of interest, when dissolved in an organic solvent. A porous solid material is impregnated with the organic phase, thus forming a membrane separating inner and outer solutions. Extraction equilibrium replaces the solubility equilibrium of the crystalline membrane in determining the selectivity.

(ii) Negatively charged mobile carrier electrodes

Negatively charged hydrophobic anions (*e.g.*, of type $(RO)_2PO_2^-$, tetra-*p*-chlorophenylborate, dinonylnaphthalene sulfonate, didecylphosphate) which, when dissolved in a suitable organic solvent and held in an inert support (*e.g.*, poly(propylene carbonate), PVC) provide membranes which are sensitive to changes in the activities of cations.

(iii) Neutral mobile carrier electrodes

Uncharged "carrier" electrodes based on solutions of molecular complexing agents of cations (e.g., ion-dipole formers; antibiotics, macrocyclic compounds or other sequestering agents) and anions (e.g., adduct formers: organotin compounds, activated carbonyl compounds and some porphyrins) which can be used in ion exchanger membrane preparations to give sensitivity and selectivity to certain cations and anions.

These electrodes are based on a large neutral molecule that can complex the ion of interest to form an aggregate that is soluble in an organic solvent. The solution so formed is then located into a porous solid to constitute the ion-selective membrane. In these electrodes ion-dipole interactions between the donor atoms and the ion are responsible for the stability of the complex.

2.1.1.3 Ion Selective field-effect transistor sensors (ISFETs)

ISFETs can be described as hybrid electronic devices consisting of an ion-selective membrane and a field effect transistor (FET) preamplifier in a single unit. They have the common features of processing central insulator of SiO_2 or Si_3N_4 surrounded by a doped semiconductor on one side, and ion exchanger (or other interfacial potential-developing membrane film or adsorption-promoting film) on the other. Only the latter side is exposed to the electrolyte solution under test.

2.1.2 Sensitized or Compound (Multiple Layer Membranes) Electrodes

It constitutes a very important group because of their inherent selectivity, as two membranes are used to generate the response, each with its own selectivity characteristics. This group of electrodes is further divided into the following two sub-headings:

2.1.2.1 Gas sensing electrodes

In gas sensing electrodes, a gas-permeable and water-impermeable membrane lies over the ISE and this solution containing acidic/basic gaseous species (e.g. NH_3, CO_2, SO_3 and NO_2), diffuses through the membrane and indicates a change in pH, detected by the glass electrode. This change is then sensed by the ion-selective electrode and is proportional to the partial pressure of the gaseous species in the sample. An exception to this classification is the hydrogen gas electrode, which responds both to the partial pressure of hydrogen and to the pH. The oxygen electrode fits under this classification although, in contrast to all other sensors, it is an amperometric and not a potentiometric device.

2.1.2.2 Enzyme substrate electrodes

These are the sensors in which an ion-selective electrode is covered with a coating containing an enzyme (between the solution and the glass electrode) which causes the reaction of an organic or inorganic substance (substrate) to produce a species to which the electrode responds. Alternatively, the sensor could be covered with a layer of substrate which reacts with the enzyme, co-factor or inhibitor to be assayed.

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

2.1.3 Metal Contact or Solid-State Ion-Selective Electrodes

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 is in contrast to typical membrane usage in which electrolyte solutions (inner filling solution and outer test solution) are in contact with opposite membrane sites.

2.2 MEMBRANE

A membrane is a phase, finite in space, which separates two other phases and exhibits individual resistance to the permeation of different species [2]. Ion selective sensors 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 can play a critical role in the performance of the sensor in a particular environment. A successful membrane needs to be generally hydrophobic, have ion-exchanger properties and contain a lipophilic ionophore that provides selectivity to the sensor.

The lack of ion-exchanger 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 behavior. 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.

2.2.1 Membrane Materials

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.

2.2.1.1 Electroactive Material (Ionophore)

Ionophore, or ion carrier, or ligand is the key component of polymeric membrane ion-selective electrodes that governs the ion selectivity and sensitivity because the molecular-level phenomenon, sensed by the ISE is the binding between the ionophore and target ion. Ideally, it forms reversible and relatively strong complex with target ion and not with the other ions. There are two kinds of ionophore, charged and neutral carrier. Various substances *viz.* inorganic and organic ion exchanger, solid electrolyte, salts of multivalent atoms, metal chelates, polyaza, polythia macrocycles, crown ethers, cryptands and calixarenes and have been used as ion carriers for the preparation of ISEs. To be used as suitable ion carrier; the active sensor 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-ligand interaction, ion-hydration and undergo rapid ion exchange at the membrane sample interface. In order to keep the membrane composition constant, the ionophore must retain within the membrane; therefore, aside from the binding centre it must contain numerous lipophilic groups. From a more mechanistic perspective, the potentiometric response of membrane-based ISEs containing a specific ionophore can be used to provide information about the mode of analyte binding as well as, at least potentially, molecular insights into the details of the relevant substrate receptor interactions.

2.2.1.2 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 obtain a variety of electrodes selective towards particular ions by doping membrane with certain ionophore. Polymer matrix are chemically inert, hydrophobic, tough, flexible, non-porous, crack resistant and should not swell in sample solutions. Silicon rubber [3], some methacrylates [4] polyurethanes [5] and polystyrene, polyamide or polyimide have been demonstrated as polymer matrices meeting this requirement, while the most commonly used polymer is poly(vinyl chloride) (PVC) due to simplicity of membrane preparation. Of the various binders used for preparing heterogeneous solid state membranes, PVC has been most widely used due to its relatively cheap cost, good mechanical properties, inertness and amenability to plasticization.

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. Thomas and Moody are the pioneers in developing PVC based electrodes. Thomas *et al.* in 1986 recommended PVC as the most significant polymer support. A detailed comparative study of

PVC with other polymeric materials in their response characteristics was provided by Moody *et al.* [6]. Buck *et al.* discussed the properties of PVC and found that the presence of dissociated fixed exchange sites contributes to the electrode response and selectivity [7, 8]. Further, Mikhelson also reviewed the advantages and disadvantages associated with the PVC matrix [9]. The incorporation of neutral carrier in a PVC matrix has provided an economical way of simplifying ISE construction.

2.2.1.3 Solvent mediator or Plasticizer

The plasticizer to be used in membranes should exhibit high lipophilicity, high molecular weight, low tendency for exudation from the polymer matrix, low vapor pressure and high capacity to dissolve the substrate and other additives present in the membrane [10]. It is well documented that the addition of plasticizers not only improves the workability of the membranes but also contributes significantly towards the improvement in the detection limit, stability and shelf life of the sensor [11]. Additionally, its viscosity and dielectric constant should be adequate. It enhances the flexibility and softness of the fabricated membrane and provides mobility of membrane constituents within the membrane phase. Being a dominating component of PVC membranes, plasticizer acts as a membrane solvent, affecting membrane selectivity through both extraction of ions into organic phase and influencing their complexation with the ionophore [12].

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. Polymeric membrane usually comprises of a matrix containing *ca.* 33 % (w/w) of PVC and 66 % of (w/w) solvent mediator. A number of organic solvents such as phthalates, sebacates, octyl ethers, acetophenone and benzyl acetate have been suitably and efficiently used as plasticizer to enhance the performance of ISEs.

2.2.1.4 Lipophilic Additive or Lipophilic Ionic Sites

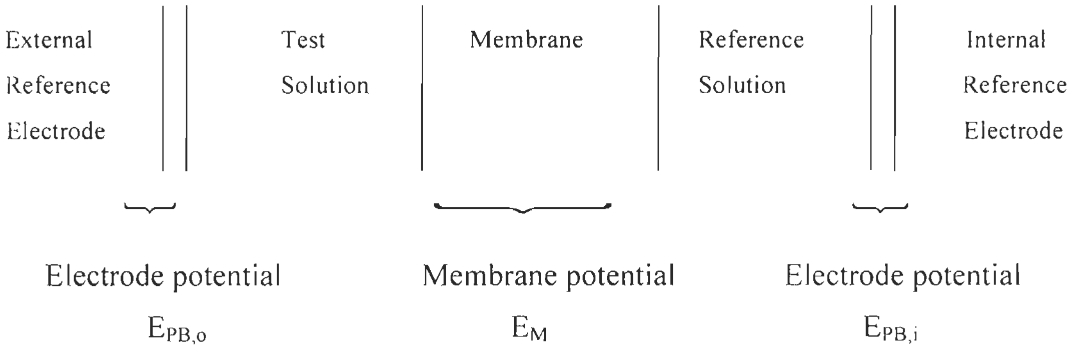
The prerequisite for obtaining a theoretical response with ISE membranes is their perm-selectivity, which means that no significant amount of counter ions may enter the membrane phase. Lipophilic ionic additive is a salt of non-exchangeable lipophilic anion/cation and an exchangeable counter ion. Their main function is to render the ion selective membrane perm selective, to optimize sensing selectivity (by defining the ratio of complexed to uncomplexed ionophore concentration in the membrane) and to reduce the bulk membrane impedance [13, 14]. The presence of lipophilic additive in ion selective membrane electrodes not only diminish the ohmic resistance and enhance the behavior but also in cases where the extraction capability is poor, increase the sensitivity of membrane electrodes. These additives may also catalyze the exchange kinetics at the sample membrane interface [15, 16].

Although the presence of the ionic sites is mandatory, membranes may function without deliberately incorporated ionic sites because of impurities in the polymer matrix or in other components.

Their concentration relative to the ionophore has an important selectivity modifying effect due to the influence of the involved equilibrium. Various tetraphenylborate derivatives are currently used as anionic additives while tetraalkylammonium salts are used as cationic additives. The charge of the proper additive is tied directly to the response mechanism of the chosen ionophore

2.3 POTENTIAL OF AN ION-EXCHANGE MEMBRANE

Ion-selective electrodes are typically investigated under zero current condition by following cell set up.



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 as

$$\mathrm{emf} = E_{\mathrm{const}} + E_{\mathrm{J}} + E_{\mathrm{M}} \qquad (1)$$

Liquid junction potential E_J originates from the different mobility of ionic species in the sample solution and in the bridge electrolyte of the reference electrode if ion-selective electrodes [17] can be kept constant by employing concentrated bridge electrolytes with similar mobilities of cations and anions (e.g. 1M KCl, NH_4NO_3, or LiOAc).

The utility of membrane electrodes depends upon the determination of *membrane potentials* E_M , which is ideally a function of the sample ion activity [18, 19]. So we will only focus on the membrane potential E_M of electrode.

Since the membrane is usually interposed between the sample and an inner reference electrolyte, it is commonly divided into three separate potential contributions, namely the phase boundary potentials at both interfaces and the diffusion potential within the ion-selective membrane.

$$E_M = E_{PB} + E_{Diff} \tag{2}$$

The potential at the membrane/inner filling solution interface can be assumed to be independent of the sample, whereas the diffusion potential within the membrane may become significant if considerable concentration gradients of ions with different mobilities arise in the membrane. If no concentration gradients occur within the membrane, diffusion potential E_{Diff} is zero. This is often the case for membranes that show theoretical Nernstian response. Phase boundary potential E_{PB} arises from a charge separation caused by the non-uniform distribution of ionic species between the organic membrane and the aqueous phase. The phase boundary potential can be derived from basic thermodynamic considerations of chemical and electrical potential contributions. The electrochemical potential, $\bar{\mu}$ for species A in aqueous phase could be written as follows [20].

$$\bar{\mu}_{A(aq)} = \mu_{A(aq)} + Z_A F \phi_{(aq)}$$

$$\bar{\mu}_{A(aq)} = \mu^{o}_{A(aq)} + 2.303\ RT\ \log a_{A(aq)} + Z_A F \phi_{(aq)} \tag{3}$$

Similarly, the electrochemical potential for the analyte ion (A) in contacting organic phase is

$$\bar{\mu}_{A(org)} = \mu_{A(org)} + Z_A F \phi_{(org)}$$

$$\bar{\mu}_{A(org)} = \mu^{o}_{A(org)} + 2.303\ RT\ \log a_{A(org)} + Z_A F \phi_{(org)} \tag{4}$$

where, μ is the chemical potential and μ^{o} is chemical potential under standard conditions, z_A is valency of analyte ion A and a_A is the activity of the uncomplexed ion A, ϕ is the electric potential and R, T and F are the universal gas constant, absolute temperature and Faraday constant respectively. It is assumed that the interfacial ion transfer and complexation processes are relatively fast and therefore, equilibrium holds at the interface so that the electrochemical potential for both phases are equal. This leads to a simple expression for the phase boundary potential, *i.e.*

$$E_{PB} = \Delta\phi = -\frac{\mu^{o}_{A(org)} - \mu^{o}_{A(aq)}}{Z_{A}F} + \frac{2.303\ RT}{Z_{A}F}\log\frac{a_{A(aq)}}{a_{A(org)}} \tag{5}$$

Thus, equation (5) indicates that the phase boundary potential is a simple function of sample ion activity ($a_{A(aq)}$) particularly if $a_{A(org)}$ is not significantly altered by the sample. The complexation of analyte ion A with the ionophore inside the organic membrane phase influences free analyte activity $a_{A(org)}$ and therefore, also the phase boundary potential [20]. However, due to the strong complexation with the ionophore, concentration of the free ion in the organic membrane is small relative to that of the complexed ions. Consequently, the concentration of the complex is approximately equal to that of the anionic sites provided by the anion discriminator and remains unaltered if an excess of ionophore is added.

This is so because, in order to maintain electroneutrality of the membrane, only as many cations could enter the membrane phase as are the anionic sites provided by the anion excluder. By combining equations (2) and (5)

$$E_{M} = E_{const} + E_{PB}$$

$$E_{Const} - \frac{\mu^{o}_{A(org)} - \mu^{o}_{A(aq)}}{Z_{A}F} - \frac{2.303\ RT}{Z_{A}F}\log a_{A(org)} + \frac{2.303\ RT}{Z_{A}F}\log a_{A(aq)} \tag{6}$$

Since $a_{A(org)}$ remains constant under the experimental conditions, it can be put together with all other sample-independent potential contributions, *i.e.* it could be included in a single term (E°). Thus, equation (6) is reduced to a well-known Nernst equation.

$$E_{M} = E^{o} + \frac{2.303\ RT}{Z_{A}F}\log a_{A(aq)} \tag{7}$$

Thus, it is clear from equation (7) that the cell potential is directly proportional to the concentration or activity of the sample ions in aqueous solution under investigation. At 25°C, the value of 2.303 RT/ z_AF is $0.059/z_A$ volts. The membrane is said to exhibit Nernstian response if the slope of a plot between cell potential and log activity comes out to be $0.059/z_A$ volts. These plots are then called Nernst plot and slope as Nernstian slope.

2.4 TERMS USED IN ISEs

Before further discussion on the performance of ion-selective electrodes some of the terms used must be defined or explained. IUPAC compendium of nomenclature [21-23] is helpful in sorting out the terms.

2.4.1 Combination Electrode/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. This assembly is represented in Fig. 2.1.

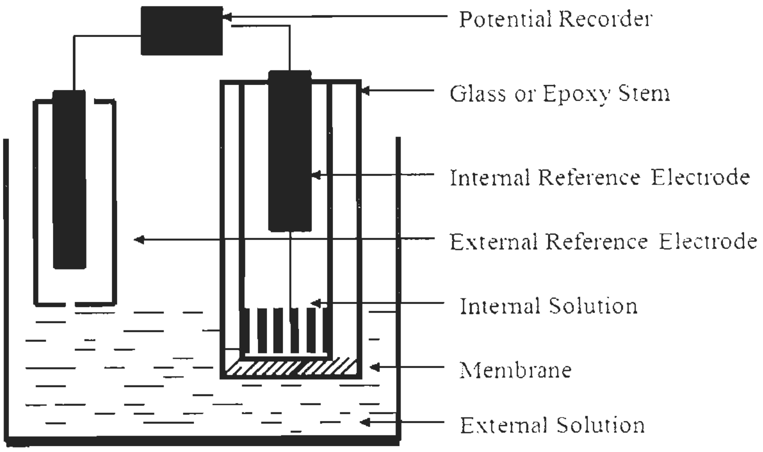


Fig. 2.1 Schematic representation of membrane electrode cell assembly

2.4.2 Calibration Graph

A calibration graph for an ion-selective electrode is defined as a plot of the potential difference between the ion-selective electrode and a reference electrode against the logarithm of the activity or concentration of the primary ion in the measurement cell. For a primary ion A, the logarithm of its activity or concentration is usually plotted along the abscissa of the graph and the cell potential is plotted along the ordinate. A calibration curve ordinarily has the shape shown in Fig. 2.2.

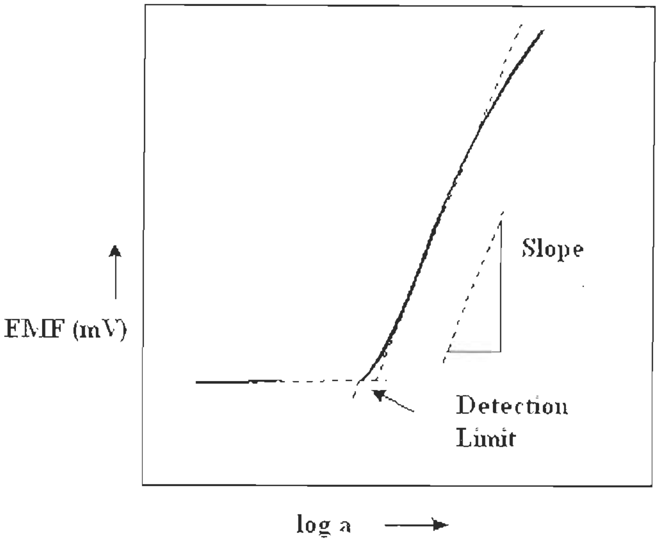


Fig 2.2 Calibration curve of ion-selective electrode

2.4.3 Limit of Detection

It may be defined as the lower activity of the target ion, A, at which the Nernstian plot of electrode potential against $-\log_{10} a_A$ begins to depart from linearity. They fall into activity ranges where the electrode starts to loose sensitivity toward the primary ion. According to the IUPAC recommendation of 1976, the detection limit is defined by the cross-section of the two extrapolated linear parts of the calibration curves (Fig. 2.2). 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.

2.4.4 Measuring Range/Linear Range/Working Concentration Range

The measuring range of ISEs is defined as the activity ratio of upper and lower detection limit and approximately corresponds to the range where 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 Fig. 2.2 is considered to be its linear part between the two dashed lines.

2.4.5 Slope

Slope is defined as the gradient of the line formed by plotting the electrode response (E_M) in millivolts against the logarithm of the activity of the measured ion. Thus, according to Nernst equation (equation 8)

$$E_M = E^o + \frac{2.303\ RT}{Z_A F} \log a_{A(aq)} \qquad (8)$$

Slope of the linear part of the calibration curve is 2.303 RT/ z_AF. This is a measure of the sensitivity of the electrode. If it is close to the Nernstian value of 59.1/z_k mV decade^{-1} activity (where, z_k is the charge of the ion) at 25°C, then it points to the ideal electrode behavior. The theoretical values of the slope is 59.1 mV decade^{-1} activity at 298 K for monovalent ion, 29.5 mV decade^{-1} activity for divalent ion and 19.7 mV decade^{-1} activity for trivalent ion.

2.4.5 Response Time

The first Recommendations by IUPAC [24] 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 ($\Delta E/\Delta t$) 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 [25]. To evaluate the reversibility of the electrodes, a similar procedure in the opposite direction can also be adopted.

2.4.6 Electrode Life Time

The working life of an ISE 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 factors such as the analysis technique used, the matrix of the samples analyzed, and the membrane composition. Loss of plasticizer, carrier, or ionic site from the polymeric film due to leaching into the sample is a primary reason for limited lifetime of the sensors. An important parameter to be considered during the active life of the electrode is how long the ISE can be used between calibrations without significant changes in the electrode parameters that will affect the accurate prediction of the target ion.

2.4.7 Drift

This is the slow, non-random change in the potential (emf) of an ion-selective electrode cell assembly with time, provided that the cell assembly is maintained in a solution of constant composition and temperature.

2.5 SELECTIVITY OF ISE MEMBRANE

Selectivity is the most important characteristics of the ISE 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 as interfering ions or foreign ions or secondary ions. In fact, no ISE responds exclusively to primary ion *i.e.*, specific to it, however, in practice it is more selective to primary ions than to interfering ions. This 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, $K_{A,B}^{Pot}$, which is defined by the semi empirical *Nicolsky-Eisenmann* equation [8]

$$E = E^{\circ} \pm \frac{2.303RT}{z_A F} \log \left[a_A + \sum K_{A,B}^{Pot} \, a_B^{z_A/z_B} \right] \tag{8}$$

where z_A, z_B, a_A and a_B are the charges and activity of ions A and B, respectively. There are a number of different methods for the determination of potentiometric selectivity coefficients, among which three methods have been however, much more widely accepted [26, 27], which are namely:

2.5.1 Separate Solution Method (SSM)
2.5.2 Mixed Solution Method (MSM)
2.5.3 Matched Potential Method (MPM)

2.5.1 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 curve is presented in Fig. 2.3. The emf of this cell E_A is related to the primary ion by the equation

$$E_A = E^0 + \frac{2.303RT}{z_A F} \log a_A \tag{9}$$

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

$$E_B = E^0 + \frac{2.303RT}{z_A F} \log K_{A,B}^{Pot} (a_B)^{z_A/z_B} \tag{10}$$

From equations (9) and (10) $K_{A,B}^{Pot}$ values are then calculated as:

$$\log K_{A,B}^{Pot} = \frac{z_A F(E_B - E_A)}{2.303\ RT} + \log\left(\frac{a_A}{a_B^{z_A/z_B}}\right) \qquad (11)$$

The term 2.303 RT/z_AF is the slope of the Nernst plot. The separate solution method, although simple to perform, is not normally used for the determination of $K_{A,B}^{Pot}$ values, because it does not represent the actual conditions under which the sensors are used. This method is recommended only if the electrode exhibits a Nernstian response.

2.5.2 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 (9). 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

$$E = E^\circ + \frac{2.303RT}{z_A F} \log \left[a_A + K_{A,B}^{Pot} (a_B)^{z_A/z_B}\right] \qquad (12)$$

From equations (9) and (12)

$$\mathrm{K}_{A,B}^{Pot} = \frac{a_A}{(a_B)^{z_A/z_B}}\left[\left(\frac{E_{A,B} - E_A}{10^{2.303RT/z_AF}}\right) - 1\right] \tag{13}$$

Thus, knowing E_A and $E_{A,B}$ 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 potentials 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 A decreases.

So in this region (QR), the response of the sensor is mixed and is due to both the ions A and B. 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 to point T. The potential corresponding to point T can be generated by constant activity of B or by the activity of A corresponding to point T. 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

$$K_{A,B}^{Pot} = \frac{a_A}{(a_B)^{z_A \; z_B}} \tag{14}$$

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 [28]. The reason behind this that the conditions prevailing at the membrane and solution interface in this method are similar to the one, which are prevalent while analyzing the sample.

2.5.3 Matched Potential Method (MPM)

The Matched Potential Method (MPM), which is independent of the Nickolsky-Eisenmann equation, was proposed by Gadzekpo and Christian [29] to overcome the difficulties for obtaining accurate selectivity coefficients when ions of unequal charge are involved. In this method, the selectivity coefficient $K_{A,B}^{Pot}$ is given by the expression

$$K_{A,B}^{Pot} = \frac{a'_A - a_A}{a_B} = \frac{\Delta a_A}{a_B} \tag{15}$$

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 curve is presented in Figure 2.5. This method provides practically realistic values of $K_{A,B}^{Pot}$. The characteristics of MPM 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. However, as this method is independent of the Nicolsky-Eisenmann 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 [30].

2.5.4 Significance of Selectivity Coefficients

The selectivity of a sensor depends on the selectivity coefficient values defined in terms of Nicolsky equation (equation 8). Ideally, it should be a constant value and called selectivity constant but it 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. The values of selectivity coefficients are higher if determined at higher concentration of interfering ions and vice-versa.

Different methods give different values of selectivity coefficients, as the conditions prevailing at the membrane-solution interface are not same [31, 32]. It is apparent from equation (8) that a value of $K_{A,B}^{Pot} = 1$ at $z_A = z_B$ indicates equal response to both A and B. Similarly, the value of $K_{A,B}^{Pot} < 1$ indicates that the electrode responds more to A in comparison to B *i.e.*, the electrode is selective to A over B. Smaller is the value of selectivity coefficient better is the selectivity. On the other hand $K_{A,B}^{Pot} > 1$ indicates that the electrode'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 $K_{A,B}^{Pot} \cong 1$ does not indicate equal response to primary and interfering ions as per equation (8), but now it depends on the values of z_A and z_B. 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 $K_{A,B}^{Pot}$ that indicates equal response to A and B irrespective of their charges.

Viteri and Diamond [33] have proposed a modification in the Nicolsky equation; they neglected the power term in the equation (8) while calculating the selectivity coefficient. The modified form of equation (12) is

$$K_{A,B}^{pot} = \frac{a_A}{a_B} \qquad (16)$$

In the present study, the selectivity coefficient values have been determined using the FIM and the MPM using equations (14) and (15), respectively.

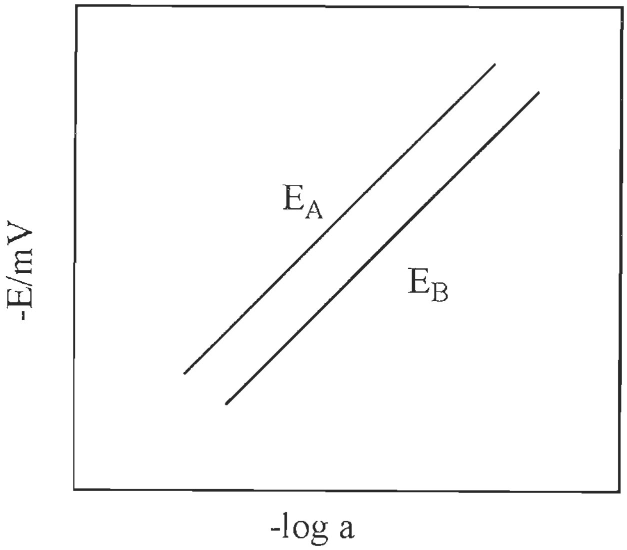


Fig. 2.3 Potential *vs.* log a_A plot illustrating the determination of selectivity – coefficient by Separate solution method (activity of B = a_B)

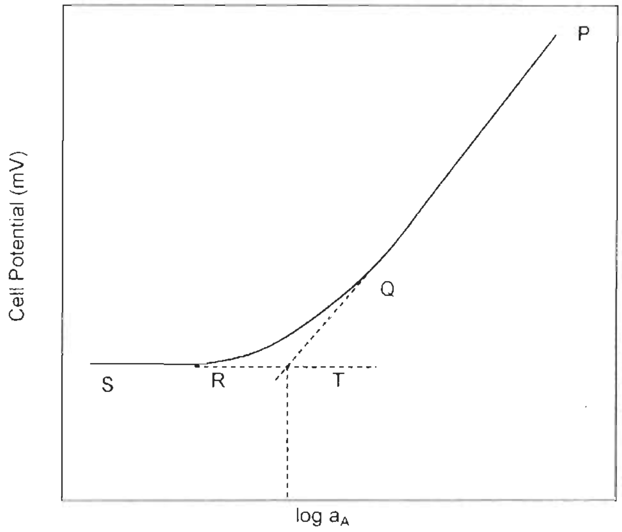


Fig. 2.4 Potential *vs.* log a_A plot illustrating the determination of selectivity -coefficient by Fixed interference method

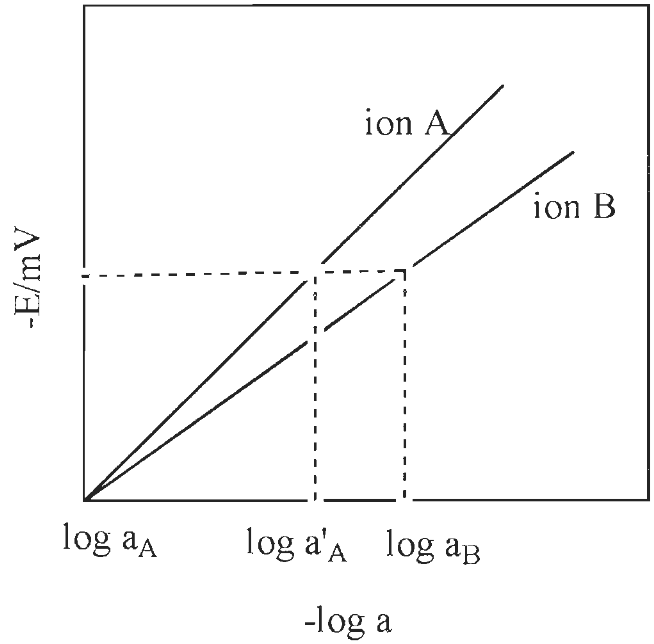


Fig. 2.5 Potential *vs.* log a_A plot illustrating the determination of selectivity -coefficient by Matched potential method (activity of B = a_B)

REFERENCES

1. Buck, R.P. and Lindner, E., "Recommendations for nomenclature of ion-selective electrodes", *Pure Appl. Chem.*, **66**, 2527 (1994).
2. Gupta, V.K. and Singh, L.P., "Ion selective electrodes for sensing metal cations", *Encyclopedia of sensors*, **5**, 133 (2006).
3. Tsujimura, Y., Sunagawa, T., Yokoyama, M. and Kimura, K., "Sodium ion-selective electrodes based on silicone-rubber membranes covalently incorporating neutral carriers", *Analyst*, **121**, 1705 (1996).
4. Qin, Y., Peper, S. and Bakker, E. "Plasticizer-free polymer membrane ion-selective electrodes containing methacrylic copolymer matrix", *Electroanalysis*, **14**, 1375 (2002).
5. Yun, S.Y., Hong, Y.K., Oh, B.K., Cha, G.S. and Nam, H., "Potentiometric properties of ion-selective electrodes membranes based on segmented polyether urethane matrices", *Anal. Chem.*, **69**, 868 (1997).
6. Moody, G.J., Saad, B.B. and Thomas, J.D.R., "Glass transition temperatures of PVC and polyacrylate materials and calcium ion-selective electrode properties", *Analyst*, **112**, 1143 (1987).
7. Horvai, G., Graf, E., Toth, K., Pungor, E. and Buck, R.P., "Plasticized poly(vinyl chloride) properties and characteristics of valinomycin electrodes. 1. High frequency resistence and dielectric properties", *Anal. Chem.*, **58**, 2737 (1986).
8. Toth, K., Graf, E., Horvai, G., Pungor, E. and Buck, R.P., "Plasticized poly(vinyl chloride) properties and characteristics of valinomycin electrodes. 2. Low frequency, surface rate and working impedence characteristics", *Anal. Chem.*, **58**, 2741 (1986).
9. Mikhelson, K.N., "Ion-selective electrodes in PVC matrix", *Sens. Actuators B*, **18**, 31 (1994).
10. Arada-Perez, M.A., Marin, L.P., Quintana, J.C. and Yazdani-Pedram, M., "Influence of different plasticizers on the response of chemical sensors based on polymeric membranes for nitrate ion determination", *Sens. Actuators B*, **89**, 262 (2003).

11. Craggs, A., Keil, L., Moody, G.J. and Thomas, J.D.R., "Evaluation of solvent mediators for ion-selective electrode membranes based on calcium bis(alkylphosphate) sensors trapped in poly(vinyl chloride) matrixes", *Talanta*, **22**, 907 (1975).
12. Sakaki, T., Harada, T., Deng, G., Kawabata, H., Kawahara, Y. and Shinkai, S. "On the selection of the optimal plasticizer for calix[n]arene-based ion-selective electrodes: Possible correlation between the ion selectivity and the "softness" of plasticizer", *J. Inclusion Phenom.*, **15**, 285 (1994).
13. Ammann, D., Pretsch, E., Simon, W., Lindler, E., Bezegh, A. and Pungor, E., "Lipophilic salts as membrane additives and their influence on the properties of macro and micro-electrodes based on neutral carriers", *Anal. Chim. Acta*, **171**, 119 (1985).
14. Gehring, P., Morf, W.E., Welti, M., Pretsch, E. and Simon, W., "Catalysis of ion transfer by tetraphenylborates in neutral carrier-based ion-selective electrodes", *Helv. Chim. Acta*, **73**, 203 (1990).
15. Rosatzin, T., Bakker, E., Suzuki, K. and Simon, W., "Lipophilic and immobilized anionic additives in solvent polymeric membranes of cation-selective chemical sensors", *Anal. Chim. Acta*, **280**, 197 (1993).
16. Wakida, S., Masadome, T., Imato, T., Shibutani, Y., Yakabe, K., Shono, T. and Asano, Y., "Additive-salt effect on low detection limit and slope sensitivity in response of potassium and sodium-selective neutral carrier based electrodes and their liquid-membrane based ion-sensitive field-effect transistor", *Anal. Sci.*, **15**, 47 (1999).
17. Mathison, S. and Bakker, E., "Effect of trans-membrane electrolyte diffusion on the detection limit of carrier-based potentiometric ion sensors", *Anal. Chem.*, **70**, 303 (1998).
18. Bailescu, G.E. and Cosofret, V.V., "Applications of ion-selective membrane electrodes in organic analysis", Ellis Horwood Ltd., Chinchester (1977).
19. Moody, G.J. and Thomas J.D.R., "Selective ion sensitive electrodes", Merrow Publishing Co. Ltd. (1971).
20. Bockris, J.O.M. and Reddy, A.K.N., "Modern electrochemistry ", vol. **1**, (1998).

21. Guilbault, G.G., Durst, R.A., Frant, M.S., Freiser, H., Hansen, E.H., Light, T.S., Pungor, E., Rechnitz, G., Rice, N.M., Rohm, T.J., Simon, W. and Thomas, J.D.R., "Recommendations for nomenclature of ion-selective electrodes", *Pure Appl. Chem.*, **48**, 129 (1975).
22. Buck, R.P. and Cosofret, V., "Recommended procedure for calibration of ion-selective electrodes", *Pure Appl. Chem.*, **65**, 1849 (1993).
23. Covington, A.K., "Terminology and conventions for microelectronic ion-selective field effect transistor devices in electrochemistry (IUPAC recommendations 1994)", *Pure Appl. Chem.*, **66**, 565 (1994).
24. "IUPAC Compendium of Analytical Nomenclature", Pergamon Press, Oxford (1978).
25. Ganjali, M.R., Norouzi, P. and Rezapour, M., "Potentiometric ion-selective sensors", *Encyclopedia of sensors*, **8**, 197 (2006).
26. Umezawa, Y., Umezawa, K. and Sato, H., "Selectivity coefficients for methods for reporting $K_{A,B}^{Pot}$ values ion-selective electrodes", *Pure Appl. Chem.*, **67**, 507 (1995).
27. Bakker, E., Pretsch, E. and Buhlmann, P., "Selectivity of potentiometric ion sensors", *Anal. Chem.*, **72**, 1127 (2000).
28. Umezawa, Y., "CRC Handbook of ion-selective electrodes: Selectivity coefficients", CRC Press, Bocca Raton, FL (1990).
29. Gadzekpo, V.P. and Christian, G.D., "Determination of selectivity coefficients of ion-selective electrodes by a matched-potential method", *Anal. Chim. Acta*, **164**, 279 (1984).
30. Horvai, G., "The matched potential method, a generic approach to characterize the differential selectivity of chemical sensors", *Sens. Actuators B*, **43**, 94 (1997).
31. Umezawa, Y., Buhlmann, P., Umezawa, K., Tohda, K. and Amemiya, S., "Potentiometric selectivity coefficients of ion selective electrodes", *Pure Appl. Chem.*, **72**, 1851 (2000).
32. Macca, C., "The current usage of selectivity coefficients for the characterization of ion-selective electrodes. A critical survey of the 2000/2001 literature", *Electroanalysis*, **15**, 997 (2003).

33. Sa'ez de Viteri, F.J. and Diamond, D., "Determination and application of ion-selective electrode model parameters using flow injection and simplex optimization", *Analyst*, **119**, 749 (1994).

Chapter 3

Membranes of macrocyclic ligands as Cation selective sensor for Transition metal ions

3.1 INTRODUCTION

The increase of metal concentration in the environment caused by natural processes and human activities, poses hazards to human and animal life. Thus, the toxic effects of metals present in environment have made it imperative to determine them in environmental samples. The determination of metals in pharmaceutical, clinical, environmental and other samples is thus important. As a result of extensive investigations, a large number of sensors have been reported for estimation of a number of heavy metal ions.

3.1.1 Nickel Ion Selective Sensor

The occurrence of nickel is widespread as it is present in effluents of a number of industries and foods of both animal and plant origin such as red meat, cotton seed, corn meal, unsaturated oils, chocolates, baking powder and certain spices. Beverages like wine, beer, milk are also a rich source of nickel. It is extensively used in a variety of commercially important industries, including stainless steel production, manufacture of coins, jewellery and nickel catalysts. The main source of nickel in aquatic systems is dissociation of rocks and soil, biological cycles and especially industrial processes and water disposal [1]. The maximum recommended concentration of nickel ions in drinking water for livestock is 2.5 mg mL^{-1} [2].

Nickel may become potential health hazard if its concentration exceeds the normal level. Ni toxicity can cause acute pneumonitis, dermatitis, asthma, cancer of lungs, stomachaches, adverse effects on blood and kidneys, disorders of central nervous system and cancer of nasal cavity and lungs [3]. Though human requirement for nickel is very low which probably does not exceed 100 μg day^{-1} but deficiency of nickel can cause low blood glucose level, abnormal bone growth, poor absorption of ferric ion and altered metabolism of calcium, Vitamin B_{12} and energy nutrients. Thus, due to vital importance of nickel in biological system and industry, a narrow window of concentration between essentiality and toxicity warrants the determination of nickel.

The first nickel-selective sensor based on Ni-dimethylglyoxime complex was reported by Pungor and coworkers [4]. Later heterogeneous membrane of nickel complex of 1,4,8,11-tetraazacyclotetradecane in araldite [5], nickel bis-(2-ethyl hexyl) phosphate in PVC [6] and nickel phosphate in paraffin and silicone rubber [7] were used for preparing Ni^{2+} selective sensors. These sensors show poor selectivity, reproducibility and exhibit non-Nernstian response. Ganjali *et al.* [8] reported 2-methyl-4-(4-methoxyphenyl)-2,6-diphenyl-2H-thiopyran based Ni^{2+} sensor which showed detection limit up to 9.0×10^{-6} M. Gupta *et al.* synthesised Schiff bases [9] and explored them as ionophores for the fabrication of PVC based membranes selective to nickel ions. This sensor works well in the concentration range of 1.6×10^{-7} to 1.0×10^{-2} M with Nernstian slope. Macrocyclic compounds which bind heavy metals selectively have also been studied as Ni^{2+} selective sensors. The sensors based on dibenzocyclamnickel (II) [10], hexa- and octamethyl-1,4,8,11-tetraazacyclotetradecane-4,11-diene-diperchlorate [11], carboxylated and methylated porphine [12] have been studied in detail with regard to selectivity, sensitivity, response time, lifetime etc. These sensors showed interference to Na^+ ions. Singh *et al.* [13] also reported a tetraazamacrocycle, dibenzo[*e*,*k*]-2,3,8,9-tetraphenyl-1,4,7,10-tetraazacyclododeca-1,3,5,7,9,11-hexaene as a potential ionophore for selective determination of Ni^{2+} ions which showed interference to Co^{2+} ions. Zamani *et al.* [14] constructed a PVC membrane electrochemical sensor based on 5-methoxy-5,6-diphenyl-4,5 dihydro-3(2H)-pyridazinethione as a novel ionophore to determine Ni^{2+} ions which exhibited the Nernstian response over concentration range of 1×10^{-6} to 1×10^{-1} M. A nickel (II) ion-selective electrode was prepared by incorporating a new N-S Schiff base ligand, glyoxal-bis(S-benzyldithiocarbazate), as a neutral carrier into the PVC matrix by Yu-Hua *et al.* [15]. This sensor exhibited Nernstian slope and showed wide working concentration range of 2.7×10^{-7} to 1×10^{-1} M.

Inspite of large amount of work has been done to develop ion-selective electrodes for the quantitative estimation of Ni^{2+} ions, still investigations are called for in this direction as the reported sensors have one or other limitations. They show poor selectivity, narrow working concentration range and exhibit high response time. In order to achieve wider applicability, these limitations need to be removed. An important requirement for the preparation of a selective ion sensor is that the electroactive material, which is used in the membranes, should exhibit high lipophilicity and strong affinity for a particular metal ion to be determined and poor affinity for others. Taking into account, the highly desirable attributes of such type of ligands, we have synthesised a macrocyclic ligand (2,9-(2-methoxyaniline)$_2$-4,11-Me$_2$-[14]-1,4,8,11-tetraene-1,5,8,12-N$_4$ (I) which can act as a suitable neutral ionophore for the preparation of polymeric membrane electrode (PME) and coated graphite electrodes (CGE) for highly selective and sensitive determination of nickel ion.

3.1.2 Cobalt Ion Selective Sensor

The need of selective determination of heavy metal ions has increased immensely during the last few decades due to the growing environmental problems. Among heavy metals, the pollution caused by cobalt is of considerable concern. Determination of cobalt assumes importance because of its widespread occurrence in sea as well as in fresh water, earth crust, meteorites, animals and plants. It is a vital trace element in animal nutrition and widely distributed in the body with high concentration in liver, bone and kidney. Cobalt is used in high-temperature alloys, in permanent magnets and its salts are useful in paint dryers as catalysts, abrasion resistant glasses, ceramics, batteries and in production of numerous pigments like cobalt blue and cobalt green, in ground coats for porcelain enamels and in electroplating industry. Cobalt, in the form of cobalamin, is an essential component of Vit. B_{12} required for the production of red blood cells and prevention of pernicious anaemia [16]. Deficiency of cobalt may cause anaemia, retarted growth and loss of apetite. On the other hand, if consumed in large doses, cobalt may be toxic and cause diarrhea, irritation of gastrointestinal tract and vomiting. Exposure to cobalt may cause lung effects, which include respiratory irritation, coughing, asthma, pulmonary edema and pneumonia. The maximum dietary tolerable level of cobalt for common livestock species is 10 ppm [17]. Occupational exposure to cobalt occurs mainly by inhalation. It is clear that monitoring of body fluids for cobalt is essential for the control of nutritional deficiencies and perhaps prevention of its toxic effect in cases of occupational exposure. As a result of its widespread use, cobalt is present in various environment samples where its determination becomes important in view of its toxic effects.

Literature survey reveals that the sensors developed for cobalt make use of chelates [18], macrocycles [19-23], extractants [24], organic resins [25,26], mercapto compounds [27], Schiff bases [28,29], isothiazoles [30], calixarenes [31,32] and variety of other ligands [33,34]. Zamani *et al.* [35] constructed a PVC membrane cobalt(II) ion-selective electrode using N'-[1-(2-thienyl)ethylidene]-2-furohydrazide as a membrane carrier. This sensor exhibited a Nernstian response for Co^{2+} ions over a working concentration range 1.0×10^{-6} to 1.0×10^{-1} M. Rezaei *et al.* [36] fabricated a Co^{2+} ion selective membrane sensor based on 3,3′-(dodecylazanediyl)bis(*N*-(2-(2-aminoethylamino)ethyl)propanamide) as a neutral carrier. This sensor works well in the wide concentration range of 6.58×10^{-7} to 1.0×10^{-1} M with limit of detection 6.82×10^{-8} M. Wardak [37] prepared Co^{2+} selective sensor by employing thiadiazole as an electroactive material and applied it to determine Co^{2+} ions in real samples. Ganjali *et al.* [38] developed Co^{2+} selective sensor by incorporating newly synthesized oxime derivative in PVC matrix. This sensor exhibited a linear potential response to cobalt activity in the concentration range of 1.0×10^{-6} to1.0×10^{-1} M with a response time of 25 s. The most reported potentiometric sensors have not been very fruitful because the developed ion-selective electrodes possess a narrow working concentration range, long response time and significant interferences from many cations. Thus, the fast, accurate and low level determination of cobalt in different samples is very important and for this purpose, good ISEs are still to be developed.

The purpose of the present work is to explore the polymeric membrane electrode and coated graphite electrode as Co^{2+} selective sensors based on two newly synthesized macrocyclic ligands *viz.* 2,3,4:9,10,11-dipyridine-1,3,5,8,10,12-hexaazacyclotetradeca-2,9-diene and 2,3,4:9,10,11-dipyridine-1,5,8,12-tetramethyl-acrylate-1,3,5,8,10,12-hexaaza cyclotetradeca-2,9-diene.

3.1.3 Zinc Ion Selective Sensor

Zinc ion is an important divalent cation in biological systems, and plays an important roles in a human body, influencing DNA synthesis, microtubule polymerization, gene expression, apoptosis, immune system function, and the activity of enzymes such as carbonic anhydrase and matrix metalloproteinase [39]. Moreover, zinc ion is also an contributory factor in neurological disorders such as epilepsy and Alzheimer's diseases |40]. Zinc is also essential to the senses of taste and smell and for growth and development. The zinc deficiency was marked by dwarfism or severe growth retardation, as well as, can result in metabolic changes such as impaired immune response, abnormal taste and abnormal dark adaptation. The foods with high content of protein are abundant source of zinc, such as shellfish, meals, liver and milk which is a good source for infants. Zinc is relatively a non-toxic element; however, it can be toxic if consumed in large quantities. For example, zinc is a metal pollutant of environment, significant concentrations of which may reduce the soil microbial activity causing phytotoxic effect [41,42] and also a common contaminant in agricultural and food wastes [43]. Zinc ions are toxic to human beings when present in concentration above 124 mg/m^3 [44]. A high zinc intake is known to produce copper-deficiency anemia by inducing the intestinal cells to synthesize large amounts of a protein that captures copper in a non-absorbable form [45]. Determination of zinc in excretive organ of the human body such as hair can reflect the cumulative status of this essential element in the body evaluating the nutrient status [46]. Thus, the determination of trace amounts of zinc is currently of great interest in many scientific fields, including medicine analysis and environmental monitoring, etc.

A large number of active compounds, for example porphyrins [47], macrocycles [48,49], sulphide drugs [50], cryptands [51], chalcogenides [52], polypyrrole [53], thiazolidin-4-one [54], N,N'- bis(acetylacetone)ethylediamine [55], and tripodal chelating ligand [56] have been explored as ionophores for construction of ion-selective sensors for Zn^{2+} ions. Rocheleaw and Purdy [57] used zinc orthophosphate and zinc mercuric thiocynate as electroactive materials on a carbon support for the fabrication of Zn^{2+} ion selective sensors. The sensors work well in the concentration range of 1.0×10^{-5} - 1.0×10^{-1} M for Zn^{2+} ion but Cu^{2+}, Cd^{2+} and Pb^{2+} ions can cause serious interference. Gholivand *et al.* prepared PVC-based bis(2-nitrophenyl)disulfide sensor for zinc ions [58]. This sensor exhibits good response to Zn^{2+} ion over a wide concentration range 2.9×10^{-7} to 3.2×10^{-2} M with a slope of 29.9 ± 0.4 mV decade^{-1} of activity. Gupta *et al.* have prepared Zn^{2+} selective sensors based on dithiophosphonic acid, dibenzo-24-crown-8 and 4-*tert*-butylcalix[4]arene as ionophores in PVC matrix [59-61]. Zamani *et al.* developed a Zn^{2+} PVC-based membrane sensor based on 3-[(2-furylmethylene)amino]-2-thioxo-1,3-thiazolidin-4-one [62] and 5,6-benzo-4,7,13,16,21,24-hexa-1,10-diazabicyclo[8,8,8]hexacos-5-ene [63]. These sensors exhibits a Nernstian behavior over a wide concentration range 1.0×10^{-6} - 1.0×10^{-1} M. Mittal *et al.* [64] fabricated Zn^{2+} ion selective electrode containing N,N′-Bis(2-dimethylaminoethyl)-N,N′-dimethyl-9,10-anthracenedimethan amine as an ionophore. This sensor works well in working concentration range of 1.0×10^{-5} - 1.0×10^{-1} M and exhibits Nernstian response with response time of 15 s.

3.2 EXPERIMENTAL

3.2.1 Reagents

All the chemicals and solvents used were of analytical reagent grade. Ethylenediamine, *o*-acetoacetanisidide, 2,6-dichloropyridine, salicylaldehyde, 1, 3-dibromopropane, 3,4-diaminotoluene were procured from Aldrich, USA. Sodium tetraphenylborate (NaTPB), dibutylphthalate (DBP), tri-n-butylphosphate (TBP), benzyl acetate (BA), dioctylphthalate (DOP), *o*-nitrophenyloctyl ether (*o*-NPOE), 1-chloronaphthalene (CN), tetrahydrofuran (THF) potassium carbonate (K_2CO_3), high molecular weight poly(vinylchloride) were purchased from Merck, Germany; methylacrylate from S. D Fine Chemicals Ltd.; potassium tetrakis *p*-(chloro phenyl)borate (KTpClPB) from Fluka, USA and were used as received. The nitrate and chloride salts of all the cations used were of analytical grade and used without any further purification. The solutions of metal salts for membrane studies were prepared in double distilled water and standardized whenever necessary.

3.2.2 Apparatus

The potential measurements were carried out using 5652 digital pH meter/millivoltmeter (ECIL, India) and Cyberscan 510 bench pH/ion/mV meter (Eutech

Instruments, Singapore). Metal concentrations were determined on a Perkin Elmer-3100 Atomic Absorption Spectrophotometer. IR spectra were recorded with a Perkin Elmer FT-IR 1000 spectrophotometer as films between KBr. The UV-Vis spectra of the compounds were recorded on a Shimadzu UV 1601 PC Double Beam Spectrophotometer using 10 mm path length silica cell. ^{1}H NMR spectra were recorded on a Bruker DRX 500 MHz spectrophotometer. The melting points were determined on Buchi SMP 20 melting point apparatus and elemental analyses were performed with Vario EL III instrument.

3.2.3 Synthesis of Ionophores

3.2.3.1 Synthesis of 2,9-(2-methoxyaniline)$_2$-4,11-Me$_2$-[14]-1,4,8,11-tetraene-1,5,8,12-N$_4$ (I)

The macrocyclic ionophore 2,9-(2-methoxyaniline)$_2$-4,11-Me$_2$-[14]-1,4,8,11-tetraene-1,5,8,12-N$_4$ (I) (Fig. 3.1) was synthesized by dissolving equimolar amounts of ethylenediamine (0.01 mol L^{-1}) and *o*-acetoacetanisidide (0.01 mol L^{-1}). Ethylenediamine was dissolved in minimum quantity of methanol and to this solution *o*-acetoacetanisidide dissolved in methanol was added dropwise with stirring. The resulting mixture was refluxed for 8 h and then was concentrated to half of its original volume on a water bath, followed by cooling and keeping aside for 1 day. The shiny creamish coloured product thus obtained was filtered off, washed with cold methanol and recrystallized from ethanol/acetonitrile (1:1) and dried in vacuo. Yield: 86 %, M.P.: 178°C. Anal. calcd. for [$C_{26}H_{34}N_6O_2$] (%): C, 67.49; H, 7.35; N, 18.17; O, 6.92; observed (%): C, 67.51; H, 7.41; N, 18.17; O, 6.92. ^{1}H NMR (CDCl$_3$, 500 MHz) δ_{ppm}: 6.82-7.29 (m, H-Ar, 8H), 4.7 (bs, NH, 2H), 3.86 (s, -OCH$_3$, 6H), 3.36-3.40 (t, N-CH$_2$-C, 8H), 2.75 (s, -C-CH$_2$-C-, 4H), 1.93 (s, -CH$_3$, 6H). IR (KBr, cm^{-1}): 1620 (C=N); 3425 (-NH); 783, 648 (-CH$_2$).

3.2.3.2 Synthesis of 2,3,4:9,10,11-dipyridine-1,3,5,8,10,12-hexaazacyclotetradeca-2,9-diene [II(a)]

The macrocyclic ionophore II(a) (Fig. 3.2) was synthesized by dissolving equimolar amounts of ethylenediamine (0.01 mol L^{-1}) and 2,6-dichloropyridine (0.01 mol L^{-1}). Ethylenediamine was dissolved in minimum quantity of methanol and to this solution 2,6-dichloropyridine dissolved in methanol was added dropwise with stirring. The resulting mixture was refluxed for 10 h in acidic medium and then was concentrated to half of its original volume on a water bath, followed by cooling and keeping aside for 1 day. A white crystalline product was obtained. Yield: 72 %. M.pt.: 138 °C. Anal. calcd. for [$C_{14}H_{18}N_6$] (%): C, 62.19; H, 6.69; N, 31.12; Observed (%): C, 62.20; H, 6.71; N, 31.09, ^{1}H NMR (MeOH, 500 MHz) δ_{ppm}: 7.02-7.64 (m, H-Ar, 6H), 2.64-2.67 (m,-C-NH-C-, 4H), 2.32 (s, -N-CH_2-C, 8H). FT-IR (KBr, cm^{-1}): 3268 (-NH str.).

3.2.3.2.1 Synthesis of 2,3,4:9,10,11-dipyridine-1,5,8,12-tetramethylacrylate-1,3,5, 8,10,12-hexaazacyclotetradeca-2,9-diene [II(b)]

The macrocyclic pendant ligand II(b) (Fig. 3.3) was synthesized from macrocycle II(a). To a stirred solution of the macrocycle II(a) (1 mmol) in 10 mL, saturated solution of anh. K_2CO_3 in anhydrous MeOH, 5 mL methylacrylate (excess amount) was added drop by drop, stirred overnight and refluxed for 24 h. The volume was then reduced to half of its initial amount and was kept in a refrigerator overnight. A creamish coloured oily product was obtained. Yield: 43 %. Anal. calcd. for [$C_{30}H_{42}N_6O_8$] (%): C, 58.60; H, 6.88; N, 13.67; O, 20.85; Observed (%): C, 58.62; H, 6.89; N, 13.67; O, 20.82. ^{1}H NMR (MeOH, 500 MHz) δ_{ppm}: 6.90-7.22 (m, H-Ar, 8H), 2.97-3.25 (m, -N-CH_2-C-, 8H), 2.52 (s, N-CH_2-CH_2-N, 8H), 2.38-2.42 (m, -C-CH_2-COOMe, 8H), 1.36 (s, -OCH_3, 12H), FT-IR (KBr, cm^{-1}): 2930 (asymmetric –CH_2- str.), 2848 (symmetric –CH_2- str.), 1747 (ester C=O str.), 1570-1382 (aromatic C=C & C=N str.), 1163 (OC-OCH_3 str.), 1109 (-OCH_3 str.).

3.2.3.3 Synthesis of 1,4-bis(2-carboxyaldehydephenoxy)butane [III]

To a stirred solution of salicylaldehyde (0.02 mol L^{-1}) and K_2CO_3 (0.01 mol L^{-1}) in DMF (100 mL), 1, 3-dibromopropane (0.01 mol L^{-1}) in DMF (40 mL) was added dropwise [65]. The reaction was continued for 10 h at 150–155 °C and then 5 h at room temperature. 200 mL distillated H_2O was added to the reaction mixture and kept in a refrigerator. Then 1 h later the precipitate was filtered and washed with 500 mL H_2O. It was then dried in air, recrystallised from EtOH and filtered under vacuum (Fig. 3.4). Yield: 16.7 g, M. Pt.: 107-109 °C, Color: Bright brown. Anal Calcd. for [$C_{17}H_{16}O_4$] (%): C, 71.82, H, 5.67, O, 22.51. Observed (%): C, 71.63, H, 5.53, O, 22.84 %. ^1H NMR (MeOH, 500 MHz) δ_{ppm}: 7.06-7.72 (m, H-Ar, 8H), 2.32-2.38 (m,-C-CH_2-C-, 2H), 4.12-4.14 (t,-O-CH_2-C-, 4H), FT-IR (KBr, cm^{-1}): 3100 m(Ar–CH), 2962, 2880 (Aliph.-CH), 1670 (C=O), 1492, 1452 (Ar–C=C), 1280, 1242 (Ar–O).

3.2.3.3.1 Synthesis of 6,7:14,15-Bzo_2-10,11-(4-methylbenzene)-[15]-6,8,12,14-tetraene-9,12-N_2-1,5-O_2 [III(a)]

The macrocyclic ligand III(a) (Fig. 3.5 (a)) was prepared by the dropwise addition of a solution of 3,4-diaminotoluene (0.01 mol L^{-1}) in MeOH (40 mL) to a stirred solution of 1,4- bis(2-carboxyaldehydephenoxy)butane (0.01 mol L^{-1}) in MeOH (60 mL). After the addition was completed, the stirring was continued for 4 h. A resulting yellow compound was filtered followed by the addition of CH_2Cl_2 which dissolved. Then, the solution was filtered and n-hexane was added to the filtered solution. A yellow compound was obtained and filtered. M. Pt.: 160 °C. Anal Calcd. for [$C_{24}H_{22}N_2O_2$] (%): C, 77.81, H, 5.99, N, 7.56, O, 8.64. Observed (%):C, 77.83, H, 6.01, N, 7.52, O, 8.64. ^1H NMR (MeOH, 500 MHz)

δ_{ppm}: 7.02-8.20 (m, H-Ar, 11H), 8.22 (s, CH=N, 2H), 2.24 (s, -CH_3, 3H), 2.30-2.37 (m,-C-CH_2-C-, 2H), 4.11-4.13 (t,-O-CH_2-C-, 4H), FT-IR (KBr, cm^{-1}): 3052 (Ar–CH), 2940, (Aliph.-CH), 1692 (C=N), 1496, 1460 (Ar–C=C), 1276, 1240 (Ar–O).

3.2.3.3.2 Synthesis of 6,7:14,15-Bzo_2-10,11-(4-methylbenzene)-[15]-6 ,14-diene-9,12-dimethylacrylate-9,12-N_2-1,5-O_2 [III(b)]

The macrocyclic pendant ligand III(b) (Fig. 3.5 (b)) was synthesized by in situ reduction of III(a) with $NaBH_4$ followed by dropwise addition of 10 mL saturated solution of anh. K_2CO_3 in anhydrous MeOH and 5 mL methylacrylate (excess amount). It was then stirred overnight and refluxed for 24 h. Then the volume was reduced half of its initial amount and was kept in a refrigerator overnight. A creamish coloured oily product was obtained. Anal. calcd. for [$C_{32}H_{38}N_2O_6$] (%): C, 70.31; H, 7.01; N, 5.12; O, 17.56; Observed (%): C, 70.33; H, 7.00; N, 5.10; O, 17.57. ^1H NMR (MeOH, 500 MHz) δ_{ppm}: 7.04-8.22 (m, H-Ar, 11H), 2.30 (s,-CH3, 3H), 2.31-2.37 (m,-C-CH_2-C-, 2H), 4.10-4.12 (t,-O-CH_2-C-, 4H), 2.48 (s, -N-CH_2-Ar-, 4H), 3.65-3.67 (t, -N-CH_2-C-, 4H), 4.62-4.64 (t, -C-CH_2-COOMe, 4H0, 3.82 (s, OCH_3, 6H), FT-IR (KBr, cm^{-1}): 3050 (Ar-CH), 2945 (Aliph.-CH), 1490, 1455 (Ar-C=C), 1285, 1245 (Ar-O), 1740 (ester C=O str.), 1160 (OC-OCH_3 str.), 1121 (-OCH_3 str.).

3.2.4 Preparation of Membranes

3.2.4.1 Preparation of Poly(vinyl chloride) Based Membranes

The nature and amount of ionophore, nature of plasticizers, plasticizer/PVC ratio and especially the nature of lipophilic additives used, are known to significantly influence the sensitivity and selectivity of the sensor [66]. Of the various binder used for preparing heterogeneous solid state membranes, PVC has been most widely used due to its relatively cheap cost, good mechanical properties, inertness and amenability to plasticization. The membranes of PVC matrix were fabricated according to the procedure described by Craggs *et al.* [67]. An important requirement for making PVC membranes of an ion selective sensor is that the ionophore, PVC, plasticizer and ionic additives should be soluble in some fast evaporating solvent. Therefore the membranes were prepared by dissolving varying amount of ionophore, PVC, plasticizers and ionic additives in THF. After thorough dissolution, the homogeneous mixture was concentrated by evaporating THF and was then poured into polyacrylate rings placed on a smooth glass plate. The solution should be poured gently so that bubbles are not formed. After the evaporation of THF, a transparent membrane of about 0.1 mm thickness was formed and removed carefully from the glass plate and glued to one end of pyrex glass tube with araldite. The ratio of membrane ingredients, time of contact and concentration of equilibrating solution were optimized so that the potential recorded were reproducible and stable within the standard deviation. Membrane to membrane reproducibility was assured carefully by following the optimum condition of fabrication. The membrane that gave reproducible results and showed best performance was selected for further studies.

3.2.4.2 Preparation of Coated Graphite Electrodes

The membrane ingredients (ionophore, PVC, plasticizer and ionic additives) were dissolved in 5 mL of THF and the solvent was evaporated to obtain a concentrated mixture. The viscous solution was then immobilized on the spectroscopic grade graphite rods of 10 mm length and 5 mm diameter by dipping the rod into the solution up to 5 mm depth, withdrawn quickly and holding it upside-down for a few seconds to allow the THF to dry out. A shielded copper wire was glued to one end of the graphite rod, and the electrode was sealed into a PVC tube of about the same diameter with epoxy resin. The process was repeated several times until a uniform coating formed on the graphite surface and the electrode was allowed to stabilize overnight. The rod was covered with paraffin film, keeping the exposed area of the membrane (5 mm) and the contact point free (open).

3.2.4.3 Preparation of Sandwich membranes

Ion-selective electrode membranes were cast as per above mentioned procedure. The blank membranes (without ionophore) of the same composition were also prepared. The sandwich membrane was made by pressing two individual membranes (ordinarily one without ionophore and one with the same components but also containing ionophore) together immediately after blotting them individually, dry with tissue paper. The obtained sandwich membrane was visibly checked for air bubbles before mounting in electrode body with the ionophore-containing segment facing the sample solution. The combined segmented membrane was then rapidly mounted on to the electrode body and studied immediately.

3.2.5 Determination of Formation Constant

A selective complexation of analyte ions by ionophores is primarily responsible for the selectivity of sensors. Despite the wide use of lipophilic and chemically immobilized ionophores in chemical sensor applications, only a limited number of experimental techniques are available to assess the binding strengths of these highly selective molecular probes directly in the polymeric matrix of the sensor. An approach to measure complex stability constants in ISE membranes relies on recording electrical potential of segmented sandwich membranes [68]. Polymeric membrane electrodes primarily respond to ion activities on both sides of the aqueous-organic phase boundary. The incorporation of an ion carrier into the membrane phase should induce a substantial potential change at the sample-membrane phase boundary, since the ion activity within the organic phase is dramatically altered. Therefore this effect could be used to determine the formation constant of the ion-ionophore complex.

It requires membrane potential measurements on two-layer sandwich membranes, where only one side contains the ionophore. If both membrane segments have the same ionic strength, it is convenient to assume that the activity coefficients for the complexed and uncomplexed ions are approximately equal. In that case, they can be omitted and the complex constant is related to the potential. In the present studies, the stability constants are investigated according to method proposed by Mi and Bakker [69] using following equation

$$\beta_{IL_n} = \left(L_T - \frac{nR_T}{Z_I} \right)^{-n} \exp\left(\frac{E_M z_I F}{RT} \right) \qquad (1)$$

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. This relationship allows for the convenient determination of formation constants of ion-ionophore complexes within the membrane phase on the basis of transient membrane potential measurements on two-layer sandwich membranes. The knowledge of formation constants of the relevant complexes is beneficial to the process of optimizing the structure of ionophores and the composition of ISE membranes for a given analyte ion.

3.2.6 Equilibration of Membranes and Potential Measurements

The membranes, fixed to one end of pyrex glass tube, were equilibrated with corresponding metal salt solution for which the membrane is to be made selective. The time of contact and concentration of equilibrating solution were optimized so that the sensors generated stable and reproducible potentials at relatively short response time.

For nickel determination, polymeric membrane electrode and coated graphite electrode based on membrane containing 2,9-(2-methoxyaniline)$_2$-4,11-Me$_2$-[14]-1,4,8,11-tetraene-1,5,8,12-N$_4$ as an ionophore with different composition were equilibrated for 2 days in 0.1 mol L^{-1} $NiCl_2$ solution. The potentials were measured by varying the concentration of $NiCl_2$ in test solution in the range 1.0×10^{-9} to 1.0×10^{-1} mol L^{-1}. Standard $NiCl_2$ solution were obtained by gradual dilution of 0.1 mol L^{-1} $NiCl_2$ solution.

For cobalt determination, polymeric membrane electrode and coated graphite electrode based on membrane containing 2,3,4:9,10,11-dipyridine-1,3,5,8,10,12-hexaaza-cyclotetra-deca-2,9-diene and 2,3,4:9,10,11-dipyridine-1,5,8,12-tetramethyl- acrylate-1,3,5,8,10,12-hexaazacyclotetradeca-2,9-diene as ionophores with different composition were equilibrated for 2 days in $Co(NO_3)_2$ solution. The potentials were measured by varying the concentration of $Co(NO_3)_2$ in test solution in the range 1.0×10^{-9} to 1.0×10^{-1} mol L^{-1}. Standard $Co(NO_3)_2$ solution were obtained by gradual dilution of 0.1 mol L^{-1} $Co(NO_3)_2$ solution.

For zinc determination, polymeric membrane electrode and coated graphite electrode based on membrane containing 6,7:14,15-Bzo$_2$-10,11-(4-methylbenzene)-[15]-6,8,12,14-tetraene-9,12-N$_2$-1,5-O$_2$ and 6,7:14,15-Bzo$_2$-10,11-(4-methylbenz ene)-[15]-6,14-diene-9,12-dimethylacrylate-9,12-N$_2$-1,5-O$_2$ as ionophores with different composition were equilibrated for 3 days in a 0.01 mol L^{-1} $Zn(NO_3)_2$ solution. The potentials were measured by varying the concentration of $Zn(NO_3)_2$ in test solution in the range 1.0×10^{-9} to 1.0×10^{-2} mol L^{-1}. Standard $Zn(NO_3)_2$ solution was obtained by gradual dilution of 0.01 mol L^{-1} $Zn(NO_3)_2$ solution.

The potential measurement for Polymeric membrane electrode (PME) were carried out at 25 ± 0.1°C using saturated calomel electrode (SCE) as reference electrode with the following cell assembly:

Hg/Hg_2Cl_2 | KCl (satd.) | (0.1 or 0.01 mol L^{-1}) metal salt solution || PVC membrane || test solution | Hg/Hg_2Cl_2 | KCl (satd.)

The potential measurement for Coated graphite electrode (CGE) were carried out at 25 ± 0.1°C using saturated calomel electrode (SCE) as reference electrode with the following cell assembly:

CGE | sample solution || $Hg/HgCl_2$ |KCl (satd.)

Activity coefficients were calculated according to the Debye-Huckel procedure, using following equation [70].

$$\log \gamma = -0.511z^2[\mu^{1/2}/(1 + 1.5\mu^{1/2}) - 0.2\mu] \quad (2)$$

where μ is the ionic strength and z is the valency.

3.3 RESULTS AND DISCUSSION

3.3.1 Membranes of 2,9-(2-methoxyaniline)$_2$-4,11-Me$_2$-[14]-1,4,8,11-tetraene-1,5,8,12-N$_4$ (I) as Ni^{2+} selective sensor

The recognition of a metal ion by a macrocyclic ligand is controlled to a large extent by a match between the size of the ligand hole and that of the metal ion. The tetraazamacrocyclic ligands form transition metal complexes of high thermodynamic stability and extreme kinetic inertness. Thus, 2,9-(2-methoxyaniline)$_2$-4,11-Me$_2$-[14]-1,4,8,11-tetraene-1,5,8,12-N$_4$ (I) was used as an ion-active phase in the preparation of membrane electrodes for transition and other metal ions and it gave a sensitive and selective response to Ni^{2+} ions.

To investigate the suitability of (I) as an ion carrier in PVC membranes, the potential responses of various membrane electrodes based on (I) for various metal ions were obtained separately. Among the different cations tested, it was found that the electrode responded to Ni^{2+} ion most selectively in terms of wide concentration range, detection limit and Nernstian slope. This is probably due to both high selective behaviour of the macrocycle for Ni^{2+} ion in comparison to other metal ions and the rapid exchange kinetics of the resulting macrocyclic-Ni(II) complex.

3.3.1.1 Optimization of membrane composition

It is well understood that the sensitivity, linearity and selectivity obtained for a given ionophore depends significantly on the membrane composition and nature of the plasticizers used [71-78]. Thus, several membranes of varying plasticizer/PVC/carrier ratios were tested.

The optimum membrane ingredient showing the most sensitive, reproducible and stable results was obtained with a plasticizer/PVC ratios of ~ 1.1 together with 6 mg of ionophore. A study of the influence of the plasticizer on the potentiometric response characteristics were conducted by using TBP, DBP, *o*-NPOE, DOP and CN and the results are shown in Fig. 3.6. It can be seen from Table 3.1, that the membrane without any plasticizer (membrane no. 1) gave a narrow working concentration range 4.8×10^{-5} to 1.0×10^{-1} mol L^{-1} with a slope of 38.4 mV $decade^{-1}$ of activity. It has been shown that the presence of lipophillic ionic additives in the ion-selective membrane sensors is necessary to introduce perm selectivity [79]. Considerable improvements were observed, when ionic additives and different plasticizers were added to the membrane ingredients and results are compiled in Table 3.1.

3.3.1.2 *Response characteristics of polymeric membrane electrode (PME) and coated graphite electrode (CGE)*

The best performance was exhibited by sensor no. 2 containing TBP as solvent mediator with the composition I: PVC: TBP: NaTPB in the ratio 6: 90:100: 4 (w/w; mg).

This sensor displayed the widest working concentration range 4.6×10^{-7} to 1.0×10^{-1} mol L^{-1} and a Nernstian slope of 29.5 ± 0.3 mV $decade^{-1}$ of activity. The limit of detection, as determined from the intersection of two extrapolated segments of the calibration curve was 2.7×10^{-7} mol L^{-1}. Thus, membrane no. 2, *i.e.* containing TBP as plasticizer was selected to prepare both the polymeric membrane electrode (PME) and the coated graphite electrode (CGE) for the Ni^{2+} ion.

The critical response characteristics of the proposed electrodes were assessed according to IUPAC recommendation [80]. The EMF response of the polymeric membrane and coated graphite electrode (Fig. 3.7) indicates their Nernstian behaviour over a wide concentration range. The slopes, linear ranges and detection limit of the resulting EMF-pNi^{2+} graphs are given in Table 3.2. The improved performance characteristics of the CGE over those of the PME presumably originate from the coated graphite technology, where an internal 1.0×10^{-1} mol L^{-1} $NiCl_2$ solution, in the case of PME, has been replaced by a copper wire of much higher electrical conductivity, in the case of CGE. A comparison of data given in Table 3.2 revealed the superiority of CGE with respect to working concentration range (7.7×10^{-8}-1.0×10^{-1} mol L^{-1}), detection limit (3.7×10^{-8} mol L^{-1}) and Nernstian slope (29.5 ± 0.2 mV $decade^{-1}$ of activity) over PME. It is well known that the higher limit of detection of PME than that of CGE is mainly due to some leakage of the internal solution into the test solution *via.* polymeric membrane [79].

3.3.1.3 Response Time and lifetime of the sensor

The response time *i.e.* the time required by the electrode assembly to generate stable and reproducible potentials was found to be 10 s for the polymeric membrane electrode and 8 s for the coated graphite electrode (Table 3.2) over the full range of concentrations. Potentials generated by the developed sensors remained stable for more than ~ 5 min after which a very slow divergence were recorded. The much higher electrical conductivity of the copper wire (in CGE) than that of the internal solution (in PME) is expected to result in lower response time of the CGE in comparison with the PME.

The polymeric membrane electrode and coated graphite electrode could be used over a period of 4 months and 5 months respectively at a stretch without observing any significant change in response time, slope and working concentration range.

3.3.1.4 Influence of pH on the sensor performance

The pH dependence of the electrodes was tested by measuring the potential response of solution containing 1.0×10^{-3} mol L^{-1} and 1.0×10^{-4} mol L^{-1} of the Ni^{2+} ion in the pH range 1.0-11.0. The pH was adjusted by using 0.1 mol L^{-1} solution of either HCl or NaOH and the results are shown in Fig. 3.8 and Fig. 3.9 for PME and CGE respectively. It can be seen that potential response for both electrodes remains constant over the pH range 3.0-8.0 and the same can be taken as the working pH range of the electrodes. The significant change in potential response observed at pH below 3.0 can be reasonably related to the response of the sensor to the hydrogen ions. On the other hand, the observed potential drift at pH values could be due to the formation of some hydroxyl complexes of Ni^{2+} ion in solution. Therefore, the best performance for the proposed sensor should be achieved in the pH range 3.0-8.0.

3.3.1.5 Interference of foreign ions on sensor performance

Potentiometric selectivity coefficient, describing the preference of the ion-selective electrodes for an interfering ion, B, relative to Ni^{2+} ion, A, was determined by the matched potential method (MPM). In MPM, the primary ion activity was taken as 1.0×10^{-2} mol L^{-1} and the activity of interfering ions were determined experimentally.

From this data, selectivity coefficients were calculated as described in section 2.5; Chapter 2. The values of selectivity coefficients so determined are presented in Table 3.3. It is immediately obvious from the values that the proposed electrodes are highly selective to Ni^{2+} ion with respect to other common cations. The selectivity coefficients are in the order of 10^{-2} (for PME) and 10^{-3} (for CGE) or lower, which seems to indicate that these cations have negligible impact on the functionality of the Ni^{2+} ion selective sensor. Meanwhile, the data given in Table 3.3 revealed that, in all cases, the selectivity coefficients obtained for the coated graphite electrode are lower than those for the polymeric membrane electrode, emphasizing the superiority of the CGE in this respect as well.

3.3.1.6 Effect of non aqueous content

The real samples may contain non-aqueous content, so the performance of the sensor was also investigated in partially non-aqueous media using 10 %, 20 %, 25 %, 30 % and 35 % (v/v) methanol-water, ethanol-water and acetonitrile-water mixtures (Table 3.4). It was found that the membranes do not show any appreciable change in working concentration range and slope in methanol-water and ethanol-water mixtures up to 25 % (v/v) non-aqueous contents, whereas in acetonitrile-water mixture, membrane could tolerate up to 20 % (v/v) non-aqueous content. However, above these mentioned non aqueous contents, the slope and working concentration range decreases appreciably, consequently reliable measurements could not be obtained. The drift in potentials in the organic phase may be probably due to swelling in membrane which was too high that membrane became mechanically weak and leaching of ionophore from membrane to non-aqueous solution took place.

3.3.1.7 Analytical Applications

3.3.1.7.1 Potentiometric Titration of nickel ion solution with standard EDTA solution

The CGE was used as an indicator electrode in the successful titration of 20 mL of Ni^{2+} ion solution (5.0×10^{-3} mol L^{-1}) with a EDTA (1.0×10^{-2} mol L^{-1}) at pH 5.5. The resulting titration curve is shown in Fig. 3.10, indicating that the amount of Ni^{2+} ion can be accurately determined with the CGE.

3.3.1.7.2 Determination of nickel ion in fruit juices

The nickel selectivity exhibited by the CGE makes it potentially useful for monitoring the low level concentration of Ni^{2+} ion in real samples. In this regard, experiments were performed to measure Ni^{2+} ion in fruit juices and wine samples. In the analysis of fruit juices, they were first centrifuged for 15 min to obtain pulp free liquid, then were filtered and diluted in 1: 20 ratio and analyzed by the proposed electrode. The results obtained have been shown in Table 3.5 and were found to be in good agreement with those obtained with Atomic Absorption Spectroscopy (AAS).

3.3.1.7.3 Determination of nickel ion in wine samples

A 10 mL portion of sample (wine) was treated with 1 mL of 65 % (v/v) HNO_3 and 2 mL of H_2O_2 in a pyrex glass tube placed in an aluminium block and heated at 100°C overnight. Aliquots of H_2O_2 were added until the solution remained transparent and clear. The solutions were left to cool at room temperature and diluted with de-ionised Milli-Q-water. The resulting solution was then analyzed by the proposed sensor and results obtained are presented in Table 3.6. The results obtained were also compared with those from AAS and revealed a satisfactory agreement between the two techniques.

3.3.1.8 Conclusion

On the basis of the results, the tetraazamacrocyclic ligand 2,9-(2-methoxyaniline)$_2$-4,11-Me$_2$-[14]-1,4,8,11-tetraene-1,5,8,12-N$_4$ can be regarded as a potential carrier for the construction of polymeric membrane electrode and coated graphite electrode to determine the low level concentration of nickel ion. The best performance was obtained for the membrane sensor having a composition of I:PVC:TBP:NaTPB in the ratio 6:90:100:4 (w/w; mg). The EMF response of the polymeric membrane electrode and the coated graphite electrode indicates their Nernstian behaviour over a wide concentration range. Proposed nickel ion selective sensor shows maximum selectivity, widest working concentration range and minimum response time. Comparison of data between polymeric membrane electrode (PME) and coated graphite electrode (CGE) revealed the superiority of CGE with regard to detection limit (3.7×10^{-8} mol L^{-1}), response time (8 s) and selectivity over PME. Thus, the coated graphite electrode was selected for the trace level determination of nickel ions in fruit juices and wine samples and can also be used as an indicator electrode in potentiometric titration.

3.3.2 Membranes of 2,3,4:9,10,11-dipyridine-1,3,5,8,10,12 hexaaza cyclotetradeca-2,9-diene [II(a)] and 2,3,4:9,10,11-dipyridine-1,5,8,12-tetramethylacrylate-1,3,5,8,10,12-hexaazacyclotetradeca-2,9-diene [II(b)] as Co^{2+} selective sensor

In preliminary experiments, II(a) and II(b) were used as neutral carriers to prepare polymeric membrane electrode for various metal ions. The potential response of the membrane electrode for different metal ions were obtained. Among different tested cations, Co^{2+} ion with the most sensitive response seems to be suitably determined with the PVC membrane based on the II(a) and II(b) with wide concentration range and a

Nernstian slope. Thus, the membranes of II(a) and II(b) were investigated primarily as Co^{2+} ion selective sensor.

3.3.2.1 Determination of Formation constant

The complexation of the II(a) and II(b) with a number of alkali, alkaline earth and transition metal ions has been investigated using segmented sandwich membrane method. The formation constants ($\log \beta_{\mathrm{IL}n}$) have been determined as described in section 3.2.5. The resulting data for the examined complexes are compiled in Table 3.7. A careful analysis of the data reveals that both the ligands II(a) and II(b) has significant cation-binding characteristics with Co^{2+} ion while all other cations tested showed a weak or negligible binding characteristics.

3.3.2.2 Optimization of membrane composition

The potentials of membranes of two macrocyclic ligands II(a) and II(b) were investigated as a function of cobalt ion concentration and the results are summarized in Tables 3.8 and 3.9 respectively. The optimization of membrane sensor is known to be highly dependent on the incorporation of additional membrane components. In order to guarantee a good membrane performance, an adequate plasticizer must show sufficient lipophilicity, no crystallization and exudation in the membrane phase. It is now well established that the plasticizer plays a vital role in the sensor performance as it is responsible for ionophore salvation and distribution in the membrane matrix, thus controlling the detection limit affecting the selectivity and sensitivity and giving the plastic membrane its proper elasticity and strength. It can be seen from Table 3.8 that the sensor no. 1 having membrane of II(a) without plasticizer exhibits linear response over a working concentration range of 3.4×10^{-5} to 1.0×10^{-1} mol L^{-1} with a slope of 28.2 mV decade^{-1} of activity. Similarly, sensor no. 13 (Table 3.9) having the membrane of II(b) without plasticizer exhibits working concentration range of 2.6×10^{-5} to 1.0×10^{-1} mol L^{-1} with a slope of 27.8 mV $decade^{-1}$ of activity. The slopes of the membranes is near Nernstian and the working concentration ranges narrow. Several membranes of varying composition were fabricated to improve the performance characteristics of the electrode by adding different plasticizers such as DBP, BA, DOP, o-NPOE and TBP as shown in Fig. 3.11 for II(a) and Fig. 3.12 for II(b). The electrodes based on II(a) and II(b) exhibited Nernstian behaviour with DOP and TBP respectively.

It is well known that the incorporation of lipophillic additive can significantly improve the selectivity of an ion sensor by decreasing the membrane resistance and co-ion interference [81]. In our experiments, we examined the effect of NaTPB and KTpClPB as suitable lipophillic additives in conjugation with ionophores II(a) and II(b) on the potentiometric response of Co^{2+} selective electrode. As is obvious from Tables 3.8 and 3.9, the use of 3 mg KTpClPB for II(a) and 2 mg NaTPB for II(b) significantly improves the performance characteristics of the membrane sensors.

The variation in potential with different amounts of ionophores was also examined and shown in Table 3.8 (sensor nos. 8, 9, 10) and Table 3.9 (sensor nos. 19, 21, 22). In this case of carrier type ion selective electrodes, the extraction equilibrium in the vicinity of the interface between the membrane and aqueous layer affects the potentiometric response of membrane. Inspite of these considerations, a carrier content of 7 mg for II(a) and 6 mg for II(b) was chosen as the optimum ionophore amount, because the surface conditions of the PVC membrane deteriorated on decreasing and increasing the carrier content.

3.3.2.3 Potentiometric calibration characteristics of the proposed cobalt sensors

The result thus obtained indicates that the electrode (no. 8) (Table 3.8) having composition II(a): PVC: DOP: KTpClPB in the ratio of 7: 35: 55: 3 (w/w; mg) exhibited a

Nernstian slope of 29.9 ± 0.2 mV decade^{-1} of activity and a concentration range of 4.6×10^{-7} to 1.0×10^{-1} mol L^{-1} with a limit of detection 2.2×10^{-7} mol L^{-1} while the best results were shown by the electrode (no. 19) (Table 3.9) having composition II(b): PVC: TBP: NaTPB in the ratio of 6: 39: 53: 2 (w/w: mg) which exhibited a Nernstian slope of 29.7 ± 0.2 mV decade^{-1} of activity over a wide concentration range of 6.0×10^{-8} to 1.0×10^{-1} mol L^{-1} with a limit of detection 4.7×10^{-8} mol L^{-1}.

3.3.2.4 Response characteristics of polymeric membrane electrode (PME) and coated graphite electrode (CGE)

The investigations on PVC based membrane of two macrocyclic ligands, *viz.* II(a) and II(b) have shown that they act as Co^{2+} selective sensors. The membrane having composition II(b): PVC: TBP: NaTPB in the ratio of 6: 39: 53: 2 (w/w: mg) which showed best response characteristics in terms of Nernstian slope, working concentration range and detection limit was selected to prepare coated graphite electrode. The EMF response of the PME and CGE (Fig. 3.13) indicates their Nernstian behaviour over a wide concentration range. A comparison of data given in Table 3.10 revealed the superiority of CGE with respect to concentration range (1.3×10^{-8} to 1.0×10^{-1} mol L^{-1}), detection limit (6.8×10^{-9} mol L^{-1}) and Nernstian slope (29.5 mV decade^{-1} of activity) over PME. The improved performance characteristics of the CGE over those of PME presumably originate from the coated graphite technology, where an internal 1.0×10^{-1} mol L^{-1} $Co(NO_3)_2$ solution, in case of PME, has been replaced by a copper wire of much higher electrical conductivity, in case of CGE.

3.3.2.5 Effect of Soaking time and lifetime

The lifetime of the electrodes were determined by soaking both PME and CGE in 0.1 mol L^{-1} $Co(NO_3)_2$ solution for interval ranging from 2 to 120 days till the electrode lost its Nernstian behaviour. This behaviour attributed to the decomposition of the ionophore and loss of other components in the membrane phase that was in contact with aqueous test solution containing cobalt ion. The response of both electrodes has been measured by recording the calibration graph at 25 °C at different intervals. The results listed in Table 3.11 shows the effect of soaking time on slope, detection limit and concentration range. It can be seen that the lifetime measured in this way was found to be 3 months for PME and 4 months for CGE during which the slope of electrode, showed only a slight change from 29.7 ± 0.2 to 23.1 ± 0.2 mV decade^{-1} of activity for PME and 29.5 ± 0.1 to 24.5 ± 0.1 mV decade^{-1} of activity for CGE.

3.3.2.6 Response time of the proposed sensors

To measure the response time of the proposed electrodes the concentration of the test solution was successively changed from 1.0×10^{-6} to 1.0×10^{-1} mol L^{-1}. The average time required for the electrodes to reach a potential response within ±1 mV of the final equilibrium value after successive immersion in a series of Co^{2+} ion solution, each having a tenfold difference in concentration was 11 s for PME (Fig. 3.14) and 8 s for CGE (Fig. 3.15). Potentials generated by the developed sensors remained stable for more than ~ 5 min after which a slow divergence was recorded.

3.3.2.7 Influence of pH on sensor performance

The pH dependence of both PME and CGE has been tested over the pH range 1.0-10.0 for 1.0×10^{-3} and 1.0×10^{-4} mol L^{-1} of Co^{2+} ion solution. The pH was adjusted by using 0.1 mol L^{-1} solution of either HCl or NaOH and the results are shown in Fig. 3.16. It can be seen that potential response for PME remains constant over pH range 2.5-8.5 and 2.0-9.0 for CGE. Therefore, the same was taken as the working pH range of the electrodes. The significant change in potential response observed at lower pH can be reasonably related to the response of the sensor to the hydrogen ions. On the other hand, the observed potential drift at higher pH values could be due to the formation of some hydroxyl complexes of Co^{2+} ion in solution.

3.3.2.8 Interference of foreign ions on sensor performance

Selectivity is perhaps the single most important characteristic of any electrode, which defines the nature of the device and the extent to which it may be employed in determination of a particular ion in the presence of other interfering ions. Potentiometric selectivity coefficients of the cobalt membrane electrodes were evaluated by a matched potential method (MPM) [82,83] and fixed Interference Method (FIM) [84]. In MPM, the selectivity coefficients were determined by measuring the change in potential upon increasing the primary ion activity from an initial value of 1.0×10^{-3} to 3.0×10^{-3} mol L^{-1} Co^{2+} ions and the activity of interfering ion added to the reference solution of Co^{2+} ion was experimentally determined. However, in the FIM, the selectivity coefficient was evaluated from potential measurement on solutions containing a fixed concentration of interfering ion (1.0×10^{-2} mol L^{-1}) and varying amount of Co^{2+} ions. The values of selectivity coefficient so determined for PME and CGE are compiled in Table 3.12. It is seen from the table that the selectivity coefficient for the interfering metal ions are sufficiently smaller than 1.0, indicating that the present sensor is significantly selective to Co^{2+} ion over other ions.

3.3.2.9 Effect of non-aqueous content

The real samples may also contain non-aqueous component, and the performance of the sensor was also investigated in partially non-aqueous media using 10 %, 20 %, 30 %, 35 % and 40 % (v/v) methanol-water, ethanol-water and acetonitrile-water mixtures (Table 3.13). It was found that the membranes did not show any appreciable change in working concentration range and slope in methanol-water and ethanol-water mixtures up to 35 % (v/v) non-aqueous contents, whereas in acetonitrile-water mixture, membrane could tolerate up to 25 % (v/v) non-aqueous content. However, above these mentioned non aqueous contents, the slope and working concentration range decreased appreciably, consequently reliable measurements could not be obtained.

3.3.2.10 Effect of ionic and non-ionic Surfactants

It is commonly known that both ionic and non-ionic surfactants interact with the polymer membrane being divided between the aqueous phase and the membrane phase and result in increased background potential and lower binding ability for the ionophore [85]. Such effects should result in deteriorated detection limits, reduced response slopes and lower selectivity for the primary ions.

In the present paper, we examined the effect of cationic (tetrabutylammonium chloride, TBC), anionic (sodium dodecyl sulfate, SDS) and nonionic (Triton X-100) surfactants on the potentiometric properties of proposed CGE based on the macrocyclic pendant ligand II(b) and the results obtained are compiled in Table 3.14. It was observed that the content of surfactants up to 1.0×10^{-4} mol L^{-1} does not cause any significant change in the response characteristics of the proposed electrode. However, concentration of the surfactants above 1.0×10^{-4} mol L^{-1} adversely affected the performance of the electrode as the selectivity, slope and working concentration range were observed to decrease.

3.3.2.11 Analytical Applications

3.3.2.11.1 Potentiometric titration of cobalt ion solution with standard EDTA solution

The analytical applicability of the electrode was evaluated by carrying out potentiometric titration of 20 mL of 5.0×10^{-3} mol L^{-1} Co^{2+} ions against

1.0×10^{-2} mol L^{-1} EDTA at pH 6 using CGE as an indicator electrode. The titration plot shown in Fig. 3.17 is of sigmoid shape that is also an indication of selectivity of electrode. The inflexion point of the plot corresponds to 1:1 stoichiometry of Co-EDTA complex.

3.3.2.11.2 Determination of cobalt ion in water samples

The proposed coated graphite electrode (CGE) was successfully applied for the direct determination of cobalt in different water samples. The results are given in Table 3.15 It was found that the cobalt contents obtained from triplicate measurements were in satisfactory agreement with those obtained by using AAS method.

3.3.2.11.3 Determination of cobalt ion in beer samples

The cobalt selectivity exhibited by the membrane electrode makes it potentially useful for monitoring the concentration of Co^{2+} ion in real samples. In this regard, experiments were performed to measure Co^{2+} ion in beer samples. Cobalt is present in trace amounts in virtually all-living tissues and thus the raw materials used for brewing barley, corn, rice and hops, are no exception. As a consequence, commercial beer normally contains a minute concentration of cobalt, usually a few hundredths of a part per million. So there is need to develop a method to check whether a beer sample contains added cobalt or not. An amount of 1 mL of 18 N H_2SO_4 was added to 50 mL of degassed beer, evaporated to dryness and 10 mL of distilled water was added. The pH was adjusted to 6.0 using either 0.1 N HCl or 0.1N NaOH. The solution was filtered and finally diluted to 50 mL with water. A beer containing known amount of cobalt was chosen. Aliquots of the working solution were added to 50 mL samples of this beer, to give known concentration of added cobalt ranging from about 0.6–1.5 ppm. The concentration of added cobalt was then determined for each sample by CGE that is presented in Table 3.16.

3.3.2.11.4 Determination of cobalt ion in pharmaceutical samples

The accuracy and applicability of the proposed CGE was also evaluated by its application for the determination of Cobalt in various pharmaceutical samples. A sample each of injectable Neurobion (Merck, India) and Sioneuron (Albert David Ltd., India) was digested with nitric acid in a covered beaker. The residue of the sample was leached with dil. H_2SO_4 and diluted to the mark in a calibrated flask. Working solutions were prepared by taking an appropriate amount of the sample and its cobalt content was determined by the proposed electrode. The results obtained are compiled in Table 3.17 and were found to be in good agreement with those obtained by AAS, thereby reflecting the utility of this sensor for determination of cobalt in real samples.

3.3.2.12 Conclusion

The investigations on PVC based membrane of two macrocyclic ligands *viz.* II(a) and II(b) shows that they are Co^{2+} selective sensors. However, of the two ligands, the sensor no. 19 based on II(b) with membrane composition II(b): PVC: TBP: NaTPB in the ratio of 6: 39: 53: 2 (w/w; mg) exhibited widest working concentration range (6.0×10^{-8} to 1.0×10^{-1} mol L^{-1}), Nernstian compliance (29.7 mV $decade^{-1}$ of activity) and high selectivity for cobalt ions. The performance of the membrane based on II(b) was compared with PME as well as with CGE. Comparison of data revealed that CGE was superior to PME with regard to detection limit (6.8×10^{-9} mol L^{-1}), response time (8 s) and selectivity. Thus, the CGE was used as indicator electrode in the potentiometric titration of Co^{2+} ions with EDTA and in determination of cobalt ions in real and pharmaceutical samples.

3.3.3 Membranes of 6,7:14,15-Bzo$_2$-10,11-(4-methylbenzene)-[15]-6,8,12,14-tetraene-9,12-N$_2$-1,5-O$_2$ [III(a)] and 6,7:14,15-Bzo$_2$-10,11-(4-methylbenzene)-[15]-6,14-diene-9,12-dimethylacrylate-9,12-N$_2$-1,5-O$_2$ [III(b)] as Zn^{2+} selective sensor

The PVC based membrane containing III(a) and III(b) as ionophores respond selectively to Zn^{2+} ions in comparison to other ions with wide working concentration range and high selectivity. Ligands for use as ionophores in a Zn^{2+} ion-selective sensor should ideally fulfill certain conditions. They should be selective to Zn^{2+} over other metal ions, should have rapid exchange kinetics and should be sufficiently lipophilic to prevent leaching of the ligand into solutions surrounding the membrane sensor. The existence of two donating nitrogens in the ligands III(a) and III(b) is expected to increase the stability of its zinc complex over other metal ions, especially alkali and alkaline earth cations [86,87]. Moreover, the presence of two methylacrylate pendant arms in III(b) can also contribute to the Zn^{2+} selectivity.

3.3.3.1 Complexation study

In preliminary experiments, the complexation of III(a) and III(b) with a number of alkali, alkaline earth, transition metal and rare earth metal ions has been investigated conductometrically in acetonitrile solutions in order to have a clue about the stability and selectivity of the resulting complexes and their stoichiometry at 25 ± 0.05 °C [88,89]. For this purpose, 25 mL of 1.0×10^{-4} mol L^{-1} cation solution was titrated against a 1.0×10^{-2} mol L^{-1} ionophore solution in acetonitrile media in order to have a clue about the stability and selectivity of the resulting complexes. The conductance of the solution was measured after each addition of ionophore until the titration plot showed a break which corresponds to the 1:1 stoichiometry of the complexes. The 1:1 binding of the protonated amines with macrocylic ligands can be expressed by the following equilibrium [90]:

$$M^{n+} + L \xrightarrow{K_f} ML^{n+} \tag{3}$$

The corresponding equilibrium constant, K_f, is given by:

$$K_f = \frac{[ML^{n+}]}{[M^{n+}]\quad[L]} \times \frac{f_{(ML^{n+})}}{f_{(M^{n+})}\ f_{(L)}} \tag{4}$$

Where $[ML^{n+}]$, $[M^{n+}]$, $[L]$ and f represents the equilibrium molar concentration of complexes, free cation, free ligand, and the activity coefficient of species indicated, respectively.

Under the dilute condition we used, the activity coefficient of unchanged ligand, $f_{(L)}$ can be reasonably assumed as unity. The use of Debye-Huckel limiting law of 1:1 electrolytes lead to the conclusion that $f_{(M^{n+})} \approx f_{(ML^{n+})}$, so the activity coefficient in equation (4) is cancelled out. Thus, the complex formation constant in terms of the molar conductance can be expressed as:

$$K_f = \frac{[ML^{n+}]}{[M^{n+}][L]} = \frac{(\Lambda_M - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_{ML})[L]} \tag{5}$$

Where

$$K_f = C_L - \frac{C_M(\Lambda_M - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_{ML})} \tag{6}$$

Here, Λ_M is the molar conductance of the cation before addition of ligand, Λ_{ML} the molar conductance of the complex, Λ_{Obs} the molar conductance of the solution during titration, C_L the analytical concentration of the ionophores added, and C_M the analytical concentration of the cation. The complex formation constants, K_f, and the molar conductance of complex, Λ_{ML}, were obtained by computer fitting of equations (5) and (6) to the molar conductance-mole ratio data, using a nonlinear least-square programs using Genetic Algorithim [91]. The logarithm of the formation constants (log K_f) of the resulting 1:1 complexes for mono, di and trivalent cations are given in Table 3.18. As seen, stability of Zn-III(a) and Zn-III(b) complexes is higher than the other cations tested. Thus, III(a) and III(b) with the most stable complex with Zn^{2+} ion is expected to act as a suitable ion-carrier for the fabrication of a Zn^{2+} ion sensor.

3.3.3.2 Determination of formation constant

Formation constant of ion-ionophore complex within the membrane phase is very important parameter that dictates the practical selectivity of the sensor. The formation constants ($\log \beta_{ILn}$) have also been determined according to segmented sandwich membrane method. The potential of such sandwich membranes remains free of diffusion-induced potential drifts for about 20 min. Standard deviations were obtained based on the measurements of sets of at least three replicate membrane disks that were made from the same parent membrane. The determined logarithm of formation constants for the examined complexes of III(a) and III(b) with different metal ions were tabulated in Table 3.18 and are compared with those obtained by Conductometric method. It can be seen from both the methods that III(a) and III(b) has stronger binding affinity for Zn^{2+} ions.

3.3.3.3 Optimization of membrane composition

The polymeric membrane electrode based on III(a) and III(b) macrocyclic ligands with different composition have been prepared and their response characteristics were evaluated according to the IUPAC recommendation [92]. The sensor no. 1 having membrane of III(a) without plasticizer exhibits linear response over a working concentration range of 4.4×10^{-5} to 1.0×10^{-2} mol L^{-1} with a slope of 27.6 ± 0.5 mV $decade^{-1}$ of activity (Table 3.19). Similarly, sensor no. 12 (Table 3.20) having the membrane of III(b) without plasticizer exhibits working concentration range of 4.1×10^{-5} to 1.0×10^{-2} mol L^{-1} with a slope of 31.6 ± 0.7 mV $decade^{-1}$ of activity. The slopes of the membranes is near Nernstian and the working concentration ranges narrow. Thus, several membranes of varying composition were fabricated to improve the performance characteristics of the electrode by adding different plasticizers such as DBP, TBP, *o*-NPOE, DOP and BA as shown in Fig. 3.18 for III(a) and Fig. 3.19 for III(b) and the results are compiled in Tables 3.19 and 3.20 respectively. Plasticizer play a vital role in the electrode performance as it is responsible for ionophore salvation and distribution in the membrane matrix, thus controlling the detection limit, affecting the selectivity and sensitivity and giving the plastic membrane its proper elasticity and strength [93,94]. The electrodes based on III(a) and III(b) exhibited Nernstian behaviour with DOP and TBP respectively. This indicates that the solvent medium of DOP and TBP is probably providing the best complexation environment between zinc ions and their respective carriers.

The influence and concentration of membrane additives was also investigated by incorporating different lipophilic additives like NaTPB and KTpClPB. As is obvious from Tables 3.19 and 3.20, the use of 1 mg NaTPB (for III(a), sensor no. 7) and 2 mg NaTPB (for III(b), sensor no. 18) significantly improves the performance characteristics of the membrane sensors in comparison to KTpClPB. This is due to fact that NaTPB acts as a charge compensating counter ion in the membrane and thus facilitate the process of ion charge transduction. On the other hand, the membranes without lipophilic salt, showed very narrow concentration range and slopes were non-Nernstian. This observation is likely due to the presence of anionic impurities within the PVC polymer matrix [95].

A carrier content of 6 mg for III(a) (Table 3.19) and 4 mg for III(b) (Table 3.20) was chosen as the optimum ionophore amount, because the surface conditions of the PVC membrane deteriorated on decreasing and increasing the carrier content. This deviation in electrode response in higher concentration of the ionophore is due to the loss of selectivity and enhanced interference of the lipophilic counter ions of the test solution as presumed in the phase boundary potential model of carrier based ISEs [96].

3.3.3.4 Potentiometric calibration characteristics of the proposed zinc sensors

The potential response of the membrane electrode having composition III(a):PVC: DOP:NaTPB in the ratio of 6:33:60:1 (w/w; mg) (sensor no. 7) depicts a rectilinear range from 2.7×10^{-6} to 1.0×10^{-2} mol L^{-1} with a limit of detection 1.2×10^{-6} mol L^{-1} and Nernstian slope of 28.6 ± 0.6 mV decade^{-1} of activity. The best results were shown by the sensor no. 18 based on III(b) containing TBP as solvent mediator with the composition III(b):PVC:TBP:NaTPB in the ratio of 4:37:57:2 (w/w; mg) exhibiting the widest working concentration range of 5.0×10^{-7} to 1.0×10^{-2} mol L^{-1}, Nernstian compliance of 28.8 ± 0.4 mV decade^{-1} of activity, low detection limit of 3.3×10^{-7} mol L^{-1} and high selectivity for Zn^{2+} ions.

3.3.3.5 Response characteristics of polymeric membrane electrode (PME) and coated graphite electrode (CGE)

The sensor no. 18 showed the Nernstian slope with wide working concentration range and low detection limit and therefore has been selected for the fabrication of coated graphite electrode. It has been reported that the replacement of inner solution of PME by solid substance like graphite rod in CGE inhibits the leakage from internal solution into the test solution and therefore improves the characteristic properties of the electrode along with its selectivity towards different secondary ions. The EMF response of the PME and CGE indicates their Nernstian behaviour over a wide concentration range as shown in Fig. 3.20. A comparison of data given in Table 3.21 revealed the superiority of CGE with respect to concentration range (1.9×10^{-7} to 1.0×10^{-2} mol L^{-1}), detection limit (7.9×10^{-8} mol L^{-1}) and Nernstian slope (29.2 ± 0.2 mV decade^{-1} of activity) over PME.

3.3.3.6 Effect of Soaking time and lifetime

Lifetime or durability of an ISE is one of the important factors in deciding the applicability of ISE. One of the criteria to assess the lifetime is the extent of leaching of the ionophore from the membrane. This in turn depends on the properties of the plasticizer and the additive being used and their compatibility with ionophore. The lifetime of the electrodes were determined by soaking both PME and CGE in 0.01 mol L^{-1} $Zn(NO_3)_2$ solution for interval ranging from 2 to 55 days till the electrode lost its Nernstian behaviour. The lifetime measured was found to be 35 days for PME and 55 days for CGE during which the slope of electrode, showed only a slight change from 28.8 ± 0.3 to 25.3 ± 0.3 mV decade^{-1} of activity for PME and 29.2 ± 0.2 to 25.4 ± 0.5 mV decade^{-1} of activity for CGE (Table 3.22).

3.3.3.7 Response time of the proposed sensors

It is well known that the response time of an ion-selective sensor is one of its most important characteristics. The response time of the electrode was determined by measuring the time required to achieve a 95 % of the steady potential. The static response time thus obtained was ~ 12 s for PME and 10 s for CGE. The sensing behaviour of the electrode remained unchanged when the potentials were recorded either from low to high concentration or vice versa.

3.3.3.8 Influence of pH on sensor performance

One of the ions present in aqueous solution is the hydrogen ion. It interferes in many instances, in the functioning of the electrode. In view of this, it is necessary to find the optimum pH range where the electrode functions without interference from the hydrogen ions. The pH dependence of polymeric membrane and coated graphite sensors based on III(b) was examined at 1.0×10^{-3} mol L^{-1} and 1.0×10^{-4} mol L^{-1} concentration of Zn^{2+} ions. The pH of the solution was varied by small addition of 0.1 mol L^{-1} solution of either HCl or NaOH and the results are depicted in Fig. 3.21. The potential response for PME remains constant over pH range 3.0-8.0 and 2.5-9.0 for CGE, beyond which some drifts in the potential were observed. The observed drift at higher pH values could be due to the formation of some hydroxyl complexes of Zn^{2+} ions in the solution and the significant change in potential response observed at lower pH can be reasonably related to the response of the sensor to the hydrogen ions.

3.3.3.9 Interference of foreign ions on sensor performance

The potentiometric selectivity coefficient of an ISE is commonly used as a quantitative expression of the ability of the electrode to respond to primary ion in the presence of interfering ions. The selectivity studies were carried out by Coated graphite electrode which exhibited the best performance characteristics in terms of working concentration range, slope, response time and life time. In the present study, the selectivity coefficients were determined using Fixed Interference Method (FIM). The selectivity coefficients were evaluated by potential measurement on solutions containing fixed concentration of interfering ion (1.0×10^{-2} mol L^{-1}) and varying concentration of Zn^{2+} ions.

The values of selectivity coefficient so determined are compiled in Table 3.23. It is quite obvious from the corresponding table that Zn^{2+} ion selective electrodes are highly selective w.r.t other common cations. The interfering effect of the cations is in the following order: $Cd^{2+} > Hg^{2+} > Na^{+} > K^{+} > Ni^{2+} > Li^{+} > Pb^{2+} > Cu^{2+} > Fe^{3+} > Cr^{3+} > Mg^{2+} > Ba^{2+} > Sr^{2+} > Ag^{+} > Co^{2+}\ Ce^{3+} > Ca^{2+}$. The selectivity coefficients are in the order of

10^{-2} or lower, which seems to indicate that these cations have negligible impact on the functionality of the Zn^{2+} sensor.

3.3.3.10 Effect of non-aqueous content

The performance of the sensor was also investigated in partially non-aqueous media using 10 %, 20 %, 30 %, 35 % and 40 % (v/v) methanol-water, ethanol-water and acetonitrile-water mixtures (Table 3.24). It was found that the membranes did not show any appreciable change in working concentration range and slope in methanol-water and ethanol-water mixtures up to 35 % (v/v) non-aqueous contents, whereas in acetonitrile-water mixture, membrane could tolerate up to 20 % (v/v) non-aqueous content. However, above these mentioned non aqueous contents, the slope and working concentration range decreased appreciably, consequently reliable measurements could not be obtained.

3.3.3.11 Analytical Applications

3.3.3.11.1 Potentiometric titration of zinc ion solution with standard EDTA solution

The analytical applicability of the electrode was evaluated by carrying out potentiometric titration of 20 mL of 1.0×10^{-3} mol L^{-1} Zn^{2+} ions against 1.0×10^{-2} mol L^{-1} EDTA at pH 5.5 using CGE as an indicator electrode (Fig. 3.22). The sensor was highly sensitive to Zn^{2+} ions and the amount of zinc ions could be accurately determined with the sensor. The point of inflexion of the plot corresponds to formation of a zinc–EDTA complex of 1:1 stoichiometry.

3.3.3.11.2 Analysis of Zn^{2+} in water samples

The Zn^{2+} ion content of 50 mL river and industrial waste water samples was determined using coated graphite electrode. The water samples were treated with 7.5 mL dil. HNO_3 (1:1) and 2.5 mL H_2O_2 (30%). The mixture was stirred, its volume was reduced to half by heating, 2.5 mL dil. HNO_3 was added, and the solution was filtered through a 0.45-μm membrane filter paper. After adjustment to pH ~ 5.5 by addition of dil HNO_3, zinc was determined by use of the sensor. The results are given in Table 3.25. It was found that the data obtained from triplicate measurements and AAS are equal ($p< 0.01$) from statistical point of view.

3.3.3.11.3 Analysis of Zn^{2+} ion in biological samples

The selectivity of zinc ions exhibited by the proposed membrane electrode makes it potentially useful for determining the concentration of Zn^{2+} ion in blood and urine samples. The blood samples were collected from a local hospital. Five millilitres of each blood sample was first dried over an IR lamp at 80–90 °C and then crushed. Five hundred milligrams of the dried blood sample was digested with $HClO_4$ and HNO_3 (in a ratio of 1:5). The digested samples were then diluted by doubly distilled water. To determine Zn^{2+} ion in urine, 5 mL urine was obtained from healthy humans and used for triplicate measurements. These samples were immediately treated or stored for a short time in the dark at 4 °C until analyzed. Samples were accurately measured into clean, dry vessels, diluted fourfold with 0.2 M HNO_3, and the pH was adjusted to ~ 5.5. The blood and urine samples were then analyzed by the proposed coated graphite electrode and results are compiled in Table 3.26. The results obtained were compared with those obtained by use of atomic-absorption spectroscopy (AAS) and found to be in good agreement.

3.3.3.11.4 Analysis of Zn^{2+} ion in milk and tea samples

The zinc content of milk has been determined by the conventional dry ashing procedure; 100 mL of milk is pipetted into a heated crucible to evaporate without frothing. After the moisture has been removed, the residue is heated strongly to 450–500°C for ~1 h. Utmost care was taken to avoid the loss by sputtering. The white ash obtained was dissolved in minimum volume of diluted nitric acid and volume was made up to 25 mL in a volumetric flask. The excess nitric acid is neutralized with dilute sodium hydroxide solution and the zinc content is determined using proposed CGE.

Two grams of the material was dry ashed at 450°C and then digested with 2 mL of 3:1 mixture of nitric and perchloric acids. The sample was heated gently almost to dryness repeated again with 2 mL of acid mixture and diluted finally to 25 mL with water. The sample was set aside for overnight and filtered to remove impurities and Zinc content is determined. The results are compiled in Table 3.27 and were found to be in good agreement with the values obtained by AAS. Hence the sensor can be successfully used for analysis of Zn^{2+} ions in real samples.

3.3.3.12 Conclusion

The macrocyclic ligands III(a) and III(b) were used as ionophores in the preparation of PVC based membranes and were found to be selective to Zn^{2+} ions. The best response characteristics were shown by the membrane having composition III(b): PVC: TBP: NaTPB in the ratio of 4: 37: 57: 2 (w/w; mg) which exhibited widest working concentration range (5.0×10^{-7} to 1.0×10^{-2} mol L^{-1}), Nernstian compliance (28.8 ± 0.3 mV decade^{-1} of activity), detection limit (3.3×10^{-7} mol L^{-1}). This membrane was selected for the fabrication of CGE. Comparison of data revealed the superiority of CGE over PME with regard to working concentration range (1.9×10^{-7} to 1.0×10^{-2} mol L^{-1}), detection limit (7.9×10^{-8} mol L^{-1}) and response time (10 s). The high selectivity of the proposed CGE made it possible to determine Zn^{2+} ions in water, biological, milk and tea samples and also used as an indicator electrode in the potentiometric titration of Zn^{2+} ions with EDTA.

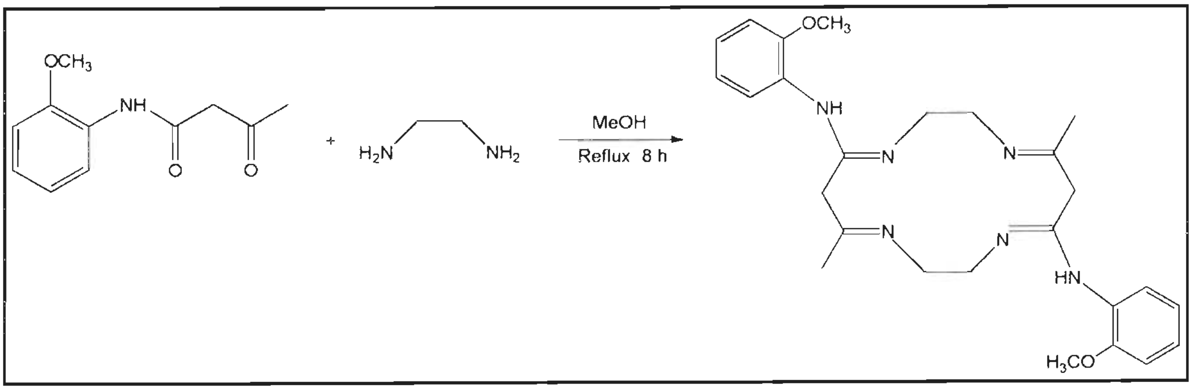


Fig. 3.1 Synthesis of 2,9-(2-methoxyaniline)$_2$-4,11-Me$_2$-[14]-1,4,8,11-tetraene-1,5,8,12-N$_4$ ionophore (I) by reaction with *o*-acetoacetanisidide and ethylenediamine in MeOH.

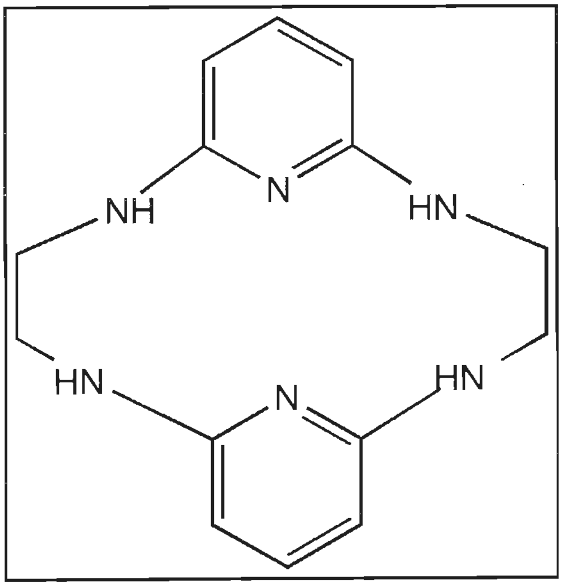


Fig. 3.2 Structure of macrocyclic ligand 2,3,4:9,10,11-dipyridine-1,3,5,8,10,12-hexa azacyclotetradeca-2,9-diene [II(a)]

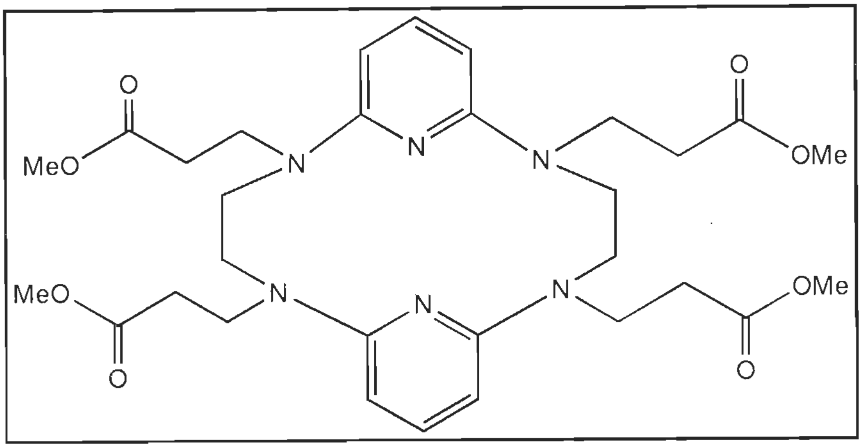


Fig. 3.3 Structure of macrocyclic pendant ligand 2,3,4:9,10,11-dipyridine- 1,5,8,12-tetramethylacrylate-1,3,5,8,10,12-hexaazacyclotetradeca-2,9-diene [II(b)]

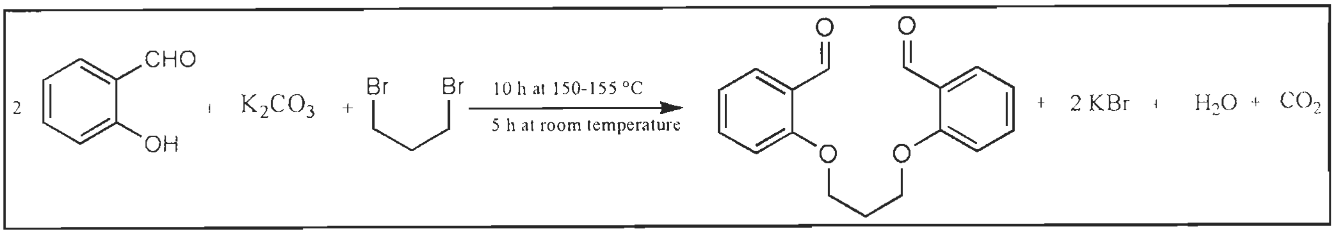


Fig. 3.4 Synthesis of 1,4-bis(2-carboxyaldehydephenoxy)butane (III)

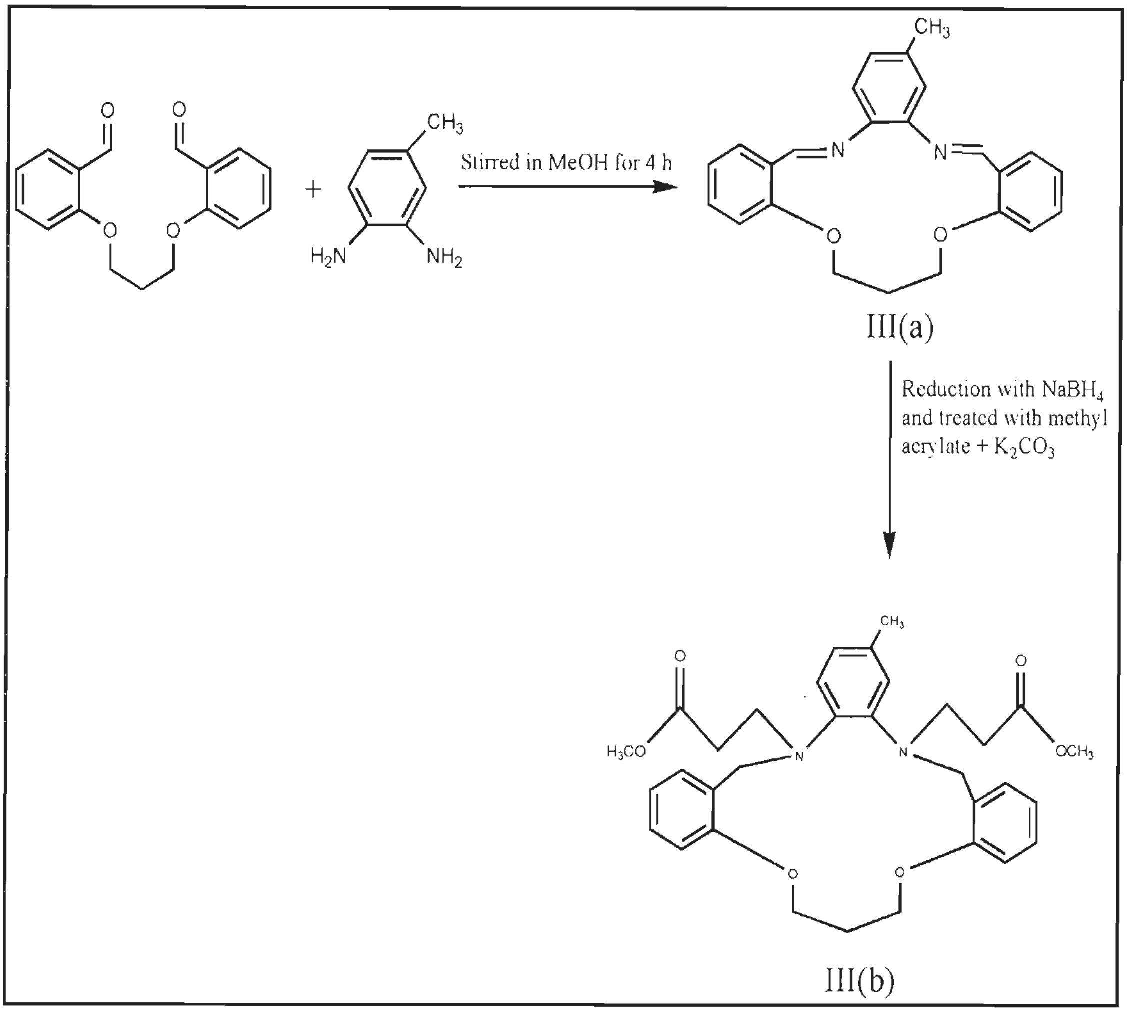


Fig. 3.5 Synthesis of 6,7:14,15-Bzo$_2$-10,11-(4-methylbenzene)-[15]-6,8,12,14-tetraene 9,12-N$_2$-1,5- O$_2$ [III(a)] and 6,7:14,15-Bzo$_2$-10,11-(4-methylbenzene)-[15]-6,14-diene-9,12- dimethylacrylate-9,12-N$_2$-1,5-O$_2$ [III(b)]

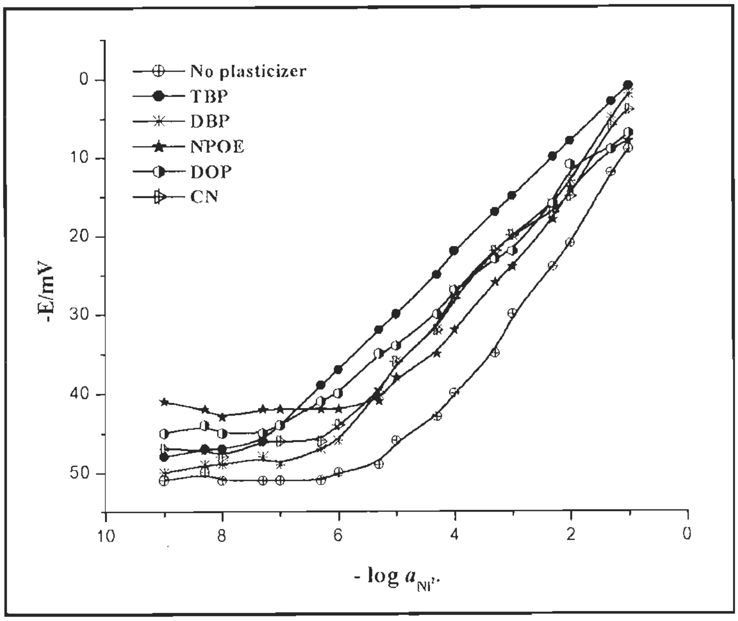


Fig. 3.6 Variation of potential of Ni^{2+} selective membrane based on (I) with different plasticizers as a function of Ni^{2+} concentration

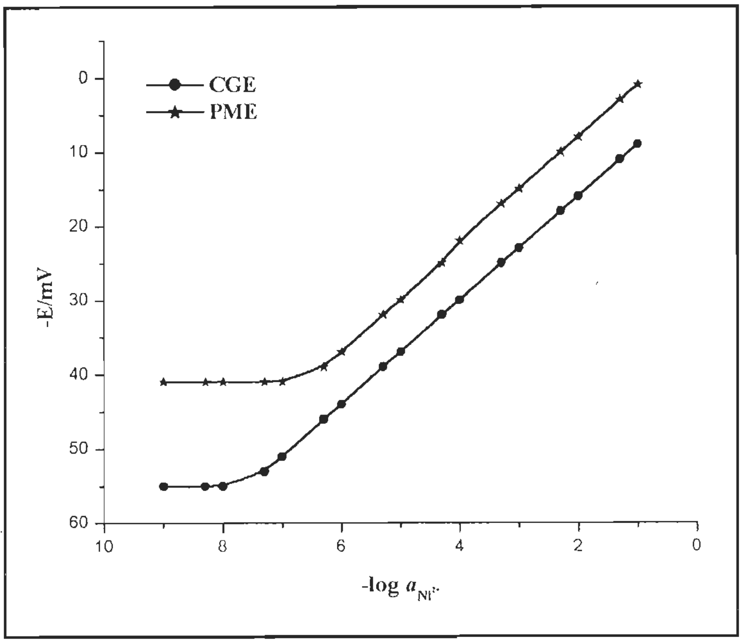


Fig. 3.7 Calibration characteristics of Ni^{2+} ion-selective electrodes (PME and CGE) based on ionophore I

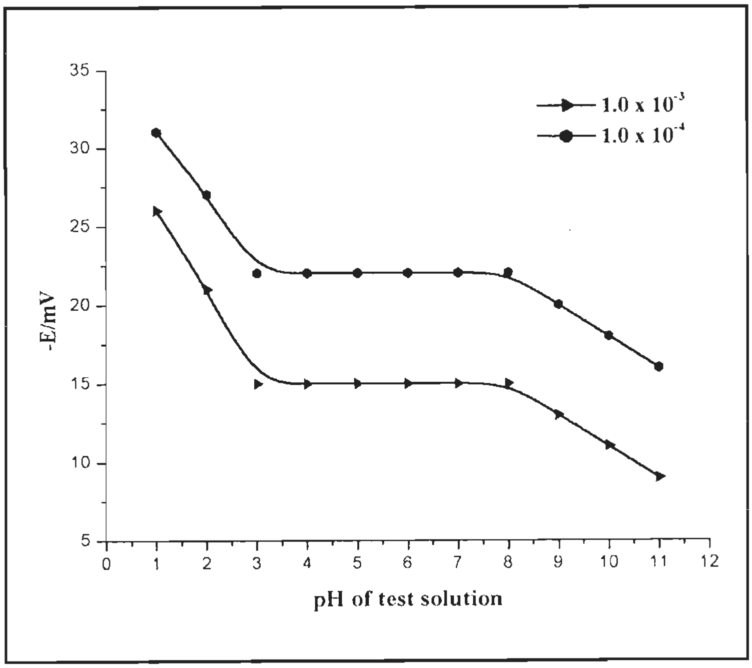


Fig. 3.8 Effect of pH of the test solutions on the potential responses of the PME at different concentrations of Ni^{2+}

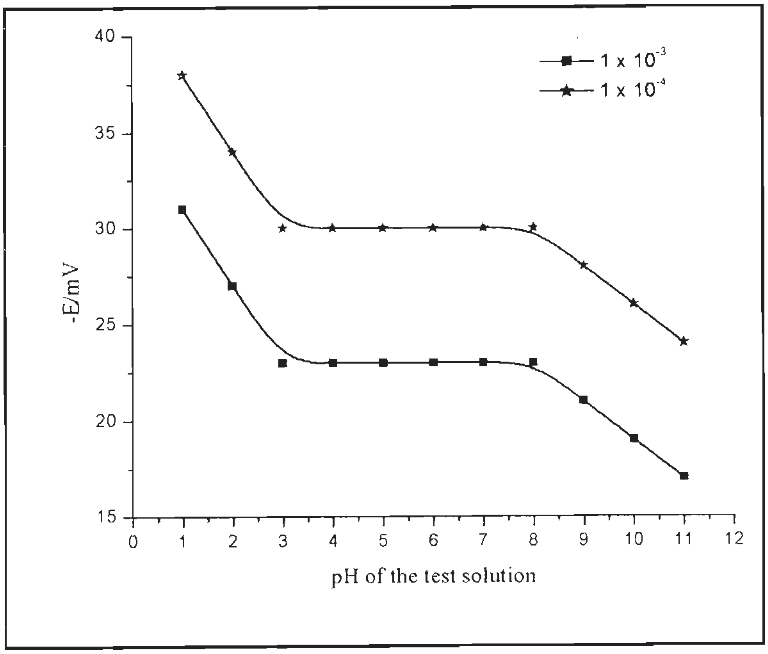


Fig. 3.9 Effect of pH of the test solutions on the potential responses of the CGE at different concentrations of Ni^{2+}

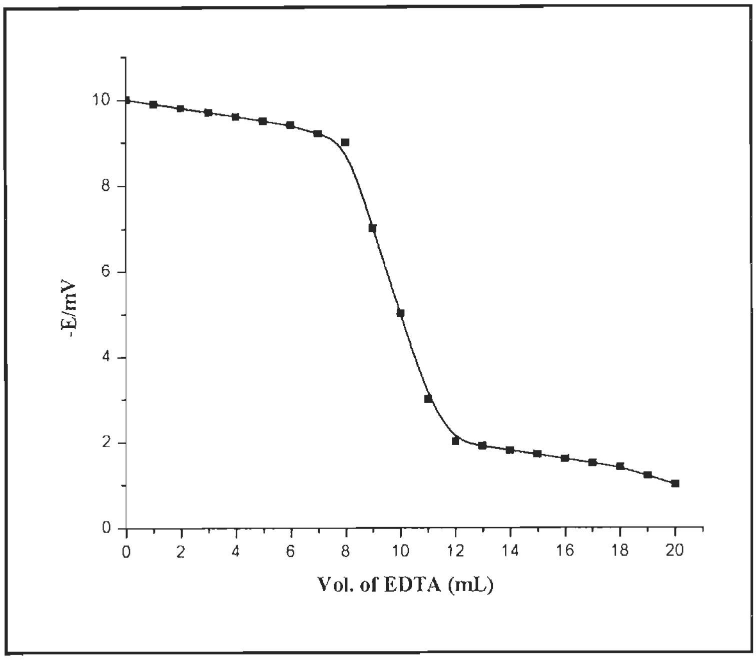


Fig. 3.10 **Potentiometric titration curve of 20 mL of 5.0 × 10^{-3} mol L^{-1} solution of Ni^{2+} ion with 1.0 × 10^{-2} mol L^{-1} EDTA at pH 5.5 using CGE as indicator electrode**

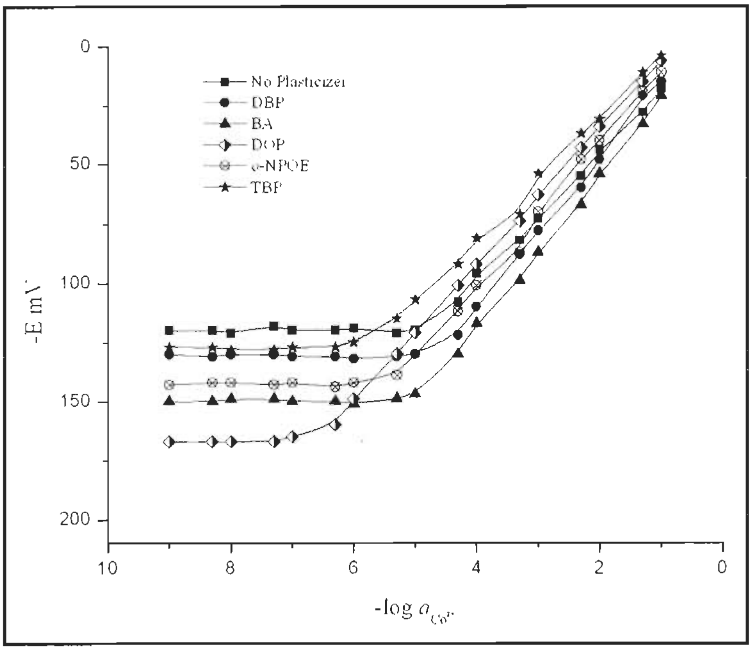


Fig. 3.11 **Variation of potential of Co^{2+} selective membrane based on II(a) with different plasticizers as a function of Co^{2+} concentration**

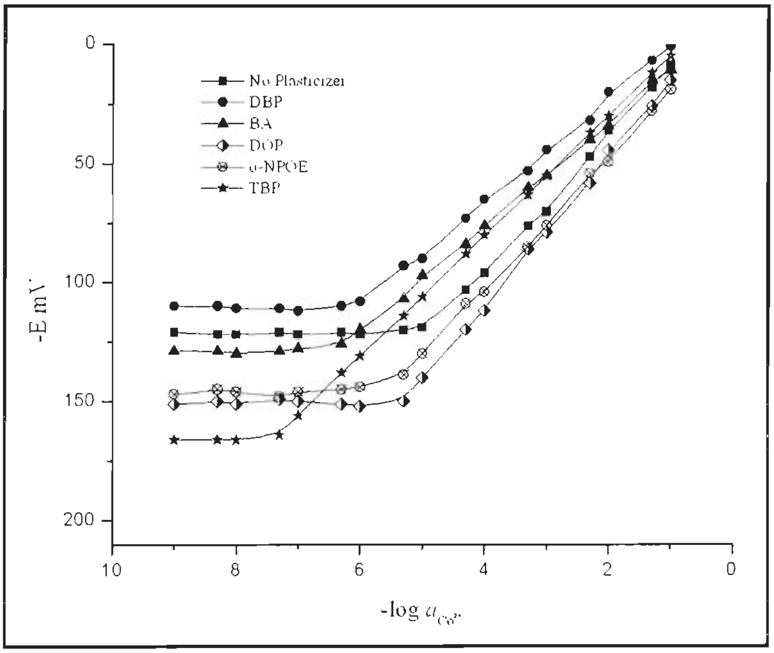


Fig. 3.12 Variation of potential of Co^{2+} selective membrane based on II(b) with different plasticizers as a function of Co^{2+} concentration

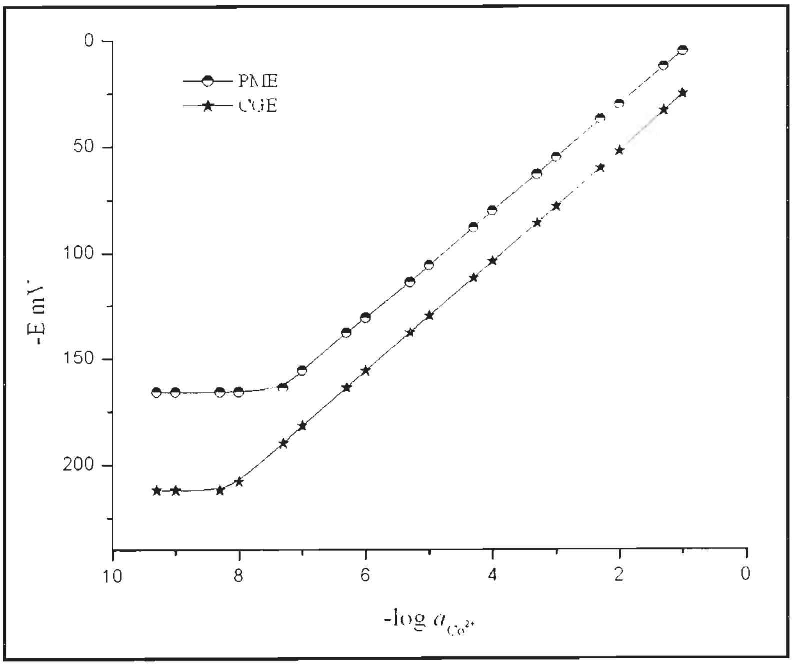


Fig. 3.13 Calibration characteristics of Co^{2+} ion-selective electrodes (PME and CGE) based on II(b)

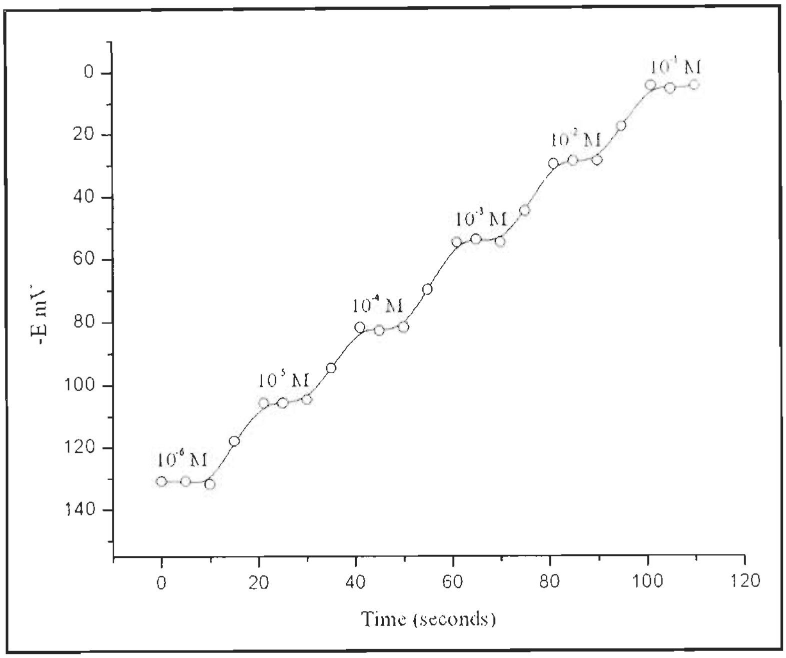


Fig. 3.14 Dynamic response of Polymeric membrane electrode based on II(b)

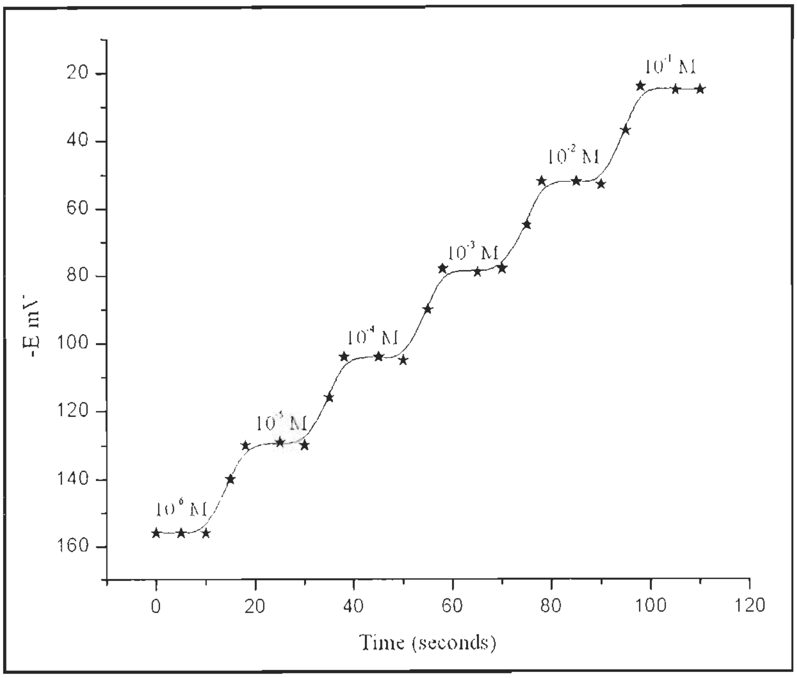


Fig. 3.15 Dynamic response of Coated graphite electrode based on II(b)

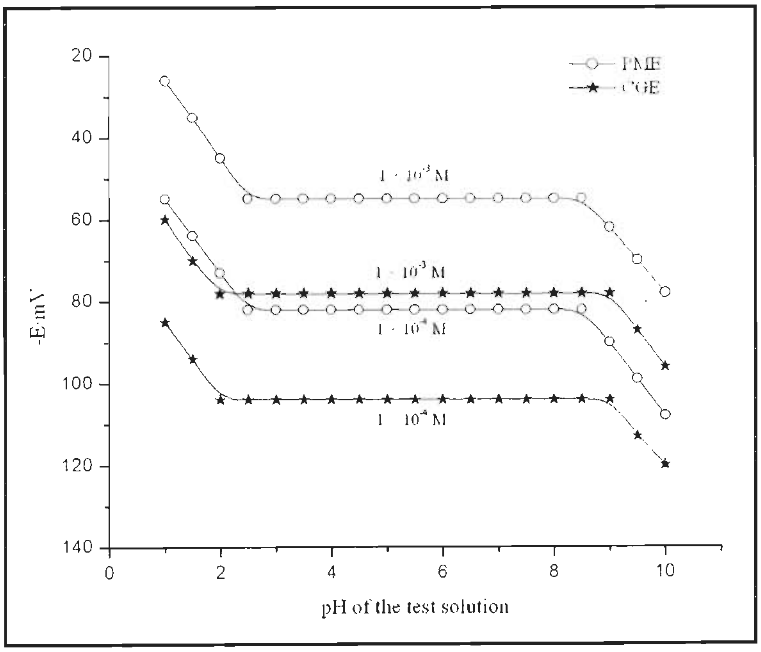


Fig. 3.16 **Effect of pH of the test solutions on the potential responses of the PME and CGE at different concentrations of Co^{2+}**

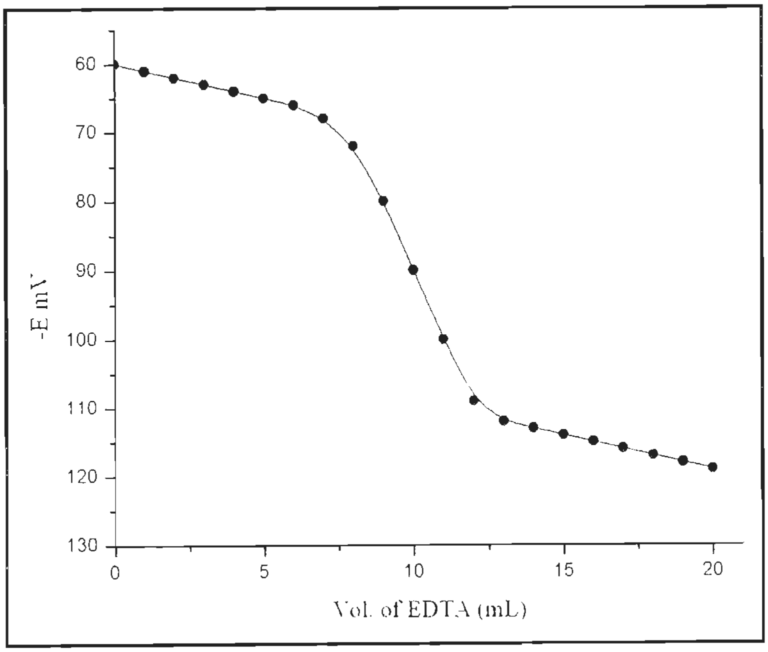


Fig. 3.17 **Potentiometric titration curve of 20 mL of 5.0×10^{-3} mol L^{-1} solution of Co^{2+} ion with 1.0×10^{-2} mol L^{-1} EDTA at pH 6.0 using CGE as indicator electrode**

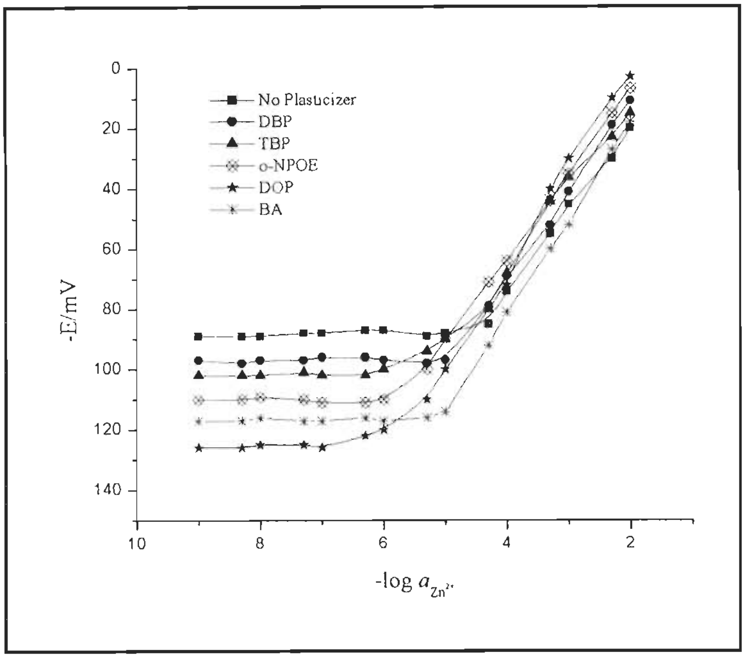


Fig. 3.18 Variation of potential of Zn^{2+} selective membrane based on III(a) with different plasticizers as a function of Zn^{2+} concentration

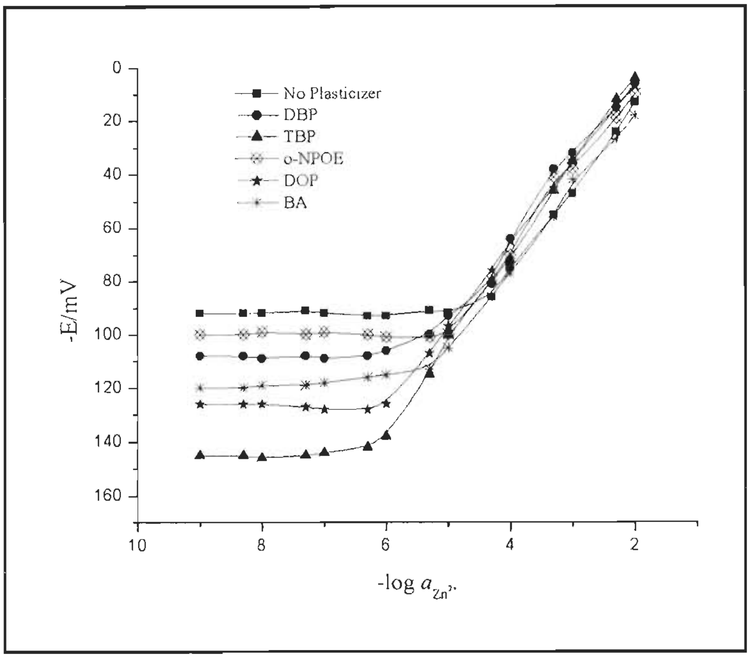


Fig. 3.19 Variation of potential of Zn^{2+} selective membrane based on III(b) with different plasticizers as a function of Zn^{2+} concentration

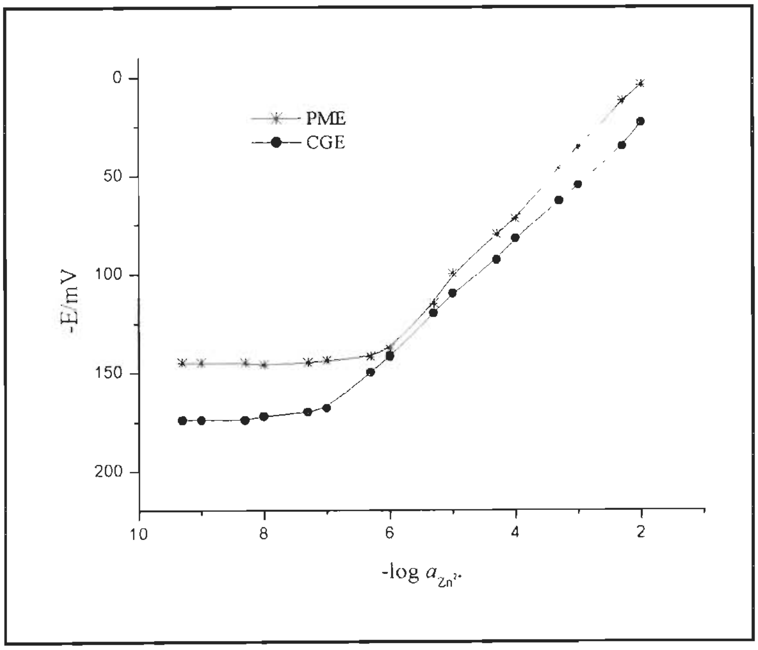


Fig. 3.20 Calibration characteristics of Zn^{2+} ion-selective electrodes (PME and CGE) based on III(b)

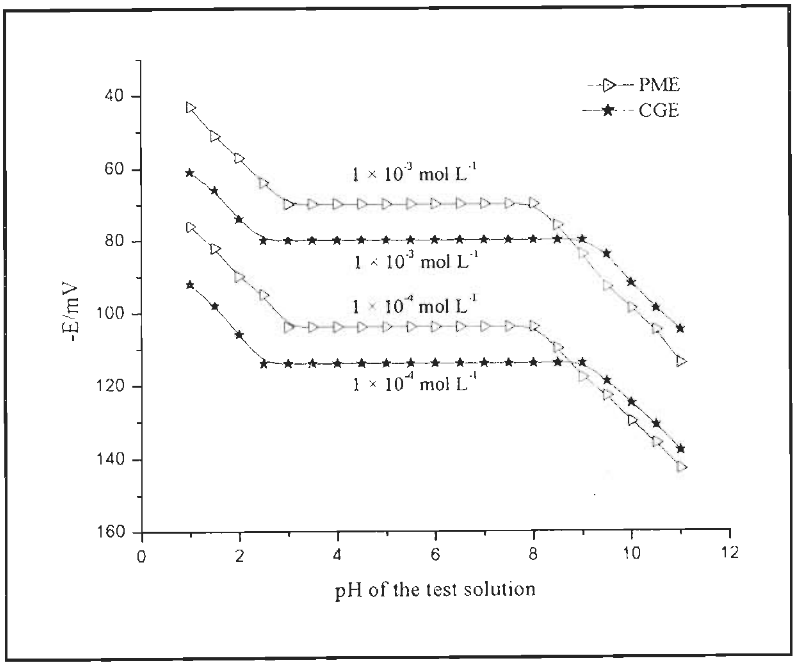


Fig. 3.21 Effect of pH of the test solutions on the potential responses of the PME and CGE at different concentration of Zn^{2+}

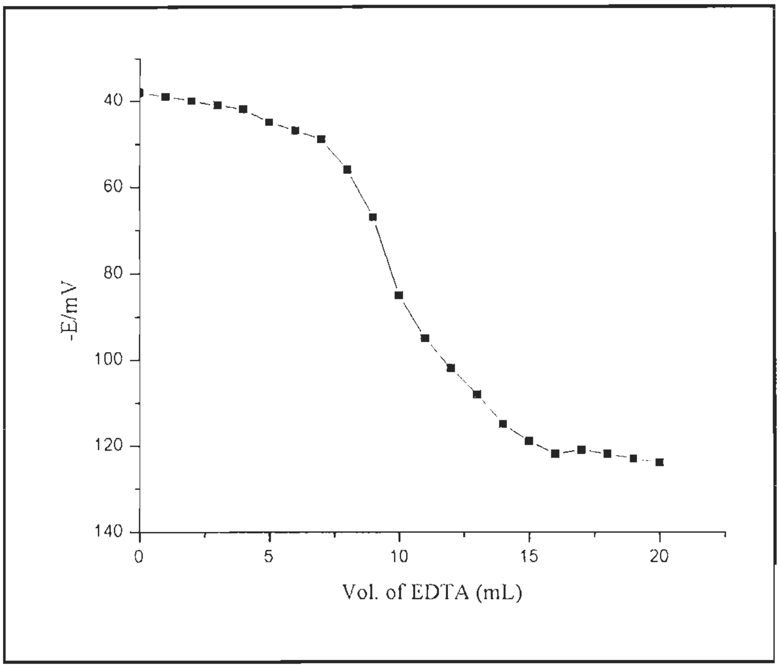


Fig. 3.22 Potentiometric titration curve of 20 mL of 1.0 × 10^{-3} mol L^{-1} solution of Zn^{2+} ion with 1.0 × 10^{-2} mol L^{-1} EDTA at pH 5.5 using CGE as indicator electrode

Table 3.1 Optimization of membrane compositions and their potentiometric response for Ni^{2+} ion selective membrane based on ionophore (I)

S.no.	Composition of membrane (w/w; mg)								Working concentration range (mol L^{-1})	Slope (mV decade^{-1} of activity)	Detection limit (mol L^{-1})
	I	PVC	NaTBP	TBP	DBP	NPOE	DOP	CN			
1	6	190	4	–	–	–	–	–	1.0×10^{-1} to 4.8×10^{-5}	38.4	3.1×10^{-6}
2	6	90	4	100	–	–	–	–	1.0×10^{-1} to 4.6×10^{-7}	29.5	2.7×10^{-7}
3	6	90	4	–	100	–	–	–	1.0×10^{-1} to 5.0×10^{-6}	37.2	2.1×10^{-6}
4	6	90	4	–	–	100	–	–	1.0×10^{-1} to 4.4×10^{-6}	31.5	7.6×10^{-6}
5	6	90	4	–	–	–	100	–	1.0×10^{-1} to 5.2×10^{-5}	44.3	2.3×10^{-5}
6	6	90	4	–	–	–	–	100	1.0×10^{-1} to 5.4×10^{-6}	33.4	1.4×10^{-6}

Table 3.2 Response characteristics of the nickel ion-selective electrodes based on PME and CGE

Properties	Values / range	
	PME	CGE
Optimized membrane composition	(I) (6 mg):PVC (90 mg): TBP (100 mg):NaTPB (4 mg)	(I) (6 mg):PVC (90 mg): TBP (100 mg):NaTPB (4 mg)
Conditioning time	2 days in 0.1 mol L^{-1} $NiCl_2$	2 days in 0.1 mol L^{-1} $NiCl_2$
Working concentration range (mol L^{-1})	4.6×10^{-7}-1.0×10^{-1}	7.7×10^{-8}-1.0×10^{-1}
Detection limit (mol L^{-1})	2.7×10^{-7}	3.7×10^{-8}
Slope (mV decade^{-1} of activity)	29.5	29.5
S.D. of slope	± 0.3	± 0.2
Response time (s)	10	8
Life span	4 months	5 months
pH range	3.0-8.0	3.0-8.0

Table 3.3 Selectivity coefficient of various interfering ions for Ni^{2+} ion-selective electrodes based on ionophore I

Metal ions	Selectivity Coefficient ($K_{A,B}^{MPM}$)	
	PME	CGE
Co^{2+}	4.6×10^{-2}	6.2×10^{-3}
Cu^{2+}	6.2×10^{-2}	6.0×10^{-3}
Na^{+}	5.5×10^{-2}	5.2×10^{-3}
Cd^{2+}	4.5×10^{-2}	4.0×10^{-3}
K^{+}	3.5×10^{-3}	1.4×10^{-3}
Ba^{2+}	4.1×10^{-3}	2.1×10^{-3}
Ca^{2+}	4.7×10^{-3}	4.2×10^{-4}
Cr^{3+}	3.4×10^{-3}	3.8×10^{-4}
Zn^{2+}	2.8×10^{-3}	3.4×10^{-4}
Sr^{2+}	2.5×10^{-3}	3.0×10^{-4}
Mn^{2+}	2.3×10^{-3}	2.7×10^{-4}
Hg^{2+}	2.2×10^{-3}	2.6×10^{-4}
Fe^{3+}	1.8×10^{-3}	2.1×10^{-4}
Pb^{2+}	1.5×10^{-3}	1.6×10^{-4}
Al^{3+}	1.2×10^{-3}	1.1×10^{-4}
Bi^{3+}	2.8×10^{-4}	4.1×10^{-5}

Table 3.4 Effect of partially non-aqueous medium on the working of Ni^{2+} selective sensor (CGE) based on I

Non-aqueous content (%; v/v)	Working concentration range (mol L^{-1})	Slope (mV $decade^{-1}$ of activity)
0	7.7×10^{-8}-1.0×10^{-1}	29.5
Methanol		
10	7.7×10^{-8}-1.0×10^{-1}	29.5
20	7.7×10^{-8}-1.0×10^{-1}	29.5
25	7.4×10^{-8}-1.0×10^{-1}	29.3
30	9.2×10^{-7}-1.0×10^{-1}	26.5
35	3.2×10^{-7}-1.0×10^{-1}	21.8
Ethanol		
10	7.7×10^{-8}-1.0×10^{-1}	29.5
20	7.7×10^{-8}-1.0×10^{-1}	29.5
25	7.1×10^{-8}-1.0×10^{-1}	29.4
30	8.7×10^{-7}-1.0×10^{-1}	25.8
35	4.1×10^{-7}-1.0×10^{-1}	19.2
Acetonitrile		
10	7.7×10^{-8}-1.0×10^{-1}	29.5
20	7.7×10^{-8}-1.0×10^{-1}	29.5
25	9.8×10^{-7}-1.0×10^{-1}	27.3
30	8.3×10^{-7}-1.0×10^{-1}	24.3
35	5.2×10^{-6}-1.0×10^{-1}	18.4

Table 3.5 Determination of Ni^{2+} ion in some fruit juice samples with the sensor (CGE) based on I

Type of juices	ISE[a] (mg L^{-1})	AAS[a] (mg L^{-1})	Confidence Limit (%)
Grapes juice	0.019 ± 0.001	0.02 ± 0.002	95
Pineapple juice	0.27 ± 0.02	0.28 ± 0.03	98
Lime juice	0.39 ± 0.01	0.40 ± 0.02	95
Lemon juice	0.019 ± 0.001	0.02 ± 0.001	95

Table 3.6 Analytical data of Ni^{2+} ion concentration in wine samples as determined with CGE and AAS

Wine samples	Concentration of Ni^{2+} as determined by ISE[a] (μg L^{-1})	Concentration of Ni^{2+} as determined by AAS[a] (μg L^{-1})	Confidence Limit (%)
Red wine	46.6 ± 0.1	46.3 ± 0.2	95
White wine	33.5 ± 0.2	33.2 ± 0.3	99
Rose wine	22.3 ± 0.1	22.1 ± 0.2	96
Champagne	17.9 ± 0.1	17.4 ± 0.3	95

[a] *Results are based on triplicate measurements*

Table 3.7 Formation constants of ionophores II(a) and II(b) with different metal ions

Metal ions	Formation constant (log $\beta_{\mathrm{IL}n}$)* ±SD	Metal ions	Formation constant (log $\beta_{\mathrm{IL}n}$)* ±SD
	II(a)		**II(b)**
Co^{2+}	5.56 ± 0.04	Co^{2+}	6.73 ± 0.01
La^{3+}	4.27 ± 0.08	La^{3+}	4.55 ± 0.05
Ce^{3+}	4.50 ± 0.07	Ce^{3+}	4.71 ± 0.13
Na^{+}	4.02 ± 0.05	Na^{+}	4.21 ± 0.03
K^{+}	3.71 ± 0.05	K^{+}	4.11 ± 0.14
Ag^{+}	3.15 ± 0.07	Ag^{+}	3.44 ± 0.04
NH_4^{+}	3.04 ± 0.06	NH_4^{+}	3.32 ± 0.08
Cd^{2+}	2.70 ± 0.04	Cd^{2+}	2.98 ± 0.07
Cr^{3+}	2.52 ± 0.07	Cr^{3+}	2.77 ± 0.02
Ca^{2+}	2.10 ± 0.09	Ca^{2+}	2.21 ± 0.14
Sr^{2+}	1.45 ± 0.04	Sr^{2+}	1.52 ± 0.07
Cu^{2+}	5.00 ± 0.06	Cu^{2+}	5.74 ± 0.03
Zn^{2+}	4.85 ± 0.05	Zn^{2+}	5.41 ± 0.12
Ni^{2+}	4.70 ± 0.05	Ni^{2+}	5.02 ± 0.08
Ba^{2+}	3.24 ± 0.05	Ba^{2+}	3.64 ± 0.02
Pb^{2+}	3.44 ± 0.04	Pb^{2+}	3.89 ± 0.06
Al^{3+}	2.33 ± 0.07	Al^{3+}	2.50 ± 0.03
Hg^{2+}	2.90 ± 0.05	Hg^{2+}	3.14 ± 0.11
Fe^{3+}	1.78 ± 0.07	Fe^{3+}	1.89 ± 0.01
Mg^{2+}	1.00 ± 0.06	Mg^{2+}	1.12 ± 0.05

Table 3.8 Optimization of membrane compositions and their potentiometric response for Co^{2+} ion selective membrane based on ionophore II(a)

S.no.	II(a) (mg)	NaTPB (mg)	KTpClPB (mg)	DBP (mg)	BA (mg)	DOP (mg)	NPOE (mg)	TBP (mg)	PVC (mg)	Working Concentration Range (mol L^{-1})	Slope (mV $decade^{-1}$ of activity)	Detection limit (mol L^{-1})
1	7	-	-	-	-	-	-	-	93	3.4×10^{-5} to 1.0×10^{-1}	28.2	1.9×10^{-5}
2	7	-	-	55	-	-	-	-	38	3.9×10^{-5} to 1.0×10^{-1}	24.7	2.1×10^{-5}
3	7	-	-	-	55	-	-	-	38	3.1×10^{-5} to 1.0×10^{-1}	33.5	1.1×10^{-5}
4	7	-	-	-	-	55	-	-	38	7.6×10^{-7} to 1.0×10^{-1}	32.0	5.2×10^{-7}
5	7	-	-	-	-	-	55	-	38	9.5×10^{-6} to 1.0×10^{-1}	31.2	4.5×10^{-6}
6	7	-	-	-	-	-	-	55	38	8.7×10^{-6} to 1.0×10^{-1}	26.7	2.1×10^{-6}
7	7	3	-	-	-	55	-	-	35	5.5×10^{-7} to 1.0×10^{-1}	31.0	3.6×10^{-7}
8	7	-	3	-	-	55	-	-	35	4.6×10^{-7} to 1.0×10^{-1}	29.9	2.2×10^{-7}
9	6	-	3	-	-	55	-	-	36	9.9×10^{-7} to 1.0×10^{-1}	34.3	7.6×10^{-7}
10	8	-	3	-	-	55	-	-	34	6.7×10^{-6} to 1.0×10^{-1}	27.9	5.4×10^{-6}
11	7	-	2	-	-	55	-	-	36	2.2×10^{-6} to 1.0×10^{-1}	25.3	1.1×10^{-6}
12	7	-	4	-	-	55	-	-	34	8.8×10^{-5} to 1.0×10^{-1}	28.7	6.3×10^{-5}

Table 3.9 Optimization of membrane compositions and their potentiometric response for Co^{2+} ion selective membrane based on ionophore II(b)

	Composition of membrane (w/w; mg)									Working concentration range (mol L^{-1})	Slope (mV $decade^{-1}$ of activity	Detection limit (mol L^{-1})
S.no	II(b)	NaTBP	KTpClPB	DBP	BA	DOP	NPOE	TBP	PVC			
13	6	-	-	-	-	-	-	-	94	2.6×10^{-5} to 1.0×10^{-1}	27.8	1.2×10^{-5}
14	6	-	-	53	-	-	-	-	41	2.2×10^{-6} to 1.0×10^{-1}	23.6	8.1×10^{-7}
15	6	-	-	-	53	-	-	-	41	9.8×10^{-7} to 1.0×10^{-1}	22.0	4.8×10^{-7}
16	6	-	-	-	-	53	-	-	41	9.1×10^{-6} to 1.0×10^{-1}	31.1	4.1×10^{-6}
17	6	-	-	-	-	-	53	-	41	8.3×10^{-6} to 1.0×10^{-1}	27.3	3.0×10^{-6}
18	6	-	-	-	-	-	-	53	41	8.1×10^{-8} to 1.0×10^{-1}	30.0	7.2×10^{-8}
19	6	2	-	-	-	-	-	53	39	6.0×10^{-8} to 1.0×10^{-1}	29.7	4.7×10^{-8}
20	6	-	2	-	-	-	-	53	39	1.8×10^{-7} to 1.0×10^{-1}	27.1	9.7×10^{-8}
21	7	2	-	-	-	-	-	53	38	4.3×10^{-7} to 1.0×10^{-1}	25.7	2.5×10^{-7}
22	5	2	-	-	-	-	-	53	40	8.7×10^{-7} to 1.0×10^{-1}	28.4	6.2×10^{-7}
23	6	1	-	-	-	-	-	53	40	1.0×10^{-7} to 1.0×10^{-1}	32.2	8.6×10^{-8}
24	6	3	-	-	-	-	-	53	38	9.8×10^{-7} to 1.0×10^{-1}	26.7	5.1×10^{-7}

Table 3.10 Response characteristics of the Co^{2+} ion-selective electrodes based on PME and CGE

Properties	Values / range	
	PME	CGE
Optimized membrane composition	II(b) (6 mg): PVC (39 mg): TBP (53 mg) : NaTPB (2 mg)	II(b) (6 mg): PVC (39 mg): TBP (53 mg) : NaTPB (2 mg)
Conditioning time	2 days in 0.1 mol L^{-1} $Co(NO_3)_2$	2 days in 0.1 mol L^{-1} $Co(NO_3)_2$
Working concentration range (mol L^{-1})	6.0×10^{-8} to 1.0×10^{-1}	1.3×10^{-8} to 1.0×10^{-1}
Detection limit (mol L^{-1})	4.7×10^{-8}	6.8×10^{-9}
Slope (mV decade^{-1} of activity)	29.7	29.5
S.D. of slope	± 0.2	± 0.1
Response time (s)	11	8
Life span	3 months	4 months
pH range	2.5-8.5	2.0-9.0

Table 3.11 Effect of Soaking time on the potential response of the Co^{2+} ion-selective electrode.

Soaking Time	Slope (mV decade^{-1} of activity)	Working Concentration Range (mol L^{-1})	Detection Limit (mol L^{-1})
PME			
2 days	29.7	6.0×10^{-8} to 1.0×10^{-1}	4.7×10^{-8}
10 days	29.7	6.5×10^{-8} to 1.0×10^{-1}	4.9×10^{-8}
25 days	29.4	7.0×10^{-8} to 1.0×10^{-1}	5.3×10^{-8}
45 days	29.2	7.9×10^{-8} to 1.0×10^{-1}	6.0×10^{-8}
70 days	28.9	8.4×10^{-8} to 1.0×10^{-1}	7.1×10^{-8}
90 days	28.5	9.7×10^{-8} to 1.0×10^{-1}	7.9×10^{-8}
95 days	23.1	4.2×10^{-7} to 1.0×10^{-1}	2.3×10^{-7}
CGE			
2 days	29.5	1.3×10^{-8} to 1.0×10^{-1}	6.8×10^{-9}
10 days	29.4	1.8×10^{-8} to 1.0×10^{-1}	7.0×10^{-9}
25 days	29.2	2.6×10^{-8} to 1.0×10^{-1}	7.3×10^{-9}
45 days	29.0	3.1×10^{-8} to 1.0×10^{-1}	7.9×10^{-9}
70 days	28.9	4.8×10^{-8} to 1.0×10^{-1}	8.4×10^{-9}
90 days	28.6	6.1×10^{-8} to 1.0×10^{-1}	8.8×10^{-9}
105 days	28.4	7.4×10^{-8} to 1.0×10^{-1}	9.0×10^{-9}
120 days	28.2	9.1×10^{-8} to 1.0×10^{-1}	9.8×10^{-9}
125 days	24.5	1.5×10^{-7} to 1.0×10^{-1}	9.4×10^{-8}

Table 3.12 Selectivity coefficient of various interfering ions for Co^{2+} selective electrode

Metal ions	Selectivity coefficient ($K_{A,B}$)			
	PME		CGE	
	FIM	MPM	FIM	MPM
La^{3+}	4.9×10^{-2}	5.6×10^{-2}	3.8×10^{-3}	4.9×10^{-3}
Ce^{3+}	4.1×10^{-2}	5.2×10^{-2}	3.2×10^{-3}	4.5×10^{-3}
Na^{+}	5.3×10^{-2}	5.9×10^{-2}	4.1×10^{-3}	5.2×10^{-3}
K^{+}	5.7×10^{-2}	6.6×10^{-2}	4.5×10^{-3}	5.8×10^{-3}
Ag^{+}	7.1×10^{-2}	7.9×10^{-2}	6.2×10^{-3}	7.0×10^{-3}
NH_4^{+}	7.8×10^{-2}	8.1×10^{-2}	6.7×10^{-3}	7.6×10^{-3}
Cd^{2+}	8.9×10^{-2}	8.8×10^{-2}	8.2×10^{-3}	8.6×10^{-3}
Cr^{3+}	9.3×10^{-2}	9.5×10^{-2}	9.1×10^{-3}	9.4×10^{-3}
Ca^{2+}	1.8×10^{-3}	2.3×10^{-3}	2.5×10^{-4}	3.1×10^{-4}
Sr^{2+}	2.7×10^{-3}	3.5×10^{-3}	4.1×10^{-4}	4.9×10^{-4}
Cu^{2+}	2.6×10^{-2}	3.1×10^{-2}	1.6×10^{-3}	2.7×10^{-3}
Zn^{2+}	3.2×10^{-2}	4.6×10^{-2}	2.3×10^{-3}	3.2×10^{-3}
Ni^{2+}	3.8×10^{-2}	4.9×10^{-2}	2.9×10^{-3}	3.8×10^{-3}
Ba^{2+}	6.6×10^{-2}	7.4×10^{-2}	5.9×10^{-3}	6.6×10^{-3}
Pb^{2+}	6.4×10^{-2}	6.9×10^{-2}	5.6×10^{-3}	6.1×10^{-3}
Al^{3+}	9.7×10^{-2}	9.9×10^{-2}	9.7×10^{-3}	9.8×10^{-3}
Hg^{2+}	8.5×10^{-2}	8.6×10^{-2}	7.3×10^{-3}	8.3×10^{-3}
Fe^{3+}	2.2×10^{-3}	2.9×10^{-3}	3.7×10^{-4}	4.3×10^{-4}
Mg^{2+}	3.0×10^{-3}	4.2×10^{-3}	5.2×10^{-4}	5.7×10^{-4}

Table 3.13 Effect of partially non-aqueous medium on the working of Co^{2+} selective sensor (CGE)

Non-aqueous content (%; v/v)	Working concentration range (mol L^{-1})	Slope (mV $decade^{-1}$ of activity)
0	1.3×10^{-8} to 1.0×10^{-1}	29.5
Methanol		
10	1.3×10^{-8} to 1.0×10^{-1}	29.5
20	1.3×10^{-8} to 1.0×10^{-1}	29.5
30	1.4×10^{-8} to 1.0×10^{-1}	29.4
35	1.6×10^{-8} to 1.0×10^{-1}	29.2
40	3.3×10^{-7} to 1.0×10^{-1}	26.5
Ethanol		
10	1.3×10^{-8} to 1.0×10^{-1}	29.5
20	1.3×10^{-8} to 1.0×10^{-1}	29.5
30	1.5×10^{-8} to 1.0×10^{-1}	29.3
35	1.8×10^{-8} to 1.0×10^{-1}	29.1
40	5.2×10^{-7} to 1.0×10^{-1}	25.2
Acetonitrile		
10	1.3×10^{-8} to 1.0×10^{-1}	29.5
20	1.6×10^{-8} to 1.0×10^{-1}	29.4
25	1.9×10^{-8} to 1.0×10^{-1}	29.1
30	1.0×10^{-7} to 1.0×10^{-1}	24.7

Table 3.14 Effect of different surfactants on the performance of Co^{2+} ion-selective electrode

Interfering ions	-log (Selectivity Coefficients)			
	Without Surfactant	With >10^{-4} mol L^{-1} CTAB	With >10^{-4} mol L^{-1} SDS	With >10^{-4} mol L^{-1} Triton X- 100
La^{3+}	2.42	2.01	2.47	2.32
Ce^{3+}	2.49	2.51	2.37	2.11
Na^{+}	2.38	1.92	2.03	2.21
K^{+}	2.34	2.30	2.22	1.98
Ag^{+}	2.20	2.15	2.05	2.13
NH_4^{+}	2.17	1.83	2.11	2.23
Cd^{2+}	2.05	2.10	2.18	2.00
Cr^{3+}	2.04	2.01	1.31	1.57
Ca^{2+}	3.60	3.57	3.17	3.22
Sr^{2+}	3.38	3.13	2.95	3.07
Cu^{2+}	2.79	2.98	2.15	2.38
Zn^{2+}	2.63	2.42	2.52	2.20
Ni^{2+}	2.53	2.61	2.49	2.01
Ba^{2+}	2.22	2.38	2.00	1.51
Pb^{2+}	2.25	2.11	1.67	1.01
Al^{3+}	2.01	1.83	1.94	2.11
Hg^{2+}	2.13	2.01	1.95	1.61
Fe^{3+}	3.43	3.71	3.05	2.77
Mg^{2+}	3.28	3.30	3.18	2.96
Slope (mV decade^{-1} of activity)	29.5	33.2	26.7	21.1
Detection limit (mol L^{-1})	6.8×10^{-9}	3.7×10^{-7}	5.3×10^{-6}	7.1×10^{-5}
Working Concentration range (mol L^{-1})	1.3×10^{-8} to 1.0×10^{-1}	6.2×10^{-7} to 1.0×10^{-1}	9.9×10^{-6} to 1.0×10^{-1}	8.7×10^{-5} to 1.0×10^{-1}

Table 3.15 Potentiometric determination of Co^{2+} ions in different water samples by CGE

Samples	ISE[a] (mg/mL)	AAS[a] (mg/mL)
Fresh water	0.58 ± 0.01	0.61 ± 0.03
River water	6.47 ± 0.02	6.46 ± 0.02
Sea water	13.26 ± 0.01	13.22 ± 0.02

[a] *Results of triplicate measurements*

Table 3.16 Potentiometric determination of Co^{2+} ion in beer by CGE

Added to beer (ppm)	Found by analysis (ppm)	Recovery (%)
0.60	0.59 ± 0.02	98
0.85	0.84 ± 0.01	99
1.00	1.00 ± 0.02	100
1.20	1.18 ± 0.03	98
1.50	1.50 ± 0.02	100

Table 3.17 Quantitative determination of cobalt in pharmaceutical samples by CGE

S.No.	Samples	Certified Value (ppm)	Cobalt Found (ppm)	
			Proposed method	AAS method
1	Neurobion (Inj.) Merck, India	21.74	21.73 ± 0.01	21.71 ± 0.02
2	Sioneuron (Inj.) Albert David Ltd., India	10.86	10.84 ± 0.02	10.82 ± 0.02

Table 3.18 The formation constants of III(a)-M^{n+} and III(b)-M^{n+} complexes using sandwich and Conductometric methods

Metal Cations	Formation constant (log β_{IL_n}) ±CI (Sandwich Method)	Formation constant (log β_{IL_n}) ±CI (Conductometric Method)	Metal Cations	Formation constant (log β_{IL_n}) ±CI (Sandwich Method)	Formation constant (log β_{IL_n}) ±CI (Conductometric Method)
	III(a)			III(b)	
Zn^{2+}	5.460 ± 0.045	6.171 ± 0.045	Zn^{2+}	6.321 ± 0.056	7.253 ± 0.022
Cd^{2+}	4.902 ± 0.033	6.004 ± 0.056	Cd^{2+}	5.773 ± 0.056	6.504 ± 0.033
Hg^{2+}	4.840 ± 0.079	5.922 ± 0.079	Hg^{2+}	5.704 ± 0.033	6.100 ± 0.045
Na^{+}	4.771 ± 0.056	5.862 ± 0.079	Na^{+}	5.622 ± 0.022	5.970 ± 0.033
K^{+}	4.601 ± 0.033	5.700 ± 0.056	K^{+}	5.462 ± 0.045	5.800 ± 0.056
Ni^{2+}	4.510 ± 0.022	5.560 ± 0.045	Ni^{2+}	5.320 ± 0.045	5.773 ± 0.079
Li^{+}	4.484 ± 0.079	5.400 ± 0.033	Li^{+}	5.241 ± 0.033	5.623 ± 0.045
Pb^{2+}	4.403 ± 0.067	5.251 ± 0.067	Pb^{2+}	5.200 ± 0.045	5.512 ± 0.045
Cu^{2+}	4.390 ± 0.067	5.011 ± 0.045	Cu^{2+}	5.150 ± 0.045	5.431 ± 0.067
Fe^{3+}	4.200 ± 0.033	4.870 ± 0.079	Fe^{3+}	5.040 ± 0.079	5.270 ± 0.033
Cr^{3+}	4.100 ± 0.045	4.643 ± 0.067	Cr^{3+}	4.970 ± 0.079	5.190 ± 0.045
Mg^{2+}	3.972 ± 0.033	4.564 ± 0.056	Mg^{2+}	4.870 ± 0.067	5.000 ± 0.079
Ba^{2+}	3.844 ± 0.033	4.484 ± 0.045	Ba^{2+}	4.634 ± 0.056	4.800 ± 0.056
Sr^{2+}	3.753 ± 0.045	4.362 ± 0.079	Sr^{2+}	4.553 ± 0.045	4.724 ± 0.033
Ag^{+}	3.532 ± 0.045	4.201 ± 0.045	Ag^{+}	4.470 ± 0.079	4.664 ± 0.045
Co^{2+}	3.422 ± 0.045	4.030 ± 0.067	Co^{2+}	4.401 ± 0.067	4.522 ± 0.056
Ce^{3+}	3.360 ± 0.079	3.950 ± 0.056	Ce^{3+}	4.321 ± 0.067	4.460 ± 0.033
Ca^{2+}	3.201 ± 0.033	3.900 ± 0.045	Ca^{2+}	4.150 ± 0.056	4.370 ± 0.033

Table 3.19 Optimization of membrane composition based on III(a) and performance in Zn^{2+} ion selective electrodes

S.No.	III(a) (mg)	Composition of membrane (w/w; mg)								Working Concentration Range (mol L^{-1})	Detection Limit (mol L^{-1})	Slope (mV $decade^{-1}$ of activity)
		NaTPB	KTpClPB	DBP	TBP	NPOE	DOP	BA	PVC			
1	6	-	-	-	-	-	-	-	94	4.4×10^{-5} to 1.0×10^{-2}	2.8×10^{-5}	27.6±0.5
2	6	-	-	60	-	-	-	-	34	2.0×10^{-5} to 1.0×10^{-2}	1.1×10^{-5}	30.5±0.6
3	6	-	-	-	60	-	-	-	34	8.1×10^{-6} to 1.0×10^{-2}	7.2×10^{-6}	25.2±0.4
4	6	-	-	-	-	60	-	-	34	4.0×10^{-6} to 1.0×10^{-2}	1.9×10^{-6}	31.4±0.4
5	6	-	-	-	-	-	60	-	34	5.6×10^{-6} to 1.0×10^{-2}	3.4×10^{-6}	28.0±0.2
6	6	-	-	-	-	-	-	60	34	1.4×10^{-5} to 1.0×10^{-2}	8.6×10^{-6}	33.1±0.7
7	6	1	-	-	-	-	60	-	33	2.7×10^{-6} to 1.0×10^{-2}	1.2×10^{-6}	28.6±0.6
8	6	-	1	-	-	-	60	-	33	6.4×10^{-5} to 1.0×10^{-2}	2.8×10^{-5}	27.9±0.3
9	6	2	-	-	-	-	60	-	32	9.0×10^{-6} to 1.0×10^{-2}	6.1×10^{-6}	28.2±0.2
10	5	1	-	-	-	-	60	-	34	6.7×10^{-6} to 1.0×10^{-2}	4.4×10^{-6}	24.2±0.5
11	7	1	-	-	-	-	60	-	32	8.8×10^{-6} to 1.0×10^{-2}	5.3×10^{-6}	26.6±0.6

Table 3.20 Optimization of membrane composition based on III(b) and performance in Zn^{2+} ion selective electrodes

S.No	III(b) (mg)	Composition of membrane (w/w; mg)								Working Concentration Range (mol L^{-1})	Detection Limit (mol L^{-1})	Slope (mV $decade^{-1}$ of activity)
		NaTPB	KTpClPB	DBP	TBP	NPOE	DOP	BA	PVC			
12	4	-	-	-	-	-	-	-	96	4.1×10^{-5} to 1.0×10^{-2}	2.6×10^{-5}	31.6±0.7
13	4	-	-	57	-	-	-	-	39	9.5×10^{-6} to 1.0×10^{-2}	8.4×10^{-6}	25.7±0.4
14	4	-	-	-	57	-	-	-	39	1.5×10^{-6} to 1.0×10^{-2}	7.5×10^{-7}	28.3±0.7
15	4	-	-	-	-	57	-	-	39	1.5×10^{-5} to 1.0×10^{-2}	9.2×10^{-6}	30.2±0.6
16	4	-	-	-	-	-	57	-	39	1.9×10^{-6} to 1.0×10^{-2}	1.0×10^{-6}	30.8±0.6
17	4	-	-	-	-	-	-	57	39	8.5×10^{-6} to 1.0×10^{-2}	7.0×10^{-6}	26.4±0.3
18	4	2	-	-	57	-	-	-	37	5.0×10^{-7} to 1.0×10^{-2}	3.3×10^{-7}	28.8±0.3
19	4	-	2	-	57	-	-	-	37	8.7×10^{-6} to 1.0×10^{-2}	4.5×10^{-6}	23.6±0.2
20	4	3	-	-	57	-	-	-	36	6.8×10^{-6} to 1.0×10^{-2}	3.8×10^{-6}	27.2±0.4
21	4	1	-	-	57	-	-	-	38	9.8×10^{-6} to 1.0×10^{-2}	7.9×10^{-6}	27.0±0.5
22	5	2	-	-	57	-	-	-	36	1.2×10^{-6} to 1.0×10^{-2}	9.2×10^{-7}	28.5±0.5
23	3	2	-	-	57	-	-	-	38	2.3×10^{-5} to 1.0×10^{-2}	9.6×10^{-6}	27.8±0.3

Table 3.21 Response characteristics of the Zn^{2+} ion-selective electrodes based on PME and CGE

Properties	Values / range	
	PME	CGE
Optimized membrane composition	III(b) (4 mg): PVC (37 mg): TBP (57 mg) : NaTPB (2 mg)	III(b) (4 mg): PVC (37 mg): TBP (57 mg) : NaTPB (2 mg)
Conditioning time	3 days in 0.01 mol L^{-1} $Zn(NO_3)_2$	3 days in 0.01 mol L^{-1} $Zn(NO_3)_2$
Working concentration range (mol L^{-1})	5.0×10^{-7} to 1.0×10^{-2}	1.9×10^{-7} to 1.0×10^{-2}
Detection limit (mol L^{-1})	3.3×10^{-7}	7.9×10^{-8}
Slope (mV decade^{-1} of activity)	28.8 ± 0.3	29.2 ± 0.2
Response time (s)	12	10
Life span	35 days	55 days
pH range	3.0-8.0	2.5-9.0

Table 3.22 Effect of Soaking time on the potential response of the Zn^{2+} ion-selective electrode

Soaking Time	Slope (mV decade^{-1} of activity)	Working Concentration Range (mol L^{-1})	Detection Limit (mol L^{-1})
PME			
2 days	28.8 ± 0.3	5.0×10^{-7} to 1.0×10^{-2}	3.3×10^{-7}
10 days	28.6 ± 0.3	5.5×10^{-7} to 1.0×10^{-2}	3.6×10^{-7}
20 days	28.4 ± 0.4	5.7×10^{-7} to 1.0×10^{-2}	3.8×10^{-7}
30 days	28.3 ± 0.2	6.0×10^{-7} to 1.0×10^{-2}	4.5×10^{-7}
35 days	28.0 ± 0.3	6.3×10^{-7} to 1.0×10^{-2}	5.3×10^{-7}
40 days	25.3 ± 0.3	8.5×10^{-6} to 1.0×10^{-2}	5.4×10^{-6}
CGE			
2 days	29.2 ± 0.2	1.9×10^{-7} to 1.0×10^{-2}	7.9×10^{-8}
10 days	29.1 ± 0.3	2.2×10^{-7} to 1.0×10^{-2}	8.1×10^{-8}
20 days	29.0 ± 0.2	2.5×10^{-7} to 1.0×10^{-2}	8.6×10^{-8}
30 days	28.8 ± 0.3	2.7×10^{-7} to 1.0×10^{-2}	8.9×10^{-8}
40 days	28.6 ± 0.2	3.0×10^{-7} to 1.0×10^{-2}	9.2×10^{-8}
50 days	28.2 ± 0.3	3.2×10^{-7} to 1.0×10^{-2}	9.6×10^{-8}
55 days	28.0 ± 0.4	3.6×10^{-7} to 1.0×10^{-2}	9.7×10^{-8}
60 days	25.4 ± 0.5	7.7×10^{-6} to 1.0×10^{-2}	2.5×10^{-8}

Table 3.23 Selectivity coefficient of various interfering ions for Zn^{2+} ion selective electrodes

Metal ions	Selectivity coefficient (-log $K_{A,B}^{FIM}$)	Metal ions	Selectivity coefficient (-log $K_{A,B}^{FIM}$)
Cd^{2+}	1.340 ± 0.045	Hg^{2+}	1.194 ± 0.056
Ni^{2+}	1.040 ± 0.022	K^{+}	1.072 ± 0.033
Pb^{2+}	2.672 ± 0.033	Li^{+}	1.021 ± 0.033
Na^{+}	1.142 ± 0.045	Cr^{3+}	2.282 ± 0.045
Mg^{2+}	2.223 ± 0.022	Sr^{2+}	2.140 ± 0.056
Fe^{3+}	2.324 ± 0.033	Ca^{2+}	2.030 ± 0.045
Cu^{2+}	2.434 ± 0.067	Ag^{+}	2.100 ± 0.033
Ba^{2+}	2.170 ± 0.033	Ce^{3+}	2.060 ± 0.033
Co^{2+}	2.080 ± 0.045		

Table 3.24 Effect of partially non-aqueous medium on the working of Zn^{2+} selective sensor (CGE)

Non-aqueous content (%; v/v)	Working concentration range (mol L^{-1})	Slope (mV $decade^{-1}$ of activity)
0	1.9×10^{-7} to 1.0×10^{-2}	29.2 ± 0.2
Methanol		
10	1.9×10^{-7} to 1.0×10^{-2}	29.2 ± 0.2
20	2.2×10^{-7} to 1.0×10^{-2}	29.0 ± 0.3
30	2.7×10^{-7} to 1.0×10^{-2}	28.8 ± 0.5
35	3.4×10^{-7} to 1.0×10^{-2}	28.6 ± 0.3
40	9.3×10^{-6} to 1.0×10^{-2}	26.5 ± 0.2
Ethanol		
10	1.9×10^{-7} to 1.0×10^{-2}	29.2 ± 0.4
20	2.4×10^{-7} to 1.0×10^{-2}	28.9 ± 0.3
30	3.9×10^{-7} to 1.0×10^{-2}	28.6 ± 0.5
35	4.3×10^{-7} to 1.0×10^{-2}	28.3 ± 0.5
40	7.1×10^{-6} to 1.0×10^{-2}	24.6 ± 0.3
Acetonitrile		
10	2.1×10^{-7} to 1.0×10^{-2}	29.0 ± 0.6
20	5.0×10^{-7} to 1.0×10^{-2}	28.5 ± 0.5
25	4.4×10^{-6} to 1.0×10^{-2}	23.4 ± 0.5

Table 3.25 Determination of Zn^{2+} ions in water samples by the proposed CGE

Sample	Ion selective electrode ± SD[a] ($\mu g\ mL^{-1}$)	AAS ± SD[a] ($\mu g\ mL^{-1}$)
Industrial waste water		
1.	18.63 ± 0.02	18.66 ± 0.03
2.	18.92 ± 0.03	18.90 ± 0.04
3.	17.54 ± 0.03	17.52 ± 0.03
River water		
1.	6.77 ± 0.04	6.74 ± 0.03
2.	6.82 ± 0.02	6.86 ± 0.03
3.	5.94 ± 0.03	5.96 ± 0.04

Table 3.26 Determination of Zn^{2+} ions in biological samples by the proposed CGE

Sample	Ion selective electrode ± SD[a] ($\mu g\ mL^{-1}$)	AAS ± SD[a] ($\mu g\ mL^{-1}$)
Blood		
1.	0.582 ± 0.04	0.580 ± 0.03
2.	0.645 ± 0.02	0.639 ± 0.04
3.	0.490 ± 0.02	0.495 ± 0.03
Urine		
1.	0.543 ± 0.03	0.538 ± 0.04
2.	0.621 ± 0.02	0.620 ± 0.03
3.	0.590 ± 0.03	0.594 ± 0.02

[a] Mean value ± standard deviation (three measurements)

Table 3.27 Determination of Zn^{2+} ions in milk and tea samples by the proposed CGE

Samples	No. of analyses	Sample ashed (mL/g)	Zn found in whole sample using ISE (µg)	Zn found in whole sample using AAS (µg)
Milk Samples				
Cow	3	100	273, 274, 279	273, 272, 276
Buffalo	3	100	224, 221, 223	225, 220, 222
Tea Samples				
Taj	3	2	129.0, 132.6, 134.1	129.4, 131.7, 134.3
Brooke Bond	3	2	77.6, 79.2, 80.7	78.1, 79.5, 80.3

REFERENCES

1. Merian, E.(ed.), Metals and their compounds in the environment, Part II, VCH, New York **22**, 1101 (1991).
2. Bohn, H.L., McNeal, B.L. and O'Connor, G.A., Soil Chemistry 2nd ed. Wiley Interscience, Chichester, 30 (1985).
3. Gupta, V.K., Jain, A.K., Singh, L.P. and Khurana, U, "Porphyrins as carrier in PVC based membrane potentiometric sensors for nickel(II)", *Anal. Chim. Acta*, **335**, 33 (1997).
4. Pungor, E., Toth, K. and Havas, J., "Nickel selective electrode based on nickel-dimethylglyoxime complex in silicone rubber", *Acta Chim. Acad. Sci. Hung.*, **48**, 17 (1996).
5. Lal, U.S., Chattopadhayaya, M.C. and Dey, A.K., "Heterogeneous ion-selective electrodes based on electroneutral ion carriers: barium(II) and nickel(II) electrodes", *J. Ind. Chem. Soc.*, **59**, 493 (1982).
6. Awasthi, S.P., Kulkarni, V.T. and Sundersane, M., "Nickel(II)-bis-2-ethylhexylphosphate as a sensor for nickel electrode", *J. Electrochem. Soc. India*, **37**, 309 (1988).
7. Buchanan, E.B. and Saego, J.L., "Study of impregnated silicone rubber membranes for potential indicating electrodes", *Anal. Chem.*, **40**, 517 (1968).
8. Ganjali, M.R., Hosseini, S.M., Javanbakht, M. and Hashemi, O.R., "Nickel(II) ion selective electrode based on 2,5-thiophenylbis(5-tert-butyl-1,3-benzooxazole)", *Anal. Lett.*, **33**, 3139 (2000).
9. Gupta, V.K., Singh, A.K. and Pal, M.K., "Nickel(II) selective sensors based on Schiff bases membranes in poly(vinyl chloride)", *Anal. Chim. Acta*, **624**, 223 (2000).
10. Gupta, V.K., Prasad, R. and Kumar, A., "Dibenzocyclam nickel(II) ionophore in PVC matrix for Ni^{2+} selective sensor", *Sensors*, **2**, 384 (2002).
11. Gupta, V.K., Jain, A.K., Singh, L.P. and Khurana, U., "Nickel(II)-selective sensors based on heterogeneous membranes of macrocyclic compounds", *Sens. Actuators B*, **40**, 15 (1997).
12. Singh, L.P. and Bhatnagar, J.M., "PVC based selective sensors for Ni^{2+} ion using carboxylated and methylated porphine", *Sensors*, **3**, 393 (2003).

13. Singh, A.K. and Saxena, P., "A PVC based membrane electrode for nickel(II) ions incorporating a tetraazamacrocycle as an ionophore", *Sens. Actuators B*, **121**, 349 (2007).
14. Zamani, H.A., Masrournia, M., Rostame-Faroge, M., Ganjali, M.R. and Behmadi, H., "Construction of Nickel (II) PVC Membrane Electrochemical Sensor Based on 5-Methoxy-5,6-Diphenyl-4,5 Dihydro-3(2H)- Pyridazinethione as a Novel Ionophore", *Sensor Letters*, **6**, 759 (2008).
15. Yu-Hua M., Ruo Y., Ya-Qin C., Xia W., Wei Z., Xin-Lu L. and Fan D., "New Ni(II) Ion-Selective Electrode Based on the N-S Schiff Base Ligand as Neutral Carrier in PVC Matrix", *Anal. Lett.*, **42**, 2411 (2009).
16. Kirk, O.R. and Othmer, F.D., "Encyclopedia of chemical technology", Wiley, **5**, 851, (1982).
17. Pais, I. and Benton, J., "The Handbook of Trace elements", St. Lucie Press, Florida, 240 (1996).
18. Ombetko, A.A., Rakhman'ko, E.M. and Lomako, V.L., "Ion selective electrode for determination of Cobalt", *Zh. Anal. Khim.*, **45**, 1592 (1990).
19. Su, Y., Wang, G., Jiang, Z. and Wang, D., "A new cobalt ion selective electrode using macrocyclic nitrogen-containing compound as a carrier", *Fenxi Huaxue*, **18**, 15 (1990).
20. Jain, A.K., Gupta, V.K., Singh, L.P. and Khurana, U., "Macrocycles based membranes for the determination of cobalt(II) ions", *Analyst*, **122**, 583 (1997).
21. Shamsipur, M., Rouhani, S., Poursaberi, T., Ganjali M.R., Sharghi, H. and Niknam, K., "Cobalt(II)-Selective Coated Graphite PVC-Membrane Electrode Based on a Recently Synthesized Dibenzopyridino-Substituted Macrocyclic Diamide", *Electroanalysis*, **14**, 729 (2002).
22. Shamsipur, M., Poursaberi, T., Rouhani, S., Niknam, K., Sharghi, H. and Ganjali, M.R., "Cobalt(II)-selective membrane electrode based on a recently synthesized benzo-substituted macrocyclic diamide", *Anal. Sci.*, **17**, 1049 (2001).
23. Singh, A.K., Singh, R.P. and Saxena, P., "Cobalt(II)-selective electrode based on a newly synthesized macrocyclic compound", *Sens. Actuators B*, **114**, 578 (2006).
24. Awasthi, S.P., Thembi, T.C., Kulkarni, V.T. and Sundareson, M., "Cobalt ion-selective electrode with bis(2-ethylhexyl)hydrogen phosphate and chelex-100 resin as sensor", *J. Electrochem. Soc. Ind.*, **49**, 23 (1991).

25. Volovik, A.M., Tomlachev, V.N. and Microshnik L.V., "Heterogeneous cobalt-selective electrode based on cellulose-acrylamide oxime-acrylhydroxamic acid polymer", *Zh. Anal. Khim.*, **40**, 481 (1985).
26. Lal, U.S., Chattopadhyaya, M.C. and Dey, A.K., "A heterogeneous cobalt(II) sensitive electrode and its applications", *Electrochimica Acta*, **26**, 283 (1981).
27. Mashhadizadeh, M.H., Momeni A. and Razavi, R., "Cobalt(II)-selective membrane electrode using a recently synthesized mercapto compound", *Anal. Chim. Acta*, **462**, 245 (2002).
28. Mashhadizadeh, M.H. and Sheikhshoaie, I., "Co^{2+}-selective membrane electrode based on the Schiff Base NADS", *Anal. Bioanal. Chem.*, **375**, 708 (2003).
29. Gupta, V.K., Singh, A.K., Mehtab, S. and Gupta, B., "A cobalt(II)-selective PVC membrane based on a Schiff base complex of N,N-bis(salicylidene)-3,4-diaminotoluene", *Anal. Chim. Acta*, **566**, 5 (2006).
30. Singh, A.K., Mehtab, S. and Saxena, P., "A novel potentiometric membrane sensor for determination of Co^{2+} based on 5-amino-3-methylisothiazol", *Sens Actuators B*, **120**, 455 (2007).
31. Gupta, V.K., Jain, A.K., Khayat, M.A., Bhargava, S.K. and Raisoni, J.R., "Electroanalytical studies on cobalt(II) selective potentiometric sensor based on bridge modified calixarene in poly(vinyl chloride)", *Electrochimica Acta*, **53**, 5409 (2008).
32. Kumar, P. and Shim, Y.B., "A novel cobalt(II)-selective potentiometric sensor based on p-(4-n-butylphenylazo)calix[4]aren", *Talanta*, **77**, 1057 (2009).
33. Pouretedal, H.R. and Keshavarz, M.H., "Cyclam modified carbon paste electrode as a potentiometric sensor for determination of cobalt (II) ions", *Chem. Res. Chin. Univ.*, **21**, 28 (2005).
34. Gupta, V.K., Chandra, S., Agarwal, S. and Lang, H. "A PVC based electrochemical sensor for cobalt(II) determination", *Proc. Ind. Nat. Sci. Acad.*, **70**, 399 (2004).
35. Zamani, H.A., Ganjali, M.R., Norouzi, P. and Adib, M., "Cobalt(II) Ion Detection in Electroplating Wastewater by a New Cobalt Ion-Selective Electrode Based on N′-[1-(2-thienyl)ethylidene]-2-furohydrazide", *Sensor letters*, **5**, 522 (2007).
36. Mehran, G., Behzad, R., Zahra S. and Javad S.G., "A Co^{2+} Selective Poly(vinyl chloride) Membrane Electrode Based on a Newly Synthesized 3,3′-

(Dodecylazanediyl)bis(*N*-(2-(2-aminoethylamino)ethyl)propan amide) Compound", *J. Chem. Eng. Data*, **55**, 2792 (2010).

37. Wardak, C., "Cobalt(II) ion selective electrode with solid contact", *Cent. Eur. J. Chem.*, **6**, 607 (2008).
38. Ganjali, M.R., Mizani, F., Emami, M., Darjezini, M., Darvich, M.R. and Yousefi, M., "Synthesis of a new oxime and its application to the construction of a highly selective and sensitive Co(II) PVC-based membrane sensor", *Anal. Sci.*, **20**, 531 (2004).
39. Berg, J.M. and Science, Y.S., "The galvanization of biology: a growing appreciation for the roles of zinc", **271**, 1081 (1996).
40. Weiss, J.H., Sensi, S.L. and Koh, J.Y., "Zn(2+): a novel ionic mediator of neural injury in brain disease", *Trends Pharmacol. Sci.*, **21**, 395 (2000).
41. Voegelin, A., Pfister, S., Scheinost, A.C., Marcus, M.A. and Kretzschmar, R., "Changes in zinc speciation in field soil after contamination with zinc oxide", *Environ. Sci. Technol.*, **39**, 6616 (2005).
42. Mertens, J., Degryse, F., Springael, D. and Smolders, E., "Zinc toxicity to nitrification in soil and soilless culture can be predicted with the same biotic ligand model", *Environ. Sci. Technol.*, **41**, 2992 (2007).
43. Callender, E. and Rice, K.C., "The Urban Environmental Gradient: Anthropogenic Influences on the Spatial and Temporal Distributions of Lead and Zinc in Sediments", *Environ. Sci. Technol.*, **34**, 232 (2000).
44. http://www.carolina.com/stcms/acrobat/stc_msds.
45. Cataldo, C.B., Bruyne, L.K.D. and Whitney, E.N. (Eds.), Nutrition and Diet Therapy, fourth ed., West Publishing Company, Minneapolis, 199 (1995).
46. Liu, R., Liu, D., Sun, A. and Liu, G., "Simultaneous determination of copper and zinc in the hair of children by pH gradient construction in a flow-injection system", *Analyst*, **120**, 569 (1995).
47. Fakhari A.R., Shamsipur, M. and Ghanbari, K., "Zinc(II)-selective membrane electrode based on tetra(2-aminophenyl) porphyrin", *Anal. Chim. Acta*, **460**, 177 (2002).
48. Singh, A.K., Jain, A.K., Saxena, P. and Mehtab, S., "Zn(II)-Selective Membrane Electrode Based on Tetraazamacrocycle [$Bzo_2Me_2Ph_2$(16)hexaeneN_4]", *Electroanalysis*, **18**, 1186 (2006).

49. Chandra, S. and Singh, D.R., "Zinc(II) selectivepoly(vinyl chloride) membrane ISE using a macrocyclic compound 1,12,14-triaza-5,8-dioxo-3(4),9(10)-dibenzoylcyclopenta deca-1,12,14-triene as neutral carrier", *J. Saudi Chem. Soc.*, **14,** 55 (2010).
50. Saleh, M.B. and Gaber A.A.A, "Novel Zinc Ion-Selective Membrane Electrode Based on Sulipride Drug", *Electroanalysis*, **13**, 104 (2001).
51. Srivastava, S.K., Gupta, V.K. and Jain, S., "PVC-Based 2,2,2-Cryptand Sensor for Zinc Ions", *Anal. Chem.*, **68**, 1272 (1996).
52. Boycheva, S.V., Vassilev, V.S. and Ivanova, Z.G., "A Zn(II) ion-selective electrode based on chalcogenide As_2Se_3–Sb_2Se_3–ZnSe and $GeSe_2$–ZnSe–ZnTe glasses", *J. Appl. Electrochem.*, **32**, 281 (2002).
53. Pandey, P.C. and Singh, G., "Electrochemical synthesis of tetraphenylborate-doped polypyrrole dependence of zinc ion sensing on the polymeric microstructure", *Sens. Actuators B*, **85**, 256 (2002).
54. Ganjali, M.R., Zamani, H.A., Norouzi, P., Adib, M., Rezapour, M. and Accedí, M., "Zn^{2+} PVC-based membrane sensor based on 3-[(2-furylmethylene) amino]-2-thioxo-1,3-thiazolidin-4-one", *Bull. Kor. Chem. Soc.*, **26,** 579 (2005).
55. Gupta, V.K., Agarwal, S., Jakob, A. and Lang, H., "Zinc-selective electrode based on N, N'-bis(acetylacetone) ethylenediimine", *Sens. Actuators B*, **114**, 812 (2006).
56. Singh, A.K., Mehtab, S., Singh, U.P. and Aggarwal, V., "Tripodal chelating ligand-based sensor for selective determination of Zn(II) in biological and environmental samples", *Anal. Bioanal. Chem.*, **388**, 1867 (2007).
57. Rocheleaw, M.J. and Purdy, W.C., "Investigations of material for making a carbon support zinc-selective electrode", *Talanta,* **37**, 307 (1990).
58. Gholivand, M.B. and Mozaffari, Y., "PVC-based bis(2-nitrophenyl)disulfide sensor for zinc ions", *Talanta*, **59**, 399 (2003).
59. Gupta, V.K., Jain, A.K., Singh, L.P. and Khurana, U., "Zn^{2+} sensor based on Zn-bis(2,4,4-trimethylpentyl)dithiophosphinic acid complex in PVC matrix", *Electrochim. Acta*, **43**, 2047 (1998).
60. Gupta, V.K., Al Khayat, M., Minocha, A.K. and Kumar, P., "Zinc(II) selective sensors based on dibenzo-24-crown-8 in PVC matrix", *Anal. Chim. Acta*, **532**, 153 (2005).

61. Gupta, V.K., Goyal, R.N., Khayat, M. A., Kumar, P. and Bachheti, N., "A new Zn(II)- selective potentiometric sensor based on 4-*tert*-butylcalix[4]arene in PVC matrix", *Talanta*, **69**, 1149 (2006).

62. Zamani, H.A., Parviz, N., Mehdi, A., Morteza, R. and Ganjali, M.R., "Zn^{2+} PVC-based membrane sensor based on 3-[(2-furylmethylene)amino]-2-thioxo-1,3-thiazolidin-4-one", *Bulletin of the Korean Chemical Society,* **26**, 579 (2005).

63. Zamani, H.A., Ganjali, M.R. and Pooyamanesh, M.J., "Zinc(II) PVC-based membrane sensor based on 5,6-benzo-4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8,8,8]hexacos-5-ene", *J. Braz. Chem. Soc.*, **17**, 149 (2006).

64. Gupta, N.R., Mittal, S., Kumar, S. and Kumar, S.K.A., "Potentiometric studies of N,N′-Bis(2-dimethylaminoethyl)-N,N′-dimethyl-9,10 anthracenedimethan- amine as a chemical sensing material for Zn(II) ions", *Materials Science and Engineering C*, **28**, 1149 (2008).

65. Ilhan, S. and Temel H., "Synthesis and spectral characterization of macrocyclic Schiff base by reaction of 2,6-diaminopyridine and 1,4- *bis* (2-carboxyaldehydephenoxy)butane and its Cu^{II}, Ni^{II}, Pb^{II}, Co^{III} and La^{III}complexes", *Transition Metal Chemistry*, **32**, 584 (2007).

66. Khayatian, G., Shariati, S. and Salimi, A., "Thallium (I) selective membrane potentiometric sensor based on dibenzyldiaza-18-crown-6", *Bull. Korean Chem. Soc.*, **24**, 421 (2003).

67. Craggs, A., Moody, G.J. and Thomas, J.D.R., "PVC matrix membrane ion selective electrode. Construction and laboratory experiments", *J. Chem. Educ.*, **51**, 541 (1974).

68. Shultz, M.M., Stefanova, O.K., Mokrov, S.B. and Mikhelson, K.N., "Potentiometric estimation of the stability constants of ion-ionophore complexes in ion-selective membranes by the sandwich membrane method: Theory, Advantages, and Limitations", *Anal. Chem.*, **74**, 510 (2002).

69. Mi, Y. and Bakker E., "Determination of complex formation constants of lipophilic neutral ionophores in solvent polymeric membranes with segmented sandwich membranes", *Anal. Chem.*, **71**, 5279 (1999).

70. Katsu, T., Ido, K., Takaishi, K. and Yokosu, H.,"Thallium (I) selective membrane electrode based on calix[6]arene or calix[5]arene derivatives", *Sensors Actuators B*, **87,** 331 (2002).

71. Park, K.M., Lee, Y.H., Jin, Y., Seo, J., Yoon, I., Lee, S.C., Park, S.B., Gong, M.S., Seo, M.L. and Lee, S.S., "Tetrathiaoxamacrocycles with dibenzo-subunits: A search for new Tl(I) and Ag(I) selective ionophore", *Supramol. Chem.*, **16**, 51 (2004).
72. Antonisse, M.M.G. and Reinhoudt, D.N., "Potentiometric ion-selective sensors", *Electroanalysis*, **11**, 1035 (1999).
73. Shahrokhian, S., Amini, M.K., Kia, R. and Tangestaninejad, S., "Salicylate-selective electrode based on Al(III) and Sn(IV) Salophens", *Anal. Chem.*, **72**, 956 (2000).
74. Shamsipur, M., Sadeghi, S., Naeimi, H. and Sharghi, H., "Iodide ion-selective PVC membrane electrode based on a recently synthesized salen Mn(II) complex", *Pol. J. Chem.*, **74**, 231 (2000).
75. Kamata, S., Bhale, A., Fukunga, Y. and Nurata, A., "Copper(II)-selective electrode using thiuram disulfide neutral carriers", *Anal. Chem.*, **60**, 2464 (1988).
76. Siswanta, D., Nagatska, K., Yamada, H., Kumakura, K., Hisamoto, H., Shichi, Y., Toshima, K. and Suzuki, K., "Structural Ion Selectivity of Thia Crown Ether Compounds with a Bulky Block Subunit and Their Application as an Ion-Sensing Component for an Ion-Selective Electrode", *Anal. Chem.*, **68**, 4166 (1996).
77. Tavakkoli, N. and Shamsipur, M., "Lead-selective membrane electrode based on dibenzopyrydino-18-crown-6", *Anal. Lett.*, **29**, 2269 (1996).
78. Javanbakht, M., Ganjali, M.R., Sharghi, H. and Shamsipur, M., "Mercury(II) ion-selective electrode based on dibenzodiazathia-18-crown-6-dione", *Electroanalysis*, **11**, 81 (1999).
79. Bakker, E., Buhlmann, P., Pretsch, E. "Carrier based ion-selective electrodes and bulk optodes.1. General characteristics", *Chem. Rev.*, **97**, 3083 (1997).
80. Analytical Chemistry Division, "I.U.P.A.C: Commission on analytical nomenclature, recommendations for nomenclature for ion selective electrodes", *Pure Appl. Chem.*, **48**, 127 (1976).
81. Morf, W.E., Kohr, G. and Simon, W., "Reduction of the anion interference in neutral carrier liquid-membrane electrodes responsive to cations", *Anal. Lett.*, **7**, 9 (1974).
82. Gadzekpo, Y.P.Y. and Christian, G.D., "Determination of selectivity coefficients of ion-selective electrodes by a matched-potential method", *Anal. Chim. Acta*, **164**, 279 (1984).
83. Umezawa, Y., Umezawa, K. and Sato, H., "Recommended methods for reporting *K* (pot, a, b) values (IUPAC Technical Report)", *Pure Appl. Chem.*, **67**, 507 (1995).

84. Sa'ez de Viteri, F.J. and Diamond, D., "Determination and application of ion-selective electrode model parameters using flow injection and simplex optimization", *Analyst*, **119,** 749 (1994).

85. Oh, H.J., Geun, S.C. and Hakhyun N., "Effect of surfactants on the electrochemical performance of cation-selective membrane electrodes", *Bull. Korean Chem. Soc.*, **24**, 37 (2003).

86. Hosseini, M., Abkenar, S.D., Ganjali, M.R. and Faridbod, F., "Determination of zinc(II) ions in waste water samples by a novel zinc sensor based on a new synthesized Schiff's base", *Materials Science and Engineering C*, **31**, 428 (2011).

87. Shamsipur, M., Rouhani, S., Ganjali, M.R., Sharghi, H. and Eshghi, H., "Zinc-selective membrane potentiometric sensor based on a recently synthesized benzo-substituted macrocyclic diamide", *Sens. Actuators B*, **59**, 30 (1999).

88. Hassani, M. and Shamsipur, M., "Conductance Study of the Thermodynamics of Ammonium Ion Complexes with Several Crown Ethers in Acetonitrile Solution", *J. Solut. Chem.*, **23**, 721 (1994).

89. Shamsipur, M. and Ganjali, M.R., "Complex formation of some anilinium ion derivatives with 18-crown-6, 1,10-diaza-18-crown-6 and cryptand C222 in acetonitrile, dimethylformamide and their 1:1 mixture", *J. Incl. Phenom. Macrocyclic Chemistry*, **28**, 315 (1997).

90. Ganjali, M.R., Davarkhah, N., Ganjali, H., Larijani, B., Norouzi, P. and Hosseini, M., "A novel europium(III) sensor based on 4E-4-(2-phenylviazenyl)-2-((E)-(2-aminoethylimino)methyl)phenol", *Intern. J. Electrochem. Sci.*, **4**, 762 (2009).

91. Deep, K., Singh, K.P., Kansal, M.L. and Mohan, C. "Real Coded Genetic Algorithm for Integer and Mixed Integer Non-linear Optimization Problems", *Appl. Math. Complexation*, **212**, 505 (2009).

92. Guilbault, G.G., Durst, R.A., Frant, M.S., Freiser, H., Hansen, E.H., Light, T.S., Pungor, E., Rechnitz, G., Rice, M.N., Rohm, T.J., Simon, W. and Thomas, J.D.R., "Recommendations for Nomenclature of Ion-Selective Electrodes", *Pure Appl. Chem.*, **48**, 127 (1976).

93. Bakker, E., Xu, A. and Pretsch, E., "Optimum composition of neutral carrier based pH electrodes", *Anal. Chim. Acta*, **295**, 253 (1994).

94. Morf, W.E., "The Principle of Ion Selective Electrodes and Membrane Transport", Elsevier, New York, (1981).

95. Gupta, V.K., Singh, A.K. and Gupta, B., "Schiff bases as cadmium (II) selective ionophores in polymeric membrane electrodes", *Anal. Chim. Acta*, **583**, 340 (2007).
96. Gupta, K.C. and D'Arc, M.J., "Effect of concentration of ion exchanger, plasticizer and molecular weight of cyanocopolymers on selectivity and sensitivity of Cu(II) ion selective electrodes", *Anal. Chim. Acta*, **437**, 199 (2001).

Chapter 4

Membranes of macrocyclic ligands as Cation selective sensor for Rare earth metal ions

4.1 INTRODUCTION

The rare earth elements (REEs) are found, usually together, in a variety of accessory minerals and occur especially in pegmatite, granites and related metamorphic igneous rocks. They are considered slightly toxic according to the Hodge-Sterner classification system [1]. Nowadays, determination of rare-earth compounds is considered necessary because of the increasing interest in bioinorganic and inorganic chemistry, increased industrial use, and also their enhanced discharge, toxic properties, and other adverse effects. In recent years, the monitoring and evaluation of REEs in some biological materials has received increasing attention, from both nutritional and toxicological point of view [2].

4.1.1 Terbium Ion selective Sensor

Terbium is an important member of the rare-earth family and is used in cathode ray tubes, magnets, optical computer memories and magnetostrictive alloys. It has been known for a long time to cause severe liver damage such as necrosis of hepatocytes [3] and liver degeneration [4] and exhibits catalytic ability in chemical reactions. Its influence on enzymatic reactions [5], their interference with Ca(II) ions [6] and the effects on Mg(II) and Mn(II)-dependent enzymes in several biological systems have been reported in the biochemical literature. Searching for effective analytical methods for terbium assay has been the subject of current analytical research.

There are few reports on Tb(III) ion-selective electrodes till date. Mohammadhossieni *et al.* reported a Tb^{3+} selective electrode based on hematoporphyrin [7] which revealed good selectivity (except for Fe^{3+} ion), wide working concentration range of 1×10^{-6} to 1×10^{-2} M with a slope of 19.8 ± 0.3 mV $decade^{-1}$ of activity. Ganjali and coworkers reported a Tb(III)-selective electrode based on bis-pyrrolidene Schiff's base [8] while Zamani *et al.* explored 4-amino-3-{2-[4-amono-6-methyl-5-oxo-4,5-dihydro-1,2,4-triazin-3-(2H)-yliden]hydrazono}–6-methyl-3,4-dihydro-1,2,4-triazin5(2H)-one [9], N, N-Dimethyl-N′,N″-bis(4-methoxyphenyl)phosphoramidate [10], 2-{2-(2-anilinocarbo thioyl)hydrazino)-2-oxoacetyl}-N-phenyl-1-hydrazinecarbothioamide [11] and N,N′-bis(5-nitrosalicylidene)-2-aminobenzylamin [12] as ionophores in the fabrication of Tb(III) selective electrodes. Gupta *et al.* prepared a polymeric membrane electrode for selective determination of Tb^{3+} ion based on S-2-benzothiazolyl-2-amino-α-(methoxyimino)-4-thiazolethiol acetate [13] which exhibited wide concentration range of 1.5×10^{-7} to 1×10^{-2} M and a fast response time of 10 s. They also reported a Tb(III) selective electrode based on N-(2-hydroxyphenyl)-3-(2-hydroxyphenyl hydroxyphenylimino)-N-phenylbutanamidine [14]. These reported electrodes possess poor performance characteristics in terms of concentration range and selectivity. Thus, it is desirable to determine terbium ions in view of their toxicity. Therefore, extensive efforts have been made to develop selective electrodes for Tb^{3+} ion.

In the present work, we have explored poly(vinylchloride) (PVC) based polymeric membrane electrode and coated graphite electrode incorporating two newly synthesized macrocyclic pendant ligands 3,4,5:12,13,14-dipyridine-2,6,11,15-tetramethyl-1,7,10,16-tetramethylacrylate-1,4,7,10,13,16-hexaazacyclooctadeca-3,13-diene and 3,4,5:12,13,14-dipyridine-2,6,11,15-tetramethyl-1,7,10,16-tetra(2-cyanoethane)-1,4,7,10,13,16-hexaaza-cyclooctadeca-3,13-diene as ionophores for selective determination of Tb^{3+} ion.

4.1.2 Ytterbium Ion Selective Sensor

Ytterbium is an important member of rare-earth family and widely used for various applications [15,16]. Although REEs, including Ytterbium, have a low acute toxicity rating, in some studies it has been found that intraperitoneal administration of this element in concentration of 0.01, 0.1 and 1% in the diet for 90 days, produced liver damage, which was more prominent in males than females. Inhalation of sesquioxide and / or trifluorides of this element also induce granulomas in the lung [17].

Few sensors are reported for ytterbium ion determination and these are based on cefixime [18], N-(2-pyridyl)-N'-(2-methoxyphenyl)-thiourea [19], 3-hydroxy-*N*-[(2-hydroxyphenyl) methylene]-2-naphthohydrazide [20], 6-methy-4-{[1-(1H-pyrrol-2-yl)methyl-idene]amino}-3-thioxo-3,4dihydro-1,2,4 triazin-5(2H)-one [21], N-(6-picolyl)-N'-(4-methoxyphenyl)-thiourea [22], 1-phenyl-3-(2-thiazolyl)-2-thiourea and 1-phenyl-3-(2-thiazolyl)-2-urea [23], 2,5-bis(5-tert-butyl-benzoxazol-2-yl)thiophene [24]. The electrode sensors reported for ytterbium exhibits narrow working concentration ranges and show interferences to various cations such as Ce^{3+}, Nd^{3+}, Gd^{3+}, and Pb^{2+}. Thus there is still a need for having good sensors for ytterbium ion determination and further efforts are required to develop it.

The purpose of the present work is to explore the use of two newly synthesized macrocyclic ligands 2,12-(2-methoxyaniline)$_2$-4,14-Me$_2$-[20]-1,4,11,14-tetraene-1,5,8,11,15,18-N$_6$ and 2,12-(2-methoxyaniline)$_2$-4,14-Me$_2$-8,18-dimethylacrylate-[20]-1,4,11,14-tetraene-1,5,8,11,15,18-N$_6$ as electroactive material in the fabrication of polymeric membrane electrode and coated graphite electrode for selective determination of Yb^{3+} ion.

4.1.3 Cerium Ion Selective Sensor

Cerium(III) is traditionally referred to as one of the rare earths. However, in reality, it is more plentiful in the earth's crust than many other elements. It is also the most widely distributed among the 'rare earths', averaging 22 mg Kg^{-1} in the earth crust [25-27]. It is found in monazite, ceric bastnaesite and silicate rocks. It has many industrial applications in the area of lightning and television, metallurgy, glass and ceramics and as one of the active components of catalytic converters in vehicles. The observation that inhalation of particles of cerium causes pneumoconiosis had generated considerable interest in the toxicology of the element [28,29]. More recently, tropical endomyocardial fibrosis, a restrictive cardiomyopathy was postulated to be the cardiac expression of cerium toxicity in combination with magnesium deficiency [30,31]. Importantly, recent observations on the mode of action of cerium at the molecular level suggested that the element may influence expression of matrix proteins like collagen in the heart and produce fibrosis. A sequel to these investigations, the determination of cerium is important from environmental and toxicological point of view.

A number of attempts have been made to develop Ce^{3+} selective sensors. Shamsipur *et al.* fabricated a PVC based conventional electrode [32] as well as coated graphite electrode [33] by employing same ionophore 1,3,5-trithiane for cerium ion determination. The conventional electrode displayed narrow working concentration range (5.0×10^{-5} -1.0×10^{-1} M) and low pH range. Karami *et al.* reported Ce^{3+} selective sensor based on N-[(Z)-2chloro-2-(1-hydroxy-1,1,1-triohenylphosphoranyl)-1-ethenyl]-4-ethyl-1-benzene sulfonamide [34] in PVC matrix. Gaber *et al.* explored the use of piperonylidine-4-[2.2] paracyclophanylamine [35] as an ionophore in the construction of cerium ion sensor. This sensor exhibited poor performance characteristics in terms of working range (2.5×10^{-5} - 1.0×10^{-1} M) and long response time (30 s). Akhond *et al.* utilized 2-aminobenzothiazole [36] in PVC matrix as sensor for Ce(III) ion In addition of these, Saleh *et al.* reported electrode for cerium ion by utilizing [4-(4-nitrobenzyl)-1-phenyl-3,5-pyrazolidinedion)] [37] as ionophore while Zamani *et al.* utilized N-[(2-hydroxyphenyl)methylidene]-2-furohydrazide [38] as an ionophore for quantification of cerium ions. Some other Ce(III) selective electrodes based on dibenzo-24-crown-8 [39], 2,5-Dioxo-4-imidazolidinyl [40] and *N,N'*-bis[2-(salicylideneamino)ethyl]ethane-1,2-diamine [41] have also been reported. However, these efforts have not been very fruitful as most of the developed electrodes have a narrow working concentration range with a near or non-Nernstian response, exhibit high response time and poor reproducibility.

In the present work, we have fabricated polymeric membrane and coated graphite electrode based on 2,3,4:12,13,14-dipyridine-1,3,5,8,11,13,15,18-octaazacycloicosa-2,12-diene and 2,3,4:12,13,14-dipyridine-1,5,8,11,15,18-hexa-methylacrylate-1,3,5,8,11, 13,15,18-octaazacycloicosa-2,12-diene macrocyclic ligands as Ce(III) selective sensors.

4.2 EXPERIMENTAL

4.2.1 Reagents

All the chemicals and solvents used were of analytical reagent grade. Barium chloride dihydrate ($BaCl_2.2H_2O$) sodium borohydride ($NaBH_4$), hydrobromic acid, sodium hydroxide (NaOH), potassium carbonate (K_2CO_3), sodium tetraphenylborate (NaTPB), dibutylphthalate (DBP), tri-n-butylphosphate (TBP), benzyl acetate (BA), dioctylphthalate (DOP), *o*-nitrophenyloctyl ether (*o*-NPOE), 1-chloronaphthalene (CN), dibutyl sebacate (DBS), tetrahydrofuran (THF) and high molecular weight poly(vinylchloride) were purchased from E. Merck (Germany); Diethylenetriamine, *o*-acetoacetanisidide, ethylenediamine, 2,6-dichloropyridine, and 2,6-diacetylpyridine from Aldrich, USA; methylacrylate and acrylonitrile were procured from S. D. Fine-Chem Ltd; potassium tetrakis *p*-(chloro phenyl)borate (KTpClPB) from Fluka, USA and were used as received. The chloride and nitrate salts of all the cations used were of analytical grade and used without any further purification. The solutions of metal salts were prepared in doubly distilled water and standardized whenever necessary.

4.2.2 Synthesis of Ionophores

4.2.2.1 Synthesis of 3,4,5:12,13,14-dipyridine-2,6,11,15-tetramethyl-1,4,7,10,13, 16-hexaazacyclooctadeca-3,13-diene (IV)

The macrocycle IV (Fig. 4.1) was synthesized following a literature method [42]. To a refluxing solution of 2,6-diacetylpyridine (1.63 g, 10 mmol) and $BaCl_2.2H_2O$ (1.22 g, 5 mmol) in anhydrous methanol (50 mL), a 10 mL methanolic solution of ethylenediamine (0.67 mL, 10 mmol) was added slowly. Then the mixture was refluxed for 10 h. After the yellow solution was allowed to cool to room temperature solid $NaBH_4$ (1 g, 27 mmol) was added slowly and carefully for in situ reduction and the flux was kept in an ice bath and was stirred for 1 h. A second addition of $NaBH_4$ (0.5 g, 13 mmol) was made and the resulting yellow-white mixture was stirred at room temperature for 1.5 h. The mixture was concentrated to dryness under reduced pressure and the crude solid was extracted with chloroform, concentrated to dryness to obtain yellow oil. The oil was dissolved in small amount of methanol and hydrobromic acid was added drop by drop until acidic pH. A white precipitate appeared. After isolation and characterization of crystalline tetrahydrobromohydric salt of ligand IV, it was dissolved in small amount of water and neutralizing with NaOH. The water solution was extracted with $CHCl_3$ (5 × 25 mL). The organic phase was dried with anhydrous Na_2SO_4 and filtered to be concentrated to dryness at reduced pressure to obtain a pale yellow highly viscous oil of desired ligand IV. Yield: 65 %. Anal. Calcd. for [$C_{22}H_{34}N_6$] (%): C, 69.11; H, 8.9; N,21.99; Observed (%): C, 69.07; H, 8.96; N, 21.97. ^{1}HNMR ($CDCl_3$, 500 MHz) δ_{ppm}: 7.6 (m, H-Ar, 2H), 7.0 (m, H-Ar, 4H), 3.8 (m, -C-CH-C-, 4H), 1.3 (m, $-CH_3$, 12H), 2.6 (m,-C-NH-C-, 4H), 2.2 (N-CH_2-C, 8H).

4.2.2.1.1 Synthesis of pendant armed macrocycle 3,4,5:12,13,14-dipyridine-2,6,11,15-tetramethyl-1,7,10,16-tetramethylacrylate-1,4,7,10,13,16-hexaazacyclooctadeca-3,13-diene IV(a)

The macrocyclic pendant ligand IV(a) (Fig. 4.2) was synthesized from macrocycle IV. To a stirred solution of the macrocycle IV (382 mg, 1 mmol) in 10 mL saturated solution of anh. K_2CO_3 in anhydrous MeOH, 5 mL methylacrylate (excess amount) was added drop by drop and then it was stirred overnight. It was refluxed for 24 h. Then the volume was reduced to half of its initial amount and 5 mL diethylether was added and kept in refrigerator overnight. A white precipitate appeared. It was filtered and washed with diethylether. The white product was dried in vacuum. Yield: 42 %, M.P.: > 300°C. Anal. calcd. For [$C_{38}H_{58}N_6O_8$] (%): C, 62.81; H, 7.99; N, 11.57; O, 17.63; Observed (%): C, 62.79; H, 8.04; N, 11.56; O, 17.61. ^{1}H NMR ($CDCl_3$, 500 MHz) δ_{ppm}: 7.26 (m, H-Ar, 2H), 7.04 (m, H-Ar, 4H), 3.68 (m, -C-CH-N-, 4H), 2.945-3.352 (m, -N-CH_2-C-, 8H), 2.476 (s, N-CH_2-CH_2-N, 8H), 2.39 (m, -C-CH_2-COOMe, 8H), 1.257 (m, -OCH_3, 12H). FT-IR (KBr, cm^{-1}): 2950 (asymmetric -CH_3 str.), 2925 (asymmetric –CH_2- str.), 2848 (symmetric –CH_2- str.), 1740 (ester C=O str.), 1573-1385 (aromatic C=C & C=N str.), 1160 (OC-OCH_3 str.), 1111 (-OCH_3 str.), 1062 (C-N str. in t-amine), 833, 768, 702, 621 (out plane bending of aromatic ring C-H).

4.2.2.1.2 Synthesis of pendant armed macrocycle 3,4,5:12,13,14-dipyridine-2,6,11,15-tetramethyl-1,7,10,16-tetra(2-cyanoethane)-1,4,7,10,13,16-hexaazacyclooctadeca-3,13-diene IV(b)

The macrocyclic pendant ligand IV(b) (Fig. 4.3) was synthesized from macrocycle IV. To a stirred solution of the macrocycle IV (382 mg, 1 mmol) in 10 mL saturated solution of anhydrous K_2CO_3 in anhydrous methanol, 5 mL (excess amount) acrylonitrile was added drop by drop. It was stirred over night. A white precipitate appeared. It was then refluxed for 10 h and reduced half of its volume & kept overnight in refrigerator. It was filtered in cold condition & washed with cold MeOH and then with diethylether. The white product was dried in vacuum. Yield: 55 %, M.P.: 190°C. . Anal. calcd. For [$C_{34}H_{46}N_{10}$] (%): C, 68.69; H, 7.74; N, 23.57; Observed (%): C, 68.66; H, 7.80; N, 23.55. ^{1}H NMR ($CDCl_3$, 500 MHz) δ_{ppm}: 7.5 (m, H-Ar, 2H), 7.1 (m, H-Ar, 4H), 3.8 (m, -C-CH-N-, 4H), 2.5 (m, -N-CH_2-C-, 8H), 2.8-2.95 (s, N-CH_2-CH_2-N, 8H), 2.5 (m, -C-CH_2-CN, 8H), 1.3 (m, -CH_3, 12H). FT-IR (KBr, cm^{-1}): 3052 (aromatic C-H str.), 2966 (asymmetric -CH_3 str.), 2929 (asymmetric –CH_2- str.), 2844 (symmetric –CH_2- str.), 2247 (-CN str.), 1618-1430 (aromatic C=N, C=C str.), 1119 (CN str. in t-amine), 825, 772, 621 (out plane bending of aromatic ring C-H).

4.2.2.2 Synthesis of 2,12-(2-methoxyaniline)$_2$-4,14-Me$_2$-[20]-1,4,11,14-tetraene-1,5,8,11,15,18-N$_6$ [V(a)]

The macrocyclic ionophore (V(a)) (Fig. 4.4) was synthesized by dissolving equimolar amounts of diethylenetriamine (0.01 mol L^{-1}) and *o*-acetoacetanisidide (0.01 mol L^{-1}). Diethylenetriamine was dissolved in minimum quantity of methanol and to this solution *o*-acetoacetanisidide dissolved in methanol was added dropwise with stirring. The resulting mixture was refluxed for 8 h and then was concentrated to half of its original volume on a water bath, followed by cooling and keeping aside for 1 day. The yellow oily product was obtained. Yield: 65 %. Anal. calcd. For [$C_{30}H_{44}N_8O_2$] (%): C, 65.63; H, 8.05; N, 20.42; O, 5.90; Observed (%): C, 65.67; H, 8.08; N, 20.42; O, 5.83. 1H NMR (MeOH, 500 MHz) δ_{ppm}: 6.82-7.29 (m, H-Ar, 8H), 4.70 (s, aromatic C-NH-, 2H), 3.86 (s, -OCH_3, 6H), 2.75 (s, -C-CH_2-C-, 4H), 1.93 (s, -CH_3, 6H), 1.8 (s, NH, 2H), 2.97-3.01 (t, N-CH_2-C, 8H), 3.35-3.39 (t, -C-CH_2-N, 8H). FT-IR (KBr, cm^{-1}): 1620 (C=N); 3425 (-NH); 783, 648 (-CH_2).

4.2.2.2.1 Synthesis of 2,12-(2-methoxyaniline)$_2$-4,14-Me$_2$-8,18-dimethylacrylate-[20]-1,4,11,14-tetraene-1,5,8,11,15,18-N$_6$ [V(b)]

The macrocyclic pendant ligand V(b) (Fig. 4.5) was synthesized from macrocycle V(a). To a stirred solution of the macrocycle V(a) (1 mmol) in 10 mL saturated solution of anh. K_2CO_3 in anhydrous MeOH, 5 mL methylacrylate (excess amount) was added drop by drop and then it was stirred overnight. Then it was refluxed for 24 h. Then the volume was reduced half of its initial amount and was kept in refrigerator overnight. A creamish coloured oily product was obtained. Yield: 43 %. Anal. calcd. For [$C_{38}H_{56}N_8O_6$] (%): C, 63.29; H, 7.81; N, 15.53; O, 13.37; Observed (%): C, 63.31; H, 7.83; N, 15.54; O, 13.32. 1H NMR (MeOH, 500 MHz) δ_{ppm}: 6.93-7.39 (m, H-Ar, 8H), 4.82 (s, aromatic C-NH-, 2H), 3.92 (s, -OCH_3, 6H), 2.45 (s, -C-CH_2-C-, 4H), 1.85 (s, -CH_3, 6H), 3.10-3.15 (t, N-CH_2-C, 8H), 3.45-3.50 (t, -C-CH_2-N, 8H), 2.94-3.12 (m, -N-CH_2-C-, 4H), 2.38 (m, -C-CH_2-COOMe, 4H), 1.25 (m, -OCH_3, 6H). FT-IR (KBr, cm^{-1}): 1625 (C=N); 3418 (-NH); 778, 652 (-CH_2), 1740 (ester C=O str.), 1160 (OC-OCH_3 str.), 1111 (-OCH_3 str.).

4.2.2.3 Synthesis of macrocyclic ligand 2,3,4:12,13,14-dipyridine-1,3,5,8,11,13,15,18-octaazacycloicosa-2,12-diene [VI(a)]

The macrocyclic ionophore VI(a) (Fig. 4.6) was synthesized by dissolving equimolar amounts of diethylenetriamine (0.01 mol L^{-1}) and 2,6-dichloropyridine (0.01 mol L^{-1}). Diethylenetriamine was dissolved in minimum quantity of methanol and to this solution 2,6-dichloropyridine dissolved in methanol was added dropwise with stirring. The resulting mixture was refluxed for 42 h in acidic medium and then was concentrated to half of its original volume on a water bath, followed by cooling and keeping aside for 1 day. A white crystalline product was obtained. Yield: 68 %. M.pt.: 158 °C. Anal. calcd. for [$C_{18}H_{28}N_8$] (%): C, 60.65; H, 7.92; N, 31.43; Observed (%): C, 60.61; H, 7.95; N, 31.44, ^{1}H NMR (MeOH, 500 MHz) δ_{ppm}: 7.62-7.74 (m, H-Ar, 6H), 3.10-3.21 (m, -N-CH_2-CH_2-N-, 16H), 1.75 (s, -NH-, 2H), 4.50 (s, Aromatic C-NH-, 4H), FT-IR (KBr, cm^{-1}): 3257 (-NH str.).

4.2.2.3.1 Synthesis of macrocyclic ligand 2,3,4:12,13,14-dipyridine-1,5,8,11,15,18-hexamethylacrylate-1,3,5,8,11,13,15,18-octaazacycloicosa-2,12-diene [VI(b)]

The macrocyclic pendant ligand VI(b) (Fig. 4.7) was synthesized from macrocycle VI(a). To a stirred solution of the macrocycle VI(a) (1 mmol) in 10 mL saturated solution of anh. K_2CO_3 in anhydrous MeOH, 5 mL methylacrylate (excess amount) was added drop by drop and then it was stirred overnight and refluxed for 48 h. Then the volume was reduced to half of its initial amount and was kept in a refrigerator overnight. A creamish coloured oily product was obtained. Yield: 40 %. Anal. calcd. for [$C_{42}H_{64}N_8O_{12}$] (%): C, 57.78; H, 7.39; N, 12.84; O, 21.99; Observed (%): C, 57.75; H, 7.42; N, 12.82; O, 22.01. ^{1}H NMR (MeOH, 500 MHz) δ_{ppm}: 7.64-7.78 (m, H-Ar, 6H), 2.75-2.90 (m, -N-CH_2-CH_2-N-, 16H), 3.25 (s, -N-CH_2-CH_2COOMe, 12H), 2.48 (s, -CH_2-CH_2-COOMe, 12H), 3.69 (s, -OCH_3, 18H). FT-IR (KBr, cm^{-1}): 1754 (ester C=O str.), 1568-1380 (aromatic C=C & C=N str.), 1110 (-OCH_3 str.).

4.2.3 Preparation of Membranes

PVC based membranes containing macrocylic ligands as electroactive material were prepared by the same procedure as reported in section 3.2.4 of Chapter 3.

4.2.4 Equilibration of Membranes and Potential Measurements

The time of contact and concentration of equilibrating solution were optimized so that the sensors generated stable and reproducible potentials at relatively short response times. For Tb^{3+} ion determination, polymeric membrane electrode and coated graphite electrode based on membrane containing 3,4,5:12,13,14-dipyridine-2,6,11,15-tetramethyl-1,7,10,16-tetramethylacrylate-1,4,7,10,13,16-hexaazacycloocta- deca-3,13-diene [IV(a)] and 3,4,5:12,13,14-dipyridine-2,6,11,15-tetramethyl-1,7,10, 16-tetra(2-cyanoethane)-1,4,7,10,13,16-hexaazacyclooctadeca-3,13-diene [IV(b)] as ionophores with different composition were equilibrated for 2 days in 0.1 mol L^{-1} $TbCl_3$ solution. The potentials were measured by varying the concentration of $TbCl_3$ in test solution in the range 1.0×10^{-9} to 1.0×10^{-1} mol L^{-1}. Standard $TbCl_3$ solution were obtained by gradual dilution of 0.1 mol L^{-1} $TbCl_3$ solution.

For Yb^{3+} ion determination, polymeric membrane electrode and coated graphite electrode based on membrane containing 2,12-(2-methoxyaniline)$_2$-4,14-Me$_2$-[20]-1,4,11,14-tetraene-1,5,8,11,15,18-N_6 [V(a)] and 2,12-(2-methoxyaniline)$_2$-4,14-Me$_2$-8,18-dimethylacrylate-[20]-1,4,11,14-tetraene-1,5,8,11,15,18-N_6 [V(b)] as ionophores with different composition were equilibrated for 3 days in 0.1 mol L^{-1} $YbCl_3$ solution. The potentials were measured by varying the concentration of $YbCl_3$ in test solution in the range 1.0×10^{-9} to 1.0×10^{-1} mol L^{-1}. Standard $YbCl_3$ solution were obtained by gradual dilution of 0.1 mol L^{-1} $YbCl_3$ solution.

For Ce^{3+} ion determination, polymeric membrane electrode and coated graphite electrode based on membrane containing 2,3,4:12,13,14-dipyridine-1,3,5,8,11,13,15,18-octaazacycloicosa-2,12-diene [VI(a)] and 2,3,4:12,13,14-dipyridine-1,5,8,11,15,18-hexamethylacrylate-1,3,5,8,11,13,15,18-octaazacycloicosa-2,12-diene [VI(b)] as ionophores with different composition were equilibrated for 3 days in 0.1 mol L^{-1} $Ce(NO_3)_3$ solution. The potentials were measured by varying the concentration of $Ce(NO_3)_3$ in test solution in the range 5.0×10^{-10} to 1.0×10^{-1} mol L^{-1}. Standard $Ce(NO_3)_3$ solution was obtained by gradual dilution of 0.1 mol L^{-1} $Ce(NO_3)_3$ solution.

The potential measurement for Polymeric membrane electrode (PME) were carried out at 25 ± 0.1°C using saturated calomel electrode (SCE) as reference electrode with the following cell assembly:

Hg/Hg_2Cl_2 | KCl (satd.) | (0.1 mol L^{-1}) metal salt solution || PVC membrane || test solution | Hg/Hg_2Cl_2 | KCl (satd.)

The potential measurement for Coated graphite electrode (CGE) were carried out at 25 ± 0.1°C using saturated calomel electrode (SCE) as reference electrode with the following cell assembly:

CGE | sample solution || $Hg/HgCl_2$ |KCl (satd.)

4.3 RESULTS AND DISCUSSION

4.3.1 Membranes of 3,4,5:12,13,14-dipyridine-2,6,11,15-tetramethyl -1,7,10,16-tetra methylacrylate-1,4,7,10,13,16-hexa aza cyclo octadeca 3,13-diene [IV(a)] and 3,4,5:12,13,14-dipyridine-2,6,11,15-tetra methyl-1, 7, 10, 16-tetra(2-cyanoethane)-1, 4, 7,10,13,16-hexaazacyclo octadeca-3,13-diene [IV(b)] as Tb^{3+} selective sensor

In preliminary experiments, various PVC membrane ion selective electrodes with synthesized macrocyclic pendant armed ligands IV(a) and IV(b) were prepared and tested for different cations. The results exhibited significantly high selectivity to Tb^{3+} ion over other cations. Hence macrocycles IV(a) and IV(b) were selected as a carrier for the preparation of Tb^{3+} selective sensors.

4.3.1.1 Determination of Formation constant

The formation constants ($\log \beta_{\mathrm{IL}n}$) for the ion-ionophore complexes have been determined as described in section 3.2.5 of Chapter 3. The complexation of IV(a) and

IV(b) with number of alkali, alkaline, transition and rare earth metal ions was investigated and the resulting data has been compiled in Table 4.1. The data revealed the significant binding characteristics of Tb^{3+} ion with macrocyclic pendant armed ligands IV(a) and IV(b) in comparison to all other cations. Therefore these ligands could be used as potential ionophores for preparing Tb^{3+} ion selective electrodes.

4.3.1.2 Optimization of membrane composition

The potentials of membrane of two macrocyclic pendant ligands IV(a) and IV(b) were investigated as a function of terbium ion concentration and the results are summarized in Table 4.2 and Table 4.3 respectively. The sensor no. 1 having membrane of IV(a) without plasticizer exhibits linear response over a working concentration range of 1.8×10^{-5} to 1.0×10^{-1} mol L^{-1} with a slope of 22.8 mV decade^{-1} of activity (Fig. 4.8). Similarly, sensor no. 13 having the membrane of IV(b) without plasticizer exhibits working concentration range of 1.1×10^{-4} to 1.0×10^{-1} mol L^{-1} with a slope of 17.2 mV decade^{-1} of activity (Fig. 4.9). The performance characteristics of the electrodes were improved by the addition of different plasticizers such as 1-CN, BA, DBP, *o*-NPOE and DOP. As it is obvious from Table 4.2 and Table 4.3, among the five different plasticizers, 1-CN for ligand IV(a) and BA for ligand IV(b) showed better sensitivity, widest dynamic range and lowest detection limits to Tb^{3+} ion than DBP, *o*-NPOE and DOP.

The potentiometric response of the electrode towards Tb^{3+} ion was also found to be dependant on the concentration of the ionophore incorporated within the membrane. Tb^{3+} selective electrode prepared with different amounts of ionophore have been evaluated and presented in Table 4.2 [for IV(a)] and Table 4.3 [for IV(b)]. An ionophore content of 6 mg for both the ligands has been chosen as an optimum ionophore amount because the surface conditions of the PVC membrane deteriorated on increasing or decreasing the carrier content.

The influence of membrane additives was also investigated by incorporating NaTPB and KTpClPB in conjugation with ionophores IV(a) and IV(b) on the potentiometric response of Tb^{3+} selective electrode. As is obvious from Table 4.2 and Table 4.3, the use of 4 mg NaTPB and 3 mg KTpClPB significantly improve the performance characteristics of the membrane sensors.

4.3.1.3 Potentiometric calibration characteristics of the proposed terbium sensors

The best electrode (no. 7) based on IV(a) having composition IV(a):PVC:1-CN:NaTPB in the ratio of 6: 32: 58: 4 (w/w; mg) exhibited Nernstian slope of 19.8 ± 0.2 mV $decade^{-1}$ of activity over a wide concentration range of 8.7×10^{-8} to 1.0×10^{-1} mol L^{-1} with a limit of detection 3.4×10^{-8} mol L^{-1} while electrode (no. 23) based on IV(b) having composition IV(b):PVC:BA:KTpClPB in the ratio of 6: 31:60:3 (w/w;mg) exhibited a Nernstian slope (19.6 ± 0.2 mV $decade^{-1}$ of activity) and concentration range of 1.7×10^{-7} to 1.0×10^{-1} mol L^{-1} with a limit of detection 1.1×10^{-7} mol L^{-1}.

4.3.1.4 Response characteristics of polymeric membrane electrode (PME) and coated graphite electrode (CGE)

The investigations on PVC based membrane of two macrocyclic pendant ligands, *viz.* IV(a) and IV(b) have shown that they act as Tb^{3+} selective sensors. However, of the two ligands, the sensor no. 7 containing 1-CN as plasticizer exhibited the best response characteristics in terms of working concentration range, detection limit and selectivity. The other sensors having BA, DBP, *o*-NPOE and DOP as plasticizers did not show much improved response characteristics. Thus, membrane containing 1-CN as plasticizer (sensor no. 7) was selected to prepare both the PME and CGE for the Tb^{3+} ion. The EMF response of the PME and CGE (Fig. 4.10) indicates their Nernstian behaviour over a wide concentration range. A comparison of data given in Table 4.4 revealed that CGE showed better response characteristics than PME in terms of working concentration range (1.0×10^{-8} to 1.0×10^{-1} mol L^{-1}), detection limit (5.7×10^{-9} mol L^{-1}), Nernstain slope (19.7 ± 0.1 mV $decade^{-1}$ of activity) and shows high selectivity for Tb^{3+} ion.

4.3.1.5 Response time and lifetime of the proposed sensors

Dynamic response time is an important factor for any ion-selective electrodes. To measure the dynamic response time of the proposed electrode the concentration of the test solution was successively changed from 1.0×10^{-6} to 1.0×10^{-1} mol L^{-1}. The average time required for the electrodes to reach a potential response within ±1 mV of the final equilibrium value after successive immersion in a series of Tb^{3+} ion solution, each having a tenfold difference in concentration is 10 s for PME (Fig. 4.11) and 8 s for CGE (Fig. 4.12).

The PME and CGE could be used over a period of 3 months and 5 months respectively at a stretch without observing any significant change in response time, slope and working concentration range. After this period, a slight change in slope and response time was observed. However, during usage, they were stored in 0.1 mol L^{-1} Tb^{3+} solution.

4.3.1.6 Influence of pH on sensor performance

The potentiometric response of the proposed sensor was found to be sensitive to pH changes. Thus, the pH dependence of the electrodes was tested by measuring the potential response of solution containing 1.0×10^{-2} mol L^{-1} and 1.0×10^{-3} mol L^{-1} of the Tb^{3+} ion in the pH range 1.0-10.0. The pH was adjusted by using 0.1 mol L^{-1} solution of either HCl or NaOH and the results are shown in Fig. 4.13 and Fig. 4.14 for PME and

CGE respectively. It can be seen that potential response for PME and CGE remains constant over pH range of 3.0-7.5 and 2.0-8.5, respectively. Therefore, the same was taken as the working pH range of the electrodes. The significant change in potential response observed at lower pH can be reasonably related to the response of the sensor to the hydrogen ions. On the other hand, the observed potential drift at higher pH values could be due to the formation of some hydroxyl complexes of Tb^{3+} ion in solution.

4.3.1.7 Interference of foreign ions on sensor performance

The most important characteristics of any ion-sensitive sensor system are its response to primary ion in presence of other ions present in the solution, which is expressed in terms of potentiometric selectivity coefficients. The potentiometric selectivity coefficients were evaluated by matched potential method (MPM), which is recommended to overcome the difficulties associated with the methods based on the Nicolsky-Eisenman equation [43]. According to this method, the specified amount of the primary ion ($a_{Tb} = 1.0 \times 10^{-5}$ mol L^{-1}) was added to the reference solution ($a'_{Tb} = 5.0 \times 10^{-5}$ mol L^{-1}) of Tb^{3+} ions, and the potential is measured at pH 5.5. In a separate experiment interfering ion concentrations ($a_B = 1 \times 10^{-4}$ to 1×10^{-1} mol L^{-1}) were added to an identical reference solution at the same pH, until the measured potential matched that obtained after the addition of the primary ions. The resulting values for both the electrodes are listed in Table 4.5. It is quite obvious that the proposed Tb^{3+} ion-selective electrodes are highly selective with respect to other common cations. The interfering effect of the cations is in the following order: $La^{3+} > Ce^{3+} > Sm^{3+} > Gd^{3+} > Yb^{3+} > K^{+} > Ba^{2+} > Sr^{2+} > Pb^{2+} > Ag^{+} > Na^{+} > Ca^{2+} > Cd^{2+} > Mg^{2+} > Cr^{3+} > Zn^{2+} > Cu^{2+} > Co^{2+} > Ni^{2+}$. The selectivity coefficients are in the order of 10^{-3} (for PME) and 10^{-4} (for

CGE) or lower, which seems to indicate that these cations have negligible impact on the functionality of the Tb^{3+} sensor.

4.3.1.8 Effect of non-aqueous content

The real samples may contain non-aqueous content, so the performance of the sensor was also investigated in partially non-aqueous media using 10 %, 20 %, 30 % and 35 % (v/v) non aqueous content in methanol-water, ethanol-water and acetonitrile-water mixtures (Table 4.6). It was found that the membranes do not show any appreciable change in working concentration range and slope in methanol-water and ethanol-water mixtures up to 30 % (v/v) non-aqueous contents, whereas in acetonitrile-water mixture, membrane could tolerate up to 20 % (v/v) non-aqueous content. However, above these mentioned non aqueous contents, the slope and working concentration range decreased drastically and the potentials were slightly irreproducible. The drift in potentials in the organic phase may be due to leaching of the ionophore at higher organic content.

4.3.1.9 Effect of surfactants on the potentiometric performance of the sensor

The presence of surfactants can result in the washing out of ionophore from the membrane to the aqueous phase, thus shortening the electrode lifetime significantly. The ionic and nonionic surfactants interact with the polymer membrane and undergo a division into the sample phase and the membrane phase enhancing the extraction of interfering ions from the sample solution leading to the decreased selectivity of the membrane. Surfactants can also disturb the measurements because of their molecule adsorption on the membrane surface, which results in potential instability and prolonged time of sensor response [44-46].

In the present paper, we examined the effect of cationic (tetrabutylammonium chloride, TBC), anionic (sodium dodecyl sulfate, SDS) and nonionic (Triton X-100) surfactants on the potentiometric properties of proposed CGE based on the macrocyclic pendant ligand IV(a) and the results obtained are compiled in Table 4.7. It was observed that the amount of surfactants up to 1.0×10^{-4} mol L^{-1} does not cause any significant change in the response characteristics of the proposed electrode. However, concentration of the surfactants above 1.0×10^{-4} mol L^{-1} adversely affects the performance of the electrode as the selectivity, slope and working concentration range were observed to decrease.

4.3.1.10 Analytical Application

4.3.1.10.1 Potentiometric titration of Tb^{3+} ion solution with standard EDTA solution

The analytical utility of the electrode was evaluated by carrying out potentiometric titration of 20 mL of 5.0×10^{-4} mol L^{-1} Tb^{3+} ions against 1.0×10^{-2} mol L^{-1} EDTA at pH 5.5 using CGE as an indicator electrode. The titration plot shown in Fig. 4.15 is of sigmoid shape that is also an indication of selectivity of electrode. The inflexion point of the plot corresponds to 1:1 stoichiometry of Terbium–EDTA complex.

4.3.1.10.2. Determination of Tb^{3+} ion in real samples

The terbium selectivity exhibited by the CGE makes it potentially useful for the determination of fluoride ion concentration in different mouth wash solutions, in toothpaste and also in grape juice. 1 g of each sample of the sodium fluoride mouth wash solutions and toothpaste was taken and diluted with distilled water in a 100 mL flask and 25 mL of this solution was titrated with a Tb^{3+} ion solution (1.0×10^{-4} mol L^{-1}) at pH 5.5. In the analysis of grape juice, it is first centrifuged for 15 min to obtain pulp free liquid and then were filtered and analyzed by the proposed electrode. The results of triplicate measurements for these samples were presented in Table 4.8. As can be seen from the table, there is a good agreement between the declared content and the determined values. The different mouthwash samples were obtained from IIT Roorkee Hospital and toothpaste from market.

4.3.1.10.3 Recovery of Tb^{3+} ions from tap water samples

The proposed CGE was also used for the recovery of Tb^{3+} ion from tap water samples and the results are summarized in Table 4.9. From the table, one can see the quantitative recovery of Tb^{3+} ions from the sample solution.

4.3.1.10.4 Determination of Tb^{3+} ion in binary mixtures

The sensor was applied to the direct monitoring of the Tb^{3+} ions in various binary mixtures because of the high selectivity and very low detection limit of the constructed Tb^{3+} sensor. Binary mixtures were prepared by adding 10 mL of 1×10^{-3} mol L^{-1} solution of cations in 1×10^{-4} mol L^{-1} Tb^{3+} ion solution. The pH was adjusted to 5.5. The results obtained are compiled in Table 4.10. It can be seen from the table that the recovery is satisfactory and in the range of 99.5 – 99.6 %.

4.3.1.11 Conclusion

The investigations on PVC-based membrane sensors based on two macrocyclic pendant ligands *viz.* 3,4,5:12,13,14-dipyridine-2,6,11,15-tetramethyl-1, 7, 10,16-tetramethylacrylate-1, 4, 7, 10, 13, 16-hexaazacyclooctadeca-4,13-diene [IV(a)] and 3,4,5:12,13,14-dipyridine-2,6,11,15-tetramethyl-1,7,10,16-tetra(2-cyanoethane)-1,4, 7, 10, 13,16-hexaazacyclooctadeca-4,13-diene [IV(b)] were used for quantification of Tb^{3+} ions. The best response characteristics were exhibited by sensor no. 7 having composition IV(a):PVC:1-CN:NaTPB in the ratio of 6:32:58:4 (w/w; mg) which showed widest working concentration range (8.7×10^{-8} to 1.0×10^{-1} mol L^{-1}), Nernstian compliance (19.8 mV decade^{-1} of activity) and high selectivity for Tb^{3+} ions. This membrane was selected to fabricate CGE which showed better detection limit (5.7×10^{-9} mol L^{-1}), response time (8 s) and selectivity over PME. Thus, the CGE was selected for determination of fluoride ions in mouth wash solutions, in toothpaste and in grape juice. The sensor was also used in direct determination of Tb^{3+} ions in tap water and various binary mixtures with quantitative results and used as indicator electrode in potentiometric titration.

4.3.2 Membranes of 2,12-(2-methoxyaniline)$_2$-4,14-Me$_2$-[20]-1,4,11,14-tetraene-1,5,8,11,15,18-N$_6$ [V(a)] and 2,12-(2-methoxy aniline)$_2$-4,14-Me$_2$-8,18-dimethylacrylate-[20]-1,4,11,14-tetraene-1,5, 8,11,15,18-N$_6$ [V(b)] as Yb^{3+} selective sensor

The macrocyclic ligands V(a) and V(b) were used as neutral carrier for the preparation of PVC-membrane electrodes for a number of metal ions, including alkali, alkaline, transition and heavy metal ions. While the slopes of the linear parts of the EMF sensor responses for all the other used cations are much lower than those expected by the Nernst equation, the resulting Yb^{3+} potential response presents Nernstian behavior.

4.3.2.1 Determination of formation constant

The determination of formation constant has been carried out to better understand the fundamental interaction between the metal ions and neutral carriers and their relationship to molecular recognition. In present studies, we have investigated the response of both the ligands towards metal ions by using segmented sandwich membrane method. It is apparent from Table 4.11 that among different metal ions, the ionophores V(a) and V(b) shows high binding characteristics with Yb^{3+} ions in comparison to other cations.

4.3.2.2 Optimization of membrane composition

The potentials of membrane of two macrocyclic ligands V(a) and V(b) were investigated as a function of ytterbium ion concentration and the results are summarized in Table 4.12 and Table 4.13 respectively. The sensor no. 1 having membrane of V(a) without plasticizer and ionic additive exhibits linear potential response over a working concentration range of 2.8×10^{-5} to 1.0×10^{-1} mol L^{-1} with a slope of 23.4 mV $decade^{-1}$ of activity. Similarly, sensor no. 13 having the membrane of V(b) without plasticizer and ionic additive exhibits linear response over a working concentration range of 1.3×10^{-5} to 1.0×10^{-1} mol L^{-1} with a slope of 20.8 mV $decade^{-1}$ of activity. The slopes of the membranes are near-Nernstian only and the working concentration ranges narrow. Thus, the performance of the membrane needs improvements. The addition of plasticizers not only improves the workability of the membranes but also contributes significantly towards the improvement in the detection limit, stability and shelf life of the sensor [47,48]. Thus, several membranes of varying composition were fabricated to improve the performance characteristics of the electrode by adding different plasticizers such as DBP, TBP, BA, DBS and *o*-NPOE as shown in Fig. 4.16 (for V(a)) and Fig. 4.17 (for V(b)). The results thus obtained indicates that the solvent medium of DBP for V(a) and BA for V(b) provides the best complexation environment between Yb^{3+} ion and their respective carriers.

The properties of ion-selective electrodes are strongly influenced by the ionic sites in their membranes. To further determine how the different lipophilic additives added to the membrane phase influence the working parameters of the electrode, a series of membranes were studied by using NaTPB and KTpClPB. As is obvious from Table 4.12 and Table 4.13, the use of 4 mg KTpClPB for V(a) and 3 mg NaTPB for V(b) significantly improves the performance characteristics of the membrane sensors.

The concentration of the ionophore in the PVC membrane is also an important parameter for evaluation of the response mechanism of neutral carrier-based ion selective sensors. Therefore the different amount of ionophores in PVC membrane was investigated and the results are summarized in Table 4.12 and Table 4.13. A carrier content of 6 mg for V(a) and 5 mg for V(b) was chosen as the optimum ionophore amount, because the surface conditions of the PVC membrane deteriorated on decreasing and increasing the carrier content.

4.3.2.3 Potentiometric calibration characteristics of the proposed ytterbium sensors

The result thus obtained indicates that the electrode (no. 8) based on V(a) having composition V(a):PVC:DBP:KTpClPB in the ratio of 6:30:60:4 (w/w; mg) exhibits a Nernstian slope (19.4 ± 0.2 mV decade^{-1} of activity) and a concentration range of 1.6×10^{-7} to 1.0×10^{-1} mol L^{-1} with a limit of detection 1.1×10^{-7} mol L^{-1} while the best results were shown by the electrode (no. 19) based on V(b) having composition V(b): PVC: BA: NaTPB in the ratio of 5:40:52:3 (w/w; mg) which exhibits a Nernstian slope of 19.8 ± 0.2 mV decade^{-1} of activity over a wide concentration range of 8.0×10^{-8} to 1.0×10^{-1} mol L^{-1} with a limit of detection 4.3×10^{-8} mol L^{-1}.

4.3.2.4 Response characteristics of polymeric membrane electrode (PME) and coated graphite electrode (CGE)

The investigations on PVC based membrane of two macrocyclic ligands, *viz.* V(a) and V(b) have shown that they act as Yb^{3+} selective sensors. However, of the two ligands, the sensor no. 19 based on V(b) containing BA as solvent mediator with the composition V(b): PVC: BA: NaTPB in the ratio of 5: 40: 52: 3 (w/w; mg) exhibit widest working concentration range and high selectivity for Yb^{3+} ions. Therefore, this membrane was selected to fabricate CGE for the Yb^{3+} ion. The CGE showed Nernstian behaviour with widest working concentration range of 9.4×10^{-9} to 1.0×10^{-1} mol L^{-1}, detection limit of 5.8×10^{-9} mol L^{-1} and Nernstian slope of 19.7 ± 0.1 mV $decade^{-1}$ of activity (Fig. 4.18). The comparison of data between both the electrodes clearly revealed the superiority of CGE in terms of working concentration range, detection limit and selectivity over PME (Table 4.14).

4.3.2.5 Response time and lifetime of the proposed sensors

Response time of both electrodes was investigated by dipping method [49-52] and was measured at various concentrations (1.0×10^{-6} to 1.0×10^{-1} mol L^{-1}) of the test solutions. The respective results are presented in Fig 4.19. It was found that the average time required for the electrodes to reach a potential response within ±1 mV of the final equilibrium value after successive immersion in a series of Yb^{3+} ion solution was 10 s for PME and 8 s for CGE.

The PME and CGE could be used for over a period of 4 months and 5 months respectively at a stretch without observing any significant change in response time, slope and working concentration range. To record the lifetime of the membrane (sensor no. 19) the potentials were checked daily, the sensing behavior of the membrane remained reasonably constant over a period of 5 months, beyond which a drift in potentials was observed because the membrane became mechanically weak and swelled up due to which leaching of ions from the membrane phase took place.

4.3.2.5 Influence of pH on sensor performance

The potentiometric response of the proposed sensor was found to be sensitive to pH changes. Thus, the pH dependence of the electrodes was tested by measuring the potential response of solution containing 1.0×10^{-3} mol L^{-1} and 1.0×10^{-4} mol L^{-1} of the Yb^{3+} ion in the pH range 1.0-10.0. The pH was adjusted by using 0.1 mol L^{-1} solution of either HCl or NaOH and the results are shown in Fig. 4.20 for PME and CGE. It can be seen that potential response for PME and CGE remains constant over pH range of 3.0-8.0 and 2.5-8.5 respectively. Therefore, the same was taken as the working pH range of the electrodes. The significant change in potential response observed at lower pH can be reasonably related to the response of the sensor to the hydrogen ions. On the other hand, the observed potential drift at higher pH values could be due to the formation of some hydroxyl complexes of Yb^{3+} ion in solution.

4.3.2.6 Interference of foreign ions on sensor performance

Selectivity is an important characteristic of a sensor that delineates the extent to which the device may be used in the estimation of analyte ion in the presence of other ions and extent of utility of any sensor in real sample measurements. In the present study, the selectivity coefficients were determined using the fixed interference method (FIM). The selectivity coefficients were evaluated by potential measurement on solutions containing fixed concentration of interfering ion (1.0×10^{-2} mol L^{-1}) and varying concentration of Yb^{3+} ions. The selectivity studies were carried out for both PME and CGE at pH 5.5 and results are summarized in Table 4.15. It is quite obvious from the data that the proposed Yb^{3+} ion-selective electrodes are highly selective with respect to other common cations. The selectivity coefficients are in the order of 10^{-3} (for PME) and 10^{-4} (for CGE), which seems to indicate that these cations have negligible impact on the functionality of the Yb^{3+} sensor. In all cases, the selectivity coefficients obtained for CGE are lower than those for the PME emphasizing the high selectivity of CGE for Yb^{3+} ion.

4.3.2.7 Effect of non-aqueous content

The functioning of CGE in non-aqueous medium was investigated by measuring its potential in methanol-water, ethanol-water and acetonitrile-water mixtures up to 10 %, 20 %, 30 % and 35 % (v/v) non-aqueous content. The working concentration range and slope determined in these mixtures are compiled in Table 4.16. It was found that the membranes do not show any appreciable change in working concentration range and slope in methanol-water and ethanol-water mixtures up to 30 % (v/v) non-aqueous content, whereas in acetonitrile-water mixture, membrane could tolerate up to 20 % (v/v) non-aqueous content.

4.3.2.8 Effect of Ionic and Nonionic Surfactants

In order to evaluate the effect of surfactants on potentiometric properties of the CGE based on ionophore V(b), the values of selectivity coefficients were determined in the presence of cationic (tetrabutylammonium chloride, TBC), anionic (sodium dodecyl sulfate, SDS) and nonionic (Triton X-100) surfactants. The results are depicted in Table 4.17. The amount of surfactant up to 1.0×10^{-4} mol L^{-1} does not cause any changes in the sensor selectivity, but the presence of surfactants greater than 1.0×10^{-4} mol L^{-1} in the sample solution adversely affects the performance of the electrode as the selectivity, slope and working concentration range were observed to decrease. This is evident because these substances undergo a division into the sample phase and the membrane phase enhancing the extraction of interfering ions from the sample solution. Correspondingly, this would result in a large measuring error or alter the original selectivity.

4.3.2.9 Analytical Application

4.3.2.9.1 Potentiometric titration of Yb^{3+} ion solution with standard EDTA solution

The analytical utility of the electrode was evaluated by carrying out potentiometric titration of 20 mL of 5.0×10^{-3} mol L^{-1} Yb^{3+} ions against 1.0×10^{-2} mol L^{-1} EDTA at pH 5.5 using CGE as an indicator electrode. The titration plot shown in Fig. 4.21 is of sigmoid shape. The inflexion point of the plot corresponds to 1:1 stoichiometry of Yb–EDTA complex.

4.3.2.9.2 Determination of fluoride ion concentration in mouthwash preparations

The proposed coated graphite electrode was used in the determination of fluoride ion concentration in mouthwash preparations. Each sample of the sodium fluoride mouthwash solutions was diluted with distilled water in a 100 mL flask and titrated with Yb^{3+} solutions (1.0×10^{-4} mol L^{-1}). The results of the triplicate measurements are presented in Table 4.18. As can be seen from the Table 4.18, there is good agreement between the declared fluoride contents and the values determined.

4.3.2.9.3 Determination of Yb^{3+} ions in wine samples

Yb^{3+} ions were used as reagent for the determination of total sulfites concentration in three different white and red wine samples. 1.0 – 2.0 g of wine sample was taken and volume made upto 10.0 mL in a volumetric flask by adding distilled water. The pH was maintained at 5.5. The resulting solution was titrated with a Yb^{3+} solution (1.0×10^{-4} mol L^{-1}). The exact amount of sulfite ion was thus evaluated from the sharp inflection point of the resulting titration curve. The results of the ISE measurements were compared with standard addition method (SAM) and summarized in Table 4.19. It is clear from the data obtained that results are in good agreement with those obtained by the SAM method and there is a satisfactory agreement between the determined value and the labeled sulfite content.

4.3.2.9.4 Determination of Yb^{3+} ion in binary mixtures

The proposed sensor was also applied to the direct monitoring of Yb^{3+} ions in various binary mixtures. Binary mixtures were prepared by adding 10 mL of

1×10^{-3} mol L^{-1} solution of cations in 1×10^{-4} mol L^{-1} ytterbium ion solution at 5.5 pH. The results are summarized in Table 4.20. As is obvious, the recovery of Yb^{3+} ions is quite quantitative (96.3-102.3%). This is due to the relatively good selectivity of the proposed electrode.

4.3.2.10 Conclusion

The present studies confirmed the selective determination of Yb^{3+} ion by 2,12-(2-methoxyaniline)$_2$-4,14-Me$_2$-[20]-1,4,11,14-tetraene-1,5,8,11,15,18-N$_6$ [V(a)] and 2, 12-(2-methoxyaniline)$_2$- 4, 14-Me$_2$- 8, 18-dimethylacrylate-[20]-1, 4, 11, 14-tetraene-1,5,8,11,15,18-N$_6$ [V(b)] incorporated in a PVC matrix. The best composition of the proposed electrode was found to be V(b):PVC:BA:NaTPB in the ratio of 5:40:52:3 (w/w; mg) which exhibited wide working concentration range (8.0×10^{-8} to 1.0×10^{-1} mol L^{-1}), Nernstian compliance (19.8 mV decade^{-1} of activity) and high selectivity for Yb^{3+} ions. The response characteristics of the CGE was found to be superior to PME w.r.t working concentration range (9.4×10^{-9} to 1.0×10^{-1} mol L^{-1}), response time (8 s) and detection limit (5.8×10^{-9} mol L^{-1}). Because of the high selectivity of CGE for Yb^{3+} ion, it is used as indicator electrode in the potentiometric titration of Yb^{3+} ions with EDTA and in determination of fluoride ions in mouthwash samples. It can also be used for determination of sulfite in wine samples and in determination of Yb^{3+} ions in various binary mixtures with quantitative results.

4.3.3 Membranes of 2,3,4:12,13,14-dipyridine-1,3,5,8,11,13,15,18-octaazacycloicosa-2,12-diene [VI(a)] and 2,3,4:12,13,14-dipyridine-1,5,8,11,15,18-hexamethylacrylate-1,3,5,8,11,13,15,18-octaazacyclo-icosa-2,12-diene [VI(b)] as Ce^{3+} selective sensor

To investigate the suitability of macrocyclic ligands VI(a) and VI(b) as ion carriers in PVC membranes, the potential responses of various membrane electrodes based on these ligands for various metal ions were obtained seperately. The best response was recorded for Ce^{3+} ion in terms of wide concentration range and slope while all other cations exhibited lower emf response.

4.3.3.1 Complexation study

In preliminary experiments, the complexation of VI(a) and VI(b) with a number of alkali, alkaline earth, transition metal and rare earth metal ions has been investigated conductometrically in acetonitrile solutions in order to obtain a knowledge about the stability and selectivity of the resulting complexes and their stoichiometry at 25 ± 0.05 °C. For this purpose, 25 mL of 1.0×10^{-4} mol L^{-1} cation solution was titrated against a 1.0×10^{-2} mol L^{-1} ionophore solution in acetonitrile media. The conductance of the solution was measured after each addition of ionophore until the titration plot in Fig. 4.22 (for VI(a) and VI(b)) showed a break which corresponds to 1:1 stoichiometry of the complexes. The conductometric titration data was further used to calculate the stability constant of the various ion-ionophore complexes formed as was discussed in Chapter 3 under section 3.3.3.1.

The logarithm of the formation constants (log K_f) of the resulting 1:1 complexes for mono, di and trivalent cations are given in Table 4.21. As seen, stability of Ce-VI(a) and Ce-VI(b) complex is higher than other cations tested. Thus, VI(a) and VI(b) with the most stable complex with Ce^{3+} ion are expected to act as a suitable ion-carrier for the fabrication of a Ce^{3+} sensor. It is also clear from the data obtained that stability constant for Ce-VI(b) is higher than Ce-VI(a) and therefore, it can be concluded that ionophore VI(b) has higher binding characteristic to Ce^{3+} ion as compared to VI(a).

4.3.3.2 Determination of formation constant

The formation constant of the ion–ionophore complex within the membrane phase was also calculated by a sandwich membrane. The logarithm of the formation constants (log β_{ILn}) for the ionophore VI(b) with different metal ions tabulated in Table 4.22 and are compared with those obtained by Conductometric method. The data obtained revealed that VI(b) forms most stable complex with Ce^{3+} ion while all other cations tested showed a weak or negligible binding characteristics. This may be due to most probably the lack of tendency for these ionophores to bind metal ions.

4.3.3.3 Optimization of membrane composition

The potential of membranes of two macrocyclic ligands VI(a) and VI(b) were investigated as a function of Ce^{3+} ion concentration and results are summarized in Table 4.23 and Table 4.24. It is seen that the sensor no. 1 having the membrane of VI(a) without plasticizer and ionic additive exhibited linear potential response over a working concentration range of 4.8×10^{-5} to 1.0×10^{-1} mol L^{-1} with a slope of 23.2 ± 0.2 mV decade^{-1} of activity. Similarly, sensor no. 13 having membrane of VI(b) without plasticizer and ionic additive exhibited linear potential response over a working concentration range of 5.0×10^{-5} to 1.0×10^{-1} mol L^{-1} with a slope of 22.8 ± 0.2 mV decade^{-1} of activity. The slopes of the membranes are near Nernstian only and the working concentration ranges narrow. Thus, the improvement in the performance was attempted by the addition of plasticizers to the membranes. The plasticizers influences the dielectric constant (ε_r) of the membrane phase and ensures high mobility of ions in the membrane [53] and it was expected to play a key role in the characteristics of the ion-selective electrode. Several membranes of varying composition were fabricated to improve the performance characteristics of the electrode by adding different plasticizers such as DBP (ε_r=6.4), TBP (ε_r=8.0), *o*-NPOE (ε_r=24.0), DOP (ε_r=5.1) and BA (ε_r = 8.0) as shown in Fig. 4.23 [for VI(a)] and Fig. 4.24 [for VI(b)]. Polar plasticizers lead to the membrane resistance reduction as compared with apolar plasticizers, which contain other functional groups with potential coordination sites which might compete with the carrier [54]. It is well established that the polarity and chemical structure of the membrane plasticizer can have a significant influence on the selectivity and dynamic response range of ISEs, although no simple correlation with polarity alone be expected. It seems that this is due to a synergism between lipophilicity and polarity. TBP [for VI(a)] and *o*-NPOE [for VI(b)] gives an intermediate value of these properties and best results were obtained. The result thus obtained indicate that the electrode no. 3 based on VI(a) having TBP as plasticizer exhibits a Nernstian slope (19.0 ± 0.3 mV decade^{-1} of activity) and a concentration range of 7.8×10^{-7}- 1.0×10^{-1} mol L^{-1} with a detection limit of 3.2×10^{-7} mol L^{-1} whereas electrode no. 16 based on VI(b) having o-NPOE as plasticizer exhibited a Nernstian slope (19.1 ± 0.2 mV decade^{-1} of activity) over a wide concentration range of 7.4×10^{-7}- 1.0×10^{-1} mol L^{-1} with a detection limit of 5.3×10^{-8} mol L^{-1}.

The properties of ion-selective electrodes (ISEs) based on neutral ionophores are strongly influenced by the ionic sites in their membranes. Although neutral carrier based ISE membranes may work properly even when they contain only a very small amount of ionic sites, the addition of a salt of lipophilic ion is advisable and beneficial for various other reasons as well. Their main function is to render the ion selective membrane perm selective, to optimize sensing selectivity (by defining the ratio of complexed to uncomplexed ionophore concentration in the membrane) and to reduce the bulk membrane impedance. In our experiments, we examined the effects of NaTPB and KTpClPB as suitable lipophilic additives in conjugation with ionophores VI(a) and VI(b) on the potentiometric response Ce^{3+} selective electrode. As is obvious from Tables 4.23 and Table 4.24, the use of 3 mg NaTPB and 2 mg KTpClPB significantly improves the performance characteristics of the membrane sensors.

The effect of the amount of ionophores incorporated in the membrane on the sensor characteristics was also investigated and results are compiled in Table 4.23 (sensor nos. 7, 9, 10) and Table 4.24 (sensor nos. 20, 21, 22). In this case of carrier type ion selective electrodes, the extraction equilibrium in the vicinity of the interface between the membrane and aqueous layer affects the potentiometric response of membrane. Inspite of these considerations, a carrier content of 7 mg for VI(a) and 6 mg for VI(b) was chosen as the optimum ionophore amount, because the surface conditions of the PVC membrane deteriorated on decreasing and increasing the carrier content.

4.3.3.4 Potentiometric calibration characteristics of the proposed cerium sensors

The result thus obtained indicates that the electrode (no. 7) having composition VI(a):PVC:TBP:NaTPB in the ratio of 7:36:54:3 (w/w; mg) exhibited a Nernstian slope of 19.2 ± 0.2 mV $decade^{-1}$ of activity and a concentration range of 5.0×10^{-7} to 1.0×10^{-1} mol L^{-1} with a limit of detection 1.9×10^{-7} mol L^{-1} while the best results were shown by the electrode (no. 20) having composition VI(b):PVC:*o*-NPOE:KTpClPB in the ratio of 6:34:58:2 (w/w: mg) which exhibited a Nernstian slope of 19.5 ± 0.2 mV $decade^{-1}$ of activity over a wide concentration range of 1.4×10^{-7} to 1.0×10^{-1} mol L^{-1} with a limit of detection 8.3×10^{-8} mol L^{-1}.

4.3.3.5 Response characteristics of polymeric membrane electrode (PME) and coated graphite electrode (CGE)

The investigations on PVC based membrane of two macrocyclic ligands, *viz.* VI(a) and VI(b) have shown that they act as Ce^{3+} selective sensors. However, of the two ligands, the sensor no. 20 based on VI(b) containing *o*-NPOE as solvent mediator with the composition VI(b):PVC:*o*-NPOE:KTpClPB in the ratio of 6:34:58:2 (w/w; mg) exhibited best response characteristics. Thus, this membrane was selected to fabricate CGE which showed much better response characteristics over PME in terms of working concentration range (1.0×10^{-8} to 1.0×10^{-1} mol L^{-1}), detection limit (7.7×10^{-9} mol L^{-1}) and high selectivity to Ce^{3+} ion (Fig. 4.25). A comparison of data between both electrodes has been summarized in Table 4.25.

4.3.3.6 Effect of Soaking time and lifetime

The lifetime of the electrodes were determined by soaking both PME and CGE in 0.1 mol L^{-1} $Ce(NO_3)_3$ solution for interval ranging from 2 to 155 days till the electrode lost its Nernstian behaviour. This behaviour is attributed to the decomposition of the ionophore and loss of other components in the membrane phase that was in contact with aqueous test solution containing Ce^{3+} ion. The response of both electrodes has been measured by recording the calibration graph at 25 °C at different intervals. The results listed in Table 4.26 shows the effect of soaking time on slope, detection limit and concentration range. It can be seen that the lifetime measured in this way was found to be 3 months for PME and 5 months for CGE during which the slope of electrode, showed only a slight change from 19.5 ± 0.2 to 16.2 ± 0.3 mV $decade^{-1}$ of activity for PME and 19.7 ± 0.1 to 15.9 ± 0.3 mV $decade^{-1}$ of activity for CGE.

4.3.3.7 Reproducibility and reversibility

The reproducibility and reversibility are two important characteristics in determining the suitability of a sensor for selective determination of the species of interest in different test solutions. The reproducibility and stability of the proposed sensors were evaluated by repeated calibration of the sensors in Ce^{3+} ion solutions. Repeated monitoring (10 determinations) of potentials over a period of 15 days in concentration range 1.0×10^{-1} to 1.0×10^{-8} mol L^{-1} with optimized membranes in sensors for each carrier, gave good reproducibility. The S.D. of slope for PME and CGE were ≤ 0.5 and ≤ 0.4 mV respectively. The S.D. of 10 replicate measurements at 1.0×10^{-3} and 1.0×10^{-6} mol L^{-1} cerium solutions were ± 0.3 and ± 0.5 mV for PME and ± 0.2 and ± 0.3 mV for CGE respectively.

4.3.3.8 Response time of the proposed sensors

The response time of the electrodes was tested by measuring the time required to achieve the steady potential. To measure the response time of the proposed electrodes the concentration of the test solution was successively changed from 1.0×10^{-6} to 1.0×10^{-1} mol L^{-1}. The resulting data shows that the time needed to reach a potential with in ± 1.0 mV of the final equilibrium value after successive immersion of a series of Ce^{3+} solution, each having a tenfold difference in concentration is 12 s for PME (Fig. 4.26) and 10 s for CGE (Fig. 4.27).

4.3.3.9 Influence of pH on sensor performance

The pH dependence of both PME and CGE has been tested over the pH range 1.0-11.0 for 1.0×10^{-3} mol L^{-1} and 1.0×10^{-4} mol L^{-1} for the Ce^{3+} ion. The pH was adjusted by using 0.1 mol L^{-1} solution of either HCl or NaOH and the results are shown in Fig. 4.28. It can be seen that potential response for PME remains constant over pH range 3.5-7.5 and

2.5-8.5 for CGE. The significant change in potential response observed at lower pH can be reasonably related to the response of the sensor to the hydrogen ions. On the other hand, the observed potential drift at higher pH values could be due to the formation of some hydroxyl complexes of Ce(III) in solution.

4.3.3.10 Interference of foreign ions on sensor performance

Selectivity is the most important characteristics as it determines the extent of utility of any sensor in real sample measurements. It gives the response of ion0sensitive sensor for the primary ion in the presence of other ions present in solution, which is expressed in terms of potentiometric selectivity coefficients. Fixed Interference Method (FIM) was used to determine the selectivity of Ce^{3+} ion with respect to alkali, alkaline, transition and rare earth metal ions. In this method, the selectivity coefficient was evaluated from potential measurement on solutions containing a fixed concentration of interfering ion (1.0×10^{-2} mol L^{-1}) and varying amount of Ce^{3+} ions as was discussed in detail in chapter 2 under section 2.5.

The values of selectivity coefficient so determined for PME and CGE are compiled in Table 4.27. It is quite obvious from the corresponding table that Ce^{3+} ion selective electrodes are highly selective with respect to other common cations. The data revealed that, in all cases, the selectivity coefficients obtained for CGE are lower than those for the PME, emphasizing the superiority of CGE in this respect as well and hence further analytical studies were carried out with it only.

4.3.3.11 Analytical Applications

4.3.3.11.1 Potentiometric titration of cerium ion solution with standard EDTA solution

The proposed coated graphite electrode was found to work well under laboratory conditions. It was used as an indicator electrode in potentiometric titration of 20.0 mL of

1.0×10^{-2} mol L^{-1} Ce^{3+} solution with 1.0×10^{-1} mol L^{-1} oxalate and fluoride solution at pH 5.5. The resulting titration curves are shown in Fig. 4.29. The exact amounts of oxalate and fluoride ions were then evaluated from the sharp inflection points of the resulting titration curve and can be determined with the proposed electrode.

4.3.3.11.2 Determination of fluoride ion in mouthwash samples by proposed CGE

Each sample of the sodium fluoride mouthwash solutions was diluted with distilled water in a 100 mL flask and titrated with Ce^{3+} ion solutions (1.0×10^{-4} mol L^{-1}). The results of the triplicate measurements are presented in Table 4.28. It is seen from the values obtained that there is good agreement between the declared fluoride contents and the values determined.

4.3.3.11.3 Determination of oxalate ion in vegetable samples and tap water samples by Ce3+ selective sensor (CGE)

Oxalates are found in a wide variety of foods such as spinach, mushroom, and beet leaves. Oxalic acid forms chelates with dietary calcium, thus rendering the calcium unavailable for absorption and assimilation. On the other hand, precipitation of calcium oxalate may lead to the formation of kidney stones. The determination of oxalate is therefore of considerable significance, especially in food and biological samples. The reported electrode was used successfully in the determination of oxalate in tap water as well as in vegetable samples *viz.* spinach and mushroom. The sample solution of spinach and mushroom were prepared as per procedure reported [55]. 3.000 g of fresh spinach or 15.0 g of fresh mushroom were cut into small pieces and pounded into paste in amortar. The paste obtained was subsequently mixed with water in a 100 mL reflux flask and boiled for 45 min, after which time the mixture was cooled. The suspension was filtered thrice through filter paper (Whatman No. 1) and the filtrate was diluted to 250 mL. To remove the interference effect of iron cations, the pH of 5.0 mL of resulted solution was adjusted to about 10 by dropwise addition of 0.1 M sodium hydroxide solution, and the solution was centrifuged at 2000 rpm for 5 min. The resulting solution was decanted and neutralized with 0.1 mol L^{-1} HCl solution and diluted in a 100 mL volumetric flask. The results are tabulated in Table 4.29.

To prepare the spiked water samples, about 20 mL of tap water was collected from a local pipe, to which a known amount of oxalate was added. The pH of the water sample was adjusted to about 10 by dropwise addition of 0.1 mol L^{-1} NaOH solution, and the solution was centrifuged. The resulting solution was decanted and neutralized with 0.1 mol L^{-1} HCl solution and diluted in a 25 mL volumetric flask. The results given in Table 4.30 suggests that recovery of oxalate is quite satisfactory and thus, we can say that proposed CGE can be used for real sample analysis.

4.3.3.12 Conclusion

The present studies confirmed the selective determination of Ce^{3+} ion by 2,3,4:12,13,14-dipyridine-1,3,5,8,11,13,15,18-octaazacycloicosa-2,12-diene [VI(a)] and 2,3,4:12,13,14-dipyridine-1,5,8,11,15,18-hexamethylacrylate-1,3,5,8,11,13,15,18-octaaza cycloicosa-2,12-diene [VI(b)] incorporated in a PVC matrix. The best composition of the proposed polymeric membrane electrode was found to be VI(b):PVC:*o*-NPOE:KTpClPB in the ratio of 6:34:58:2 (w/w; mg). The sensor developed using this ionophore exhibited working concentration range of 1.4×10^{-7} to 1.0×10^{-1} mol L^{-1}, detection limit of 8.3×10^{-8} mol L^{-1} with Nernstiaan slope 19.5 ± 0.3 mV $decade^{-1}$ of activity. This performance of this sensor was also compared with coated graphite electrode which showed better results than PME with respect to the working concentration range (1.0×10^{-8} to 1.0×10^{-1} mol L^{-1}), low detection limit

(7.7×10^{-9} mol L^{-1}), fast response time (10 s) and high selectivity for Ce^{3+} ion. The response characteristics of the proposed CGE are best as compared to the previously reported electrodes that make it superior potentiometric device. It also offers a practical sensing and the determination of Ce^{3+} ion in vegetable and tap water samples as well as in potentiometric titration of Ce^{3+} ion with EDTA.

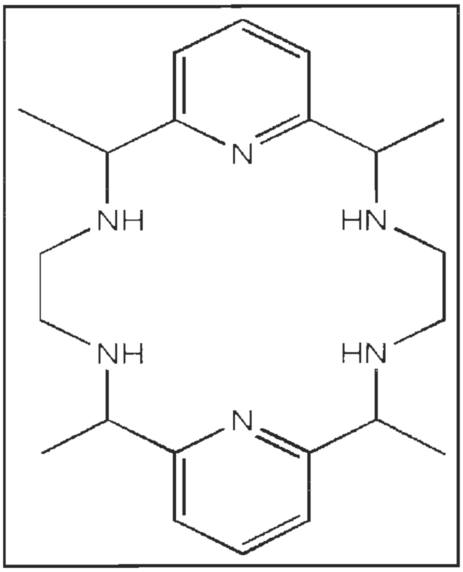


Fig. 4.1 Structure of macrocyclic ligand 3, 4 ,5 : 12 ,13, 14-dipyridine-2, 6, 11, 15-tetramethyl-1,4,7,10,13,16-hexaazacyclooctadeca-3,13-diene (IV)

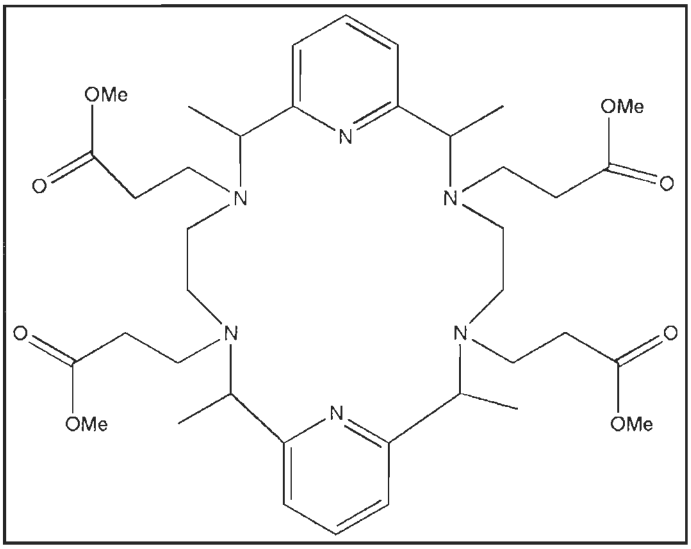


Fig. 4.2 Structure of macrocyclic pendant ligand 3,4,5:12,13,14-dipyridine- 2,6,11,15-tetramethyl-1,7,10,16-tetramethylacrylate-1,4,7,10,13,16-hexa azacyclooctadeca-3,13-diene [IV(a)]

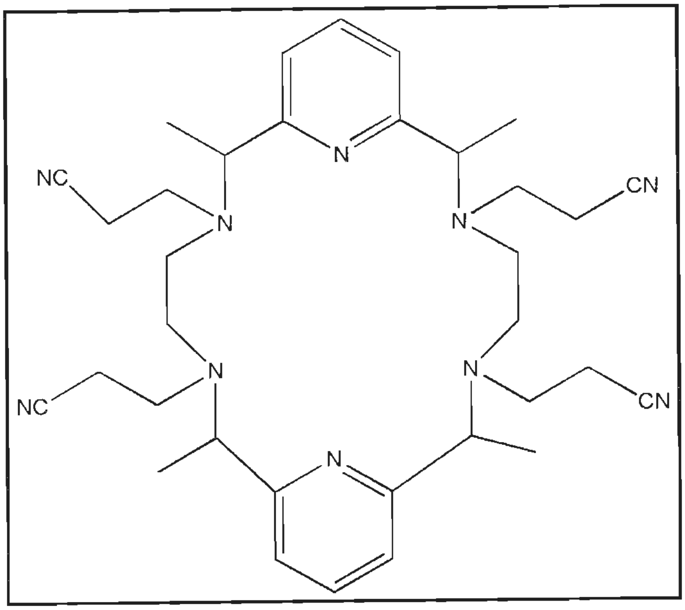


Fig. 4.3 Structure of macrocyclic pendant ligand 3,4,5:12,13,14-dipyridine- 2,6,11,15-tetramethyl-1,7,10,16-tetra(2-cyanoethane)-1,4,7,10,13,16-hexaaza cyclo octa deca-3, 13-diene [IV(b)]

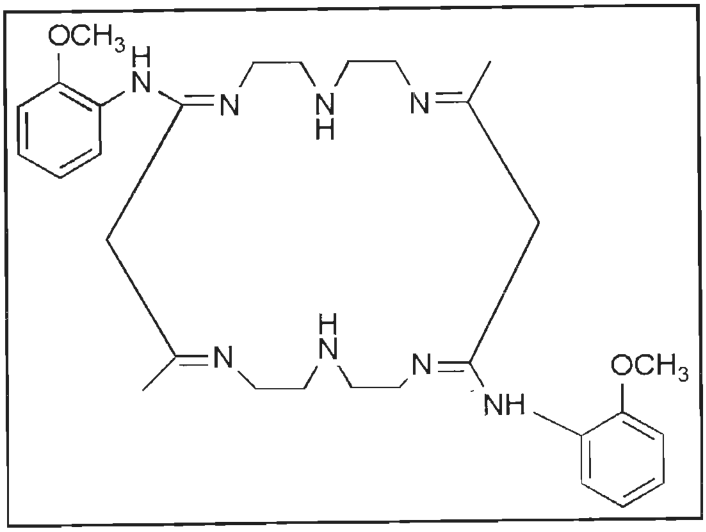


Fig. 4.4 Structure of macrocyclic ligand 2,12-(2-methoxyaniline)$_2$-4,14-Me$_2$-[20]-1,4,11,14-tetraene-1,5,8,11,15,18-N$_6$ [V(a)]

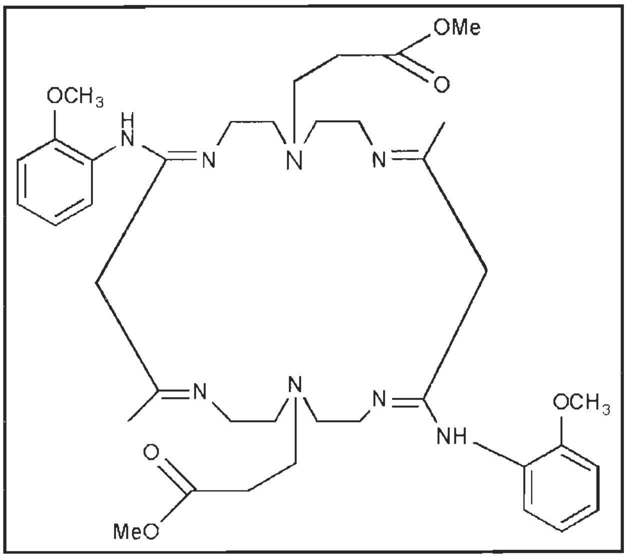


Fig. 4.5 Structure of macrocyclic pendant ligand 2,12-(2-methoxyaniline)$_2$-4,14-Me$_2$-8,18-dimethylacrylate-[20]-1,4,11,14-tetraene-1,5,8,11,15,18-N$_6$ [V(b)]

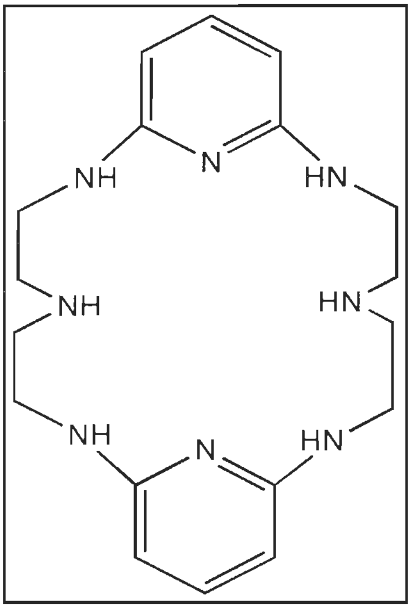


Fig. 4.6 Structure of macrocyclic ligand 2,3,4:12,13,14-dipyridine-1,3,5, 8,11, 13, 15,18-octaazacycloicosa-2,12-diene [VI(a)]

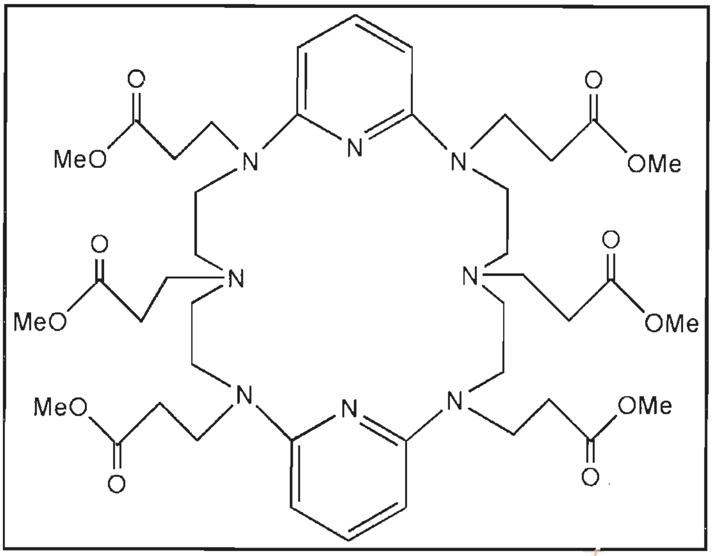


Fig. 4.7 Structure of macrocyclic pendant ligand 2,3,4:12,13,14-dipyridine-1,5, 8, 11,15,18-hexamethylacrylate-1,3,5,8,11,13,15,18-octaazacycloicosa-2,12-diene [VI(b)]

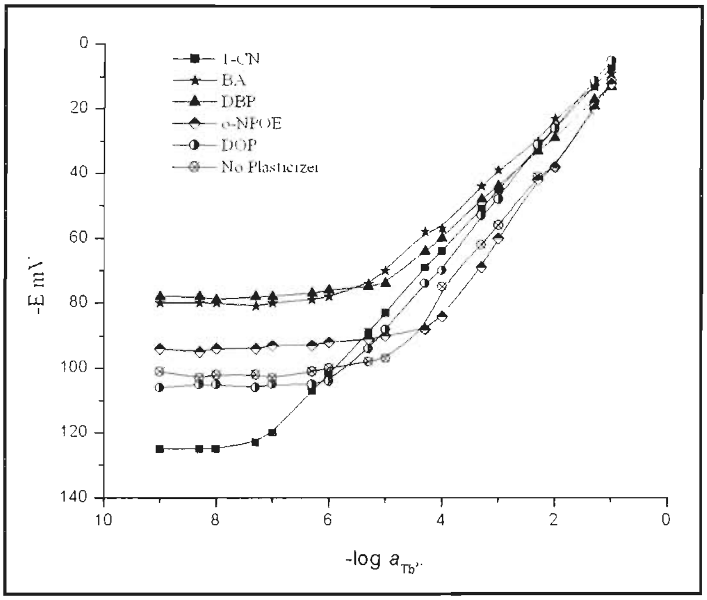


Fig. 4.8 Variation of potential of Tb^{3+} selective membrane based on IV(a) with different plasticizers as a function of Tb^{3+} concentration

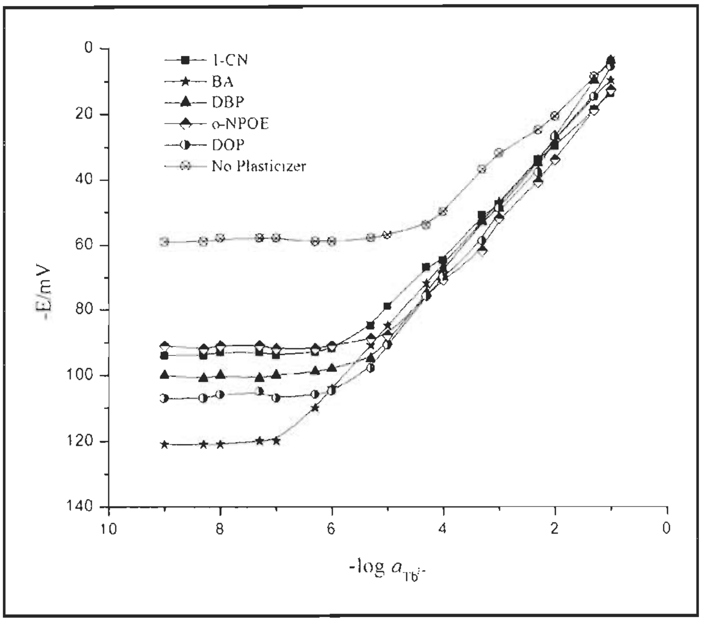


Fig. 4.9 Variation of potential of Tb^{3+} selective membrane based on IV(b) with different plasticizers as a function of Tb^{3+} concentration

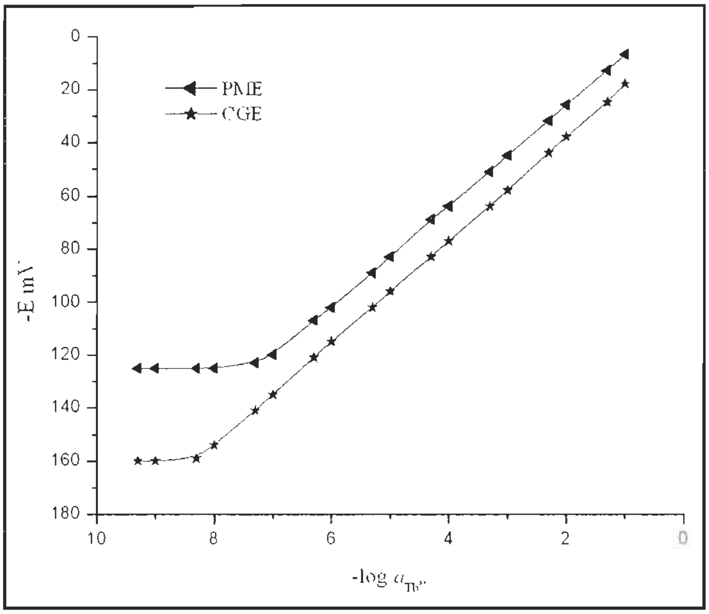


Fig. 4.10 Calibration characteristics of Tb^{3+} selective electrodes (PME and CGE) based on IV(a)

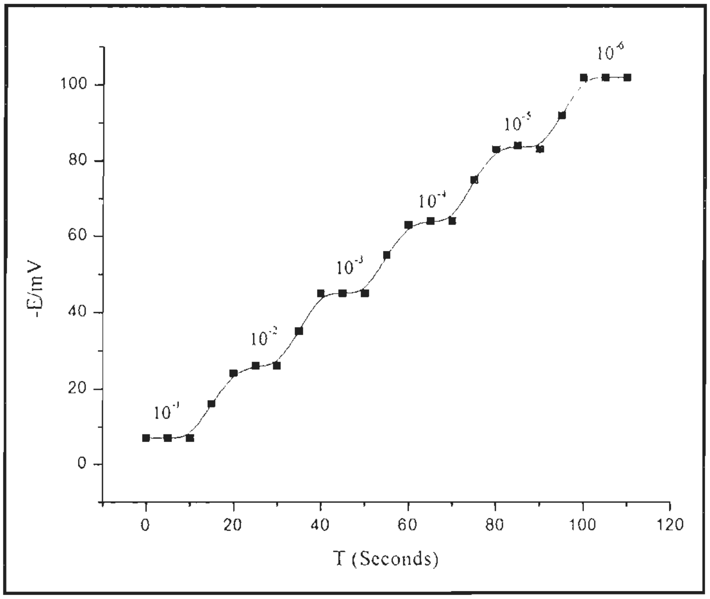


Fig. 4.11 Dynamic response of Polymeric membrane electrode based on IV(a)

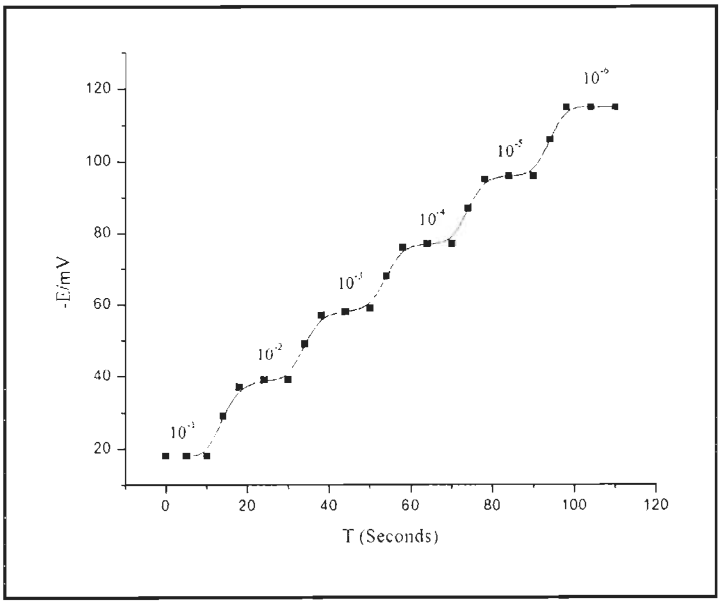


Fig. 4.12 Dynamic response of coated graphite electrode based on IV(a)

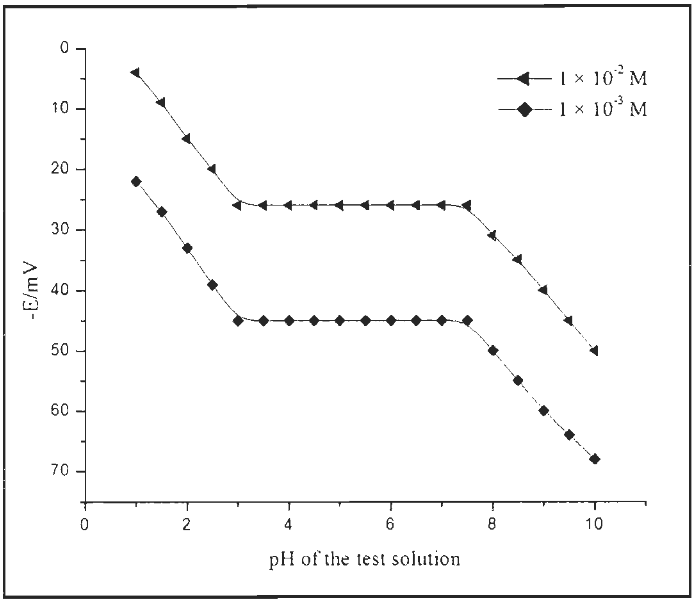


Fig. 4.13 Effect of pH of the test solutions on the potential responses of the PME at different concentration of Tb^{3+}

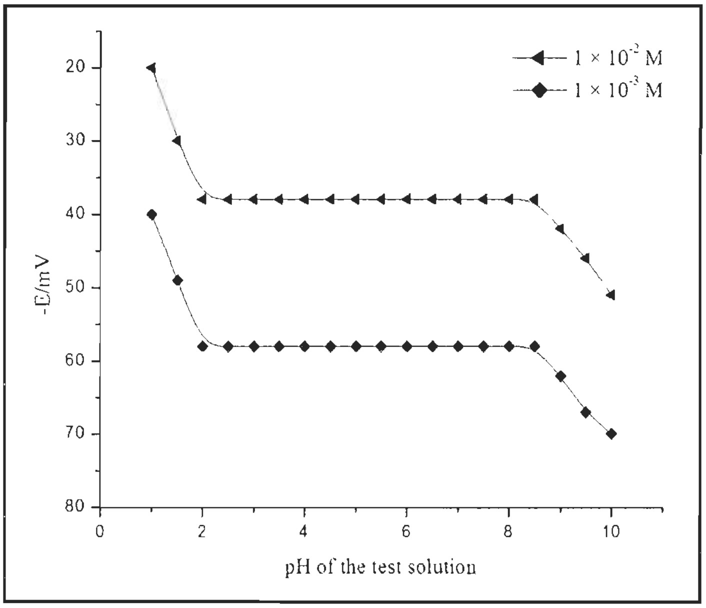


Fig. 4.14 Effect of pH of the test solutions on the potential responses of the CGE at different concentration of Tb^{3+}

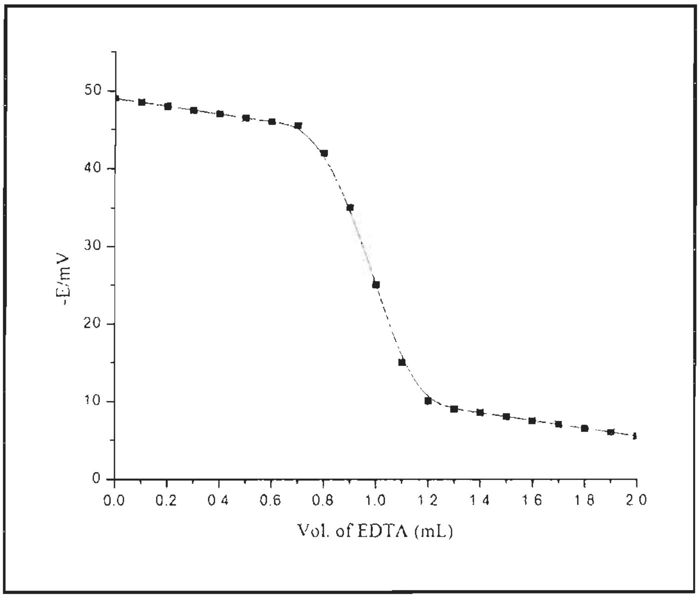


Fig. 4.15 Potentiometric titration curve of 20 mL of 5.0 × 10^{-4} mol L^{-1} solution of Tb^{3+} ion with 1.0 × 10^{-2} mol L^{-1} EDTA at pH 5.5 using CGE as indicator Electrode

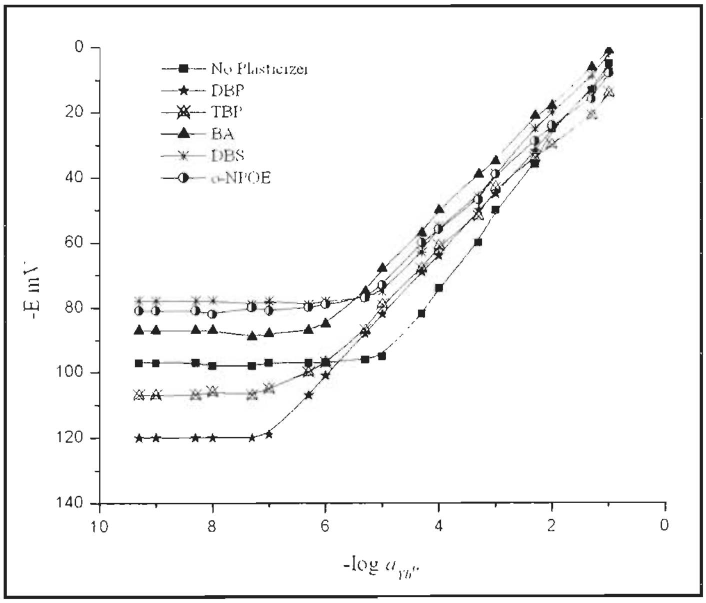


Fig. 4.16 Variation of potential of Yb^{3+} selective membrane based on V(a) with different plasticizers as a function of Yb^{3+} concentration

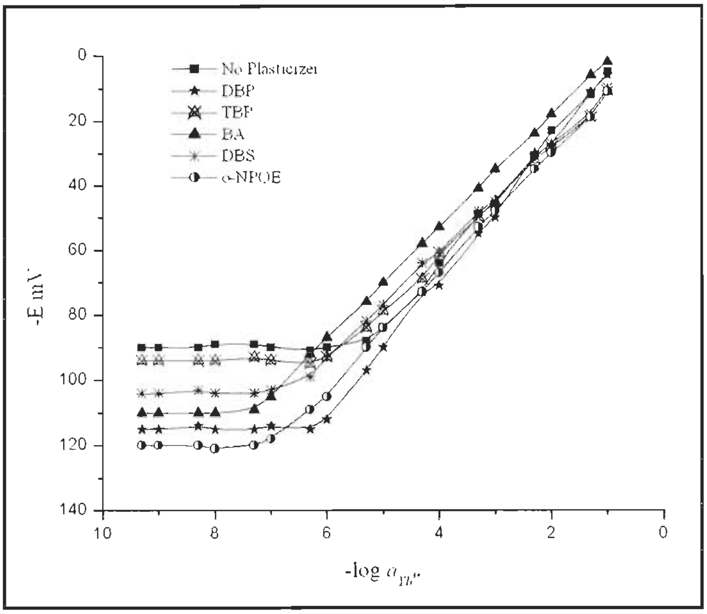


Fig. 4.17 Variation of potential of Yb^{3+} selective membrane based on V(b) with different plasticizers as a function of Yb^{3+} concentration

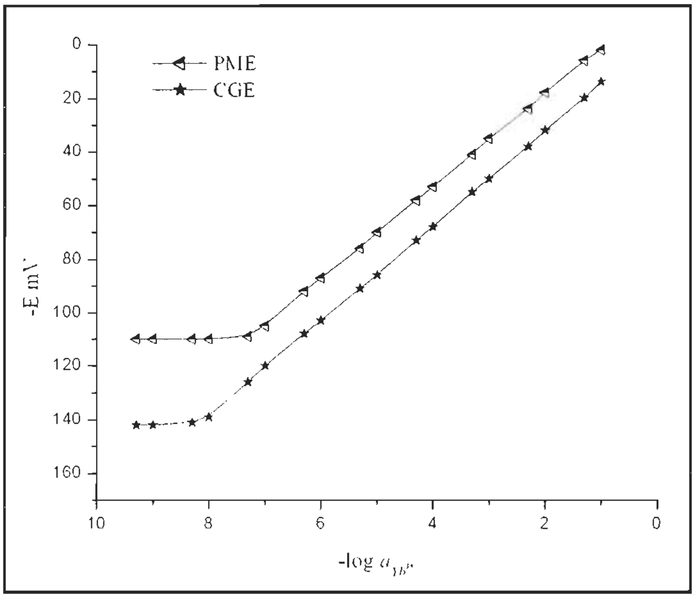


Fig. 4.18 Calibration characteristics of Yb^{3+} selective electrodes (PME and CGE) based on V(b)

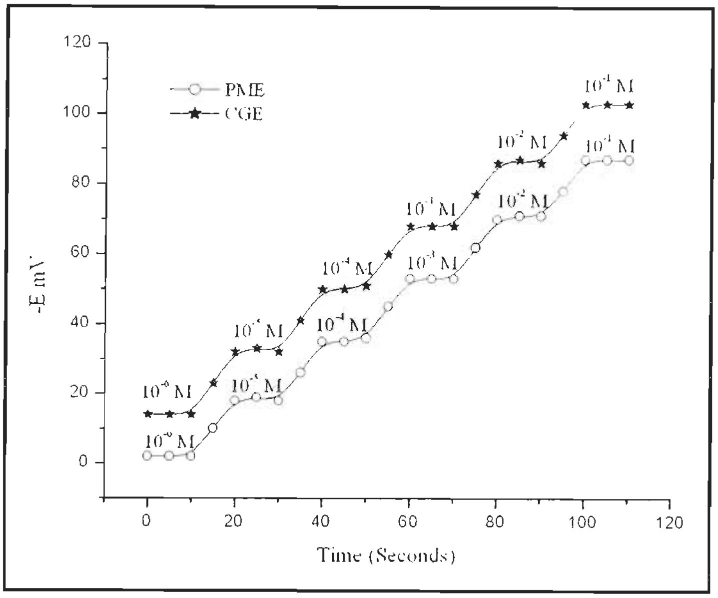


Fig. 4.19 Dynamic response of PME and CGE based on V(b)

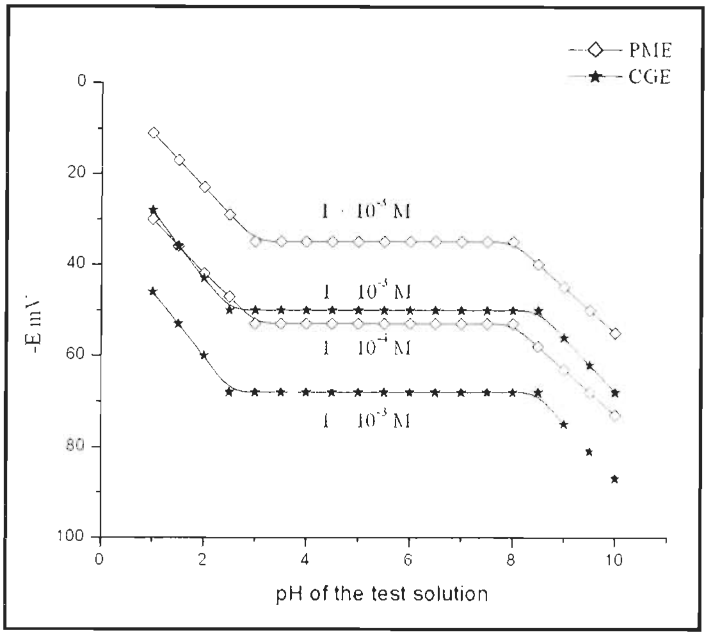


Fig. 4.20 Effect of pH of the test solutions on the potential responses of the PME and CGE

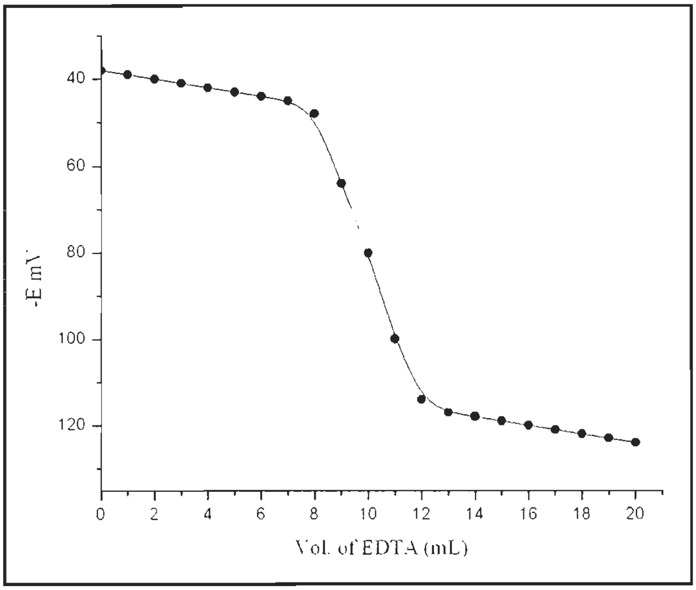


Fig. 4.21 Potentiometric titration curve of 20 mL of 5.0 × 10^{-3} mol L^{-1} solution of Yb^{3+} ion with 1.0 × 10^{-2} mol L^{-1} EDTA at pH 5.5 using CGE as indicator electrode

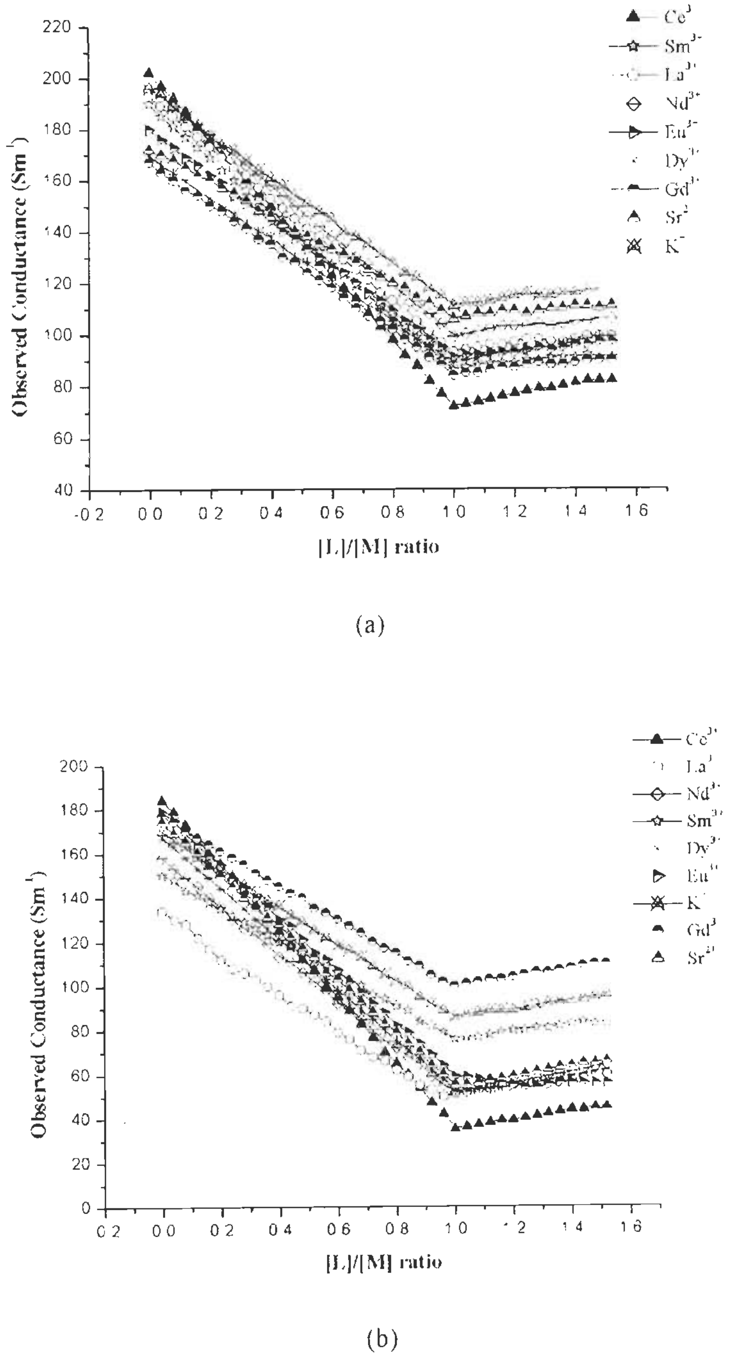


Fig. 4.22 Conductometric study of ion-ionophore complexes (a) with [VI(a)] (b) with [VI(b)]

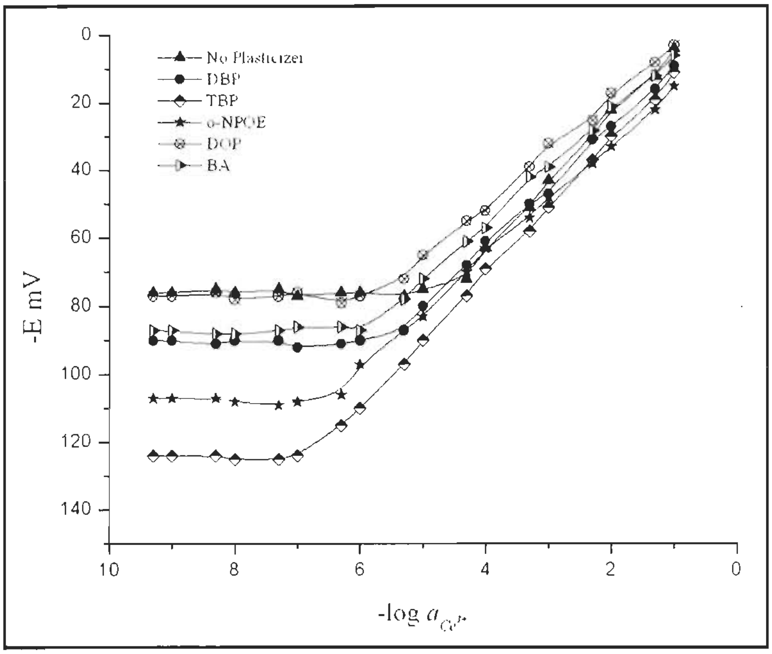


Fig. 4.23 Variation of potential of Ce^{3+} selective membrane based on VI(a) with different plasticizers as a function of Ce^{3+} concentration

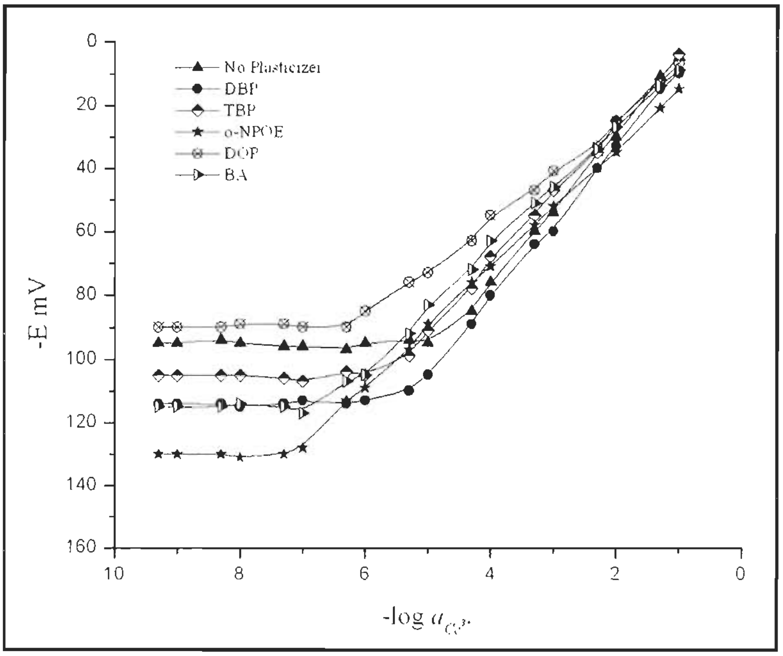


Fig. 4.24 Variation of potential of Ce^{3+} selective membrane based on VI(b) with different plasticizers as a function of Ce^{3+} concentration

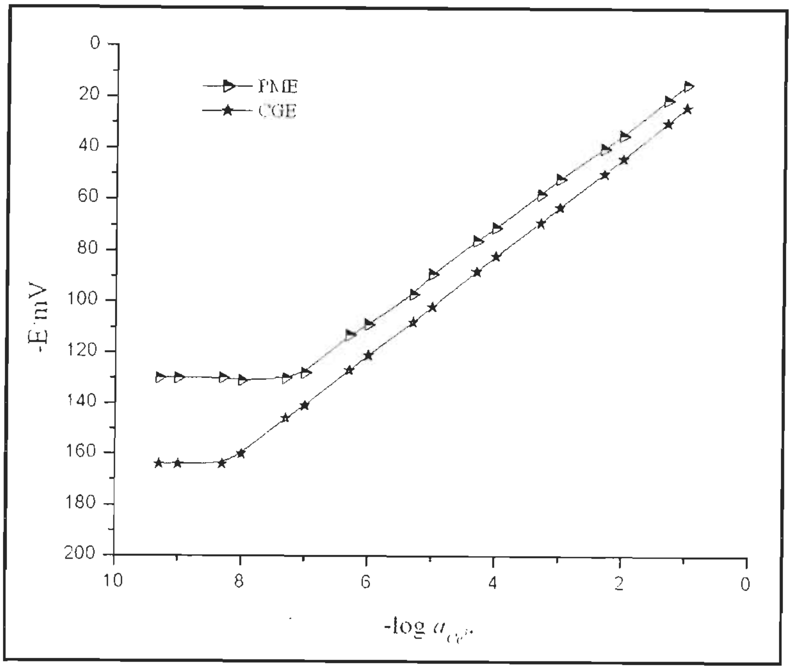


Fig. 4.25 Calibration characteristics of Ce^{3+} selective electrodes (PME and CGE) based on VI(b)

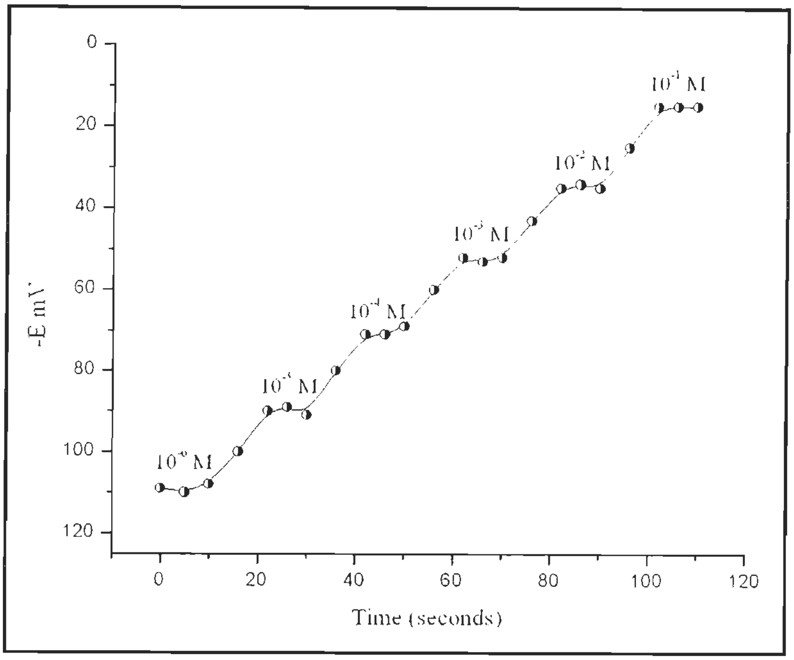


Fig. 4.26 Dynamic response of Polymeric membrane electrode based on VI(b)

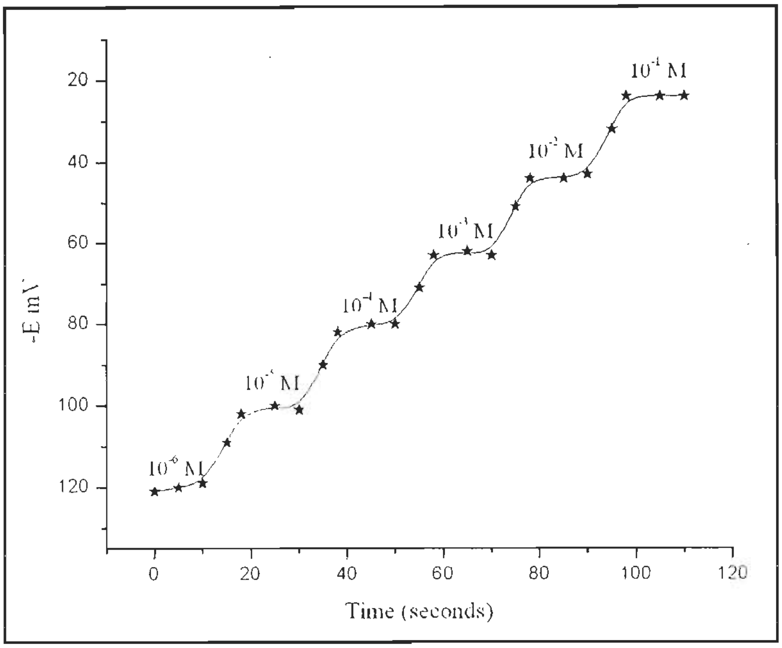


Fig. 4.27 Dynamic response of Coated graphite electrode based on VI(b)

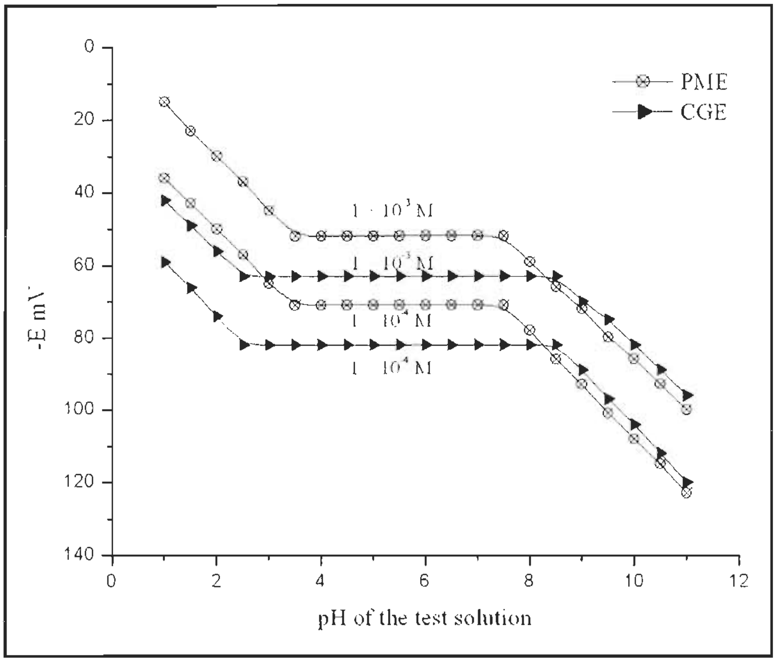


Fig. 4.28 Effect of pH of the test solutions on the potential responses of the PME and CGE at different concentration of Ce^{3+}

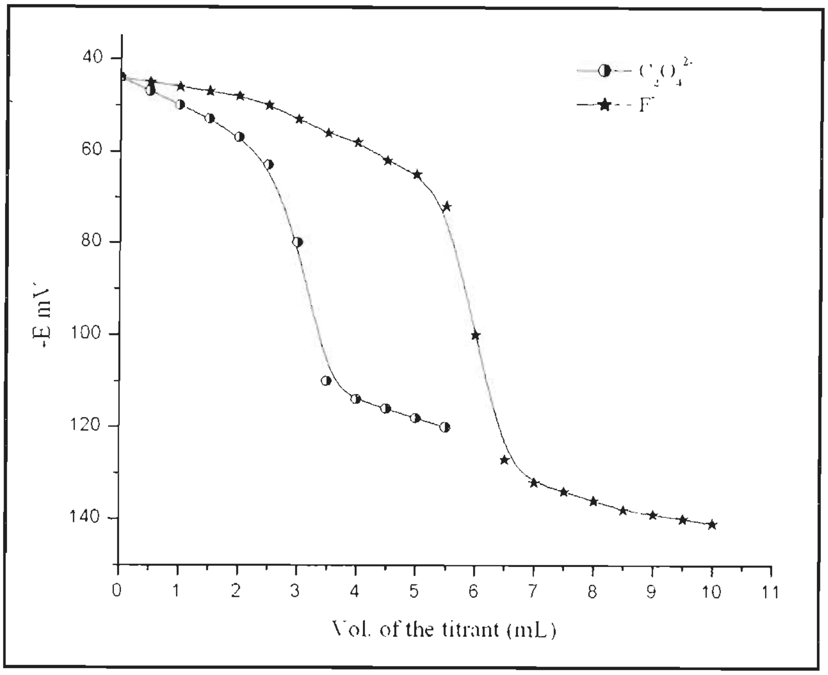


Fig. 4.29 Application of Ce^{3+} ion-selective electrode based on VI(b) in potentiometric titration of 20 mL of 1.0×10^{-2} mol L^{-1} Ce^{3+} solution with 0.1 mol L^{-1} oxalate and fluoride ion solution

Table 4.1 Formation constant of IV(a) and IV(b) with different metal ions

Metal ions	Formation constant ($\log K_f$)* ±SD	Metal ions	Formation constant ($\log K_f$)* ±SD
	IV(a)		IV(b)
Tb^{3+}	6.85 ± 0.02	Tb^{3+}	5.19 ± 0.03
La^{3+}	5.16 ± 0.05	La^{3+}	4.87 ± 0.04
Ce^{3+}	4.76 ± 0.05	Ce^{3+}	4.35 ± 0.06
Sm^{3+}	4.25 ± 0.04	Sm^{3+}	4.01 ± 0.05
Gd^{3+}	3.58 ± 0.02	Gd^{3+}	3.28 ± 0.04
Yb^{3+}	3.07 ± 0.03	Yb^{3+}	2.95 ± 0.04
K^{+}	2.93 ± 0.06	K^{+}	2.80 ± 0.05
Ba^{2+}	2.65 ± 0.05	Ba^{2+}	2.45 ± 0.09
Sr^{2+}	2.58 ± 0.11	Sr^{2+}	2.33 ± 0.07
Pb^{2+}	2.47 ± 0.15	Pb^{2+}	2.20 ± 0.05
Ag^{+}	2.42 ± 0.08	Ag^{+}	2.04 ± 0.04
Na^{+}	2.38 ± 0.06	Na^{+}	1.95 ± 0.06
Ca^{2+}	2.17 ± 0.12	Ca^{2+}	1.82 ± 0.05
Cd^{2+}	2.06 ± 0.14	Cd^{2+}	1.70 ± 0.05
Mg^{2+}	1.82 ± 0.02	Mg^{2+}	1.58 ± 0.07
Cr^{3+}	1.66 ± 0.13	Cr^{3+}	1.45 ± 0.03
Zn^{2+}	1.55 ± 0.09	Zn^{2+}	1.31 ± 0.11
Cu^{2+}	1.35 ± 0.07	Cu^{2+}	1.20 ± 0.05
Co^{2+}	1.02 ± 0.05	Co^{2+}	0.90 ± 0.07
Ni^{2+}	0.98 ± 0.03	Ni^{2+}	0.79 ± 0.09

Table 4.2 Optimization of membrane compositions and their potentiometric response for Tb^{3+} ion selective membrane based on ionophore IV(a)

S.no.	Composition of membrane (w/w; mg)									Working concentration range (mol L^{-1})	Slope (mV $decade^{-1}$ of activity)	Detection limit (mol L^{-1})
	IV (a)	NaTBP	KTpClPB	CN	BA	DBP	NPOE	DOP	PVC			
1	6	-	-	-	-	-	-	-	94	1.8×10^{-5} to 1.0×10^{-1}	22.8	7.4×10^{-6}
2	6	-	-	58	-	-	-	-	36	1.0×10^{-7} to 1.0×10^{-1}	19.3	8.1×10^{-8}
3	6	-	-	-	58	-	-	-	36	5.2×10^{-6} to 1.0×10^{-1}	16.2	2.0×10^{-6}
4	6	-	-	-	-	58	-	-	36	1.6×10^{-5} to 1.0×10^{-1}	15.9	8.9×10^{-6}
5	6	-	-	-	-	-	58	-	36	1.0×10^{-4} to 1.0×10^{-1}	17.3	3.9×10^{-5}
6	6	-	-	-	-	-	-	58	36	1.4×10^{-6} to 1.0×10^{-1}	21.5	8.4×10^{-7}
7	6	4	-	58	-	-	-	-	32	8.7×10^{-8} to 1.0×10^{-1}	19.8	3.4×10^{-8}
8	6	-	4	58	-	-	-	-	32	7.4×10^{-6} to 1.0×10^{-1}	22.1	4.1×10^{-6}
9	5	4	-	58	-	-	-	-	33	7.0×10^{-6} to 1.0×10^{-1}	14.4	4.6×10^{-7}
10	7	4	-	58	-	-	-	-	31	9.0×10^{-6} to 1.0×10^{-1}	18.6	7.0×10^{-7}
11	6	4	-	58	-	-	-	-	33	2.2×10^{-7} to 1.0×10^{-1}	23.8	1.1×10^{-7}
12	6	4	-	58	-	-	-	-	31	5.7×10^{-6} to 1.0×10^{-1}	13.2	2.4×10^{-6}

Table 4.3 Optimization of membrane compositions and their potentiometric response for Tb^{3+} ion selective membrane based on ionophore IV(b)

S.no.	Composition of membrane (w/w; mg)									Working concentration range (mol L^{-1})	Slope (mV $decade^{-1}$ of activity)	Detection limit (mol L^{-1})
	IV (b)	NaTBP	KTpClPB	CN	BA	DBP	NPOE	DOP	PVC			
13	6	-	-	-	-	-	-	-	94	1.1×10^{-4} to 1.0×10^{-1}	17.2	2.9×10^{-5}
14	6	-	-	60	-	-	-	-	34	5.7×10^{-6} to 1.0×10^{-1}	16.8	1.5×10^{-6}
15	6	-	-	-	60	-	-	-	34	9.5×10^{-7} to 1.0×10^{-1}	19.1	6.0×10^{-7}
16	6	-	-	-	-	60	-	-	34	9.6×10^{-6} to 1.0×10^{-1}	22.3	8.4×10^{-6}
17	6	-	-	-	-	-	60	-	34	1.5×10^{-5} to 1.0×10^{-1}	18.1	8.5×10^{-6}
18	6	-	-	-	-	-	-	60	34	5.8×10^{-6} to 1.0×10^{-1}	20.2	2.2×10^{-6}
19	6	4	-	-	60	-	-	-	30	8.3×10^{-6} to 1.0×10^{-1}	23.0	7.1×10^{-6}
20	6	-	4	-	60	-	-	-	30	5.6×10^{-7} to 1.0×10^{-1}	19.0	4.2×10^{-7}
21	7	-	4	-	60	-	-	-	29	7.1×10^{-6} to 1.0×10^{-1}	21.4	4.5×10^{-6}
22	5	-	4	-	60	-	-	-	31	1.0×10^{-6} to 1.0×10^{-1}	14.5	9.1×10^{-7}
23	6	-	3	-	60	-	-	-	31	1.7×10^{-7} to 1.0×10^{-1}	19.6	1.1×10^{-7}
24	6	-	5	-	60	-	-	-	29	3.8×10^{-6} to 1.0×10^{-1}	16.8	1.4×10^{-6}

Table 4.4 Response characteristics of the terbium ion-selective electrodes based on PME and CGE

Properties	Values / range	
	PME	CGE
Optimized membrane composition	(IV(a)) (6 mg): PVC (32 mg): CN (58 mg) : NaTPB (4 mg)	(IV(a)) (6 mg): PVC (32 mg): CN (58 mg) : NaTPB (4 mg)
Conditioning time	2 days in 0.1 mol L^{-1} $TbCl_3$	2 days in 0.1 mol L^{-1} $TbCl_3$
Working concentration range (mol L^{-1})	8.7×10^{-8}-1.0×10^{-1}	1.0×10^{-8}-1.0×10^{-1}
Detection limit (mol L^{-1})	3.4×10^{-8}	5.7×10^{-9}
Slope (mV $decade^{-1}$ of activity)	19.8	19.7
S.D. of slope	± 0.2	± 0.1
Response time (s)	10	8
Life span	3 months	5 months
pH range	3.0-7.5	2.0-8.5

Table 4.5 Selectivity coefficient of various interfering ions for Tb^{3+} ion selective electrodes

Interfering cations	Selectivity Coefficient ($K_{A,B}^{MPM}$)	
	PME	CGE
La^{3+}	1.9×10^{-2}	4.3×10^{-3}
Ce^{3+}	2.7×10^{-2}	7.5×10^{-3}
Sm^{3+}	2.3×10^{-3}	2.8×10^{-4}
Gd^{3+}	2.8×10^{-3}	3.3×10^{-4}
Yb^{3+}	3.1×10^{-3}	4.2×10^{-4}
K^{+}	4.7×10^{-3}	5.1×10^{-4}
Ba^{2+}	5.9×10^{-3}	6.3×10^{-4}
Sr^{2+}	6.4×10^{-3}	7.3×10^{-4}
Pb^{2+}	7.2×10^{-3}	9.8×10^{-4}
Ag^{+}	7.7×10^{-3}	1.9×10^{-5}
Na^{+}	8.3×10^{-3}	2.5×10^{-5}
Ca^{2+}	1.6×10^{-4}	3.1×10^{-5}
Cd^{2+}	2.1×10^{-4}	4.6×10^{-5}
Mg^{2+}	3.6×10^{-4}	5.8×10^{-5}
Cr^{3+}	4.7×10^{-4}	8.1×10^{-5}
Zn^{2+}	5.2×10^{-4}	2.7×10^{-6}
Cu^{2+}	6.5×10^{-4}	3.9×10^{-6}
Co^{2+}	7.2×10^{-4}	5.4×10^{-6}
Ni^{2+}	8.1×10^{-4}	9.3×10^{-6}

Table 4.6 Effect of partially non-aqueous medium on the working of Tb^{3+} ion selective sensor (CGE)

Non-aqueous content (%; v/v)	Working concentration range (mol L^{-1})	Slope (mV decade^{-1} of activity)
0	1.0×10^{-8}-1.0×10^{-1}	19.7
Methanol		
10	1.0×10^{-8}-1.0×10^{-1}	19.7
20	1.0×10^{-8}-1.0×10^{-1}	19.7
30	6.3×10^{-8}-1.0×10^{-1}	19.5
35	9.2×10^{-7}-1.0×10^{-1}	18.1
Ethanol		
10	1.0×10^{-8}-1.0×10^{-1}	19.7
20	1.0×10^{-8}-1.0×10^{-1}	19.7
30	5.5×10^{-8}-1.0×10^{-1}	19.6
35	8.9×10^{-7}-1.0×10^{-1}	17.4
Acetonitrile		
10	1.0×10^{-8}-1.0×10^{-1}	19.7
20	7.1×10^{-8}-1.0×10^{-1}	19.3
30	6.9×10^{-7}-1.0×10^{-1}	17.9
35	9.8×10^{-6}-1.0×10^{-1}	12.3

Table 4.7 Effect of different surfactants on the performance of Tb^{3+} selective electrode

Interfering ions	-log (Selectivity Coefficients)			
	Without Surfactant	**With $>10^{-4}$ mol L^{-1} CTAB**	**With $>10^{-4}$ mol L^{-1} SDS**	**With $>10^{-4}$ mol L^{-1} Triton X- 100**
La^{3+}	2.4	2.0	1.5	1.1
Ce^{3+}	2.1	1.7	0.9	1.2
Sm^{3+}	3.6	1.8	2.2	2.8
Gd^{3+}	3.5	3.1	1.4	2.4
Yb^{3+}	3.4	2.1	2.3	1.5
K^{+}	3.3	2.4	1.3	2.0
Ba^{2++}	3.2	1.3	1.6	1.9
Sr^{2+}	3.1	2.3	2.8	2.1
Pb^{2+}	3.0	1.6	2.2	1.2
Ag^{+}	4.7	3.8	2.6	1.3
Na^{+}	4.6	3.5	4.4	2.4
Ca^{2+}	4.5	3.7	2.5	1.4
Cd^{2+}	4.3	2.3	3.8	3.0
Mg^{2+}	4.2	2.9	1.6	1.1
Cr^{3+}	4.1	3.7	3.0	2.5
Zn^{2+}	5.6	5.1	4.8	2.8
Cu^{2+}	5.4	4.4	3.2	1.9
Co^{2+}	5.3	3.3	4.1	3.2
Ni^{2+}	5.0	2.1	0.9	1.6
Slope (mV $decade^{-1}$ of activity)	19.7	20.2	26.5	17.8
Detection limit (mol L^{-1})	5.7×10^{-9}	6.9×10^{-6}	5.0×10^{-5}	8.8×10^{-5}
Working Concentration range (mol L^{-1})	1.0×10^{-8} – 1.0×10^{-1}	1.3×10^{-6} – 1.0×10^{-1}	7.8×10^{-5} – 1.0×10^{-1}	1.3×10^{-4} – 1.0×10^{-1}

Table 4.8 Determination of fluoride ions in various samples by CGE

Sample No	Sample	Labelled (%)	Found (%)*
1	Senquel AD	0.2	0.2 ± 0.01
2	Chlorhexidine Gluconate	0.2	0.2 ± 0.02
3	Fluoriguard mouthwash	0.05	0.05 ± 0.01
4	Listerine mouthwash	0.022	0.021 ± 0.002
5	Colgate Total Toothpaste	0.24	0.22 ± 0.02
6	Grape juice	6.8 ppm	(6.78 ± 0.01) ppm

* Mean value ± standard deviation (three measurements)

Table 4.9 Recovery of Tb^{3+} ions from tap water samples by the proposed coated graphite electrode

S. No.	Tb^{3+} added (mol L^{-1})	Tb^{3+} ± SD* found (mol L^{-1})	Recovery (%)
1	1.0×10^{-2}	$(0.99 \pm 0.01) \times 10^{-2}$	99.0
2	5.0×10^{-2}	$(4.86 \pm 0.03) \times 10^{-2}$	97.2
3	2.0×10^{-3}	$(1.99 \pm 0.02) \times 10^{-3}$	99.5
4	5.0×10^{-3}	$(4.98 \pm 0.05) \times 10^{-3}$	99.6
5	1.0×10^{-4}	$(0.97 \pm 0.02) \times 10^{-4}$	97.0
6	5.0×10^{-5}	$(4.80 \pm 0.04) \times 10^{-5}$	96.3

* Mean value ± standard deviation (three measurements)

Table 4.10 Determination of Tb^{3+} ions in various binary mixtures by the proposed CGE

Tb^{3+} (mol L^{-1})	Added cation (mol L^{-1})	Recovery ± SD* (%)
1.0×10^{-4}	Co^{2+} (1.0×10^{-3})	101.9 ± 0.2
1.0×10^{-4}	Ca^{2+} (1.0×10^{-3})	99.5 ± 0.1
1.0×10^{-4}	Ba^{2+} (1.0×10^{-3})	98.2 ± 0.3
1.0×10^{-4}	Pb^{2+} (1.0×10^{-3})	98.6 ± 0.2
1.0×10^{-4}	Cr^{3+} (1.0×10^{-3})	99.8 ± 0.1
1.0×10^{-4}	Na^{+} (1.0×10^{-3})	99.1 ± 0.1
1.0×10^{-4}	La^{3+} (1.0×10^{-3})	96.2 ± 0.5
1.0×10^{-4}	Yb^{3+} (1.0×10^{-3})	97.3 ± 0.4
1.0×10^{-4}	Ce^{3+} (1.0×10^{-3})	96.8 ± 0.3
1.0×10^{-4}	Sm^{3+} (1.0×10^{-3})	97.0 ± 0.3
1.0×10^{-4}	Ni^{2+} (1.0×10^{-3})	102.6 ± 0.1
1.0×10^{-4}	K^{+} (1.0×10^{-3})	97.8 ± 0.2

Table 4.11 Formation constants of V(a) and V(b) with different metal ions

Metal ions	Formation constant (log K_f)* ±SD	Metal ions	Formation constant (log K_f)* ±SD
	V(a)		V(b)
Yb^{3+}	6.05 ± 0.05	Yb^{3+}	7.82 ± 0.02
Sm^{3+}	5.96 ± 0.04	Sm^{3+}	6.13 ± 0.08
Tb^{3+}	5.10 ± 0.02	Tb^{3+}	5.22 ± 0.06
Dy^{3+}	4.95 ± 0.05	Dy^{3+}	5.10 ± 0.14
La^{3+}	4.64 ± 0.04	La^{3+}	4.88 ± 0.09
Na^{+}	4.51 ± 0.01	Na^{+}	4.63 ± 0.07
K^{+}	4.20 ± 0.05	K^{+}	4.31 ± 0.05
Gd^{3+}	4.05 ± 0.04	Gd^{3+}	4.12 ± 0.05
Sr^{2+}	3.86 ± 0.04	Sr^{2+}	3.99 ± 0.11
Nd^{3+}	3.47 ± 0.02	Nd^{3+}	3.62 ± 0.02
Ni^{2+}	3.30 ± 0.04	Ni^{2+}	3.45 ± 0.04
Al^{3+}	2.90 ± 0.06	Al^{3+}	3.02 ± 0.05
Ce^{3+}	2.75 ± 0.07	Ce^{3+}	2.86 ± 0.03
Ca^{2+}	2.64 ± 0.05	Ca^{2+}	2.73 ± 0.13
Mg^{2+}	2.41 ± 0.09	Mg^{2+}	2.52 ± 0.06
Zn^{2+}	2.27 ± 0.06	Zn^{2+}	2.38 ± 0.03
Cu^{2+}	2.00 ± 0.03	Cu^{2+}	2.19 ± 0.08
Cd^{2+}	1.86 ± 0.05	Cd^{2+}	1.92 ± 0.13
Hg^{2+}	1.38 ± 0.11	Hg^{2+}	1.53 ± 0.08

* Mean value ± standard deviation (three measurements)

Table 4.12 Optimization of membrane compositions and their potentiometric response for Yb^{3+} ion selective membrane based ionophore V(a)

S.no	Composition of membrane (w/w; mg)									Working concentration range (mol L^{-1})	Slope (mV $decade^{-1}$ of activity	Detection limit (mol L^{-1})
	V (a)	NaTBP	KTpClPB	DBP	TBP	BA	DBS	NPOE	PVC			
1	6	-	-	-	-	-	-	-	94	2.8×10^{-5} to 1.0×10^{-1}	23.4	1.1×10^{-5}
2	6	-	-	60	-	-	-	-	34	8.5×10^{-7} to 1.0×10^{-1}	18.9	3.2×10^{-7}
3	6	-	-	-	60	-	-	-	34	3.8×10^{-6} to 1.0×10^{-1}	16.7	3.5×10^{-7}
4	6	-	-	-	-	60	-	-	34	1.5×10^{-6} to 1.0×10^{-1}	17.3	8.0×10^{-7}
5	6	-	-	-	-	-	60	-	34	2.1×10^{-5} to 1.0×10^{-1}	18.6	9.3×10^{-6}
6	6	-	-	-	-	-	-	60	34	1.4×10^{-5} to 1.0×10^{-1}	16.3	4.1×10^{-6}
7	6	4	-	60	-	-	-	-	30	1.0×10^{-6} to 1.0×10^{-1}	19.1	8.8×10^{-7}
8	6	-	4	60	-	-	-	-	30	1.6×10^{-7} to 1.0×10^{-1}	19.4	1.1×10^{-7}
9	5	-	4	60	-	-	-	-	31	9.3×10^{-6} to 1.0×10^{-1}	22.4	4.2×10^{-6}
10	7	-	4	60	-	-	-	-	29	4.9×10^{-6} to 1.0×10^{-1}	15.5	1.2×10^{-6}
11	6	-	3	60	-	-	-	-	31	7.3×10^{-7} to 1.0×10^{-1}	18.6	4.5×10^{-7}
12	6	-	5	60	-	-	-	-	29	2.1×10^{-6} to 1.0×10^{-1}	16.8	9.9×10^{-7}

Table 4.13 Optimization of membrane compositions and their potentiometric response for Yb^{3+} ion selective membrane based on ionophore V(b)

S.no.	Composition of membrane (w/w; mg)									Working concentration range (mol L^{-1})	Slope (mV $decade^{-1}$ of activity	Detection limit (mol L^{-1})
	V (b)	NaTBP	KTpClPB	DBP	TBP	BA	DBS	NPOE	PVC			
13	5	-	-	-	-	-	-	-	95	1.3×10^{-5} to 1.0×10^{-1}	20.8	6.2×10^{-6}
14	5	-	-	52	-	-	-	-	43	1.2×10^{-6} to 1.0×10^{-1}	21.0	8.2×10^{-7}
15	5	-	-	-	52	-	-	-	43	3.8×10^{-6} to 1.0×10^{-1}	16.4	1.0×10^{-6}
16	5	-	-	-	-	52	-	-	43	1.1×10^{-7} to 1.0×10^{-1}	18.6	9.0×10^{-8}
17	5	-	-	-	-	-	52	-	43	1.3×10^{-6} to 1.0×10^{-1}	14.5	2.5×10^{-7}
18	5	-	-	-	-	-	-	52	43	6.2×10^{-7} to 1.0×10^{-1}	18.5	1.0×10^{-7}
19	5	3	-	-	-	52	-	-	40	8.0×10^{-8} to 1.0×10^{-1}	19.8	4.3×10^{-8}
20	5	-	3	-	-	52	-	-	40	4.5×10^{-6} to 1.0×10^{-1}	18.0	9.8×10^{-7}
21	4	3	-	-	-	52	-	-	41	8.9×10^{-7} to 1.0×10^{-1}	18.4	6.2×10^{-7}
22	6	3	-	-	-	52	-	-	39	4.6×10^{-5} to 1.0×10^{-1}	14.4	3.2×10^{-5}
23	5	4	-	-	-	52	-	-	39	7.7×10^{-6} to 1.0×10^{-1}	21.3	3.0×10^{-6}
24	5	5	-	-	-	52	-	-	38	9.5×10^{-6} to 1.0×10^{-1}	21.9	7.3×10^{-6}
25	5	2	-	-	-	52	-	-	41	5.8×10^{-7} to 1.0×10^{-1}	17.7	4.6×10^{-6}
26	5	1	-	-	-	52	-	-	42	8.2×10^{-6} to 1.0×10^{-1}	16.3	3.4×10^{-6}

Table 4.14 Response characteristics of the ytterbium ion-selective electrodes based on PME and CGE

Properties	Values / range	
	PME	CGE
Optimized membrane composition	V(b) (5 mg): PVC (40 mg): BA (52 mg) : NaTPB (3 mg)	V(b) (5 mg): PVC (40 mg): BA (52 mg) : NaTPB (3 mg)
Conditioning time	3 days in 0.1 mol L^{-1} $YbCl_3$	3 days in 0.1 mol L^{-1} $YbCl_3$
Working concentration range (mol L^{-1})	8.0×10^{-8}-1.0×10^{-1}	9.4×10^{-9}-1.0×10^{-1}
Detection limit (mol L^{-1})	4.3×10^{-8}	5.8×10^{-9}
Slope (mV $decade^{-1}$ of activity)	19.8	19.7
S.D. of slope	± 0.2	± 0.1
Response time (s)	10	8
Life span	4 months	5 months
pH range	3.0-8.0	2.5-8.5

Table 4.15 Selectivity coefficient of various interfering ions for Yb^{3+} selective electrodes

Metal ions	Selectivity Coefficient ($K_{A,B}^{FIM}$)	
	PME	CGE
Dy^{3+}	3.78×10^{-3}	2.80×10^{-3}
Na^{+}	6.28×10^{-3}	3.66×10^{-3}
Sm^{3+}	1.42×10^{-2}	1.03×10^{-3}
Gd^{3+}	7.62×10^{-3}	5.02×10^{-3}
Tb^{3+}	3.23×10^{-2}	1.89×10^{-3}
Nd^{3+}	8.03×10^{-3}	5.88×10^{-3}
La^{3+}	5.12×10^{-3}	3.02×10^{-3}
Sr^{2+}	8.25×10^{-3}	5.47×10^{-3}
K^{+}	7.15×10^{-3}	4.31×10^{-3}
Al^{3+}	9.26×10^{-3}	6.90×10^{-3}
Ni^{2+}	8.82×10^{-3}	6.34×10^{-3}
Ce^{3+}	7.12×10^{-3}	5.53×10^{-4}
Mg^{2+}	8.69×10^{-3}	6.44×10^{-4}
Ca^{2+}	7.55×10^{-3}	6.18×10^{-4}
Zn^{2+}	8.61×10^{-3}	7.52×10^{-4}
Cd^{2+}	8.15×10^{-4}	8.02×10^{-4}
Cu^{2+}	9.84×10^{-3}	7.96×10^{-4}
Hg^{2+}	9.04×10^{-4}	8.54×10^{-4}

Table 4.16 Effect of partially non-aqueous medium on the working of Yb^{3+} selective sensor (CGE)

Non-aqueous content (%; v/v)	Working concentration range (mol L^{-1})	Slope (mV $decade^{-1}$ of activity)
0	9.4×10^{-9}-1.0×10^{-1}	19.7
Methanol		
10	9.4×10^{-9}-1.0×10^{-1}	19.7
20	9.4×10^{-9}-1.0×10^{-1}	19.7
30	9.6×10^{-9}-1.0×10^{-1}	19.6
35	3.3×10^{-7}-1.0×10^{-1}	17.0
Ethanol		
10	9.4×10^{-9}-1.0×10^{-1}	19.7
20	9.4×10^{-9}-1.0×10^{-1}	19.7
30	9.5×10^{-9}-1.0×10^{-1}	19.4
35	4.8×10^{-7}-1.0×10^{-1}	17.5
Acetonitrile		
10	9.4×10^{-9}-1.0×10^{-1}	19.7
20	9.9×10^{-9}-1.0×10^{-1}	19.1
30	5.2×10^{-8}-1.0×10^{-1}	15.9
35	8.1×10^{-7}-1.0×10^{-1}	16.4

Table 4.17 Effect of different surfactants on the performance of Yb^{3+} selective electrode

Interfering ions	**-log (Selectivity Coefficients)**			
	Without Surfactant	**With >10^{-4} M TBC**	**With >10^{-4} M SDS**	**With >10^{-4} M Triton X- 100**
Dy^{3+}	2.55	2.32	2.40	2.04
Na^{+}	2.43	2.01	2.42	1.58
Sm^{3+}	2.98	2.11	2.23	2.04
Gd^{3+}	2.29	2.09	1.31	2.03
Tb^{3+}	2.72	2.00	2.15	2.31
Mg^{2+}	2.23	1.59	2.04	1.23
La^{3+}	2.51	2.15	2.30	2.00
Sr^{2+}	2.26	2.10	2.08	1.35
K^{+}	2.36	1.63	2.01	2.20
Al^{3+}	2.16	1.46	2.08	0.61
Ni^{2+}	2.19	1.62	2.08	2.23
Ce^{3+}	3.25	2.93	2.82	2.41
Nd^{3+}	3.19	3.12	2.88	1.29
Ca^{2+}	3.20	2.98	3.03	3.22
Zn^{2+}	3.12	2.67	2.30	3.01
Cd^{2+}	3.07	2.52	1.26	2.69
Cu^{2+}	3.09	2.74	3.12	3.01
Hg^{2+}	3.06	2.11	2.00	2.86
Slope (mV $decade^{-1}$ of activity)	19.7	20.3	22.9	18.1
Detection limit (mol L^{-1})	5.8×10^{-9}	6.2×10^{-7}	5.5×10^{-6}	2.2×10^{-5}
Working Concentration range (mol L^{-1})	9.4×10^{-9} – 1.0×10^{-1}	5.4×10^{-8} – 1.0×10^{-1}	9.2×10^{-7} – 1.0×10^{-1}	5.1×10^{-6} – 1.0×10^{-1}

Table 4.18 Determination of fluoride ions in various samples by CGE.

Sample No	Sample	Labelled (%)	Found (%)
1	Senquel AD	0.2	0.2 ± 0.01
2	Chlorhexidine Gluconate	0.2	0.2 ± 0.01
3	Fluoriguard mouthwash	0.05	0.05 ± 0.002
4	Listerine mouthwash	0.022	0.021 ± 0.001

Table 4.19 Sulfite determination in the wine samples by proposed CGE

Sulfite wine samples	Labeled ($\mu g\ mL^{-1}$)	Found by proposed sensor ± SD* ($\mu g\ mL^{-1}$)	Added sulfite in wine samples ($\mu g\ mL^{-1}$)	Found sulfite after addition ± SD* (by proposed sensor, $\mu g\ mL^{-1}$)
Red wine	0.20	0.20 ± 0.02	0.10	0.28 ± 0.02
Red wine	0.20	0.19 ± 0.01	0.20	0.39 ± 0.01
Red wine	0.20	0.19 ± 0.02	0.30	0.48 ± 0.01
White wine	0.35	0.34 ± 0.02	0.10	0.43 ± 0.03
White wine	0.35	0.35 ± 0.01	0.20	0.54 ± 0.01
White wine	0.35	0.35 ± 0.03	0.30	0.64 ± 0.03

SD* was the average of three measurements

Table 4.20 Determination of Yb^{3+} ions in various binary mixtures by the proposed CGE

Yb^{3+} (mol L^{-1})	Added cation (mol L^{-1})	Recovery ± SD* (%)
1.0×10^{-4}	Cd^{2+} (1.0×10^{-3})	102.3 ± 0.2
1.0×10^{-4}	Ce^{3+} (1.0×10^{-3})	99.9 ± 0.3
1.0×10^{-4}	Sr^{2+} (1.0×10^{-3})	98.6 ± 0.1
1.0×10^{-4}	Zn^{2+} (1.0×10^{-3})	101.6 ± 0.5
1.0×10^{-4}	Ni^{2+} (1.0×10^{-3})	99.1 ± 0.3
1.0×10^{-4}	Gd^{3+} (1.0×10^{-3})	98.0 ± 0.4
1.0×10^{-4}	Ca^{2+} (1.0×10^{-3})	100.1 ± 0.2
1.0×10^{-4}	K^{+} (1.0×10^{-3})	97.8 ± 0.4
1.0×10^{-4}	La^{3+} (1.0×10^{-3})	97.0 ± 0.1
1.0×10^{-4}	Tb^{3+} (1.0×10^{-3})	96.6 ± 0.1
1.0×10^{-4}	Na^{+} (1.0×10^{-3})	97.4 ± 0.6
1.0×10^{-4}	Sm^{3+} (1.0×10^{-3})	96.3 ± 0.4

Table 4.21 The formation constants of VI(a)-M^{n+} and VI(b)-M^{n+} complexes using conductometric studies

Metal ions	Formation constant (log K_f)* ±SD	Metal ions	Formation constant (log K_f)* ±SD
	VI(a)		VI(b)
Ce^{3+}	5.98 ± 0.05	Ce^{3+}	6.19 ± 0.03
La^{3+}	3.93 ± 0.04	La^{3+}	4.18 ± 0.04
Sm^{3+}	3.78 ± 0.03	Sm^{3+}	4.00 ± 0.02
Dy^{3+}	3.21 ± 0.04	Dy^{3+}	3.66 ± 0.05
K^{+}	3.09 ± 0.06	K^{+}	3.58 ± 0.04
Na^{+}	2.97 ± 0.04	Na^{+}	3.05 ± 0.01
Gd^{3+}	2.74 ± 0.08	Gd^{3+}	2.95 ± 0.05
Sr^{2+}	2.01 ± 0.05	Sr^{2+}	2.88 ± 0.04
Nd^{3+}	1.96 ± 0.01	Nd^{3+}	2.75 ± 0.04
Pb^{2+}	1.84 ± 0.08	Pb^{2+}	2.60 ± 0.02
Eu^{3+}	1.70 ± 0.06	Eu^{3+}	2.20 ± 0.04
Mg^{2+}	1.62 ± 0.07	Mg^{2+}	2.01 ± 0.06
Ni^{2+}	1.55 ± 0.04	Ni^{2+}	1.99 ± 0.02
Cu^{2+}	1.42 ± 0.05	Cu^{2+}	1.87 ± 0.05
Zn^{2+}	1.36 ± 0.03	Zn^{2+}	1.72 ± 0.02
Ca^{2+}	1.29 ± 0.04	Ca^{2+}	1.68 ± 0.03
Ba^{2+}	1.10 ± 0.04	Ba^{2+}	1.50 ± 0.03
Cd^{2+}	1.00 ± 0.07	Cd^{2+}	1.18 ± 0.05
Co^{2+}	0.86 ± 0.06	Co^{2+}	1.07 ± 0.07
Hg^{2+}	0.70 ± 0.04	Hg^{2+}	0.94 ± 0.02

* Mean value ± standard deviation (three measurements)

Table 4.22 The formation constants of VI(b)-M^{n+} complexes using Sandwich membrane method

Metal ions	Formation constant ($\log \beta_{\mathrm{IL}n}$)* ±SD	Metal ions	Formation constant ($\log \beta_{\mathrm{IL}n}$)* ±SD
Ce^{3+}	6.23 ± 0.02	Eu^{3+}	2.47 ± 0.09
La^{3+}	4.21 ± 0.05	Mg^{2+}	2.26 ± 0.05
Sm^{3+}	4.08 ± 0.12	Ni^{2+}	2.18 ± 0.12
Dy^{3+}	3.89 ± 0.06	Cu^{2+}	2.03 ± 0.08
K^{+}	3.62 ± 0.05	Zn^{2+}	1.94 ± 0.06
Na^{+}	3.11 ± 0.02	Ca^{2+}	1.73 ± 0.02
Gd^{3+}	3.00 ± 0.04	Ba^{2+}	1.64 ± 0.04
Sr^{2+}	2.91 ± 0.13	Cd^{2+}	1.33 ± 0.08
Nd^{3+}	2.82 ± 0.07	Co^{2+}	1.25 ± 0.09
Pb^{2+}	2.67 ± 0.15	Hg^{2+}	1.11 ± 0.11

* Mean value ± standard deviation (three measurements)

Table 4.23 Optimization of membrane compositions and their potentiometric response for Ce^{3+} ion selective membrane based on ionophore VI(a)

S.no.	Composition of membrane (w/w; mg)									Working Concentration range (mol L^{-1})	Slope (mV $decade^{-1}$ of activity)	Detection limit (mol L^{-1})
	VI (a)	NaTBP	KTpClPB	DBP	TBP	NPOE	DOP	BA	PVC			
1	7	-	-	-	-	-	-	-	93	4.8×10^{-5} to 1.0×10^{-1}	23.2 ± 0.2	2.7×10^{-5}
2	7	-	-	54	-	-	-	-	39	6.4×10^{-6} to 1.0×10^{-1}	17.3 ± 0.4	3.0×10^{-6}
3	7	-	-	-	54	-	-	-	39	7.8×10^{-7} to 1.0×10^{-1}	19.0 ± 0.3	3.2×10^{-7}
4	7	-	-	-	-	54	-	-	39	6.5×10^{-7} to 1.0×10^{-1}	18.2 ± 0.2	4.1×10^{-7}
5	7	-	-	-	-	-	54	-	39	4.9×10^{-6} to 1.0×10^{-1}	15.8 ± 0.2	2.2×10^{-6}
6	7	-	-	-	-	-	-	54	39	3.0×10^{-6} to 1.0×10^{-1}	16.7 ± 0.3	1.1×10^{-6}
7	7	3	-	-	54	-	-	-	36	5.0×10^{-7} to 1.0×10^{-1}	19.2 ± 0.2	1.9×10^{-7}
8	7	-	3	-	54	-	-	-	36	8.6×10^{-6} to 1.0×10^{-1}	20.7 ± 0.3	6.4×10^{-6}
9	6	3	-	-	54	-	-	-	37	5.8×10^{-6} to 1.0×10^{-1}	18.8 ± 0.3	3.4×10^{-6}
10	8	3	-	-	54	-	-	-	35	3.6×10^{-5} to 1.0×10^{-1}	15.4 ± 0.2	1.4×10^{-5}
11	7	4	-	-	54	-	-	-	35	9.3×10^{-6} to 1.0×10^{-1}	17.8 ± 0.4	7.5×10^{-6}
12	7	2	-	-	54	-	-	-	37	7.8×10^{-6} to 1.0×10^{-1}	18.5 ± 0.4	5.3×10^{-6}

Table 4.24 Optimization of membrane compositions and their potentiometric response for Ce^{3+} ion selective membrane based on ionophore VI(b)

S.no.	Composition of membrane (w/w; mg)									Working concentration range (mol L^{-1})	Slope (mV $decade^{-1}$ of activity)	Detection limit (mol L^{-1})
	VI(b)	NaTBP	KTpClPB	DBP	TBP	NPOE	DOP	BA	PVC			
13	6	-	-	-	-	-	-	-	94	5.0×10^{-5} to 1.0×10^{-1}	22.8 ± 0.3	2.0×10^{-5}
14	6	-	-	58	-	-	-	-	36	8.4×10^{-6} to 1.0×10^{-1}	25.3 ± 0.3	3.9×10^{-6}
15	6	-	-	-	58	-	-	-	36	4.9×10^{-6} to 1.0×10^{-1}	22.7 ± 0.4	2.4×10^{-6}
16	6	-	-	-	-	58	-	-	36	7.4×10^{-7} to 1.0×10^{-1}	19.1 ± 0.2	5.3×10^{-8}
17	6	-	-	-	-	-	58	-	36	1.4×10^{-6} to 1.0×10^{-1}	17.5 ± 0.2	8.6×10^{-7}
18	6	-	-	-	-	-	-	58	36	9.8×10^{-7} to 1.0×10^{-1}	23.2 ± 0.3	2.6×10^{-7}
19	6	2	-	-	-	58	-	-	34	7.5×10^{-6} to 1.0×10^{-1}	20.7 ± 0.2	5.1×10^{-6}
20	6	-	2	-	-	58	-	-	34	1.4×10^{-7} to 1.0×10^{-1}	19.5 ± 0.2	8.3×10^{-8}
21	7	-	2	-	-	58	-	-	33	9.8×10^{-6} to 1.0×10^{-1}	21.3 ± 0.4	7.3×10^{-6}
22	5	-	2	-	-	58	-	-	35	3.6×10^{-6} to 1.0×10^{-1}	18.4 ± 0.4	1.2×10^{-6}
23	6	-	3	-	-	58	-	-	33	3.6×10^{-5} to 1.0×10^{-1}	17.2 ± 0.3	1.2×10^{-5}
24	6	-	1	-	-	58	-	-	35	6.4×10^{-5} to 1.0×10^{-1}	18.9 ± 0.3	3.8×10^{-5}

Table 4.25 Response characteristics of the cerium ion-selective electrodes based on PME and CGE

Properties	Values / range	
	PME	CGE
Optimized membrane composition	VI(b) (6 mg): PVC (34 mg): *o*-NPOE (58 mg) : KTpClPB (2 mg)	VI(b) (6 mg): PVC (34 mg): *o*-NPOE (58 mg) : KTpClPB (2 mg)
Conditioning time	3 days in 0.1 mol L^{-1} $Ce(NO_3)_3$	3 days in 0.1 mol L^{-1} $Ce(NO_3)_3$
Working concentration range (mol L^{-1})	1.4×10^{-7} to 1.0×10^{-1}	1.0×10^{-8} to 1.0×10^{-1}
Detection limit (mol L^{-1})	8.3×10^{-8}	7.7×10^{-9}
Slope (mV decade^{-1} of activity)	19.5	19.7
S.D. of slope	± 0.3	± 0.1
Response time (s)	12	10
Life span	3 months	5 months
pH range	3.5-7.5	2.5-8.5

Table 4.26 Effect of Soaking time on the potential response of the Ce^{3+} selective electrode

Soaking Time	Slope (mV decade^{-1} of activity)	Working Concentration Range (mol L^{-1})	Detection Limit (mol L^{-1})
PME			
2 days	19.5 ± 0.2	1.4×10^{-7} to 1.0×10^{-1}	8.3×10^{-8}
10 days	19.5 ± 0.2	1.7×10^{-7} to 1.0×10^{-1}	8.8×10^{-8}
25 days	19.3 ± 0.3	2.2×10^{-7} to 1.0×10^{-1}	9.0×10^{-8}
45 days	19.1 ± 0.2	3.8×10^{-7} to 1.0×10^{-1}	9.2×10^{-8}
70 days	18.8 ± 0.3	5.1×10^{-7} to 1.0×10^{-1}	9.6×10^{-8}
90 days	18.6 ± 0.4	7.5×10^{-7} to 1.0×10^{-1}	9.8×10^{-8}
95 days	16.2 ± 0.3	9.8×10^{-6} to 1.0×10^{-1}	2.5×10^{-7}
CGE			
2 days	19.7 ± 0.1	1.0×10^{-8} to 1.0×10^{-1}	7.7×10^{-9}
10 days	19.6 ± 0.3	1.8×10^{-8} to 1.0×10^{-1}	8.0×10^{-9}
25 days	19.4 ± 0.2	2.3×10^{-8} to 1.0×10^{-1}	8.1×10^{-9}
45 days	19.2 ± 0.2	2.9×10^{-8} to 1.0×10^{-1}	8.6×10^{-9}
70 days	19.1 ± 0.1	3.5×10^{-8} to 1.0×10^{-1}	8.8×10^{-9}
90 days	19.0 ± 0.3	4.2×10^{-8} to 1.0×10^{-1}	9.0×10^{-9}
105 days	18.8 ± 0.2	5.1×10^{-8} to 1.0×10^{-1}	9.2×10^{-9}
120 days	18.6 ± 0.1	5.6×10^{-8} to 1.0×10^{-1}	9.5×10^{-9}
135 days	18.5 ± 0.3	6.4×10^{-8} to 1.0×10^{-1}	9.9×10^{-9}
150 days	18.4 ± 0.2	7.3×10^{-8} to 1.0×10^{-1}	1.1×10^{-8}
155 days	15.9 ± 0.3	4.5×10^{-7} to 1.0×10^{-1}	2.6×10^{-7}

Table 4.27 Selectivity coefficient of various interfering ions for Ce^{3+} selective electrodes

Metal ions	Selectivity Coefficient ($K_{A,B}^{FIM}$)	
	PME	CGE
La^{3+}	3.4×10^{-2}	4.2×10^{-3}
Dy^{3+}	5.5×10^{-2}	6.2×10^{-3}
Sm^{3+}	4.8×10^{-2}	5.9×10^{-3}
Gd^{3+}	7.4×10^{-2}	7.1×10^{-3}
Nd^{3+}	8.1×10^{-2}	7.6×10^{-3}
Pb^{2+}	8.8×10^{-2}	7.8×10^{-3}
K^{+}	5.9×10^{-2}	6.5×10^{-3}
Ba^{2+}	4.5×10^{-3}	3.5×10^{-4}
Sr^{2+}	7.7×10^{-2}	7.4×10^{-3}
Eu^{3+}	9.0×10^{-2}	8.4×10^{-3}
Na^{+}	6.8×10^{-2}	6.9×10^{-3}
Ca^{2+}	3.9×10^{-3}	2.9×10^{-4}
Cd^{2+}	4.9×10^{-3}	4.4×10^{-4}
Cu^{2+}	2.7×10^{-3}	9.9×10^{-3}
Zn^{2+}	3.1×10^{-3}	2.6×10^{-4}
Mg^{2+}	9.4×10^{-2}	8.7×10^{-3}
Co^{2+}	5.4×10^{-3}	4.8×10^{-4}
Ni^{2+}	9.9×10^{-2}	9.0×10^{-3}
Hg^{2+}	6.9×10^{-3}	5.6×10^{-4}

Table 4.28 Determination of fluoride ions in various mouthwash samples by CGE

Sample No	Sample	Labelled (%)	Found (%)
1	Senquel AD	0.2	0.19 ± 0.01
2	Chlorhexidine Gluconate	0.2	0.2 ± 0.01
3	Fluoriguard mouthwash	0.05	0.048 ± 0.002
4	Listerine mouthwash	0.022	0.021 ± 0.001

Table 4.29 Determination of Oxalate in vegetable samples by CGE

Sample	Added ($\mu g\ mL^{-1}$)	Found by CGE * ($\mu g\ mL^{-1}$)	Recovery (%)	Content in Sample ($mg\ g^{-1}$) *	
				This method	Standard method [61]
Spinach	-	0.78 ± 0.02	-	12.5 ± 0.3	12.8 ± 0.2
	0.20	1.01 ± 0.01	103.0		
	0.40	1.16 ± 0.03	98.3		
Mushroom	-	0.90 ± 0.03	-	2.9 ± 0.2	3.2 ± 0.3
	0.30	1.25 ± 0.02	104.1		
	0.50	1.39 ± 0.01	99.2		

* Mean value ± standard deviation (three measurements)

Table 4.30 Analysis of spiked water samples by the proposed CGE

Sample	Oxalate Added (μg mL^{-1})	Oxalate Found (μg mL^{-1})	Recovery (%)
Tap Water	0.20	0.19 ± 0.02	95.0
Tap Water	0.60	0.60 ± 0.03	100.0
Tap Water	1.20	1.18 ± 0.01	98.3

REFERENCES

1. Gschneidner, K.A. and Erying, L., "Handbook on the physics and chemistry of the Rare earths", Vol. 1, North Holand Publishing Co. Amsterdam, (1979).
2. Kirk, R.E. and Othmes, D.F., Encyclopedia of Chemical Technology, Wiley, New York 19 (1928) 851.
3. Yongxing, W., Xiaorong, W. and Zichum, H., "Genotoxicity of lanthanum(III) and gadolinium(III) in human peripheral blood lymphocytes", *Bull. Environ. Contam. Toxicol.*, **64**, 611 (2000).
4. Magnusson, G., "The behaviour of certain lanthanum's in rats", *Acta Pharmacol. Toxicol.*, **3**, 1 (1963).
5. Snyder, F., Cress, E.A. and Kyker, G.C., "Liver lipid response to intravenous rare earths in rats", *J. Lipid Res.*, **1**, 125 (1959).
6. Gomez, J.E., Birnbaum, E.R. and Darnall, D.W., "The metal ion acceleration of the conversion of trypsinogen to trysin. Lanthanide ions as calcium substitutes", *Biochem.*, **13**, 3745 (1974).
7. Mohammadhossieni M., Zamani, H,A. And Nekoei, M., "Terbium(III) Ion-Selective Electrochemical Sensor Based on Hematoporphyrin", *Anal. lett.*, **42,** 298 (2009).
8. Ganjali, M.R., Ghesmi, A., Hosseini, M., Pourjavid, M.R., Rezapour, M., Shamsipur, M. and Salavati-Niasari, M., "Novel terbium(III) sensor based on a new bis- pyrrolidene Schiff's base", *Sens. Actuators B*, **105**, 334 (2005).
9. Zamani, H.A., Rajabzadeh, G. and Ganjali, M.R., "Construction of a novel potentiometric terbium(III) membrane sensor and its application for the determination of terbium ion in binary mixture and fluoride ion in a mouthwash preparation", *J. Braz. Chem. Soc.*, **17**, 1297 (2006).
10. Zamani, H.A., Ganjali, M.R., Norouzi, P. Tadjarodi, A. and Shahsavani, E., "Determination of terbium(III) ions in phosphate rock samples by a Tb^{3+} PVC membrane sensor based on N, N-Dimethyl-N',N"-bis(4-methoxy phenyl)phosphoramidate", *Material Sci. and Engg.* C, **28**, 1489 (2008).

11. Zamani, H.A. and Ganjali, M.R.," Tb^{3+} PVC-Membrane Electrode Based on 2-{2-(2-Anilinocarbothioyl)hydrazino)- 2-oxoacetyl}-N-phenyl-1-hydrazinecarbothioamide", *Anal. lett.*, **42**, 1958 (2009).

12. Zamani, H.A., Zabihi, M.S., Rohani, M., asadabadi, A.Z., Ganjai, M.R., Faridbod, F. and Meghdadi, S., "Quantitative monitoring of terbium ion by a Tb^{3+} selective electrode based on a new schiff's base", *Material Sci. and Engineering C*, **31**, 409 (2011).

13. Gupta, V.K., Singh, A.K. and Gupta, B., "Electroanalytical performance of terbium(III)-selective sensor based on a neutral ionophore in environmental and medicine samples", *Anal. Bioanal. Chem.*, **390**, 2171 (2008).

14. Gupta, V.K., Pal, M.K. and Sharma, R.A., "Comparative studies on Tb(III)-selective PVC membrane sensors", *Talanta*, **82**, 1136 (2010).

15. V. Gapontsev, IPG Photonics Debuts High-Power Fibre. Pigtailed Lase Systems, Vol. 15, Electromanufacturing, Boston, NA, 2002.

16. D. Woods, Shining Light on Optical Networking, Vol. 13, Network Comput. Manhasset, 2002, p. 63.

17. C.A. Hampel, R. Book, The Encyclopedia of the Chemical Elements Corporation, New York 1968.

18. Ganjali, M.R., Naji, L., Poursaberi, T., Shamsipur, M. and Haghgoo, S., "Ytterbium(III)-selective membrane electrode based on cefixime", *Anal. Chim. Acta* **475,** 59 (2003).

19. Ganjali, M.R, Rasoolipour, S., Rezapour, M., Norouzi, P., Tajarodi, A. and Hanifehpour, Y., "Novel ytterbium(III) selective membrane sensor based on N-(2-pyridyl)-N'-(2-methoxyphenyl)-thiourea as an excellent carrier and its application to determination of fluoride in mouth wash preparation samples", *Electroanalysis* **17,** 1534 (2005)

20. Ganjali, M.R., Norouzi, P., Tamaddon, A. and Adib, M., "Nano-level monitoring of ytterbium(III) by a novel ytterbium(III) membrane sensor based on 3-hydroxy-N'-[(2-hydroxyphenyl) methylene]-2-naphthohydrazide", *Sens. Actuat. B*, **114**, 855 (2006).

21. Berny, F. and Wipff, G., "Interaction of M^{3+} lanthanide cations with amide, urea, thioamide and thiourea ligands: a quantum mechanical study", *J. Chem. Soc. Perkin Trans.*, **2**, 73 (2001).

22. Zamani, H.A., Rajabzadeh, G. and Ganjali, M.R., "Construction of a novel potentiometric terbium(III) membrane sensor and its application for the determination of terbium ion in binary mixture and fluoride ion in a mouth wash preparation", *Talanta* **72**, 1093 (2007).

23. Ganjali, M.R., Norouzi, P., Ghorbani, H., Larijani, B., Tadjaroeli, A. and Hanifehpour, Y., *Canadian Journal of Anal. Sci. And Spectroscopy,* **51**, 6 (2006).

24. Ebrahimi, M. And Zamani, H.A.,"Determination of Ytterbium(III) ions in soil and sediment samples by a new polymeric Yb3+-PVC membrane sensor", *Anal. lett.,* **42**, 1041 (2009).

25. F. A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, 3rd ed., (Wiley Eastern, New Delhi, 1976), p. 422.

26. F. W. Oehme, Toxicity of Heavy Metals in the Environment (Marcel Dekker, New York, 1979) p. 971.

27. Abbasi, S.A., "Spectrophotometric determination of trimipramine using cerium(IV) sulphate(VI) and potassium idate (VII)", *Int. J. Environ. Anal. Chem.*, **34**, 181 (1998).

28. Venugopal, B. and Luckey, T.D.,"Toxicity of Group III metals. In Venugopal B and Luckey TD (Ed.) Metal toxicity in mammals", Plenum Press, New York, pp. 101-173 (1978).

29. Vocatura, G., Colombo, F., Zanoni, M., Rodi, F. and Sabbioni, E.P., "Human exposure to heavy metals: Rare earth pneumoconiosis in occupational workers", *Chest*, **83**, 780 (1983).

30. Valiathan, M.S., Kartha, C.C., Eapen, J.T., Dang, H.S. and Sunta, C.M., "A geochemical basis for endomyocardial fibrosis", *Cardiovasc. Res.*, **23**, 647 (1989).

31. Valiathan, M.S. and Kartha, C.C., "Endomyocardial fibrosis: The possible connection with myocardial levels of magnesium and cerium", *Int. J. Cardiol.*, **28**, 1 (1990).

32. Shamsipur, M., Yousefi, M. and Ganjali, M.R., "PVC-based 1,3,5-trithiane sensor for cerium(III) ions", *Anal.Chem.*, **72**, 2391 (2000).

33. Shamsipur, M., Yousefi, M., Hosseini, M. and Ganjali, M.R., "PVC-based 1,3,5-trithiane coated graphite electrode for determination of cerium(III) ions", *Anal. Lett.*, **34**, 2249 (2001).

34. Karami, H., Mousavi, M.F., Shamsipur, M., Yavari, I. and Alizadeh, A.A., "A new ion-selective electrode for potentiometric determination of Ce(III)", *Anal. Lett.*, **36**, 1065 (2003).

35. Gaber, A.A.A., "Novel PVC membrane sensor for selective determination of cerium(III) Ions", *Anal. Lett.*, **36**, 2585 (2003).

36. Akhond, M., Najafi, M.B. and Tashkhourian, J., "A new cerium(III)-selective membrane electrode based on 2-aminobenzothiazole", *Sens. Actuators B*, **99**, 410 (2004).

37. Saleh, M.B., Gaber, A.A.A., Khalaf, M.M.R. and Tawfeek, A.M., "A new ion-selective electrode for potentiometric determination of Ce(III) ions", *Sens. Actuators B*, **119**, 275 (2006).

38. Zamani, H.A., Ganjali, M.R. and Adib, M., "Construction of a highly selective PVC-based membrane sensor for Ce(III) ions", *Sens. Actuators B*, **120**, 545 (2007).

39. Mittal, S.K., Kumar, S.K.A. and Sharma, H.K., "Cerium(III)-selective membrane electrode based on dibenzo-24-crown-8 as a neutral carrier", *E-J. of Chemistry,* 7, 849 (2010).

40. Abedi, M.R., Zamani, H.A., Ganjali, M.R. and Norouzi, P., "Determination of cerium(III) ions in soil and sediment samples by Ce(III) PVC-based membrane electrode based on 2,5-dioxo-4-imidazoildinyl", *Intern. J. Environ. Anal. Chem.*, **88**, 353 (2008).

41. Gupta, V.K., Singh, A.K., Gupta, B., "A cerium(III) selective poly(vinyl chloride) membrane sensor based on a Schiff base complex of N,N-bis[2-(salicylideneamino)ethyl]ethane-1,2-diamine", *Anal. Chim. Acta*, **575**, 198 (2006).

42. Rothermel, G.L., Miao, J.L., Hill, A.L. and Jackels, S.C., "Macrocyclic ligands with 18-membered rings containing pyridine or furan groups: preparation, protonation, and complexation by metal ions", *Inorg. Chem.*, **31**, 4854 (1992).

43. Shultz, M.M., Stefanova, O.K., Mokrov, S.B. and Mikhelson, K.N., "Potentiometric Estimation of the Stability Constants of Ion–Ionophore Complexes in Ion-Selective Membranes by the Sandwich Membrane Method: Theory, Advantages, and Limitations", *Anal. Chem.*, **74**, 510 (2002).

44. Birch, B.J. and Cockroft, R.N., "Analysis of ionic surfactants in the detergent industry using ion-selective electrodes", *Ion-Sel. Electrode Rev.*, **3**, 1 (1981).

45. Szczepaniak, W. and Ren., M., "Selectivity of liquid membrane electrode based on mercurated polystyrene as ion-exchanger to anionic surfactants and soaps", *Electroanalysis*, **6**, 341 (1994).

46. Gabrielli, C., Hemery, P., Letellier, P., Masure, M., Perrot, H. and Rahmi, M.I., "Investigation of ionic surfactant-selective electrodes by EIS", *Electrochim. Acta*, 47, 2117 (2002).

47. Norov, S.K., Gulamova, M.T., Zhukov, A.F., Norova, G.M. and Mamedova, Y.G., "Electrode characteristics of membranes based on dibenzo-18-crown-6 derivatives", *Zh. Anal. Khim.*, **43**, 986 (1988).

48. Erden, S., Demirel, A., Memon, S., Yilmaz, M., Canel, E. and Kilie, E., "Using of hydrogen ion-selective poly(vinyl chloride) membrane electrode based on calix[4]arene as thiocyanate ion-selective electrode", *Sens. Actuators B*, **113**, 290 (2006).

49. Macca, C., "Response time of ion-selective electrodes: current usuage versus IUPAC recommendations", *Anal. Chim. Acta.*, **512**, 183 (2004).

50. Karlberg, B., "Time lag of ion-exchange in the gel layer of hydrogen-ion selective glass electrodes", *J. Electroanal. Chem.*, **49**, 1 (1974).

51. Morf, W.E., Lindner, E. And Simon, W., "Theoretical treatment of the dynamic response of ion-selective membrane electrodes", *Anal. Chem.*, **47**, 1596 (1975).

52. Hawkings, R.C., Corriveau, L.P.V., Kushneriuk, S.A. and Wong, P.Y., "Dynamic response of the fluoride ion-selective electrode", *Anal. Chim. Acta*, **102**, 61 (1978).

53. Anker, P., Wieland, E., Ammann, D., Dohner, R.E., Asper, R. and Simon, W., "Neutral carrier based ion-selective electrode for the determination of total calcium in blood serum", *Anal. Chem.*, **53**, 1970 (1981).

54. Eugster, R., Rrosatzin, T., Rusterholz, B., Aebersold, B., Pedrazza, U., Ruegg, D., Schmid, A., Spichiger, U.F. and Simon, W., "Plasticizers for liquid polymeric membranes of ion-selective chemical sensors", *Anal. Chim. Acta*, **289**, 1 (1994).

55. Chamjangali, M.A., Razavian, L.S., Yousefi, M. and Amin, A.H., "Determination of trace amounts of oxalate in vegetable and water samples using a new kinetic-catalytic reaction system", *Spectrochimica Acta Part A*, **73**, 112 (2009).

Chapter 5

Membranes of macrocyclic ligands
as
Anion selective sensor

5.1 INTRODUCTION

The field of ion-selective membrane research is a vigorous and ever-expanding one. Recently there has been much focus on the construction of anion selective electrodes that function on the basis of chemical recognition principle [1,2]. Ion-selective electrodes are also of obvious interest because they help to translate the chemistry of new substrate-binding systems into tools that can be used to selectively recognize various target species in the presence of potentially interfering analytes. It is well known that selectivity of such sensors is mainly determined by the relative hydration energy of ions, according to the so called Hofmeister series [3]. The main component of a membrane, which makes possible the fabrication of electrodes with selectivity patterns different from the Hofmeister series, is ionophore. Thus, the investigation of new ionophores, especially with enhanced selectivity towards hydrophilic ions, is still a subject of much effort and research. In comparison to the variety of host molecules as cation receptors, selective receptors for anions are much less. The detection and quantification of anions is important in biology and environmental chemistry as a consequence of the role played by anions in environmental and chemical processes. The design of host molecules capable of binding selectively to anionic guests is a notoriously challenging area and consequently has given rise to a plethora of imaginative and ingenious systems designed to tackle the problem [4,5]. Thus there is a high demand for anion selective electrodes which can be employed in analysis of water, medicine, food, environmental monitoring and biotechnology.

5.1.1 Thiocyanate Ion selective Sensor

Anions sensing and recognition remains a challenging task because of the limited availability of suitable molecular hosts for anions. In order to have a selective sensor for thiocyanate, the most important requirement is to have an ionophore in the sensor which show high affinity towards thiocyanate ion and poor for the other anions. Thiocyanate has been extensively used for various purposes, such as in dyeing, photography, medicine, catalysis, prevention of erosion, etc. It is usually present in low concentrations in human serum, saliva and urine as a result of the digestion of some vegetables (cabbage, turnip, kale) [6] of the genus Brassica containing glucosinolates or by intake of thiocyanate-containing foods such as milk and cheese [7]. Higher concentration of thiocyanate ion, which is a metabolic product of cyanides, arises from tobacco smoke. In this respect, the concentration level of thiocyanate is considered to be a good probe to distinguish between smokers and non-smokers. Saliva of nonsmokers contains thiocyanate concentrations between 0.5 and 2 mg/L while in smokers concentrations as high as 6 mg/L can be found. Human plasma levels are 2 to 3 mg/L in nonsmokers and 9 to 12 mg/L in smokers [8]. Another important sample where the determination of the thiocyanate anion is of interest is in water, especially wastewaters. At low pH values, thiocyanate contained wastewater, when discharged into natural waters, converts thiocyanate into cyanide ion in the presence of oxidants and thereby causes profound damage to the aquatic life. Thiocyanate is administered as drug in the treatment of thyroid conditions [9] and to achieve an optimal antibacterial effect of the lactoperoxidase system in milk [10]. Therefore, an accurate, simple and rapid method for the determination of thiocyanate is desired for application in the field of medicine, life sciences and environment [11].

Thus, development of ion-selective sensors for thiocyanate ions is of considerable interest. Buhlmann *et al.* [12] reported thiocyanate-selective electrodes based on the dinuclear zinc(II) complex of a Bis-N,O-bidentate Schiff base, while Chandra and coworkers [13] reported thiocyanate sensor based on copper and nickel complexes of para-tolualdehydesemicarbazone as carrier which exhibited a linear response over the range of 1.0×10^{-7} to 1.0×10^{-1} M with a slope of 52.0 ± 0.3 mV decade^{-1} of activity. Wu *et al.* [14]

proposed another electrode for selective determination of thiocyanate ions based on N,N'-(aminoethyl)ethylenediamide bis(2-benzoideneimine) binuclear copper(II) complex as a neutral carrier while Dong and coworkers [15] developed a thiocyanate sensor based on an amide-linked manganese diporphyrin xanthene which showed working concentration range of 2.4×10^{-6} to 1.0×10^{-1} M with a response time of less than 60 s. Shorkrollahi *et al.* [16] utilized Cobalt(III) complex with Schiff base as a charge carrier for detection of thiocyanate ions in water and biological samples. Highly selective thiocyanate sensor based on N-salicylidene-benzylamineato copper(II) complexes was proposed by Wang and coworkers [17] which exhibited working concentration range of 9.0×10^{-7} to 1.0×10^{-1} with a detection limit of 7.0×10^{-7} M. Hassan *et al.* [18] used copper(II)-2-(5-bromo-2-pyridylazo)-5-diethylamino phenol complex in thiocyanate selective sensor which exhibits detection limit of 5.6×10^{-6} M and a calibration slope of -57.5 ± 0.5 mV decade^{-1} of activity. Xu *et al.* [19] developed thiocyanate sensor by using hydroxycitronellal (o-aminobenzoic acid) copper(II) and salicylaldehyde (o-aminobenzoic acid) copper(II) as neutral carriers. This sensor exhibited Nernstian slope of -57.3 mV decade^{-1} of activity over working concentration range of 1.0×10^{-6} to 1.0×10^{-1} M. Liu *et al.* [20] developed a thiocyanate selective polyvinyl chloride membrane electrode based on copper(II) complex with 2-amino-thiourea-bis(salicylaldehyde) base as carrier which showed linear response over 1.4×10^{-7} to 1.0×10^{-1} M with a detection limit of 5.6×10^{-8} M. Sun and coworkers [21] designed another thiocyanate electrode using N,N'-bis(5-bromosalicylidene)-2,6-pyridinediamine copper (II) complex as a carrier which exhibited Nernstian slope of 58.5 mV decade^{-1} of activity with a detection limit of 2.0×10^{-6} M. A variety of other electroactive materials were used by various group of researchers [22-43] for the preparation of thiocyanate electrode. The sensors based on these ionophores exhibited in many cases narrow working concentration range or non Nernstian response or very short functional lifetime due to the degradation of ionophore molecules.

In the present work, we have investigated the use of zinc complexes of 6,7:14,15-Bzo_2-10,11-(4-methylbenzene)-[15]-6,8,12,14-tetraene-9,12-N_2-1,5-O_2 [VII(a)] and 6,7:14,15-Bzo_2-10,11-(4-methylbenzene)-[15]-6,14-diene-9,12-dimethylacrylate-9,12-N_2-1,5-O_2 [VII(b)] as ionophores for the construction of a plasticized PVC membrane based polymeric membrane and coated graphite electrode for simple, selective and rapid determination of thiocyanate ion with high selectivity.

5.1.2 Perchlorate Ion Selective sensor

Perchlorate is receiving increased attention as an inorganic contaminant in soils, groundwaters, surface waters, and irrigation waters used for crop production. It is emerging as a new persistent inorganic contaminant because of its specific properties, such as high water solubilities, mobility and considerable stability [44]. The United States Environmental Protection Agency (EPA) is currently assessing the risks posed by perchlorate in the environment and has placed perchlorate on the Contaminant Candidate List [45] and the Unregulated Contaminant Monitoring Rule [46]. One of the major sources of this environmental contamination is the manufacture and improper storage and disposal of ammonium perchlorate which is used as a primary component in solid propellant for rockets, missiles, fireworks [47-49], or explosives in various military munitions and air bag inflators [50]. It has also been found in food products, soil, milk, fertilizers, plants and in human urine. It is known that the perchlorate salts have been used to treat patients with hyperactive thyroid glands and to carry out diagonistic tests [51] and as a thyreostatic drugs and growth promoters in cattle fattening [52].

A number of potentiometric sensors based on a variety of ionophores have been reported in the literature. Rezaei *et al.* synthesized bis(dibenzoylmethanato) Ni(II) complex and used it as an ionophore for the determination of perchlorate ions in water and human urine samples [53]. They also reported another electrode for the quantification of ClO_4^- ions based on bis(dibenzoylmethanato) Co(II) complex [54]. This electrode exhibited working concentration range of 8.0×10^{-7} to 1.0×10^{-1} M with a Nernstian slope of 60.3 ± 0.5 mV decade^{-1} of activity. The response time of this sensor is fast (≤ 5 s) and can be used for 2 months. Soleymanpour *et al.* fabricated the polymeric membrane electrode and coated glassy carbon electrodes based on platinum (II) complexes which exhibited the wide working concentration range and high selectivity towards ClO_4^- ion relative to a variety of other common anions [55,56]. Mahajan *et al.* [57] developed perchlorate selective electrode based on surfactant ion-pair complex (dodecyltrimethylammonium-perchlorate) which exhibited Nernstian response over working concentration range of 5.0×10^{-6} to 1.0×10^{-1} M with detection limit of 2.51×10^{-6} M. Zarei *et al.* [58] developed a perchlorate selective sensor based on bis(dimethylgolyoximato)nitritopyridineCo(III) for determination of ClO_4^- ion in waste water and human urine samples. This sensor showed working concentration range of 1.0×10^{-6} to 1.0×10^{-1} M and a sub Nernstian slope of 41.36 mV decade^{-1} of activity. Shokrollahi and coworkers [59] used Co(III)-Schiff base $[Co(5\text{-}NO_2\text{-}Salen)(PBu_3)]ClO_4{\cdot}H_2O$ as a new carrier for construction of perchlorate-selective electrode by incorporating the membrane ingredients on the surface of a graphite electrodes has been reported. The proposed electrode shows a linear potential response to perchlorate ion in the range 1.0×10^{-6} to 5.0×10^{-1} M with a slope of (59.4 ± 0.9) mV decade^{-1} of activity with a low detection limit of 5.0×10^{-7} M and good perchlorate selectivity over the wide variety of other anions. Canel *et al.* [60] prepared perchlorate selective electrode using 5,11,17,23-tetra-tert-butyl-25,26,27,28-tetracyanomethoxy-calix[4]arene as an ionophore in PVC membrane which exhibited a linear response over the range 1.0×10^{-5} to 5.0×10^{-1} M. Several perchlorate selective electrodes have been reported based on ion-association complexes between perchlorate anions and different organic compounds (long-chain quaternary ammonium ions, organic bases, organic dyes and metal chelates) [61-70]. Most of these ion-selective electrodes are not sensitive and selective enough to permit selective measurement of low levels of perchlorate and are susceptible to interferences from other common anions such as IO_4^-, NO_3^-, SCN^-, I^- and MnO_4^- ions.

In the present work, we have investigated the use of zinc complexes of 6,7:13,14-Dibenzo-2, 4, 9, 11-tetramethyl-1, 5, 8, 12-tetraazacyclotetradecane-1, 4, 6, 8, 11, 13-hexaene [VIII(a)] and 6,7:13,14-Dibenzo-2,4,9,11-tetramethyl-1,5,8,12-tetra methylacrylate-1,5,8,12-tetraazacyclotetra-decane-6,13-diene [VIII(b)] as ionophores for the construction of a plasticized PVC membrane based polymeric membrane and coated graphite electrode for simple, selective and rapid determination of perchlorate.

5.2 EXPERIMENTAL

5.2.1 Reagents

Reagent grade hexadecyltrimethylammonium bromide (HTAB), dibutylphthalate (DBP), tri-n-butylphosphate (TBP), benzyl acetate (BA), dioctylphthalate (DOP), *o*-nitrophenyloctyl ether (*o*-NPOE), potassium carbonate (K_2CO_3), zinc(II) acetate dihydrate, tetrahydrofuran (THF) and high molecular weight poly(vinylchloride) were purchased from E. Merck (Germany) and used as received. Salicylaldehyde, 1, 3-dibromopropane, 3,4-diaminotoluene, o-phenylenediamine, acetylacetone were procured from Aldrich (USA) and methylacrylate from S. D Fine Chemicals Ltd. Reagent grade sodium and potassium salts of all anions used were of highest purity available from SRL (Mumbai) and used without any further purification except for vacuum drying over P_2O_5. Trishydroxymethylaminomethane (TRIS), Glycine (Gly) and 2-morpholinoethanesulfonic acid (MES) were purchased from Fluka. 0.05 M Gly adjusted for pH less then 4 with 0.1 M HCl solution. MES-NaOH buffer were prepared by titrating 50 mM solution of the acid form with concentrated sodium hydroxide to a pH-values of 4.00±0.01, 5.00±0.01 and 6.00±0.01. TRIS-SO4 buffer was prepared by titrating 50 mM of the basic form of TRIS using concentrated solution of H_2SO_4 to pH-values of greater then 6.00. Triply distilled water was used for the preparation of all aqueous solutions. Anionic salt solutions were prepared in doubly distilled water and standardized whenever necessary.

5.2.2 Synthesis of Ionophores

5.2.2.1 Synthesis of 1,4-bis(2-carboxyaldehydephenoxy)butane (VII)

To a stirred solution of salicylaldehyde (0.02 mol L^{-1}) and K_2CO_3 (0.01 mol L^{-1}) in DMF (100 mL) was added dropwise 1, 3-dibromopropane (0.01 mol L^{-1}) in DMF (40 mL) [71]. The reaction was continued for 10 h at 150–155 °C and then 5 h at room temperature. After the addition was completed then added 200 mL distillated H_2O and was put in a refrigerator. Then 1 h later the precipitate was filtered and washed with 500 mL H_2O. It was then dried in air, recrystallised from EtOH and filtered under vacuum. Yield: 16.7 g, M. Pt.: 107 °C, Color: Bright brown. Anal Calcd. for [$C_{17}H_{16}O_4$] (%): C, 71.82, H, 5.67, O, 22.51. Observed (%): C, 71.63, H, 5.53, O, 22.84 %. ^{1}H NMR (MeOH, 500 MHz) δ_{ppm}: 7.06-7.72 (m, H-Ar, 8H), 2.32-2.38 (m,-C-CH_2-C-, 2H), 4.12-4.14 (t,-O-CH_2-C-, 4H), FT-IR (KBr, cm^{-1}): 3100 m(Ar–CH), 2962, 2880 (Aliph.-CH), 1670 (C=O), 1492, 1452 (Ar–C=C), 1280, 1242 (Ar–O).

5.2.2.1.1 Synthesis of Zn complex of 6,7:14,15-Bzo$_2$-10,11-(4-methylbenzene)-[15]-6,8,12,14-tetraene-9,12-N$_2$-1,5-O$_2$ [VII(a)]

The zinc complex of 6,7:14,15-Bzo$_2$-10,11-(4-methylbenzene)-[15]-6,8,12,14-tetra ene-9,12-N$_2$-1,5-O$_2$ [VII(a)] (Fig. 5.1 (a)) was synthesized by dissolving 1,4-bis(2-carboxyaldehyde- phenoxy)butane (0.05 mol L^{-1}) and Zn(II)acetate dihydrate (0.05 mol L^{-1}) in 50 mL of distilled methanol in a 250 mL round bottom flask. The mixture was stirred and to this a solution of 3,4-diaminotoluene (0.05 mol L^{-1}) in 30 mL methanol was added dropwise over a period of 1 h. After the addition was completed, the stirring was continued for 2 h. A light yellow coloured microcrystalline compound was filtered and washed with EtOH, $CHCl_3$ and Et_2O, respectively, then dried in air. Yield: 45%. Anal Calcd. For [$C_{24}H_{22}N_2O_2Zn$] (%): C, 66.08, H, 5.16, N, 6.41, O, 7.33, Zn, 15.02. Observed (%):C, 66.14, H, 5.09, N, 6.43, O, 7.34, Zn, 15.0. ^{1}H NMR (MeOH, 500 MHz) δ_{ppm}: 6.95-7.62 (m, H-Ar, 11H), 8.28 (s, CH=N, 2H), 2.20 (s, -CH_3, 3H), 2.28-2.36 (m,-C-CH_2-C-, 2H), 4.10-4.13 (t,-O-CH_2-C-, 4H), FT-IR (KBr, cm^{-1}): 3055 (Ar–CH), 2940, (Aliph.-CH), 1690 (C=N), 1492, 14601 (Ar–C=C), 1273, 1242 (Ar–O).

5.2.2.1.2 Synthesis of Zn complex of 6,7:14,15-Bzo$_2$-10,11-(4-methylbenzene)-[15]-6,14-diene-9,12-dimethylacrylate-9,12-N$_2$-1,5-O$_2$ [VII(b)]

The Zn complex of 6,7:14,15-Bzo$_2$-10,11-(4-methylbenzene)-[15]-6,14-diene-9,12-dimethylacrylate-9,12-N$_2$-1,5-O$_2$ [VII(b)] (Fig. 5.1 (b)) was synthesised by in situ reduction of VII(a) with $NaBH_4$ followed by dropwise addition of 10 mL saturated solution of anh. K_2CO_3 in anhydrous MeOH and 5 mL methylacrylate (excess amount). It was then stirred overnight and refluxed for 24 h. The volume was then reduced to half of its initial amount and was kept in refrigerator for 1 day. A creamish coloured compound was obtained. Anal. calcd. for [$C_{34}H_{44}N_2O_6Zn$] (%): C, 63.54; H, 6.98; N, 4.36; O, 14.95;

Zn, 10.17; Observed (%): C, 63.60; H, 6.91; N, 4.36; O, 14.95; Zn, 10.18. ^{1}H NMR (MeOH, 500 MHz) δ_{ppm}: 7.07-8.23 (m, H-Ar, 11H), 2.32 (s,-CH_3, 3H), 2.29-2.32 (m,-C-CH_2-C-, 2H), 4.14-4.16 (t,-O-CH_2-C-, 4H), 2.25 (s, -N-CH_2-Ar-, 4H), 2.73-2.75 (t, -N-CH_2-C-, 4H), 4.33-4.35 (t, -C-CH_2-COOMe, 4H), 3.86 (s, OCH_3, 6H), FT-IR (KBr, cm^{-1}): 3056 (Ar-CH), 2944 (Aliph.-CH), 1288, 1251 (Ar-O), 1739 (ester C=O str.), 1120 (-OCH_3 str.).

5.2.2.2 Synthesis of Zn complex of 6,7:13,14-Dibenzo-2,4,9,11-tetramethyl-1,5,8,12-tetraazacyclotetradecane-1,4,6,8,11,13-hexaene [VIII(a)]

The Zn complex of macrocyclic ionophore VIII(a) (Fig. 5.2 (a)) was synthesized by dissolving *o*-phenylenediamine (0.05 mol L^{-1}) and Zn(II)acetate dihydrate (0.05 mol L^{-1}) in 50 mL of distilled methanol in a 250 mL round bottom flask. The mixture was stirred and to this a solution of acetylacetone (0.05 mol L^{-1}) in 30 mL methanol was added dropwise over a period of 1 h. After the addition was completed, the stirring was continued for 3 h. The resulting mixture was concentrated to half of its original volume and keeping aside for 1 day. A brown coloured product was obtained. Yield: 60 %. Anal. calcd. for [$C_{22}H_{24}N_4Zn$] (%): C, 64.58; H, 5.81; N, 13.72; Zn, 15.89. Observed (%): C, 64.47; H, 5.90; N, 13.67, Zn, 15.95. ^{1}H NMR (MeOH, 500 MHz) δ_{ppm}: 7.27-7.62 (m, H-Ar, 8H), 1.14 (s, -CH_3, 12H), 1.52 (s, -CH_2, 4H). FT-IR (KBr, cm^{-1}): 1692 (C=N), 1510, 1495 (Ar-C=C), 3035 (Ar-CH), 2946 (Aliph-CH).

5.2.2.2.1 Synthesis of Zn complex of 6,7:13,14-Dibenzo-2,4,9,11-tetramethyl-1,5,8,12-tetramethylacrylate-1,5,8,12-tetraazacyclotetra-decane-6,13-diene [VIII(b)]

The Zn complex of macrocyclic pendant ligand VIII(b) (Fig. 5.2 (b)) was synthesised by in situ reduction of VIII(a) with $NaBH_4$ followed by dropwise addition of 10 mL saturated solution of K_2CO_3 in anhydrous MeOH and 5 mL methylacrylate (excess amount). It was then stirred overnight at 0°C under a nitrogen atmosphere and refluxed for 24 h. The volume was then reduced to half of its initial amount and was kept in refrigerator for 1 day. A yellow coloured compound was obtained. Yield: 42 %. Anal. calcd. for [$C_{38}H_{64}N_4O_4Zn$] (%): C, 64.73; H, 9.10; N, 7.56; O, 9.15; Zn, 9.46. Observed (%): C, 64.73; H, 9.13; N, 7.93; O, 9.06, Zn, 9.26. ^{1}H NMR (MeOH, 500 MHz) δ_{ppm}: 6.95-7.38 (m, H-Ar, 8H), 3.24 (s, -OCH_3, 12H), 1.23 (s, -CH_3, 12H), 2.79-2.86 (m, -N-CH-C-, 4H), 1.54-1.79 (m,-C-CH_2-C-, 4H), 3.35 (m, -N-CH_2-C-, 8H), 3.37 (m, -C-CH_2-OCH_3, 8H), 1.60-1.68 (m, -C-CH_2-C(OCH_3), 8H)._FT-IR KBr, cm^{-1}): 3016 (Ar-CH), 1739 (ester C=O str.), 2940 (Aliph-CH), 1125 (-OCH_3 str.).

5.2.3 Preparation of Membranes

PVC based membranes containing macrocylic ligands as electroactive material were prepared by the same procedure as reported in section 3.2.4 of Chapter 3.

5.2.4 Equilibration of Membranes and Potential Measurements

The time of contact and concentration of equilibrating solution were optimized so that the sensors generated stable and reproducible potentials at relatively short response times. For thiocyanate ion determination, polymeric membrane electrode and coated graphite electrode based on membrane containing zinc complex of 6,7:14,15-Bzo_2-10,11-(4-methylbenzene)-[15]-6,8,12,14-tetraene-9,12-N_2-1,5-O_2 [VII(a)] and zinc complex of 6,7:14,15-Bzo_2-10,11-(4-methylbenzene)-[15]-6,14-diene-9,12-dimethylacrylate-9,12-N_2-1,5-O_2 [VII(b)] as ionophores with different composition were equilibrated for 2 days in 0.01 mol L^{-1} NaSCN solution. The potentials were measured by varying the concentration of NaSCN in test solution in the range 5.0 × 10^{-10} to 1.0 × 10^{-2} mol L^{-1}. Standard NaSCN solution were obtained by gradual dilution of 0.01 mol L^{-1} NaSCN solution.

For perchlorate ion determination, polymeric membrane electrode and coated graphite electrode based on membrane containing zinc complexes of 6,7:13,14-Dibenzo-2,4,9,11-tetramethyl-1,5,8,12-tetraazacyclotetradecane-1,4,6,8,11,13-hexa- ene [VIII(a)] and 6,7:13,14-Dibenzo-2,4,9,11-tetramethyl-1,5,8,12-tetramethyl acrylate-1,5,8,12-tetraazacyclotetradecane-6,13-diene [VIII(b)] as ionophores with different composition were equilibrated for 2 days in 1.0 × 10^{-2} mol L^{-1} $KClO_4$ solution. The potentials were measured by varying the concentration of $KClO_4$ in test solution in the range 5.0 × 10^{-10} to 1.0 × 10^{-2} mol L^{-1}. Standard $KClO_4$ solution were obtained by gradual dilution of 0.01 mol L^{-1} $KClO_4$ solution.

The potential measurement for Polymeric membrane electrode (PME) were carried out at 25 ± 0.1°C using saturated calomel electrode (SCE) as reference electrode with the following cell assembly:

Hg/Hg_2Cl_2 | KCl (satd.) | (0.1 or 0.01 mol L^{-1}) metal salt solution || PVC membrane || test solution | Hg/Hg_2Cl_2 | KCl (satd.)

The potential measurement for Coated graphite electrode (CGE) were carried out at 25 ± 0.1°C using saturated calomel electrode (SCE) as reference electrode with the following cell assembly:

CGE | sample solution || $Hg/HgCl_2$ |KCl (satd.)

5.3 RESULTS AND DISCUSSION

5.3.1 Membranes of zinc complexes of 6,7:14,15-Bzo$_2$-10,11-(4-methylbenzene)-[15]-6,8,12,14-tetraene-9,12-N$_2$-1,5-O$_2$ [VII(a)] and 6, 7: 14,15-Bzo$_2$-10,11-(4-methylbenzene)-[15]-6,14-diene-9,12-dimethylacrylate-9,12-N$_2$-1,5-O$_2$ [VII(b)] as SCN$^-$ selective sensor

In order to understand the affinity of ionophores VII(a) and VII(b) for various anions, spectroscopic studies on the interaction of SCN$^-$ with VII(a) and VII(b) were carried out and the results obtained are now discussed.

5.3.1.1 Spectroscopic studies of ionophores VII(a) and VII(b) with thiocyanate ions

In order to investigate the selective interaction of VII(a) and VII(b) as potential ion carriers with different anion species, the ultraviolet spectral studies were carried out in acetonitrile solutions. The ionophores VII(a) and VII(b) of concentration 1×10^{-4} mol L^{-1} gives the absorption peaks at 259.6, 311.4 nm and 291.0, 359.5 nm respectively. On addition of equimolar solution of SCN$^-$ (1×10^{-4} mol L^{-1}) to the VII(a) and VII(b) gave peaks at 263.9, 321.5 nm and 296.1, 351.9, 445.3 nm respectively (Fig. 5.3). The substantial increase in the absorbance after the contact with a carrier solution of the thiocyanate-containing phase suggested that the absorbing species has increased in size and the axial coordination might have taken place [72,73]. These changes in the UV-vis spectrum gives evidence of the specific interaction between the ionophores VII(a) and VII(b) and SCN$^-$.

The stoichiometry of the metal complexes was examined by the mole ratio method. The absorbance-mole ratio plot obtained for VII(a) and VII(b) revealed a pronounced inflexion point at a thiocyanate-to-ionophore ratio of about 1, indicating the formation of 1:1 adduct between the two species in solution. At the same time, the effect of other anions on the spectrum of the carrier was investigated and no detectable changes in the corresponding UV-vis spectra were observed.

5.3.1.2 Determination of formation constant

The determination of formation constant has been carried out to better understand the fundamental interaction between metal ions, neutral molecules and their relationship to molecular recognition. In present studies we have investigated the responses of zinc complexes of 6,7:14,15-Bzo$_2$-10,11-(4-methylbenzene)-[15]-6,8,12,14-tetraene-9,12-N$_2$-1,5-O$_2$ [VII(a)] and 6,7:14,15-Bzo$_2$-10,11-(4-methylbenzene)-[15]-6,14-diene-9,12-dimethylacrylate-9,12-N$_2$-1,5-O$_2$ [VII(b)] towards various anions by using segmented sandwich membrane method as described in section 3.2.5 of Chapter 3. The determined formation constants for the examined different complexes were recorded in Table 5.1. The values logarithm of formation constants (log $\beta_{\mathrm{IL}n}$) indicates that the ligands VII(a) and VII(b) forms most stable complex with thiocyanate ion *i.e.* (4.67 ± 0.04 for VII(a)-SCN^-) and (5.91 ± 0.03 for VII(b)-SCN^-) and complexes of comparatively poor stability with other metal anions (log $\beta_{\mathrm{M,I}}$ = 1.74-3.89). Because of their high affinity towards thiocyanate ion, VII(a) and VII(b) were used as potential ionophores in the preparation of thiocyanate ion selective electrode. The preferential response of the ionophores used towards SCN^- is believed to be associated with the coordination of thiocyanate with the metal centre in the macrocyclic Zn(II) complexes [VII(a) and VII(b)], and it is the relative affinity of the SCN^- as suitable ligand for Zn(II) that dictates the observed selectivity pattern of the electrodes.

5.3.1.3 Optimization of membrane composition

In preliminary experiments, the ionophores VII(a) and VII(b) were used as carriers to prepare PVC-based membranes for a variety of metal anions. Various membrane electrodes were prepared and conditioned in different anion solutions. The potentiometric response of these electrodes was observed and the best response was recorded for SCN^- ions while all other anions exhibited lower emf response. This may be due to the selective behaviour of the ionophores against SCN^- ions in comparison to the other anions and the rapid exchange kinetics of the resulting ligand–metal ion complex. Therefore, this membrane was used to develop a thiocyanate ions selective sensor. As the properties of membranes depends not only on the nature of an ionophore, but also are strongly influenced by the nature and amount of the solvent mediator, the plasticizer/PVC ratio and especially, the nature of additive used [74]. Thus to optimize potentiometric performance of thiocyanate selective electrode various PVC membrane based on VII(a) and VII(b) were prepared and investigated. The membrane containing only electroactive material VII(a) in the PVC matrix exhibited a narrow working concentration range of 9.8×10^{-5} to 1.0×10^{-2} mol L^{-1} with a slope of 68.3 ± 0.3 mV $decade^{-1}$ of activity (Fig. 5.4). Similarly the membrane containing VII(b) in the PVC matrix exhibited a narrow working concentration range of 2.3×10^{-5} to 1.0×10^{-2} mol L^{-1} with a slope of 66.1 ± 0.2 mV $decade^{-1}$ of activity (Fig. 5.5). Thus, the improvement in the performance was attempted by the addition of plasticizers and lipophilic charged additives to the membranes. It is well known that lipophilic charged additives like cation excluders enhance the sensitivity and selectivity of anion selective membrane by reducing the ohmic resistance [75,76]. Also, in case of PVC-based membranes, plasticizers compatible with the ionophore, can provide a smooth surface to the membrane and thus enhance the response characteristics. It can also improve the dielectric constant of the polymeric membrane and also the movement of ionophore and its metal complex [77]. Therefore, effect of the addition of cation excluder (HTAB) and plasticizers like DBP, DOP, TEP, TBP, CN, and DBBP on the performance of the membranes was also studied and the results are compiled in Table 5.2 and Table 5.3 for VII(a) and VII(b) respectively.

5.3.1.4 Potentiometric calibration characteristics of the proposed thiocyanate sensors

The membrane based on VII(a) containing DOP as plasticizer (Composition VII(a):PVC:DOP:HTAB in the ratio of 5:38:55:2) (sensor no. 7) exhibited a Nernstian slope 57.6 ± 0.3 mV decade^{-1} of activity over a wide working concentration range of 6.9×10^{-7} to 1.0×10^{-2} mol L^{-1} with detection limit of 4.5×10^{-7} mol L^{-1}. The best results are shown by sensor no. 18 based on VII(b) containing o-NPOE as the plasticizer having the composition VII(b):PVC:*o*-NPOE:HTAB in the ratio of 6:33:59:2. This sensor exhibited the Nernstian slope of 58.2 ± 0.3 mV decade^{-1} of activity over a wide working concentration range of 4.4×10^{-7} to 1.0×10^{-2} mol L^{-1} with detection limit of 2.2×10^{-7} mol L^{-1}.

5.3.1.4 Response characteristics of polymeric membrane electrode (PME) and coated graphite electrode (CGE)

The polymeric membrane electrode (PME) based on membrane having composition VII(b):PVC:*o*-NPOE:HTAB in the ratio of 6:33:59:2 exhibited Nernstian response over a wide working concentration range and high selectivity for thiocyanate ions. It was, therefore, decided to prepare the coated graphite electrode (CGE) for thiocyanate ion based on the membrane having above composition and its potentiometric response was recorded (Fig. 5.6). It was found that CGE exhibited better results over PME w. r. t Nernstian slope (59.0 ± 0.2) mV decade^{-1} activity, wide concentration range of 8.9×10^{-8} to 1.0×10^{-2} mol L^{-1} and detection limit of 6.7×10^{-8} mol L^{-1} (Table 5.4).

5.3.1.5 Response time and lifetime of the proposed sensors

The response time of the electrode was measured after successive immersion of the electrode in a series of SCN^- solutions, in each of which the SCN^- concentration increased tenfold from 1.0×10^{-6} to 1.0×10^{-2} mol L^{-1}. The resulting data showed that the time needed to reach a potential within ± 1.0 mV of the final equilibrium value after successive immersion in a series of thiocyanate solution is 10 s for PME (Fig. 5.7) and 8 s for CGE (Fig. 5.8).

The PME and CGE could be used over a period of 2 months and 3 months respectively at a stretch without observing any significant change in response time, slope and working concentration range. However, during usage, they were stored in 1×10^{-2} mol L^{-1} NaSCN solution.

5.3.1.6 Influence of pH on sensors performance

The pH of the sample solution is an important factor, often influencing the response of ion-selective electrodes. To adjust pH, MES-NaOH buffer, for pH-values of 4.00 ± 0.01, 5.00 ± 0.01 and 6.00 ± 0.01 and 0.05 mol L^{-1} Gly/HCl buffer for pH less than 4 were used. TRIS-SO_4 buffer for pH-values of greater than 6.00 were prepared and examined as background electrolyte solutions for potentiometric measurements. The pH dependence of both PME and CGE has been tested over the pH range 1.0-11.0 for 1.0×10^{-3} and 1.0×10^{-4} mol L^{-1} of the thiocyanate ions. It was found that potential response for PME remains constant over pH range 3.0-7.5 and 2.5-8.0 for CGE (Fig. 5.9). Therefore, the same was taken as the working pH range of the electrodes. Variation of the potential at lower pH could be related to protonation of SCN^- in the aqueous phase and ionophore in the membrane phase, which results in a loss of its ability to interact with the ionophore. At higher pH, the potential drop may be due to interference of hydroxide ions.

5.3.1.7 Effect of Soaking time and lifetime

The lifetime of the electrodes were determined by soaking both PME and CGE in 1×10^{-2} mol L^{-1} NaSCN solution for interval ranging from 2 to 95 days till the electrode lost its Nernstian behaviour. This behaviour attributed to the decomposition of the ionophore and loss of other components in the membrane phase that was in contact with aqueous test solution containing thiocyanate ion. The response of both electrodes has been measured by recording the calibration graph at 25 °C at different intervals. It was found that the lifetime measured in this way was found to be 2 months for PME and 3 months for CGE after which the slope of electrode, changes from 58.2 ± 0.3 to 52.1 ± 0.5 mV $decade^{-1}$ of activity for PME and 59.0 ± 0.2 to 53.7 ± 0.2 mV $decade^{-1}$ of activity for CGE (Table 5.5).

5.3.1.8 Interference of foreign ions on sensor performance

Selectivity of solvent polymeric membrane ion-selective electrodes is quantitatively related to equilibrium at the interface between sample and the electrode membrane. In this work, the selectivity coefficients of the electrode towards different anionic species were evaluated by using the fixed interference method (FIM). The selectivity coefficient was evaluated from potential measurement on solutions containing a fixed concentration of interfering ion (1.0×10^{-2} mol L^{-1}) and varying amount of SCN^- ions. The data obtained was summarized in Table 5.6.

It is evident from Table 5.6 that both electrodes, PME and CGE have relatively high selectivity towards SCN^- relative to anions such as perchlorate, iodide, salicylate, and several other common anions. It is interesting to note that the observed selectivity pattern for the SCN^--ISE significantly differs from so called Hofmeister selectivity sequence. The reason that the selectivity coefficients of this electrode do not comply with the Hofmeister series, and shows anti-hofmeister behaviour, is thought to be due to possible interaction of the anions with Zn [78]. According to hard-soft acid and base (HSAB) theorem, interaction of SCN^- with complex is via nitrogen. These results emphasize the superiority of CGE in this respect as well over PME and hence further studies were carried out with it only.

5.3.1.9 Analytical Applications

5.3.1.9.1 Potentiometric titration of thiocyanate ion solution with $AgNO_3$ solution

The proposed CGE was used as an indicator electrode in the potentiometric titration of 20 mL of 1.0×10^{-3} mol L^{-1} NaSCN with 1.0×10^{-2} mol L^{-1} $AgNO_3$ at pH 5.5. As can be seen from Fig. 5.9, the amount of thiocyanate ion in solution can be accurately determined from the titration curve providing a sharp end point.

5.3.1.9.2 Determination of thiocyanate ions in biological samples

The high degree of thiocyanate selectivity exhibited by the CGE makes it potentially useful for monitoring low concentration levels of thiocyanate in biological samples. Experimental results have shown that the urinary and salivary thiocyanate concentration is higher for smokers than non-smokers, so that thiocyanate has historically been monitored as an assessment of the effectiveness of cigarette smoking cession program. Thus, experiments were carried out to determine the feasibility of using the proposed electrode to measure thiocyanate in urine and saliva samples. The samples were first diluted to 1:10 and adjusted to pH 5.5 with MES/NaOH buffer and were analysed by CGE. The results are compiled in Table 5.7.

5.3.1.9.3 Determination of thiocyanate ions in water samples

The practical applicability of the proposed sensor was also checked in river water. The river water sample was used directly by adjusting the pH to 5.5 using dil. HCl solution. The results of the triplicate measurements are presented in Table 5.8.

It can be seen from Table 5.7 and Table 5.8 that the amount of thiocyanate ion evaluated with the help of the electrode are in good agreement with those obtained by the standard colorimetric method, thereby reflecting the utility of the proposed sensor.

5.3.1.10 Conclusion

On the basis of the results discussed in this paper, VII(a) and VII(b) can be regarded as carriers for the construction of thiocyanate selective electrode. The comparison of data reveals that CGE is superior to PME with regard to working concentration range (8.9×10^{-8} to 1.0×10^{-2} mol L^{-1}), detection limit (6.7×10^{-8} mol L^{-1}), response time (8 s) and selectivity. The high degree of thiocyanate selectivity by the CGE makes it potentially useful for monitoring concentration levels of thiocyanate in different water and biological samples and also as an indicator electrode in potentiometric titration of SCN^- ion.

5.3.2 Membranes of zinc complexes of 6,7:13,14-Dibenzo-2,4,9,11-tetramethyl-1, 5, 8, 12-tetraazacyclotetradecane-1, 4, 6, 8, 11, 13-hexaene [VIII(a)] and 6,7:13,14-Dibenzo-2,4,9,11-tetramethyl-1,5,8,12-tetra methylacrylate- 1, 5, 8, 12-tetraazacyclotetradecane- 6, 13-diene [VII(b)] as ClO_4^- selective sensor

In preliminary experiments, the ionophores VIII(a) and VIII(b) were used as carriers to prepare PVC-based membranes for some anions. Various membrane electrodes were prepared and conditioned in different anion solutions. The potentiometric response of these electrodes was observed and the best response was recorded for perchlorate ions while all other anions exhibited lower emf response. This may be due to the selective behaviour of the ionophores towards perchlorate ions in comparison to the other anions and the rapid exchange kinetics of the resulting ligand–metal ion complex. Therefore, this membrane was used to develop a perchlorate ions selective sensor.

5.3.2.1 Complexation Study

It is well established that the selective interaction of an analyte anion and a lipophilic ion carrier within the membrane is essential for the development of anion-selective membranes. The anion selectivity is mainly governed by a specific interaction between the central metal and the anions rather than the lipophilicity of the anions or a simple opposite charge interaction with anions [79]. The preferential response of the ionophore used towards ClO_4^- is believed to be associated with the coordination of perchlorate to the metal center in the complex VIII(a) and VIII(b), and it is the relative affinity of the ClO_4^- as a suitable ligand for Zn(II) that dictates the observed selectivity pattern of the electrodes.

In a preliminary study to learn about the affinity of the ligands [VIII(a) and VIII(b)] for different metal anions, a condutometric titration was carried out where a 20 mL of 1.0×10^{-4} mol L^{-1} anion solution was titrated with ligand solution of 1.0×10^{-3} mol L^{-1} and the conductance of the mixture was measured after each addition of ligand. It was observed that among various metal anions studied, conductance of perchlorate ion solution showed maximum variation on the addition of ligands. The change in conductance of ClO_4^- solution as a function of $[I]/[ClO_4^-]$ ratio is shown in Fig. 5.11. It is seen that the conductance decreases in the beginning on the addition of the ligand which shows that ClO_4^- ions are strongly interacting with the added ligand. A stage comes when interaction of ligands to the complex is complete and further addition of the ligand does not change the conductance of the mixture. The breaks in the plots show the stoichiometry of the complex formed. It is seen from these breaks that these ligands form 1:1 complex with ClO_4^- .The conductometric titration data was further used to calculate the stability constant of the various ion-ionophore complexes formed as calculated in Chapter 3 under section 3.3.3.1 and the results are summarized in Table 5.9. It can be seen from the table that VIII(a) and VIII(b) with the most stable complex with ClO_4^- ion is expected to act as a suitable ion-carriers for the fabrication of perchlorate ion sensor.

5.3.2.2 Determination of formation constant

The formation constants ($\log \beta_{\mathrm{IL}n}$) have been determined according to segmented sandwich membrane method. The potential of such sandwich membranes remains free of diffusion-induced potential drifts for about 20 min. Standard deviations were obtained based on the measurements of sets of at least three replicate membrane disks that were made from the same parent membrane. The determined logarithm of formation constants for the examined complexes of VIII(a) and VIII(b) with different anions were tabulated in Table 5.9. The results showed that VIII(a) and VIII(b) forms most stable complex with ClO_4^- ion having logarithm of formation constants ($\log \beta_{\mathrm{IL}n}$) 4.92 ± 0.04 and 5.47 ± 0.03 respectively. The $\log \beta_{\mathrm{IL}n}$ value for other complexes are comparatively smaller. The higher stability constant of ClO_4^- complexes with VIII(a) and VIII(b) is an indication that both the ligands have high affinity for ClO_4^- ions compared to other anions. Thus the data obtained from the both methods *i.e.* conductometric method and sandwich membrane method revealed that ligands VIII(a) and VIII(b) are potential ionophores for preparing ClO_4^- ion selective electrodes.

5.3.2.3 Optimization of membrane composition

The potential of the membranes of two macrocyclic ligands VIII(a) and VIII(b) were investigated as a function of perchlorate ion concentration and results are summarized in Table 5.10 and Table 5.11. It is seen from Table 5.10 that the sensor no. 1 having the membrane of VIII(a) without plasticizer and ionic additive exhibited linear potential response over a working concentration range of 7.5×10^{-5}-1.0×10^{-2} mol L^{-1} with a slope of 52.1 ± 0.5 mV decade^{-1} of activity. Similarly, sensor no. 11 (Table 5.11) having membrane of VIII(b) without plasticizer and ionic additive exhibited linear potential response over a working concentration range of 5.4×10^{-5} - 1.0×10^{-2} mol L^{-1} with a slope of 54.2 ± 0.4 mV decade^{-1} of activity. The slopes of the membranes are near- Nernstian only and the working concentration range is narrow. On the grounds that the plasticizer nature affects the dielectric constant of the membrane, the mobility of the ionophore molecule and the state of the ligand, it is expected for the plasticizers to play a key role in the determination of the ion-selective characteristics. This is the reason why in the present work five plasticizers, namely DBP, TBP, o-NPOE, DOP and BA, were added in varying amounts to the membrane matrix. Thus, several membranes of varying composition were fabricated to improve the performance characteristics of the electrode by adding different plasticizers as shown in Fig. 5.12 for VIII(a) and Fig. 5.13 for VIII(b) and the results are compiled in Tables 5.10 and Table 5.11 respectively. The electrodes based on VIII(a) and VIII(b) exhibited good Nernstian behaviour with TBP and BA respectively. This indicates that the solvent medium of TBP and BA is probably providing the best complexation environment between perchlorate ions and their respective carriers.

The addition of lipophilic cationic additive in anion selective membranes is necessary to introduce permselectivity [80]. The influence and concentration of the membrane additives was also investigated by incorporating HTAB into the membranes.

The potentiometric sensitivity of the membranes based on both carriers was greatly improved in the presence of HTAB as a lipophilic cationic additive, compared to the membranes with no additive at all. As is obvious from Tables 5.10 and Table 5.11, the use of 1 mg HTAB (for VIII(a), sensor no. 8) and 2 mg HTAB (for VIII(b), sensor no. 18) significantly improves the performance characteristics of the membrane sensors. This is due to fact that HTAB acts as a charge compensating counter ion in the membrane and thus facilitate the process of ion charge transduction. On the other hand, the membranes without lipophilic salt, showed very narrow concentration range and slopes were non-Nernstian.

The effect of the amount of ionophores incorporated in the membrane on the sensor characteristics was also investigated and results are compiled in Tables 5.10 (sensor nos. 8, 9, 10) and Table 5.11 (sensor nos. 18, 20, 21). A carrier content of 6 mg for VIII(a) and 7 mg for VIII(b) was chosen as the optimum ionophore amount, because the surface conditions of the PVC membrane deteriorated on decreasing and increasing the carrier content. This deviation in electrode response in higher concentration of the ionophore is due to the loss of selectivity and enhanced interference of the lipophilic counter ions of the test solution as presumed in the phase boundary potential model of carrier based ISEs.

5.3.2.4 Potentiometric calibration characteristics of the proposed perchlorate ion sensors

The investigations on PVC based membrane of two macrocyclic ligands, *viz.* VIII(a) and VIII(b) have shown that they act as perchlorate selective sensors. The membrane based on VIII(a) having composition VIII(a):PVC:TBP:HTAB in the ratio of 6:38:55:1 (w/w; mg) (sensor no. 8) exhibited Nernstian slope of (57.3 ± 0.5 mVdecade^{-1} of activity) and a working concentration range of 1.0×10^{-6} to 1.0×10^{-2} mol L^{-1} with a detection limit of 8.2×10^{-7} mol L^{-1} while the best results are shown by electrode no. 18 based on VIII(b) having composition VIII(b):PVC:BA:HTAB in the ratio of 7:32:59:2 (w/w; mg) which exhibited a Nernstian slope of 58.7 ± 0.3 mV decade^{-1} of activity over a wide concentration range of 8.3×10^{-7} to 1.0×10^{-2} mol L^{-1} with a detection limit of 5.4×10^{-7} mol L^{-1}.

5.3.2.5 Response characteristics of polymeric membrane electrode (PME) and coated graphite electrode (CGE)

The membrane having composition VIII(b):PVC:BA:HTAB in the ratio of 7:32:59:2 (w/w; mg) which showed best response characteristics for PME in terms of working concentration range and selectivity was selected to fabricate CGE. It was found that CGE exhibited better results over PME with respect to Nernstian slope (59.3 ± 0.2) mV decade^{-1} activity, wide concentration range of 1.0×10^{-7} to 1.0×10^{-2} mol L^{-1} and detection limit of 8.4×10^{-8} mol L^{-1} (Fig. 5.14). The comparison of data between both the electrodes has been compiled in Table 5.12.

5.3.2.6 Dynamic response time and lifetime of the proposed sensors

The response time of the electrodes was determined by measuring the time required to achieve a steady state potential (within ±1 mV) after successive immersion of the electrodes in a series of perchlorate ion solutions, each having a 10-fold increase in concentration from 1.0×10^{-6} to 1.0×10^{-2} mol L^{-1}. The typical potential–time plots for PME and CGE are shown in Fig. 5.15 and Fig. 5.16 respectively, which gives an idea that the response time for the PME is 12 s whereas that for the CGE is 9 s.

The lifetime of the electrodes was determined by soaking both PME and CGE in 0.01 mol L^{-1} $KClO_4$ solution for interval ranging from 2 to 65 days till the electrode lost its Nernstian behaviour. This behaviour attributed to the decomposition of the ionophore and loss of other components in the membrane phase that was in contact with aqueous test solution containing perchlorate ion. The lifetime of PME and CGE was found to be 30 days and 65 days respectively. The electrodes were stored in 0.01 mol L^{-1} perchlorate ion solution when not in use.

5.3.2.7 Influence of pH on sensors performance

The pH of the sample solution is an important factor, often influencing the response of ion-selective electrodes. Thus, the effect of pH on the perchlorate response characteristics of electrodes (PME and CGE) was investigated by measuring the potentials in 1.0×10^{-3} and 1.0×10^{-4} mol L^{-1} perchlorate ion solution at different pH values varied from 1.0-11.0. The pH of the solution was adjusted by addition of 0.1 mol L^{-1} solution of either HCl or NaOH and the results are shown in Fig. 5.17. The potential response for PME and CGE remains constant over pH range of 3.0-8.0 and 2.5-9.0 respectively. Therefore, the same was taken as the working pH range of the electrodes. The significant change in potential response observed at lower pH (<) can be reasonably related to the response of the sensor to the ClO_4^- and Cl^- ions. On the other hand, the observed potential drift at higher pH (>) values could be due to the interference by the hydroxide ions.

5.3.2.8 Effect of non-aqueous media

The performance of the sensor was also investigated in partially non-aqueous media using 10 %, 20 %, 25 % and 30 % (v/v) methanol-water, ethanol-water and acetonitrile-water mixtures (Table 5.13). It was found that the membranes did not show any appreciable change in working concentration range and slope in methanol-water and ethanol-water mixtures up to 25 % (v/v) non-aqueous contents, whereas in acetonitrile-water mixture, membrane could tolerate up to 15 % (v/v) non-aqueous content. However, above these mentioned non aqueous contents, the slope and working concentration range decreased appreciably, consequently reliable measurements could not be obtained.

5.3.2.9 Interference of foreign ions on sensor performance

The most important characteristics of any ion-selective electrode, is its relative response for the primary ion over other ions present in the solution which is expressed in terms of the potentiometric selectivity coefficients $K_{A,B}^{pot}$, describing the preference of the membrane for an interfering ion relative to perchlorate ion. In this work, the selectivity coefficients of the electrode towards different anionic species were evaluated by using the fixed interference method (FIM). For this purpose, a fixed concentration of interfering ion ($a_B = 1.0 \times 10^{-2}$ mol L^{-1}) was added to the primary perchlorate ion solutions ranging from 1.0×10^{-9} to 1.0×10^{-2} mol L^{-1} and the potentials were measured. The potential values obtained were plotted versus the activity of the perchlorate ion. The linear portions of the potential response curve were extrapolated and the value of $a_{ClO_4^-}$ obtained from the intersection point. Potentiometric selectivity coefficients were then calculated using the expression as discussed in section 2.5 of Chapter 2. The selectivity coefficients are shown in Table 5.14.

As it is evident from the data in Table 5.14, the coated graphite electrode based on VIII(b) has relatively high selectivity towards ClO_4^- relative to anions such as thiocyanate, iodide, salicylate, and several other common anions. The interfering effect of the ions is in the following order: $SCN^- > I^- > Br^- > NO_3^- > SO_4^{2-} > Cl^- > CN^- > F^- > MnO_4^- > IO_3^- > NO_2^- > HPO_4^{2-} > CH_3COO^- > CO_3^{2-} > H_2PO_4^- > Sal^- > Cr_2O_7^{2-}$. From the analysis of selectivity co-efficient data, it is quite clear that none of the secondary ions had been found to be interfering in the normal functioning of the proposed perchlorate ion selective electrode. It is interesting to note that the observed selectivity pattern for the ClO_4^--ISE significantly differs from so called Hofmeister selectivity sequence. The reason that the selectivity coefficients of this electrode do not comply with the Hofmeister series, and shows anti-hofmeister behaviour, is thought to be due to possible interaction of the anions with Zn.

5.3.2.10 Analytical Applications

5.3.2.10.1 Determination of perchlorate ions in water and biological samples

To assess the applicability of the membrane electrode for real samples an attempt was made to determine ClO_4^- ion in several water and biological samples using the standard addition method. The proposed electrode was applied to the recovery of perchlorate ion from river and tap water and human urine samples with satisfactory results. The results are summarized in Table 5.15. Good recoveries were obtained in all samples. It was also used for the determination of perchlorate ion in presence of other anions and the results are compiled in Table 5.16. The results indicate that the proposed electrode can be successfully applied to the determination of perchlorate ion at concentrations normally present in different matrices.

5.3.2.11 Conclusion

The present studies confirmed the selective determination of ClO_4^- ion by zinc complexes of 6,7:13,14-Dibenzo-2,4,9,11-tetramethyl-1,5,8,12-tetraazacyclotetra decane-1,4,6,8,11,13-hexaene [VIII(a)] and 6,7:13,14-Dibenzo-2,4,9,11-tetramethyl-1,5,8,12-tetramethylacrylate-1,5,8,12-tetraazacyclotetradecane-6,13-diene [VIII(b)| incorporated in a PVC matrix. The best composition of the proposed polymeric membrane electrode was found to be VIII(b):PVC:BA:HTAB in the ratio of 7:32:59:2 (w/w; mg). The polymeric membrane electrode developed using this ionophore exhibited working concentration range of 8.3×10^{-7} to 1.0×10^{-2} mol L^{-1}, detection limit of 5.4×10^{-7} mol L^{-1} with

Nernstian slope 58.7 ± 0.3 mV decade^{-1} of activity. The performance of this sensor was also compared with coated graphite electrode which showed better results than PME with respect to the working concentration range (1.0×10^{-7} to 1.0×10^{-2} mol L^{-1}), low detection limit (8.4×10^{-8} mol L^{-1}), fast response time (9 s) and high selectivity for ClO_4^- ion. The response characteristics of the proposed CGE are best as compared to the previously reported electrodes that make it superior potentiometric device. The high degree of perchlorate selectivity by the CGE makes it potentially useful for monitoring concentration levels of perchlorate in different water and biological samples.

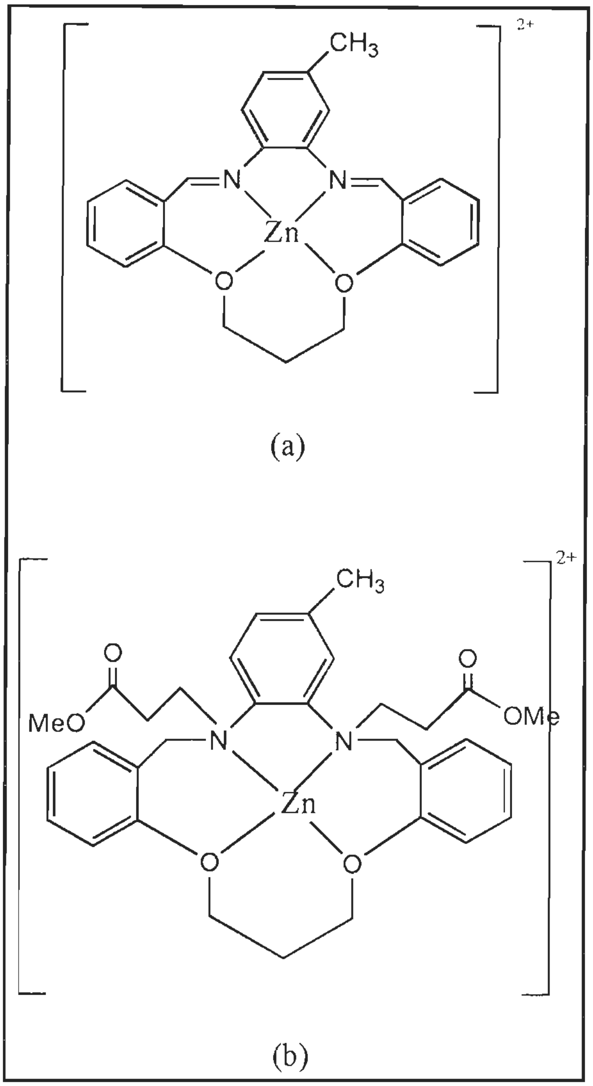


Fig. 5.1 (a) Zinc complex of 6,7:14,15-Bzo$_2$-10,11-(4-methylbenzene)-[15]- 6,8,12,14-tetraene-9,12-N$_2$-1,5-O$_2$ [VII(a)]

(b) Zinc complex of 6,7:14,15-Bzo$_2$-10,11-(4-methylbenzene)-[15]-6,14-diene-9,12-dimethylacrylate-9,12-N$_2$-1,5-O$_2$ [VII(b)]

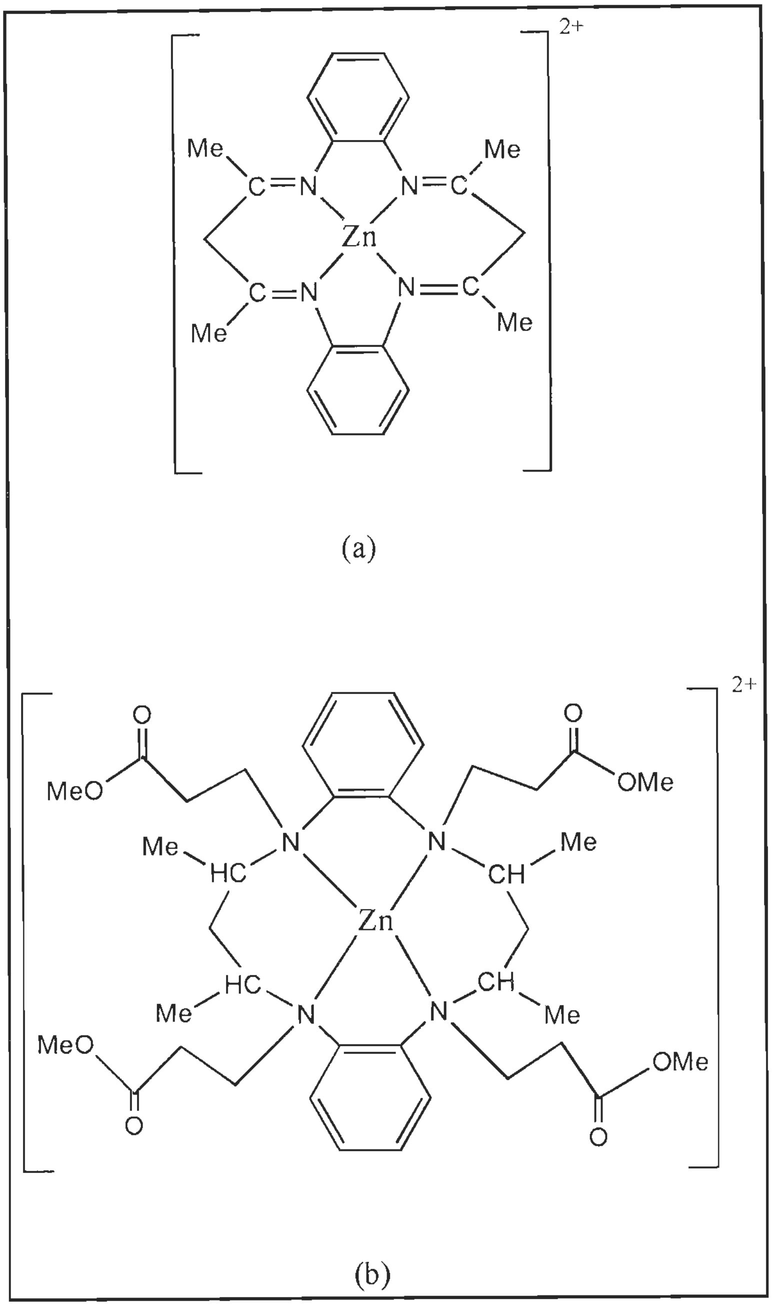


Fig. 5.2 (a) Structure of zinc complex of 6,7:13,14-Dibenzo-2,4,9,11-tetramethyl-1,5,8,12-tetraazacyclotetradecane-1,4,6,8,11,13-hexaene [VIII(a)]

(b) Structure of zinc complex of 6,7:13,14-Dibenzo-2,4,9,11-tetramethyl-1,5,8,12-tetramethylacrylate-1,5,8,12-tetraazacyclotetradecane-6,13-diene [VIII(b)]

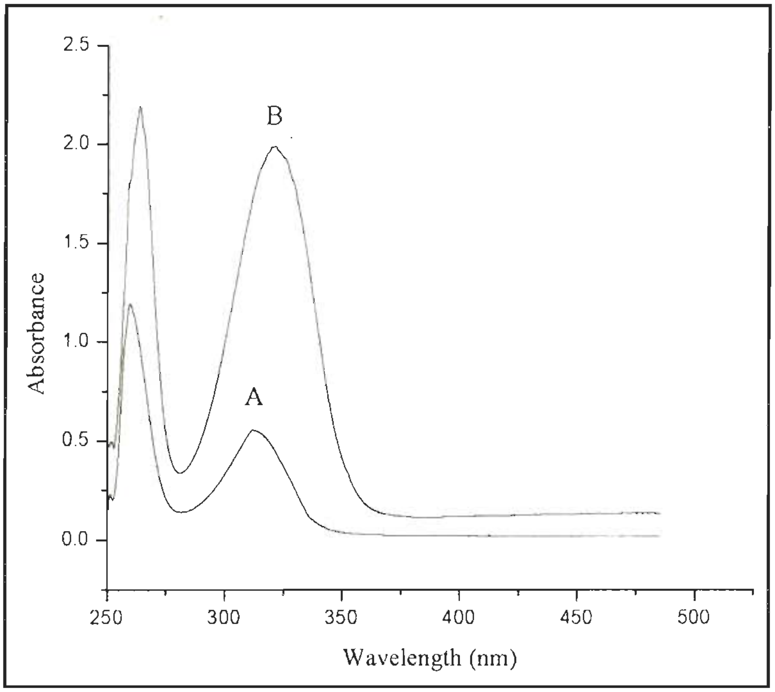


Fig. 5.3 UV-Vis spectra of 1×10^{-4} mol L^{-1} ionophore [VII(a)] (A), Mixture of VII(a) and SCN^- ion solution (B), 1×10^{-4} mol L^{-1} ionophore [VII(b)] (C), Mixture of VII(b) and SCN^- ion solution (D)

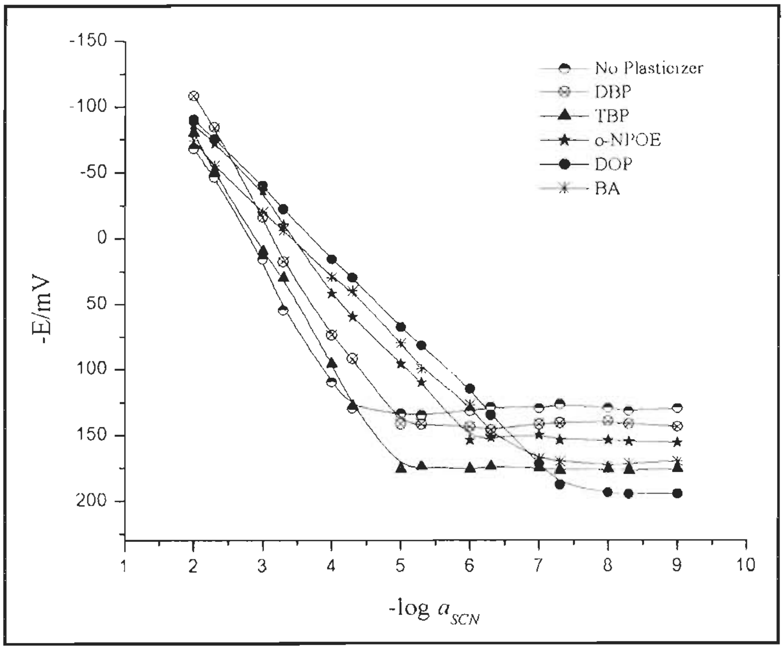


Fig. 5.4 Variation of potential of thiocyanate selective membrane based on VII(a) with different plasticizers as a function of SCN^- concentration

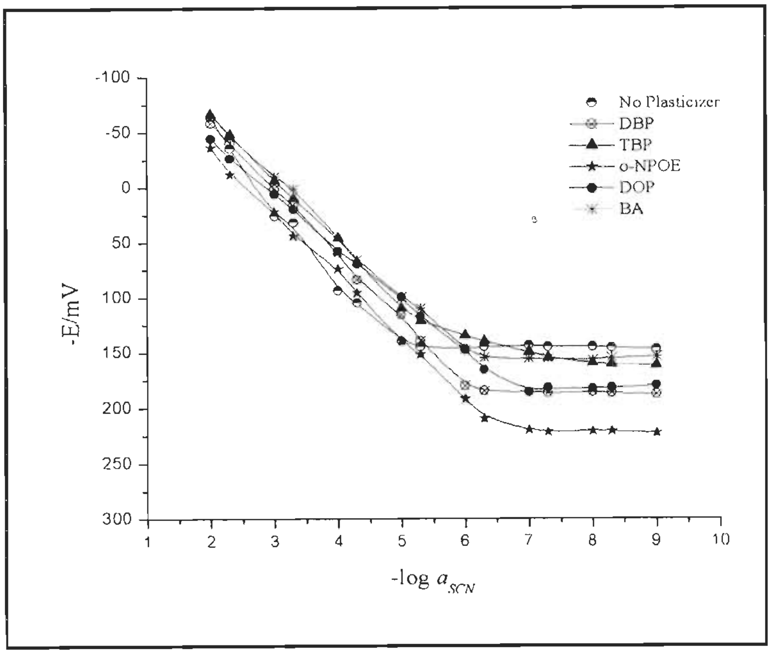


Fig. 5.5 Variation of potential of thiocyanate selective membrane based on VII(b) with different plasticizers as a function of SCN$^-$ concentration

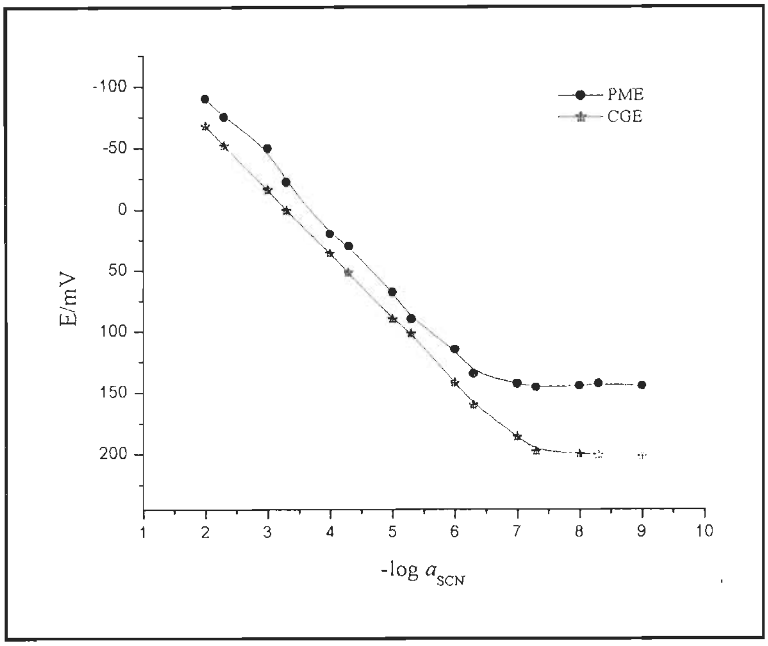


Fig. 5.6 Calibration characteristics of thiocyanate selective electrodes (PME and CGE) based on VII(b)

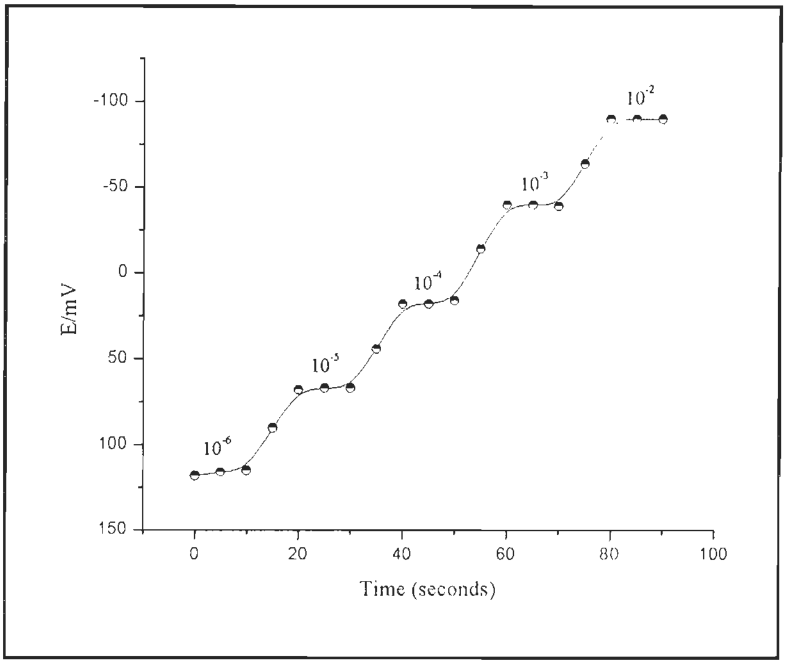


Fig. 5.7 Dynamic response of Polymeric membrane electrode based on VII(b)

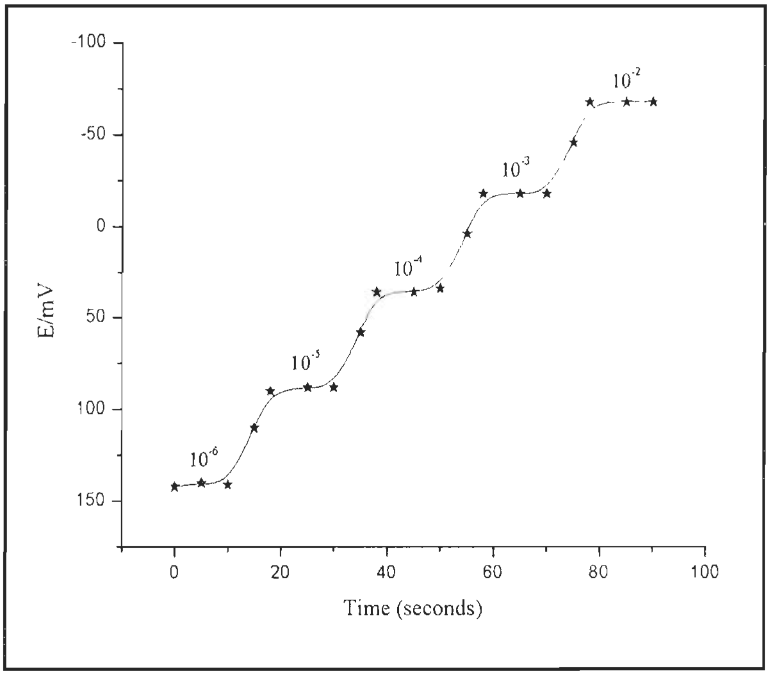


Fig. 5.8 Dynamic response of Coated graphite electrode based on VII(b)

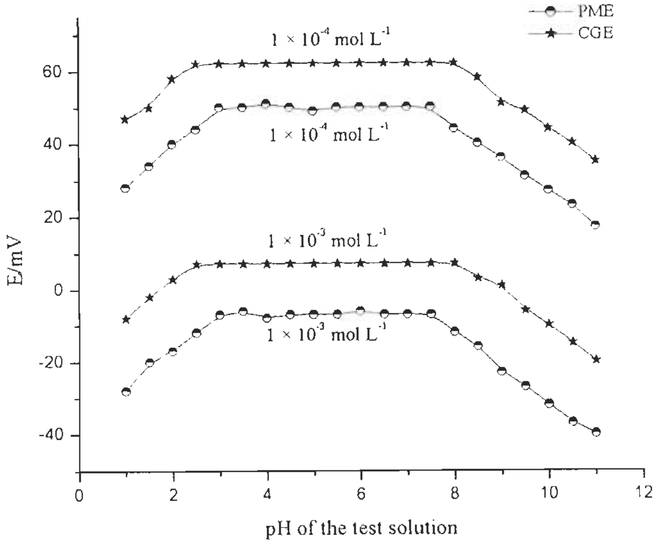


Fig. 5.9 Effect of pH of the test solutions on the potential responses of the PME and CGE at different concentration of SCN^-

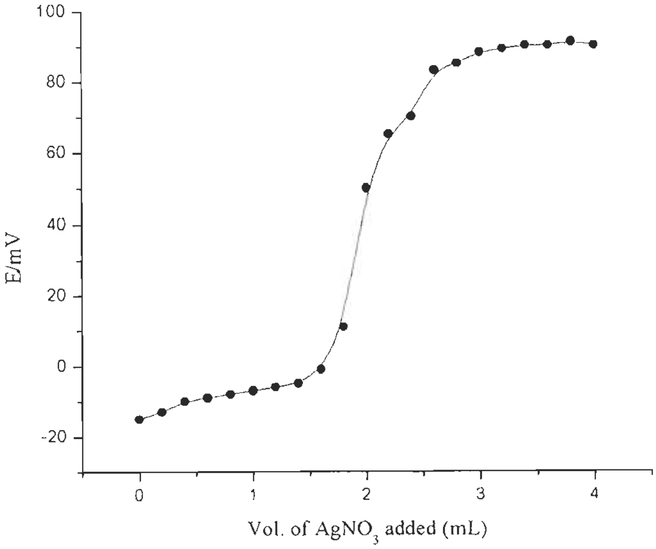


Fig. 5.10 Titration curve of 20 mL of 1.0 × 10^{-3} mol L^{-1} NaSCN with 1.0×10^{-2} mol L^{-1} $AgNO_3$ at pH 5.5

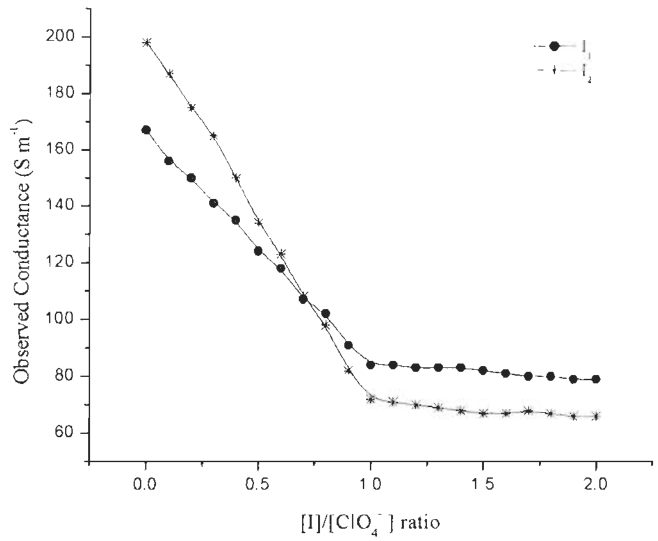


Fig. 5.11 Conductometric plot showing 1:1 stoichiometric ratio of perchlorate ion with ligands VIII(a) and VIII(b)

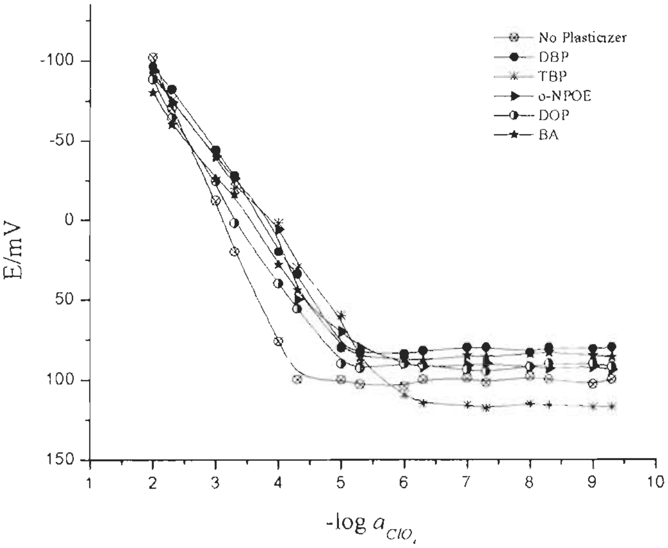


Fig. 5.12 Variation of potential of perchlorate selective membrane based on VIII(a) with different plasticizers as a function of ClO$_4^-$ concentration

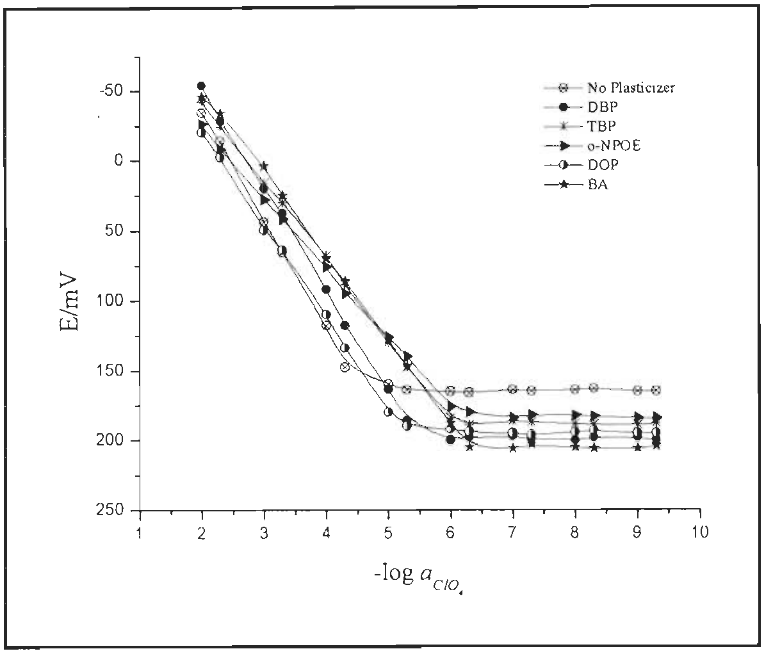


Fig. 5.13 Variation of potential of perchlorate selective membrane based on VIII(b) with different plasticizers as a function of ClO_4^- concentration

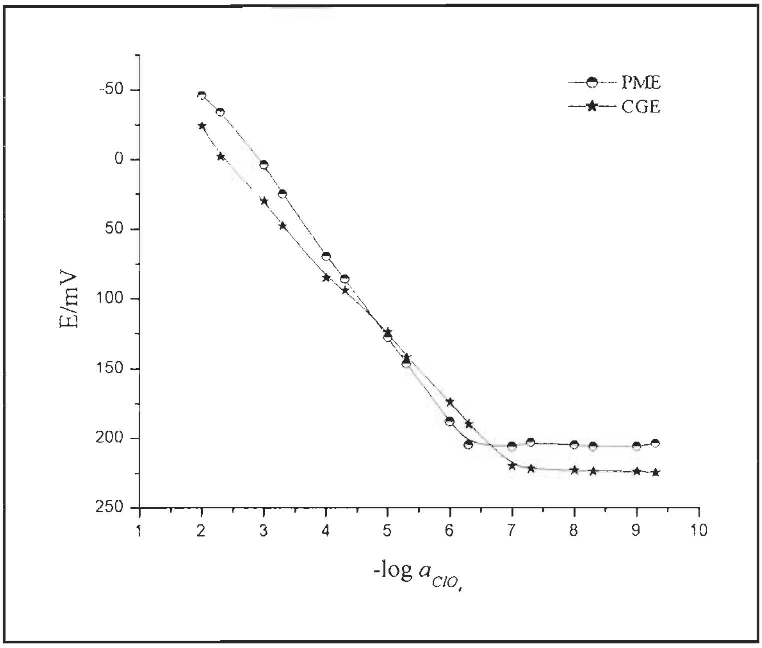


Fig. 5.14 Calibration characteristics of perchlorate ion selective electrodes (PME and CGE) based on VIII(b)

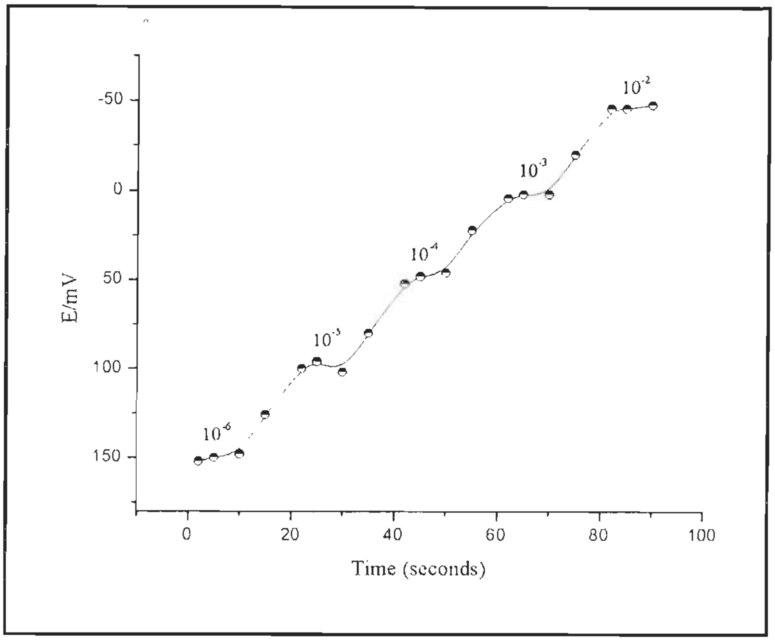


Fig. 5.15 Dynamic response of Polymeric membrane electrode based on VIII(b)

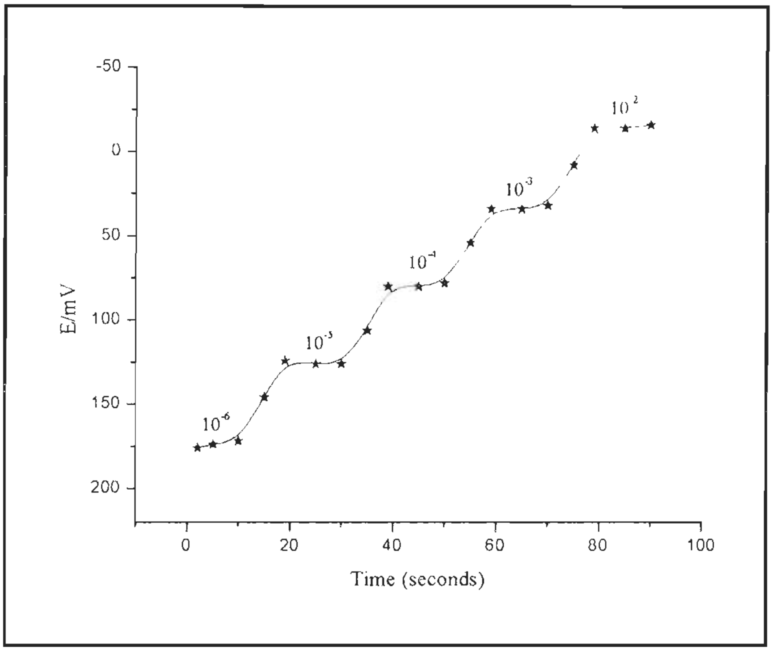


Fig. 5.16 Dynamic response of Coated graphite electrode based on VIII(b)

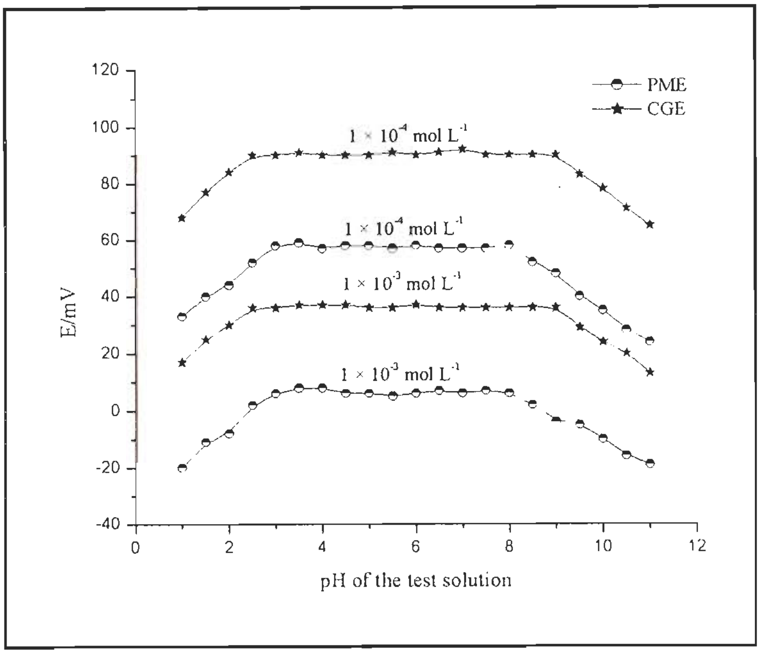


Fig. 5.17 Effect of pH of the test solutions on the potential responses of the PME and CGE at different concentration of ClO_4^-

Table 5.1 The formation constants of VII(a)-M^{n-} and VII(b)-M^{n-}complexes using Sandwich method

Metal anions	**Formation constant (log β_{IL_n})* ±SD**	**Metal anions**	**Formation constant (log β_{IL_n})* ±SD**
	VII(a)		**VII(b)**
SCN^-	4.67 ± 0.04	SCN^-	5.91 ± 0.03
ClO_4^-	3.89 ± 0.04	ClO_4^-	4.00 ± 0.05
I^-	3.66 ± 0.03	I^-	3.82 ± 0.03
NO_3^-	3.53 ± 0.04	NO_3^-	3.73 ± 0.05
Br^-	3.41 ± 0.06	Br^-	3.66 ± 0.05
Sal^-	3.26 ± 0.07	Sal^-	3.49 ± 0.07
CN^-	3.10 ± 0.06	CN^-	3.37 ± 0.04
Cl^-	2.97 ± 0.05	Cl^-	3.30 ± 0.05
NO_2^-	2.90 ± 0.04	NO_2^-	3.24 ± 0.05
F^-	2.85 ± 0.05	F^-	3.18 ± 0.03
$H_2PO_4^-$	2.70 ± 0.06	$H_2PO_4^-$	3.04 ± 0.02
MnO_4^-	2.66 ± 0.04	MnO_4^-	2.97 ± 0.04
$S_2O_3^{2-}$	2.54 ± 0.04	$S_2O_3^{2-}$	2.84 ± 0.07
SO_4^{2-}	2.48 ± 0.05	SO_4^{2-}	2.70 ± 0.07
PO_4^{3-}	2.30 ± 0.03	PO_4^{3-}	2.53 ± 0.05
$Cr_2O_7^{2-}$	2.17 ± 0.03	$Cr_2O_7^{2-}$	2.42 ± 0.06
$C_2O_4^{2-}$	1.99 ± 0.04	$C_2O_4^{2-}$	2.33 ± 0.04
CH_3COO^-	1.74 ± 0.06	CH_3COO^-	1.92 ± 0.04

* Mean value ± standard deviation (three measurements)

Table 5.2 Composition and response characterisitics of Thiocyanate ion-selective polymeric membrane electrode based on VII(a)

S.No.	Composition of membrane (w/w; mg)								Working concentration range (mol L^{-1})	Slope (mV decade^{-1} of activity)	Detection limit (mol L^{-1})
	VII(a) (mg)	HTAB	DBP	TBP	*o*-NPOE	DOP	BA	PVC			
1	5	-	-	-	-	-	-	95	9.8×10^{-5} to 1.0×10^{-2}	68.3 ± 0.3	6.6×10^{-5}
2	5	-	55	-	-	-	-	40	3.6×10^{-5} to 1.0×10^{-2}	66.7 ± 0.4	1.5×10^{-5}
3	5	-	-	55	-	-	-	40	2.1×10^{-5} to 1.0×10^{-2}	55.9 ± 0.3	1.3×10^{-5}
4	5	-	-	-	55	-	-	40	2.5×10^{-6} to 1.0×10^{-2}	69.2 ± 0.6	1.4×10^{-6}
5	5	-	-	-	-	55	-	40	7.4×10^{-7} to 1.0×10^{-2}	56.4 ± 0.4	5.1×10^{-7}
6	5	-	-	-	-	-	55	40	3.9×10^{-6} to 1.0×10^{-2}	52.6 ± 0.5	1.6×10^{-6}
7	5	2	-	-	-	55	-	38	6.9×10^{-7} to 1.0×10^{-2}	57.6 ± 0.3	4.5×10^{-7}
8	5	1	-	-	-	55	-	39	9.2×10^{-7} to 1.0×10^{-2}	54.3 ± 0.3	7.1×10^{-7}
9	5	3	-	-	-	55	-	37	6.4×10^{-6} to 1.0×10^{-2}	62.3 ± 0.3	3.6×10^{-6}
10	6	2	-	-	-	55	-	37	8.5×10^{-6} to 1.0×10^{-2}	66.1 ± 0.2	6.2×10^{-6}
11	4	2	-	-	-	55	-	36	3.4×10^{-6} to 1.0×10^{-2}	65.7 ± 0.5	2.6×10^{-6}

Table 5.3 Composition and response characterisitics of Thiocyanate ion-selective polymeric membrane electrode based on VII(b)

S.No.	Composition of membrane (w/w; mg)								Working concentration range (mol L^{-1})	Slope (mV decade^{-1} of activity)	Detection limit (mol L^{-1})
	VII(b) (mg)	HTAB	DBP	TBP	*o*-NPOE	DOP	BA	PVC			
12	6	-	-	-	-	-	-	94	2.3×10^{-5} to 1.0×10^{-2}	66.1 ± 0.2	1.5×10^{-5}
13	6	-	59	-	-	-	-	35	1.6×10^{-6} to 1.0×10^{-2}	62.7 ± 0.2	9.3×10^{-7}
14	6	-	-	59	-	-	-	35	4.1×10^{-6} to 1.0×10^{-2}	57.2 ± 0.3	1.0×10^{-6}
15	6	-	-	-	59	-	-	35	5.7×10^{-7} to 1.0×10^{-2}	57.0 ± 0.6	4.5×10^{-7}
16	6	-	-	-	-	59	-	35	4.2×10^{-6} to 1.0×10^{-2}	64.7 ± 0.3	2.3×10^{-6}
17	6	-	-	-	-	-	59	35	9.7×10^{-7} to 1.0×10^{-2}	56.4 ± 0.5	7.0×10^{-7}
18	6	2	-	-	59	-	-	33	4.4×10^{-7} to 1.0×10^{-2}	58.2 ± 0.3	2.2×10^{-7}
19	6	1	-	-	59	-	-	34	6.2×10^{-7} to 1.0×10^{-2}	56.1 ± 0.3	4.7×10^{-7}
20	6	3	-	-	59	-	-	32	5.3×10^{-6} to 1.0×10^{-2}	67.7 ± 0.3	3.8×10^{-6}
21	7	2	-	-	59	-	-	32	9.4×10^{-7} to 1.0×10^{-2}	62.8 ± 0.2	8.6×10^{-7}
22	5	2	-	-	59	-	-	34	4.7×10^{-6} to 1.0×10^{-2}	66.7 ± 0.2	1.8×10^{-6}

Table 5.4 Response characteristics of the thiocyanate ion-selective electrodes based on PME and CGE

Properties	Values / range	
	PME	CGE
Optimized membrane composition	VII(b) (6 mg): PVC (33 mg): *o*-NPOE (59 mg) : HTAB (2 mg)	VII(b) (6 mg): PVC (33 mg): *o*-NPOE (59 mg) : HTAB (2 mg)
Conditioning time	2 days in 0.01 mol L^{-1} NaSCN	1 day in 0.01 mol L^{-1} NaSCN
Working concentration range (mol L^{-1})	4.4×10^{-7} to 1.0×10^{-2}	8.9×10^{-8} to 1.0×10^{-2}
Detection limit (mol L^{-1})	2.2×10^{-7}	6.7×10^{-8}
Slope (mV $decade^{-1}$ of activity)	58.2 ± 0.3	59.0 ± 0.2
Response time (s)	10	8
Life span	2 months	3 months
pH range	3.0-7.5	2.5-8.0

Table 5.5 Selectivity coefficient of various interfering anions for thiocyanate selective electrodes.

Metal anions	Selectivity Coefficient ($K_{A,B}^{FIM}$)	
	PME	CGE
ClO_4^-	6.7×10^{-2}	3.3×10^{-3}
I^-	7.9×10^{-2}	3.9×10^{-3}
NO_3^-	9.1×10^{-2}	4.1×10^{-3}
Br^-	1.3×10^{-3}	6.4×10^{-3}
Sal^-	1.9×10^{-3}	8.8×10^{-3}
CN^-	2.7×10^{-3}	2.6×10^{-4}
Cl^-	3.2×10^{-3}	4.2×10^{-4}
NO_2^-	4.9×10^{-3}	5.8×10^{-4}
F^-	5.2×10^{-3}	6.7×10^{-4}
$H_2PO_4^-$	6.8×10^{-3}	6.9×10^{-4}
MnO_4^-	7.4×10^{-3}	7.3×10^{-4}
$S_2O_3^{2-}$	8.2×10^{-3}	7.9×10^{-4}
SO_4^{2-}	8.6×10^{-3}	8.2×10^{-4}
PO_4^{3-}	9.3×10^{-3}	8.8×10^{-4}
$Cr_2O_7^{2-}$	9.7×10^{-3}	9.3×10^{-4}
$C_2O_4^{2-}$	2.3×10^{-4}	9.9×10^{-4}
CH_3COO^-	3.0×10^{-4}	3.4×10^{-5}
CrO_4^-	3.6×10^{-4}	4.1×10^{-5}

Table 5.6 Effect of Soaking time on the potential response of the thiocyanate selective electrode

Soaking Time	Slope (mV decade^{-1} of activity)	Working Concentration Range (mol L^{-1})	Detection Limit (mol L^{-1})
PME			
2 days	58.2 ± 0.3	4.4×10^{-7} to 1.0×10^{-2}	2.2×10^{-7}
10 days	58.0 ± 0.4	4.6×10^{-7} to 1.0×10^{-2}	2.3×10^{-7}
25 days	57.6 ± 0.3	5.3×10^{-7} to 1.0×10^{-2}	2.7×10^{-7}
45 days	57.2 ± 0.2	5.9×10^{-7} to 1.0×10^{-2}	3.1×10^{-7}
60 days	56.4 ± 0.4	6.6×10^{-7} to 1.0×10^{-2}	4.5×10^{-7}
65 days	52.1 ± 0.5	4.7×10^{-6} to 1.0×10^{-2}	1.3×10^{-6}
CGE			
2 days	59.0 ± 0.2	8.9×10^{-8} to 1.0×10^{-2}	6.7×10^{-8}
10 days	59.0 ± 0.3	9.1×10^{-8} to 1.0×10^{-2}	6.9×10^{-8}
25 days	58.9 ± 0.2	9.3×10^{-8} to 1.0×10^{-2}	7.0×10^{-8}
45 days	58.5 ± 0.2	9.6×10^{-8} to 1.0×10^{-2}	7.2×10^{-8}
70 days	58.2 ± 0.4	9.9×10^{-8} to 1.0×10^{-2}	8.0×10^{-8}
90 days	57.9 ± 0.3	1.0×10^{-7} to 1.0×10^{-2}	8.9×10^{-8}
95 days	53.7 ± 0.2	5.2×10^{-6} to 1.0×10^{-2}	3.5×10^{-6}

Table 5.7 Comparison of results of proposed electrode and colorimetric methods for determination of SCN⁻ (µg/mL) in saliva and urine samples of smokers and non-smokers

Sample no.	Smokers (µg/mL)		Sample no.	Non-smokers (µg/mL)	
	Electrode	Colorimetric		Electrode	Colorimetric
Saliva					
1	21.6 ± 0.4	21.2 ± 0.3	4	4.6 ± 0.2	4.7 ± 0.5
2	17.5 ± 0.3	17.5 ± 0.4	5	5.3 ± 0.4	5.6 ± 0.5
3	20.4 ± 0.3	20.8 ± 0.6	6	4.9 ± 0.2	5.0 ± 0.3
Urine					
1	8.4 ± 0.3	8.2 ± 0.4	4	1.9 ± 0.3	1.9 ± 0.6
2	7.5 ± 0.2	7.4 ± 0.5	5	2.3 ± 0.2	2.3 ± 0.6
3	6.9 ± 0.4	6.9 ± 0.5	6	1.2 ± 0.4	1.4 ± 0.5

Table 5.8 Determination of SCN⁻ ions in river samples by the proposed CGE

Samples	Proposed thiocyanate sensor (µg/mL)	Colorimetric method (µg/mL)
1	0.90 ± 0.2	0.92 ± 0.5
2	0.84 ± 0.2	0.88 ± 0.4
3	0.96 ± 0.3	0.97 ± 0.5

Table 5.9 Formation constants of different metal complexes with ionophores VIII(a) and VIII(b)

Anions	Formation constant ($\log \beta_{\mathrm{IL}n}$) ± SD (Conductometric Method)	Formation constant ($\log \beta_{\mathrm{IL}n}$) ± SD (Sandwich Method)	Anions	Formation constant ($\log \beta_{\mathrm{IL}n}$) ± SD (Conductometric Method)	Formation constant ($\log \beta_{\mathrm{IL}n}$) ± SD (Sandwich Method)
	VIII(a)			VIII(b)	
ClO_4^-	4.92 ± 0.04	4.85 ± 0.05	ClO_4^-	5.47 ± 0.03	5.40 ± 0.03
SCN^-	3.67 ± 0.07	3.64 ± 0.06	SCN^-	3.94 ± 0.07	3.87 ± 0.02
I^-	3.44 ± 0.04	3.46 ± 0.04	I^-	3.75 ± 0.05	3.66 ± 0.04
Br	3.35 ± 0.04	3.31 ± 0.04	Br^-	3.43 ± 0.04	3.40 ± 0.04
NO_3	3.11 ± 0.07	3.10 ± 0.03	NO_3^-	3.24 ± 0.08	3.25 ± 0.05
SO_4^{2}	2.99 ± 0.06	2.92 ± 0.02	SO_4^{2-}	3.18 ± 0.04	3.20 ± 0.06
Cl^-	2.92 ± 0.03	2.87 ± 0.03	Cl^-	3.00 ± 0.03	2.96 ± 0.06
CN^-	2.80 ± 0.03	2.81 ± 0.05	CN^-	2.96 ± 0.03	2.88 ± 0.07
F^-	2.65 ± 0.03	2.60 ± 0.05	F^-	2.90 ± 0.04	2.80 ± 0.04
MnO_4^-	2.59 ± 0.02	2.51 ± 0.07	MnO_4^-	2.88 ± 0.05	2.77 ± 0.05
IO_3^-	2.50 ± 0.06	2.44 ± 0.07	IO_3^-	2.76 ± 0.06	2.68 ± 0.05
NO_2^-	2.42 ± 0.03	2.35 ± 0.08	NO_2^-	2.70 ± 0.03	2.64 ± 0.03
HPO_4^{2-}	2.36 ± 0.02	2.30 ± 0.06	HPO_4^{2-}	2.62 ± 0.04	2.59 ± 0.03
CH_3COO^-	2.24 ± 0.05	2.25 ± 0.05	CH_3COO^-	2.52 ± 0.07	2.54 ± 0.04
CO_3^{2-}	2.18 ± 0.06	2.14 ± 0.05	CO_3^{2-}	2.41 ± 0.06	2.40 ± 0.02
$H_2PO_4^-$	2.05 ± 0.05	2.00 ± 0.04	$H_2PO_4^-$	2.37 ± 0.03	2.35 ± 0.04
Sal	1.84 ± 0.04	1.85 ± 0.03	Sal^-	2.24 ± 0.04	2.25 ± 0.03
$Cr_2O_7^{2}$	1.77 ± 0.03	1.76 ± 0.03	$Cr_2O_7^{2-}$	2.15 ± 0.06	2.12 ± 0.05

Table 5.10 Composition and response characteristics of Perchlorate ion-selective polymeric membrane electrode based on VIII(a)

S.No.	Composition of membrane (w/w; mg)								Working concentration range (mol L^{-1})	Slope (mV decade^{-1} of activity)	Detection limit (mol L^{-1})
	VIII(a) (mg)	HTAB	DBP	TBP	*o*-NPOE	DOP	BA	PVC			
1	6	-	-	-	-	-	-	94	7.5×10^{-5} to 1.0×10^{-2}	52.1 ± 0.5	5.0×10^{-5}
2	6	-	55	-	-	-	-	39	1.1×10^{-5} to 1.0×10^{-2}	50.5 ± 0.2	8.0×10^{-6}
3	6	-	-	55	-	-	-	39	2.8×10^{-6} to 1.0×10^{-2}	54.6 ± 0.2	1.3×10^{-6}
4	6	-	-	-	55	-	-	39	7.9×10^{-6} to 1.0×10^{-2}	67.3 ± 0.6	3.8×10^{-6}
5	6	-	-	-	-	55	-	39	2.5×10^{-5} to 1.0×10^{-2}	64.2 ± 0.4	1.1×10^{-5}
6	6	-	-	-	-	-	55	39	9.3×10^{-6} to 1.0×10^{-2}	51.7 ± 0.5	7.5×10^{-6}
7	6	2	-	55	-	-	-	37	7.9×10^{-7} to 1.0×10^{-2}	55.1 ± 0.3	6.3×10^{-7}
8	6	1	-	55	-	-	-	38	1.0×10^{-6} to 1.0×10^{-2}	57.3 ± 0.5	8.2×10^{-7}
9	7	1	-	55	-	-	-	37	8.4×10^{-6} to 1.0×10^{-2}	65.3 ± 0.3	6.9×10^{-6}
10	5	1	-	55	-	-	-	39	3.5×10^{-6} to 1.0×10^{-2}	51.3 ± 0.2	1.2×10^{-6}

Table 5.11 Composition and response characterisitics of perchlorate ion-selective polymeric membrane electrode based on VIII(b)

S.No.	Composition of membrane (w/w; mg)								Working concentration range (mol L^{-1})	Slope (mV decade^{-1} of activity)	Detection limit (mol L^{-1})
	VIII(b) (mg)	HTAB	DBP	TBP	*o*-NPOE	DOP	BA	PVC			
11	7	-	-	-	-	-	-	93	5.4×10^{-5} to 1.0×10^{-2}	54.2 ± 0.4	2.8×10^{-5}
12	7	-	59	-	-	-	-	34	1.2×10^{-5} to 1.0×10^{-2}	52.7 ± 0.3	3.8×10^{-6}
13	7	-	-	59	-	-	-	34	3.4×10^{-6} to 1.0×10^{-2}	51.4 ± 0.2	1.1×10^{-6}
14	7	-	-	-	59	-	-	34	1.3×10^{-6} to 1.0×10^{-2}	66.7 ± 0.4	7.4×10^{-7}
15	7	-	-	-	-	59	-	34	1.1×10^{-5} to 1.0×10^{-2}	63.3 ± 0.2	6.5×10^{-6}
16	7	-	-	-	-	-	59	34	9.7×10^{-7} to 1.0×10^{-2}	56.7 ± 0.2	7.3×10^{-7}
17	7	1	-	-	-	-	59	33	9.1×10^{-7} to 1.0×10^{-2}	57.2 ± 0.3	6.5×10^{-7}
18	7	2	-	-	-	-	59	32	8.3×10^{-7} to 1.0×10^{-2}	58.7 ± 0.3	5.4×10^{-7}
19	7	3	-	-	-	-	59	31	9.8×10^{-7} to 1.0×10^{-2}	62.7 ± 0.4	8.2×10^{-7}
20	6	2	-	-	-	-	59	33	8.7×10^{-6} to 1.0×10^{-2}	63.9 ± 0.2	1.3×10^{-7}
21	8	2	-	-	-	-	59	34	4.3×10^{-6} to 1.0×10^{-2}	53.4 ± 0.2	1.9×10^{-6}

Table 5.12 Response characteristics of the perchlorate ion-selective electrodes based on PME and CGE

Properties	**Values / range**	
	PME	**CGE**
Optimized membrane composition	VIII(b) (7 mg): PVC (32 mg): BA (59 mg) : HTAB (2 mg)	VIII(b) (7 mg): PVC (32 mg): BA (59 mg) : HTAB (2 mg)
Conditioning time	2 days in 0.01 mol L^{-1} $KClO_4$	1 day in 0.01 mol L^{-1} $KClO_4$
Working concentration range (mol L^{-1})	8.3×10^{-7} to 1.0×10^{-2}	1.0×10^{-7} to 1.0×10^{-2}
Detection limit (mol L^{-1})	5.4×10^{-7}	8.4×10^{-8}
Slope (mV $decade^{-1}$ of activity)	58.7 ± 0.3	59.3 ± 0.2
Response time (s)	12	9
Life span	30 days	65 days
pH range	3.0-8.0	2.5-9.0

Table 5.13 Effect of partially non-aqueous medium on the working of perchlorate ion selective sensor by proposed CGE.

Non-aqueous content (%; v/v)	Working concentration range (mol L^{-1})	Slope (mV $decade^{-1}$ of activity)
0	1.0×10^{-7} to 1.0×10^{-2}	59.3 ± 0.2
Methanol		
10	1.1×10^{-7} to 1.0×10^{-2}	59.1 ± 0.3
20	2.2×10^{-7} to 1.0×10^{-2}	58.8 ± 0.3
25	4.9×10^{-7} to 1.0×10^{-2}	58.6 ± 0.5
30	5.9×10^{-6} to 1.0×10^{-2}	49.9 ± 0.4
Ethanol		
10	1.3×10^{-7} to 1.0×10^{-2}	59.2 ± 0.3
20	2.5×10^{-7} to 1.0×10^{-2}	59.0 ± 0.4
25	6.0×10^{-7} to 1.0×10^{-2}	58.6 ± 0.5
30	6.7×10^{-6} to 1.0×10^{-2}	45.3 ± 0.6
Acetonitrile		
10	1.8×10^{-7} to 1.0×10^{-2}	58.9 ± 0.5
15	7.2×10^{-7} to 1.0×10^{-2}	58.3 ± 0.5
20	9.5×10^{-6} to 1.0×10^{-2}	40.7 ± 0.7

Table 5.14 Selectivity coefficient of various interfering anions for perchlorate selective electrodes determined by CGE

Interfering anions	Selectivity coefficient ($K_{A,B}^{FIM}$)	Interfering anions	Selectivity coefficient ($K_{A,B}^{FIM}$)
SCN^-	3.63×10^{-2}	IO_3^-	3.16×10^{-3}
I^-	4.78×10^{-2}	NO_2^-	3.80×10^{-3}
Br^-	5.88×10^{-2}	HPO_4^{2-}	4.26×10^{-3}
NO_3^-	6.43×10^{-2}	CH_3COO^-	5.75×10^{-3}
SO_4^{2-}	7.76×10^{-2}	CO_3^{2-}	6.60×10^{-3}
Cl^-	8.12×10^{-2}	$H_2PO_4^-$	7.24×10^{-3}
CN^-	8.91×10^{-2}	Sal^-	7.94×10^{-3}
F^-	9.77×10^{-2}	$Cr_2O_7^{2-}$	8.51×10^{-3}
MnO_4^-	2.75×10^{-3}		

Table 5.15 Determination of perchlorate ions in water and human urine samples by the proposed CGE

Samples	Perchlorate (μg ml^{-1})		
	Added	Found	Recovery (%)
Tap water	5	4.82 ± 0.05	96.4
	10	9.76 ± 0.07	97.6
	100	98.20 ± 0.05	98.2
River water	5	4.96 ± 0.04	99.2
	10	9.85 ± 0.08	98.5
	100	98.36 ± 0.06	98.4
Human Urine	5	4.79 ± 0.05	95.8
	10	9.68 ± 0.09	96.8
	100	97.94 ± 0.11	97.9

Table 5.16 Determination of perchlorate ion in the presence of other anions (1000 μg mL^{-1})

Samples	Perchlorate (μg mL^{-1})		Error (%)
	Added	Found	
SCN^-	1000	1056	5.6
Br^-	1000	1048	4.8
SO_4^{2-}	1000	1040	4.0
Cl^-	1000	1033	3.3
CN^-	1000	1029	2.9
F^-	1000	1020	2.0
IO_3^-	1000	1014	1.4
NO_2^-	1000	1010	1.0
CO_3^{2-}	1000	1005	0.5
Sal^-	1000	1003	0.3

REFERENCES

1. Bakker, E., Buhlmann, P. and Pretsch, E., "Polymer membrane ion-selective electrodes-What are the limits", *Electroanalysis*, **11**, 915 (1999).
2. DeMeulenaere, R.L., Onsrud, P. and Arnold, M.A., "Selectivity for phosphate and citrate with benzyltin-based polymer membrane electrodes", *Electroanalysis*, **5**, 833 (1993).
3. Hofmeister, F., "Zur Lehre von der Wirkung der Salze II, Arch", *Exp. Patol. Pharmakol.*, **24** 247 (1888).
4. Chen, P., Shen, J., Barbe, J. -M., Guilard, R., Gros, C.P. and Kadish, K.M., "Electrochemistry, spectroelectrochemistry and ligand binding properties of cobalt porphyrin-corrole dyads", *Abstracts, 62nd Southwest Regional Meeting of the Am. Chem. Soc.*, **19**, 594 (2006).
5. Baumgartner, M.R., Schmalle, H. and Dubler, E., "The interaction of transition metals with the coenzyme lipophlic acid: synthesis, structure and characterization of copper and zinc complexes", *Inorg. Chim. Acta,* **252**, 319 (1996).
6. Weuffen W, Franzke C and Turkow B "The alimentary ingestion, analysis and biological significance of thiocyanate", *Nahrung*, **28**, 341 (1984).
7. Bliss R.E. and O'Connell K.A., "Problems with thiocyanate as an index of smoking status: a critical review with suggestions for improving the usefulness of biochemical measures in smoking cessation research", *Health Psychol.*, **3**, 563 (1984).
8. Maliszewski, P.M. and Bass, H.E., "Thiocyanate in body fluids of smokers and nonsmokers", *J. Appl. Physiol.*, **8**, 289 (1955).
9. Bandtsen, A.B. and Hansen, E.H., "Spectrophotometric flow injection determination of trace amounts of thiocyanate based on reaction with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol and dichromate: assay of the thiocyanate level in saliva from smokers and non-smokers", *Analyst*, **161**, 647 (1991).
10. Bjorck, L., Claesson, O, Schulthess, W., "The lactoperoxidase-thiocyanate-hydrogen peroxide system as temporary preservative for raw milk in developing countries", *Milchwissenschaft*, **34**, 726 (1979).

11. Li, Q., Wei, W. and Liu, Q., "Indirect determination of thiocyanate with ammonium sulfate and ethanol by extraction flotation of copper", *Analyst*, **125**, 1885 (2000).
12. Buhlmann, P., Yahya, L. and Endress, R., "Ion-selective electrodes for thiocyanate based on the dinuclear zinc(II) complex of a Bis-N,O-bidentate Schiff base", *Electroanalysis*, **16**, 973 (2004).
13. Chandra, S., Rawat, A. and Sarkar, A., "Thiocyanate-Selective PVC Membrane Electrode Based on Copper and Nickel Complexes of Para-tolualdehydesemicarbazone as Carrier", *Analytical letters*, **41**, 3058 (2008).
14. Wu, X., Chai, Y.Q., Yuan, R., Ye, G.R. and Zhou, W., "Highly Selective Thiocyanate Electrode Based on Bis-bebzion Schiff Base Binuclear Copper(II) Complex as Neutral Carrier", *Analytical letters*, **41**, 890 (2008).
15. Dong, Y.Y., Li, C.Y., Zhang, X.B., Yu, R.Q. and Shen, G.L., "A Novel Potentiometric Sensor for Thiocyanate Based on an Amide-Linked Manganese Diporphyrin Xanthene", *Electroanalysis*, **20**, 1769 (2008).
16. Shokrollahi, A., Ghaedi, M., Ghaedi, H. and Kianfar, A.H., "Thiocyanate-selective membrane electrode based on cobalt(III) Schiff base as a charge carrier", *Intern. J. Environ. Anal. Chem*, **88**, 841 (2008).
17. Wang, F.C., Chai, Y.Q. and Yuan, R., "Thiocyanate-Selective Electrode Based on N-salicylidene-benzylamineato Copper(II) Complex", Russian J. of *Electrochemistry*, **44**, 272 (2008).
18. Hassan, S.S.M., Badr, I.H.A., Kamel, A.H. and Mohamed, M.S., A novel poly(vinylchloride) matrix membrane sensor for Batch and flow injection determinations of thiocyanate, cyanide and some metal ions", *Analytical Sciences*, **25**, 911 (2009).
19. Xu, W.J., Zhang, Y., Chai, Y.Q. and Yuan, R., "Preparation and characterization of thiocyanate-selective electrodes based on new complexes of copper(II) as neutral carriers", *Desalination*, **249**, 139 (2009).
20. Liu, H.A., Xu, G., Ren, L.Y. and Dong, W.L., "Research and application of thiocyanate-selective polyviny chloride membrane electrode based on copper(II) complex with 2-amino-thiourea-bis(salicylaldehyde) base as carrier", *Fenxi Huaxue*, **38**, 1801 (2010).

21. Sun, Z.Y., Fenf, L.J. and Xiang, C.H., "Preparation of a highly selective thiocyanate electrode with N,N'-bis(5-bromosalicylidene)-2,6-pyridinediamine copper (II) complex as the carrier", *Xinan Daxue Xuebao*, **32**, 68 (2010).
22. Amini, M.K., Shahrokhian, S. and Tangestaninejad, S., "Thiocyanate-selective electrodes based on nickel and iron phthalocyanines", *Anal. Chim. Acta*, **402**, 137 (1999).
23. Poursberi, T., Salavati-Niasari, M., Khodabakhsh, S., Hajiagha-Babei, L., Shamsipur, M., Yousefi, M., Rouhani, S. and Ganjali, M.R., "A selective membrane electrode for thiocyanate ion based on a copper-1,8-dimethyl-1,3,6,8,10,13-azacyclotetradecane complex as ionophore", *Anal. Lett.*, **34**, 2621 (2001).
24. Hassan, S.S.M., Abou, G.M.H., Amr, A.E. and Mohamed, A.H.K., "Novel thiocyanate-selective membrane sensors based on di-, tetra-, and hexa-imidepyridine ionophores", *Anal. Chim. Acta*, **482**, 9 (2003).
25. Erden, S., Demirel, A., Memon, S., Yilmaz, M., Canel, E. and Kilic, E., "Using of hydrogen ion-selective poly(vinyl chloride) membrane electrode based on calix[4]arene as thiocyanate ion-selective electrode", *Sens. Actuat. B*, **113**, 290 (2006).
26. Ardakani, M.M., Sadeghi, A. and Salavati-Niasari, M., "Highly selective thiocyanate membrane electrode based on butane-2,3-dione bis(salicylhydrazonato)zinc(II) complex", *Talanta*, **66**, 837 (2005).
27. Xu, W.J., Chai, Y.Q., Yuan, R. and Liu, S.L., "A novel thiocyanate-selective electrode based on a zinc-phthalocyanine complex", *Anal. Bioanal. Chem.*, **385**, 926 (2006).
28. Segui, M.J., Lizondo-Sabater, J., Martinez-Manez, R., Sancen´on, F. and Soto, J., "Linear polyamines as carriers in thiocyanate-selective membrane electrodes", *Talanta*, **68**, 1182 (2006).
29. Ganjali, M.R., Yousefi, M., Javanbakht, M., Poursaberi, T., Niasari, M.S., Babaei, L. H., Latifi, E. and Shamsipur, M., "Determination of SCN^- in urine and saliva of smokers and non-smokers by SCN^--selective polymeric membrane containing a nickel(II)-azamacrocycle complex coated on a graphite electrode", *Anal. Sci.*, **18**, 887 (2002).

30. Amini, M.K., Rafi, A., Ghaedi, M., Habibi, M.H. and Zohory, M.M., "Bis(2-mercaptobenzoxazolato)mercury(II) and bis(2-pyridinethiolato)mercury(II) complexes as carriers for thiocyanate selective electrodes", *Microchem. J.*, **75**, 143 (2003).

31. Shamsipur, M., Ershad, S., Samadi, N., Rezvani, A.R. and Haddadzadeh, H., "The first use of a Rh(III) complex as a novel ionophore for thiocyanate-selective polymeric membrane electrodes", *Talanta*, **65**, 991 (2005).

32. Khorasani, J.H., Amini, M.K., Motaghi, H., Tangestaninejad, S. and Moghadam, M., "Manganese porphyrin derivatives as ionophores for thiocyanate-selective electrodes: the influence of porphyrin substituents and additives on the response properties", *Sens. Actuators B: Chem.*, **87**, 448 (2002).

33. Chai, Y.Q., Dai, J.Y., Yuan, R., Zhong, X., Liu, Y. and Tang, D.P., "Highly thiocyanate-selective membrane electrodes based on the N,N'-bis-(benzaldehyde)-glycine copper(II) complex as a neutral carrier", *Desalination*, **180**, 207 (2005).

34. Arvand, M., Zanjanchi, M.A. and Heydari, L., "Novel thiocyanate-selective membrane sensor based on crown ether-cetyltrimethyl ammonium thiocyanate ion-pair as a suitable ionophore", *Sens. Actuators B: Chem.*, **122**, 301 (2007).

35. Zamani, H.A., Malekzadegan, F. and Ganjali, M.R., "Highly selective and sensitive thiocyanate membrane electrode based on nickel(II)-1,4,8,11,15,18,22,25-octabutoxyphthalocyanine", Analytica Chimica Acta, 555, 336 (2006).

36. Luo, E.P., Chai, Y.Q. and Yuan, R., "Unsymmetrical Tetradentate Schiff Bases Copper (II) Complex as Neutral Carrier for Thiocyanate-Selective Electrode", *Analytical letters*, **40**, 369 (2007).

37. Ardakani, M.M., Jamshipour, M., Naeimi, H. And Moradi, L., "Thiocyanate Ion-selective PVC Membrane Electrode Based on *N,N'*-Ethylene-bis(4-methylsalicylidineiminato)nickel(II)", *Analytical Sciences*, **22**, 1221 (2006).

38. Valdes, M. and Garcia, M.D., "Determination of Thiocyanate within Physiological Fluids and Environmental Samples: Current Practice and Future Trends", *Critical Reviews in Analytical Chemistry*, **34**, 23 (2004).

39. Yuan, J.D.R., Chai, Y., An, L., Zhong, X., Liu, Y. and Tang, D., "Highly Thiocyanate-Selective PVC Membrane Electrode Based on Lipophilic Ferrocene

Derivative", *Electroanalysis*, **17**, 1865 (2005).

40. Xu, L., Yuan, R., Chai, Y.Q. and Fu, Y.Z., "Novel Membrane Potentiometric Thiocyanate Sensor Based on Tribenzyltin(IV) Dithiocarbamate", *Electroanalysis*, **17**, 1003 (2005).
41. Ardakani, M.M., Salavati-Niasari, M. and Sadeghi, A., "Novel selective thiocyanate PVC membrane electrode based on new Schiff base complex of 2.2-[(1,3-dimethyl-1,3-propanediylidene)dinitrilo]bis-benzenethiolato cadmium(II)", *New J. Chem.*, **28**, 595 (2004).
42. Singh, A.K., Singh, U.P., Mehtab, S. and Aggarwal, V., "Thiocyanate selective sensor based on tripodal zinc complex for direct determination of thiocyanate in biological samples", *Sensors and Actuators B*, **125**, 453 (2007).
43. Vlascici, D., Cosma, E.F. and Spiridon, O.B., "A New Composition for Co(II)-porphyrin-based Membranes used in Thiocyanate-selective Electrodes", *Sensors*, **6**, 892 (2006).
44. Canas, J.E., Cheng, Q.Q., Tian, K. and Anderson, T.A., "Optimization of operating conditions for the determination of perchlorate in biological samples using preconcentration/preelution ion chromatography", *J. Chromatogr. A*, **20**, 102 (2006).
45. Perciasepe, R., "Announcement of the drinking water contaminant candidate list; notice", *Fed. Regist., Part III. U.S. Environmental Protection Agency*, **63**, 10273 (1998).
46. Browner, C., "Revisions to unregulated contaminant monitoring regulation for public water systems; final rule", *Fed. Regist., Part II. U. S. Environmental Protection Agency. 40 CFR parts 9, 141 and 142*, **42**, 11372 (2000).
47. Urbansky, E.T., "Perchlorate Chemistry: Implications for Analysis and Remediation", *Biochem. J.*, **2**, 81 (1998).
48. Urbansky, E.T. and Schock, M.R., "Issues in managing the risks associated with perchlorate in drinking water", *J. Environ. Manage.*, **56**, 79 (1999).
49. Magnuson, M.L., Urbansky, E.T. and Kelty, C.A., "Determination of perchlorate at trace levels in drinking water by ion- pair extraction with electrospray ionization mass spectrometry", *Anal. Chem.*, **72**, 25 (2000).
50. U.S. Environmental Protection Agency: Federal Facilities Restoration and Reuse: Perchlorate, http://www.epa.gov/fedfac/documents/perchlorate.htm.

51. Logan, B.E., "A review of chlorate- and perchlorate-respiring microorganisms", *Bioremediation. J.*, 2, 69 (1998).
52. Batjoens, P., De Brabander, H.F. and T'Kindt, L., "Ion chromatographic determination of perchlorate in cattle urine", *Anal. Chim. Acta*, **275**, 335 (1993).
53. Rezaei, B., Meghdadi, S. and Nafisi, V., "Fast response and selective perchlorate polymeric membrane electrode based on bis(dibenzoylmethanato) nickel(II) complex as a neutral carrier", *Sens. Actuators B*, **121**, 600 (2007).
54. Rezaei, B., Meghdadi, S. and Bagherpour, S., "Perchlorate-selective polymeric membrane electrode based on bis(dibenzoyl methanato)cobalt(II) complex as a neutral carrier", *Journal of Hazardous Materials*, **161**, (2009) 641.
55. Soleymanpour, A., Hamidiasl, E. and Nabavizadeh, S.M., "Perchlorate selective membrane electrodes based on synthesized platinum(II) complexes for low-level concentration measurements", *Sensors and Actuators B*, **120**, 447 (2007).
56. Soleymanpour, A., Garaili, B. and Nabarizadeh, S.M., "Perchlorate selective membrane electrodes based on a platinum complex", *Monatsh Chem*, **139** 1439 (2008).
57. Mahajan R.K., Nandni, D. and Puri, R.K., "Novel perchlorate selective electrode based on neutral surfactant ion-pair complex of dodecyltrimethylammonium-perchlorate", *Analytical letters*, **43**, 2114 (2010).
58. Zarei, G. and Zonouzi, F., "Complex of Co(III) as receptor molecule for development of a new perchlorate-selective polymeric membrane electrode", *Asian Journal of Chemistry*, **21**, 6819 (2009).
59. Shokrollahi, A., Ghaedi, M., Rajabi, H.R. and Kianfar, A.H., "Highly Selective Perchlorate Membrane Electrode Based on Cobalt(III) Schiff Base as a Neutral Carrier", *Chinese J. Chemistry*, **27**, 258 (2009).
60. Canel, E., Erden, S., Demirel, A., Memon, S., Yilmaz, M., Canel, E. and Kilic, E., "A hydrogen ion-selective poly(vinyl chloride) membrane electrode based on calix[4]arene as a perchlorate ion-selective electrode", *Turkish J. Chemistry*, **32**, 323 (2008).
61. B'uhlmann, P., Pretsch, E. and Bakker, E., "Carrier-Based Ion-Selective Electrodes and Bulk Optodes. 2. Ionophores for Potentiometric and Optical sensors", *Chem. Rev.*, **98**, 1593 (1998).

62. Erich, D., Schaller, U. and Meyerhoff, M.E., "Response characteristics of anion-selective polymer membrane electrodes based on gallium(III), indium(III) and thallium(III) porphyrins", *Anal. Sci.*, **14**, 79 (1998).

63. Coetzee, C.J. and Freiser, H., Liquid–liquid membrane electrodes based on brilliant green perchlorate", *Anal. Chem.*, **40**, 1128 (1969).

64. B"ack, S., "Selectivity studies on anion-selective membrane electrodes", *Anal. Chem.*, **44**, 1696 (1972).

65. Segui, M.J., Sabater, J.L.,. Manez, R.M., Sancenon, F. and Soto, J., "A perchlorate-selective membrane electrode based on a Cu(II) complex of the ligand 1,4,8,11-tetra(n-octyl)-1,4,8,11-tetraazacyclotetradecane", *Analyst*, **127**, 387 (2002).

66. Ganjali, M.R., Yousefi, M., Poursaberi, T., Naji, L., Salavati-Niasari, M. and Shamsipur, M., "Highly selective and sensitive perchlorate sensors based on some recently synthesized Ni(II)-hexaazacyclotetradecane complexes", *Electroanalysis*, **15**, 1476 (2003).

67. Zanjanchi, M.A., Arvand, M., Akbari, M., Tabatabaeian, K. and Zaraei, G., "Perchlorate-selective polymeric membrane electrode based on a cobaloxime as a suitable carrier", *Sens. Actuators B*, **113**, 304 (2006).

68. Ardakani, M.M., Jalayer, M., Naeimi, H. and Zare, H.R., "Perchlorate-selective membrane electrode based on a new complex of uranil", *Anal. Bioanal. Chem.*, **381**, 1186 (2005).

69. Sabater, J.L., Segui, M.J., Lloris, J.M., Manez, R.M., Pardo T., Sancenon, F. and Soto, J., "New membrane perchlorate-selective electrodes containing polyazacycloalkanes as carriers", *Sens. Actuators B*, **101**, 20 (2004).

70. Ganjali, M.R., Norouzi, P., Faridbod, F., Yousefi, M., Naji, L. and Niasari, M.S., "Perchlorate–selective membrane sensors based on two nickelhexaazamacrocycle complexes", *Sens Actuators B*, **120**, 494 (2007).

71. Ilhan S., Temel H., Ziyadanogullari R. and Sekerci M., "Synthesis and spectral characterization of macrocyclic Schiff base by reaction of 2,6-diaminopyridine and 1,4- *bis* (2-carboxyaldehydephenoxy)butane and its Cu^{II}, Ni^{II}, Pb^{II}, Co^{III} and La^{III} complexes", Transition Met. Chem., **32**, 584 (2007).

72. Gao, D., Gu, J., Yu, R.Q. and Zheng, G.D., "Nitrite-sensitive liquid membrane electrodes based on metalloporphyrin derivatives", *Analyst*, **12**, 499 (1995)

73. Malinowska, E. and Meyerhoff, M.E., "Role of axial ligation on potentiometric response of Co(III) tetraphenylporphyrin-doped polymeric membrane to nitrite ions", *Anal. Chim. Acta*, **300**, 33, (1995).

74. Arvand-Barmchi, M., Mousavi, M.F., Zanjanchi, M.A. and Shamsipour, M., "A new dodecylsulfate -selective supported liquid membrane electrode based on its N-cetylpydinium ion-pair", *Microchem. J.*, **74**, 149 (2003).

75. Kim, J.H., Kim, Y.G., Lee, K.H., Kang, S.W. and Koh, K.N., "Size selective molecular recognition of calix[4]arenes in Langmuir-Blodgett monolayers", *Synth. Met.*, **117**, 145 (2001).

76. Ammanmm, D., Pretsch, E., Simon, W., Lindler, E., Bezegh, A. and Pungor, E., "Lipophilic salts as membrane additives and their influence on the properties of macro- and microelectrodes based on neutral carriers", *Anal. Chim. Acta*, **171**, 119 (1985).

77. Ankere, P., Wieland, E., Ammann, D., Dohner, R.E., Asper, R. and Simon, W., "Neutral carrier based ion-selective electrode for the determination of total calcium in blood serum", *Anal. Chem.*, **53**, 1970 (1981).

78. Daunert, S., Wallace, S., Florido, A., Bachas, L.G., "Anion-selective electrodes based on electropolymerized porphyrin films", *Anal. Chem.*, **63**, 1676 (1991).

79. Kawakami, J.M., Aoto, H., Takeda, N., Fujimori, K. and Shibutani, Y., "Anion Selectivities of Dibutyltin Dihalides as Neutral Carriers for Ion-Selective Electrodes", *Anal. Sci.*, **16**, 303 (2000).

80. Schaller, U., Bakker, E., Spichiger, U.E. and Pretsch, E., "Ionic additives for ion-selective electrodes based on electrically charged carriers", *Anal. Chem.*, **66**, 391 (1994).