SYNTHESIS AND ELECTROANALYTICAL STUDIES OF SOME CHELATING IONOPHORES

A THESIS

Submitted in partial fulfilment of the
requirements for the award of the degree
of
DOCTOR OF PHILOSOPHY
in
CHEMISTRY

by

JITENDRA

DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY ROORKEE
ROORKEE-247 667 (INDIA)
JULY, 2011

INDIAN INSTITUTE OF TECHNOLOGY ROORKEE
ROORKEE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled, **"SYNTHESIS AND ELECTROANALYTICAL STUDIES OF SOME CHELATING IONOPHORES"** 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, 2006 to July, 2011 under the supervision of Dr. A. K. Singh, Professor and Dr. A. K. Jain, Emeritus 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/University.

Jitendra
(JITENDRA)

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

18/7/2011
(Ajay K. Jain)
Supervisor

(Ashok K. Singh)
Supervisor

Date: 18.07.2011

The Ph.D. Viva-Voice examination of **Mr. Jitendra,** Research Scholar, has been held on Oct.13., 2011

Signature of Supervisors

Signature of External Examiner

ABSTRACT

Rapid industrialization and urbanization has no doubt improved the quality of life. However its adverse effects are severe pollution of air, water and soil due to mobilization of several harmful metals and organic pollutants into the environment. Environmental pollution by toxic metals is well recognized and their toxicity leads to the accumulation of toxins in our tissues and organs. Presence of metals trace concentration in animal life is useful but at higher concentration toxic effects appears and life is subjected to many nutritional deficiencies, neurological disorders and can even lead to autoimmune disorders, cancer and other debilitating chronic diseases. It is normally difficult for anyone to avoid exposure to harmful metals as they are widely prevalent in environment due to their presence in almost all products of modern consumerism *viz.* construction materials, cosmetics, medicines, processed foods, variety of fuel and various agricultural products. In view of toxicity of these metals and their understood occurrence in the environment, it is important to monitor these pollutants. A number of analytical techniques such as Atomic Absorption Spectrometry, Inductive Coupled Plasma-Mass Spectrometry, Ion Chromatography, Flame Photometry, Cyclic voltametry, isotopic dilution, radiometric activation analysis are available for quantitative analysis of metals present in the environmental samples. These techniques provide accurate results but their maintenance and operational cost is high and requires adequate expertise and large scale infrastructure back up. Thus, the analysis is generally limited to laboratory level only. A reliable, low cost, quick and portable analytical technique is often required especially for the analysis of large number of samples and such requirements are often met with ion selective electrodes (ISEs) to a significant extent. The technique is generally non-destructive, adaptable to small sample volume with possible applications in real-time

analysis. Moreover, analysis of coloured and viscous samples can also be carried out easily. Further the technique involves a number of advantages such as simple set up, low cost and very convenient to use for online measurement. Due to these advantages the determination of concentration of a particular ion using an ISE has taken a leading place among all electrochemical methods of analysis. ISEs find application in a variety of fields like clinical, environmental, industrial, agricultural and process monitoring, as well as detectors in HPLC and capillary electrophoresis. As a result, a number of good ion sensors have been developed and marketed which are now convenient tools for analysis. These ion sensors have been used for the quantification of metals in food products, biological fluids, soil, effluents and wastewater.

Membrane ion selective electrodes consist of a semi-permeable membrane that separates two solutions of different concentrations of an appropriate electrolyte and responds selectively to particular ion, even in the presence of other ions. The membrane constituent is normally an active ion-exchanger ingredient generally called an ionophore or electroactive material. In spite of great utility of ion sensors in analysis, it has not been possible to prepare them for many ions of importance, mainly due to the non availability of good ionophores. It is obvious that the development of good ion sensors requires an ionophore which has high affinity for a particular cation/anion and poor for others but such materials are not available in abundance. Due to importance of ion sensors various types of materials such as solid electrolytes, inorganic and organic ion exchangers, insoluble salts of multivalent metals, metal chelates, macrocycles, calixarenes, Schiff base, hydrogen bonding receptors, other neutral carriers have been used as ionophores for the development of ion selective electrodes. In recent past, intensive studies on the design and synthesis of highly selective and sensitive ion-carriers as sensory molecules and their applications as ion-selective electrodes for the routine assessments of various ions have been reported. However, many of these electrodes have not been very successful as they exhibit a significant interference to other ions, poor sensitivity and selectivity, high response time and function over a limited pH range. Therefore, it is desirable to further explore different materials for the preparation of membranes which may act as selective sensor for target ions.

The development of potentiometric membrane-based ion sensor with analytically useful selectivity remains a formidable challenge. Work for developing new ISEs of high selectivity is always a useful goal. We have, therefore, explored some newly synthesized and previously reported compounds as ionophores and used their membranes as ISEs for some metals. For the sake of convenience, simplicity and clarity, the work embodied in the thesis has been organized as following six chapters.

First Chapter; *General Introduction*:

It presents an up-to-date review of the literature on 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.

Second Chapter; *Theory and Methodology of Ion Selective Electrodes*:

This encompasses classification of ISEs, theory of membrane electrodes, its potentials and terms used in the study of ion selective electrode. The concept of the selectivity of ion selective membranes and methods of its determination has also been discussed.

Third Chapter; *Schiff base as copper ion selective electrodes*:

It is reported that Schiff base have been widely used as chelating ligands in the coordination chemistry of transition metals and some of them show selective affinity for metals. It is, therefore, possible to use Schiff bases as selective ionophores in the preparation of membrane electrodes of better characteristics. To test this possibility in a realistic fashion, we investigated them as potential sensory component for the development of membrane ion-selective electrodes. In this chapter, the synthesis and characterization of 2-[{(2-hydroxyphenyl)imino}methyl]-phenol (L_1) and 2-[{(3-hydroxyphenyl)imino}methyl]-phenol (L_2), and their analytical application as ionophores for the fabrication of Cu^{2+} ion selective electrodes are described. Polymeric membranes electrodes (PME) of L_1 and L_2 have been prepared and investigated as Cu^{2+}-selective sensors. Poly (vinyl chloride) (PVC) was used as matrix for the sensor's design and influence of the other membrane components *i.e.* ionophore, plasticizer and the lipophilic additive that are known to have a dramatic effect on sensor's performance have also been evaluated. Effect of various plasticizers *viz.*, dibutyl phthalate (DBP), dibutyl sebacate (DBS), benzyl acetate (BA), *o*-nitrophenyloctylether (*o*-NPOE) was studied in detail and improved performance was observed in several instances by the addition of oleic acid (OA) as anion excluder. Optimum performance for the electrodes based on L_1 was observed with membrane having ingredients in composition L_1:DBS:OA:PVC ≡ 6:54:10:30 (%, w/w). This sensor worked satisfactorily in the concentration range 3.2×10^{-8} to 1.0×10^{-2} mol L^{-1} with a Nernstian slope of 29.5 mV decade^{-1} of $a_{Cu}{}^{2+}$ and having the detection limit as 2.0×10^{-8} mol L^{-1} (1.27 ng mL^{-1}). Optimization of membrane composition of the electrodes based on L_2 showed that the membrane having composition L_2:DBP:OA:PVC ≡ 6:54:10:30 (%, w/w) exhibit the Nernstian slope (29.6 ± 0.5 mVdecade^{-1} of $a_{Cu}{}^{2+}$) and showed linear potential response in the concentration range of $2.5 \times 10^{-7} - 1.9 \times 10^{-2}$ mol L^{-1} with limit of detection 1.2×10^{-7} mol L^{-1}. Wide pH range (3.0 – 8.5), fast response time (5 s), good performance in presence of small amounts of (up to 20 % v/v) non-aqueous contents and adequate shelf life (3 months) indicate the utility of the proposed sensors. The selectivity coefficients for these electrodes were determined by matched potential method (MPM) and the results indicate their selective response for Cu^{2+} ions over various interfering ion. However, it was found that the sensor based on ionophore (L_1) has good selectivity over the sensor based on ionophore (L_2). These electrodes could be successfully used for the determination of copper in edible oils, tomato plant material; river water and as an indicator electrode in potentiometric titration of copper ion with EDTA.

Fourth Chapter; *Gd^{3+} ion-selective coated graphite electrode based on N_5 donor chelating ligand*:

This chapter incorporates investigation on the use of a N_5 donor chelating ligand as ionophore in the preparation of membrane electrode selective to Gd^{3+}. Chelating ligand 2,6-Bis-[1-{N-cyanoethyl,N-(2-methylpridyl)}aminoethyl]pyridine (L_3) having five nitrogen donor sites for complexation with cations has been synthesized. Stability studies of the several metal-ligand complexes showed that L_3 has high affinity towards Gd^{3+} ion and therefore, it was used as a potential ionophore for the preparation of coated graphite Gd^{3+} ion selective electrode. Among several electrodes prepared, the one having membrane of composition L_3:NaTPB:PVC:*o*-NPOE ≡ 8:4:30:58 (%, w/w) gave best performance over the widest working concentration range of $2.8 \times 10^{-7} - 5.0 \times 10^{-2}$ mol L^{-1} showing Nernstian behaviour (19.6 ± 0.3 mV $decade^{-1}$) with lower limit of detection as 6.3×10^{-8} mol L^{-1}. Furthermore, it showed a fast response time (12 s) and can be used for 2.5 months without significant divergence in its characteristics. Further, the electrode can tolerate the concentration of different surfactants up to 1.0×10^{-4} mol L^{-1} and can be used successfully in ethanol 30 % (v/v) and methanol and acetonitrile 10 % (v/v) water mixture. The useful pH range of this electrode for the detection of Gd^{3+} in a solution is

2.0 to 8.0. The potentiometric selectivity coefficients of the electrode were evaluated by IUPAC recommended fixed interference method (FIM) and matched potential method (MPM) and it was found that the electrode is sufficiently selective for Gd^{3+} over many cations and could be used for the determination of Gd^{3+} ions in waste water and rock samples. It could also be used successfully as an indicator electrode in the potentiometric titration of $GdCl_3$ with EDTA.

Fifth chapter; *Nd^{3+}ion-selective coated graphite electrodes based on lariat ethers*:

This chapter describes the synthesis of novel lariat ethers viz 1,5–di(cyanoethane)-2,4: 7,8:13,14-tribenzo-1,5-diaza-9,12-dioxacyclopentadeca-2,7,13-triene (L_4) and 1,5-di (cyanoethane)-2,3, 4-pyridine-7,8:13,14-dibenzo-1,3, 5-triaza-9, 12-dioxa cyclopentadeca-2,7,13-triene (L_5) and their application as potential ionophores for the fabrication of Nd^{3+} selective and sensitive coated graphite electrodes. Complexation study of the two ionophores towards various metal ions in acetonitrile solutions revealed the formation of 1:1 metal-ionophore complexes. A number of PVC based coated graphite electrodes (CGEs) of L_4 with different plasticizers and lipophilic additives were prepared and explored as Nd^{3+} selective electrodes. The results showed that optimized membrane composition for the electrode based on L_4 was found to be; L_4:*o*-NPOE:NaTPB:PVC ≡ 5:57:3:35 (%, w/w). This electrode exhibited good performance over the wide working concentration range $8.4 \times 10^{-8} - 3.1 \times 10^{-2}$ mol L^{-1} with Nernstian slope (19.8 ± 0.4 mVdecade^{-1} of $a_{Nd^{3+}}$) and low detection limit (3.8×10^{-8} mol L^{-1}). However, the electrode based on L_5 having optimum membrane composition of its ingredients L_5:*o*-NPOE:NaTPB:PVC ≡ 5:53:3:39 (%, w/w) performed best over the widest working concentration range of $4.6 \times 10^{-8} - 5.0 \times 10^{-2}$ mol L^{-1} with Nernstian slope

(19.7 ± 0.5 mVdecade^{-1} of a_{Nd}^{3+}) and low detection limit (1.6 × 10^{-8} mol L^{-1}). The potentiometric response of these electrodes was excellent in the range of pH 3.5 to 7.6 and they showed fast response time of 14 s and 10 s, for L_4 and L_5 based CGEs, respectively with a shelf life of three months without significant divergence in the performance characteristics. They could also tolerate up to 20 % (v/v) methanol, ethanol and acetonitrile, if present in the test solution. The presence of cationic and anionic surfactants at 1.0 × 10^{-4} mol L^{-1} or above caused significant interference in the performance of the electrodes. Further, the values of selectivity coefficients determined by FIM indicate that the proposed electrodes are efficiently selective over a number of monovalent (Ag^+, Na^+, K^+ , Li^+), divalent (Hg^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Mg^{2+}, Ca^{2+}, Zn^{2+}, Cu^{2+}) and trivalent ions (Gd^{3+}, Pr^{3+}, Ce^{3+}, La^{3+}, Tb^{3+}, Dy^{3+} Sm^{3+} and Yb^{3+}). However, higher concentration of Co^{2+}, La^{3+}, Pr^{3+} and Yb^{3+} caused some interference. These electrodes were used successfully as indicator electrodes in the potentiometric titration of Nd^{3+} against EDTA and also direct determination of Nd^{3+} ions from binary mixtures and water samples.

Sixth chapter; *Cd^{2+} ion-selective electrodes based on N_4, N_2S_2 and N_2O_2 type chelating ligands*:

This chapter describes the synthesis, characterisation and analytical application of three chelating compounds N^1,N^2 -dicyanoethyl-N^1,N^2-bis(pyridine-2-ylmethyl)benzene-1,2-diamine [L_6], N^1,N^2-dicyanoethyl-N^1,N^2-bis(thiophen-2-ylmethyl) benzene-1, 2-diamine [L_7] and N^1,N^2-dicyanoethyl-N^1,N^2-bis(furan-2-ylmethyl)benzene-1,2-diamine [L_8]. Membranes having constituents PVC, plasticizers, lipophilic anionic additives and the ionophores were coated on the surface of spectroscopic graphite rods and their potential response investigations carried out. The electrodes having membranes of different compositions were investigated and it was found that the among all the electrodes of L_6, the one having membrane composition in the ratio L_6:*o*-NPOE:NaTPB:PVC as 4:51:2.5:42.5 (%, w/w) performed best *i.e.* worked over a wide working concentration range 2.5×10^{-7} - 1.0×10^{-1} mol L^{-1} with Nernstian slope 29.5±0.07 mV $decade^{-1}$ and low detection limit 7.8×10^{-8} mol L^{-1}. This electrode generated constant potential in the pH range 2.0 to 8.0 with a fast response time (12 s) and shelf life of 4 weeks. The CGE based on L_7 having membrane composition L_7:*o*-NPOE:NaTPB:PVC ≡ 3:52.5:1.5:43 (%, w/w) performed best i.e. widest linear working concentration range 1.7×10^{-8} - 1.0×10^{-1} mol L^{-1} with Nernstian slope 29.6±0.08 mV $decade^{-1}$ and lower detection limit as 7.0×10^{-9} mol L^{-1}. The useful pH range of this electrode was observed to be 2.6 to 8.0. This electrode showed a fast response time of 7 s towards Cd^{2+} ion and the potentiometric characteristics of the electrode do not change significantly over a period of 6 weeks. A similar optimization of membrane composition of the electrodes based on L_8 showed that the electrode with composition L_8:*o*-NPOE:NaTPB:PVC ≡ 7:49:3.5:40.5 (%, w/w) showed best performance in terms of wide working concentration range (4.6×10^{-7} - 5.0×10^{-2} mol L^{-1}), Nernstian slope (29.8± 0.05 mV $decade^{-1}$) and low detection limit (8.4×10^{-8} mol L^{-1}). The response of the electrode is fast (17 s) and can work satisfactorily in the pH range 3.0 to 7.5 with a shelf life of 4 weeks. Selectivity coefficients of the electrodes were evaluated by FIM and the results showed that these electrodes have high selectivity towards Cd^{2+} over a large number of cations and could tolerate upto 20 % (v/v) non-aqueous impurity. In view of high sensitivity and selectivity, the utility of these electrodes was tested in the potentiometric determination of Cd^{2+} in medicinal plants, soil and industrial waste water. They could also be used successfully as an indicator electrode in the potentiometric titration of Cd^{2+} against EDTA.

Thus, the present investigations on the membranes of Schiff's bases, chelating ligands and lariat ethers have resulted in the development of selective and sensitive sensors for Cu^{2+}, Gd^{3+}, Nd^{3+} and Cd^{2+} ions. The investigated sensors of metal ions have been found to be better than reported sensors with respect to various response characteristics and resulted in the availability of some improved and novel ion sensors which can be used successfully for analytical purposes. Thus, the present work adds to our knowledge in the field of chemical sensors.

ACKNOWLEDGEMENTS

A journey is easier when you travel together. Interdependence is certainly more valuable than independence. This thesis is a result of five years of work through inspiration and perspiration, whereby I have been accompanied and supported by many people to successfully trail the path of research. It is a pleasant aspect that I now have the opportunity to express my gratitude for all of them.

I am highly indebted to **Prof. A.K. Singh** and **Prof. A.K. Jain**, my supervisors, for their excellent guidance, cooperation, motivation, invigorating discussions and encouragement. I consider myself fortunate to have had an opportunity to work under their guidance and enrich from their vast knowledge and experiences. I acknowledge with great pleasure my deep sense of gratitude to them for their constructive criticism and an inspirational impetus in designing and execution of this research problem.

I am highly grateful to Prof. V.K Gupta and Prof. Kamaluddin, the present and the former Head of the Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee for providing me with the necessary facilities and support to carry out these investigations.

I am thankful to Mr. Abdul Haq and Mr. V.P Saxena for their technical assistance in the department. Thanks are also due to the official staff in the Department, especially to Mr. O.P. Dhama, Mr. Ram Kumar, Shri Tyagi ji for all the official help. Sincere thanks to Madanpal ji, Amar Singh ji, Tilakram ji, and Ramesh ji for timely help.

I sincerely thank my ex lab seniors: Dr. Barkha Gupta and Dr. Sameena Mehtab, who always inspired me during this period. My most sincere appreciation and thanks are due to my juniors: *Mr. Koteswara Rao Bandi* and *Mr. Manoj Sahani* who played a very important role during the evolution process of my thesis. Without their support, it was difficult for me to do it at the right time. I wish to extend a word of acknowledgement to my lab mates Nivedita, Prerna and Anjali for helping me in whatever little way they could.

I express my wholehearted indebtness to my friends Dr. Vaibhave, Dr. Vinay, Dr. Pooja, Dr. Aditi, Dr. Virender, Dr. Vipin, Dr. Aftab, and Dr. Ashok for their uncompromising support and encouragement during all times of my research work. I extend my heartfelt appreciation to my friends Ramswaroop, Pramod, Raman, Ajay, Deepak, Atul, Chetan and Subhash whose encouragement, cooperation helped in the completion of this work.

I express my deep gratitude towards my **Mummy** and late **Papa** for their blessing which always acted as a guiding star for me at every stage of my work, and helped me to scale new heights. I thank my brothers *Nitin* and *Manoj*; and sister *Rashmi* for unconditional support and encouragement to pursue my interest. These pages wouldn't be sufficient to mention the enormous hard work of my parents who has made to educate me and to take care of my entire requirements. I am in dearth of proper words to express my abounding feeling to my in-laws for their unflinching support, encouragement and the love they showed on me at every stage.

Last but not least, I am greatly indebted to my devoted love *Manisha* for supporting me in every adverse situation. She forms the backbone and origin of my happiness. Her love and support without any complaint or regret enabled me to complete this Ph.D. work. She took every responsibility and suffered to take care of me and my studies. I cherish the way that she always brings a smile on my face even when the going becomes tough.

I am also thankful to the financial assistance from Council of Scientific and Industrial Research, New Delhi, in the form of Junior and Senior Research Fellowship during my research work. I would not have imagined the situation without their help and assistantship. I would like to thank almighty who instilled in me the courage, confidence and patience to fulfill my task. It is only his will that I am able to complete my research on *"Synthesis and electroanalytical studies of some chelating ionophores"*

Dated: 18/07/2011

Jitendra
(JITENDRA)

LIST OF PUBLICATIONS

1. **Jitendra Singh**, A.K. Singh, A.K. Jain and S. Mehtab, "Development of an electrochemical sensor based on Schiff base for Cu(II) determination at nano level in river water and edible materials", *International Journal of Environmental and Analytical Chemistry*, **89**, 1081–1098, 2009.
2. **Jitendra Singh**, A. K. Singh and A .K. Jain, "Novel coated graphite electrode for the selective determination of Gd(III) in rock s and waste water samples" *Electrochimica Acta*, **54**, 5640–5647, (2009).
3. **Jitendra Singh**, A. K. Singh and A. K. Jain, "Highly selective Nd(III) sensors: Novel Macrocyclic compounds for potentiometric determination of Neodymium" *Electroanalysis*, **22**, 2443–2452, (2010).
4. **Jitendra Singh**, A. K. Singh and A. K. Jain, "Fabrication of novel coated graphite electrodes for selective nanolevel determination of Cd^{2+} ions in biological and environmental samples", *Electrochemica Acta*, (Accepted)
5. **Jitendra Singh**, A.K. Singh, S. Mehtab, U.P. Singh and V. Aggarwal, "Tripodal Cadmium complex and Macrocyclic ligand based sensors for Phosphate ion determination in environmental samples", *Electroanalysis*, **20**, 1186–1193, (2008).

CONTENTS

Chapter 1 General Introduction

Chapter 2 Theory and Methodology of Ion Selective Electrodes

Chapter 3 Schiff Bases As Copper Ion-Selective Electrodes

Chapter 4 Gd^{3+} Ion-Selective Coated Graphite Electrode Based On N_5 Donor Chelating Ligand

Chapter 5 Nd^{3+}Ion-Selective Coated Graphite Electrodes Based On Lariat Ethers

Chapter 6 Cd^{2+} Ion-Selective Electrodes Based On N_4, N_2S_2 and N_2O_2 Type Chelating Ligands

Chapter 1

General Introduction

1.1 Introduction

Attempts to produce better products for comfortable life have caused serious environmental problems which have a great influence on our life-style, corporate activities, national management and international cooperation in the world. Environmental toxicology caused by industrialization is threatening the existence of human and natural habitats to a great extent. The technological development has brought a dramatic rise in emissions of anthropogenic pollutants. Moreover, today we have opened Pandora's Box by spreading toxic metals throughout our environment by fossil fuel consumption, heavy metals mining, smelting, fertilizer applications and municipal waste incineration. Heavy metals constitute an important group of pollutants causing severe toxic effects at higher concentration. Therefore, it is necessary to monitor the concentration of heavy metals in environmental and biological samples for assurance against acute intoxication. Apart from the direct threat to health or the environment, metal contamination can cause economic and financial damage indirectly.

Thus the importance of clean environment is being increasingly recognized and it has become mandatory for various agencies to monitor the environment so as to keep the level of pollution below permissible limits. As a result, environmental analysis has become an area of intense interest for scientists and the public alike. The field of environmental science has evolved, with the growing concern for the welfare of the environment requiring qualitative and quantitative knowledge on the nature, concentration and temporal changes in pollutants. These demands have led to the development of many important analytical approaches. The realization of importance of analytical methods in present day life has led to vigorous efforts by chemists and instrumentalists to develop new instruments, techniques and procedures so as to make analysis convenient, fast, reliable and selective [1-7]. Various instrumental techniques such as flame atomic absorption spectrometry (FAAS), electrothermal atomic absorption spectrometry (ETAAS), atomic fluorescence spectrometry (AFS), inductively coupled plasma-atomic Emission Spectrometry (ICP-AES), inductively coupled plasma–mass spectrometry (ICP-MS), high performance liquid chromatography (HPLC), spectrphotometry, anodic stripping voltammetry (ASV) and many more has become available for determining the concentration of metal ions in aqueous solutions [8-16]. Although, these methods provide sensitive and reproducible results, but often requirement of chemical manipulation of the sample and expensive infrastructure make these techniques redundant for routine and 'on-line' analysis of a large number of samples. Besides this, the use of these techniques can be problematic and erroneous in coloured and turbid solutions.

Thus, a reliable, low cost, quick and portable analytical technique is often required especially for the analysis of large number of samples and such requirements are met often with ion selective electrodes (ISEs) to a significant extent. Ion-selective electrodes are the electrochemical sensors of longest history and allow the assessment of free ion activities. Ion-selective electrodes (ISEs) are in many respects ideal sensors for use in the analysis of industrial and environmental samples. Much of the current knowledge collected during the past decades presents that this area of analytical chemistry is being intensively developed as they enjoy a number of advantages over other methods of analysis [17-20]. The most attractive features of this technique are insensitivity to sample color, viscosity or suspended solids, rapid response to changes in determinant concentration, and possible use in a very wide concentration range. Moreover, their fabrication in the laboratory is quite easy and so they have been widely used for the quantification of many ionic and non-ionic species present in aqueous samples. As a result of analytical requirements, a number of commercially available ISEs have been developed as convenient tools for analysis which can be directly used for metal ion determination in food products, biological fluids, effluents, wastewater, soil, fertilizers etc. [21, 22]. Therefore, utility and simplicity of ion selective electrodes has made them useful in the analysis of samples in various fields including clinical, environmental, industrial and agricultural studies.

The essential part of a carrier-based ISE is the ion sensitive solvent polymeric membrane, physically a water-immiscible liquid of high viscosity that is commonly placed between two aqueous phases, i.e., the sample and the internal electrolyte solution. An ion selective electrode selectively responds to the activity/concentration of the target ion and usually covers an extraordinarily large sensitivity range, from 0.1 M to 1 nM. The measured potential, obtained with optimized membrane electrodes, can be directly related to the free ion activity of the analyte in the sample. ISEs are characterized by the fact that the electrochemical response is usually dominated by one ionic species present in the solution, known as the primary ion (analyte ion/target ion) even in the presence of other interfering ions. The wide use of ISEs in routine analysis is accompanied by a search for more selective membrane materials and also on theoretical studies of the mechanism of functioning of these sensors [23-25]. A successful polymeric ion selective membrane needs to be generally hydrophobic, contains conventionally an ionophore (ion carrier), a lipophilic salt as ion exchanger (additive) and a membrane solvent (plasticizer). The majority of modern polymeric ISEs are based on neutral carriers, making the ionophore the key component of an ion selective membrane which is capable of reversibly binding with ions and also catalyzes ion transport across hydrophobic membranes. One of the most important features of ISEs is the selectivity towards a specific analyte. The ionophore is primarily responsible for the ion selectivity of the sensor by selectively and reversibly binding the analyte of interest. The ion-ionophore interactions based on their ion-exchange property or size-exclusion of the ionophore, determine selectivity of an ion sensor and its proper functioning towards a specific ion.

Potentiometric ISEs based on plasticized polymeric membranes that contain highly selective ionophores are widely used for the routine assessments of many important ions [26]. 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. The creation of cavities and cleft in the ionophore are complementary to the size and charge of a particular ion leading to selective interactions. The design of host molecules capable of binding selectively to an ionic guest is a challenging area and consequently has given rise to a plethora of imaginative and ingenious systems designed to tackle the problem [27].

Development of ISEs continued to be exciting and expanding areas of analytical research. Apart from the classical potentiometric response, new transduction schemes for the solvent polymeric membranes have been proposed, making the detection of new analytes possible, allowing comprehensive instrumental control over sensing characteristics and introducing new detection principles. The aim of most research associated with ISEs is to produce miniaturized, solid-state devices, with rapid, sensitive response and exquisite selectivity that can be mass produced at low cost. The application of ISEs is still flourishing with the aim of improving their performance and reaching better understanding of their response mechanism. Thorough evaluation of the response is essential to forecast the chances of success of novel ISEs, which are proposed at constant rate in the current literature.

1.2 Historical Review of Ion-selective Electrodes

The occurrence of electric potential was first noticed by Luigi Galvani in 1791 while dissecting a frog. In 1848, du Bois-Reymond proposed that living cell membranes have properties similar to an electrode of galvanic cell. However, the scientific basis to this phenomenon was given in 1890 when W. Ostwald proposed that the semi-permeability of the membrane was the main cause of potential generation [28]. The first landmark in the history of ISEs was the discovery of hydrogen ion sensing glass electrode in 1906 by Cremer. Besides glass, other materials were also investigated with passage of time to develop ISEs. Efforts in this direction were initiated by Kolthoff and Sanders [29] in 1937 who made first silver halide disk sensors. In the early 1960s, E. Pungor [30] published his work on Ag-I based heterogeneous membrane electrodes which were the basis for first commercial solid state ISEs. These electrodes exhibited good selectivity and Nernstian response and were the first truly selective electrodes (non-glass) to be developed, which gave a thermodynamically reversible response with respect to the primary ion. Many workers continued their research towards the preparation of various ISEs of heterogeneous membranes consisting of an active material supported in an inert matrix of silicone rubber [31, 32]. However, active and widespread interest in research in the field of ISEs was generated with the discovery of fluoride ISEs by Frant and co-workers [33]. The fluoride ISE they developed was based on lanthanum fluoride doped with europium fluoride and considered as the second best electrode after glass electrode.

A wide-ranging research was started after this not only in the field of precipitate based ion-selective electrodes but also on the application of complexing agents based liquid membrane electrodes [34, 35]. Bloch and co-workers introduced the first ionophore-based solvent polymeric membrane based on PVC [36], a matrix still widely used today as it provides a user friendly, robust membrane matrix and can be plasticized with polar and non-polar water immiscible solvents. The procedure for compounding, casting, drying and mounting PVC membranes was developed by Moody *et al* [37]. Finally, the birth of host-guest chemistry [38-40] played an important role to explore different materials in developing ISEs for various cations and anions.

1.3 Classification of Ion-Selective Electrodes

According to IUPAC recommendations [41], ion-selective electrodes are classified in the following categories according to the physical state of the substances forming the electrode membrane, or possibly according to the nature of the substances affecting the ion exchange in the membrane.

1.3.1 Primary electrodes
1.3.2 Sensitized or Compound (multiple layer membrane) electrodes
1.3.3 All-solid-state ion-selective electrodes

1.3.1 Primary electrodes

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

1.3.1.1 Solid membrane electrodes

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

a. *Glass electrodes*

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

b. *Homogenous solid state electrodes*

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

c. *Heterogeneous solid state electrodes*

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

1.3.1.2 Liquid membrane electrodes

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

1.3.2 Sensitized or Compound (multiple layer membrane) electrodes

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

1.3.2.1 Gas sensing electrodes

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

1.3.2.2 Enzyme substrate electrodes

These are the electrodes in which an ion-selective membrane 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 that can be sensed by the electrode. Alternatively, the electrode 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-selective glass membrane electrode.

1.3.3 All-solid-state ion-selective electrodes

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

1.4 Literature Survey

Ever since the discovery of glass electrode for pH determination, ion-selective electrodes have aroused a great deal of interest from both theoretical and practical points of view and their role in analytical chemistry has been steadily increasing. In recent years, the field of ISEs is perhaps one of the most eminent examples for interdisciplinary research in analytical chemistry. A number of books [42-51] and some significant papers [52-57] have appeared in the recent past. Progress in this field including theory, methodology, and applications of ISEs has been described in the periodic reviews [58-69]. 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 various ions, are presented here.

1.4.1 Alkali metal ion-selective electrodes

There has been appreciable interest in the development of ISEs using neutral carriers for the analysis of alkali metal ions in environmental, medical, and clinical fields. Lithium ion selective electrodes belong to the most investigated type because of its prophylactic and therapeutic action in various affective disorders. Gadzekpo and coworkers [70, 71] have reported 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. Fiedler *et al.* [72] introduced the first Li^+- selective electrodes based on *N,N′*-diheptyl-*N,N′*-5,5-tetramethyl-3,7-dioxanonanediamide. This electrode worked in the range of 1.0 M to 0.01 mM and showed high selectivity over sodium, potassium, magnesium and calcium. In 1981, Zhulov *et al.* [73] developed an important Li^+-selective sensor using neutral carrier *N,N,N′,N′*-tetra-isobutylcyolohexaneo-1,2-dicarboxamide with PVC as binder. This sensor showed working concentration range of 1.0×10^{-5} to 1.0×10^{-1} mol L^{-1} and was selective for Li^+ over other alkali and alkaline earth metal ions.

Later on, some other neutral carriers, *N,N′*-dicyclohexyl-*N′,N′*-diisobutyl-cis-cyclo hexanedicarbonylamide [74], 6,6-dibenzyl-1,4,8,11-tetraoxacyclotetradecane [75], l-phenyl-3-methyl-4-benzoyl-5-pyrazolone [76], crown ether derivatives [77, 78] and 1,10-phenanthroline derivatives [79], macrocycles [80] were also investigated as suitable ionophores to develop Li^+-selective sensors. All these sensors were of comparable performance. Gupta *et al.* [81] reported a Li^+-selective sensor based on a carbosiloxane dendrimer. The sensor showed a working concentration range of 2.5×10^{-5}–1.0×10^{-1} mol L^{-1} of Li^+ with a slope of 52.0 mV decade^{-1} of $a_{Li}{}^+$ and was used for the determination of Li^+ in blood serum.

A major interest for Na^+ analysis with ISEs comes from clinical chemistry. Most of the reported Na^+ selective sensors developed are based on neutral carriers. The sensors prepared by Wu *et al.* [82] based on triglycollic bisdiamides in PVC matrix performed well and showed good selectivity for Na^+ over other alkali and alkaline earth metals and could be used for the determination of sodium in water with high magnesium content. The sensors based on the membranes of crown ethers such as bis-[(3n+l)-crown-n]ether derivatives [83], dibenzo-16-crown-5 derivatives [84], 16-crown-5-derivatives [85], bis-(12-crown-4)methylmalonates [86], benzyloxymethyl-11-crown-3 [87] and azo- and azoxycrown compounds with sulphur atoms in long side chains [88] 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 [89], calix[4]arene derivatives [90], triestermonoacid derivative of p-tert-butylcalix[4]arene [91]. All these sensors show high selectivity for Na^+ as calix[4]arene compounds exhibit an optimum cavity size for complexation with Na^+ and have been used for Na^+ determination in biological fluids. Recently, Kimura *et al.* [92] designed several sol-gel derived membranes selective to Na^+ which encapsulate valinomycin and bis-(crownether) as well as calix[4]arene ester and amide derivatives electroactive materials, while Kim *et al.* [93] tried lipophilic trimesters of calix[4]arene and calix[4]quinine to develop Na^+ selective sensors. These membranes showed good sensitivity, selectivity and low response time.

A major interest for K^+ analysis comes from clinical chemistry because changes in K^+ concentration in human serum bring along the risk of acute cardiac arrhythmia. A number of ISEs have been developed for K^+ in view of its importance in clinical chemistry. Fiedler and Ruzika [94] developed the first successful and commercially available sensor for potassium ion by using valinomycin, an electroneutral carrier. Since then many researchers [95-98] have developed neutral carrier based ISEs for K^+. A number of K^+ selective sensors based on crown ethers viz., cis- and trans-bis-(crown ethers) [99], bis-(15-crown-5) [100], 4'-picrylamino-5'-nitrobenzo-18-crown-6 [101] and 4-acryloylamidobenzo-15-crown-5 and 4-acryloylamidobenzo-18-crown-6 [102] have been prepared. All these sensors show high selectivity for K^+ over other alkali and alkaline earth metals and have been used for determining potassium in biological fluids. Yan *et al.* [103] used calix[6]arene hexaester for the preparation of membranes and investigated its applicability to determine K^+ in human serum. Recently, Katsu *et al.* [104] 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^+. Bobacka *et al.* [105, 106] introduced solid state potassium ion selective electrodes using carbon nanotubes as ion-to-electron transducer in polymer membranes.

The development of ISEs for Rb^+ has received relatively less attention mainly because of their conspicuous absence in biological systems. However, still some sensors have been reported. Cosgrove *et al.* [107] reported a valinomycin based sensor selective for Rb^+

and used it to determine rubidium in yeast cells. Singh and co-workers [108] used epoxy resin based membranes of rubidium tungustoarsenate to develop Rb^+-selective sensor. The sensors prepared were not highly selective but could be used for its determination by potentiometric titration procedure. A solid membrane electrode for the determination of Rb^+ selectively in the concentration range 4.0×10^{-5} - 1.0×10^{-1} mol L^{-1} was reported by Shrivastava and co-workers [109]. Another Rb^+ selective sensor was developed by Saleh *et al.* [110] using indanopyrazalo[l, 5-a] pyrimidines as electroactive material which showed Nernstian response in the narrow concentration range of 1.0×10^{-4} - 1.0×10^{-1} mol L^{-1}. Yang *et al.* [111] used decylidene bis-(4-benzo-15-crown-5) ether to develop Rb^+ selective sensor. It exhibited a near Nernstian response in the concentration range of 5.0×10^{-5} - 1.0×10^{-1} mol L^{-1} with detection limit down to 20 μM. Hyun *et al.* [112] explored binaphthyl-based crown ether derivatives as ionophores in the preparation of Rb^+-selective polymeric membrane electrodes which worked in the linear concentration range 1.0×10^{-5} - 1.0×10^{-1} mol L^{-1}.

Cesium has also received much attention during the last two decades and various ionophores were reported for the development of Cs^+-selective electrodes. Wang *et al.* [113] found 15-crown-5-phosphotungustic acid precipitate selective for Cs^+. It showed Nernstian response in the concentration range of 1.0×10^{-4} - 1.0×10^{-1} mol L^{-1}. Several crown ether derivatives *viz.*, 14 and 15-crown formazans [114] and calix[4]crown ether-ester [115] showed good selectivity for Cs^+ over a number of ions. Cs^+-selective electrodes based on several calixarenes *viz.*, calix[6]arene tetraester derivatives [116], bridged bis-calix[4]arenes [117], 1,3-bis-bridged cofacial-calix[6]crowns [118], crown bridged thiacalix[4]arenes [119], have also been reported. Shamsipur *et al.* [120] reported a 16-membered macrocylic diamide as a Cs^+-selective ionophore while Ganjali and co-workers [121] used a cavitand as Cs^+- selective ionophore. Saleh *et al.* [122] developed a Cs^+-selective sensor using cephalexin antibiotic drug as ionophore and a new Cs^+-selective graphite rod electrode based on Cs-Molybdophosphate was reported by Arida *et al.* [123]. Recently, a Cs^+-selective electrode, having longest lifetime of nine months, based on 5-(4'-nitrophenylazo)25,27-bis-(2-propyloxy)26,28-dihydroxycalix[4]arene has been reported by Ramanjaneyulu and co-workers [124] while Sadeghi *et al.* [125] fabricated a Cs^+-selective polymeric membrane coated graphite electrode based on 4',4"(5') di-tert-butyl di-benzo-18-crown-6.

1.4.2 Alkaline earth metal ion-selective electrodes

Considerable efforts have been made by researchers to develop selective sensors for alkaline earth metal ions due to their occurrence in diverse samples. As such, a large number of sensors for these ions have been reported. A brief review on IESs for these metals is given in the following paragraphs.

Among alkaline earth metal ions, beryllium has received less attention 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 [126] used phosphate ester ionophores to prepare Be^{2+} selective sensors. Ganjali *et al.* employed 2,4-dinitrophenylhydrazine-benzo-9-crown-3 [127], naphtho-9-crown-3 [128], 2, 3, 5, 6, 8, 9-hexahydro-1,4,7,10-benzotetraoxa cyclododecine-12-carbaldehyde-12-(2,4-dinitrophenyl)hydrazine [129] and 4-nitrobenzo-9-crown-3-ether [130] to develop Be^{2+}- selective sensors. The sensors [130] showed Nernstian response to Be^{2+} and worked in the concentration range of 1.0×10^{-10} - 1.0×10^{-4} with a limit of detection 3.5×10^{-11} mol L^{-1} (350 pg/L). Shamsipur *et al.* [131] developed graphite coated Be^{2+}-selective sensors based on a macrocyclic diamide, 15-diaza-3,4:12,13-dibenzo-5,8,11-

trioxabicyclo [13,2,2] heptadecane-2,14-dione and compared its characteristics with polymeric membrane electrode.

The major challange in the design of Mg^{2+} ionophores lies in the discrimination of Ca^{2+}. A Mg^{2+}-selective sensor was prepared by Saleh *et al.* [132] using phenylene bis-(ditolyl phosphineoxide) in PVC matrix which showed high selectivity for Mg^{2+} over Ca^{2+} in the concentration range of 6.0×10^{-5} - 1.0×10^{-1} mol L^{-1}. Further, Mg(II)oxinate [133] and 1-(*N,N*-dicyclohexylcarbamoyl)-2-(*N,N*-dioctadecylcarbamoyl)ethyl phosphonic acid monomethyl ester [134] were also used as ionophores for magnesium selective sensors. These sensors exhibited linear potential response towards Mg^{2+} ions with reasonably good selectivity. Gupta *et al.* reported Mg^{2+}-selective sensors based on benzo-15-crown-5 [135] and magnesium-tetrazaporphyrin complex [136]. Both the sensors exhibited excellent selectivity for Mg^{2+} over other cations. Aggarwal *et al.* [137] carried out studies on zirconium(IV) selenomolybdate gel based Mg^{2+}-selective heterogeneous membrane sensor.

Development of a convenient method for the determination of calcium ions has been an area of extensive research because of its widespread occurrence in biological and environmental system. Initial attempts to develop a calcium selective sensor were not successful. The useful Ca^{2+}-selective sensors were developed by Thomas and coworkers [138] by incorporating Ca-bis-(2,6-dinitro-4[l,l,3,3-tetramethyl(butyl)])phenoxide and Ca-bis-(di[l,l, 3,3-tetramethyl(butylphenyl)]) phosphate in PVC. Later on, various organophosphates, such as di(2-ethylhexyl) phosphate [139], Ca-di(n-octylphenyl) phosphate [140], Ca-bis-(4-octylphenyl) phosphate [141] and polyaniline functionalized with bis-[4-(l,1,3,3-tetramethyl(butyl phenyl)]phosphate [142] were employed as electroactive material for Ca^{2+} selective sensors. Some of these sensors respond to Ca^{2+} over a wide concentration range (down to 1 nM) with a fast response time but the selectivity of these sensors was not good. Kumar *et al.* [143] developed Ca^{2+}-selective membrane sensor based on dibenzo-18-crown-6. Singh *et al.* [144] developed highly Ca^{2+}-selective potentiometric sensor based on furildioxime as neutral carrier while Jain *et al.* [145] reported p-isopropylcalix[6]arene based sensor for the selective determination of calcium.

Determination of barium is important as it is present in various drugs. In the begining, non- ionic Antrarox CO-880 and its barium complex [146] were used to construct Ba^{2+} selective sensors. Gupta *et al.* [147] used dibenzo-24-crown-8 to develop a highly selective sensor for Ba^{2+} which exhibited linear response in the range of 14 μM - 0.1 M. Saleh [148] reported a Ba^{2+} selective sensor using neutral bidentate organo phosphorous compounds. Singh *et al.* [149] reported 2,3,4-pyridine-1,3,5,7,12-pentaazacyclopentadeca-3-ene as a Ba^{2+} selective ionophore. Othman *et al.* [150] used complex ion associate of barium(II)-Rose Bengal as an ionophore for preparing Ba^{2+}-selective PVC membrane sensor which exhibited fast linear potential response for Ba^{2+} ions over the concentration range 5.0×0^{-5} to 1.0×10^{-1} mol L^{-1} with a Nernstian slope of 28.5 ± 0.4 mV $decade^{-1}$ of activity. Recently, Zamani *et al.* [151] constructed a Ba^{2+}-selective sensor based on 3-deoxy-erythro-hexos-2-ulosebis-(thiosemicarbazone) which showed high selectivity for Ba^{2+} over 1.0×10^{-6} to 1.0×10^{-2} mol L^{-1} with a lower detection limit of 5.6×10^{-7} mol L^{-1}.

The first Sr^{2+}-selective sensor was developed by Baumann [152] using strontium complex of nonylphenoxypoly(ethyleneoxy)ethanol as electroactive material but it exhibited higher selectivity for Ba^{2+} over Sr^{2+}. Qian *et al.* [153] reported a Sr^{2+}-selective sensor based on tetracyclohexyl-2,6-pyridine-bis-(methyleneoxyacetamide) as ionophore which showed strong interference to Pb^{2+} and Ag^{+} ions. The sensor based on the membrane of dibenzo-30-

crown-10 [154] was also found to be Sr^{2+} selective. Gupta *et al.* [155] used 5,11,17,23,9,35-hexakis (1,1,3,3-tetramethyl butyl)-37, 38, 39, 40, 41, 42-hexakis-(carboxymethoxy)-calix-[6]arene to prepare Sr^{2+}-selective sensors. Potentiometric membrane sensor based on 6-(4-nitrophenyl)-2-phenyl-4,4-dipropyl-3,5-diaza-bicyclo[3,1,0]hex-2-ene was developed by Zanjanchi *et al.* [156] for trace level detection of Sr^{2+} ions. Zamani and co-workers [157] used 2,3-diphenylquinoxaline-4',4"-dioxytriethylene glycol as a suitable ionophore for preparing Sr^{2+}-selective sensor which exhibited a linear dynamic range 1.0×10^{-6}-1.0×10^{-2} mol L^{-1} with a Nernstian slope of 29.9 mV $decade^{-1}$ of $a_{Sr}{}^{2+}$ and a detection limit of 6.7×10^{-7} mol L^{-1}. Guo *et al.* [158] explored 1-benzothiazol-3-benzoyl-thiocarbamide as neutral carrier for the fabrication of fast response Sr^{2+} selective polymeric membrane sensor which exhibits Nernstian response to Sr^{2+} over 4.0×10^{-7} to 1.0×10^{-1} mol L^{-1} with a detection limit of 2.5×10^{-7} mol L^{-1} and a slope of 30.1 ± 0.1 mV $decade^{-1}$ of $a_{Sr}{}^{2+}$.

1.4.3 Transition metal ion-selective electrodes

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

Several neutral carriers *viz.*, glyoxal bis-(2-hydroxyanil) [159], 2,3,8,9-tetraphenyl-1,4, 7,10-tetraazacyclododeca-1, 3, 7, 9-tetraene [160], 1, 3-diamino-2-hydroxypropane-*N,N,N′,N′*-tetraacetic acid [161], 4-amino-3-hydrazino-6-methyl-1,2,4-triazin-5-one [162] were explored as Cr^{3+}-selective sensors. Recently, Schiff bases [163, 164] have also been reported as highly selective ionophores for chromium ion determinations.

Pungor and coworkers reported the first nickel-selective electrode based on Ni-dimethylglyoxime complex [165]. Recently, a number of ionophores *viz.*, 5,7,12,14-tetramethyl dibenzotetraazaannulene [166], dibenzo-18-crown-6 [167], Schiff bases [168, 169] have been reported for selective determination of nickel in various samples. Lai and coworkers [170] reported the first neutral carrier Ag^{+}-selective electrode based on dithiacrown ether. Since then a number of Ag^{+} ISEs involving mainly calixarene derivatives [171-174], crown ethers [175, 176], Schiff bases [177, 178] and sulphur donor neutral and macrocyclic ligands [179, 180] have been reported.

Amongst heavy metal ions, the determination of mercury is probably most important to analysts in view of its acute toxicity. Hg^{2+}-selective sensor based on 1-(2′-aminoaryl)-4,4,6-trimethyl-1,4,5,6-tetrahydro-6-hydroxy pyrimidine-2-thiol [181] and 2-amino-6-purinethiol and 5-amino-1,3,4-thiadiazole-2-thiol [182] as a chelating ionophores exhibited better performance characteristics. Saleh *et al.* [183] developed a highly selective ethylenediamine-bis-(thiophenecarboxaldehyde) based Hg^{2+} sensor which showed Nernstian response with a low detection limit 7.0×10^{-8} mol L^{-1}. Recently, Hosseini *et al.* [184] reported a calix[4]arene derivative as an ionophore in the preparation of Hg^{2+}-selective sensor which exhibited Nernstian response in the linear range of 1.0×10^{-6} to 1.0×10^{-1} mol L^{-1} and detection limit of 4.0×10^{-7} mol L^{-1}.

Manganese is essential micronutrient for various organisms but is toxic at higher concentration level. There has been little work done on manganese selective sensors. Lal and coworkers explored cation exchange resin (Dowex 50WX-4) for fabrication of Mn^{2+}-selective sensor [185]. The sensor worked in concentration range of 1.0×10^{-5} - 1.0×10^{-1} mol L^{-1} with long response time. A Schiff base was used by Gupta *et al.* [186] exhibited response to Mn^{2+} over the range 1.25×10^{-5} to 1.0×10^{-1} mol L^{-1}. A recently reported Mn^{2+}-selective electrode, based on N-(2-picolinamidoethyl)-picolinamide, showed high response to Mn^{2+} over the concentration range of 1.0×10^{-5} to 1.0×10^{-1} mol L^{-1} with Nernstian slope of 29.3 ± 0.5 mV decade^{-1} of $a_{Mn}{}^{2+}$ and detection limit of 8.0×10^{-6} mol L^{-1}.

There are only few reports of Fe^{3+}-selective sensors in the literature. Mashhadizadeh and co-workers [187] explored 2-[(2-hydroxy-1-propenyl-buta-1,3-dienylimino)-methyl]-4-*p*-tolyazophenol as ionophore for fabrication of Fe^{3+}-selective sensor but this sensor showed super-Nernstain response. Recently, Ekmekci *et al.* [188] reported Fe^{3+} selective sensor based on benzo-18-crown-6 crown ether as an ionophore. Zamani *et al.* explored N-(2-hydroxyethyl)ethylenediamine-N,N',N''-triacetic acid [189], 5-amino-3-methyl-1-phenyl-1H-pyrazole-4-carboxamide [190], di-tert-butylazodicarboxylate [191]. These sensors showed very low detection limits.

A number of Zn^{2+}-selective sensors based on a variety of ionophores have been reported in the past few decades. A new Zn^{2+}-selective potentiometric sensor based on 4-tert-butylcalix[4]arene [192] worked over the concentration range 9.8×10^{-6} to 1.0×10^{-1} mol L^{-1} with a near-Nernstian slope of 28.0±1.0 mV decade^{-1} of $a_{Zn}{}^{2+}$ and low detection limit 5.0×10^{-7} mol L^{-1}. Singh *et al.* [193] explored tripodal chelating ligand-based Zn^{2+}-selective sensor which exhibited good selectivity to Zn^{2+} ions over a wide concentration range; 1.4×10^{-7} to

1.0×10^{-1} mol L^{-1} with a low limit of detection of 9.5×10^{-8} mol L^{-1}. Zn^{2+}-selective potentiometric sensor based on 3-hydroxy-2-naphthoichydrazide [194] exhibited a Nernstian response over a concentration range of 1.8×10^{-7} - 3.6×10^{-1} mol L^{-1}, with a detection limit of 1.1×10^{-7} mol L^{-1}. Singh *et al.* [195] introduced electrochemical sensors based on pendant armed macrocyclic ligand for the determination of Zn^{2+} ions. Worldwide toxicity of lead has made its monitoring desirable for the analysts.

Thus, a number of Pb^{2+}-selective sensors have been reported using a variety of sensing agents. Some of the recently reported Pb^{2+} ISEs are discussed here briefly. A PVC membrane Pb^{2+}-selective electrode was constructed using 1,10-dibenzyl-1,10-diaza-18-crown-6 as membrane carrier [196]. This electrode had fast Nernstian response for Pb^{2+} over the working range 5.0×10^{-5} to 1.0×10^{-2} mol L^{-1} and showed long shelf life of more than ten months. Bhat *et al.* [197] constructed coated wire lead ion selective electrode using 5, 11, 17, 23, 29, 35-hexa-tert-butyl-37, 38, 39, 40, 41, 42-hexahydroxycalix[6]arene.This electrode exhibited linear Nernstian response over the range 1×10^{-6} to 1×10^{-1} mol L^{-1} with a slope of 30.0 ± 1.0 mV decade^{-1} of $a_{Pb}{}^{2+}$ and a detection limit of 6×10^{-7} mol L^{-1}. Gupta *et al.* [198] used N,N'-dibenzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane as an ionophore for preparing Pb^{2+} selective sensor which exhibits a Nernstian response for Pb^{2+} over a wide concentration range of 8.2×10^{-6} to 1.0×10^{-1} mol L^{-1} with a slope of 30.0 ± 0.1 mV decade^{-1} of $a_{Pb}{}^{2+}$. Wilson *et al.* [199] reported PVC membrane ion selective electrodes for Pb(II) ion based on 1,3-bis-(N'-benzoylthioureido)benzene and 1,3-bis-(N'-furoylthioureido)benzene. Both the electrodes exhibited fast Nernstian response over a wide working concentration range.

Ganjali *et al.* [200] developed Co^{2+} selective sensor by incorporating newly synthesized oxime derivative in PVC matrix. The sensor exhibited a linear potential response to log ${a_{Co}}^{2+}$ in the concentration range of 1.0×10^{-6} - 1.0×10^{-1} mol L^{-1} with a high response time of 25 s. A bridge modified 4-tert-butylthiacalix[4]arene was employed by Jain *et al.* [201] as electroactive material in the preparation of cobalt selective sensor which performed linearly in the range 5.3×10^{-6} to 1.0×10^{-1} mol L^{-1} with near-Nernstian slope of 30.0 mV $decade^{-1}$ of ${a_{Co}}^{2+}$ and a detection limit of approximately 0.3 ppm. Kumar *et al.* [202] used *p*-(4-n-butylphenylazo)calix[4]arene as an electroactive material for the fabrication of a new Co^{2+}-selective sensor which exhibited a fast linear response with the detection limit of 4.0×10^{-6} mol L^{-1}. Recently, a Schiff base has been explored successfully for determination of vanadyl ions by Ganjali and coworkers [203].

1.4.4 Rare earth metal ion-selective electrodes

Rare-Earths also called as lanthanides are an important group of 15 trivalent metals. They usually have magnetic, catalytic and optic properties therefore they are used widely in industry. Rare-Earths have a less toxicity rating; however, their intraperitoneal administration affects metabolic processes. Industrial sources of lanthanides are potentially hazardous to human health, and therefore, there is a growing demand for determination of these metal ions. Considerable efforts have been made by researchers to develop selective sensors for rare-earths [204]. A detailed literature on Gd^{3+} and Nd^{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.

Akhond *et al.* utilized 2-aminobenzothiazole [205] in PVC matrix as a suitable ionophore for preparing Ce^{3+} selective sensor. An addition to the family of Ce^{3+} sensors was made by Saleh *et al.* by utilizing [4-(4-nitrobenzyl)-1-phenyl-3,5-pyrazolidinedion)] [206] as electroactive material while Zamani *et al.* utilized N-[(2-hydroxyphenyl)methylidene]-2-furohydrazide [207] for developing cerium ion sensor. Abedi *et al.* [208] used 2,5-Dioxo-4-imidazolidinyl as an excellent sensing material in the preparation of a PVC membrane for a Ce^{3+}-selective sensor. The developed sensor exhibited a wide linear response with a slope of 19.6 ± 0.3 mV decade^{-1} of $a_{Ce}{}^{3+}$ over the concentration range of 1.0×10^{-6} to 1.0×10^{-1} mol L^{-1} and detection limit is 5.7×10^{-7} mol L^{-1}.

Zamani *et al.* [209] explored 4-amino-3-{2-[4-amino-6-methyl-5-oxo-4,5-dihydro-1,2,4-triazin-3(2H)-yliden]hydrazono}-6-methyl-3,4-dihydro-1,2,4-triazin-5(2H)-one (ATO) as a suitable ionophore for determination of terbium ions. The sensor performed satisfactorily in the concentration range of 1.0×10^{-6} to 1.0×10^{-1} mol L^{-1} with Nernstian slope 19.4±0.5 mV per decade of $a_{Tb}{}^{3+}$ and detection limit 8.6×10^{-7} mol L^{-1}. Singh *et al.* [210] reported macrocyclic pendant ligands for development of Ce^{3+}-selective electrodes. Coated graphite electrode based on 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 showed fast linear response with a detection limit of 5.7×10^{-9} mol L^{-1}. Gupta *et al.* [211] a new terbium selective sensor based on N-(2-hydroxyphenyl)-3-(2-hydroxyphenylhydroxyphenylimino)-N-phenylbutanamidine.

Ganjali *et al.* [212] reported a Sm^{3+}-selective coated graphite electrode which showed very high selectivity to Sm^{3+}. 3-{[2-oxo-1(2H)-acenaphthylenyliden]amino}-2-thioxo-1, 3-thiazolidin-4-one [213] and 2-[(E)-1-(1H-pyrrol-2-yl)methylidene]-1-hydrazinecarbothio amide [214] have also been reported as a suitable ionophores for preparation of Sm^{3+}-selective sensor. 2-ethoxy-1-ethoxycarbonyl-1,2-dihydroquinoline [215] was used as a suitable neutral ionophore for the preparation of a highly selective Sm^{3+} membrane sensor. This sensor exhibited a Nernstian response over a concentration range 1.0×10^{-6} to 1.0×10^{-2} mol L^{-1} with a detection limit of 5.0×10^{-7} mol L^{-1}.

Ion selective sensors for some other rare earth metal ions *viz.*, for La^{3+} [216], Yb^{3+} [217], Dy^{3+} [218], Eu^{3+} [219], Ho^{3+} [220], Tm^{3+} [221], UO_2^{2+} [222], Pr^{3+} [223], Lu^{3+} [224] and Er^{3+} [225] *etc.*, have also been reported. All these sensors exhibited good selectivity for the primary ion over a sufficiently wide working concentration range and have a low response time.

1.4.5 Anion selective electrodes

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.* [226]. The sensor exhibited working concentration range of 10 μM - 10 mM and detection limit up to 0.6 μM. Pandey *et al.* [227] designed a steroid based imidazolium receptor as a recognition material for fluoride ions. Kang *et al.* [228] developed a fluoride-selective PVC membrane electrode based on scandium(III) octaethylporphyrin as a highly selective ionophore. Membrane sensors based on [tetrakis(4-*N,N*-dimethylaminobenzene)porphyrinato]manganese(III) acetate [229] and cobalt-salophen complex [230] have been developed which responded selectively to I^- ions. Pandey *et al.* [231] synthesized click bile acid polymers to stabilize silver nanoparticles which were showed iodide sensing properties. Similarly, attempts have also been made to prepare chloride selective sensors by using different ionophores such as lanthanidetris(b-diketonates) [232] and 2-(1-H-imidazo[4,5-f] [1,10]-phenanthroline-2-yl)-

6methoxyphenol [233]. Singh *et al.* [234] developed a novel bromide selective polymeric membrane electrode based on Zn(II) complex.

Schwarz *et al.* [235] prepared NO_3^--selective sensor using tridodecylmethyl-ammonium nitrate as electroactive material and applied it for *in-situ* determination of NO_3^- in ground water and drinking water. Developement of NO_3^--selective membrane sensors based on various electroactive materials such as (2-hydroxyanil)acetylacetonelead (II) [236], tris(2-aminoethyl)amine [237] and doped polypyrrole films utilizing carbon fibers as a substrate [238].

Herman and Rechnitz reported first carbonate selective membrane sensors based on the tri-fluoroacetyl-*p*-butylbenzene derivatives [239]. However, the applicability of these sensors has often been limited because of interference caused by lipophilic anions such as salicylate, perchlorate, and thiocyanate. Asymmetric membrane technology was utilized to prevent salicylate from responding to carbonate sensitive membranes in serum carbon dioxide measurements [240]. Recently, Lee *et al.* [241] used urea-functionalized calix[4]arenes as carriers for carbonate selective sensor. The sensor exhibited a linear response over a narrow concentration range (5.0×10^{-4} to 1.0×10^{-1} mol L^{-1}) with a slope of 29.2 mV $decade^{-1}$ of activity. Jain *et al.* [242] reported hydrogen bonding diamide receptor *N,N'*-bis(2,4-dinitrophenyl)isophthalohydrazide as highly selective ionophore for carbonate ion. This sensor worked well over a wide concentration range 1.3×10^{-7} to 1.0×10^{-3} mol L^{-1} with Nernstian slope (29.0 mV $decade^{-1}$ of activity) and a response time of approximately 7 s.

Ganjali *et al.* reported complex of Zn(II) Schiff base[243] and pyrylium perchlorate [244] as suitable ionophores to develop SO_4^{2-}-selective sensors. These sensors were used as an indicator electrode in the potentiometric titration of SO_4^{2-} with barium. Blikova *et al.* [245] 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. Mazloum *et al.* [246] reported ClO_4^- selective membrane sensor based on a new complex of uranil and applied it for the determination of ClO_4^- in urine and water. Ganjali *et al.* [247] reported perchlorate salts of Ni(II) complexes of 1,3,5,8,10,13-hexaazacyclotetradecane and 1,8-tert-butyl-1,3,5,8,10,13-hexaazacyclotetradecane as suitable ionophores in construction of perchlorate selective membrane electrodes. Singh *et al.* [248] reported a potentiometric thiocyanate-selective sensor based on zinc-tris(N-tert-butyl-2-thioimidazolyl)hydroborate complex as a neutral carrier. The sensor exhibited significantly enhanced selectivity towards thiocyanate ions over the concentration range 6.3×10^{-7} to 1.0×10^{-2} mol L^{-1} with a lower detection limit of 3.16×10^{-7} mol L^{-1} and a Nernstian slope of 59.4±1.1 mV $decade^{-1}$ of activity.

Arsenite selective sensor was prepared by Gupta *et al.* [249] using 5,10,15,20-tetrakis(4-methoxyphenyl)porphyrinatocobalt(II) as electroactive material which showed linear potential response in the concentration range of 7.9×10^{-5} - 1.0×10^{-1} mol L^{-1} with a slope of 28.8 mV $decade^{-1}$ of activity. C-thiophenecalix[4]resorcinarene was employed as a suitable ionophore in PVC matrix for the preparation of CrO_4^{2-}-selective sensor by Jain and co-workers [250]. This sensor exhibited wide concentration range 5.6×10^{-6} - 1.0×10^{-1} mol L^{-1} with Nernstian slope of 29.0 mV $decade^{-1}$ of activity. Polyvinyl chloride (PVC) based membranes using macrocyclic dithioxamide receptor were also prepared and explored as HPO_4^{2-}-selective sensors [251]. Rawat *et al.* [252] developed a highly selective potentiometric oxalate ion sensor using Ni(II)[bis-(m-aminoacetophenone)ethylenediamine] as an ion carrier. The sensor showed Nernstian response with improved linear range 1×10^{-1} - 1×10^{-7} mol L^{-1} giving a relatively fast response within 10 s.

1.4.6 Miscellaneous electrodes

Besides inorganic ions, efforts have also been made to develop sensors for gases and organic species. Arnold *et al.* [253] worked on the determination of glucose in a synthetic biological matrix. Stefan and co-workers [254] constructed potentiometric enantioselective membrane electrodes for the assessment of l-proline. Kumar *et al.* [255] developed a conductimetric immunosensor based on poly(3, 4-ethylenedioxythiophene). A nicotine-selective sensor [256] 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 [257]. The NH_3 gas sensors have been used in the analysis of fresh water, effluents and sewage; similarly CO_2 sensor for blood analysis, SO_2 sensor for food and beverages and NOx for the measurement of nitrite in soil extracts and water samples. Electrochemical immunosensors were developed by Guilbault *et al.* [258] for the detection of 19-nortestosterone and methyltestosterone in bovine urine. Guilard and co-workers [259] designed a new colorimetric molecular sensor based on a 1,8-diaminoanthraquinone which exhibited efficient binding for lead ion in water and allowed naked-eye detection. Glennon *et al.* [260] synthesized and electropolymerized N-acetyltyramine with a negatively charged sulfobutylether-β-cyclodextrin on a boron-doped diamond (BDD) electrode followed by the electropolymerization of pyrrole to form a stable and permselective film for selective dopamine detection.

1.5 THE PROBLEM

An overview of literature already presented reveals that a number of ion selective electrodes for alkali, alkaline earth, heavy metals and anions have been reported. For every single ion, a number of sensors using different materials are reported. This is due to the fact that researchers have tried to improve working concentration range, selectivity, life time and response time of already reported ISEs using newer materials. However, for most of the ions, even the best sensor so far developed is not the final word and can always be improved in some respect with the availability of newer selective materials. Further, literature survey shows that the most of the sensors reported for Cu^{2+}, Gd^{3+}, Nd^{3+} and Cd^{2+} metal ions are not of very high selectivity and generally show high response time and limited working concentration range. As the determination of these ions is important, attempts have been made to develop new ISEs for these metal ions which show improved performance compared to the existing ones.

The performance of any ISEs depends mainly on the selectivity of the ionophore (electroactive component) present in the membrane. It is important and essential that ionophore used should have high affinity for a particular cation/anion and poor for others. Such ionophores are likely to act as a selective sensor for the ion to which they show high affinity. The high affinity of an ionophore for a particular ion may be due to various processes such as selective ion exchange, sorption, ion-ionophore complexation or hydrogen bonding. The problem is that very few materials are available which show high affinity to a particular ion as a result of either of these processes. However, the newer materials such as calixarenes, porphyrins, dendrimers, Schiff bases, macrocyclic compounds various types of metal chelates and hydrogen bonding receptors are being continually synthesized and few of them have shown selective response to only a limited number of cations/anions. In the present investigations, some of such materials have been explored as ionophores for the fabrication of polymeric membrane and coated graphite ion selective electrodes for Cu^{2+}, Gd^{3+}, Nd^{3+}, and Cd^{2+} metal ions. The efforts have been successful to a significant extent as evident from the results reported in the following chapters. The efforts have been successful to a significant extent as evident from the results reported in the following chapters.

- Schiff bases are the compounds of great interest in the field of ion selective electrodes as they provide different donor atoms, cavity size and ligand geometry to guest ions. In view of the aforesaid applications, we thought it's worthwhile to synthesize some Schiff's base ligands and to explore as molecular recognition materials for selective determination of Cu^{2+} ions. Therefore, Polymeric membrane electrodes (PME) of 2-[{(2-hydroxyphenyl)imino}methyl]-phenol (L_1) and 2-[{(3-hydroxy phenyl)imino} methyl]-phenol (L_2), have been prepared and investigated as Cu^{2+}-selective sensors. The results obtained are given in Third Chapter, which clearly demonstrates that efforts have been largely successful.

- Chelating ligand 2,6-Bis-[1-{N-cyanoethyl,N-(2-methylpridyl)}aminoethyl] pyridine (L_3) having five nitrogen donor sites for complexation with cations was synthesized. The stability constants of its complexes with various metal ions were determined and it was found that that L_3 has high affinity towards Gd^{3+} ion. Therefore, it was used as a potential ionophore for the preparation of coated graphite Gd^{3+}-selective electrode. The results of these studies, given in Fourth Chapter, clearly indicate that efforts have been successful to a significant extent and the developed Gd^{3+}-selective coated graphite electrode show better performance than the existing ones in various respects.

- Novel lariat ethers *viz.*, 1,5–di(cyanoethane)-2,4:7,8:13,14-tribenzo-1,5-diaza-9,12-dioxacyclopentadeca-2, 7, 13-triene (L_4) and 1, 5-di(cyanoethane)-2, 3, 4-pyridine-7,8:13,14-dibenzo-1,3,5-triaza-9,12-dioxacyclopentadeca-2,7,13-triene (L_5) were synthesized and used as highly selective ionophores in the potentiometric determination of neodymium. Complexation study of these ligands with several metal ions revealed their high affinity for Nd^{3+} compared to others. A number of PVC based coated graphite electrodes of L_4 and L_5 were prepared and explored as Nd^{3+} selective electrodes. The results obtained are incorporated in Fifth Chapter which indicates that efforts are successful to a significant extent and newly developed ISEs show better performance than the existing ones in various respects.

- Three chelating compounds N^1,N^2-dicyanoethyl-N^1,N^2-bis-(pyridine-2-ylmethyl) benzene-1,2-diamine [L_6], N^1,N^2-dicyanoethyl-N^1,N-bis-(thiophen-2-ylmethyl) benzene-1,2-diamine [L_7] and N^1,N^2-dicyanoethyl-N^1,N^2-bis-(furan-2-ylmethyl) benzene-1,2-diamine [L_8] were synthesized and employed as electroactive material in the fabrication of coated graphite electrodes as Cd^{2+}-selective sensors. The results obtained from the potentiometric studies of these electrodes are compiled in Sixth Chapter which indicates that these are important addition to the existing set of cadmium selective electrodes.

References

1. Mark, H.H., Kevin, J.J., Susan, L.R., John, Z., Howard, W., Kim, C., Dana, G. and Duane, T., "A novel chemical detector using cermet sensors and pattern recognition methods for toxic industrial chemicals", *Sens. Actuators, B*, **116**, 135 (2006).
2. Elisabetta, M. and Cosimino, M., "Electrochemical detection of the toxic organohalide 2,4-DB using a Co-porphyrin based electrosynthesized molecularly imprinted polymer", *Sens. Actuators, B*, **148**, 186 (2010).
3. Dabke, R.B., Contractor, A.Q. and Chawla, H.M., "Molecular recognition-application to the detection of toxic metal ions", *Trans. SAEST*, **29**, 216 (1994).
4. Iqbal, S.S., Mayo, M.W., Bruno, J.G., Bronk, B.V., Batt, C.A. and Chambers, J.P., "A review of molecular recognition technologies for detection of biological threat agents", *Biosens. Bioelectron*, **15**, 549 (2000).
5. Prabhakaran, D., Nanjo, H. and Matsunaga, H., "Naked eye sensor on polyvinyl chloride platform of chromo-ionophore molecular assemblies: A smart way for the colorimetric sensing of toxic metal ions", *Anal. Chim. Acta*, **601**, 108 (2007).
6. Singh, R.P., Oh, B.K. and Choi, J.W., "Application of peptide nucleic acid towards development of nanobiosensor arrays", *Bioelectrochem.*, **79**, 153 (2010).
7. Liu, Q., Cai, H., Xu, Y., Xiao, L., Yang, M. and Wang P., "Detection of heavy metal toxicity using cardiac cell-based biosensor", *Biosens. Bioelectron,* **22**, 3224 (2007).
8. Soylak, M. and Aydin, A., "Determination of some heavy metals in food and environmental samples by flame atomic absorption spectrometry after coprecipitation", *Food Chem. Toxicol.*, **49**, 1242 (2011).
9. Sanchez-Moreno, R.A., Gismera, M.J., Sevilla, M.T. and Procopio, J.R., "Direct and rapid determination of ultratrace heavy metals in solid plant materials by ET-AAS ultrasonic-assisted slurry sampling", *Phytochem. Anal.*, **21**, 340 (2010).
10. Wu, H., Jin, Y., Luo, M. and Bi, S., "A simple and sensitive flow-injection on-line preconcentration coupled with hydride generation atomic fluorescence spectrometry for the determination of ultra-trace lead in water, wine, and rice", *Anal. Sci.*, **23**, 1109 (2007).

11. Tu, Q., Wang, T. and Antonucci, V., "High-efficiency sample preparation with dimethylformamide for multi-element determination in pharmaceutical materials by ICP-AES", *J. Pharm. Biomed. Anal.*, **52**, 311 (2010).
12. Li, S., Lin, L., Zheng, F. and Wang, Q., "Metal bioavailability and risk assessment from edible brown alga laminaria japonica, using biomimetic digestion and absorption system and determination by ICP-MS", *J. Agri. Food Chem.*, **59**, 822 (2011).
13. Zhang, X., Geng, P., Liu, H., Teng, Y., Liu, Y., Wang, Q., Zhang, W., Jin, L. and Jiang, L., "Development of an electrochemical immunoassay for rapid detection of E. coli using anodic stripping voltammetry based on Cu and Au nanoparticles as antibody labels", *Biosens. Bioelectron.*, **24**, 2155 (2009).
14. Lin, H., Huang, Z.J., Hu, Q., Yang, G. and Zhang, G., "Determination of palladium, platinum, and rhodium by HPLC with online column enrichment using 4-carboxylphenyl-thiorhodanine as a precolumn derivatization reagent", *J. Anal. Chem.*, **62**, 58 (2007).
15. Van Staden, J.F. and Tlowana, S.I., "Spectrophotometric determination of chloride in mineral and drinking waters using sequential injection analysis", *Fresenius. J. Anal. Chem.*, **371**, 396 (2001).
16. Kumar, S.S., Lokesh, S.V., Puttaiah, E.T., Sherigara, B.S. and Babu, K.H., "Analysis of trace metals in river Tunga of Karnataka by differential pulse anodic stripping voltametry (DPASV)", *Nat. Environ. Pollut. Tech.*, **5**, 425 (2006).
17. Huang, H. and Dasgupta, P.K., "Fast voltammetric sensors for the measurement of soil water activity", *Electroanalysis*, **7**, 626 (1995).
18. Vallieres, C., Gray, J., Poncin, S. and Matlosz, M., "Single conducting polymer nanowire based sequence-specific, base-pair-length dependant label-free DNA sensor", *Electroanalysis*, **10**, 191 (1998).
19. Kim, J., Kang, D.M., Shin, S.C., Choi, Y.M., Kim, S.J. and Lee, S.S., "Functional polyterthiophene-appended uranyl-salophen complex: Electropolymerization and ion-selective response for monohydrogen phosphate", *Anal. Chim. Acta.*, **614**, 85 (2008).
20. Noh, H.B., Kumar, P., Biswas, T.K., Kim, D.S. and Shim, Y.B., "Improved performance of an amperometric biosensor with polydiaminonaphthalene on electrochemically deposited Au nanoparticles", *Electroanalysis*, **22**, 632 (2010)

21. Ganjali, M.R., Norouzi, P. and Rezapour, M., "Potentiometric ion-selective sensors", *Encyclopedia of Sensors*, **4**, (2006).

22. Egorov, V.V., Rakhman'ko, E.M. and Ratko A.A., "Anion-selective electrodes liquid membranes", *Encyclopedia of Sensors*, **1**, (2006).

23. Moody, G.J., "Mechanistic studies of ion-selective electrodes", *J. Biomed. Eng.*, **7**, 183 (1985).

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

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

26. Nägele, M., Bakker, E. and Pretsch E., "General description of the simultaneous response of potentiometric ionophore-based sensors to ions of different charge, *Anal. Chem.*, **71**, 1041 (1999).

27. Baumgartner, M.R., Schmalle, H. and Dubler, E., "The interaction of transition metals with the coenzyme lipophilic acid: synthesis, structure and characterization of copper and zinc complexes", *Inorg. Chim. Acta*, **252**, 319 (1996).

28. Koryata, J., "Theory and applications of ion selective electrodes", *Anal. Chim. Acta*, **61**, 329 (1972).

29. Kolthoff, I.M. and Sanders, H.L., "Electric potentials at crystal surfaces, and at silver halide surfaces", *J. Am. Chem. Soc.*, **59**, 416 (1937).

30. Pungor, E. and Hollos-Rokosinyi, E., "Use of membrane electrodes in the study of ion concentration", *Acta Chim. Acad. Sci. Hung.*, **27**, 63 (1961).

31. Rechnitz, G.A., Lin, Z.F. and Zamochnick, S.B., "Potentiometric measurements with SO_4^{2-} and PO_4^{3-} sensitive membrane electrodes", *Anal. Lett.*, **1**, 1532 (1967).

32. Macdonald, A.M.U. and Toth, K., "The development of fluoride-sensitive membrane electrodes: Part I. Membranes containing thorium, lanthanum or calcium fluoride", *Anal. Chim. Acta*, **41**, 99 (1968).

33. Frant, M.S. and Ross, J.W., "Electrodes for sensing fluoride ion activity in solution", *Science*, **154**, 1553 (1966).

34. Stefanac, Z. and Simon, W., "Ion specific electrochemical behavior of macrotetrolides in membranes", *Microchem. J.*, **12**, 125 (1967).

35. Higuchi, T., Illian, C.R. and Tossounian, J.L., "Plastic electrodes specific for organic ions", *Anal. Chem.*, **42**, 1674 (1970).
36. Bloch, R., Shatkay, A. and Saroff, H.A., "Fabrication and evaluation of membranes as specific electrodes for calcium ions", *Biophys. J.*, **7**, 865 (1967).
37. 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).
38. Pedersen, C.J., "Cyclic polyethers and their complexes with metal salts", *J. Am. Chem. Soc.*, **89**, 2495 (1967).
39. Farago, M.E., "Thallium(I) complexes with some macrocyclic "crown" polyethers", *Inorg. Chim. Acta*, **23**, 211 (1977).
40. Whittingham, M.S., "Chemistry of intercalation compounds: Metal guests in chalcogenide hosts", *Prog. Solid State Chem.*, **12**, 41 (1978).
41. Buck, R.P. and Lindner, E., "Recommendations for nomenclature of ion-selective electrodes", *Pure Appl. Chem.*, **66**, 2527 (1994).
42. Durst, R.A., "*Ion-selective electrodes*", Natl. Bur. Standards Spec. Publ., Washington (1969).
43. Moody, G.J. and Thomas, J.D.R., "*Selective ion-sensitive electrodes*", Merrow, Watford (1971).
44. Morf. W.E., "*The principles of ion-selective electrodes and of membrane transport*", Elsevier Scientific Publishing Co., New York (1981).
45. Florido, A., "*Dynamic characteristics of ion-selective electrodes*", CRC Press (1988).
46. Buck, R.P. and Lindner, E., "Recommendation for nomenclature of ion-selective electrode", *Pure Appl. Chem.*, **66**, 2527 (1994).
47. Cattrall, R.W., "*Chemical sensors*", Oxford University Press, Oxford (1997).
48. Lakshminarayanaiah, N., "*Membrane electrodes*", Academic Press, New York (1976).
49. Diamond, D., "*Principles of chemical and biological Sensors*", Wiley Interscience Publ., New York (1998).
50. Stefan, R.I. and van Stead, J.F., "*Electrochemical sensors in bioanalysis*", Marcel Dekker, New York (2001).

51. Fry, C. and Langley, S.E.M., "Ion-selective electrodes for biological systems", Taylor & Francis, Amsterdam, Netherland (2001).

52. Buck, R.P., "Electrochemistry of ion selective electrodes", *Sens. Actuators*, **1**, 197 (1981).

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

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

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

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

57. 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).

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

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

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

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

62. Arnold, M. A. and Solsky, R.L., "Ion selective electrodes", *Anal. Chem.*, **58**, 84R (1986).

63. Janata, J., Josowicz, M. and DeVaney, D. M., "Chemical sensors", *Anal. Chem.*, **66**, 207R (1994).

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

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

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

67. Bakker, E. and Pretsch, E., "Modern Potentiometry", *Angew. Chem. Int. Ed.*, **46**, 5660 (2007).

68. Bobacka, J., Ivaska, A. and Lewenstam, A., "Potentiometric ion sensors", *Chem. Rev.*, **108**, 329 (2008).

69. Privett, B.J., Shin, J.H. and Schoenfisch M.H., "Electrochemical sensors", *Anal. Chem.*, **82**, 4723 (2010).

70. 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).

71. Gadzekpo, V.P.Y., Moody, G.J. and Thomas, J.D.R., "Coated-wire lithium ion-selective electrodes based on polyalkoxylate complexes", *Analyst*, **110**, 1381 (1985).

72. Guggi, M., Fiedler, U., Pretsch, E. and Simon, W., "A lithium ion-selective electrode based on a neutral carrier", *Anal. Lett.*, **8**, 857 (1975).

73. 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).

74. 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).

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

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

77. Kobiro, K., Tobe, Y. and Watanabe, K., "Highly selective lithium-ion electrode based on decalino-14-crown-4", *Anal. Lett.*, **26**, 49 (1993).

78. Kang, Y.R., Lee, K.M., Nam, H., Cha, G.S., Jung, S.O. and Kim, J.S., "Lithium ion-selective electrodes employing tetrahydrofuran-based 16-crown-4 derivatives as neutral carriers", *Analyst*, **122**, 1445 (1997).

79. Sun, L., Okada, T., Collin, J. and Sugihara, H., "PVC membrane lithium-selective electrodes based on oligomethylene-bridged bis-l,10-phenanthroline derivatives", *Anal. Chim. Acta*, **329**, 57 (1996).

80. Park, Y.S., Choi, H., Kim, M.G., Park, Y.J., Yoon, N.S. and Bell, T.W., "A D_2-symmetric tetraamide macrocycle based on 1, 1', 4, 4'-tetrahydro[3, 3'(2H, 2'H)-spirobiquinoline]-2, 2'-dione: synthesis and selectivity for lithium over sodium and alkaline earth ions", *Tetrahedron*, **62**, 8696 (2006).

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

82. 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).

83. 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).

84. 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).

85. Suzuki, K., Hayashi, K., Tohda, K., Watanabe, K., Ouchi, M., Hakushi, T. and Inoue, Y., "Sodium ion selective electrodes based on lipophilic 16-crown-5-derivatives", *Anal. Lett.*, **24**, 1085 (1991).

86. Kimura, K., Yoshinaga, M., Funaki, K., Shibutani, Y., Yakabe, K., Shono, T., Kasai, M., Muzufune, H. and Tanaka, M., "Effect of a-substituents on ion selectivity of bis (12-crown-4)methylmalonates as neutral carriers for sodium-ion-selective electrodes", *Anal. Sci.*, **12**, 67 (1996).

87. Shen, S.L. and Shibutani, Y., "Preparation of a benzyloxymethyl-11-crown-3 sodium ion- selective electrode", *Fenxi Huaxue*, **25**, 1300 (1997).

88. 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).

89. 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).

90. 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).

91. Crady, T., Cadogan, A., Mckittrick, T., Harris, S.J., Diamond, D. and McKervey, M.A., "Sodium-selective electrodes based on triestermonoacid derivatives of p-tert-butyl calix[4]arene comparison with tetraestercalix[4]arene ionophores", *Anal. Chim. Acta*, **336**, 1 (1996).

92. 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).

93. Kim, Y.D., Jeong, H., Kang, S.O., Nam, K.C. and Jeon, S., "Polymeric membrane sodium ion-selective electrodes based on calix[4]arene trimesters", *Bull. Korean Chem. Soc.*, **22**, 405 (2001).

94. 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).

95. Momma, T., Komba, S.I., Yammamota, M., Osaka, T. and Yamauchi, S., "All solid-state potassium-selective electrode using double-layer film of polypyrrole/polyanion composite and plasiticized poly(vinyl chloride) containing valinomycin", *Sens. Actuators, B*, **25**, 724 (1995).

96. Saleh, M.B., Taha, F. and Aof, G.S., "Potentiometric potassium selectivity of polymer membrane electrodes prepared with organo-phosphine ligands", *Electroanalysis*, **7**, 770 (1995).

97. 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).

98. Oosaki, S., Kawai, Y., Yajima, S. and Kimura, K., "Neutral-carrier-type potassium ion-selective electrodes based on polymer-supported liquid-crystal membranes for practical use", *Anal. Sci.*, **20**, 1165 (2004).

99. 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).

100. Chung, T.D., Chang, S.K., Park, J. and Kim, H., "New potassium selective electrode based on an ionophore bis(15-crown-5-ether) derived from xanthene-4,5-dicarboxylic acid", *Anal. Sci.*, **13**, 325 (1997).

101. Lee, D. and Thomas, J.D.R., "4'-picrylamino-5'-nitrobenzo-18-crown-6 as a sensing agent in potassium ion-selective electrode membranes", *Talanta*, **41**, 901 (1994).

102. Heng, L.Y. and Hall, E.A.H., "One-step synthesis of K^+-selective methacrylie-acrylic copolymers containing grafted ionophore and requiring no plasticizer", *Electroanalysis*, **12**, 178 (2000).

103. 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).

104. 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).

105. Mousavi, Z., Bobacka, J., Lewenstam, A. and Ivaska, A., "Poly(3,4-ethylenedioxythiophene) (PEDOT) doped with carbon nanotubes as ion-to-electron transducer in polymer membrane-based potassium ion-selective electrodes", *J. Electroanal. Chem.*, **633**, 246 (2009).

106. Mousavi, Z., Teter, A., Lewenstam, A., Maj-Zurawska, M., Ivaska, A. and Bobacka, J., "Comparison of multi-walled carbon nanotubes and poly(3-octylthiophene) as ion-to-electron transducers in all-solid-state potassium ion-selective electrodes", *Electroanalysis*, **23**, 1352 (2011).

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

108. 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).

109. Srivastava, S.K., Kumar, S. and Kumar, S., "Selective determination of rubidium ions by a solid membrane electrode", *J. Electroanal. Chem. Interfacial Electrochem.*, **161**, 345 (1984).

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

111. Yang, Y.H., Bi, Y.M., Liu, M., Fu, J. and Xi, Z.W., "Preparation of a decylidene bis (4-benzo-15-crown-5)ether membrane rubidium (I) electrode", *Microchem. J.*, **55**, 348 (1997).

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

113. Glennon, J.D., Mulcahy, D., Murphy, W.S. and Fallon, M.G., "Cesium ion-selective electrodes based on crowned benzoquinones", *Analyst*, **121**, 127 (1996).

114. Borosoum, B.N., Khella, S.K., Elwaby, A.H.M., Abbas, A.A. and Ibrahim, Y.A., "Evaluation of some new 14- and 15-crown formazans as carrier in Cs ion selective electrode", *Talanta*, **47**, 1215 (1998).

115. Mahajan, R.K., Kumar, M., Sharma, V. and Kaur, I., "Cesium ion selective electrode based on calix[4]crown ether-ester", *Talanta*, **61**, 757 (2003).

116. Oh, H., Choi, E.M., Jeong, H., Nam, K.C. and Jeon, S., "Poly(vinyl chloride) membrane cesium ion-selective electrodes based on lipophilic calix[6]arene tetraester derivatives", *Talanta*, **53**, 535 (2000).

117. Chen, L., Ju, H., Zeng, X., He, X. and Zhang, Z., "Cesium selective electrodes based on novel double flexible spacers bridged biscalix[4]arenes", *Anal. Chim. Acta*, **447**, 41 (2001).

118. Jeon, S., Yeo, H., Lee, H.K., Ko, S.W. and Nam, K.C., "Novel cesium-selective electrodes based on lipophilic 1,3-bisbridged cofacial-calix[6]crowns", *Electroanalysis*, **16**, 472 (2004).

119. Bereczki, R., Csokai, V., Gruen, A., Bitter, I. and Toth, K., "Crown bridged thiacalix[4]arenes as cesium-selective ionophores in solvent polymeric membrane electrodes", *Anal. Chim. Acta*, **569**, 42 (2006).

120. Shamsipur, M., Kazemi, S.Y., Sharghi, H. and Niknam, K., "Cesium-selective membrane electrode based on a recently synthesized 16-membered macrocyclic diamide", *Fresenius J. Anal. Chem.*, **371**, 1104 (2001).

121. Ganjali, M.R., Norouzi, P., Emami, M., Golmohammadi, M. and Mouradzadegun, A., "Novel cesium membrane sensor based on a cavitand", *J. Chinese Chem. Soc.*, **53**, 1209 (2006).

122. 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).

123. Arida, H., Aglan, R.F. and El-Reefy, S.A., "A New Cesium ion selective graphite rod electrode based on Cs-molybdophosphate", *Anal. Lett.*, **37**, 21 (2004).

124. Ramanjaneyulu, P.S., Singh, P., Sayi, Y.S., Chawla, H.M. and Ramakumar, K.L.,"Ion selective electrode for cesium based on 5-(4'-nitrophenylazo)25,27-bis(2-propyloxy)26, 28-dihydroxycalix[4]arene", *J. Hazard. Mater.*, **175**, 1031 (2010).

125. Sadeghi, S. and Fathi, F., "Polymeric membrane coated graphite cesium selective electrode based on 4', 4''(5') di-tert-butyl di-benzo-18-crown-6", *J. Inclusion Phenom. Macrocyclic Chem.*, **67**, 91 (2010).

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

127. Ganjali, M.R., Daftari, A., Pourjavid, M.R., Rastegar, M.F. and Moghimi, A., "Novel Be(II) membrane electrode-based on a derivative of benzo-9-crown-3", *M. Grp. Met. Chem.*, **25**, 669 (2002).

128. Ganjali, M.R., Daftari, A., Faal-Rastegar, M. and Moghimi, A., "Novel potentiometric sensor for monitoring beryllium based on naphtho-9-crown-3", *Anal. Sci.*, **19**, 353 (2003).

129. 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-l,4,7,10-benzotetraoxacyclododecine-12-carbaldehyde-12-(2,4-dinitrophenyl) hydrazine", *Sens. Actuators, B*, **100**, 315 (2004).

130. Ganjali, M.R., Norouzi, P., Dinarvand, R., Faribod, F. and Moghimi, A., "Subnanomolar determination of a beryllium ion by a novel Be(II) microsensor based on 4-nitrobenzo-9-crown-3-ether", *J. Anal. Chem.*, **63**, 684 (2008).

131. Shamsipur, M., Soleymanpour, A., Akhond, M. and Sharghi, H., "New macrocyclic diamides as neutral ionophores for highly selective and sensitive PVC-membrane electrodes for Be^{2+} ion", *Electroanalysis*, **16**, 282 (2004).

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

133. Kumari, P.J. and Chattopadhyaya, M.C., "A novel coated wire magnesium(II) ion-selective electrode: Determination of magnesium in dolomite sample", *J. Ind. Chem. Soc.*, **77**, 358 (2000).

134. 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).

135. Gupta, V.K., Chandra, S. and Mangla, R., "Magnesium-selective electrodes", *Sens. Actuators, B*, **86**, 235 (2002).

136. Gupta, V.K., Prasad, R. and Kumar, A., "Magnesium-tetrazaporphyrin incorporated PVC matrix as a new material for fabrication of Mg^{2+} selective potentiometric sensor", *Talanta*, **63**, 1027 (2004).

137. Gupta, A.P., Ikram, S. and Agarwal, H., "Studies on zirconium(IV) selenomolybdate gel based Mg(II) ion selective heterogeneous membrane sensor-determination of water hardness", *J. Sci. Ind. Res.*, **61**, 61 (2002).

138. Khalil, S.A.H., Moody, G.J., Thomas, J.D.R. and Lima, J.L.F.C., "Epoxy-based all solid state poly(vinyl chloride) matrix membrane calcium ion selective micro electrodes", *Analyst*, **111**, 611 (1986).

139. Lindfors, T. and Ivaska, A., "All solid state calcium-selective electrodes prepared of soluble electrically conducting polyaniline and di(2-ethylhexyl)phosphate with ETH 1001 as neutral carrier", *Anal. Chim. Acta*, **404**, 101 (2000).

140. 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).

141. Qi, D. and Zhuang, Y., "Development of PVC matrix membrane calcium ion-selective microelectrode", *Fenxi Huaxue*, **13**, 34 (1985).

142. Lindfors, T. and Ivaska, A., "Calcium-selective electrode based on polyaniline functionalized with bis[4-(1,1,3,3-tetramethylbutyl)pheny]phosphate", *Anal. Chim. Acta*, **437**, 171 (2001).

143. Kumar, A. and Mittal, S.K., "PVC based dibenzo-18-crown-6 electrode for Ca(II) ions", *Sens. Actuators, B*, **99**, 340 (2004).

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

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

146. 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).

147. Gupta, V.K., Jain, A.K., Khurana, U. and Singh, L.P., "A PVC based neutral carrier and organic exchanger membranes as sensors for the determination of barium(II) and strontium(II)", *Sens. Actuators, B*, **55**, 201 (1999).

148. Saleh, M.B., "Neutral bidentate organophosphorous compounds as novel ionophores for potentiometric membrane sensors", *Fresenius' J. Anal. Chem.*, **367**, 530 (2000).

149. Singh, A.K., Singh, R., Singh, R.P. and Saxena, P., "Novel potentiometric sensor for monitoring barium(II) based on 2,3,4-pyridine-1,3,5,7,12-pentaazacyclopentadeca-3-ene", *Sens. Actuators, B*, **B106**, 779 (2005).

150. 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).

151. Zamani, H.A., Hamed-Mosavian, M.T., Aminzadeh, E., Ganjali, M.R., Ghaemy, M., Behmadi, H. and Faridbod, F., "Construction of barium(II) PVC membrane electrochemical sensor based on 3-deoxy-erythro-hexos-2-ulose bis(thiosemincarbazone) as a novel ionophore", *Desalination*, **250**, 56 (2010).

152. Baumann, E.W., "Preparation and properties of strontium selective electrode", *Anal. Chem.*, **47**, 959 (1975).

153. Qian, G.Y., Wu, M.B., Wu, G.L., Huang, S., Yan, Y.J. and Tian, B.Z., "Strontium ISE based on the diamides with pyridine ring as ionophore", *Talanta*, **47**, 1149 (1998).

154. Ganjali, M.R., Kiani, R., Yousefi, M. and Faal-Rastegar, M., "Novel Potentiometric strontium membrane sensor based on dibenzo-30-crown-10", *Anal. Lett.*, **36**, 2123 (2003).

155. 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).

156. Zanjanchi, M.A., Arvand, M., Islamnezhad, A. and Mahmoodi, N.O., "Novel potentiometric membrane sensor based on 6-(4-nitrophenyl)-2-phenyl-4,4-dipropyl-3,5-diaza-bicyclo[3,1,0] hex-2-ene for detection of strontium (II) ions at trace levels", *Talanta*, **74**, 125 (2007).

157. Zamani, H.A., Masrournia, 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", *Mater. Sci. Eng.*, C, **29**, 976 (2009).

158. 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", *Sens. Lett.*, **8**, 596 (2010).

159. Gholivand, M.B. and Sharifpour, F., "Chromium(III) ion-selective electrode based on glyoxal bis(2-hydroxyanil)", *Talanta*, **60**, 707 (2003).

160. Singh, A.K., Singh, R. and Saxena, P., "Tetraazacyclohexadeca macrocyclic ligand as a neutral carrier in a Cr ion-selective electrode", *Sensors*, **4**, 187 (2004).

161. Abedi, M.R., Zamani, H.A., Ganjali, M.R. and Norouzi, P., "Cr(III) ion-selective membrane sensor based on 1,3-diamino-2-hydroxypropane-N,N,N',N'-tetraacetic acid", *Sens. Lett.*, **5**, 516 (2007).

162. Zamani, H.A., Rajabzadeh, G. and Ganjali, M.R., "Highly selective and sensitive chromium (III) membrane sensors based on 4-amino-3-hydrazino-6-methyl-1,2,4-triazin-5-one as a new neutral ionophores", *Sens. Actuators, B*, **119**, 41 (2006).

163. Singh, A.K., Gupta, V.K. and Gupta, B., "Chromium(III) selective membrane sensors based on Schiff bases as chelating ionophores", *Anal. Chim. Acta*, **585**, 171 (2007).

164. Moghimi, A., "Cr(III) selective PVC membrane electrodes based on Schiff base 1-(2-pyridylazo)2-naphthol complex as an ionophore", *Middle East J. Sci. Res.*, **7**, 147 (2011).

165. Pungor, E., Toth, K. and Harvas, J., "Nickel-selective electrode based on nickel dimethyl glyoxime complex in silicone rubber", *Acta Chim. Acad. Sci. Hung.*, **48**, 17 (1966).

166. Gupta, V.K., Prasad, R., Kumar, P. and Mangla, R., "New nickel(II) selective potentiometric sensor based on 5,7,12,14-tetramethyldibenzotetraazaannulene in a poly(vinyl chloride) matrix", *Anal. Chim. Acta*, **420**, 19 (2000).

167. Gupta, V.K., Goyal, R.N., Agarwal, S., Kumar, P. and Bachheti, N., "Nickel(II)-selective sensor based on dibenzo-18-crown-6 in PVC matrix", *Talanta*, **71**, 795 (2007).

168. Gupta, V.K., Singh, A.K. and Pal, M.K., "Ni(II) selective sensors based on Schiff bases membranes in poly(vinyl chloride)", *Anal. Chim. Acta*, **624**, 223 (2008).

169. Gowri, M., Selvi, J. T., Priya, P.A. and Shanthi, G., "Potentiometric determination of nickel(II) ion using nickel triphenyl phosphine complex of N-(1-phenyl-3-methyl-4-benzoyl-75-hydroxy pyrazolin)-2-amino phenol imine Schiff base", *J. Ultra Chem.*, **5**, 149 (2009).

170. Lai, M.T. and Shih, J.S., "Mercury(II) and silver(I) ion-selective electrodes based on dithia crown ethers", *Analyst*, **111**, 891 (1986).

171. 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).

172. Mahajan, R.K., Kaur, I. and Kumar, M., "Silver ion-selective electrodes employing Schiff base p-tert-butylcalix[4]arene derivatives as neutral carriers", *Sens. Actuators, B*, **91**, 26 (2003).

173. Ngeontae, W., Janrungroatsakul, W., Morakot, N., Aeungmaitrepirom, W. and Tuntulani, T., "New silver selective electrode fabricated from benzothiazolecalix[4]arene: Speciation analysis of silver nanoparticles", *Sens. Actuators, B*, **134**, 377 (2008).

174. Aghaie, M., Giahi, M., Aghaie, H. and Atryan, A., "Silver(I)-selective membrane potentiometric sensor based on two recently synthesized ionophores containing calix[4]arene", *Russ. J. Electrochem.*, **45**, 804 (2009).

175. Gupta, V.K., Pal, M.K. and Singh, A.K., "Comparative study of Ag(I) elective poly(vinyl chloride) membrane sensors based on newly developed Schiff-base lariat ethers derived from 4,13-diaza-18-crown-6", *Anal. Chim. Acta*, **631**, 161 (2009).

176. Zhang, J., Ding, J., Yin, T., Hu, X., Yu, S. and Qin, W., "Synthesis and characterization of monoazathiacrown ethers as ionophores for polymeric membrane silver-selective electrodes", *Talanta*, **81**, 1056 (2010).

177. Seo, H., Jeong, E., Ahmed, M.S., Lee, H.K. and Jeon, S., "Polymeric membrane silver-ion selective electrodes based on Schiff base N,N'-bis(pyridin-2-ylmethylene) benzene-1,2-diamine", *Bull. Korean Chem. Soc.*, **31**, 1699 (2010).

178. Jeong, E., Ahmed, M.S., Jeong, H., Lee, E. and Jeon, S., "Novel silver(I) ion selective PVC membrane electrode based on the Schiff base (N2E,N2'E)-N2,N2'-bis(thiophen-2-ylmethylene)-1,1'-binaphthyl-2,2'-diamine", *Bull. Korean Chem. Soc.*, **32**, 800 (2011).

179. Mittal, S.K., Kumar, S.K.A., Gupta, N.R., Ocak, M. and Ocak, U., "Silver selective electrode based on liquid membrane containing $N_2S_2O_2$ macrocycle as ionophore", *Indian J. Chem., Sect. A: Inorg., Bio-inorg., Phys., Theor. Anal. Chem.*, **47A**, 1676 (2008).

180. Ganjali, M.R., Norouzi, P., Alizadeh, T. and Adib, M., "Ion recognition: synthesis of 2-methyl-2,4-di(2-thienyl)-2,3-dihydro-1H-1,5-benzodiazepine and its application in construction of a highly selective and sensitive Ag^+ membrane sensors", *J. Braz. Chem. Soc.*, **17**, 1217 (2006).

181. Singh, L.P. and Bhatnagar, J.M., "Chelating ionophore based electrochemical sensor for Hg(II) ions", *J. Appl. Electrochem.*, **34**, 391 (2004).

182. Gupta, V.K., Singh, A.K., Khayat, M.A. and Gupta, B., "Neutral carriers based polymeric membrane electrodes for selective determination of mercury (II)", *Anal. Chim. Acta*, **590**, 81 (2007).

183. Saleh, M., Soliman, E., Abdel G.A. and Ahmed, S., "A novel Hg(II) PVC membrane sensor based on simple ionophore ethylenediamine bis-thiophenecarboxaldehyde", *Anal. Lett.*, **39**, 659 (2006).

184. Hosseini, M., Rahimi, M., Sadeghi, H.B., Taghvaei-Ganjali, S., Abkenar, S.D. and Ganjali, M.R., "Determination of Hg(II) ions in water samples by a novel Hg(II) sensor, based on calix[4]arene derivative", *Int. J. Environ. Anal. Chem.*, **89**, 407 (2009).

185. 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).

186. Gupta, V.K., Jain, A.K. and Maheshwari, G., "Manganese(II) selective PVC based membrane sensor using a Schiff base", *Talanta*, **72**, 49 (2007).

187. Mashhadizadeh, M.H., Shoaei, I.S. and Monadi, N., "A novel selective membrane potentiometric sensor for direct determination of Fe(III) in the presence of Fe(II)", *Talanta*, **64**, 1048 (2004).

188. 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).

189. Zamani, H.A., Hamed-Mosavian, M.T., Hamidfar, E., Ganjali, M.R. and Norouzi, P., "A novel iron(III)-PVC membrane potentiometric sensor based on N-(2-hydroxyethyl) ethylenediamine-N,N',N"-triacetic acid", *Mater. Sci. Eng., C*, **28**, 1551 (2008).

190. Zamani, H.A., Rajabzadeh, G. and Ganjali, M.R., "Fabrication of an iron-PVC membrane sensor based on 5-amino-3-methyl-1-phenyl-1H-pyrazole-4-carboxamide", *Sens. Lett.*, **7**, 114 (2009).

191. 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", *Mater. Sci. Eng., C*, **31**, 574 (2011).

192. Gupta, V.K., Goyal, R.N., Al Khayat, M., 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).

193. 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).

194. Gholivand, M.B., Shahlaei, M. and Pourhossein, A., "New Zn(II)-selective potentiometric sensor based on 3-hydroxy-2-naphthoic hydrazide", *Sens. Lett.*, **7**, 119 (2009).

195. Singh, P., Singh, A.K. and Jain, A.K., "Electrochemical sensors for the determination of Zn^{2+} ions based on pendant armed macrocyclic ligand", *Electrochim. Acta*, **56**, 5386 (2011).

196. Mousavi, M.F., Sahari, S., Alizadeh, N. and Shamsipur, M., "Lead ion-selective membrane electrode based on 1,10-dibenzyl-1,10-diaza-18-crown-6", *Anal. Chim. Acta*, **414**, 189 (2000).

197. Bhat, V.S., Ijeri, V.S. and Srivastava, A.K., "Coated wire lead(II) selective potentiometric sensor based on 4-tert-butylcalix[6]arene", *Sens. Actuators, B*, **99**, 98 (2004).

198. Gupta, V.K., Jain, A.K. and Kumar, P., "PVC-based membranes of N,N'-dibenzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane as Pb(II)-selective sensor", *Sens. Actuators, B*, **B120**, 259 (2006).

199. Wilson, D., de-los Angeles, A.M., Alegret, S. and del Valle, M., "Lead(II) ion selective electrodes with PVC membranes based on two bis-thioureas as ionophores: 1,3-bis(N'-benzoylthioureido)benzene and 1,3-bis(N'-furoylthioureido)benzene", *J. Hazard. Mater.*, **181**, 140 (2010).

200. 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).

201. 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)", *Electrochim. Acta*, **53**, 5409 (2008).

202. Kumar, P. and Shim, Y., "A novel cobalt(II)-selective potentiometric sensor based on p-(4-n-butylphenylazo)calix[4]arene", *Talanta*, **77**, 1057 (2009).

203. 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).

204. Kumar, R., Sharma, H.K., Dogra, P. and Kumar, P., "Ion selective electrodes for rare earth metal ions", *Res. J. Chem. Environ.*, **14,** 96 (2010).

205. 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).

206. 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).

207. 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).

208. 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-imidazolidinyl", *Int. J. Environ. Anal. Chem.*, **88**, 353 (2008).

209. 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).

210. Singh, A.K., Singh, P., Banerjee, S. and Mehtab, S., "Development of electrochemical sensors for nano scale Tb(III) ion determination based on pendant macrocyclic ligands", *Anal. Chim. Acta*, **633**, 109 (2009).

211. Gupta, V.K., Pal, M.K. and Sharma, R.A., "Comparative studies on Tb(III)-selective PVC membrane sensors", *Talanta*, **82**, 1136 (2010).

212. Ganjali, M.R., Rezapour, M., Pourjavid, M.R. and Haghgoo, S., "ppt Level detection of samarium (III) with a coated graphite sensor based on an antibiotic", *Anal. Sci.*, **20**, 1007 (2004).

213. Zamani, H.A., Ganjali, M.R. and Adib, M., "Fabrication of a new samarium(III) ion-selective electrode based on 3-{[2-oxo-1(2H)-acenaphthylenyliden]amino}-2-thioxo-1,3-thiazolidin-4-one", *J. Brazil. Chem. Soc.*, **18**, 215 (2007).

214. Zamani, H.A., "Determination of fluoride ions in mouthwash samples by a PVC membrane samarium(III) sensor", *Anal. Lett.*, **42**, 615 (2009).

215. Naddaf, E. and Zamani, H.A., "Samarium(III)-PVC-membrane sensor based on ethoxy-1-ethoxycarbonyl-1,2-dihydroquinoline", *Anal. Lett.*, **42**, 2838 (2009).

216. Islamnezhad, A., Zanjanchi, M.A., Shariati, S. and Abri, A., "A fast response membrane sensor based on ethyl 1,2,3,4-tetrahydro-6-methyl-4-phenyl-2-thioxo-pyrimidine-5-carboxylate for detection of lanthanum (III) ions at wide concentration range", *Acta Chim. Slov.*, **58**, 46 (2011).

217. Singh, A.K., Jain, A.K. and Mehtab, S., "Ytterbium-selective polymeric membrane electrode based on substituted urea and thiourea as a suitable carrier", *Anal. Chim. Acta*, **597**, 322 (2007).

218. Zamani, H.A. and Mohaddeszadeh, M., "Determination of dysprosium(III) ion in soil and sediment samples by an original potentiometric dysprosium(III) membrane sensor", *Anal. Lett.*, **41**, 2710 (2008).

219. Ganjali, M.R., Norouzi, P., Daftari, A., Faridbod, F. and Salavati-Niasari, M., "Fabrication of a highly selective Eu(III) membrane sensor based on a new S-N hexadentates Schiff's base", *Sens. Actuators, B*, **B120**, 673 (2007).

220. Ganjali, M.R., Nemati, R., Faridbod, F., Norouzi, P. and Darviche, F., "Lanthanide recognition: a Ho^{3+} potentiometric membrane sensor", *Int. J. Electrochem. Sci.*, **3**, 1288 (2008).

221. Ganjali, M.R., Norouzi, P., Farrokhi, R., Faridbod, F., Larijani, B. and Meghdadi, S., "Lanthanide recognition: determination of thulium(III) ions in presence of other rare earth elements by a thulium(III) sensor based on 4-methyl-1,2-bis(2-Pyridinecarboxamido) benzene as a sensing material", *Anal. Lett.*, **41**, 2322 (2008).

222. Shamsipur, M., Zargoosh, K., Mizani, F., Eshghi, H. and Rostami, F., "A novel PVC-membrane optical sensor for highly sensitive and selective determination of UO_2^{2+} ion based on a recently synthesized benzo-substituted macrocyclic diamide and dibenzoylmethane", *Spectrochim. Acta, Part A*, **77A**, 319 (2010).

223. Gupta, V.K., Goyal, R.N., Pal, M.K. and Sharma, R.A., "Comparative studies of praseodymium(III) selective sensors based on newly synthesized Schiff's bases", *Anal. Chim. Acta*, **653**, 161 (2009).

224. Zamani, H.A., Rohani, M., Saleh Z. M., Ganjali, M.R. and Salavati-Niasari, M., "A novel lutetium(III) PVC membrane sensor based on a new symmetric S-N Schiff's base for Lu(III) analysis in real sample", *Mater. Sci. Eng., C*, **30**, 917 (2010).

225. Zamani, H.A., "Erbium(III) PVC membrane sensor based on N-(benzyloxycarbolyloxy) succinimide as a new neutral ionophore", *Chin. Chem. Lett.*, **22**, 346 (2011).

226. Newman, J.D., Pirzad, R., Cowell, D.C. and Dowman, A.A., "Development of a polycrystalline fluoride ion-selective electrode", *Analyst*, **114**, 1579 (1989).

227. Pandey, P.S. and Chahar, M., "Design of steroid-based imidazolium receptors for fluoride ion recognition", *Tetrahedron*, **64**, 6488 (2008).

228. Kang, Y., Lutz, C., Hong, S. A., Sung, D., Lee, J.S., Shin, J.H., Nam, H., Cha, G.S. and Meyerhoff, M.E., "Development of a fluoride-selective electrode based on scandium(III) octaethylporphyrin in a plasticized polymeric membrane", *Bull. Korean Chem. Soc.*, **31**, 1601 (2010).

229. 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).

230. Zare, H.R., Memarzadeh, F., Gorji, A. and Ardakani, M.M., "Iodide-selective membrane electrode based on salophen complex of cobalt (III)", *J. Braz. Chem. Soc.*, **16**, 571 (2005).

231. Pandey, P.S., Kumar, A. and Chhatra, R., "Synthesis of click bile acid polymers and their application in stabilization of silver nanoparticles showing iodide sensing property", *Org. lett.*, **12,** 24 (2010).

232. 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. Commun.*, 2238 (2003).

233. Gupta, V.K., Goyal, R. N. and Sharma, R.A., "Chloride selective potentiometric sensor based on a newly synthesized hydrogen bonding anion receptor", *Electrochim Acta*, **54**, 4216 (2009).

234. Singh, A.K., Mehtab S., and Saxena, Puja., "A novel bromide selective polymeric membrane electrode based on Zn(II) complex", *Talanta*, **69**, 1143 (2006).

235. 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).

236. Asghari, A., Amini, M.K., Mansour, H.R., Salavati-Niasari, M. and Rajabi, M., "Nitrate-selective membrane electrode based on bis(2-hydroxyanil) acetylacetone lead(II) neutral carrier", *Anal. Sci.*, **19**, 1121 (2003).

237. 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).

238. Bendikov, T.A., Kim, J. and Harmon, T.C., "Development and environmental application of a nitrate selective microsensor based on doped polypyrrole films", *Sens. Actuators, B*, **B106**, 512 (2005).

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

240. 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. Actuators, B*, **32**, 161 (1996).

241. Lee, H.K., Oh, H., Nam, K.C. and Jeon, S., "Urea-functionalized calix[4]arenes as carriers for carbonate-selective electrodes", *Sens. Actuators, B*, **106**, 207 (2005).

242. Jain, A.K., Gupta, V.K. and Raisoni, J.R., "Anion recognition using newly synthesized hydrogen bonding diamide receptors: PVC based sensors for carbonate", *Electrochim. Acta*, **52**, 951 (2006).

243. Ganjali, M.R., Rezapour, M., Pourjavid, M.R., Salavati-Niasari, M. and Poursaberi, T., "A novel potentiometric membrane sensor for quick determination of trace amount of SO_4^{2-} based on a zinc-Schiff base", *Anal. Lett.*, **36**, 881 (2003).

244. Ganjali, M.R., Shirvani-Arani, S., Nourozi, P., Salimzadeh, D., Faal-Rastegar, M. and Moghimi, A., "A novel sulfate polymeric membrane sensor based on a new bis-pyrylium derivative", *Electroanalysis*, **16**, 1009 (2004).

245. 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).

246. Mazloum A.M., Jalayer M., Naeimi H., Zare H.R. and Moradi, L., "Perchlorate-selective membrane electrode based on a new complex of uranil", *Anal. Bioanal. Chem.*, **381**, 1186 (2005).

247. Ganjali, M.R., Norouzi, P., Faridbod, F., Yousefi, M., Naji, L. and Salavati-Niasari, M., "Perchlorate-selective membrane sensors based on two nickel-hexaazamacrocycle complexes", *Sens. Actuators, B*, **B120**, 494 (2007).

248. 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", *Sens. Actuators, B*, **B125**, 453 (2007).

249. 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).

250. Jain, A. K., Gupta, V. K., Singh, L. P., Srivastava, P. and Raisoni, J.R., "Anion recognition through novel C-thiophenecalix[4]resorcinarene: PVC based sensor for chromate ions", *Talanta*, **65**, 716 (2005).

251. Jain, A.K., Gupta, V.K. and Raisoni, J.R., "A newly synthesized macrocyclic dithioxamide receptor for phosphate sensing", *Talanta,* **69**, 1007 (2006).

252. Rawat, A., Chandra, S. and Sarkar, A., "Highly selective potentiometric oxalate ion sensors based on Ni(II) bis-(m-aminoacetophenone)ethylenediamine", *Chinese J. Chem.,* **28**, 1140 (2010).

253. Arnold, M.A., Cingo, N.A. and Small, G.W., "Determination of glucose in a synthetic biological matrix with decimated time-domain filtered near-infrared interferogram data", *Vib. Spectrosc.*, **23**, 103 (2000).

254. Van-Staden, J.F., Stefan, R.I. and Aboul-Enein, H.Y., "A new construction for potentiometric, enantioselective membrane electrodes, and use for l-proline assay" *Anal. Lett*., **31,** 11 (1998).

255. Contractor, A.Q., Srivastava, D.N., Kumar, A. and Kanungo, M., "Conductimetric immunosensor based on poly(3,4-ethylenedioxythiophene)", *Chem. Commun*., 680 (2002).

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

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

258. Guilbault G.G., Conneely G., Aherne M. and Lu H., "Electrochemical immunosensors for the detection of 19-nortestosterone and methyltestosterone in bovine urine", *Sens. Actuators, B*, **121**, 103 (2007).

259. Guilard, R., Ranyuk, E., Bessmertnykh, A., Denat, F., Averin, A. and Beletskaya, I., "Diaminoanthraquinone-linked polyazamacrocycles: Efficient and simple colorimetric sensor for lead ion in aqueous solution", *Org. Lett.*, **11**, 987 (2009).

260. Glennon J.D., Shang F., Zhou, L., Mahmoud, K.A., Hrapovic, S., Liu, Y., Moynihan, H.A. and Luon, J.H.T., "Selective nanomolar detection of dopamine using a boron-doped diamond electrode modified with an electropolymerized sulfobutylether-β-cyclodextrin-doped poly(N-acetyltyramine) and polypyrrole composite film", *Anal. Chem*., **81**, 4089 (2009).

Chapter 2

Theory and Methodology of Ion Selective Electrodes

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

2.1 Potential of an Ion Exchange Membrane

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

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

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

First term on the right hand side of the equation (1) gives the thermodynamic limiting value of the concentration potential, *i.e.,* Donnan potential while the second term denotes the diffusion potential due to co-ion flux in the membrane. However, if the membrane is considered to be ideally permselective (t_y^-=0), then equation (1) takes the form of the Nernst equation:

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

The equation (2) represents Donnan potential for an ideally permselective membrane. The sign will be +ve for cation selective and –ve for anion selective membranes. It can also be said that it gives thermodynamic limiting value of the concentration potential. The following cell set up is generally used for the measurement of membrane potential using saturated calomel electrodes (SCE) or other reference electrodes.

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

2 $E_{L(2)}$

1 $E_{L(1)}$

Generally, compartment 1 contains reference or internal solution whose concentration is kept constant. The saturated calomel electrode dipped in this solution is known as internal reference electrode. The membrane together with internal solution and internal reference electrode is known as membrane electrode or membrane sensor. The saturated calomel electrode dipped in external solution, which is usually referred to as test solution or sample, is known as external reference electrode. The electromotive force (emf) across this cell is the sum of all individual potential contributions. Many of these are sample-independent and the measured emf can usually be described by the following expression

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

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

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

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

(For cation exchange membrane)

The values of $E_{L(1)}$ and $E_{L(2)}$ are small and generally remain constant. Also the term $\frac{2.303RT}{Z_A F} \log (a_A)_1$ remains constant if the concentration of internal solution is not changed.

Therefore, in a given experimental setup, all the terms in parenthesis of equation (4) are constant and can be substituted by a constant E_0'. The value of E_0' would change only when experimental conditions are changed. The equation (4) is reduced to well-known Nernst equation:

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

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

2.2 Terms Used In ISEs

Before further discussion on the performance of ion-selective electrodes, some of the terms used need to be defined. IUPAC compendium of nomenclature [6 - 8] is helpful in sorting out the terms.

2.2.1 Membrane

A membrane is a phase, finite in space, which separates two other phases and exhibits resistance to the permeation of different species [9]. Ion selective electrodes generally employ homogeneous/heterogeneous membranes of chemical compounds. The capability to differentiate between various permeating species is the principal characteristics of a membrane used in electrochemical sensors. This differentiation leads to the formation of an electrical double layer, which is the source of electric potential. The potential developed is basically due to two processes: (i) different mobilities of the ions through the membrane resulting in the generation of diffusion potential, (ii) Donnan or phase boundary potential arising from non-transport of one or more kind of ions. The potential developed is a function of activity ratios of the exchangeable ions on the two sides of the membrane.

Therefore, it can be used to determine the activity of an unknown solution. For the satisfactory performance of the membrane, the diffusion potential should be absent or be minimal. The membrane plays a critical role in the performance of the sensor in a particular environment. A successful membrane needs to be generally hydrophobic, have ion-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.

2.2.2 Membrane Components

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

i. Electroactive Material (Ionophore)

Ionophore or ion carrier is the key components of polymeric membrane ion-selective electrodes that govern the ion selectivity and sensitivity 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. Various substances *viz.,* inorganic and organic ion exchanger, solid electrolyte, salts of multivalent atoms, metal chelates, polyaza, polythia macrocycles, crown ethers, cryptands and calixarenes which have been used as ion carriers for the preparation of ISEs.

To be used as suitable ion carrier; the electroactive material should be physically compatible with the matrix, have a low solubility product, must exhibit some electrical conductivity, have balance between the free energies of ion-ionophore interaction and high conformational flexibility in order to guarantee rapid ion exchange at the membrane sample interface. To keep the concentration on ionophore constant in the membrane, the ionophore must retain within the membrane; therefore, aside from the binding centre it must contain numerous lipophilic groups to enhance its lipophilicity. Depending upon the nature of ionophore, ISEs can be classified into three different classes: (i) Neutral carrier based ion-selective electrodes (ii) Charged carrier based ion-selective electrodes (iii) ion exchanger based ion-selective electrodes. Schematic representation of the equilibria between sample, ion-selective membrane, and inner filling solution for three important classes of solvent polymeric ion-selective membranes is shown in Figure 2.1 which shows formation of ion-ionophore complex in the membrane phase [10].

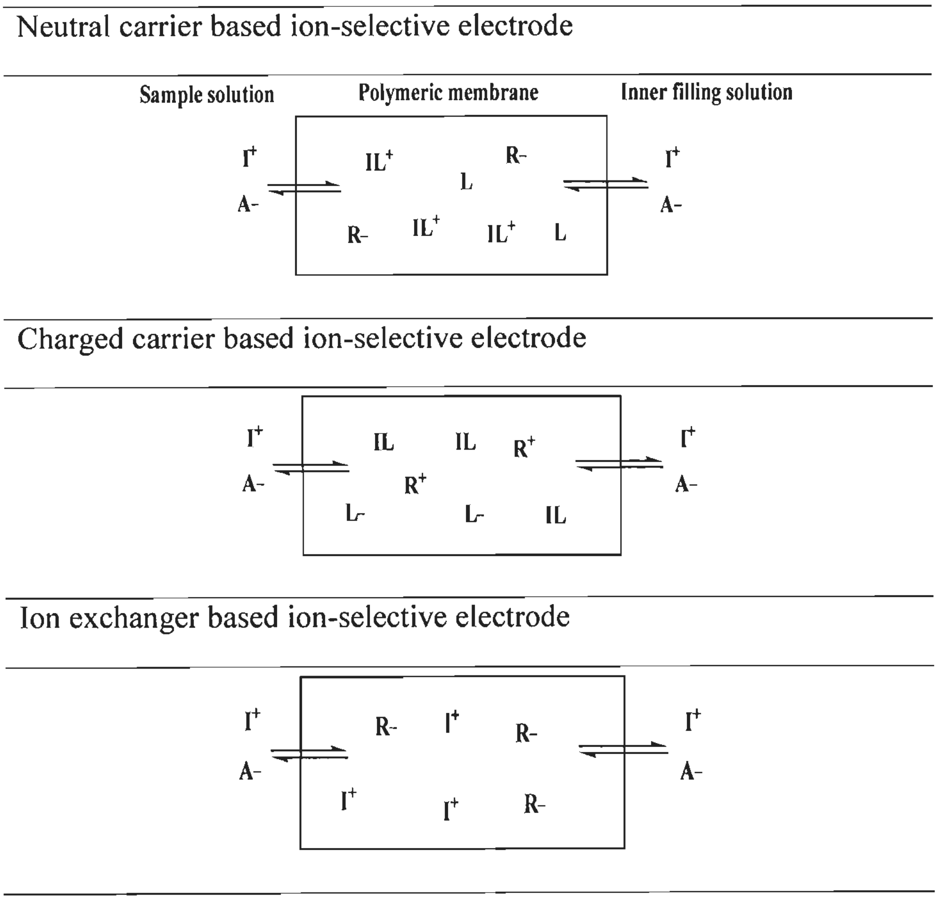


Figure 2.1: Representation of equilibria between sample membrane and inner filling solution: Top: electrically neutral carrier (L) and lipophilic cation exchanger (R-); center: charged carrier (L-) and anion exchanger (R+); and bottom: cation exchanger (R-)

ii. *Polymeric (Inert) Matrix*

The matrix used provides an inert base that imparts physical-mechanical stability and elasticity to the membrane. As it was mentioned above, polymer membrane gives a unique opportunity to obtain a variety of electrodes selective towards particular ions by doping membrane with certain ionophore. Polymer matrix should be chemically inert, hydrophobic, flexible, non-porous; stable and crack resistant. Moreover, it should not swell in sample solutions. Polymers as homogenous membrane matrices first came in use with charged carriers. Poly(vinyl chloride) (PVC) [11], Silicon rubber [12], some methacrylates [13], polyurethanes [14] and polystyrene [15] have been demonstrated as polymer matrices meeting this requirement. However, the most commonly used polymer is PVC due to simplicity of membrane preparation. 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. Moody *et al.* [16] discussed a detailed comparative study of PVC with other polymeric materials and their influence on the performance characteristics of Ca^{2+}-selective electrode was determined. Buck *et al.* [17, 18] discussed the properties of PVC and found that the presence of dissociated fixed exchange sites contributes to the electrode response and selectivity. Further, Mikhelson also reviewed the advantages and disadvantages associated with the PVC matrix [19]. The incorporation of neutral carrier in a PVC matrix has provided an economical way of simplifying ISE construction.

iii. Solvent mediator or Plasticizer

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

It is well documented that the addition of plasticizers 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. 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 [21, 22].

In order to obtain a homogeneous organic phase, plasticizer must be compatible with the polymer and other membrane constituents have to be soluble in it. The main classes of plasticizers for polymeric ISEs are defined by now comprise lipophilic esters and ethers [23]. Polymeric membranes usually comprise of a matrix containing *ca.* 33 % (w/w) of PVC and 66 % of (w/w) plasticizer. A number of organic solvents such as phthalates, dioctylsebacate, 2-nitrophelyl octyl ether, acetophenone and benzyl acetate have been suitably and efficiently used as plasticizer to enhance the performance of ISEs.

iv. *Lipophilic additive or lipophilic ionic sites*

The prerequisite for obtaining a theoretical response with ISE membranes is their perm-selectivity, which means that no significant amount of counter ions may enter the membrane phase. Lipophilic ionic additive is a salt of non-exchangeable lipophilic anion/cation and an exchangeable counter ion. Their main function is to render the ion selective membrane permselective by reducing interference due to foreign ions, to optimize sensing selectivity (by defining the ratio of complexed to uncomplexed ionophore concentration in the membrane) and to reduce the bulk membrane impedance [24, 25]. Besides, the presence of lipophilic additive in ion selective membrane not only diminishes the ohmic resistance but also increase the sensitivity of membrane electrodes. These additives may also catalyze the exchange kinetics at the sample-membrane interface [26, 27].

Thus, the concentration of additive relative to the ionophore has an important selectivity modifying characteristic due to the influence of the involved equilibrium. Lipophilic ion exchangers traditionally used for polymeric membrane preparation are the anionic tetraphenylborate derivatives *viz.,* sodium tetrakis-[3,5-bis- (1,1,1,3,3,3-hexafluoro-2-methoxy-2-propyl)-phenyl]borate trihydrate (NaHFPB), sodium tetraphenyl borate (NaTPB) and potassium tetrakis p-(chloro phenyl)borate (KTpClPB) and the cationic tetraalkylammonium salts *viz.,* tridodecyl methylammonium chloride (TDDMACl), hexadecyl trimethylammonium bromide (HTAB) and tributylammonium chloride (TBAC). The charges on both lipophilic ions are localized on a single (boron or nitrogen) atom, but the steric inaccessibility of the charged centre, due to bulky substituents, may inhibit ion-pair formation in the membrane and provide, when necessary, non-specific interactions between ionic sites and sample ions.

2.2.3 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. A simple format of the assembly is represented schematically in Figure 2.2.

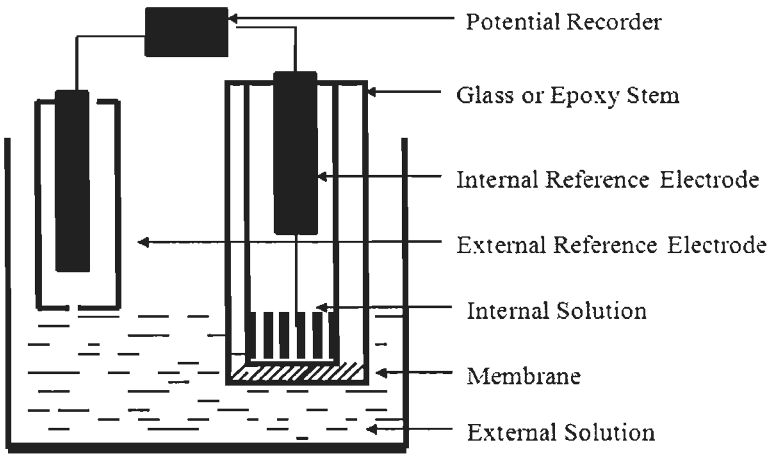


Figure 2.2: Schematic representation of membrane electrode cell assembly

2.2.4 Calibration curve

The cell potential of the assembly is changed when the activity of the solution of primary ion is altered. A plot between cell potential and logarithm of the activity or concentration of the primary ion is normally referred as calibration curve. It determines the performance characteristics of the ion selective electrode and is used in the determination of primary ion concentration. For a primary ion A, the logarithm of its activity (log a_A) is usually plotted along the abscissa of the graph and the cell potential is plotted along the ordinate. A Typical calibration curve ordinarily is shown in Figure 2.3.

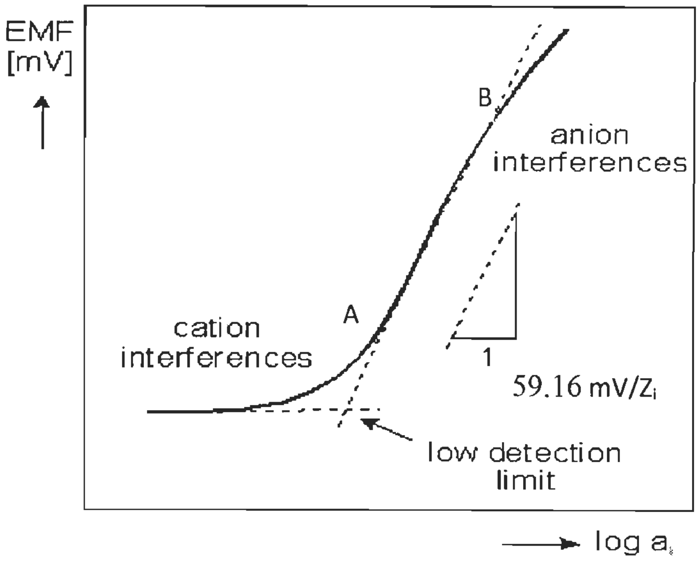


Figure 2.3: Calibration Curve of an ion-selective electrode

2.2.5 Limit of detection

According to the IUPAC recommendation of 1976, detection limit can be defined as the minimum concentration that can be determined for the primary ion. It is obtained from the point of intersection of two extrapolated linear segments of the calibration curve as shown in Figure 2.3. The potential response of ISEs becomes stable below the detection limit.

2.2.6 Measuring range/Linear range/Working concentration range

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

2.2.7 Slope of the ISE

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

$$E_{cell} = E_0' + \frac{2.303RT}{Z_A F}\log(a_A)$$

If the slope is equal to 2.303 RT/ z_AF, the slope is normally called Nernstian slope. If the slope of an ISE Nernstian, it is said that the electrode behaviour is ideal. The theoretical values of the slope is 59.1 mV decade^{-1} 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.

2.2.8 Response time

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

According to it, the response time is the time elapses between the instant at which an ion-selective electrode and a reference electrode are brought into contact with a sample solution and the first instant at which emf/time slope ($\Delta E/\Delta t$) 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 [29]. To evaluate the reversibility of the electrodes, a similar procedure in the opposite direction can also be adopted.

2.2.9 Lifetime of ISE

The lifetime of an ion-selective electrode may be defined as the time interval between the conditioning of the membrane and the moment when at least one parameter of the functionality characteristics of the device changes detrimentally. The working shelf life of an 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 the nature of the samples analyzed and the lipophilicity of the ingredients of ion selective membrane. The continuous loss of plasticizer, ionophore or ionic site from the polymeric film into the sample due to an increasing period of exposure finally results in a breakdown of the ion measuring capacity of the system and hence, a primary reason for limited lifetime of ion selective electrodes [30].

2.2.10 Drift

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

2.2 Potentiometric Selectivity

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. The ion for which the sensor is designed is called primary ion and all other ions are referred to as interfering ions or foreign ions or secondary ions. In fact, no 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. Therefore, it is a necessary parameter to determine as it indicates the commercial potential of any sensor. The degree of selectivity of the sensor for primary ions A, with respect to interfering ion B, is expressed in terms of potentiometric selectivity coefficient ($K_{A,B}^{Pot}$) which is defined by the semi-empirical Nicolsky-Eisenmann equation (6)

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

where z_A, z_B, a_A and a_B are the charges and activity of ions A and B, respectively. It is apparent from equation (6) that a value of $K_{A,B}^{Pot} = 1$ 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 sensor responds more to A in comparison to B *i.e.,* the sensor is selective to A over B. Smaller is the value of selectivity coefficient better is the selectivity. On the other hand, $K_{A,B}^{Pot} > 1$ indicates that the sensor's response is more towards B rather than A and in such a case it is said that the ion B causes considerable interference.

When the charges $z_A \neq z_B$, the values of selectivity coefficient $K^{Pot}_{A,B} \cong 1$ does not indicate equal response to primary and interfering ions as per equation (6), but now it depends on the values of z_A and z_B. For different values of z_A and z_B, $K^{Pot}_{A,B}$ values showing equal response to both A and B have been computed from equation (6) at an activity of 1.0×10^{-2} mol L^{-1} of B and are summarized in Table 2.1.

Table2.1: Selectivity coefficient values ($K^{Pot}_{A,B}$) indicating equal response of the sensor to both primary (A) and interfering ion (B) at an activity of 1.0×10^{-2} M of B.

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

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

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

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

Thus, it is seen from Table 2.1 and 2.2 that the discussion of the selectivity of the sensors is rather difficult. At an activity of 1.0×10^{-2} mol L^{-1}, with z_A=z_B=1, $K^{Pot}_{A,B}$>1 indicate interference but with z_A=2 and z_B=1, $K^{Pot}_{A,B}$>1, does not indicate any serious interference. The interference becomes serious when $K^{Pot}_{A,B}$>100. As a matter of fact, with z_A=2 and z_B=1, a value of $K^{Pot}_{A,B}$ upto 100 means that sensor is more selective to A compared to B. Similar problem also exists when z_A=1, z_B=2 or z_A=2, z_B=3 *etc*. In order to make it easy to appreciate the relative selectivity of the sensor when large number of ions of different charges are involved, it would be better to have only a single value of $K^{Pot}_{A,B}$ that indicates equal response to A and B irrespective of their charges. Viteri and Diamond [31] have proposed a modification in the Nicolsky equation. They neglected the power term from the equation (6) and reported the data. The selectivity coefficient data reported in this way (*i.e.*, by neglecting the power term, z_A/z_B) comes out to be on a scale for which $K^{Pot}_{A,B}$ =1 indicates equal response for both A and B irrespective of their charges.

It is important to emphasize that selectivity coefficient values signify the selectivity only at the conditions of determination but in actual practice the interference caused depends on the relative concentration of the primary and interfering ions and other experimental conditions. Though the selectivity coefficient may not reflect exactly the interference level but still it is a very important parameter to estimate the likely performance of a sensor. However, it has been seen that the deviation between the expected performance of a sensor on the basis of selectivity coefficient and the experimental performance is not large. Therefore, it is necessary to evaluate the performance of a sensor in the presence of other ions by determining selectivity coefficient. A number of methods have been described to determine selectivity coefficient [32-34] and are grouped into the following categories.

2.2.1 Separate Solution Method (SSM)
2.2.2 Mixed Solution Method (MSM)
2.2.3 Matched Potential Method (MPM)

2.2.1 **Separate solution method (SSM)**

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

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

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

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

From equations (7) and (8)

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

When $E_A = E_B$

$$K_{A,B}^{Pot} = \frac{a_A}{(a_B)^{z_A/z_B}} \tag{10}$$

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 ion selective electrode is used [35].

2.2.2 Mixed solution method (MSM)

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

Procedure I (Fixed Primary Method)

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

$$E_{AB} = E° + \frac{2.303RT}{z_A F} \log \left[a_A + K_{A,B}^{Pot} (a_B)^{z_A/z_B} \right] \tag{11}$$

From equations (7) and (11)

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

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

Procedure II (Fixed Interference Method)

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

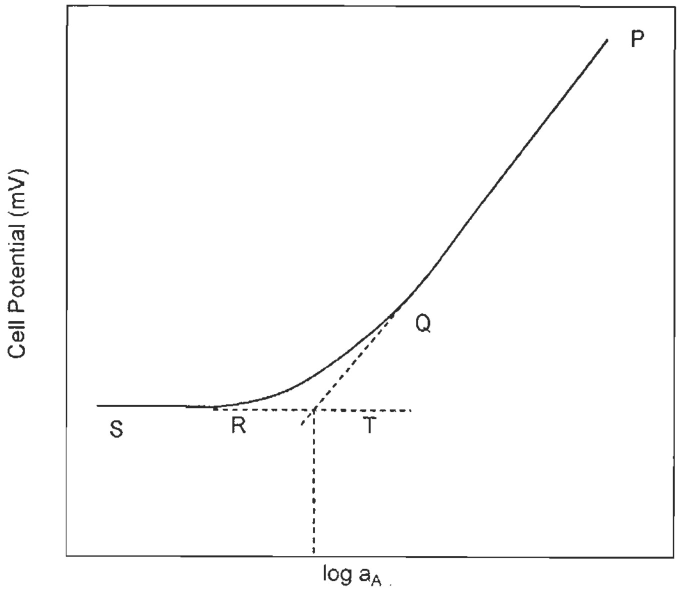


Figure 2.4: Potential *vs.* ($\log_{10}$ a_A) plot illustrating the determination of selectivity coefficient by Fixed interference method

This plot generally has three distinct regions. In the first region PQ, the linear response of the sensor indicates that it is responding only to primary ion, A, with no interference caused by B in this concentration range. In the second region QR, deviation from linearity is caused because now the sensor is also responding to the activity of B as the concentration of primary ion decreases. So in this region (QR), the response of the sensor is mixed and is due to both the ions A and B. The third region RS of the plot is linear and the potential is constant. Constancy in the potential indicates that the sensor is now only responding to interfering ion B with no contribution arising due to primary ion, A. This generally occurs at lower activity of A. As the activity of B is constant and A is not affecting the potential in this concentration range, the potential of the sensor remains constant. The linear portion PQ and RS are then extrapolated and meet at the intersection point T. The potential corresponding to point T can be generated by constant activity of B or by the activity of A. Thus, for point T, E_A is equal to E_B (E_A is generated by A of activity a_A and E_B by B of activity a_B). Under this condition of E_A=E_B, the $K_{A,\ B}$ can be calculated by the following equation (10) already derived under separate solution method.

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

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

2.2.3 Matched potential method (MPM)

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

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

and is determined by measuring the change in potential upon increasing by a definite amount the primary ion activity from an initial value of a_A to a'_A and a_B represents the activity of interfering ion added to same reference solution of activity a_A which brings about same potential change. The potential response curve obtained in the matched potential method is shown in Figure 2.5. This method provides practically realistic values of $K_{A,B}^{Pot}$. The characteristics of Matched Potential Method are that the charge number on primary and interfering ions is not taken into consideration and Nernstian responses are assumed neither

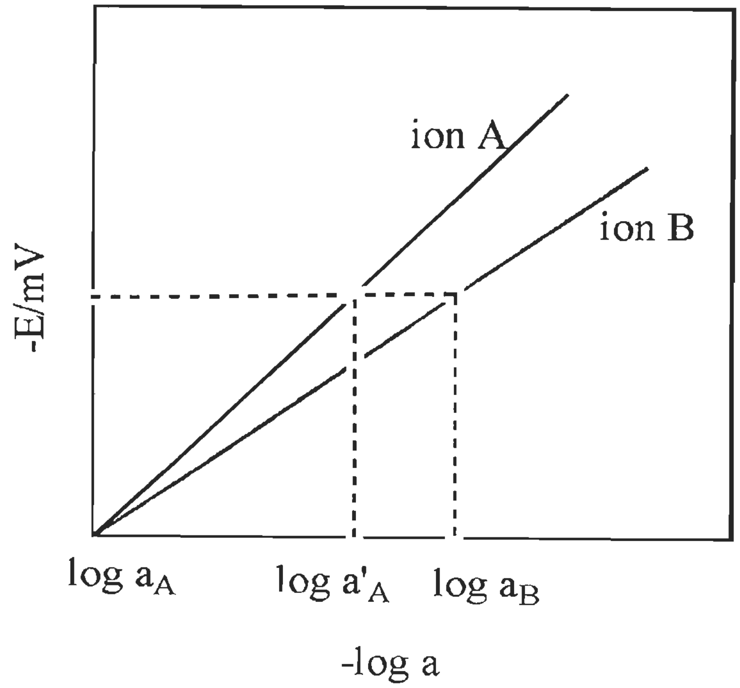


Figure 2.5: Potential *vs.* log a_A plot illustrating the determination of selectivity coefficient by Matched potential method (activity of B = a_B)

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 [39].

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

References

1. Baiulescu, G.E. and Cosofret, V.V., "Applications of ion-selective membrane electrodes in organic analysis", Ellis Horwood Ltd., Chinchester (1977).
2. Moody, G.J. and Thomas J.D.R., "Selective ion sensitive electrodes", Merrow Publishing Co. Ltd. (1971).
3. Bailey, P.L., "Analysis with ion-selective electrodes", 2nd Ed., Heyden, London (1980).
4. IUPAC, Analytical Chemistry Division, "Commission on Analytical Nomenclature", *Pure Appl. Chem.*, **48**, 127 (1976).
5. Inczedy, J., Lingyel, T. and Ure, A.M., "Compendium of analytical nomenclature, definitive rules 1997", Blackwell Science, Oxford, UK (1998).
6. Buck, R.P. and Lindner, E., "Recommendations for nomenclature of ion-selective electrodes", *Pure Appl. Chem.*, **66**, 2527 (1994).
7. Buck, R.P. and Cosofret, V., "Recommended procedure for calibration of ion-selective electrodes", *Pure Appl. Chem.*, **65**, 1849 (1993).
8. 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).
9. Gupta, V.K. and Singh, L.P., "Ion selective electrodes for sensing metal cations", *Encyclopedia of sensors*, **5**, 133 (2006).
10. Mikhailov, S.M., Shvarev, A. and Bakker. E.E., "New trends in ion-selective electrodes", *Electrochemical Sensors, Biosensors and Their Biomedical Applications*, 17, (2008).
11. Moody, G. J., Oke, R.B. and Thomas, J.D.R., "Calcium-sensitive electrode based on a liquid ion exchanger in a poly(vinyl chloride) matrix", *Analyst*, **95**, 910 (1970).
12. 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).
13. Qin, Y., Peper, S. and Bakker, E.E., "Plasticizer-free polymer membrane ion-selective electrodes containing methacrylic copolymer matrix", *Electroanalysis*, **14**, 1375 (2002).

14. 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).

15. Singh, A.K., Bhattacharjee, G., Singh, M. and Chandra, S., "A new macrocyclic polystyrene-based membrane sensor for zinc", *Electroanalysis*, **9**, 1005 (1997).

16. 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).

17. 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).

18. 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).

19. Mikhelson, K.N., "Ion-selective electrodes in PVC matrix", *Sens. Actuators, B*, **18**, 31 (1994).

20. Simon, M. A. and Kusy, R.P., "The molecular, physical and mechanical properties of highly plasticized poly(vinyl chloride) membranes", *Polymer*, **34**, 5106 (1993).

21. 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).

22. 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).

23. Eugster, R., Rosatzin, T., Rusterholz, B., Aebersold, B., Pedrazza, U., Ruegg, D., Schmid, A., Spichiger, U.E. and Simon, W., "Plasticizers for liquid polymeric membranes of ion-selective chemical sensors", *Anal. Chim. Acta*, **289**, 1 (1994).

24. Morf, W.E., Kahr, G. and Simon, W., "Reduction of the anion interference in neutral carrier liquid-membrane electrodes responsive to cations", *Anal. Lett.*, 7, 9 (1974).

25. Petrukhin, O.M., Kharitonov, A.B., Frakiisky, E.V., Urusov, Y.I., Zhukov, A.F., Shipway, A.N. and Baulin, V.N., "The effect of lipophilic anionic additives on detection limits of ion-selective electrodes based on ionophores with phosphoryl complexing groups", *Sens. Actuators, B*, **76**, 653 (2001).
26. 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).
27. 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).
28. "IUPAC Compendium of Analytical Nomenclature", Pergamon Press, Oxford (1978).
29. Ganjali, M.R., Norouzi, P. and Rezapour, M., "Potentiometric ion-selective sensors", *Encyclopedia of sensors*, **8**, 197 (2006).
30. 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).
31. de Viteri, F.J.S. and Diamond, D., "Determination and application of ion-selective electrode model parameters using flow injection and simplex optimization", *Analyst*, **119**, 749 (1994).
32. Umezawa, Y., "CRC handbook of ion-selective electrodes: selectivity coefficients", CRC Press, Bocca Raton, FL (1990).
33. Umezawa, Y., Umezawa, K. and Sato, H., "Selectivity coefficients for ion selective electrodes: Recommended methods for reporting values", *Pure Appl. Chem.*, **67**, 507 (1995).
34. Macca, C., "Determination of potentiometric selectivity", *Anal. Chim. Acta*, **321,** 1 (1996).
35. Buck, R.P. and Lindner, E., "Recommendation for nomenclature of ion-selective electrode", *Pure Appl. Chem.*, **66**, 2527 (1994).
36. Bakker, E., Pretsch, E. and Bühlmann, P., "Selectivity of potentiometric ion sensors", *Anal. Chem.*, **72**, 1127 (2000).

37. Bakker, E., "Selectivity of liquid membrane ion-selective electrodes", *Electroanalysis,* **9**, 7 (1997).

38. 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).

39. Horvai, G., "The matched potential method, a generic approach to characterize the differential selectivity of chemical sensors", *Sens. Actuators, B*, **43**, 94 (1997).

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

41. Umezawa, Y., Buhlmann, P., Umezawa, K., Tohda, K. and Amemiya, S., "Potentiometric selectivity coefficients of ion selective electrodes", *Pure Appl. Chem.*, **72**, 1851 (2000).

42. 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).

Chapter 3

Schiff Bases As Copper Ion-Selective Electrodes

3.1 Introduction

The design and synthesis of ligands that, upon coordination with metal ions can induce high selectivity and sensitivity constitute an important issue in modern coordination chemistry. In this context, Schiff base ligands are topical in connection and they have played a special role as chelating ligands in main group and transition metal coordination chemistry, due to their stability under a variety of oxidative and reductive conditions, and to the fact that imine ligands are border line between hard and soft Lewis bases [1, 2]. These ligands have been amongst the most thoroughly studied in the past few years. For following reasons, Schiff bases have been found to be among the most attractive ligands.

- The steric and electronic effect around the metal core can be finely tuned by an appropriate selection of electron withdrawing or electron donating substituents incorporated into the Schiff bases. As a consequence of this, these are able to stabilize different metals in various oxidation states, controlling the performance of metals in a large variety of useful catalytic transformations.
- The two donor atoms, N and O, of the chelated Schiff base exert two opposite electronic effects: the phenolate oxygen is a hard donor known to stabilize the higher oxidation state of the metal atom whereas the imine nitrogen is a soft donor and accordingly will stabilize the lower oxidation states of the metal ion [3].
- Schiff bases are currently prepared in high yield through one step procedures *via* condensation of common aldehydes with amines, in practically quantitative yields [4] and have good solubility in common solvents.

They are used in diverse range of applications such as in organic synthesis [5-7], as liquid crystals [8], as heterogeneous catalysts [9], as well as in many biological aspects, *viz.*, proteins, visual pigment [10], enzymic aldolization [11], decarboxylation reactions [12], in pyridoxal phosphate degradation [13] and mechanistic investigations of the drugs used in pharmacology, biochemistry and physiology [14]. These ligands have proved to be very effective in constructing supramolecular architectures such as coordination polymers, double helixes and triple helicates. Schiff bases are potential anticancer drugs and when administered as their metal complexes, the anticancer activity of these complexes is enhanced in comparison to the free ligand. They can accommodate different metal centres involving various coordination modes allowing successful synthesis of homo and heterometallic complexes with varied stereochemistry [15]. This feature is employed for modelling active sites in biological systems [16].

Additionally, they are widely used for analytical purposes such as their use as extracting agents in liquid-liquid [17], solid phase [18] and cloud-point extraction techniques [19]. The ability of these ligands to reversibly bind oxygen [20], their catalytic activity in the hydrogenation of olefins [21] and photochemical properties [22] has also been reported. However, the latest research has revealed that these entities provide the opportunity to design new systems for selective recognition of specific metal ions [23]. The lipophilic ability of Schiff bases provide geometric and cavity control for host guest complexation modulation and thus produces remarkable selectivity, sensitivity and stability for a specific ion. Potentiometric sensors comprising Schiff bases ligands as electroactive ingredient into PVC-membranes, for the fabrication of a variety of cations [24-29] and anions [30-35], have been reported. The subsequent discussion shows that the determination of Cu^{2+} ions is important and a number of ISEs have been developed using different materials for this purpose.

Copper is an essential trace element and present in all land and marine organisms. It is widely used for industrial, agricultural and domestic purposes and is therefore widely distributed in the environment. It is a proven fact that copper plays an important role in many biological processes, such as blood formation and functioning of various enzymes but its maximum tolerable level is 2.0 mg L^{-1} [36-38]. However, relatively higher concentration of copper can be tolerated by human beings but its excessive intake manifests in certain diseases in humans such as gastrointestinal catarrh, hypoglycaemia, Menke's syndrome and Wilson's disease [39, 40]. Thus, the determination of copper at low level concentration is important in view of its utility as well as toxicity.

Cu^{2+} ion-selective electrodes

Due to urgent need for selective potentiometric determination of trace amounts of copper ions, especially in food and water samples, a variety of ion carriers have been used as ionophores in the construction of ion selective electrodes (ISEs) for Cu^{2+} determination [41-68]. A mixture of $CuS-Ag_2S$ was used as electroactive material to prepare copper selective electrodes by early workers [69, 70] but these electrodes showed significant interferences to Hg^{2+}, Hg^{+}, Ag^{+} and Fe^{3+}. Later on, Kamata *et al.* developed Cu^{2+}- selective sensors using solid membranes of thiuramdisulfide [71], xylene-bis-(diethyldithiocarbamate) [72] and *o*-xylenebis-(dithiocarbamate) [73] but these sensors worked in the narrow concentration range of 1.0×10^{-5} - 1.0×10^{-1} mol L^{-1}. Xia *et al.* [74] reported a Cu^{2+}-selective sensor based on *N,N'*-(1,4-butylediene)-1-thiauram disulphide which exhibited a working concentration range of 0.8 μM - 10 mM. Jain *et al.* [75] reported PVC based membrane sensors incorporating 3,5,7,7,10,12,14,14-octamethyl-1,4, 8,ll-tetraazacyclotetradeca-4,ll-diene diperchlorate and 5,7,7,12,14,14-hexamethyl-1, 4, 8, 11-tetrazacyclotetradeca-4,ll-diene dipercholrate which worked in the concentration range of 10 μM - 0.1 M. Various Schiff bases *viz.*, *bis*-thiophenalpropanediamine [76], diphenylisocyanatebis(acetylacetone) ethylenediimine [77], salens [78], *bis*-(2-hydroxyacetophenone)butane-2,3-dihydrazone [79], 1,2-*bis*(E-2-hydroxybenzylidene-amino)anthracene-9,10-dione [80], 2,2′-[1,2-ethanediylbis(nitriloethylidene)]bis(1-naphthalene) [81] and Schiff base complexes [82-85] have also been used as excellent neutral ion carriers in the construction of highly selective Cu^{2+} membrane electrodes. Ganjali *et al.* [86] reported a highly selective membrane coated graphite electrode based on a novel Schiff base *bis*-2-thiophenal propanediamine (TPDA) for Cu^{2+} ion determination in black tea. This electrode worked over a wide working concentration range (1.0×10^{-1} to 6.0×10^{-8} mol L^{-1}) with a detection limit of 3.0×10^{-8} mol L^{-1}. Chandra *et al.* developed Cu^{2+}-selective electrodes using a Zinc Complex [87], 8,11,14-triaza-1, 4-dioxo,5(6), 16(17)-dibenzocycloseptadecane [88] and 1, 2, 5, 6, 8, 11-hexaazacyclododeca-7, 12-dione-2, 4, 8, 10-tetraene [89] as selective ionophores. Sadeghi *et al.* [90] investigated the potentiometric response characteristics of a new Cu^{2+}-membrane electrode based on erythromycinethyl succinate (EES). The electrode exhibited a Nernstian response to Cu^{2+} over the activity range 1.5×10^{-2} to 2.0×10^{-6} mol L^{-1} with a detection limit of 6.3×10^{-7} mol L^{-1}. Shamsipur *et al.* [91] developed Cu^{2+}-selective PVC membrane (PME) and coated graphite electrode (CGE) based on a benzo-substituted macrocyclic diamide. Some other neutral ligands [92-101] were explored as sensing materials for the development of Cu^{2+} selective sensors by many researchers. Thus, the review of literature reveals that the most of the reported Cu^{2+}-ion selective sensors generally show some limitations; (i) poor detection limit, (ii) narrow working concentration range, (iii) interference to some ions, (iv) narrow useful pH range and (v) slow response. It is, therefore, still necessary to have better performing sensors for quantitative determination of copper in view of its toxicity. Taking an account of the highly desirable attributes of Schiff bases, we have also explored 2-[{(2-hydroxyphenyl)imino}methyl]-phenol (L_1, Figure 1) and 2-[{(3-hydroxyphenyl)-imino}methyl]-phenol (L_2, Figure 2) as highly selective and sensitive ionophores for preparing ISEs for Cu^{2+} ions. As a result, PVC based membranes electrodes of these ionophores were fabricated using different plasticizers and investigated as Cu^{2+}-selective sensors for the estimation of Cu^{2+} ions in various samples. The results of these investigations are presented in this Chapter.

3.2 Experimental

3.2.1 Reagents

Reagent grade, oleic acid (OA), dibutyl phthalate (DBP), dibutyl sebacate (DBS), benzyl acetate (BA), *o*-nitrophenyloctylether (*o*-NPOE), tetrahydrofuran (THF) and high molecular weight PVC were procured from E. Merck (Mumbai) and used as received. 2-aminophenol, 3-aminophenol, Glaxo Ltd. (Mumbai) and salicylaldehyde, Loba Chemie Ltd. (Mumbai) were reagent grade and used as received. AR grade Copper nitrate and other metal salts (E. Merck) was used throughout. Double distilled water was used to prepare stock solution (0.1 M) of metals which was then diluted to prepare solutions of different concentrations.

3.2.2 Apparatus and instrumentation

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 in real samples were determined on a Perkin Elmer-3100 Atomic Absorption Spectrophotometer. Infrared spectra of ligands were recorded as KBr discs on a FTIR, Nexus, Thermo Nicolet in the range 4000-650 cm^{-1}. A Shimadzu UV 1601 PC Double Beam Spectrophotometer, with a 10 mm path length silica cell, was used for recording the UV-Vis spectra of ligands. ^{1}H NMR spectra were recorded on a Bruker DRX 500 MHz spectrometer at the Institute Instrumentation Centre, Indian Institute of Technology, Roorkee. 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 Schiff's bases

The ligands L_1 and L_2 were synthesized according to reported method [102].

3.2.3.1 Synthesis of 2-[{(2-hydroxyphenyl)imino}methyl]-phenol [L_1]

2-Aminophenol (0.218 g, 2 mmol) was dissolved in 50 ml dried ethanol at elevated temperature under nitrogen atmosphere. Salicylaldehyde (0.244 g, 2 mmol) in ethanol was added drop-wise to this solution. The reaction mixture was heated under refluxing condition. Orange precipitates were observed within 10 min. Reaction was continued for 1 h. Precipitates were filtered, washed with toluene and dried in a vacuum oven at 60 °C, orange crystals were obtained. m.p. 110°C. Elemental *Anal. Calc.* for $C_{13}H_{11}NO_2$: C, 73.23; H, 5.20; N, 6.57. Found: C, 73.28; H, 5.33; N, 6.61 %. IR(KBr, cm^{-1}) 1614 (s, $\nu_{C=N}$). 3453(m, ν_{O-H}), ^{1}H NMR ($CDCl_3$, δ/ppm): 6.7-7.3 (m, 8H), 8.5 (s, 1H), 11.3 (s, 2H).

3.2.3.2 Synthesis of 2-[{(3-hydroxyphenyl)imino}methyl]-phenol [L_2]

3-Aminophenol (0.218 g, 2 mmol) was dissolved in 50 ml dried ethanol at elevated temperature under nitrogen atmosphere. Salicylaldehyde (0.244 g, 2 mmol) in ethanol was added drop-wise to this solution. The reaction mixture was heated under refluxing condition for 2 h. Orange yellow precipitates were observed. Precipitates were filtered and washed with toluene, and dried in a vacuum at room temperature (≈ 30°C), orange yellow crystals were obtained. m.p. 125°C. *Anal. Calc.* for $C_{13}H_{11}NO_2$: C, 73.23; H, 5.20; N, 6.57. Found: C, 74.28; H, 5.14; N, 6.22 %. IR (KBr, cm^{-1}) 1620 ($\nu_{C=N}$). 3664 (m, $\nu_{O\text{-}H}$), ^1H NMR ($CDCl_3$, δ/ppm): 6.8-7.8 (m, 8H), 8.3 (s, 1H), 11.3 (s, 2H)

3.2.4 Preparation of polymeric membranes electrodes

In the present work ion sensitive membranes of the PVC matrix were fabricated according to the procedure described by Craggs *et al.* [103]. An important requirement for making PVC membranes of an ion selective electrode is that the membrane ingredients should be soluble in some fast evaporating solvent. The ionophores, PVC, different plasticizers and anionic additives, used in the present investigations, were found to be soluble in THF. Therefore, a number of membrane cocktails were formulated by dissolving varying amounts of membrane components (PVC, Ionophore, Plasticizer and liphophilic additive) in 5 mL THF. After thorough dissolution, the homogeneous mixture was concentrated to about 2 mL by evaporating THF and it was then poured into polyacrylate rings placed on a smooth glass plate. The solution should be poured gently so that bubbles are not formed. A pad of filter papers and a heavy weight are then placed on top of the ring and it was left for one day at room temperature to allow complete evaporation of THF. After the evaporation of solvent, a transparent membrane was obtained which was removed carefully from the glass plate. It was attached to one end of Pyrex glass tube with araldite.

Besides the critical role of the nature of ion carrier in preparing membrane electrodes, some other important parameters for PVC based membrane electrodes, such as amount of ionophore, nature of solvent mediator, plasticizer/PVC ratio and nature of additive used are known to significantly influence the sensitivity and selectivity. Therefore, the ratio of membrane ingredients, time of contact and concentration of equilibrating solution was optimized to provide membranes which gave reproducible results and best performance. Blank membranes having only PVC were also prepared to observe whether any background potentials being produced due to binding material or not. The membrane that gave reproducible results and best performance was selected for detailed studies.

3.2.5 Preparation of sandwich membranes

Ion-selective electrode membranes were cast from above mentioned procedure. The blank membranes (without ionophore) having same composition of other ingredients were also prepared. The sandwich membrane was made by fusing two individual membranes (ordinarily one without ionophore and one with the same components and an additional ionophore) together with pressure from a metal spatula immediately after blotting them individually dry with tissue paper. The drying step is necessary to avoid an aqueous phase between the two membrane segments. The combined segmented membrane was then rapidly mounted into the electrode body with the ionophore-containing segment facing the sample solution. The obtained sandwich membrane was visibly checked for air bubbles before mounting in electrode body. The segmented sandwich membrane technique was reported to be a simple method to investigate the binding properties in the membrane.

3.2.6 Equilibration of membranes and potential measurements

The membranes were equilibrated for 4 days in 1.0×10^{-1} mol L^{-1} $Cu(NO_3)_2$ solution. The potentials were measured by varying the concentration of $Cu(NO_3)_2$ in test solution in the range $1.0 \times 10^{-8} - 1.0 \times 10^{-1}$ mol L^{-1}. Each solution was stirred and the potential reading was recorded when it became stable, and then plotted as logarithmic function of Cu^{2+} cation activity. The activities of metal ions were calculated using the following modified form of the Debye–Huckel equation:

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

where μ is the ionic strength and Z the valency.

The potential were measured out at 25 ± 0.1°C using saturated calomel electrodes (SCE) as reference electrodes with the following cell assembly:

Hg/Hg_2Cl_2| KCl (satd)|0.1 M $Cu(NO_3)_2$ ||PVC membrane||test solution|Hg/Hg_2Cl_2| KCl

3.2.7 Determination of stability constant

A selective complexation of analyte ions by ionophores is primarily responsible for the selectivity of an ion electrode. Stability constant of the ion–ionophore complex within the membrane phase is an important parameter that indicates the practical selectivity of the electrode. Despite the wide use of lipophilic and chemically immobilized ionophores in chemical electrode 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 electrode. A different approach to measure stability constants of ion-ionophore complexes in ISE membranes depends on recording electrical potential of segmented sandwich membranes [104]. 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 due to complexation with the sample ions. Therefore, this effect could be used to determine the formation/stability constant of the ion-ionophore complex.

Thus, the ion-ionophore complex formation constants were evaluated by a potentiometric sandwich membrane method [105]. In this method, the membrane potential measurement is carried out using a two-layer sandwich membrane, where only one side contains the ionophore. This sandwich membrane electrode was brought in contact with the aqueous ion solution, having identical concentration on both sides, and the change in cell potential was recorded.

On the other hand the cell potential of another membrane having no ionophore was measured. As reported in the method, the membrane potential (E_M) is determined by subtracting the cell potential for a membrane without ionophore from that of the sandwich membrane. The formation constant is then calculated from the following equation:

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

where L_T is the total concentration of ionophore in the membrane segment, R_T is the concentration of lipophilic ionic site additives, n is the ion–ionophore complex stoichiometry, and R, T and F are the gas constant, the absolute temperature, and the Faraday constant. The ion I 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 if ion pairing can be neglected. 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 given analyte ions.

3.3 Results and Discussion

3.3.1 Evaluation of stability constants

In preliminary experiments, the complexation of the (L_1) and (L_2) with a number of metal ions was investigated using segmented sandwich membrane method. The Stability constants (log β_{ML_n}) of several metal complexes of L_1 and L_2 were determined as described in section 3.2.5. The resulting values of stability constants for the examined complexes are compiled Table 3.1. A careful analysis of the values show that the Schiff bases L_1 and L_2 interact strongly with Cu^{2+} ion (stability constant 7.14 for CuL_1 complex and 4.38 for CuL_2 complex) but show moderately weak interaction with other metals such as Co, Ni, Fe, Hg, Cd, Mg, Pb, Zn, Ag, La, Na, Ca (having stability constant of metal complexes in the range 3.82-0.66). As under identical conditions of measurement Schiff base L_1 and L_2 have high affinity of complexation with Cu^{2+} ion, the two ligands can be used for the development of Cu^{2+}-selective electrodes.

3.3.2 Optimization of membrane composition

Various components which are usually present in membrane are binder (matrix material), ionophore, plasticizer and anion excluding additive. It is well known that the composition [106-108] of the membrane affects the performance of the electrode. The performance characteristics which render an electrode better are wide working concentration range, low response time and Nernstian slope. In terms of these parameters, various membranes of different compositions were prepared by dissolving varying amounts of ionophore (L_1 and L_2), PVC, anion excluder (NaTPB) with various plasticizers viz., *o*-NPOE, DBP, BA and DBS in THF and their potential response to Cu^{2+} ion in the concentration range $1.0 \times 10^{-8} - 1.0\times 10^{-1}$ mol L^{-1} was measured. The performance characteristics determined from the potential response plots are given in

Tables 3.2 and 3.3. It is seen from the Tables that the blank membranes no. 1 and 11, having only plasticizer, additives and PVC show very poor response to Cu^{2+} with a very small slope and short working range (6.2×10^{-3}- 1.0×10^{-1} mol L^{-1}). The membranes no. 2 and 12 which only have ionophore show an increased slope (21.6 mV decade $^{-1}$ and 20.4 mV decade $^{-1}$ of $a_{Cu}{}^{2+}$ respectively) and working concentration range (5.2×10^{-5}–1.0×10^{-2} mol L^{-1} with L_1 and 7.5×10^{-5}–1.0×10^{-2} mol L^{-1} with L_2) indicating the selectivity of ionophores. Though in the presence of ionophore the response of membrane electrodes is better as compared to blank membranes but the slope is sub-Nernstian and the working concentration range is still much shorter. Therefore the electrodes need improvement with regard to performance.

The membrane no. 3 to 10 for L_1 having different compositions were prepared and investigated and their performance characteristics also gathered in Table 3.2. It is well established that a plasticizer with good lipophilicity and capacity to dissolve the membrane components tend to improve the performance of electrode with regard to sensitivity, selectivity, working concentration range and response time [109]. This is because the plasticizer forms a liquid organic phase through which the cations can easily extract into the membrane. Therefore the performance of PVC based membranes of L_1 and L_2 was examined in the presence of different plasticizers *viz.*, *o*-NPOE, DBP, BA and DBS in PVC matrix and their potential response plots are shown in Figures 3.3 and 3.4. A perusal of Table 3.2 shows that the addition of plasticizers improves the slope and broadens the working concentration range. However, the membrane electrode no. 3 of L_1 with DBS plasticizer shows better characteristics in terms of slope (27.9 mV decade $^{-1}$ of $a_{Cu}{}^{2+}$) and working concentration range (4.0×10^{-7}-1.0×10^{-2} mol L^{-1}). The performance of this membrane electrode was further improved by adding oleic acid as a lipophilic anion additive. The use of 10 % (w/w) oleic acid (OA) was found suitable for the electrodes based on ionophore L_1 and the electrode no. 7 having membrane composition L_1:DBS:OA:PVC ratio as 6:54:10:30 (%, w/w) shows the best performance characteristics with regard to Nernstian slope (29.5 mV decade^{-1} of $a_{Cu}{}^{2+}$) and widest activity range (3.2×10^{-8} -1.0×10^{-1} mol L^{-1}). In the 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 membranes [110]. Therefore, the effect of amount of ionophore was also seen and it was found that 6 % (w/w) amount of the ionophore (L_1) is optimum with regard to all performance parameters. It can be seen from the Table 3.2 that both the slope and the working concentration range were affected as the amount of ionophore was changed from its optimum concentration.

Similarly the membranes no. 13 to 20 of L_2 having different compositions were also prepared and their performance characteristics are gathered in Table 3.3. The additive used in these preparations was more lipophilic NaTPB (3 %, w/w). It is seen that in this case also the addition of plasticizers improves the performance characteristic of membrane electrode. However, the effect of DBP is the best and 8 % (w/w) amount of ionophore is optimum with regard to all performance parameters. Hence, the membrane no. 17 having composition L_2:DBP:NaTPB:PVC ratio as 8:58:3:31 (%, w/w) was observed to perform best as it exhibited the widest working concentration range (2.2×10^{-7} - 1.0×10^{-2} mol L^{-1}) with Nernstian slope (29.6 mV decade^{-1}).

The experimentally determined results show that DBS gives better results with L_1 and DBP is better for L_2. This is due to a synergism between lipophilicity and polarity and the best results are obtained when these properties gain an intermediate value. The use of NaTPB with L_2 was to enhance the selectivity of the membrane electrodes and to promote the exchange kinetics at the sample membrane interface.

3.3.3 Potentiometric calibration characteristics of electrodes

The calibration curve (Figure 3.5) for the two copper ion selective electrodes indicate that the electrode no. 7 based on L_1 exhibits Nernstian slope (29.5 ± 0.5 mV decade^{-1} of $a_{Cu}{}^{2+}$) over a wide concentration range of 3.2×10^{-8} - 1.0×10^{-1} mol L^{-1} with a detection limit of 2.0×10^{-8} mol L^{-1}, while electrode no. 17 based on L_2 exhibits a Nernstian slope (29.6 ± 0.5 mV decade^{-1} of $a_{Cu}{}^{2+}$) and linear concentration range of $2.2 \times 10^{-7} - 1.0 \times 10^{-2}$ mol L^{-1} with limit of detection as 1.2×10^{-7} mol L^{-1}.

3.3.4 Effect of internal solution and equilibration time

According to generally adopted ion electrode response formalism, the influence of the concentration of internal solution on the potential response of the polymeric membrane electrode based on L_1 and L_2 was studied. The concentration of copper nitrate solution was varied from 1.0×10^{-1} to 1.0×10^{-3} mol L^{-1} and the potential response of the electrode was obtained. It was found that the best results in terms of slope and working concentration range were obtained with internal solution of activity 1.0×10^{-1} mol L^{-1}. Thus, 1.0×10^{-1} mol L^{-1} concentration of the reference solution was quite appropriate for the smooth functioning of the proposed electrode. The membrane to be used in ISEs should generate noiseless and reproducible potential. These characteristics generally depend on the optimizing ratio of membrane ingredients, time of contact and concentration of equilibrating solution. Imperfect equilibration gives rise to erratic potential and large response time. Studies revealed that a minimum of 4 days equilibration was necessary for generating reproducible and stable potentials in 0.1 M Cu^{2+} solution for this sensor.

3.3.5 Potentials response of the electrodes based on L_1 and L_2 to various cations

A number of PVC membrane electrodes based on Schiff bases L_1 and L_2 were prepared under optimum conditions and the potential response characteristics of the electrodes were evaluated for various metal ions. A perusal of working concentration range, slope and detection limit of potential response curve for these cations are presented in Figures 3.6 and 3.7. It was observed from these figures that the membrane electrodes based on two ionophores gave linear potential response over a wide concentration range for Cu^{2+} ion whereas for the other cations the response is poor with narrow working concentration range. It appears that these electrodes are responding to Cu^{2+} strongly as compared to many ions studied. The preferential response toward Cu^{2+} ion is believed to be associated with the strong complexation of Cu^{2+} with the donor sites of the ligands.

3.3.6 Potentiometric selectivity of the polymeric membrane electrodes

Selectivity is the most important characteristic as it determines the extent of utility of any electrode in real sample measurements. It gives the response of ion-selective electrode for the primary ion in the presence of other ions present in solution, which is expressed in terms of the potentiometric selectivity coefficients. Potentiometric selectivity coefficient ($K_{Cu,B}^{Pot}$) for the Cu^{2+} selective electrodes were determined by the IUPAC recommended Matched potential method (MPM). This method has an advantage of removing limitations imposed by Nicolsky-Eisenman equation while calculating selectivity coefficient by other methods. These limitations include non-Nernstian behavior of interfering ion and problem of inequality of charges of primary and interfering ions. According to this method, change in potential of a reference solution of primary ion of activity; $a_{Cu^{2+}} = 1.0 \times 10^{-4}$ mol L^{-1} is noted with addition of primary ions of specified activity ($a_{Cu}^{2+} = 5.0 \times 10^{-4}$ mol L^{-1}). In a separate experiment, interfering ions ($a_B = 1.0 \times 10^{-2}$ mol L^{-1}) were kept on being added in small amounts to the identical reference solution until the change in potential is same as that produced by adding primary ion. The amount of interfering ion added producing same change was noted and the selectivity coefficients were calculated using equation (13) of section 2.3.3 as described in Chapter 2. The selectivity coefficients so calculated for the electrodes based on ionophores L_1 and L_2 are listed in Table 3.4. A value of 1.0 for selectivity coefficient shows equal response of the electrode both to primary and interfering ions. The values of selectivity coefficient those are smaller than 1.0, show that the electrode is selective to primary ions over interfering ions. It is seen from the Table 3.4 that the selectivity coefficients are of the order of 10^{-3} or smaller, indicating that the electrode is appreciably selective to Cu^{2+} ions over a number of foreign ions studied.

3.3.7 Influence of pH on the Performance of the Electrodes

The dependence of potential response of the electrodes was investigated over the pH range 1.0 to 12.0 for 1.0×10^{-2} mol L^{-1} and 1.0×10^{-3} mol L^{-1} Cu^{2+} solution. The operational pH range was studied by varying the pH of the test solution with 0.1 M nitric acid or sodium hydroxide. The effect of change in the pH of the solutions on the potential response of the electrodes is shown in Figure 3.8 and 3.9. A close examination of these figures shows that the potentials are independent of pH in the range 3.0 – 8.5 and 3.2 – 7.5 for electrode no. 7 and 17 respectively. Therefore, the same was taken as the useful working pH range of the electrodes based on L_1 and L_2. The change in potential below pH 3 and 3.2 is apparently due to the interference of H^+ and above pH 8.5 and 7.5 due to strong hydrolysis of Cu^{2+} ions.

3.3.8 Determination of response time of the proposed electrodes

It is well known that the response time of an ISE is an important factor in its evaluation. Response time of an ion selective electrode is defined as the length of time between the instant at which the ISE and a reference electrode are brought into contact with a sample solution and the first instant at which the cell gives a constant potential. To measure the response time of the proposed electrodes the concentration of the test solution was successively changed from 1.0×10^{-7} mol L^{-1} to 1.0×10^{-2} mol L^{-1}. The results depicted in Figure 3.10 and 3.11 show that the time needed to reach a potential within ± 1 mV of the final equilibrium value after successive immersion of the electrodes in a series of Cu^{2+} ions, each having a ten-fold difference in concentration, is 7 s for electrode no. 7 and 10 s for electrode no. 17. This indicates fast exchange kinetics of complexation-decomplexation of Cu^{2+} ions with the ionophores L_1 and L_2 at the sample-membrane interface. To evaluate the reversibility of the electrode, a similar procedure in the opposite direction was adopted. The measurements were performed in the sequence of high-to-low (1.0×10^{-2} mol L^{-1} - 1.0×10^{-7} mol L^{-1}) sample concentrations and the results showed that the potentiometric response of the electrodes were reversible. Reproducibility of the electrode was examined by using a set of similarly constructed electrodes under the optimum conditions. The result showed good reproducibility (± 0.6 mV) for the electrode.

3.3.9 Determination of lifetime of the electrodes

The deviation from the Nernstian behaviour has been ascribed to decomposition of the ionophore and loss of other components in the membrane phase that contacts aqueous test solution [111]. To investigate the lifetime of the electrodes, the potential response characteristics of these electrodes were measured from time to time over a period of 100 days. It is important to mention that electrodes were stored in 0.1 mol L^{-1} Cu^{2+} solution when not in use. During this period, the potential response of both electrodes was measured by recording the calibration graph at different time intervals. The results summarised in Tables 3.5 and 3.6, showed the effect of soaking time on the performance characteristics of the electrodes. It was observed that up to 90 days there is no significant change in the slope and working concentration range of electrode no. 7 whereas this period is 45 days for electrode no. 17. Above this period the performance of both the electrodes started deteriorating. Thus the shelf- life of the electrodes can be taken as 3 and 1.5 months for the electrode no. 7 and 17 respectively.

3.3.10 Effect of non-aqueous content on the performance of the electrodes

The real samples may contain non-aqueous content, so the performance of the electrodes was also investigated in partially non-aqueous solutions of methanol-water, ethanol-water and acetone-water mixtures containing 10 %, 20 %, 25 %, 30 % and 35 % (v/v) non-aqueous impurities. The performance characteristics of the electrodes were measured in each solution and the results are summarized in Table 3.7. It was found that the electrodes do not show any appreciable change in working concentration range and slope in non-aqueous mixtures containing up to 25 % (v/v) organic impurities, but acetone affected the performance of the electrodes more than others. However, above 25 % (v/v) non-aqueous content, the potentials showed drift with time both in working concentration range and slope which may be probably due to leaching of the ionophore at higher organic content.

3.4 Analytical Applications

The high selectivity and sensitivity showed by the electrode no. 7 and 17 based on L_1 and L_2 for Cu^{2+} makes them potentially useful for monitoring the concentration of

Cu^{2+} in various samples. Trace levels of copper, present in edible oils, tomato plant material and river water were analyzed by AAS and the proposed electrode.

3.4.1 Estimation of Cu^{2+} in edible oils and tomato plant leaves

The oil and plant samples were ashed and the residue was dissolved in dilute hydrochloric acid and then it was diluted to 50 mL. The pH of the test solution was adjusted to 5.0 and Cu^{2+} concentration was determined by AAS and the proposed electrodes. The results obtained by two different analytical techniques are compiled in Table 3.8.

3.4.2 Determination of Cu^{2+} in the Ganga river water

The electrodes were also successfully applied to determine copper directly in the Ganga river water sample. The water sample was acidified with 0.1 M HCl to adjust the pH of the sample at 5.0. The results obtained from the triplicate measurements are compared with those determined by atomic adsorption spectrometry (AAS) and are summarized in Table 3.8.

It was observed from the Table 3.8 that there is a close agreement between the results obtained by AAS and the proposed electrodes. It shows that the estimation of copper by the proposed electrodes is reliable. Thus the electrodes can be used successfully to determine Cu^{2+} ion concentration in tomato plant, edible oils and river water and also in other samples.

3.4.3 Potentiometric titration

The electrodes were also found useful as indicator electrodes in potentiometric titration of Cu^{2+} against EDTA under laboratory condition. A 10 ml solution of 5.0×10^{-3} M Cu^{2+} was titrated against a 1.0×10^{-2} M EDTA solution at pH 6. As indicated from

Figures 3.12 and 3.13, a sharp inflection point, corresponding to 1:1 stoichiometry was observed in the titration plot.

3.5 Conclusion

Two Schiff bases, *viz.*, 2-[{(2-hydroxyphenyl)imino}methyl]-phenol [L_1] and 2-[{(3-hydroxyphenyl)imino}methyl]-phenol [L_2] were found to show strong affinity for Cu^{2+} and hence, they can be used as selective ionophores for preparing Cu^{2+} ion selective electrodes PVC based membrane electrodes based on L_1 and L_2 showed good selectivity towards Cu^{2+} and wider working concentration range (3.2×10^{-8} to 1.0×10^{-1} mol L^{-1} and 2.2×10^{-7} to 1.0×10^{-2} mol L^{-1}) with fast response times 7 and 10 s respectively. A comparison of the proposed electrodes with reported ISEs (Table 3.9) show that the electrodes show better performance characteristics than most reported ISEs in terms of working concentration range, detection limit, response time and selectivity. Most reported electrodes show interference to Na^+ [44], Cd^{2+} [44, 50], Ag^+ [50, 51], Hg^{2+} [81, 50], Pb^{2+} [44, 49], Zn^{2+} [47, 48], Co^{2+} [44, 50] where as the proposed electrode show better selectivity with respect to these ions, therefore superior to them. However, there are only few reported electrodes [51, 79, 86] which show similar selectivity but have poor sensitivity (higher detection limit). Thus the proposed electrode is better when compared to the reported electrodes in terms of working concentration range, detection limit and response time.

The utility of the proposed electrodes was demonstrated by using them to determine copper in various samples (edible oils, tomato plant material, and river water) and hence, the availability of these electrodes can be termed as a good addition to the family of Cu^{2+} ion selective electrodes.

Tables

Table 3.1: Stability constants of various ion-ionophore complexes with L_1 and L_2

Cation (M^{n+})	Stability constants (log β_{ML}) (n=2)	
	L_1	L_2
Cu^{2+}	7.14	4.38
Co^{2+}	3.27	2.98
Ni^{2+}	3.82	3.62
Fe^{2+}	3.71	2.02
Hg^{2+}	1.76	1.61
Cd^{2+}	1.72	1.68
Mg^{2+}	1.62	0.74
Pb^{2+}	1.60	0.69
Zn^{2+}	1.57	1.32
Ag^{+}	1.43	0.85
Ca^{2+}	1.22	0.96
Na^{+}	0.97	0.72
La^{3+}	0.83	0.66

* n – Ligand to metal ratio

Table 3.2: Potentiometric response characteristics of Cu^{2+} PVC membrane sensors based on ionophore L_1.

Electrode No.	Composition of membrane (%, w/w)				Slope (mV decade^{-1} of $a_{Cu}{}^{2+}$)	Linear range (mol L^{-1})
	Ionophore	Plasticizer	Additive	PVC		
1	-	60	10, OA	30	<9.2	6.2×10^{-3}-1.0×10^{-1}
2	6, L_1	-	-	94	21.6	5.2×10^{-5}-1.0×10^{-2}
3	6, L_1	54, DBS	-	40	27.9	4.0×10^{-7}-1.0×10^{-2}
4	6, L_1	54, BA	-	40	23.9	7.4×10^{-6}-5.0×10^{-2}
5	6, L_1	54, DBP	-	40	22.3	7.8×10^{-6}- 2.0×10^{-2}
6	6, L_1	54, NPOE	-	40	20.8	2.8×10^{-6}-3.0×10^{-2}
7	6, L_1	54, DBS	10, OA	30	29.5	3.2×10^{-8}-1.0×10^{-1}
8	5, L_1	54, DBS	10, OA	31	26.8	1.3×10^{-7}-1.0×10^{-2}
9	4, L_1	54, DBS	10, OA	32	25.4	9.6×10^{-7}-1.0×10^{-2}
10	6, L_1	-	10, OA	84	21.3	1.5×10^{-5}-1.0×10^{-2}

Table 3.3: Potentiometric response characteristics of Cu^{2+} PVC membrane sensors based on ionophore L_2.

Electrode No.	Composition of membrane (%, w/w)				Slope (mV decade^{-1} of $a_{Cu}{}^{2+}$)	Linear range (mol L^{-1})
	Ionophore	Plasticizer	Additive	PVC		
11	-	60	3, NaTPB	37	<14.2	1.5×10^{-3}-1.0×10^{-1}
12	8, L_2	-	-	92	20.4	7.5×10^{-5}-1.0×10^{-2}
13	8, L_2	58, DBP	-	34	27.3	3.1×10^{-6}-1.0×10^{-2}
14	8, L_2	58, NPOE	-	34	33.1	8.3×10^{-6}-7.2×10^{-2}
15	8, L_2	58, DBS	-	34	35.3	5.2×10^{-6}- 4.0×10^{-2}
16	8, L_2	58, BA	-	34	34.9	6.5×10^{-6}-7.0×10^{-2}
17	8, L_2	58, DBP	3, NaTPB	31	29.6	2.2×10^{-7}-1.0×10^{-2}
18	7, L_2	58, DBP	3, NaTPB	32	26.4	8.8×10^{-6}-1.0×10^{-2}
19	6, L_2	58, DBP	3, NaTPB	33	24.8	4.2×10^{-6}-1.0×10^{-2}
20	8, L_2	-	3, NaTPB	89	20.5	1.0×10^{-5}-1.0×10^{-2}

Table 3.4: Selectivity coefficients of Cu^{2+}-selective electrodes for various interfering ions by MPM

Interfering ions (B)	Selectivity Coefficients ($K^{Pot}_{A,B}$)	
	Electrode no. 7	Electrode no. 17
Co^{2+}	6.4×10^{-3}	7.3×10^{-4}
Ni^{2+}	2.3×10^{-3}	1.2×10^{-3}
Fe^{2+}	1.6×10^{-4}	1.8×10^{-3}
Hg^{2+}	7.2×10^{-5}	2.8×10^{-5}
Cd^{2+}	4.6×10^{-5}	5.2×10^{-5}
Mg^{2+}	3.2×10^{-5}	9.4×10^{-6}
Pb^{2+}	2.6×10^{-5}	8.4×10^{-6}
Zn^{2+}	1.8×10^{-5}	3.2×10^{-5}
Ag^{+}	1.3×10^{-5}	4.3×10^{-5}
La^{3+}	8.8×10^{-6}	7.9×10^{-6}
Na^{2+}	7.3×10^{-6}	7.6×10^{-6}
Ca^{2+}	6.5×10^{-5}	3.3×10^{-3}

Table 3.5: Effect of soaking time on the potential response of the electrode no. 7

Soaking time (Days)	Slope (mV decade^{-1} $a_{Cu}{}^{2+}$)	Working concentration range (mol L^{-1})	Detection limit (mol L^{-1})
15	29.5	3.2×10^{-8}-1.0×10^{-1}	2.0×10^{-8}
30	29.5	3.2×10^{-8}-1.0×10^{-1}	2.0×10^{-8}
45	29.3	3.6×10^{-8}-1.0×10^{-1}	2.2×10^{-8}
60	29.2	3.6×10^{-8}-1.0×10^{-1}	2.3×10^{-8}
90	28.9	4.1×10^{-8}-1.0×10^{-1}	2.9×10^{-8}
95	23.8	8.7×10^{-7}-5.0×10^{-2}	1.9×10^{-7}
100	26.3	9.6×10^{-6}-1.0×10^{-3}	5.3×10^{-7}

Table 3.6: Effect of soaking time on the potential response of the electrode no. 17

Soaking time (Days)	Slope (mV decade^{-1} of $a_{Cu}{}^{2+}$)	Working concentration range (mol L^{-1})	Detection limit (mol L^{-1})
15 days	29.6	2.5×10^{-7}-1.9×10^{-2}	1.2×10^{-7}
30 days	29.2	2.5×10^{-7}-1.9×10^{-2}	1.3×10^{-7}
45 days	28.5	6.8×10^{-7}-1.9×10^{-2}	7.1×10^{-7}
60 days	27.2	2.5×10^{-6}-1.9×10^{-2}	1.9×10^{-6}
90 days	26.9	3.5×10^{-6}-1.9×10^{-2}	2.3×10^{-5}
95 days	25.2	2.3×10^{-5}-1.0×10^{-2}	1.5×10^{-5}
100 days	24.4	7.3×10^{-5}-1.0×10^{-2}	4.5×10^{-5}

Table 3.7: Effect of partially non-aqueous medium on the performance of Cu^{2+} electrodes no.7 and 17).

Non-aqueous content (% v/v)	Working concentration range (mol L^{-1})	Slope (mV $decade^{-1}$ of a_{Cu}^{2+})	Working concentration range (mol L^{-1})	Slope (mV $decade^{-1}$ of a_{Cu}^{2+})
0	3.2×10^{-8}-1.0×10^{-1}	29.5±0.5	2.2×10^{-7}-1.0×10^{-2}	29.6±0.5
Methanol				
10	3.2×10^{-8}-1.0×10^{-1}	29.5	2.2×10^{-7}-1.0×10^{-2}	29.6
20	3.2×10^{-8}-1.0×10^{-1}	29.5	2.4×10^{-7}-1.0×10^{-2}	29.4
25	5.0×10^{-8}-1.0×10^{-1}	29.1	2.4×10^{-7}-1.0×10^{-2}	29.4
30	9.2×10^{-7}-5.0×10^{-3}	24.2	1.2×10^{-6}-5.0×10^{-2}	28.1
35	3.2×10^{-6}-1.0×10^{-3}	22.6	6.4×10^{-5}-1.0×10^{-2}	23.9
Ethanol				
10	3.2×10^{-8}-1.0×10^{-1}	29.5	2.2×10^{-7}-1.0×10^{-2}	29.6
20	3.2×10^{-8}-1.0×10^{-1}	29.5	2.2×10^{-7}-1.0×10^{-2}	29.6
25	3.8×10^{-8}-2.3×10^{-1}	29.3	2.8×10^{-7}-5.0×10^{-2}	29.2
30	6.2×10^{-7}-5.0×10^{-2}	24.6	9.4×10^{-7}-5.5×10^{-2}	25.1
35	5.0×10^{-6}-2.0×10^{-3}	23.9	2.0×10^{-6}-2.0×10^{-3}	24.3
Acetone				
10	3.2×10^{-8}-1.0×10^{-1}	29.5	2.4×10^{-7}-5.0×10^{-2}	29.4
20	5.1×10^{-8}-1.0×10^{-1}	29.1	3.1×10^{-7}-1.0×10^{-2}	29.1
25	6.2×10^{-8}-3.0×10^{-1}	28.9	5.2×10^{-7}-5.0×10^{-2}	28.6
30	8.2×10^{-6}-2.4×10^{-2}	25.6	1.2×10^{-6}-5.0×10^{-3}	23.9
35	7.3×10^{-6}-5.0×10^{-2}	22.8	7.3×10^{-5}-5.0×10^{-3}	20.8

Table 3.8: Quantification of copper in edible oils, plant material and water samples using AAS and proposed Cu^{2+} selective electrodes no. 7 and 17

Sample	Copper found by AAS (μg/ml)[a]	Copper Found by electrode no. 7 (μg/ml) [a] (%, RSD)	Copper Found by electrode no.17 (μg/ml) [a] (%, RSD)
Soya bean oil	0.90 ± 0.06	0.93 ± 0.02 (2.15)	0.91 ± 0.01 (1.09)
Sunflower oil	0.97 ± 0.08	0.96 ± 0.02 (2.08)	0.94 ± 0.05 (5.32)
Tomato plant leaves	121 ± 2.1	122 ± 1.3 (1.06)	119 ± 0.8 (0.67)
River water sample	14.9 ± 0.5	15.3 ± 0.7 (4.58)	15.2 ± 1.2 (7.89)

[a] *Average of three replicate measurements*

Table 3.9: Comparison of the proposed Cu^{2+}-selective electrodes with the reported electrode

Ref. no.	Linear range (M)	Slope (mV/decade of activity)	Detection limit (M)	Selectivity coefficients (-log $K^{Pot}_{Cu,B}$)	pH range	Response time (s)
100	8.0×10^{-6}-1.0×10^{-1}	29.5	3.0×10^{-6}	Mg^{2+}(2.3),Sr^{2+}(2.1),Ba^{2+}(2.1), Co^{2+}(2.2),Cd^{2+}(2.2),Pb^{2+}(0.5), Zn^{2+}(2.3), Zn^{2+}(2.2)	3.0-6.5	15
44	7.9×10^{-6}-1.0×10^{-1}	29.9	7.0×10^{-6}	Ba^{2+}(0.6), Co^{2+}(0.2),Pb^{2+}(0.6), Ag^{+}(0.6), NH_4^{+}(0.6), Li^{+}(0.7), Na^{+}(0.2), K^{+}(0.2)	2.1-6.3	11
47	1.0×10^{-5}-1.0×10^{-2}	25.9	2.1×10^{-7}	Sr^{2+}(2.8), Ba^{2+}(3.0), Ni^{2+}(2.5), Co^{2+}(2.7),Hg^{2+}(2.5),Cd^{2+}(2.4), Zn^{2+}(1.7), Pb^{2+} (0.5)	4.5-7.0	15
48	1.0×10^{-6}-1.0×10^{-1}	28.2	5.0×10^{-7}	Ni^{2+}(3.0),Co^{2+}(3.0),Cd^{2+}(2.9), Zn^{2+}(1.7), NH_4^{+}(2.5), Li^{+}(2.3), K^{+}(2.9), Mg^{2+}(2.4)	3.3-6.5	10
81	5.0×10^{-8}-2.0×10^{-2}	29.8	3.1×10^{-6}	Mg^{2+}(3.0),Ni^{2+}(1.5),Co^{2+}(2.1), Cd^{2+}(2.1),Zn^{2+}(2.1),Na^{+}(1.3), Hg^{2+}(1.2), Pb^{2+}(2.4)	4.0-7.0	5
77	6.0×10^{-8}-1.0×10^{-1}	29.8	6.0×10^{-7}	Ca^{2+}(3.4),Mg^{2+}(3.5),Ni^{2+}(3.7), Co^{2+}(3.6),Cd^{2+}(3.5), Zn^{2+}(3.4), K^{+}(3.7), Pb^{2+}(3.7).	3.0-7.5	15
49	1.0×10^{-6}-1.0×10^{-1}	29.0	1.4×10^{-7}	Ca^{2+}(3.6),Ni^{2+}(3.2),Co^{2+}(4.0), Pb^{2+}(0.7), Zn^{2+}(2.2), K^{+}(2.3), Mg^{2+}(3.6), Na^{+}(2.6)	3.2-5.5	9
50	5.0×10^{-8}-1.0×10^{-2}	29.5	4.0×10^{-8}	Ni^{2+}(2.9),Co^{2+}(1.1),Cd^{2+}(2.2), Pb^{2+}(1.5),Zn^{2+}(2.4), Hg^{2+}(0.8), Ag^{+}(0.5), Na^{+}(2.9).	3.0-9.5	12
86	6.0×10^{-8}-1.0×10^{-1}	29.1	3.0×10^{-8}	Co^{2+}(3.4),Pb^{2+}(3.4),Zn^{2+}(3.77), Ni^{2+}(3.6), Cd^{2+} 3.9), Sr^{2+} (4.1), Na^{+} (4.0), K^{+} (4.00)	2.8-5.8	<15
51	1.0×10^{-7} -1.0×10^{-3}	28.1	6.3×10^{-8}	Ag^{+}(0.0),Ni^{2+}(4.2),Co^{2+}(5.2), Zn^{2+}(4.7),Fe^{3+}(4.9),Mn^{2+}(5.2), Cd^{2+}(4.3)	5.3-7.2	6
27	5.0×10^{-8} - 1.0×10^{-2}	29.6	3.0×10^{-8}	Co^{2+}(4.4),Pb^{2+}(4.6),Zn^{2+}(4.5), Ni^{2+}(4.5),Hg^{2+}(4.9),Ag^{+}(5.1), Li^{+}(5.7),Gd^{3+}(4.6)	2.8-5.8	<15
Present work	3.2×10^{-8} - 1.0×10^{-2}	29.5	2.0×10^{-8}	Co^{2+}(2.2),Ni^{2+}(3.6),Fe^{2+}(3.8), Hg^{2+}(4.1),Cd^{2+}(4.3),Mg^{2+}(4.5), Pb^{2+}(4.6),Zn^{2+}(4.7)	3.0-8.5	5
Present work	2.5×10^{-7} - 1.9×10^{-2}	29.6	1.2×10^{-7}	Co^{2+}(3.1),Ni^{2+}(2.9),Fe^{2+}(2.7), Hg^{2+}(4.5),Cd^{2+}(4.8),Mg^{2+}(4.5), Pb^{2+}(5.0), Ag^{+}(4.5)	3.0-8.5	5

Figures

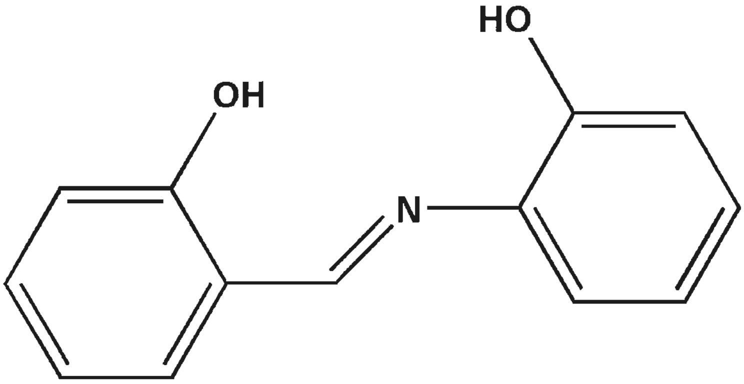


Figure 3.1: Structure of 2-[{(2-hydroxyphenyl)imino}methyl]-phenol [L_1]

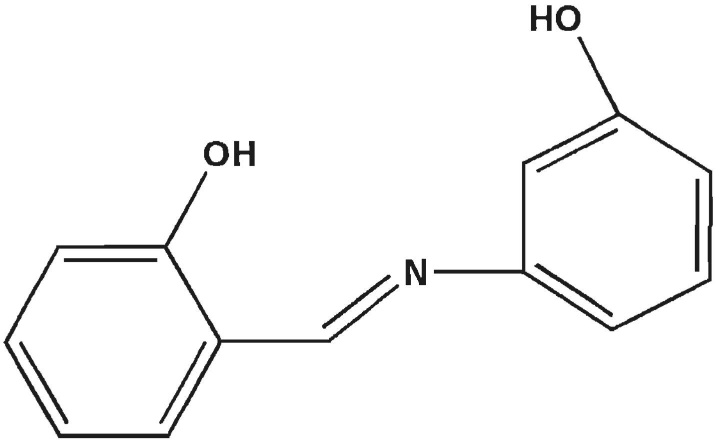


Figure 3.2: Structure of 2-[{(3-hydroxyphenyl)imino}methyl]-phenol [L_2]

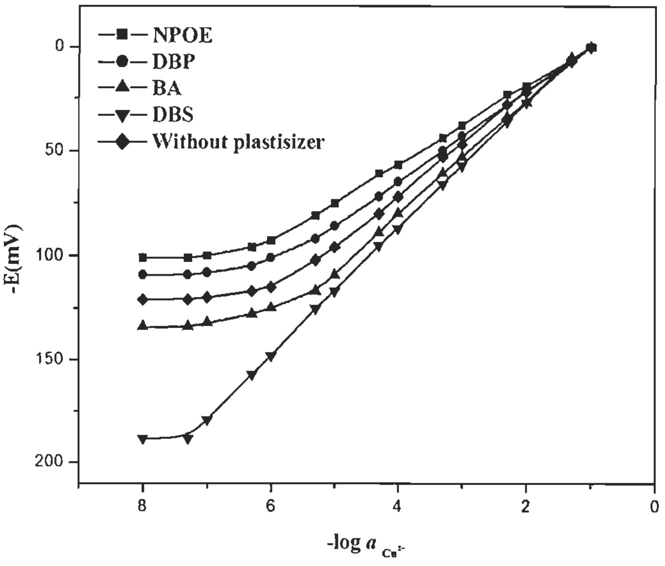


Figure 3.3: Potential responses of Cu^{2+} membrane sensors based on L_1 with different plasticizer

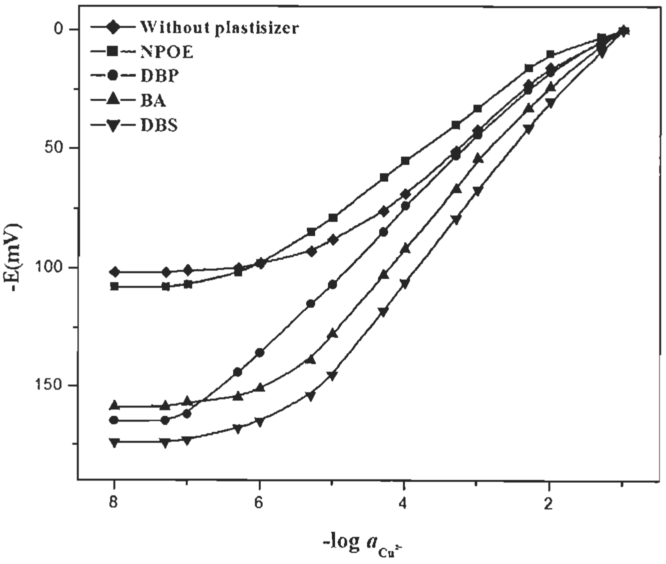


Figure 3.4: Potential responses of Cu^{2+} membrane sensors based on L_2 with different plasticizer

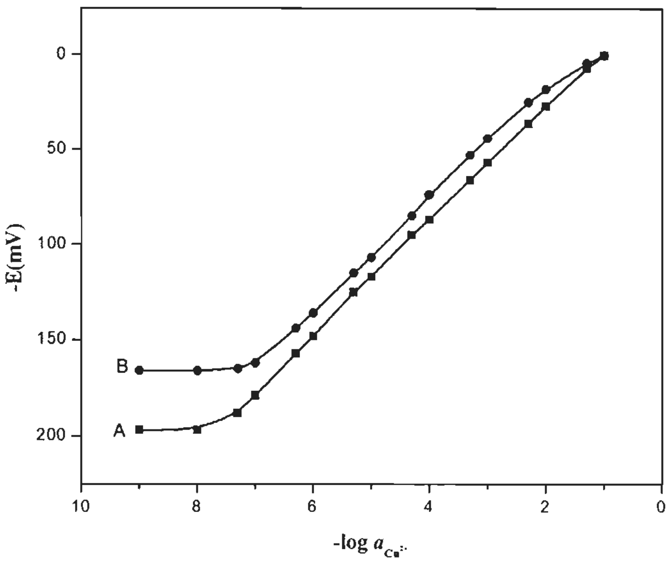


Figure 3.5: Calibration plot for copper ion selective electrodes: (A) for sensor no. 7 (B) for sensor no. 17

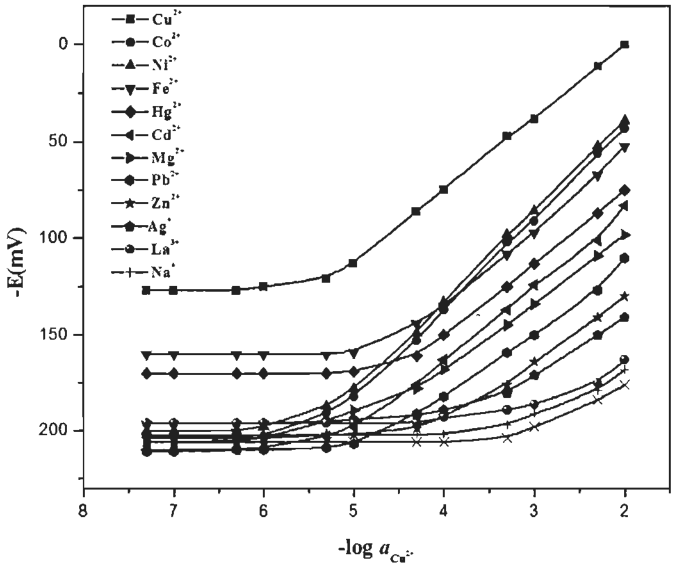


Figure 3.6: Potentiometric response of membrane sensors based on L_1 for different cations

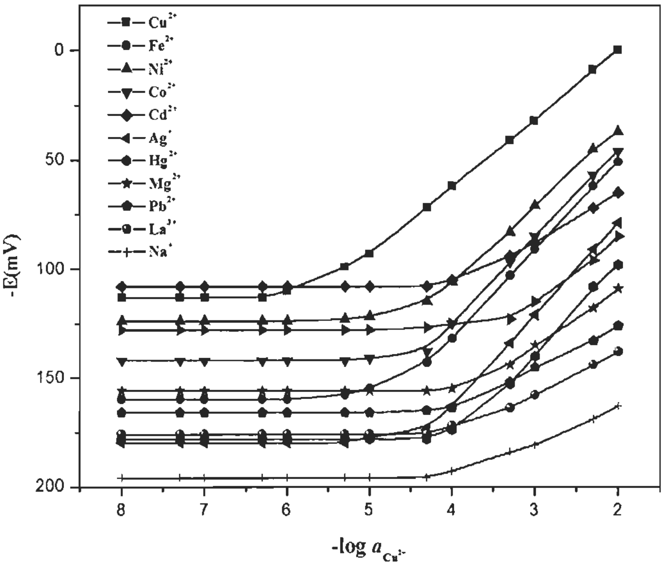


Figure 3.7: Potentiometric response of membrane sensors based on L_2 for different cations

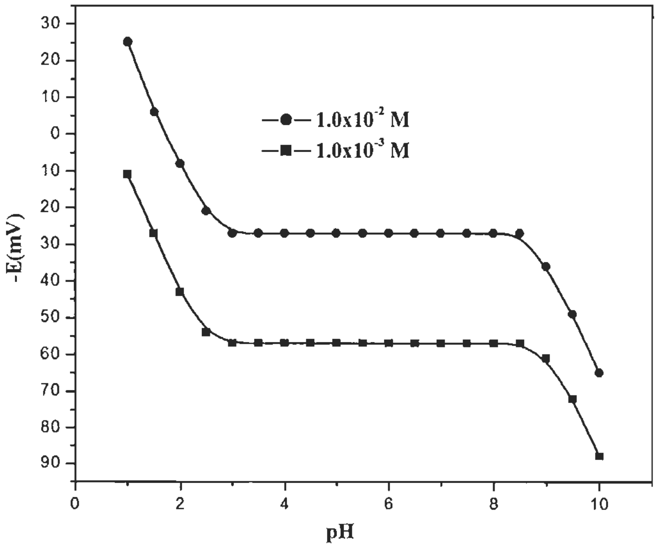


Figure 3.8: Effect of pH on cell potential of sensor no. 15 based on L_1 at 1.0×10^{-2} M and 1.0×10^{-3} M respectively

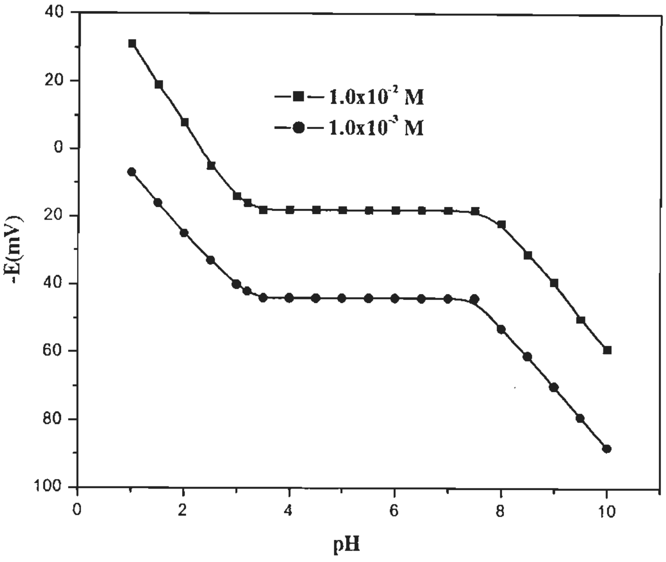


Figure 3.9: Effect of pH on cell potential of sensor no. 25 based on L_2 at 1.0×10^{-2} M and 1.0×10^{-3} M respectively.

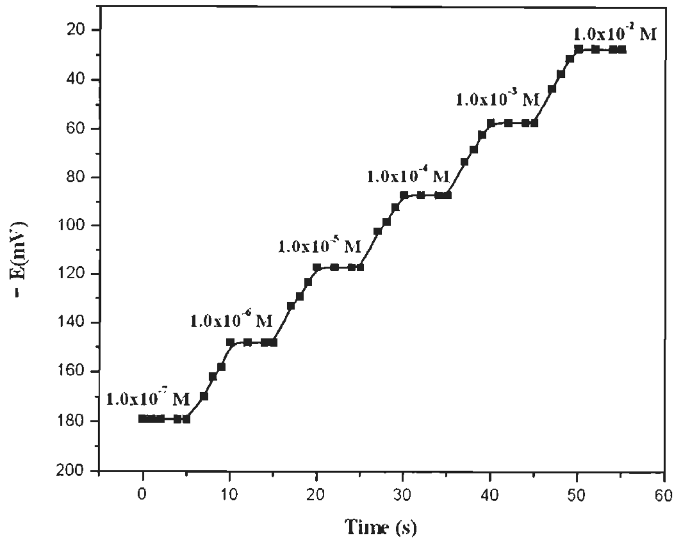


Figure 3.10: Dynamic response time of the copper electrode based on L_1 (sensor no. 7) for ten-fold step changes in concentration of Cu^{2+}

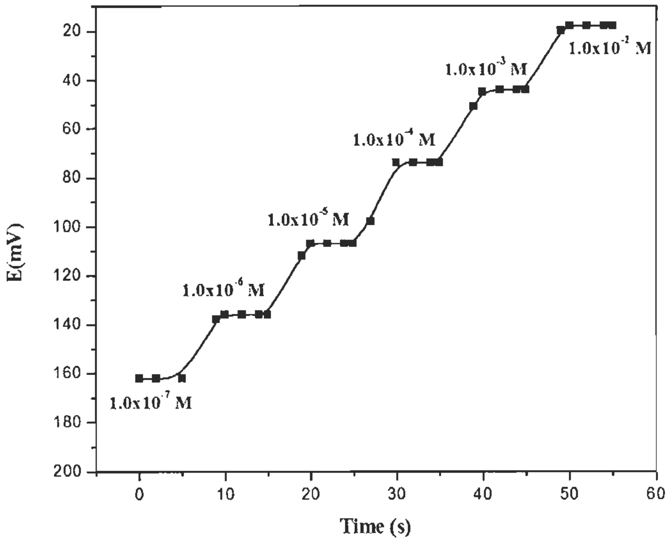


Figure 3.11: Dynamic response time of the copper electrode based on L_2 (sensor no. 17) for ten-fold step changes in concentration of Cu^{2+}

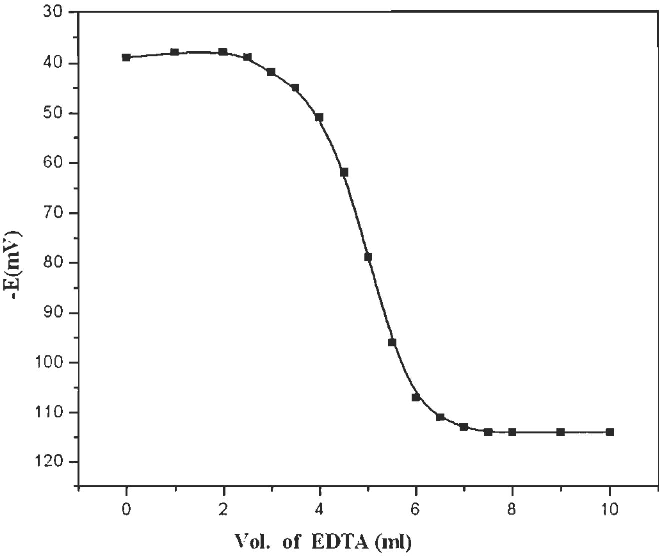


Figure 3.12: Potentiometric titration curve for 10 ml of 5.0×10^{-3} M Cu^{2+} with 1.0×10^{-2} M EDTA, at constant pH range 6 using the proposed sensor no. 7

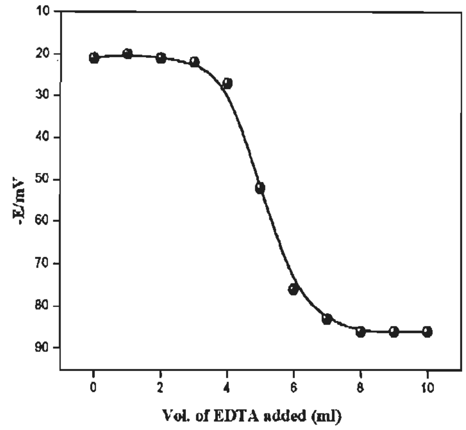


Figure 3.13: Potentiometric titration curve for 10 ml of 5.0 × 10^{-3} M Cu^{2+} with 1.0 × 10^{-2} M EDTA, at constant pH range 6 using the proposed sensor no. 17

References

1. Garnovskii, A.D., Nivorozhkin, A.L. and Minkin, V.I., "Ligand environment and the structure of Schiff bases adducts and tetracoordinated-chelates", *Coord. Chem. Rev.*, **126**, 1 (1993).
2. Ziessel, R.,"Schiff-based bipyridine ligands: Unusual coordination features and mesomorphic behaviour", *Coord. Chem. Rev.*, **216**, 195 (2001).
3. Drozdzak, R., Allaert, B., Ledoux, N., Dragutan, I., Dragutan, V. and Verpoort, F., "Ruthenium complexes bearing bidentate Schiff base ligands as efficient catalysts for organic and polymer syntheses", *Coord. Chem. Rev.*, **249**, 3055 (2005).
4. Guerriero, P., Tamburini, S. and Vigato, P.A., "From mononuclear to polynuclear macroacyclic complexes", *Coord. Chem. Rev.*, **139**, 17 (1995).
5. Katsuki, T., "Catalytic asymmetric oxidations using optically active (salen) manganese(III) complexes as catalysts", *Coord. Chem. Rev.*, **140**, 109 (1995).
6. Ito, Y.N. and Katsuki, T., "Asymmetric catalysis of new generation chiral metallosalen complexes", *Bull. Chem. Soc. Jpn.*, **72**, 603 (1999).
7. Pospisil, P.J., Carsten, D.H. and Jacobsen, E.N., "X-ray structural studies of highly enantioselective Mn(salen) epoxidation catalysts", *Chem. Eur. J.*, **2**, 974 (1996).
8. Hoshino, N., "X-Ray structural studies of highly enantioselective Mn(salen) epoxidation catalysts", *Coord. Chem. Rev.*, **174**, 77 (1998).
9. Canali, L. and Sherrington, D.C., "Utilization of homogeneous and supported chiral metal(salen) complexes in asymmetric catalysis", *Chem. Soc. Rev.*, **28**, 85 (1999).
10. Morton, R.A. and Pitt, G.A.J., "Rhodopsin. IX. pH and the hydrolysis of indicator yellow", *Biochem. J.*, **59**, 128 (1955).
11. Grazi, E., Rowley, R.T., Cheng, T., Tchola, O. and Horecker, B.L., "The mechanism of action of aldolases III. Schiff base formation with lysine", *Biochem. Biophys. Res. Commun.*, **9**, 38 (1962).
12. Fridovitch, I. and Westheimer, F.H., "On the mechanism of the enzymatic decarboxylation of acetoacetate",*J. Am. Chem. Soc.*, **84**, 3208 (1962).
13. Hammes, G.G. and Fasella, P., "A kinetic study of glutamic-aspartic transaminase", *J. Am. Chem. Soc.*, **84**, 4644 (1962).

14. Morvay, C.J. and Herczeg, O., "Study of 5-nitro-2-furaldehyde derivatives, II. Preparation, spectra and antibacterial activities of Schiff bases with sulfonamides", *Acta. Phys. Chem.*, **31**, 717 (1985).

15. Chowdhury, C.R., Dey, S.K., Mondal, N., Mitra, S., Mahalli, S.O.G. and Malik, K.M.A., "Synthesis and structural characteization of [Ni($Me_2NCH_2CH_2CH_2N=CHC_6H_4O)_2$]", *J. Chem. Crystallogr.*, **31**, 57 (2002).

16. Kolodziej, A.F., "The chemistry of nickel-containing enzymes", *Prog. Inorg. Chem.*, **41**, 493 (1994).

17. Hirayama, H., Takeuchi, I., Honjo, T., Kubono, K. and Kokusen, H., "Ion-pair extraction system for the mutual separation of lanthanides using divalent quadridentate schiff bases", *Anal. Chem.*, **69**, 4814 (1997).

18. Shamspur, T., Sheikhshoaie, I. and Mashhadizadeh, M.H., "Flame atomic absorption spectroscopy (FAAS) determination of iron(III) after preconcentration on to modified analcime zeolite with 5-((4-nitrophenylazo)-*N*-(2,4′-dimethoxyphenyl))salicylaldimine by column method", *J. Anal. At. Spectrom.*, **20**, 476 (2005).

19. Shemirani, F., Abkenar, S.D., Mirroshandel, A.A., Salavati-Niasari, M. and Kozania, R.R., "Preconcentration and speciation of chromium in water samples by atomic absorption spectrometry after cloud-point extraction", *Anal. Sci.*, **19**, 1453 (2003).

20. Jones, R.D., Summerville, R.D. and Basolo, F., "Synthetic oxygen carriers related to biological systems", *Chem. Rev.*, **79**, 139 (1979).

21. Henrici-Olive, G. and Olive, S., "The chemistry of the catalyzed hydrogenation of carbon monoxide", Springer, Berlin (1984).

22. Osman, A.H., "Synthesis and characterization of cobalt(II) and nickel(II) complexes of some Schiff bases derived from 3-hydrazino-6-methyl[1,2,4]triazin-5(4H)one", *Trans. Met. Chem.*, **31**, 35 (2006).

23. Peng, X., Tang, X., Qin, W., Dou, W., Guo, Y., Zheng, J., Liu, W. and Wang, D., "Aroylhydrazone derivative as fluorescent sensor for highly selective recognition of Zn^{2+} ions: Syntheses, characterization, crystal structures and spectroscopic properties", *Dalton Trans.*, **40,** 5271 (2011).

24. Abbaspour, A., Esmaeilbeig, A.R., Jarrahpour, A.A., Khajeh, B. and Kia, R., "Aluminium(III)-selective electrode based on a newly synthesized tetradentate Schiff base", *Talanta*, **58**, 397 (2002).

25. Mahajan, R.K., Kaur, I. and Kumar, M., "Silver ion-selective electrodes employing Schiff base *p*-tert-butyl calix[4]arene derivatives as neutral carriers", *Sens. Actuators, B*, **91**, 26 (2003).

26. Shamsipur, M., Saeidi, M., Yari, A., Yaganeh-Faal, A., Mashhadizadeh, M.H., Azimi, G., Naeimi, H. and Sharghi, H., "UO_2^{2+} ion-selective membrane electrode based on a naphthol-derivative Schiff's base 2,2'-[1,2-ethandiylbis (nitriloethylidene)]bis(1-naphthalene)", *Bull. Kor. Chem. Soc.*, **25**, 629 (2004).

27. Jain, A.K., Gupta, V.K., Ganeshpure, P.A. and Raisoni, J.R., "Ni(II)-selective ion sensors of salen type Schiff base chelates", *Anal. Chim. Acta.*, **553**, 177 (2005).

28. Gupta, V.K., Agarwal, S., Jakob, A. and Lang, H., "A zinc-selective electrode based on N,N'-bis(acetylacetone)ethylenediimine", *Sens. Actuators, B*, **114**, 812 (2006).

29. Gupta, V.K., Jain, A.K. and Maheshwari, G., "Manganese(II) selective PVC based membrane sensor using a Schiff base", *Talanta*, **72**, 49 (2007).

30. Ying, M., Yuan, R., Li, Z., Song, Y., Li, W., Lin, H., Shen, G. and Yu, R., "Thiocyanate selective electrode based on cobalt(II) complexes of pyrazolone heterocyclic Schiff bases", *Fresenius J. Anal. Chem.*, **361**, 437 (1998).

31. Shamsipur, M., Soleymanpour, A., Akhond, M., Sharghi, H. and Naseri, M.A., "Iodide-selective carbon paste electrodes based on recently synthesized Schiff base complexes of Fe(III)", *Anal. Chim. Acta*, **450**, 37 (2001).

32. Ganjali, M.R., Norouzi, P., Gol-Mohammadi, M., Mizani, F., Poursaberi, T., Salavati-Niasari, M., Shamsipur, M., Hosseini, M. and Javanbakht, M., "Sulfate-selective PVC membrane electrode based on a strontium Schiff base complex", *Annali di Chimica*, **93**, 679 (2003).

33. Mitchell-Koch, J.T., Malinowska, E. and Meyerhoff, M.E., "Gallium(III) Schiff base complexes as novel ionophores for fluoride selective polymeric membrane electrodes", *Electroanalysis*, **17**, 1347 (2005).

34. Kumar, K.G., John, K.S. and Indira, C.J., "A chloride ion selective potentiometric sensor based on a polymeric Schiff base complex", *Ind. J. Chem. Techno.*, **13**, 13 (2006).

35. Ye, G., Chai, Y., Yuan, R., Zhou, L., Li, Y. and Zhang, L., "Salicylate ion-selective electrode based on new tetranuclear copper complexes of *o*-vanillin-methionine as neutral carriers", *Anal. Sci.*, **23**, 171 (2007).

36. Tyrala, E.E., Brodsky, N.L. and Auerbach, V.H., "Urinary copper losses in infants receiving free amino acid solutions", *Am. J. Clin. Nutr.*, **35**, 342 (1982).

37. Svediene, N., Sheina, N.M. and Silasie, G.V., "Liquid and solid-state copper-selective electrodes with a membrane based on N-aryl-substituted hydroxamic acid chelates", *Zh. Anal. Khim.*, **46**, 339 (1991).

38. Faust, S.D. and Aly, O.M., "Adsorption processes for water treatment", Butterworth, London, 1987.

39. Bull P.C. and Cox D.W., "Wilson disease and Menkes disease: new handles on heavy-metal transport", *Trends Genet.*, **10**, 246 (1994).

40. Schaefer, M. and Gitlin, G.D., "Genetic disorders of membrane transport. IV. Wilson's disease and Menkes disease", *Am. J. Phsiol*, **276,** 311 (1999).

41. Kamata, S., Yamasaki, Y., Higo, M., Bhale, A. and Fukunaga, Y.," Copper(II)-selective electrodes based on macrocyclic polythiaethers", *Analyst*, **113**, 45 (1988).

42. Kouljenovic, J., Martinac, V. and Radic, N., "Ion-sensitive behaviour of silver sulphide-based solid-state copper(II) and iodide electrodes in partially aqueous systems", *Anal. Chim. Acta*, **231**, 137 (1990).

43. 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).

44. Gupta, V.K., Prasad, R. and Kumar, A., "Preparation of ethambutol–copper(II) complex and fabrication of PVC based membrane potentiometric sensor for copper", *Talanta*, **60**, 149 (2003).

45. Szigeti, Z., Bitter, I., Toth, K., Latkoczy, C., Fliegel, D.J., Gunther, D. and Pretsch, E., "A novel polymeric membrane electrode for the potentiometric analysis of Cu^{2+} in drinking water", *Anal. Chim. Acta*, **532**, 129 (2005).

46. Jain, A.K., Gupta, V.K., Singh, L.P. and Raisoni, J.R., "Chelating ionophore based membrane sensors for copper(II) ions", *Talanta*, **66**, 1355 (2005).

47. Hassan, S.S.M., Elnemma, E.M. and Mohamed, A.H.K., "Novel potentiometric copper(II) selective membrane sensors based on cyclic tetrapeptide derivatives as neutral ionophores", *Talanta*, **66**, 1034 (2005).

48. Firooz, A.R., Mazloum, M., Safari, J. and Amini, M.K., "Coated wire copper(II)-selective electrode based on phenylglyoxal-alphamonoxime ionophores", *Anal. Bioanal. Chem.*, **372**, 718 (2002).

49. Kamata, S., Murata, H., Kubo, Y. and Bhale, A., "Copper(II)-selective membrane electrodes based on o-xylylene bis(dithiocarbamates) as neutral carriers", *Analyst*, **114**, 1029 (1989).

50. Singh, A.K., Mehtab, S. and Jain, A.K., "Selective electrochemical sensor for copper (II) ion based on chelating ionophores", *Anal. Chim. Acta*, **575**, 25 (2006).

51. Wakida, S., Sato, N. and Saito, K., "Copper(II)-selective electrodes based on a novel charged carrier and preliminary application of field-effect transistor type checker", *Sens. Actuators, B*, **30**, 187 (2008).

52. Marcin, O., Agata, M. and Krzysztof, M., "Accumulation of Cu(II) cations in poly(3,4-ethylenedioxythiophene) films doped by hexacyanoferrate anions and its application in Cu^{2+} selective electrodes with PVC based membranes", *Electrochim. Acta*, **51**, 2298 (2006).

53. 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).

54. Xia, S., Xiao, D., Yuan, H., Cheng, B., Yuan, F. and Yu, R., "Copper(II) ion-sensitive electrode using chemical vapor deposited Nb-Ge superconducting films", *Anal. Chim. Acta*, **382**, 151 (1999).

55. 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).

56. Abbaspour, A. and Kamyabi, M.A, "Copper(II)-selective electrode based on dithioacetal", *Anal. Chim. Acta*, **455**, 225 (2002).

57. Yoshimoto, S., Mukai, H., Kitano, T. and Sohrin, Y., "Copper(II)-selective membrane electrode based on hydrotris(3-isopropylpyrazolyl)methane in a poly(vinyl chloride) matrix", *Anal. Chim. Acta*, **494**, 207 (2003).

58. Mittal, S.K., Kumar, A.S.K., Gupta, N., Kaur, S. and Kumar, S., "8-Hydroxyquinoline based neutral tripodal ionophore as a copper(II) selective electrode and the effect of remote substituents on electrode properties", *Anal. Chim. Acta*, **585**, 161 (2007).
59. Kopylovich, M.N., Mahmudov, K.T. and Pombeiro, A.J.L., "Poly(vinyl) chloride membrane copper-selective electrode based on 1-phenyl-2-(2-hydroxyphenylhydrazo) butane-1,3-dione", *J. Hazard. mater.*, **186**, 1154 (2011).
60. Shamsipur, M., Rouhani, S., Ganjali, M.R., Eshghi, H. and Sharghi, H., "Copper(II)-selective membrane electrode based on a recently synthesized macrocyclic diamide", *Microchem. J.*, **63**, 202 (1999).
61. Cali, C., Foix, D., Taillades, G., Siebert, E., Gonbeau, D., Pradel, A. and Ribes, M., "Copper (II) selective electrode based on chalcogenide materials: Study of the membrane/solution interface with electrochemical impedance spectroscopy and X-ray photoelectron spectroscopy", *Mater. Sci. Eng.*, *C*, **21**, 3 (2002).
62. Pandey, P. C., "Copper (II) ion sensor based on electropolymerized undoped-polyindole modified electrode", *Sens. Actuators, B*, **54**, 210 (1999).
63. Mashhadizadeh, M.H., Mostafavi, A., Razavi, R. and Shamsipur, M., "Highly selective Cu(II) PVC membrane electrode based on 3,6,9,14-tetrathiabicyclo[9.2.1]tetradeca-11,13-diene as a suitable neutral ionophore", *Sens. Actuators, B*, **86**, 222 (2002).
64. Gupta, V.K., Jain, A.K., Maheshwari, G., Lang, H. and Ishtaiwi, Z., "Copper(II)-selective potentiometric sensors based on porphyrins in PVC matrix", *Sens. Actuators, B*, **117**, 99 (2002).
65. Park, S.J., Shon, O.J., Rim, J.A., Lee, J. K., Kim, J.S., Nam, H. and Kim, H., "Calixazacrown ethers for copper(II) ion-selective electrode", *Talanta*, **55**, 297 (2001).
66. Gholivand, M.B. and Nozari, N., "Copper(II)-selective electrode using 2,2'-dithiodianiline as neutral carrier", *Talanta*, **54**, 597 (2001).
67. Shamsipur, M., Javanbakht, M., Mousavi, M.F., Ganjali, M.R., Lippolis, V., Garau, A. and Tei, L., "Copper(II)-selective membrane electrodes based on some recently synthesized mixed aza-thioether crowns containing a 1,10-phenanthroline sub-unit", *Talanta*, **55**, 1047 (2001).

68. Gupta, V.K., Goyal, R.N., Bachheti, N., Singh, L.P. and Agarwal, S., "A copper-selective electrode based on bis(acetylacetone)propylenediimine", *Talanta*, **68**, 193 (2005).

69. Van de Leest, R.E., "Solid state ion-selective electrode for metal ions", *Analyst,* **102**, 509 (1977).

70. 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).

71. Kamata, S., Bhale, A., Fukunaga, Y. and Murata, H., "Copper(II)-selective electrode using thiuram disulfide neutral carriers", *Anal. Chem.,* **60**, 2464 (1988).

72. Kamata, S., Ogawa, F. and Fukumoto, M., "Xylene bis(dimethyldithiocarbamate) as a neutral carrier for copper (II)-selective membrane electrodes", *Chem. Lett.,* 533 (1987).

73. Kamata, S., Murata, H., Kubo, Y. and Bhale, A., "Copper(II)-selective membrane electrodes based on o-xylylene bis(dithiocarbamates) as neutral carriers", *Analyst,* **114**, 1029 (1989).

74. Xia, S.X., Xiao, D. and Yu, R.Q., "Copper ion sensitive membrane electrode based on thiauram derivative as carriers", *Fenxi Huaxue,* **22**, 892 (1994).

75. 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).

76. Poursaberi, T., Hajiagha-Babei, L., Yousefi, M., Rouhani, S., Shamsipur, M., Kargar-Razi, M., Moghimi, A., Aghabozorg, H. and Ganjali, M.R., "The synthesis of a new thiophene-derivative Schiff base and its use in preparation of copper-ion selective electrodes", *Electroanalysis,* **13**, 1513 (2001).

77. Ganjali, M.R., Emami, M. and Salavati-Nisari, M., "Novel copper(II)-selective sensor based on a new hexadentate Schiff s base", *Bull. Kor. Chem. Soc.,* **23**, 1394 (2002).

78. Fakhari, A.R., Raji, T.A. and Naeimi, H., "Copper-selective PVC membrane electrodes based on salens as carriers" *Sens. Actuators, B,* **104**, 317 (2005).

79. Gholivand, M.B., Rahimi-Nasrabadi, M., Ganjali, M.R. and Salavati-Niasari, M., "Highly selective and sensitive copper membrane electrode based on a new synthesized Schiff base", *Talanta,* **73**, 553 (2007).

80. 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-hydroxybenzylidenen-amino)anthracene-9,10-dione complex as an ionophore", *Bull. Chem. Soc. Jpn.*, **31**, 401 (2010).

81. Alizadeh, N., Ershad, S., Naeimi, H., Sharghi, H. and Shamsipur, M., "Copper(II)-selective membrane electrode based on a recently synthesized naphthol-derivative Schiff's base", *Fresen. J. Anal. Chem.*, **365**, 511 (1999).

82. Singh, L.P. and Bhatnagar, J.M., "Copper(II) selective electrochemical sensor based on Schiff Base complexes", *Talanta*, **64**, 313 (2004).

83. Tastekin, M., Tunali, F., Atakol, O. and Kilic, E., "Copper(II)-selective membrane electrodes based on Cu(II)-schiff base complexes as an ionophore", *Rev. Anal. Chem.*, **26**, 155 (2007).

84. Chandra, S., Singh, C.K. and Agarwal, H., "Polymeric membrane ion-selective electrode for copper(II) ions based on CuII-cyclohexaneone thiosemicarbazone complex", *J. Ind. Chem. Soc.*, **84**, 291 (2007).

85. Jeong, D.C., Lee, H.K. and Jeon, S., "Highly copper(II)-selective PVC membrane based on a schiff base complex of N,N'-bis-pyridin-2-ylmethylene-naphthalene-1,8-diamine as an ionophore", *Bull. Kor. Chem. Soc.*, **27**, 1593 (2006).

86. Ganjali, M.R., Poursaberi, T., Babaei, L.H., Rouhani, S., Yousefi, M., Kargar-Razi, M., Moghimi, A., Aghabozorg, H. and Shamsipur, M., "Highly selective and sensitive copper(II) membrane coated graphite electrode based on a recently synthesized Schiff's base", *Anal. Chim. Acta*, **440**, 81 (2001).

87. Chandra, S., Sharma, K., Kumar, A. and Tomar, P.K., "Cu(II) selective PVC membrane electrode based on zinc complex of acetophenonethiosemicarbazone (ZATSC) as an ionophore", *Der Pharma Chemica*, **2**, 256 (2010).

88. Chandra, S., Singh, D.R. and Agarwal, H., "Novel Cu(II) selective PVC electrode based on 8,11,14-triaza-1,4-dioxo-5(6), 16(17)-dibenzocycloseptadecane as an ionophore", *Int. J. Pure Appl. Chem.*, **2**, 415 (2007).

89. Chandra, S., Singh, C.K., Agarwal, H. and Agarwal, R.K., "A copper(II)-selective PVC membrane electrode based on a macrocyclic ligand, 1,2,5,6,8,11-hexaazacyclododeca-7,12-dione-2,4,8,10-tetraene", *Anal. Sci.*, **23**, 683 (2007).

90. Sadeghi, S. and Jahani, M., "New copper(II) ion-selective membrane electrode based on erythromycin ethyl succinate as a neutral ionophore", *Anal. Lett.*, **42**, 2026 (2009).

91. Shamsipur, M., Mizani, F., Saboury, A.A., Sharghi, H. and Khalifeh, R., "Highly selective and sensitive membrane sensors for copper(II) ion based on a new benzo-substituted macrocyclic diamide 5,6,7,8,9,10-hexahydro-2H-1,13,4,7,10-benzo-dioxatriazacyclopentadecine-3, 11(4H, 12H)-dione", *Electroanalysis*, **19**, 587 (2007).

92. Ganjali, M.R., Golmohammadi, M., Yousefi, M., Norouzi, P., Salavati-Niasari, M. and Javanbakht, M., "Novel PVC-based copper(II) membrane sensor based on 2-(1'-(4'-(1"-hydroxy-2"-naphthyl)methyleneamino)butyliminomethyl)-1-naphthol", *Anal. Sci.*, **19**, 223 (2003).

93. Akhond, M., Ghaedi, M. and Tashkhourian, J., "Development of a new copper(II) ion-selective poly(vinyl chloride) membrane electrode based on 2-mercaptobenzoxazole", *Bull. Kor. Chem. Soc.*, **26**, 882 (2005).

94. Zamani, H.A., Rajabzadeh, G., Ganjali, M.R. and Khatami, S.M., "Highly selective and sensitive copper(II) membrane sensors based on 6-methyl-4-(1-phenylmethylidene) amino-3-thioxo-1,2,4-triazin-5-one as a new neutral ionophore", *Electroanalysis*, **17**, 2260 (2005).

95. Akhond, M., Najafi, M.B., Sharghi, H., Tashkhourian, J. and Naiemi, H., "Novel copper(II)-selective membrane electrode based on a new synthesized Schiff base", *J. Chin. Chem. Soc.*, **54**, 331 (2007).

96. Mahajan, R.K. and Sood, P., "Novel copper(II)-selective electrode based on 2,2':5',2"-terthiophene in PVC matrix", *Int. J. Electrochem. Sci.*, **2**, 832 (2007).

97. Zamani, H.A., Rajabzadeh, G., Firouz, A. and Ganjali, M.R., "Determination of copper(II) in wastewater by electroplating samples using a PVC-membrane copper(II)-selective electrode", *J. Anal. Chem.*, **62**, 1080 (2007).

98. Buzuk, M., Brinic, S., Generalic, E. and Bralic, M., "Copper(II) ion selective PVC membrane electrode based on S,S'-bis(2-aminophenyl)ethanebis(thioate)", *Crot. Chem. Acta*, **82**, 801 (2009).

99. Lee, C., Kim, D.W., Kim, J., Yang, M.H., Choi, M.Y. and Kim, J.S., "Copper ion selective membrane electrode based on bis(salphenH$_2$) derivatives", *Sens. Lett.*, **8**, 297 (2010).

100. Sadeghi, S., Eslahi, M., Naseri, M.A., Naeimi, H., Sharghi, H. and Shameli, A., "Copper ion selective membrane electrodes based on some Schiff base derivatives", *Electroanalysis*, **15**, 1327 (2003).

101. Sadeghi, S., Gafarzadeh, A. and Naeimi, H., "PVC-based Cu (II)-Schiff base complex membrane coated graphite electrode for the determination of the triiodide ion", *J. Anal. Chem.*, **61**, 677 (2006).

102. Freeman, D.C. and White, C.E., "The Structure and characteristics of the fluorescent metal chelates of o,o'-dihydroxyazo compounds", *J. Am. Chem. Soc.*, **78**, 2678 (1956).

103. Craggs, A., Moody, G.J. and Thomas, J.D.R., "Procedure for the construction of all solid state PVC membrane electrodes", *J. Chem. Edu.*, **51**, 541 (1974).

104. 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).

105. 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).

106. 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).

107. Tavakkoli, N. and Shamsipur, M., "Lead-selective membrane electrode based on dibenzopyrydino-18-crown-6", *Anal. Lett.*, **29**, 2269 (1996).

108. Javanbakht, M., Ganjali, M.R., Eshghi, H., Sharghi H. and Shamsipur, M., "Mercury(II) ion-selective electrode based on dibenzo-diazathia-18-crown-6-dione", *Electroanalysis*, **11**, 81 (1999).

109. Jadhav, S. and Bakker, E., "Selectivity behavior and multianalyte detection capability of voltammetric ionophore-based plasticized polymeric membrane sensors", *Anal. Chem.*, **73**, 80 (2001).

110. IUPAC Analytical Chemistry Division, *Pure Appl. Chem.*, **48**, 127 (1976).

111. Bulhlmann, P., Umezawa. Y., Rondinini, S., Vertova, A., Pigliucci, A. and Bertesago L., "Lifetime of ion-selective electrodes based on charged ionophore", *Anal. Chem.*, **72**, 1843 (2000).

Chapter 4

Gd^{3+} Ion-Selective Coated Graphite Electrode Based On N_5 Donor Chelating Ligand

4.1. Introduction

Gadolinium is a lanthanide element and occurs in trace amounts in the mineral gadolinite. Unlike other rare earths, gadolinium is relatively stable in dry air and is chiefly used in petroleum industries to produce catalysers, in nuclear research as neutron absorber, in steel industries and polishing glassware. Gadolinium compounds are also used as phosphors in the manufacture of color-television picture tubes. Because of their paramagnetic properties, solutions of organic gadolinium compounds are used as intravenous radio-contrast agent in medical field to enhance image quality of the magnetic resonance imaging (MRI) of all anatomic regions. They are excreted non-metabolized from the organism *via* urine. They generally, pass through waste water treatment plant and contaminate surface water [1].

Free gadolinium ion is an inorganic blocker as its ionic radius (107.8 pm) is very close to that of Ca^{2+} ion (114 pm). Thus it inhibits physiological processes which depend upon Ca^{2+} influx as well as the activity of some enzymes [2]. It may also depress the reticuloendothelial system and has been found to increase the expression of hepatic cytokines [3]. In view of toxic effects of gadolinium, it is important to determine it in environmental samples.

A number of analytical techniques [4-12] have been used for its determination but they are all very sophisticated expensive, time consuming and require large infrastructure back up and expertise. Hence these are not very appropriate for monitoring of large number of environmental samples in the field. However, ion selective electrodes (ISEs) are the ideal choice for the analysis of large number of environmental samples as they provide a low cost, fast and convenient method with no chemical manipulations. As such there has been intensive activity in developing ion selective electrodes for many metal ions.

Gd^{3+} ion-selective electrodes

A number of good electrodes have been reported for many toxic metals. However, development of good selective electrodes for lanthanides has lagged behind and only few good lanthanides selective electrodes have been reported [13-24]. A detailed literature survey showed availability of only a limited number of ionophores which were used in developing Gd^{3+}-selective sensors. Zhang *et al.* [25, 26] reported the first Gd^{3+} sensors based on functional polymers as the electroactive material. These electrodes worked over a narrow linear range with higher slopes and short pH range. Ganjali *et al.* [27] used antibiotic omeprazole for preparing Gd^{3+} sensor. This sensor has a linear dynamic range of 1.0×10^{-5} - 1.0×10^{-1} mol L^{-1} with a Nernstian slope of 19.3 ± 0.3 mV $decade^{-1}$ of a_{Gd}^{3+}.

Shamsipur *et al.* [28] used a Schiff base 2-[{3-[(2-sulfanylphenyl)imino)-1-methylbutylidene}amino]phenyl hydrosulfide for developing a Gd^{3+} selective sensor. The electrode showed Nernstian response with a detection limit of 3.0×10^{-6} mol L^{-1} and worked well in the pH range of 4.0-8.0. A pentadentate Schiff base Bis(thiophenal)pyridine-2,6-diamine (BPD) was used by Ganjali *et al.* [29] as an excellent ion carrier to prepare Gd^{3+} selective membrane electrode. The resulting sensor worked linearly in the range 1.0×10^{-6} - 1.0×10^{-1} mol L^{-1} with a Nernstian slope of 19.4 ± 0.4 mV $decade^{-1}$ of a_{Gd}^{3+} and detection limit as 7.0×10^{-7} mol L^{-1} (110 ng mL^{-1}). Norouzi *et al.* [30] developed a highly selective and sensitive Gd^{3+} membrane sensor based on N-(2-pyridyl)-N'-(4-nitrophenyl)thiourea as an excellent neutral ion carrier. This sensor exhibited a Nernstian slope of 19.95 ± 0.3 mV per decade of a_{Gd}^{3+} over the concentration range of 3.0×10^{-7} to 1.0×10^{-1} mol L^{-1} with a detection limit of 3.0×10^{-7} mol L^{-1}. Zamani *et al.* [31] used 6-methyl-4-{[1-(2-thienyl) methylidene] amino}-3-thioxo-3, 4-dihydro-1, 2, 4-triazin-5-(2H)-one as an ionophore for the preparation of Gd^{3+} selective electrode. This electrode worked in the range of 1.0×10^{-6}-1.0×10^{-1} mol L^{-1}

with Nernstian slope of 19.8 ± 0.2 mV per decade of $a_{Gd}{}^{3+}$ and a detection limit as 5.8×10^{-7} mol L^{-1}. Faridbod *et al.* [32] constructed the first asymmetric microsensor based on N-(2-pyridyl)-N'-(4-nitrophenyl)thiourea. This sensor exhibited a Nernstian slope of 17.46±0.3 mV decade^{-1} of $a_{Gd}{}^{3+}$ over the concentration range of 1.0×10^{-8} to 1.0×10^{-3} mol L^{-1} and a detection limit of 3.0×10^{-9} mol L^{-1} of Gd^{3+} ions. A critical examination of literature show that, in general, most of the reported gadolinium electrodes are not good enough as they show short working concentration range, low sensitivity and poor selectivity. It is, therefore, necessary to prepare a more sensitive and selective gadolinium electrode for its determination in various samples.

In order to have a selective sensor for any metal ion, the most important requirement is to have an ionophore in the sensor membranes, which show high affinity towards that metal ion and poor for others. The availability of such materials is limited and thus quest for new materials capable of specific and effective recognition of metal ions is a topic of current interest and represents a challenging task. Neutral chelating carriers have characteristics of being uncharged, lipophilic and undergoing reversible complexation with selected cations and promoting cation transfers between the aqueous phase and the organic membrane phase by means of carrier transport. Also the use of neutral chelating ligands as electroactive component in membrane sensors generated widespread interest because they exhibit high complexation or extraction selectivity for a particular ion, enough conformational flexibility for rapid ion exchange, high lipophilicity to remain in membrane phase and moderate molecular weight to allow high mobility [33]. In view of these facts, we have, therefore, taken up investigation in this direction.

In the present study, we synthesized a pentadentate neutral chelating ligand having N donor sites along with cyanopropyl pendant arms and explored this ligand as an ionophore for developing ion selective electrode. The stability studies of a this newly synthesized pendant (L_3) exhibited that the ligand form most stable complex with Gd^{3+} ion as compared to other metal ions studied. Thus due to the high affinity of the ligand towards gadolinium it was used as a potential ionophore for preparing gadolinium selective electrode. Membranes having different compositions of PVC, a plasticizer *o*-nitrophenyloctylether (NPOE), sodium tetraphenylborate (NaTPB) as anionic additive and the ionophore (L_3) were coated on the graphite surface and investigated them as gadolinium selective electrodes. The results are reported in the present communication.

4.2. Experimental

4.2.1 Chemicals and reagents

Reagent grade oleic acid (OA), sodium tetraphenylborate (NaTPB), dibutyl phthalate (DBP), benzyl acetate (BA), *o*-nitrophenyloctylether (*o*-NPOE), dioctylpthalate (DOP), dioctylsebacate (DOS), tetrahydrofuran (THF) and high molecular weight PVC were procured from E. Merck (Mumbai) and used as received. 2,6-diacetylpyridine, 2-(aminmethyl)pyridine, extra pure $GdCl_3$, Potassiumtetrakis(4-chlorophenyl) borate (KTpClPB), Triton X-100 from Sigma-Adlrich (Steinheim, Germany), acrylonitrile, sodiumdodecylsulphate (SDS), cetyl trimethylammonium bromide (CTAB) and Brij-35 from Loba Chemie (Mumbai) were reagent grade materials. Double distilled water was used to prepare stock solution (0.1 M) of metal salts which was then diluted to prepare solutions of different concentrations. The nitrate and chloride salts of all the cations used were of analytical grade. The metal solutions were standardized wherever necessary.

4.2.2 Apparatus and instrumentation

All the apparatus and instruments used have been described in section 3.2.2 of Chapter 3. A conductivity meter model Cyberscan 510, provided with a dip-type cell (K_{cell} = 1.0), was used for conductance measurements.

4.2.3 Synthesis of 2,6-Bis-[1-{N-cycnopropyl,N-(2-methylpridyl)}aminoethyl]pyridine [L_3]

The reaction scheme for the synthesis of the ligand (L_3) is shown in Figure 4.1 which involves two steps.

Step 1

2, 6-diacetylpyridine (0.326 g, 2 mmol) was dissolved in 50 mL dried methanol at room temperature under nitrogen atmosphere. 2-aminomethyl pyridine (0.432 g, 4 mmol) in methanol was added drop-wise to this solution. The reaction mixture was heated under refluxing condition for 6 hrs. The yellow solution was then allowed to cool to room temperature. Solid $NaBH_4$ (0.076 g, 2 mmol) was added slowly and carefully for *in situ* reduction keeping the reaction system in an ice bath and was stirred for 1 h. The reaction was interrupted with the addition of HCl to the reaction mixture until pH 4 was reached. The solvent was removed under vacuum and 25 mL water was added to the residue. The reactants were extracted with CH_2Cl_2. The aqueous phase was separated and its pH was adjusted to 10 using Na_2CO_3. Finally the product was extracted with CH_2Cl_2. Anhydrous $MgSO_4$ was added to the organic phase. After filtering, the solvent was removed under vacuum. The product (A), brown solid, was obtained in 60 % yield. *Anal. Calc.* for $C_{21}H_{25}N_5$: C, 72.52; H, 7.19; N, 20.15. Found: C, 72.28; H, 7.14; N, 21.06 %. IR(KBr, cm^{-1}) 1244 (s, $\nu_{C—N}$), 3213 (s, $\nu_{N—H}$), ^1H NMR ($CDCl_3$, δ/ppm): 7.0-7.3 (m, 11H), 2.6 (m, 2H), 1.3 (d, 6H), 3.8 (m, 2H), 2.2(m, 4H).

Step 2

10 ml saturated solution of anhydrous K_2CO_3 in anhydrous methanol was added to the methanolic solution of 347 mg (1 mmol) of Product (A), obtained in step 1. 5 ml (excess amount) acrylonitrile was added drop by drop to this mixture. The solution was stirred 3 hrs and then refluxed for 10 hrs. The volume of the reaction mixture was reduced and then it was kept overnight in refrigerator. The compound 2,6-Bis-[1-{N-cycnopropyl,N-(2-methylpridyl)}aminoethyl]pyridine [L_3] separated as white precipitate which was filtered and washed with cold methanol. The white product was dried in vacuum.

Yield: 48 %. *Anal. Calc.* for $C_{27}H_{31}N_7$: C, 71.52; H, 6.84; N, 21.63. Found: C, 71.60; H, 6.92; N, 21.48 %. IR(KBr, cm^{-1}) 2248 (s, $\nu_{-C\equiv N}$), ^1H NMR ($CDCl_3$, δ/ppm): 7.2- 7.6 (m, 11H), 1.3 (d, 6H), 3.8 (m, 2H), 2.1 (m, 4H), 2.5 (m, $4H_{CH2—CN}$), 2.8 (m, $4H_{-CH2—N}$).

4.2.4 Preparation of coated graphite electrodes

The membrane ingredients (ionophore, anion additives, PVC and plasticizers) were dissolved in 5 mL of tetrahydrofuran and the solvent was evaporated to obtain a concentrated mixture. Spectroscopic grade graphite electrodes of 5 mm diameter and 15 mm long were polished and a copper wire was glued to one end of the electrode. The other end of the electrode was then dipped into the concentrated membrane solution and left overnight. The solvent evaporated off and a thin PVC film formed on the graphite electrode surface. Various compositions of membrane solutions were tried and preliminary investigations revealed that the membrane composition having 8 mg of ionophore (L_3), 4 mg of NaTPB, 58 mg of NPOE and 30 mg of PVC was optimum with regard to good performance of the electrode. In order to make the electrode handy the graphite electrode was then sealed in a glass tube with epoxy resin, taking care that the electrode portion having membrane layer remained exposed.

4.2.5 Preparation of polymeric membrane electrodes

PVC based membrane electrodes of this ionophore were also fabricated by the same procedure as reported in *section 3.2.4* of Chapter 3. The fabrication of segmented sandwich membranes were carried out as described in *section 3.2.5* of Chapter 3.

4.2.6 Conditioning of electrodes and potential measurements

Prior to potential measurements, all the prepared electrodes were equilibrated to obtain stable and reproducible potential. The coated graphite electrodes were equilibrated in 1 mM $GdCl_3$ solution for four days before starting the mesurement. For measuring potentials the coated electrode was dipped into the test solution to which a calomel electrode was also connected. The potentials of the following cell setup were measured by varying the concentration of $GdCl_3$ solution in the range 1.0×10^{-9}–1.0×10^{-1} M on a Orion 4 star pH meter at $25 \pm 0.1\ ^0C$.

CGE || Test solution || Hg/Hg_2Cl_2 | KCl (saturated)

4.2.7 Determination of formation constant

The ion-ionophore binding mode in the form of formation constants was calculated by Sandwich membrane method following the same procedure as described in *section 3.2.7* of Chapter 3.

4.3 Results and Discussion

4.3.1 Preliminary complexation study

The complexation of the pendant (L_3) with a number of cations was investigated conductometrically in an acetonitrile solution, at 25 ± 0.05 °C, in order to obtain a clue about the stability and selectivity of the resulting complexes and there stoichiometry. In this experiment, 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. The conductance of the solution was measured after each addition of ionophore until the titration plot (Figure 4.2) showed a sharp break and further, no significant change was observed in conductance of the solution. It can be seen from the Figure that the breaks in the titration plot indicate 1:1 stoichiometry of metal-ligand complexes. The complexation of gadolinium with ionophore is shown in Figure 4.3.

4.3.2 Evaluation of formation constants

The values of formation constants (Table 4.1), for ion-ionophore complexes, obtained by sandwich membrane method indicate that the value of formation constant is highest ($\log\beta_{Gd,L} = 6.68$) for the complex of Gd^{3+} with ligand whereas lower values ($\log\beta_{M,L} = 4.92$–0.39) were obtained in case of other metal ions. It can be concluded from these results that the ligand forms most stable complex with gadolinium and complexes of comparatively poor stability with other metal ions. Because of its high affinity towards Gd^{3+} ion, we thought it desirable to explore this ligand as a potential ionophore in the preparation Gd^{3+} ion selective electrode.

4.3.3 Optimization of membrane composition

Various studies have shown that the composition of membrane affects the performance characteristics significantly [34, 35]. Thus the performance of the present electrode was evaluated for different compositions to obtain the one showing best results with regard to all potentiometric characteristics.

The influence of the ionophore concentration on the potential response was first looked into PVC membranes by varying ionophore concentration up to 10 % (w/w) amount. The potentials of these PVC coated electrodes were determined as a function of Gd^{3+} ion concentration in the range 1.0×10^{-9} - 1.0×10^{-1} M and their performance characteristics are specified in Table 4.2. It is evident from the results that the electrode (CGE-1) with 8 % (w/w) ionophore exhibits linear working concentration range (9.7×10^{-5} - 1.0×10^{-2} mol L^{-1}) and non-Nernstian slope (12.8 mV decade^{-1} of a_{Gd}^{3+}). However, when the ionophore concentration was increased further up to 10 % (w/w), the performance of the electrode were not improved but started deteriorating showing some decrease in slope which may be due to some non-homogeneity and possible saturation of ionophore in the membrane. Further, the blank electrode (CGE-10) in Table 4.2, having zero ionophore concentration, does not perform well in view of narrow working concentration range ($8.5\times10^{-4} - 1.0\times10^{-2}$ mol L^{-1}), small slope (8.5 mV decade^{-1} of a_{Gd}^{3+}) and high detection limit (2.8×10^{-4} mol L^{-1}). Thus ionophore contributes to the generation of potentials and in all further studies ionophore amount in the membrane was kept at 8 % (w/w).

It is well established that the plasticizer improves the performance characteristics of membrane sensors as they change the polarity of the membrane phase [36]. Therefore, further it was attempted to improve the performance characteristics of the electrode by adding different plasticizers such as DOP, DBP, BA, *o*-NPOE, and DOS. The potential response of the membrane coated graphite electrodes prepared by adding these plasticizers and 8 % (w/w) ionophore is shown in Figure 4.4 and the performance characteristics from these plots are summarized in Table 4.2. It can be seen that the electrode (CGE-1) containing 8 % ionophore and no plasticizer responds only over a short working concentration range with non-Nernstian slope; whereas the addition of all plasticizers increases the slope and broadens the working range (CGE-2 to 6). The results indicate that, of the four plasticizers studied, *o*-NPOE plasticizer improves the performance to maximum extent. The optimum amount of this plasticizer was found to be 58 % (w/w) and CGE-6 responded to Gd^{3+} over a wider working concentration range ($3.4\times10^{-6} - 1.0\times10^{-2}$ mol L^{-1}) with the increased slope (16.9 mV decade^{-1}

of a_{Gd}^{3+}). In case of other plasticizers, the performance characteristics of the electrodes (CGE-2 to 5) were inferior to that containing *o*-NPOE. This appear due to optimum polarity imparted by *o*-NPOE to the membrane and also a result of differences in the electrode mechanism [37] as well as good extraction of Gd^{3+} ions with *o*-NPOE.

The improvement in the performance of this sensor was further attempted by employing different anion additives in the membrane composition as impart perm-selectivity to the electrode by eliminating the anion interference in neutral carrier based cation selective electrodes [38, 39]. The potential response of the electrode was greatly enhanced in the presence of lipophilic additive NaTPB but there was no significant improvement in the performance characteristics of the coated membrane electrode when OA and KTpClPB were used. Previous studies have shown that there is an optimal concentration of lipophilic anion additive in the membrane phase that gives the best electrode performance. Our studies have revealed that electrode no. 9 having 4 % (w/w) NaTPB is the best of all electrodes studied in this investigation as it responds over the widest working concentration range compared to others and shows Nernstian behaviour.

4.3.4 Potentiometric response characteristics of the proposed electrode

Thus the results obtained from the optimization of the amount of membrane ingredients have shown that the best performance was shown by the coated graphite electrode no. 9 having composition of its ingredients in the ratio L_3:NaTPB:PVC:NPOE as 8:4:30:58 (%, w/w). The calibration graph of this sensor is given in Figure 4.5 which shows that this electrode gives a linear response to the activity of Gd^{3+} over the widest working concentration range of 2.8×10^{-7} - 5.0×10^{-2} mol L^{-1} with a Nernstian slope of 19.6 ± 0.3 mV $decade^{-1}$ of a_{Gd}^{3+}. The limit of detection, as determined from the intersection of the two linear segments of the calibration graph, was 6.3×10^{-8} mol L^{-1}. The S.D. of five replicate potential measurements for a series of solutions having Gd^{3+} ion concentration in the range of 1.0×10^{-9} – 1.0×10^{-1} mol L^{-1} was ± 0.4 mV.

4.3.5 Potential – pH profile of the electrode

The influence of pH on the potential response of the electrode at 1.0×10^{-4} mol L^{-1} and 1.0×10^{-3} mol L^{-1} $GdCl_3$ solutions over a pH range of 1.0 to 10.0 was studied and the results were shown in Figure 4.6. The operational pH range was studied by varying the pH of the test solution with 0.1 M HNO_3/NaOH. It was observed from the pH-potential curve that the potential does not change with pH in the range of 2.0 to 8.0 for the $GdCl_3$ solutions studied. At pH less than 2, the change in potentials may be due to protonation of ionophore whereas above pH 8 the potential drift may appear due to hydrolysis of gadolinium salt [41].

4.3.6 Potentiometric selectivity of the electrode

The most important characteristic of any ion-sensitive electrode system is its response to the primary ion in the presence of other ions present in the solution, which is expressed in terms of the potentiometric selectivity coefficients. The experimental selectivity coefficients depend on the activity and the method of their determination. In the present study the potentiometric selectivity coefficients ($K_{A,B}^{Pot}$) of the proposed coated graphite electrode (CGE-9) toward different cations (M^{n+}) were evaluated by using Fixed interference method (FIM) as well as the Matched potential method (MPM) as described in Chapter 2.

In FIM, the selectivity coefficients were evaluated using *equation (10)* given in Chapter 2. The calibration plot obtained from potential measurement on solutions containing a fixed concentration of interfering ion (1.0×10^{-2} mol L^{-1}) and varying the concentration of Gd^{3+} ions solutions in the range of 1.0×10^{-9} to 1.0×10^{-1} mol L^{-1}, was used to determine the activity of the primary (Gd^{3+}) ion.

However, in MPM, the selectivity coefficients were determined by measuring the change in potential upon increasing 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 the reference solution of primary ion of activity (a_A) which also generates the same potential change. In the present study, a_A and a'_A were 1.0×10^{-3} mol L^{-1} and 5.0×10^{-3} M Gd^{3+} and a_B was experimentally determined at pH 6.0. The selectivity coefficients were obtained by putting all the values in *equation (13)* given in Chapter 2. The values of selectivity coefficient determined by these methods are compiled in Table 4.3. It is seen from the Table 4.3 that the selectivity coefficients determined by both these methods are of the order of 10^{-3} or lower which indicates that the electrode is highly selective to Gd^{3+} ion over many alkali, alkaline earth, transition and rare earth elements.

It is further concluded from the values listed in Tables 4.1 and 4.3 that there is an adverse relationship between formation constants and selectivity coefficients. The comparison between these values reflects that the selectivity coefficients are smaller for those metals which form weaker complexes in comparison to gadolinium.

4.3.7 Response time of the proposed coated graphite electrode

Response time is an important factor for an ion sensitive electrode which determines its utility in a measurement. Thorough evaluation of the response time is essential to forecast the chances of success of novel ISEs. In our study, we used the dipping method [42] to determine the response time of the CGE-9 and the average response time required for the Gd^{3+} electrode to reach a potential of final equilibrium value after successive immersion of CGE-9 in $GdCl_3$ solutions, ranging from 1.0×10^{-2} M to 1.0×10^{-6} M, each having a ten fold difference in concentration was measured. The potential measurement sequence was from the lower (1.0×10^{-6} M) to the higher (1.0×10^{-2} M) concentration and the standard deviation of 10 replicate measurements was ± 0.72 mV. In Figure 4.7, actual potential versus time plot is traced which shows that the response time of the electrode to give a stable potential over the entire concentration range is approximately 12 s.

4.3.8 Determination of lifetime of the proposed electrode

The major factor limiting the lifetime of the ion selective membrane in potentiometric measurements is the loss of components into the contacting aqueous solutions. For continuous monitoring with membranes electrodes, especially ionophore must be sufficiently lipophilic to ensure a long and stable response of the ion-selective electrode [43]. The lifetime of the electrode was studied over a 4 months period. During this period, the electrode was daily used for extended period (2 h per day), and the performance characteristics of the electrode, working concentration range, slopes and detection limit, were measured from the potentiometric calibration plots. After two and half month, a little changes were observed in the slope (from 19.6 to 19.1 mV decade^{-1} of $a_{Gd^{3+}}$) and detection limit (from 6.3×10^{-8} to 7.2×10^{-7} M, respectively) and the results of this study are shown in Table 4.4. The reproducibility of the Gd^{3+} electrode (CGE-9) was also investigated. The standard deviations of 10 replicate measurements at 1.0×10^{-3} and 1.0×10^{-4} mol L^{-1} were ± 0.3 and ±0.4 respectively. The life time study reveals that the proposed electrode can be successfully used for 2.5 months for the monitoring of Gd^{3+} in solution.

4.3.9 Comparison of polymeric membrane electrode and coated graphite electrode

Polymeric membrane electrode (PME) was also prepared having the similar membrane composition as that of the coated graphite electrode (CGE). The performance characteristics of this electrodes were also investigated as Gd^{3+}-selective electrode and the studies showed that PME exhibit the linear working concentration range (9.5×10^{-7} to 1.0×10^{-2} mol L^{-1}) with Nernstian slope (19.5 ± 0.3 mV decade^{-1} of $a_{Gd}{}^{3+}$) and low detection limit (4.1×10^{-7} mol L^{-1}). A comparison data of the performance characteristics of PME and CGE is given in Table 4.5. The results revealed the superiority of CGE over PME with respect to higher working concentration range, low detection limit and fast response time. 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} $GdCl_3$ solution as in case of PME, has been replaced by a copper wire of much higher electrical conductivity as in case of CGE. The higher limit of detection of PME than CGE may be due to some leakage of the internal solution into the test solution.

4.3.10 Effect of non-aqueous media on the performance of the electrode

The functioning of the electrode has also been investigated in partially nonaqueous media using acetonitrile–water, methanol–water and ethanol–water mixtures of different concentration (10 %, 20 % and 30 %, v/v) and the results obtained from potential response plots are compiled in Table 4.6. It is observed that in the presence up to 30 % (v/v) ethanol, the slope as well as working concentration range does not change significantly. However, drastic changes were observed in case of methanol and acetonitrile. It was found that only 10 % (v/v) amount of these two non-aqueous could be tolerated. Therefore, the electrode is not suitable for using in methanol–water and acetonitrile–water mixtures above their 10 % (v/v) concentration as the potentiometric characteristics are significantly affected. This may be due to greater solubility of the ionophore in methanol and acetonitrile which causes leaching of ionophore from the membrane phase. However, the electrode can be satisfactorily used in ethanol-water mixture containing up to 30 % (v/v) impurity of ethanol in aqueous solution of Gd^{3+}.

4.3.10 Influence of surfactants on performance of the electrode

Surfactants are widely used in households and in various industries. Thus, they are present in water samples and might affect the determination of Gd^{3+} by an ion selective electrode. Surfactants are surface active molecules and have a tendency to accumulate and adsorb at any interface. Thus the surfactants present in solution are likely to get concentrated at the electrode surface and therefore affect the performance of the electrode. Correspondingly, this would result in a large measuring error or alter the original selectivity [44, 45].

In this study, the effect of ionic (CTAB, SDS) and non-ionic (Triton-X-100, Brij-35) surfactants on potentiometric characteristics of the Gd^{3+}-selective electrode (CGE-9) was determined with varying concentrations of these surfactants. The results calculated from the calibration curve are given in Table 4.7. It was observed that the content of the each surfactant greater than 1.0×10^{-4} M affected the potential response as well as selectivity of the electrode. In the presence of these surfactants, the electrode showed remarkable difference in slope, working concentration range and detection limit from the original values obtained without any surfactant. The selectivity coefficients were also calculated for some trivalent ions (Sm^{3+}, Nd^{3+}, La^{3+}, Pr^{3+}, Tm^{3+}, Tb^{3+}, Ce^{3+}) and their values were observed to decrease; even near to unity in some cases, showing a change in the selectivity behavior of the electrode.

4.4 Analytical Application

The selectivity for gadolinium ions exhibited by this electrode (CGE-9) makes it potentially useful for monitoring the concentration of Gd^{3+} ion in various real samples.

4.4.1 Potentiometric titration

The electrode was used successfully for the end point determination in the potentiometric titration of $GdCl_3$ against EDTA solution. A 20 ml of 1.0×10^{-4} mol L^{-1} solution of Gd^{3+} was titrated against 1.0×10^{-3} mol L^{-1} EDTA solution at pH 5.0. The titration plot obtained (Figure 4.8) is of sigmoid shape which supports the results that the electrode is selective to Gd^{3+} ion and the inflexion point corresponds to 1:1 stoichiometry of Gd^{3+}- EDTA complex. Therefore, this electrode can be used as an indicator electrode for the potentiometric determination of Gd^{3+} ion.

4.4.2 Determination of gadolinium in water samples

The electrode was also successfully applied to determine gadolinium directly in the water samples taken from river Yamuna, Delhi and waste water from Bhaba Atomic Research Centre (BARC) Mumbai, India. The water samples were acidified with 0.1 M HNO_3 to adjust pH at 6. The results obtained from the triplicate measurements are in close agreement with those determined by ICP-MS and are summarized in Table 4.8.

4.4.3. Determination of gadolinium in rock samples

Three rock samples of Dolerite DNC-1, Granite G-2 and Marine Mud MAG-1 were collected from North Eastern Hills and Tamilnadu region in India. The sample material (2 g) was stirred overnight with 5 mL concentrated HF. Then a mixture of 3 mL hydrochloric acid and 2 mL nitric acid were added and the sample was heated in a Teflon beaker at 140°C for 6 hrs. The sample was then diluted to 50 mL. The digested samples were diluted 20 times before measurement and the pH was adjusted at 6. The results of the ISE measurements were compared with those obtained by ICP-MS and are summarized in Table 4.8. The results showed a good agreement between the two analytical techniques. Thus the electrode can be used successfully to determine Gd^{3+} ion concentration in real samples.

4.5 Conclusion

Of the various coated graphite electrodes prepared with different composition of membrane ingredients, it was found that the electrode no. 9 having membrane composition of its ingredients in the ratio L_3:NaTPB:PVC:NPOE as 8:4:30:58 (%, w/w) performed best with regard to all the performance characteristics. This electrode exhibits Nernstian response to Gd^{3+} ion over a wide concentration range ($2.8 \times 10^{-7} - 5.0 \times 10^{-2}$ mol L^{-1}) with slope 19.6 mV decade^{-1} of $a_{Gd}{}^{3+}$ and works well over a pH range of 2 to 8. The proposed electrode shows a fast response time (12 s) and can be used up to two and half months without significant divergence in its characteristics. The electrode shows excellent selectivity for gadolinium over several alkali, alkaline and heavy metal ions. It can tolerate 1.0×10^{-4} M concentration of surfactants and also performs satisfactorily in partially non-aqueous solutions with 30 % (v/v) ethanol and 10 % (v/v) methanol and acetonitrile impurities. The electrode could be used successfully as an indicator electrode in the potentiometric titration against EDTA. The selectivity of the electrode permitted its use in the determination of Gd^{3+} ion in water and rock samples. It can be seen from the comparison Table 4.9 that the proposed electrode is superior to the reported Gd^{3+} sensors as it responds over a wide working concentration range, shows better selectivity and lower detection limit. Therefore, this electrode is a useful addition to the family of Gd^{3+} ion selective sensors.

Tables

Table 4.1: Formation constants of ion-ionophore complexes of L_3 with different metal ions

Cations	Formation constant ($\log \beta_{ILn}$) ± SD	Cations	Formation constant ($\log \beta_{ILn}$) ± SD
Gd^{3+}	6.68 ± 0.3	Zn^{2+}	1.55 ± 0.6
Sm^{3+}	4.92 ± 0.4	Cd^{2+}	1.33 ± 0.4
Nd^{3+}	4.65 ± 0.2	Co^{2+}	0.86 ± 0.8
La^{3+}	3.58 ± 0.5	Ni^{2+}	0.67 ± 0.4
Ce^{3+}	2.27 ± 0.4	Ca^{2+}	0.39 ±1.2
Pr^{3+}	2.65 ± 0.3	Ag^{+}	0.54 ± 0.8
Tm^{3+}	2.18 ± 0.5	Na^{+}	1.78 ± 0.5
Tb^{3+}	2.57 ± 0.2	K^{+}	2.18 ± 0.8
Cu^{2+}	2.16 ± 1.2	Sr^{2+}	1.35 ± 0.5

Table 4.2: Optimization of membrane ingredients and their performance characteristics as Gd^{3+} ion selective electrode

CGE No.	Membrane composition (%, w/w)				Working concentration range (mol L^{-1})	Slope (mV decade^{-1} of a_{Gd}^{3+})	Detection limit (mol L^{-1})
	Ionophore	Additive	Plasticizer	PVC			
1	8	-	-	92	$9.7 \times 10^{-5} - 1.0 \times 10^{-2}$	12.8	7.8×10^{-5}
2	8	-	58, DOS	30	$8.7 \times 10^{-5} - 1.0 \times 10^{-2}$	13.2	5.9×10^{-5}
3	8	-	58, BA	30	$8.2 \times 10^{-6} - 1.0 \times 10^{-2}$	14.5	6.3×10^{-6}
4	8	-	58, DOP	30	$7.9 \times 10^{-6} - 1.0 \times 10^{-2}$	15.7	4.5×10^{-6}
5	8	-	58, DBP	30	$6.5 \times 10^{-6} - 1.0 \times 10^{-2}$	16. 1	3.8×10^{-6}
6	8	-	58, NPOE	34	$3.4 \times 10^{-6} - 1.0 \times 10^{-2}$	16. 9	2.2×10^{-6}
7	8	4,KTpClPB	58, NPOE	30	$9.5 \times 10^{-6} - 1.0 \times 10^{-2}$	16.8	4.0×10^{-6}
8	8	10, OA	52, NPOE	30	$6.2 \times 10^{-5} - 1.0 \times 10^{-2}$	15.4	5.4×10^{-5}
9	8	4, NaTPB	58, NPOE	30	$2.8 \times 10^{-7} - 5.0 \times 10^{-2}$	19.6	6.3×10^{-8}
10	-	4, NaTPB	58, NPOE	38	$8.5 \times 10^{-4} - 1.0 \times 10^{-2}$	8.5	2.8×10^{-4}
11	6	4, NaTPB	58, NPOE	32	$5.0 \times 10^{-6} - 1.0 \times 10^{-2}$	17.3	3.2×10^{-6}
12	7	4, NaTPB	58, NPOE	31	$5.2 \times 10^{-6} - 1.0 \times 10^{-2}$	17.8	3.9×10^{-6}
13	9	4, NaTPB	58, NPOE	29	$9.8 \times 10^{-7} - 5.0 \times 10^{-2}$	18.6	2.4×10^{-7}
14	10	4, NaTPB	58, NPOE	28	$3.4 \times 10^{-6} - 1.0 \times 10^{-2}$	18.1	2.0×10^{-6}

Table 4.3: Potentiometric selectivity coefficients values for Gd^{3+}-selective electrode

Interfering ion (B)	Selectivity coefficient ($K^{Pot}_{Gd^{3+},B}$)	
	FIM	MPM
Sm^{3+}	8.9×10^{-3}	7.2×10^{-3}
Nd^{3+}	5.9×10^{-3}	4.5×10^{-3}
La^{3+}	6.1×10^{-4}	8.9×10^{-4}
Ce^{3+}	6.4×10^{-4}	4.8×10^{-4}
Pr^{3+}	3.8×10^{-4}	2.6×10^{-4}
Tm^{3+}	8.6×10^{-4}	6.2×10^{-4}
Tb^{3+}	9.1×10^{-4}	7.5×10^{-4}
Cu^{2+}	4.2×10^{-4}	2.9×10^{-4}
Zn^{2+}	7.8×10^{-5}	5.5×10^{-5}
Cd^{2+}	7.5×10^{-5}	4.9×10^{-5}
Co^{2+}	8.9×10^{-5}	6.5×10^{-5}
Ni^{2+}	4.5×10^{-5}	2.7×10^{-5}
Ca^{2+}	5.4×10^{-5}	3.4×10^{-5}
Ag^{+}	2.8×10^{-4}	1.3×10^{-5}
Na^{+}	9.2×10^{-5}	6.7×10^{-5}
K^{+}	9.5×10^{-5}	3.8×10^{-5}
Sr^{2+}	8.0×10^{-5}	7.3×10^{-5}

Table 4.4: Lifetime study of the proposed Gd^{3+}-selective coated graphite electrode

Time	Slope (mV $decade^{-1}$ of $a_{Gd^{3+}}$)	Detection limit (mol L^{-1})	Working concentration range (mol L^{-1})
7 days	19.6 ± 0.1	6.3×10^{-8}	2.8×10^{-7} - 5.0×10^{-2}
15 days	19.5 ± 0.3	6.3×10^{-8}	2.8×10^{-7} - 5.0×10^{-2}
1 month	19.3 ± 0.4	6.8×10^{-8}	3.0×10^{-7} - 5.0×10^{-2}
1.5 months	19.3 ± 0.2	7.2×10^{-8}	4.4×10^{-7} - 5.0×10^{-2}
2 months	19.3 ± 0.3	7.6×10^{-8}	5.1×10^{-7} - 5.0×10^{-2}
2.5 months	19.1 ± 0.4	7.2×10^{-8}	6.5×10^{-7} - 5.0×10^{-2}
3 months	18.8 ± 0.5	9.8×10^{-7}	3.9×10^{-6} - 5.0×10^{-2}
3.5 months	17.9 ± 0.1	2.5×10^{-6}	4.7×10^{-6}- 1.0×10^{-2}
4 months	16.2 ± 0.3	1.4×10^{-6}	6.4×10^{-6}- 1.0×10^{-2}

Table 4.5: Potentiometric characteristics of polymeric membrane electrode and coated graphite electrode

Potentiometric Characteristics	PME	CGE
Membrane Composition	L_3:NaTPB:PVC:NPOE as 8:4:30:58 (%, w/w)	L_3:NaTPB:PVC:NPOE as 8:4:30:58 (%, w/w)
Equilibration time	2 days in 0.1 M $GdCl_3$	4 days in 1 mM $GdCl_3$
Working concentration range (mol L^{-1})	9.5×10^{-7} - 1.0×10^{-2}	2.8×10^{-7} – 5.0×10^{-2}
Detection limit (mol L^{-1}	4.1×10^{-7}	6.3×10^{-8}
Slope (mV decade^{-1} of a_{Gd}^{3+}	19.5	19.6
Response time (s)	26	12
Lifetime	1.5 months	2.5 months
pH range	2.5-8.0	2.0-8.0

Table 4.6: The effect of partially non-aqueous media on the performance of Gd^{3+} electrode

Non-aqueous content (%, v/v)	Working concentration range (mol L^{-1})	Slope (mV decade^{-1} of a_{Gd}^{3+})
0	2.8×10^{-7} — 5.0×10^{-2}	19.6
Methanol		
10	9.6×10^{-7} — 5.0×10^{-2}	18.9
20	4.5×10^{-6} — 1.0×10^{-2}	17.1
30	7.9×10^{-6} — 1.0×10^{-2}	16.5
Ethanol		
10	4.2×10^{-7} — 5.0×10^{-2}	19.3
20	4.5×10^{-7} — 5.0×10^{-2}	19.3
30	6.3×10^{-7} — 1.0×10^{-2}	19.0
Acetonitrile		
10	7.0×10^{-7} — 5.0×10^{-2}	19.1
20	4.2×10^{-6} — 1.0×10^{-2}	17.8
30	5.5×10^{-6} — 1.0×10^{-2}	16.8

Table 4.7: Effect of different surfactants on the performance of Gd^{3+}-selective electrode

Interfering ions	- log (Selectivity Coefficients)				
	Without surfactant	With $>10^{-4}$ M CTAB	With $>10^{-4}$ M SDS	With $>10^{-4}$ M Triton X- 100	With $>10^{-4}$ M Brij-35
Sm^{3+}	2.1	1.2	1.8	0.8	1.3
Nd^{3+}	2.3	1.1	1.5	1.7	1.9
La^{3+}	3.0	1.6	2.1	1.2	1.4
Ce^{3+}	3.3	1.3	2.3	2.0	2.1
Pr^{3+}	3.6	1.8	2.1	2.5	1.8
Tm^{3+}	3.2	1.4	1.7	1.9	1.4
Tb^{3+}	3.1	2.2	2.8	2.0	2.3
Slope (mV decade^{-1} of $a_{Gd}{}^{3+}$)	19.6	17.8	20.9	18.3	22.5
Detection Limit (mol L^{-1})	6.3×10^{-8}	1.9×10^{-6}	5.4×10^{-6}	2.4×10^{-6}	8.8×10^{-6}
Working concentration range (mol L^{-1})	2.8×10^{-7}- 5.0×10^{-2}	4.3×10^{-6} – 1.0×10^{-2}	8.0×10^{-6} – 1.0×10^{-2}	7.0×10^{-6} – 1.0×10^{-2}	1.3×10^{-5} – 1.0×10^{-2}

Table 4.8: Potentiometric determination of Gd^{3+} ion in different water and rock samples

Sample	ISE (μg L^{-1})	ICP-MS (μg L^{-1})
Water Samples		
(i) River water	0.213 ± 0.05	0.225 ± 0.02
(ii) Waste water	0.681 ± 0.02	0.627 ± 0.03
Rock Samples		
(i) Dolerite DNC-1	1.8 ± 0.01	1.82 ± 0.04
(ii) Granite G-2	2.2 ± 0.03	2.06 ± 0.50
(iii) Marine Mud MAG-1	3.5 ± 0.02	3.23 ± 0.02

Table 4.9: Comparison of the proposed Gd^{3+}-selective coated graphite electrode with the reported electrodes

Ref. No.	Detection limit (mol L^{-1})	Selectivity coefficients (-log $K^{Pot}_{Gd^{3+},B}$)	Working concentration range (mol L^{-1})	pH range	Slope (mV decade^{-1} of $a_{Gd}{}^{3+}$)
This work	6.3×10^{-8}	Sm^{3+}(2.1), Nd^{3+}(2.3), La^{3+}(3.0), Ce^{3+}(3.3), Pr^{3+}(3.6), Yb^{3+}(3.2), Tb^{3+}(3.1),K^+(4.2)	2.8×10^{-7} – 5.0×10^{-2}	2.0 – 8.0	19.6 ± 0.3
27	5.0×10^{-6}	Ce^{3+}(1.6), La^{3+}(2.5), Sm^{3+}(2.3), Yb^{3+}(2.6) Cd^{2+}(1.5), K^+(2.0), Ag^+(2.6), Cu^{2+}(1.9)	1.0×10^{-5} – 1.0×10^{-1}	4.0 – 10.0	19.3 ± 0.3
28	3.0×10^{-6}	Ce^{3+}(2.5), La^{3+}(2.4), Sm^{3+}(2.2), Yb^{3+}(2.3) Cu^{2+}(2.3), Tb^{3+}(1.4), Ag^+(2.6), Cu^{2+}(1.9)	1.0×10^{-5} – 1.0×10^{-1}	4.0 – 8.0	19.8 ± 0.3
29	7.0×10^{-7}	Ce^{3+}(1.1), La^{3+}(2.2), Sm^{3+}(2.0), Yb^{3+}(2.4) Cd^{2+}(2.5), K^+(2.8), Ag^+(2.1), Cu^{2+}(2.9)	1.0×10^{-6} – 1.0×10^{-1}	3.5 – 8.0	19.4 ± 0.4
31	5.8×10^{-7}	Ce^{3+}(2.6), La^{3+}(2.1), Sm^{3+}(1.3), Yb^{3+}(1.6) Cd^{2+}(1.2), K^+(2.3), Ag^+(2.2), Cu^{2+}(3.9)	1.0×10^{-6} – 1.0×10^{-2}	3.2 – 8.7	19.8 ± 0.2
30	3.0×10^{-7}	Ce^{3+}(1.8), La^{3+}(1.5), Sm^{3+}(2.6), Yb^{3+}(2.7) Cd^{2+}(3.5), K^+(3.0), Ag^+(2.8), Cu^{2+}(2.2)	3.0×10^{-7} – 1.0×10^{-1}	4.0 – 9.0	19.95 ± 0.3

Figures

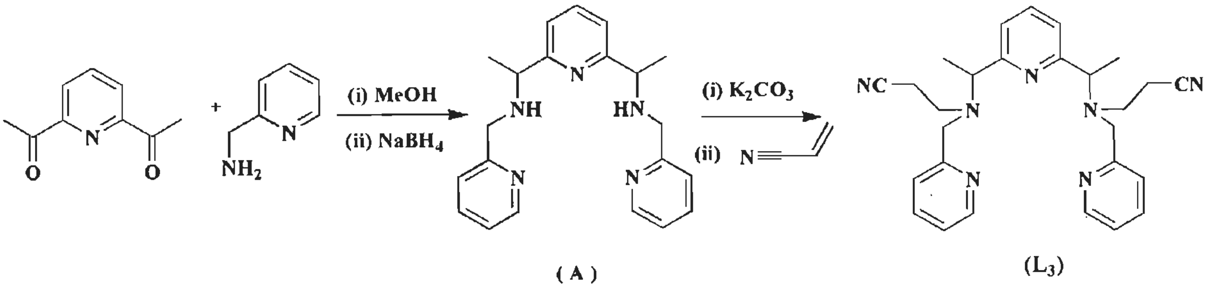


Figure 4.1: Reaction scheme for the synthesis of 2,6-Bis-[1-{*N*-cyanopropyl, *N*-(2-methylpridyl)}aminoethyl]pyridine [L$_3$]

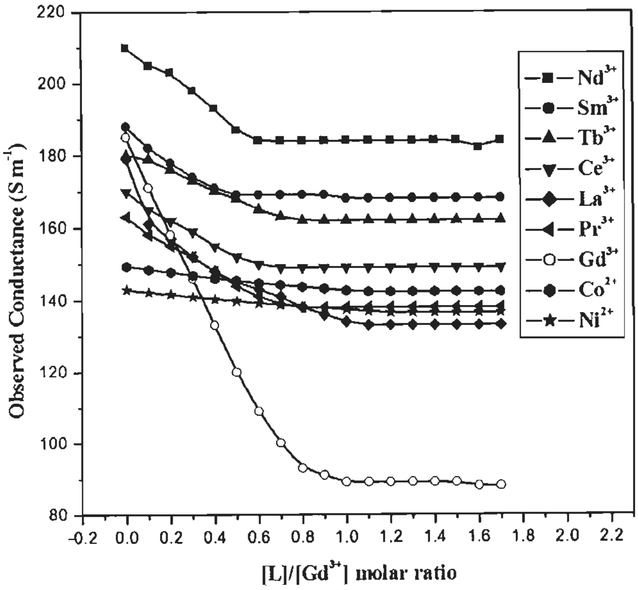


Figure 4.2: The variation in the conductance of the metal ion solution with the addition of ligand L$_3$

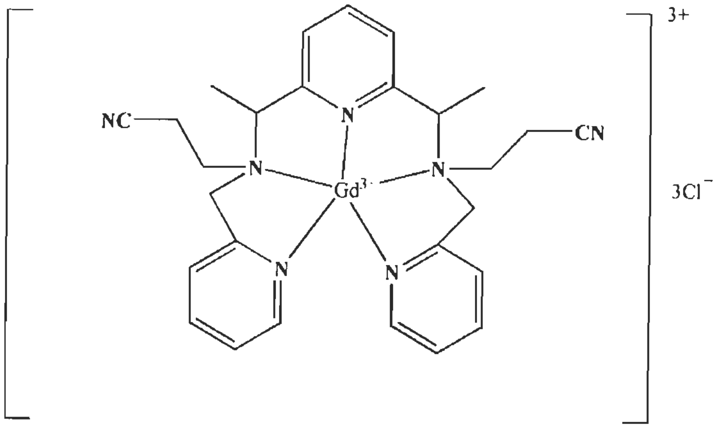


Figure 4.3: Structure of Gadolinium(III) complex

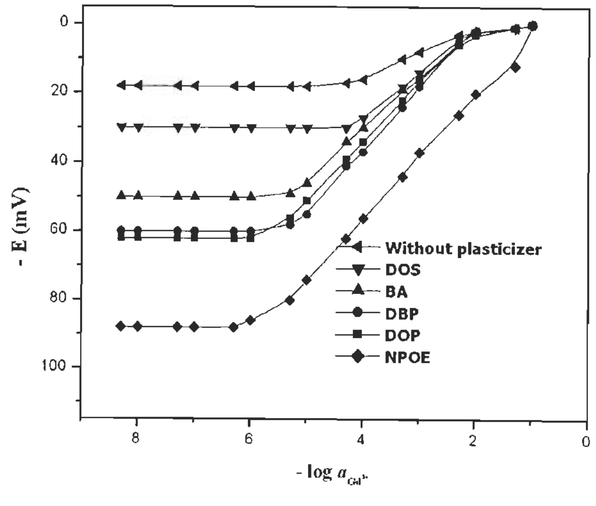


Figure 4.4: Potential responses of Gd^{3+} membrane electrodes based on L_3 with different plasticizers.

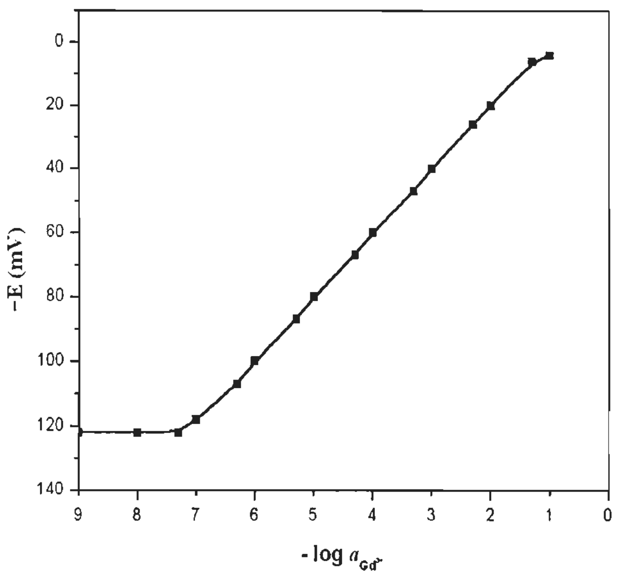


Figure 4.5: Calibration plot for Gd^{3+} ion-selective electrode CGE-9

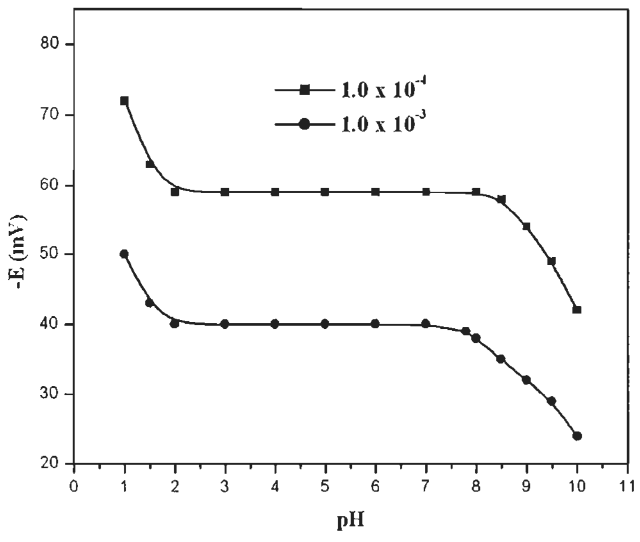


Figure 4.6: Effect of pH on the performance of the electrode no. 9 at 1.0×10^{-3} M and 1.0×10^{-4} M respectively.

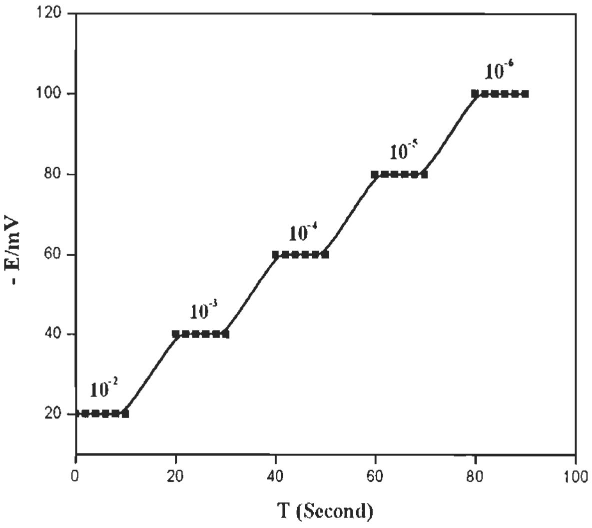


Figure 4.7: Dynamic response time of the Gd^{3+} selective electrode CGE-9 for Ten-fold change in Gd^{3+} ion concentration.

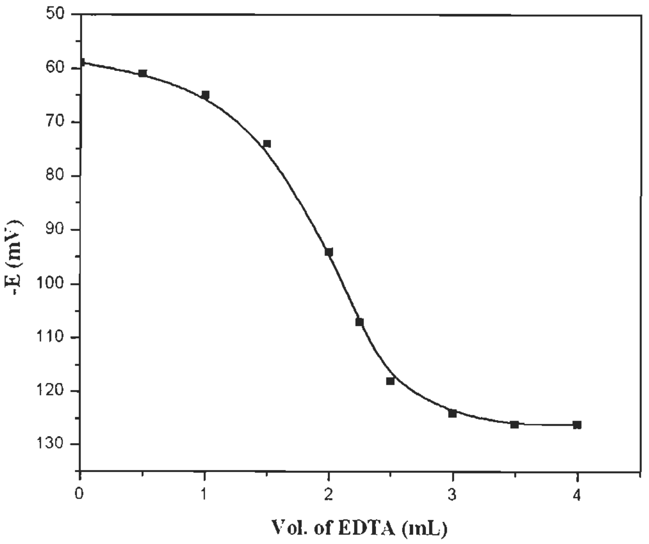


Figure 4.8: Potentiometric titration curve for 20 mL of 1.0×10^{-4} M Gd^{3+} with 1.0×10^{-3} M EDTA, at constant pH 5 using the proposed electrode CGE-9

References

1. Caravan, P., Ellison, J.J., McMurry, T.J. and Lauffer, R.B., "Gadolinium(III) chelates as MRI contrast agents: structure, dynamics, and applications", *Chem. Rev.*, **99**, 2293 (1999).
2. Idee, J.M., Port, M., Raynal, I., Schaefer, M., Le, G.S. and Corot, C., "Clinical and biological consequences of transmetallation induced by contrast agents for magnetic resonance imaging: a review", *Fundam. Clin. Pharmacol.*, **20**, 563 (2006).
3. Evans, C.H., "Biochemistry of the lanthanides", Plenum Press, New York, (1990).
4. Shibata, N., Fudagawa, N. and Kubota, M., "Electrothermal vaporization using a tungsten furnace for the determination of rare-earth elements by inductively coupled plasma mass spectrometry", *Anal. Chem.*, **63**, 636 (1991).
5. Hennebrüder, K., Wennrich, R., Mattusch, J., Stärk, Hans-J. and Engewald, W., "Determination of gadolinium in river water by SPE preconcentration and ICP-MS", *Talanta*, **63**, 309 (2004).
6. Normann, P.T., Joffe, P., Martinsen, I. and Thomsen, H.S., "Quantification of gadodiamide as Gd in serum, peritoneal dialysate and feces by inductively coupled plasma atomic emission spectroscopy and comparative analysis by high-performance liquid chromatography", *J. Pharm. Biomed. Anal.*, **22**, 939 (2000).
7. Moyer, E.S. and McCarthy, W. J., "Evaluation of electron spin resonance for quantitative determinations of Gadolinium, Chromium, Iron, Copper and Manganese", *Anal. Chim. Acta*, **48**, 79 (1969).
8. McCown, J.J. and Larsen, R.P., "Radiochemical determination of total rare earths by liquid-liquid extraction", *Anal. Chem.*, **33**, 1003 (1961).
9. Bertram-Berg, A., Mainka, E. and Ache, H.J., "Determination of gadolinium in aquous solutions by time-resolved fluorimetry", *Fresenius. J. Anal. Chem.*, **333**, 766 (1989).
10. Mazzucotelli, A., De, P.F., Magi, E. and Frache, R., "Interferences of major elements in the determination of rare earth elements by inductively coupled plasma atomic emission spectroscopy", *Anal. Sci.*, **8**, 189 (1992).
11. Cornell. D.H., "Rare earths from supernova to superconductor", *Pure Appl. Chem.*, **65**, 2453 (1993).

12. Marsh, R.H. and Allie, W., "Precision determination of gadolinium in cadmium fluoride by neutron activation analysis", *Anal. Chim. Acta*, **45**, 179 (1969).

13. Ganjali, M.R., Pourjavid, M.R., Rezapour, M. and Haghgoo, S., "Novel samarium(III) selective membrane sensor based on glipizid", *Sens. Actuators, B,* **89**, 21 (2002).

14. Shamsipur, M., Hosseini, M., Alizadeh, K., Talebpour, Z., Mousavi, M.F., Ganjali, M.R., Arca, M. and Lippolis, V., "PVC membrane and coated graphite potentiometric sensors based on Et4todit for selective determination of samarium(III)", *Anal. Chem.*, **75**, 5680 (2003).

15. Ganjali, M.R., Rezapour, M., Pourjavid, M.R. and Haghgoo, S., "ppt level detection of samarium (III) with a coated graphite sensor based on an antibiotic", *Anal. Sci.*, **20**, 1007 (2004).

16. Ganjali, M.R., Akbar, V., Ghorbani, M., Norouzi, P. and Ahmadi, A., "Fluoride determination in some mouth wash preparations by a novel La(III) graphite coated membrane sensor based on amitraz", *Anal. Chim. Acta*, **531**, 185 (2005).

17. 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. Actuators*, B**, 114**, 855 (2006).

18. Ganjali, M.R., Mirnaghi, F.S., Norouzi, P. and Adib, M., "Novel Pr(III)-selective membrane sensor based on a new hydrazide derivative", *Sens. Actuators, B,* **115**, 374 (2006).

19. Ganjali, M.R., Norouzi, P., Alizadeh, T. and Adib, M., "Application of 8-amino-N-(2-hydroxybenzylidene)naphthylamine as a neutral ionophore in the construction of a lanthanum ion-selective sensor", *Anal. Chim. Acta*, **576**, 275 (2006).

20. Ganjali, M.R., Norouzi, P., Tamaddon, A. and Husain, S.W., "Novel Tm(III) membrane sensor based on 2,2'-dianiline disulfide and its application for the fluoride monitoring of mouth wash preparations", *Bull. Korean. Chem. Soc.*, **27**, 1418 (2006).

21. Ganjali, M.R., Faridbod, F., Norouzi, P. and Adib, M., "A novel Er(III) sensor based on a new hydrazone for the monitoring of Er(III) ions", *Sens. Actuators, B,* **120**, 119 (2006).

22. Ganjali, M.R., Norouzi, P., Akabri-Adergani, B., Riahi, S. and Larijani, B., "An asymmetric lutetium(III) microsensor based on N-(2-furylmethylene) pyridine-2,6-diamine for determination of lutetium(III) ions", *Anal. Lett.*, **40**, 1923 (2007).

23. Ganjali, M.R., Norouzi, P., Faridbod, F., Hajiabdollah, N., Larijani, B. and Hanifehpour, Y., "Procaine as a sensing material for determination of dysprosium(III) ions in presence of other rare-earth elements in biological and environmental samples", *Anal. Lett.*, **40**, 2544 (2007).

24. 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-methoxyphenyl) phosphoramidate", *Electrochim. Acta*, **53**, 1870 (2007).

25. Wu, J. and Zhang, Y., "Gadolinium ion-selective electrode and its application in flow injection analysis", *Fenxi Huaxue*, **20**, 611 (1992).

26. Wu, J., Zhang, Y., Li, W., Che, J., Yan, M. and Sun, J., "Functional polymer membrane electrode. Development of the gadolinium ion-selective electrode", *Zhongguo Xitu Xuebao*, **3**, 27 (1985).

27. Ganjali, M.R., Tahami, M., Shamsipur, M., Poursaberi, T., Haghgoo, S. and Hosseini, M., "Novel gadolinium PVC-based membrane sensor based on omeprazole as an antibiotic", *Electroanalysis*, **15**, 1038 (2003).

28. Ganjali, M.R., Emami, M., Rezapour, M., Shamsipur, M., Maddah, B., Salavati-Niasari, M., Hosseini, M. and Talebpoui, Z., "Novel gadolinium poly(vinyl chloride) membrane sensor based on a new S-N Schiff's base", *Anal. Chim. Acta*, **495**, 51 (2003).

29. Ganjali, M.R., Rezapour, M., Norouzi, P. and Salavati-Niasari, M., "A new pentadentate S-N schiffs' base as a novel ionophore in construction of a novel Gd(III) membrane sensor", *Electroanalysis*, **17**, 2032 (2005).

30. Norouzi, P., Ganjali, M.R., Alizadeh, T., Tajarodi, A. and Hanifehpour, Y., "Fabrication of a highly selective and sensitive Gd(III)-PVC membrane sensor based on N-(2-pyridyl)-N'-(4-nitrophenyl)thiourea", *Sens. Actuators*, B, **120**, 487 (2007).

31. 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).

32. Faridbod, F., Ganjali, M.R., Labbafi, S. and Norouzi, P., "Lanthanide recognition: development of an asymetric gadolinium microsensor based on N-(2-pyridyl)-N'-(4-nitrophenyl)thiourea", *Anal. Lett.*, **41**, 2972 (2008).

33. Brzozka, Z., "Transition metal ion-selective membrane electrodes based on complexing compounds with heteroatoms. Part I. Complexing compounds containing nitrogen atoms", *Analyst*, **113**, 891 (1988).

34. Mi, Y., Mathison, S., Goines, R., Logue, A. and Bakker, E., "Detection limit of polymeric membrane potentiometric ion sensors: How can we go down to trace levels", *Anal. Chim. Acta*, **397**, 103 (1999).

35. Meier, P.C., Morf, W.E., Laubli, M. and Simon, W., "Evaluation of the optimum composition of neutral carrier membrane electrodes with incorporated cation-exchanger sites", *Anal. Chim. Acta*, **156**, 1 (1984).

36. Shawish, H.M.A., Saadeh, S.M., Al-Dalou, A.R., Ghalwa, N.A. and Assi, A.A.A., "Optimization of tramadol–PVC membrane electrodes using miscellaneous plasticizers and ion-pair complexes", *Mater. Sci. Eng. C*, **31**, 300 (2011).

37. Jagur, G.J., Marian, S. and Vofsi, D., "Mechanism of a selective permeation of ions through solvent polymeric membranes", *Sep. Sci.*, **8**, 33 (1973).

38. Morf, W.E., Ammann, D. and Simon, W., "Elimination of the anion interference in neutral carrier cation-selective membrane electrodes", *Chimia*, **28**, 65 (1974).

39. Żubrowska, M., Wróblewski, W. and Wojciechowski, K., "The effect of lipophilic salts on surface charge in polymeric ion-selective electrodes", *Electrochim. Acta*, **56**, 6114 (2011).

40. Ammann, D., Pretsch, E., Simon, W., Lindner, 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).

41. Gratzl, M., Rakiás, F., Horvai, G., Tóth, K. and Pungor, E., "Effect of pH on the response of a cyanide ion-selective electrode", *Anal. Chim. Acta*, **102**, 85 (1978).

42. Macca, C., "Response time of ion-selective electrodes. Current usage versus IUPAC recommendations", *Anal. Chim. Acta*, **512**, 183 (2004).

43. Bakker, E. and Pretsch, E., "Lipophilicity of tetraphenylborate derivatives as anionic sites in neutral carrier-based solvent polymeric membranes and lifetime of corresponding ion-selective electrochemical and optical sensors", *Anal. Chim. Acta*, **309**, 7 (1995).

44. Fujinaga, T., Okazaki, S. and Freiser, H., "Ion selective electrodes responsive to anionic detergents", *Anal. Chem.*, **46**, 1842 (1974).

45. Espadas, T.C., Bakker, E., Barker, S. and Meyerhoff, M.E., "Influence of nonionic surfactants on the potentiometric response of hydrogen ion-selective polymeric membrane electrodes", *Anal. Chem.*, **68**, 1623 (1996).

Chapter 5

Nd^{3+} Ion-Selective Coated Graphite Electrodes Based On Lariat Ethers

5.1 Introduction

Metals are used both for domestic and industrial purposes. As a result they occur in environment and cause harmful effects on human and animal health. Therefore, the detection of metal ions is important from biological, environmental and industrial point of view. Thus, it is desirable to develop analytical approaches which could allow the quantification of these ions. Nowadays apart from transition elements, rare earth elements (REEs) are also industrially important and have posed significant challenge to the environmentalists as they are enough toxic. 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 [1-5]. Similar to other rare earths, neodymium is moderately toxic and irritating to eyes and long term exposure to neodymium may cause lung embolisms and cell membrane damage which has negative influence on reproduction and function of the nervous system [6, 7]. Neodymium is widely used in the preparation of colour televisions, fluorescent and energy saving lamps, modern vehicles components, data storing devices, loudspeakers and in petrol-producing industries. The widespread use of neodymium results in its occurrence in many environmental samples where its estimation is de needed. A number of instrumental techniques [8-18] are commonly used for low-level determination of rare-earth ions in solution.

Nowadays, there has been much focus on the construction of ion selective electrodes that function on the basis of chemical recognition principle because they can help to translate the chemistry of new substrate-binding systems into tools that can be used to recognize selectively various target species in the presence of potentially interfering analytes. Therefore efforts have been made from time to time to develop good ISEs of higher sensitivity and selectivity.

The recognition elements which can be utilized as suitable carriers for construction of membrane sensors have characteristics of suitable size and specific metal ligand interaction. The quest for ligands that might offer new opportunities for applications or provide insight into fundamental chemical processes is always of interest. Electrically neutral lipophilic ligands containing a certain number of binding sites of high solvating ability can behave as ionophore to prepare ion-selective membrane to detect different cations. The membranes of neutral ionophores have been successfully used as ISEs for many metals [19-30]. However their potential in the determination of rare earths has not been fully realized due to non availability of suitable ionophores. Therefore, advances have been made in the design of molecular hosts capable of selectively binding ionic guests and consequently have given rise to a plethora of imaginative and ingenious molecular receptors.

In recent times, macrocyclic chemistry has undergone significant expansion which has resulted in designing macrocyclic ligands with interesting and selective coordination properties, thus opening up the possibilities of preparing good ionophores for rare earths. Many intensive studies on the synthesis of highly selective ionophores as sensory molecules for ion-selective electrodes have been reported and much interest has been focused on macrocyclic compounds [31]. The design and function of synthesized macrocyclic carrier for cationic selective membrane sensors are usually based on the structure and size of ion carrier, the stability and its ability to extract the target ion into the membrane phase. Macrocyclic compounds could be easily functionalized with additional chelating moieties to enhance their selectivity and with branched alkyl chains to increase ionophore lipophilicity and to avoid crystallization in the membrane [32]. Also the introduction of functionalized pendant coordinating arms into the macrocyclic framework can lead to important changes in the complexation capability of the ligands providing: additional coordinating functions, enhancing the metal ion selectivity and the stability of metal complexes or promoting the formation of supramolecular structures with different properties and applications [33 - 40].

Synthetic macrocycles are a growing class of compounds with varying chemistry, a wide range of different molecular topologies and sets of donor atoms. The literature shows that macrocyclic compounds containing varying combination of nitrogen (N), oxygen (O) and sulfur (S) as donor sites tend to form stable complexes with lanthanides [41]. In this study, we have synthesized two novel pendant macrocyclic ligands (L_4 and L_5) and explored them as potential ionophores for preparing Nd^{3+} selective sensors. The subsequent discussion reveals that there are only limited reports in the preparation of neodymium ISEs.

Nd^{3+} ion-selective electrodes

A PVC-based sensor for Nd^{3+} ions based on chelating inorganic ion-exchange resin tetracycline-sorbed zirconium (IV) tungstophosphate as an electroactive material was prepared by Aggarwal *et al.* [42] this sensor exhibited the linear working concentration range ($1.0 \times 10^{-1} - 5.0 \times 10^{-5}$ mol L^{-1}) with detection limit as 1.0×10^{-5} mol L^{-1}. The proposed membrane sensor exhibited good selectivity over other metal ions and used in the determination of Nd^{3+} in Sibaiya phosphate ore. Shamsipur *et al.* [43] carried out spectrofluorometric complexation of 5-pyridino-2,8-dithia[9](2,9)-1,10-phenanthrolinephane towards various REEs and found the stability of metal complexes in the order of $Nd^{3+} > Yb^{3+} > Gd^{3+} > Sm^{3+} > La^{3+}$. Further they used this neutral ionophore for the preparation of polymeric Nd^{3+} selective electrode which exhibited Nernstian response over a wide concentration range (1.0×10^{-6}-1.0×10^{-2} mol L^{-1}) with a low limit of detection 1.0×10^{-6} mol L^{-1}. This electrode showed a fast response time of approximately 5 s and could be used in the extraction of Nd^{3+} ions from tap water samples.

Ganjali *et al.* [44] reported a Nd^{3+}-selective polymeric membrane sensors based on 2-{[(6-aminopyridin-2-yl)imino]methyl}phenol. The sensor showed a Nernstian slope of 19.6 ± 0.3 mV $decade^{-1}$ over the concentration range of 1.0×10^{-5} - 1.0×10^{-2} mol L^{-1} and a detection limit of 2.0×10^{-6} mol L^{-1} of Nd^{3+} ions. This sensor showed advantages of low resistance, fast response time, good selectivity and the potentials were independent of pH in the range 3.5 to 8.5. Norouzi *et al.* [45] used N-(2-furylmethylene) pyridine-2,6-diamine as an excellent ionophore in the construction of Nd^{3+}-selective polymeric membrane electrode. The sensor response was Nernstian (slope of 19.6 ± 0.3 mV per decade of $a_{Nd}{}^{3+}$) over a wide concentration range (1.0×10^{-5} - 1.0×10^{-2} mol L^{-1}) with a detection limit of 7.0×10^{-6} mol L^{-1}. The sensor responds sharply within 15 s and showed a considerable lifetime of six weeks in the pH range of 4.0 - 8.0. Behmadi *et al.* [46] reported Nd^{3+}-selective PVC membrane electrode containing benzyl-bisthiosemicarbazone as a suitable ion carrier. This electrode exhibited Nernstian response for the Nd^{3+} ions over a wide concentration range, 1.0×10^{-2} - 1.0×10^{-6} mol L^{-1}, with a detection limit of 6.2×10^{-7} mol L^{-1} in the pH range of 3.7 - 8.3. The electrode revealed high selectivity, fast response time (10 s), considerable lifetime (6 weeks) and could be used for the determination of neodymium in soil and sediment samples. Chandra *et al.* [47] developed a polymeric membrane Nd^{3+}-selective electrode using 11,13-Diaza-4,7,12-trioxo-2(3),8(9)-dibenzoyl-cyclotetridecane-1,11-diene (DATODBCT) as an excellent ionophore. The electrode showed Nernstian response (slope of 19.4 ± 0.3 mV per decade of $a_{Nd}{}^{3+}$) in the concentration range 1.0×10^{-8} to 1.0×10^{-1} mol L^{-1} with a detection limit of 8.0×10^{-7} mol L^{-1} in the pH range of 3.0 - 7.0. Gupta *et al.* [48] used two neutral Ionophores *N, N'*-bis((1H-pyrrol-2-yl)methylene)cyclohexane-1, 2-diamine and 3, 3'-(cyclohexane-1, 2-diylbis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)-bis(5-hydroxymethyl)-pyridine-2-ol) for the construction of Nd^{3+}-selective electrodes. The electrode exhibited significantly enhanced selectivity towards Nd^{3+} in the concentration range 5.0×10^{-7} to 1.0×10^{-2} mol L^{-1} with a detection limit of 1.0×10^{-7} mol L^{-1} and a Nernstian compliance (19.8 ± 0.3 mV $decade^{-1}$ of activity). *p*-toluenesuifonyl-serine-neodymium(III) complex was used by Liu *et al.* [49] as an electroactive material to prepare a Nd^{3+}-selective PVC membrane electrode which had good Nernstian response to neodymium ion in the concentration range of 1.0×10^{-6} - 1.0×10^{-2} mol L^{-1}. The slope of calibration curve was 19.3 mV $decade^{-1}$ of a_{Nd}^{3+} with the detection limit 6.31×10^{-7} mol L^{-1} and it could be used in the determination of neodymium in simulated samples. Kumar *et al.* [50] prepared Nd^{3+}-selective electrodes by using Sn(IV) antimonotungstate (SnSbW) and Zr(IV) antimonotungstate (ZrSbW) as electroactive materials and epoxy resin as a binder. The electrode based on SnSbW shows potential response to Nd^{3+} in the concentration range of 1.0×10^{-4} to 1.0×10^{-1} mol L^{-1} with a super-Nernstian slope of 40.0 mV $decade^{-1}$ of a_{Nd}^{3+} and the potentials remained stable in the pH range 3.0-9.0 whereas the electrode based on ZrSbW worked in the concentration range of 1.0×10^{-5} to 1.0×10^{-1} mol L^{-1} with a near-Nernstian slope (25.0 mV $decade^{-1}$ of a_{Nd}^{3+}) and the potentials were independent of pH in the range 2.9-9.9. Menon *et al.* [51] reported Nd^{3+}-selective PVC membrane electrode containing azocalix[4]arene as a suitable ionophore. The electrode exhibited Nernstian response for Nd^{3+} with slope of 19.8 ± 0.2 mV $decade^{-1}$ over a wide linear range of 4.0×10^{-8} to 1.0×10^{-1} mol L^{-1} and low detection limit 1.0×10^{-8} mol L^{-1}. Having advantages of fast response time (10 s), long shelf life (four months) and wide pH range 4.0 to 8.0, this electrode was employed for the detection of neodymium ions in industrial waste water as well as in lake water. Zamani *et al.* [52] used *N,N'*-bis(quinoline-2-carboxamido)-4,5-dimethylbenzene as an ionophore for fabricating Nd^{3+}-selective sensor which exhibited Nernstian response to Nd^{3+} ions in the concentration range of 5.0×10^{-6} to 1.0×10^{-2} mol L^{-1} with slope of 19.5±0.4

mV decade^{-1} of a_{Nd}^{3+} and detection limit of 4.8×10^{-6} mol L^{-1}. The proposed sensor showed high selectivity, fast response time (l0 s) wide pH range (2.9 to 9.2) and could be used for ten weeks without significant change in its potential response.

Even the reported electrodes show narrow linear working concentration range and poor detection limit. Therefore a better ion-selective electrode needs to be developed for neodymium estimation. The results presented in this chapter show that attempts to prepare PVC coated graphite electrodes as Nd^{3+}-selective sensors based on two novel ionophores have been successful.

5.2. Experimental

5.2.1 Reagents

Reagent grade sodium tetraphenylborate (NaTPB), potassium tetrakis *p*-(chloro phenyl)borate (KTpClPB), dibutylphthalate (DBP), benzyl acetate (BA), dioctylphthalate (DOP), *o*-nitrophenyloctylether (*o*-NPOE), dioctylsebacate (DBS), acetophenone (AP) tetrahydrofuran (THF), sodium borohydride ($NaBH_4$), sodium hydroxide, potassium carbonate and high molecular weight poly vinylchloride were purchased from E. Merck (Germany) and used as received. 2, 6-diaminopyridine, *m*-phenylenediamine and acrylonitrile were procured from Across organics (USA). Triton X-100 from Sigma-Adlrich (Steinheim, Germany), sodiumdodecylsulphate (SDS) and tetrabutylammonium chloride (TBC) from Loba Chemie (Mumbai) were reagent grade materials. The metal chlorides were of analytical grade and used without further purification and their solutions were prepared in doubly distilled water. The solutions were standardized wherever necessary.

5.2.2 Apparatus and instrumentation

All the apparatus and instruments used have been described in section 3.2.2 of Chapter 3. A conductivity meter model Cyberscan 510 was also used for conductance measurements provided with a dip-type cell ($K_{cell} = 1.0$).

5.2.3 Synthesis of Lariat ethers

A detailed synthesis scheme of the two macrocyclic ligands is shown in Figure 5.1. Dialdehyde [1,2-bis(2-carboxyaldehydephenoxy)ethane] used as the precursor, was synthesized according to the reported method [53]. Novel lariat ethers were synthesized by following the previous procedure [54] and characterized as follows.

5.2.3.1 Synthesis of 1, 5-di(cyanoethane)-2,4:7,8:13,14-tribenzo-1, 5-diaza-9, 12-dioxa cyclopentadeca-2,7,13-triene (L_4)

In a 100 mL round bottom flask equipped with a reflux condenser, 2.70 g (10 mmol) of 1, 2-bis(2-carboxyaldehydephenoxy)ethane were dissolved in 20 mL of Methanol. 1.08 g (10 mmol) of m–phenylenediamine in MeOH (20 mL) was added in one portion and the content was refluxed for 10 h after vigorous stirring for 2 h. After evaporation of the solvent, yellow product (A) was obtained. Anal. calcd. for [$C_{22}H_{18}N_2O_2$] (%): C, 77.17; H, 5.30; N, 8.18; O, 9.35 Observed (%): C, 78.66; H, 5.43; N, 8.55; O, 7.36. ^{1}H NMR (DMSO, 500 MHz) δ_{ppm}: 4.6 (m, –O-CH_2, 4H), 7.1–7.6 (m, H-Ar, 12 H), 10.23 (s, -CH=N, 2H),. FT-IR (KBr, cm^{-1}): 1622 ν(-C=N). To the solution of the macrocycle A (0.342 g, 1 mmol) in 10 mL MeOH, solid $NaBH_4$ (0.5 g, 13 mmol) was added slowly, keeping the flask in an ice bath, and stirred for 1 h. A second addition of $NaBH_4$ (0.27 g, 7 mmol) was made and the resulting solution was stirred at room temperature for 2 h along with the addition of anhydrous K_2CO_3 (1 g). 5 mL (excess amount) acrylonitrile was added drop by drop and the solution was stirred overnight followed by refluxing for 10 h. After reducing the volume under vacuum, the solution was kept overnight in refrigerator and a white solid was obtained. It was then filtered and washed with water followed by cold MeOH. The product (Figure 5.2) was dried in vacuum and finally purified by column chromatography.

Yield: 49 %, mp 147°C. Anal. calcd. for [$C_{28}H_{28}N_4O_2$] (%): C, 74.31; H, 6.24; N, 12.38; O, 7.07; Observed (%): C, 73.86; H, 6.82; N, 12.45; O, 6.86. ^{1}H NMR (DMSO, 500 MHz) δ_{ppm}: 7.0–7.7 (m, H-Ar, 12H), 4.6 (m, -Ar-CH_2-N-, 4H), 2.5 (t, -C-CH_2-CN, 4H), 3.6 (t, -N-CH_2-C-, 4H), 4.5 (t, O-CH_2-, 4H),. FT-IR (KBr, cm^{-1}): 3048 (aromatic C-H str.), 2920 (asymmetric –CH_2– str.), 2872 (symmetric –CH_2– str.), 2253 (–CN str.).

5.2.3.2 Synthesis of 1, 5-di(cyanoethane)-2,3,4-pyridine-7,8:13,14-dibenzo-1,3,5-triaza-9, 12-dioxacyclopentadeca-2,7,13-triene (L_5)

2, 6-diaminopyridine (1.09 g, 10 mmol) was added to 20 mL methanolic solution of dialdehyde (2.70 g, 10 mmol) in one portion and the content was stirred for 2 h followed by refluxing for 10 h. After cooling, the solvent was evaporated off and the crude dark yellow product (B) was obtained. Anal. calcd. for [$C_{21}H_{17}N_3O_2$] (%): C, 73.45; H, 4.99; N, 12.24; O, 9.32 Observed (%): C, 73.49; H, 5.08; N, 11.73; O, 9.70. ^{1}H NMR (DMSO, 500 MHz) δ_{ppm} : 4.2 (m, –O-CH_2, 4H), 6.9–7.9 (m, H-Ar, 11 H), 9.5 (s, -CH=N, 2H),. FT-IR (KBr, cm^{-1}): 1628 ν(-C=N). To 10 mL methanolic solution of macrocycle (B) (0.343 g, 1 mmol), solid $NaBH_4$ (0.5 g, 13 mmol) was added slowly with constant stirring and the flask was kept in an ice bath. A second addition of $NaBH_4$ (0.27 g, 7 mmol) was made and the resulting solution was stirred at room temperature for 2 h along with the addition of anhydrous K_2CO_3 (1 g). Acrylonitrile (5 mL) was added drop by drop and then the solution was stirred over night followed by refluxing for 12 h. It was concentrated under vacuum and kept in refrigerator, a brown precipitate was obtained. The product (Figure 5.3) was filtered and washed with water and cold MeOH. It was dried under vacuum and purified by column chromatography.

Yield: 52 %, mp 169°C. Anal. calcd. For [$C_{27}H_{27}N_5O_2$] (%): C, 71.50; H, 6.00; N, 15.44; O, 7.06 Observed (%): C, 70.86; H, 6.08; N, 15.23;O, 7.87. ^{1}H NMR (DMSO, 500 MHz) δ_{ppm}: 6.7–7.2 (m, H-Ar, 11H), 4.5 (s, -Ar-CH_2-N-, 4H), 2.7 (t, -C-CH_2-CN, 4H), 3.5 (t, -N-CH_2-C-, 4H), 4.3 (t, O-CH_2-, 4H),. FT-IR (KBr, cm^{-1}): 3042 (aromatic C-H str.), 2924 (asymmetric –CH_2– str.), 2863 (symmetric –CH_2– str.), 2248 (–CN str.).

5.2.4 Preparation of coated graphite electrodes

The membrane ingredients (ionophore, anion additives, PVC and plasticizers) were dissolved in 5 mL of tetrahydrofuran and the solvent was partly 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 with a fixed copper wire at the top, 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. 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 exposed.

5.2.5 Preparation of polymeric membrane electrodes

PVC based membrane electrodes of two lariat ethers were fabricated by the same procedure as reported in *section 3.2.4* of Chapter 3. The fabrication of segmented sandwich membranes were carried out as described in *section 3.2.5* of Chapter 3.

5.2.6 Equilibration of electrodes and potential measurement

The time of contact and concentration of equilibrating solution were optimized in order to get stable and reproducible potentials at relatively short response time. Each electrode was pre-conditioned before potentiometric measurements by soaking it in 1.0×10^{-3} mol L^{-1} $NdCl_3$ solution for 24 h prior to use. The potentials were measured by varying the concentration of $NdCl_3$ solution in the range 1.0×10^{-1} to 1.0×10^{-9} mol L^{-1}. Standard $NdCl_3$ solutions were obtained by gradual dilution of 0.1 mol L^{-1} $NdCl_3$ solution. EMF measurements with the coated graphite electrode were carried out on Century CP 901 digital pH meter at 25 ± 0.1°C using saturated calomel electrode (SCE) as reference electrode by the following cell setup:

Coated graphite electrode || Sample solution || $Hg/HgCl_2$ |KCl (satd.)

Activity coefficients were calculated according to the Debye-Huckel procedure, using the equation (1) given in *section 3.2.6* of Chapter 3.

5.2.7 Determination of formation constant

The formation constants of ion-ionophore complexes within the membrane phase were calculated by the same procedure as described in *section 3.2.7* of Chapter 3.

5.2.8 Aqueous layer test

The formation of aqueous layer between the membrane and the solid contact was tested as introduced by E. Lindner [55]. The best performing electrodes were modified by applying self assembled monolayer (SAM) of a redox active compound (4-mercaptobenzoic acid) on the graphite surface before casting the membrane. These electrodes were sequentially exposed to concentrated solutions (c = 0.1 mol L^{-1}) of Nd^{3+} and La^{3+} ions and the potentials were recorded as a function of time.

5.3 Results and Discussion

5.3.1 Preliminary conductometric Study

The complexation of L_4 and L_5 with a number of cations was investigated conductometrically in acetonitrile solution, 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 the ionophore until the titration plot showed a break. The variation of conductance as a function of ligand to metal ratio is shown in Figures 5.4 and 5.5. It is seen from the figures that the conductance variation for Tb, Sm, Gd, Dy is minimal indicating that either these metals cannot form complex with the ligands or forming the complex of weak stability. On the other hand the conductance titration plots for Nd, Pr, La, show a significant variation in conductance and giving a sharp break which gives the molar ratio for the interaction of metal ions with these ligands. From the breaks in the plots, it is clear that the metal-ligand stoichiometry for these complexes is 1:1.

5.3.2 Evaluation of formation constants

The formation constants of the resulting 1:1 metal-ionophore complexes were then calculated according to sandwich membrane method. The results, gathered in Table 5.1, show that the two ligands form most stable complex with Nd^{3+} having formation constants 8.72 and 9.08 for L_4 and L_5 respectively. The formation constant values for other metals are much smaller. The higher stability constant of Nd^{3+} complexes with L_4 and L_5 is an indication that both ligands have high affinity for Nd^{3+} ions compared to other metals. Therefore these ligands are potential ionophores for preparing Nd^{3+} ion selective electrodes. The subsequent results show that the coated graphite electrodes of L_4 and L_5 act as sufficiently selective Nd^{3+} sensors.

5.3.3 Optimization of membrane composition

It is well known that the membrane composition of ion selective electrodes significantly affects their performance [56, 57]. Therefore a number of electrodes having different composition were prepared and studied. The composition of the membranes was varied by taking the ingredients in different relative amounts. The potential response of the coated graphite electrodes containing only ionophores and PVC was first investigated and the results are summarized in Tables 5.2 and 5.3 respectively. In these studies the concentration of ionophores was varied in the range 2-8 % (w/w) and found that the electrodes having ionophore concentration 5 % (w/w) gave the best performance. It is seen from Tables 5.2 and 5.3 that the electrode no. 1 and 16 respond to Nd^{3+} ions linearly in the concentration range 7.1×10^{-6}–5.0×10^{-2} and 3.1×10^{-6}–1.0×10^{-2} mol L^{-1} with sub-Nernstian slope 15.9 and 16.6 mV decade^{-1} of a_{Nd}^{3+}, respectively. Next it was thought necessary to improve the performance of the electrodes with regard to slope and working concentration range. It is established [58] that the addition of plasticizer generally improves the performance of ion selective electrode systems due to their influence on the dielectric constant of the membrane phase. Therefore, in this study, the effect of addition of six plasticizers *viz* *o*-NPOE, BA, AP, DBP, DOP and DBS was looked into and the responses obtained with the plasticized membranes are given in Figures 5.6 and 5.7. It is clear from the performance characteristics of the electrode no. 2 to 7 (Table 5.2) and electrode no. 17 to 22 (Table 5.3) that the addition of plasticizers generally increases the slope and widens the working concentration range. The best effect is obtained for *o*-NPOE as the electrode no. 2 and 17 having NPOE plasticized membranes give the wider linear range, 1.0×10^{-7}–5.0×10^{-2} and 1.6×10^{-7}–1.0×10^{-1}mol L^{-1} with near Nernstian slope 18.0 and 18.8 mV decade^{-1} of a_{Nd}^{3+}, respectively. Therefore, in further studies NPOE was used as plasticizer. The better performance of *o*-NPOE plasticized electrodes (CGE-2 and 17) could be due to high dielectric constant of the plasticizer which helped to increase the polarity of the membrane and to reduce the leaching of membrane components.

The improvement in the performance of these electrodes was further attempted by adding lipophilic anion additives which generally suppress the interference by sample anions [59]. The effect of two additives NaTPB and KTpClPB was looked into the potentiometric response of Nd^{3+}-selective electrodes and the results showed that both the additives improved the performance of these CGEs. However of the two additives NaTPB performs better and CGE no. 9 and 24, containing 3 % (w/w) NaTPB, gave the best performance of all the membranes studied so far in terms of widest concentration range with Nernstian slope and low detection limit.

Thus at this stage the studies have shown that the ingredients producing best membranes along with ionophores (L_4 and L_5) are additive NaTPB, Plasticizer o-NPOE and PVC as inert Matrix. Further improvisation in the potentiometric characteristics of CGE-9 and 24 was tried by changing the amount of ionophores only. The results show that the presence of higher amounts of ionophore does not in anyway enhance the performance of these electrodes but rather adversely affect the performance by decreasing the slope and shortening the linear range. Thus the optimum amount of the ionophores in these studies is found to be 5 % (w/w). From these studies it is reasonable to conclude that the electrodes of optimum compositions L_4:NPOE:NaTPB:PVC as 5:57:3:35 (%, w/w) (CGE-9) and L_5:NPOE:NaTPB:PVC ratio as 5:53:3:39 (%, w/w) (CGE-24) perform best in all respects. The potential response calibration curve for the electrodes CGE-9 and CGE-24 is shown in Figure 5.8.

Further it was observed from aqueous layer test that there was no drift in the potentials with time. A comparison of the performance characteristics of SAM modified coated graphite electrodes with those of CGE-9 and CGE-24 is given in Table 5.4. Applying a self assembled monolayer of redox active compound did not improve the performance characteristics of CGE-9 and CGE-24 significantly; however, stable potential values were obtained for SAM modified graphite electrodes. Therefore the possibility of the formation of undesirable aqueous layer between the ion selective membrane and its solid contact can be neglected. Therefore all further studies were carried out with CGE- 9 and 24.

5.3.4 Effect of pH on the performance of the electrodes

The effect of pH on the performance of the two coated graphite electrodes was investigated by measuring the potential in a 1.0×10^{-3} mol L^{-1} $NdCl_3$ solution at different pH values from 1 to 10. The pH was adjusted with 0.1 M HCl/NaOH and the potential response obtained at different pH are shown in Figure 5.9. It is seen from this figure that the potentials remain constant in the pH range 3.5 to 7.6. At pH value above 7.6, the potentials start decreasing which appear probably due to the formation of metal hydroxide species in the system [60]. Similarly in the acidic range, i.e., at pH less than 3.5, the response of these electrodes increased rather irregularly with decreasing the pH of the solution. At such high acidities, the membrane may extract H^+ ions in addition to Nd(III) ions [61] due to the protonation of donor sites of the ligands. Thus these Nd(III) selective CGEs were found to perform successfully in the pH range 3.5-7.6.

5.3.5 Potentiometric selectivity

The selectivity is one of the most important characteristics of an ion sensor which determines its utility for analytical purpose. The potentiometric selectivity coefficient values for the electrodes (CGE- 9 and 24) were determined according to FIM Following the fixed interference method, a fixed concentration of interfering ion (a_B =1.0×10^{-2} mol L^{-1}) was added to the primary Nd^{3+} ion solutions of concentration ranging from 1.0×10^{-8} to 1.0×10^{-2} mol L^{-1} and the potentials were measured. The potential values obtained were plotted versus the activity of the primary ion. Potentiometric selectivity coefficients were determined graphically using the expression discussed in chapter 2 and the results obtained are reported in Table 5.5. The values of selectivity coefficients show that these electrodes are selective to Nd^{3+} over monovalent (Ag^{+}, Na^{+}, K^{+} , Li^{+}) and divalent (Hg^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Mg^{2+}, Ca^{2+}, Zn^{2+}, Cu^{2+}) ions. High stability of the Nd^{3+} complexes of the two lariat ethers accounts for the selectivity of these electrodes towards Nd^{3+} over other interfering ions. However the selectivity coefficient values for cobalt are not very small and thus, estimation of neodymium can be done only in presence of small amounts of Co^{2+}. In order to estimate the extent of interference caused by cobalt, the performance of the two electrodes was checked in presence of different concentrations of Co^{2+} and the results (Figures 5.10 and 5.11) showed that the two electrodes do not exhibit significant change in their performance characteristics at lower concentrations of Co^{2+} ion. When the concentration of Co^{2+} is increased up to 1.0 × 10^{-2} mol L^{-1}, interference causes a shortening of linear working concentration range and elevation in detection limits with increased value of slope as determined from the potential response curve. However it was found that the presence of 5.0×10^{-3} mol L^{-1} Co^{2+} can be tolerated over the entire concentration range for the two electrodes. Further selectivity coefficient values indicate that the electrodes are also selective to Nd^{3+} ion over a number of lanthanides (Gd^{3+}, Pr^{3+}, Ce^{3+}, La^{3+}, Tb^{3+}, Dy^{3+} Sm^{3+} and Yb^{3+}). However, between the two electrodes CGE-24 based on L_5 was found better regarding selectivity as CGE-9 based on L_4 showed significant interference to La^{3+}, Pr^{3+} and Yb^{3+}. Thus the two electrodes can be used for neodymium estimation in presence of these rare earths. However, for CGE-9 the concentration of La^{3+}, Pr^{3+} and Yb^{3+} should not exceed than 1.0×10^{-2} mol L^{-1} while estimating neodymium in view of not very high selectivity of this sensor.

5.3.6 Determination of response time and lifetime

The response time of the two coated graphite electrodes was determined [62] by measuring the time required to achieve a steady state potential (within ±1 mV) after successive immersion of the electrodes in a series of neodymium ion solutions, each having a ten-fold increase in concentration ranging from 1.0×10^{-6} to 1.0×10^{-2} mol L^{-1}. The electrodes were dipped in the test solutions successively and the potential was measured with respect to time. The typical potential-time plots for the two electrodes are shown in Figures 5.12 and 5.13. It is concluded from the figures that the response time for the electrode (CGE-9) based on L_4 is 14 s where as for the electrode (CGE-24) based on L_5 it is 10 s. The potential readings remained constant for about 3 min after which a slow divergence was observed. A similar procedure was adopted, in a sequence of high to low sample concentration, in order to evaluate the reversibility of the sensor.

The loss of membrane components from the electrode is the major cause for the short lifetime of the polymer membrane electrodes [63]. The lifetime of the electrodes was measured by monitoring the change in slope and working range with time. In order to determine the durability of the electrodes, they were tested daily over a period 4.5 months and their characteristics were observed. The results showed (Table 5.6) that the two electrodes have a long lifetime and can be used successfully for 3 months after which some change is observed in their performance characteristics towards Nd^{3+} ion due to swelling of membrane and leaching of membrane components on continuous usage. The reproducibility of the Nd^{3+} electrode was also investigated and the standard deviations of 10 replicate measurements at 1.0×10^{-3} mol L^{-1} were ± 0.3 and ± 0.4 mV, for CGE- 9 and 24 respectively. However when not in use, the electrodes were stored in 1.0 mM $NdCl_3$ solution.

5.3.7 Effect of surfactants on the performance of CGEs

Surfactants are highly surface active molecules and affect the performance of the electrode as they have a tendency to accumulate and adsorb at the sample membrane interface [64]. In order to evaluate the effect of surfactants on potentiometric properties of the CGEs based on the ionophores L_4 and L_5, their basic analytical parameters were determined in the presence of cationic (TBC), anionic (SDS) and nonionic (Triton X–100) surfactants and the results are summarized in Table 5.7. It can be seen from the results that the effect of surfactants was negligible at their concentration below 10^{-4} M, however at concentration 10^{-4} M or above they start adversely affecting the performance of the electrodes showing decreased slope, narrow working concentration range and increased detection limit. Further the selectivity of the electrodes also decreased in the presence of surfactants. The high interference is probably due to the adsorption of surfactant molecules at the membrane solution interface.

5.3.8 Effect of partially non-aqueous mixtures

The performance of the two electrodes was also investigated in partially non-aqueous media using acetonitrile–water, methanol–water and ethanol–water mixtures and the results showed (Table 5.8) that the two electrodes tolerate up to 20% (v/v) non-aqueous content. However at higher non-aqueous content the performance of the electrodes started deteriorating which should be due to the leaching of ionophores from the membrane phase.

The electrode performance also affected when the electrodes were stored in non-aqueous solution for one week and the membrane got damaged after ten days of storage.

5.3.9 Comparisons of proposed CGEs with reported sensors

The performance characteristics of the prepared electrodes (CGE - 9 and 24) were compared with the other Nd^{3+} ion selective electrodes based on various ionophores and shown in Table 5.9. The comparative study of the two CGEs based on L_4 and L_5 reveals that they are superior over the previously reported Nd^{3+}-selective electrodes with regard to their wide working range and low detection limit. However, their selectivity is comparable to the reported electrodes.

5.4 Analytical Applications

5.4.1 Determination of Nd^{3+} in mixed binary solutions

The proposed CGEs were used to determine Nd^{3+} in various binary mixtures, prepared by adding 10 mL of 5.0×10^{-3} mol L^{-1} solution of different cations to 1.0×10^{-4} mol L^{-1} neodymium ion solution at 5.0 pH. The results are summarized in Table 5.10. The recovery of Nd^{3+} ions from the binary test samples is satisfactory which shows high selectivity of these electrodes for Nd^{3+} ions over the foreign ions.

5.4.2 Potentiometric titration

The analytical utility of these electrodes was also evaluated by carrying out potentiometric titration of 20 mL of 5.0×10^{-3} mol L^{-1} Nd^{3+} against 1.0×10^{-2} mol L^{-1} EDTA at pH 5.0. The titration plots (Figure 5.14) are of sigmoid shapes that indicates high selectivity of these electrodes for Nd^{3+}.

5.4.3 Determination of neodymium in real samples

The proposed electrodes were also used for the detection of Nd^{3+} ions in Ganga (Roorkee) and Yamuna (Delhi) river and in the waste water taken from the Chemistry Department of IIT Roorkee. The potentiometric results, given in Table 5.11 are in close agreement with those obtained by atomic absorption spectrometry.

5.5 Conclusions

Nd^{3+} ion selectivity of two novel pendent macrocycles has been looked into using them as ionophore in the membrane coated graphite electrodes. Among all the electrodes prepared with different membrane compositions, CGE-9 and 24 incorporating *o*-NPOE as solvent mediator and NaTPB as anionic exchanger performed best. Their good performance characteristics towards Nd^{3+} ion were, wide working concentration range (8.4×10^{-8} - 3.1×10^{-2} and 4.6×10^{-8} - 5.0×10^{-2} mol L^{-1}), Nernstian slope (19.8 ± 0.4 and 19.7 ± 0.5 mV decade^{-1} of $a_{Nd^{3+}}$), low detection limit (3.8×10^{-8} and 1.6×10^{-8} mol L^{-1}), wide useful pH range (3.5 to 7.6), fast response time of 14 s (for CGE-9) and 10 s (for CGE-24) with a shelf life of three months. They could also tolerate up to 20 % (v/v) non-aqueous content (methanol, ethanol and acetonitrile) in the test solution. The presence of surfactants at 1.0×10^{-4} mol L^{-1} or above caused significant interference in the performance of the electrodes. Further the electrodes were found to be sufficiently selective over a number of metal ions and could therefore be used for the analysis of Nd^{3+} ions in various binary solutions. These electrodes could be used in successful determination of Nd^{3+} ions in water samples and also as indicator electrodes in the potentiometric titration of Nd^{3+} with EDTA.

Tables

Table 5.1: Formation constants of ion-ionophores complexes of L_4 and L_5 with different metal ions

Metal ions (M^{n+})	Stability Constants	
	($\log \beta_{ML1}$) ± σ	($\log \beta_{ML2}$) ± σ
Nd^{3+}	8.72 ± 0.4	9.08 ± 0.3
Pr^{3+}	3.80 ± 0.4	3.26 ± 0.2
La^{3+}	3.11 ± 0.4	3.23 ± 0.7
Yb^{3+}	3.61 ± 0.5	3.49 ± 0.5
Tb^{3+}	2.12 ± 1.1	2.67 ± 0.8
Sm^{3+}	2.48 ± 0.4	2.32 ± 0.4
Gd^{3+}	2.06 ± 0.9	2.16 ± 0.4
Dy^{3+}	2.31 ± 1.3	2.19 ± 1.6
Co^{2+}	5.14 ± 0.2	5.38 ± 0.4
Cu^{2+}	2.02 ± 0.9	2.04 ± 1.2
Ni^{2+}	1.96 ± 0.6	2.13 ± 1.4
Ca^{2+}	1.29 ± 0.3	1.48 ± 0.8
Na^{+}	1.05 ± 0.8	1.66 ± 0.3
Ag^{+}	1.16 ± 0.6	1.28 ± 0.4

σ standard deviation

Table 5.2: Potentiometric response characteristics of the electrodes based on L_4 towards Nd^{3+} ion

CGEs	Membrane composition (%, w/w)				Linear working range (mol L^{-1})	Slope (mV $decade^{-1}$)	Detection limit (mol L^{-1})
	L_4	Additive	Plasticizer	PVC			
1	5	–		95	7.1×10^{-6} - 5.0×10^{-2}	15.9	4.4×10^{-6}
2	5	–	57, NPOE	38	1.0×10^{-7} - 5.0×10^{-2}	18.0	8.0×10^{-8}
3	5	–	57, AP	38	9.4×10^{-7} - 1.0×10^{-1}	17.3	5.0×10^{-7}
4	5	–	57, DBP	38	1.7×10^{-6} - 1.0×10^{-2}	16.9	7.9×10^{-7}
5	5	–	57, DOP	38	6.2×10^{-6} - 3.1×10^{-2}	16.6	2.8×10^{-6}
6	5	–	57, BA	38	7.4×10^{-6} - 1.0×10^{-1}	16.5	3.1×10^{-6}
7	5	–	57, DBS	38	5.8×10^{-6} - 1.0×10^{-1}	16.2	4.2×10^{-6}
8	5	3, KTpClPB	57, NPOE	35	3.7×10^{-7} - 1.0×10^{-2}	18.4	1.3×10^{-7}
9	5	3, NaTPB	57, NPOE	35	8.4×10^{-8} - 3.1×10^{-2}	19.8	3.8×10^{-8}
10	5	3.5, NaTPB	57, NPOE	34.5	9.8×10^{-8} - 1.0×10^{-2}	20.3	6.6×10^{-8}
11	5	4, NaTPB	57, NPOE	34	5.6×10^{-7} - 1.0×10^{-2}	22.5	1.2×10^{-7}
12	4	3, NaTPB	57, NPOE	36	2.2×10^{-6} - 5.0×10^{-2}	18.3	6.8×10^{-7}
13	6	3, NaTPB	57, NPOE	34	1.8×10^{-7} - 1.0×10^{-2}	19.2	9.2×10^{-8}
14	8	3, NaTPB	57, NPOE	32	7.2×10^{-7} - 1.0×10^{-1}	18.6	3.7×10^{-7}
15	–	3, NaTPB	57, NPOE	40	3.1×10^{-3} - 1.0×10^{-1}	6.6	8.2×10^{-4}

Table 5.3: Potentiometric response characteristics of the electrodes based on L_5 towards Nd^{3+} ion

CGEs	Membrane composition (%, w/w)				Linear working range (mol L^{-1})	Slope (mV $decade^{-1}$)	Detection limit (mol L^{-1})
	L_5	Additive	Plasticizer	PVC			
16	5	–		95	3.1×10^{-6}-1.0×10^{-2}	16.6	6.3×10^{-7}
17	5	–	53, NPOE	42	1.6×10^{-7}-1.0×10^{-1}	18.8	6.8×10^{-8}
18	5	–	53, AP	42	7.9×10^{-7}-3.1×10^{-2}	17.8	5.1×10^{-7}
19	5	–	53, DBP	42	2.4×10^{-6}-3.1×10^{-2}	17.1	1.0×10^{-6}
20	5	–	53, BA	42	5.0×10^{-6}-1.0×10^{-1}	17.3	4.2×10^{-6}
21	5	–	53, DOP	42	5.2×10^{-6}-5.0×10^{-2}	17.0	4.0×10^{-6}
22	5	–	53, DBS	42	7.8×10^{-6}-5.0×10^{-2}	16.8	4.2×10^{-6}
23	5	3, KTpClPB	53, NPOE	39	6.2×10^{-7}-1.0×10^{-1}	18.8	3.9×10^{-7}
24	5	3, NaTPB	53, NPOE	39	4.6×10^{-8}-5.0×10^{-2}	19.7	1.6×10^{-8}
25	5	3.5, NaTPB	53, NPOE	38.5	8.1×10^{-8}-1.0×10^{-2}	19.9	4.1×10^{-8}
26	5	4, NaTPB	53, NPOE	38	7.2×10^{-7}-1.0×10^{-1}	23.5	5.4×10^{-7}
27	4	3, NaTPB	53, NPOE	40	4.6×10^{-7}-1.0×10^{-2}	19.1	1.3×10^{-7}
28	6	3, NaTPB	53, NPOE	38	2.3×10^{-7}-5.0×10^{-2}	18.9	7.8×10^{-8}
29	8	3, NaTPB	53, NPOE	36	3.1×10^{-7}-1.0×10^{-2}	17.4	1.0×10^{-7}
30	–	3, NaTPB	53, NPOE	44	2.4×10^{-3}-1.0×10^{-1}	5.9	8.2×10^{-4}

Table 5.4: Comparison of proposed electrodes with the SAM modified graphite electrodes

Characteristic of electrode	Without SAM		With SAM	
	CGE-9	CGE-24	MCGE-9	MCGE-24
Slope	19.8± 0.4	19.7± 0.5	20.1± 0.03	19.8 ± 0.1
Linear range	8.4×10^{-8} -3.1×10^{-2}	4.6×10^{-8} -5.0×10^{-2}	7.9×10^{-8} -2.0×10^{-2}	5.4×10^{-8} -1.0×10^{-2}
Detection limit	3.8×10^{-8}	1.6×10^{-8}	3.1×10^{-8}	2.8×10^{-8}

Table 5.5: Potentiometric Selectivity Coefficients of various interfering ions

Interfering ions	Selectivity Coefficients (–Log $K_{Nd^{3+}, B}$)			
	CGE - 9		CGE - 24	
	FIM	MPM	FIM	MPM
La^{3+}	1.6 ± 0.1	1.2 ± 0.2	2.0 ± 0.2	2.1 ± 0.1
Pr^{3+}	1.8 ± 0.3	2.3 ± 0.1	2.1 ± 0.2	2.4 ± 0.4
Yb^{3+}	2.1 ± 0.1	2.5 ± 0.3	2.3 ± 0.1	2.7 ± 0.1
Tb^{3+}	2.3 ± 0.2	2.1 ± 0.3	2.2 ± 0.4	3.0 ± 0.2
Sm^{3+}	2.3 ± 0.1	2.8 ± 0.2	2.1 ± 0.2	2.3 ± 0.4
Gd^{3+}	2.4 ± 0.2	2.1 ± 0.3	2.1 ± 0.1	2.0 ± 0.2
Dy^{3+}	2.6 ± 0.3	2.2 ± 0.2	2.7 ± 0.1	2.3 ± 0.2
Co^{2+}	1.1 ± 0.3	0.8 ± 0.2	1.2 ± 0.1	1.4 ± 0.3
Cu^{2+}	4.1 ± 0.2	4.0 ± 0.3	4.3 ± 0.1	3.9 ± 0.2
Hg^{2+}	4.3 ± 0.2	4.0 ± 0.2	4.4 ± 0.2	4.0 ± 0.2
Ce^{3+}	4.3 ± 0.1	4.3 ± 0.1	4.5 ± 0.3	4.1 ± 0.2
Zn^{2+}	4.4 ± 0.2	3.6 ± 0.1	3.3 ± 0.2	3.3 ± 0.4
Cd^{2+}	4.3 ± 0.1	3.5 ± 0.2	3.2 ± 0.3	3.2 ± 0.2
Ni^{2+}	4.2 ± 0.3	3.8 ± 0.2	4.1 ± 0.1	4.0 ± 0.4
Ca^{2+}	4.5 ± 0.1	4.0 ± 0.2	4.0 ± 0.3	3.7 ± 0.2
Na^{+}	3.8 ± 0.3	3.5 ± 0.2	3.6 ± 0.2	3.3 ± 0.2
Ag^{+}	3.6 ± 0.2	2.9 ± 0.3	3.4 ± 0.2	2.7 ± 0.1
K^{+}	4.1 ± 0.2	3.8 ± 0.2	3.6 ± 0.1	3.5 ± 0.1
Li^{+}	4.4 ± 0.1	4.1 ± 0.1	3.8 ± 0.1	3.5 ± 0.2

Table 5.6: Determination of Lifetime of the proposed electrodes

	CGE – 9		CGE - 24	
Time	Slope (mV Decade^{-1})	Detection limit (mol L^{-1})	Slope (mV Decade^{-1})	Detection limit (mol L^{-1})
5 days	19.8 ± 0.4	3.8×10^{-8}	19.7 ± 0.5	1.6×10^{-8}
10 days	19.8 ± 0.4	3.8×10^{-8}	19.7 ± 0.5	1.6×10^{-8}
20 days	19.8 ± 0.6	3.8×10^{-8}	19.7 ± 0.5	1.6×10^{-8}
1 month	19.8 ± 0.6	4.0×10^{-8}	19.7 ± 0.6	1.6×10^{-8}
1.5 month	19.8 ± 0.8	4.0×10^{-8}	19.7 ± 0.3	1.8×10^{-8}
2 month	19.5 ± 0.4	4.4×10^{-8}	19.7 ± 0.4	2.1×10^{-8}
2.5 month	19.3 ± 0.7	4.6×10^{-8}	19.4 ± 0.5	2.8×10^{-8}
3 month	19.1 ± 0.6	1.1×10^{-7}	19.2 ± 0.8	3.6×10^{-8}
3.5 month	18.6 ± 0.5	1.8×10^{-6}	17.9 ± 0.9	6.5×10^{-6}
4 month	17.3 ± 0.4	4.5×10^{-6}	16.8 ± 0.4	8.3×10^{-6}
4.5 month	16.7 ± 0.4	7.8×10^{-6}	16.9 ± 0.4	8.8×10^{-6}

Table 5.7: Effect of surfactants on the performance of the proposed electrodes

	Test Sample	Slope (mV Decade^{-1})	Detection Limit (mol L^{-1})	$-\log K_{Nd^{3+}, La}$		$-\log K_{Nd^{3+}, Co}$	
				FIM	MPM	FIM	MPM
CGE - 9	No Surfactant	19.8 ± 0.4	3.8×10^{-8}	1.6 ± 0.1	1.2 ± 0.2	1.1 ± 0.3	0.8 ± 0.2
	10^{-4} M TBC	17.8	4.6×10^{-6}	1.2 ± 0.2	0.7 ± 0.1	0.7 ± 0.2	0.5 ± 0.3
	10^{-4} M SDS	18.1	4.2×10^{-6}	1.1 ± 0.1	1.0 ± 0.3	0.9 ± 0.1	0.6 ± 0.2
	10^{-4} M Triton X–100	17.5	3.9×10^{-6}	0.9 ± 0.1	0.6 ± 0.1	1.2 ± 0.4	0.7 ± 0.1
CGE – 24	No Surfactant	19.7 ± 0.5	1.6×10^{-8}	2.0 ± 0.2	2.1 ± 0.1	1.2 ± 0.1	1.4 ± 0.3
	10^{-4} M TBC	18.2	9.3×10^{-7}	0.9 ± 0.1	0.8 ± 0.1	1.0 ± 0.2	0.6 ± 0.1
	10^{-4} M SDS	17.3	1.8×10^{-6}	1.1 ± 0.3	0.9 ± 0.2	0.8 ± 0.1	1.0 ± 0.4
	10^{-4} M Triton X–100	17.7	7.8×10^{-7}	1.1 ± 0.1	0.7 ± 0.3	1.0 ± 0.1	0.5 ± 0.2

Table 5.8: Effect of non- aqueous content on the performance of the electrodes

Non-aqueous content (%,v/v)	CGE – 9		CGE - 24	
	Slope (mV decade^{-1})	Detection limit (mol L^{-1})	Slope (mV decade^{-1})	Detection limit (mol L^{-1})
0	19.8 ± 0.4	3.8×10^{-8}	19.7 ± 0.5	1.6×10^{-8}
Acetonitrile				
10	19.8 ± 0.6	3.8×10^{-8}	19.7 ± 0.6	1.6×10^{-8}
15	19.6 ± 0.2	4.0×10^{-8}	19.6 ± 0.5	1.9×10^{-8}
20	19.3 ± 0.5	4.4×10^{-8}	19.4 ± 0.3	2.7×10^{-8}
25	18.9 ± 0.4	1.8×10^{-7}	17.9 ± 0.2	6.8×10^{-6}
30	16.4 ± 0.3	4.6×10^{-6}	16.7 ± 0.4	8.5×10^{-6}
Methanol				
10	19.8 ± 0.6	3.8×10^{-8}	19.7 ± 0.6	1.6×10^{-8}
15	19.8 ± 0.2	3.8×10^{-8}	19.5 ± 0.3	3.9×10^{-8}
20	19.6 ± 0.5	4.1×10^{-8}	19.5 ± 0.2	3.8×10^{-8}
25	17.9 ± 0.3	1.8×10^{-7}	18.0 ± 0.5	5.3×10^{-6}
30	16.6 ± 0.3	4.4×10^{-6}	16.3 ± 0.3	8.8×10^{-6}
Ethanol				
10	19.8 ± 0.6	3.8×10^{-8}	19.7 ± 0.6	1.6×10^{-8}
15	19.8 ± 0.5	3.9×10^{-8}	19.4 ± 0.5	2.4×10^{-8}
20	19.3 ± 0.5	4.4×10^{-8}	19.4 ± 0.3	2.4×10^{-8}
25	17.4 ± 0.2	2.8×10^{-6}	17.9 ± 0.2	6.8×10^{-6}
30	16.3 ± 0.4	4.7×10^{-6}	17.1 ± 0.4	9.5×10^{-6}

Table 5.9: Comparison of Nd^{3+}-selective electrodes with the reported electrodes

Ref. No.	Slope (mV decade^{-1})	Linear range (mol L^{-1})	Detection limit (mol L^{-1})	pH range	$-\log K_{Nd^{3+},B}$ (FIM)
CGE – 9	19.8 ± 0.4	8.4×10^{-8} -3.1×10^{-2}	3.8×10^{-8}	3.5–8.0	La^{3+} (1.6), Yb^{3+}(1.7), Tb^{3+}(2.3), Ce^{3+}(4.3) Dy^{3+}(2.6), Gd^{3+}(2.4), Co^{2+} (1.1), Zn^{2+}(4.4) Cu^{2+}(4.1), Ni^{2+}(4.2), Ag^{+}(3.6), Na^{+}(3.8)
CGE – 24	19.7 ± 0.5	4.6×10^{-8} -5.0×10^{-2}	1.6×10^{-8}	3.5–8.0	La^{3+} (2.0), Yb^{3+}(1.9), Tb^{3+}(2.2), Ce^{3+}(4.5) Dy^{3+}(2.7), Gd^{3+}(2.1), Co^{2+}(1.2), Zn^{2+}(3.3) Cu^{2+}(4.3), Ca^{2+}(4.0), K^{+}(3.6), Na^{+}(3.6)
43	20.1 ± 0.2	1.0×10^{-6} -1.0×10^{-2}	7.9×10^{-7}	4.0–6.5	La^{3+} (1.5), Yb^{3+}(1.2),Sm^{3+}(1.9),Ce^{3+}(1.3), Gd^{3+}(1.3), Co^{2+} (1.7),Zn^{2+}(1.5),Cu^{2+}(1.4), Ni^{2+}(1.9), Ag^{+}(1.4), Na^{+}(1.4)
45	19.6 ± 0.3	1.0×10^{-5} -1.0×10^{-2}	7.0×10^{-6}	4.0–8.0	La^{3+} (1.7), Yb^{3+}(2.3), Sm^{3+}(1.7) Dy^{3+}(2.3), Gd^{3+}(1.9), Cu^{2+}(2.1), K^{+}(2.7), Na^{+}(2.9)
44	19.6 ± 0.3	1.0×10^{-5} -1.0×10^{-2}	2.0×10^{-6}	3.5–8.5	La^{3+} (1.6), Yb^{3+}(2.2), Sm^{3+}(1.6),Ce^{3+}(1.6) Dy^{3+}(2.1), Gd^{3+}(1.8),Cu^{2+}(2.1), Ca^{2+}(2.4), K^{+}(2.6), Na^{+}(2.7)
46	19.7 ± 0.4	1.0×10^{-6} -1.0×10^{-2}	6.2×10^{-7}	3.7–8.3	La^{3+} (2.1), Tb^{3+}(2.9),Sm^{3+}(3.5),Dy^{3+}(2.0), Gd^{3+}(2.1), Co^{2+} (3.3),Zn^{2+}(3.1),Cu^{2+}(3.1), Ni^{2+}(2.9), Ag^{+}(2.2), Na^{+}(3.0), Hg^{2+}(2.3)
48	19.8 ± 0.3	5.0×10^{-7}– 1.0×10^{-2}	1.0×10^{-7}	4.0–8.0	La^{3+}(3.8), Tb^{3+}(3.2), Sm^{3+}(3.8), Dy^{3+}(4.5), Gd^{3+}(3.6), Tb^{3+}(4.4), Co^{2+} (2.4)

Table 5.10: Determination of Nd^{3+} ions in various binary mixtures by the proposed coated graphite electrodes (CGEs)

Nd^{3+} ion concentration (M)	Added cation concentration (M)	Recovery (%) ± σ	
		CGE- 9	CGE-24
1.0×10^{-4}	La^{3+} (5.0×10^{-3})	96.8 ± 0.3	97.8 ± 0.4
1.0×10^{-4}	Yb^{3+} (5.0×10^{-3})	97.3 ± 0.3	97.6 ± 0.3
1.0×10^{-4}	Tb^{3+} (5.0×10^{-3})	99.2 ± 0.5	99.4 ± 0.6
1.0×10^{-4}	Gd^{3+} (5.0×10^{-3})	99.5 ± 0.1	100.5 ± 0.8
1.0×10^{-4}	Dy^{3+} (5.0×10^{-3})	98.4 ± 0.9	101.6 ± 0.2
1.0×10^{-4}	Co^{2+} (5.0×10^{-3})	97.4 ± 0.2	96.9 ± 0.1
1.0×10^{-4}	Cu^{2+} (5.0×10^{-3})	100.2 ± 0.1	101.5 ± 0.3
1.0×10^{-4}	Hg^{2+} (5.0×10^{-3})	99.6 ± 0.3	99.1 ± 0.2
1.0×10^{-4}	Zn^{2+} (5.0×10^{-3})	99.3 ± 0.5	98.8 ± 0.6
1.0×10^{-4}	Cd^{2+} (5.0×10^{-3})	99.5 ± 0.4	99.2 ± 0.2

T able 5.11: Quantitative determination of Nd^{3+} in water samples

Sample	Added Nd^{3+} ion concentration (ppm)	Found by CGEs (ppm)		Found by AAS (ppm)
		CGE-9	CGE-24	
Ganga water	5.00	5.32	5.06	4.97
Yamuna water	5.00	5.14	5.10	5.25
Waste water	5.00	4.88	5.36	5.20

Figures

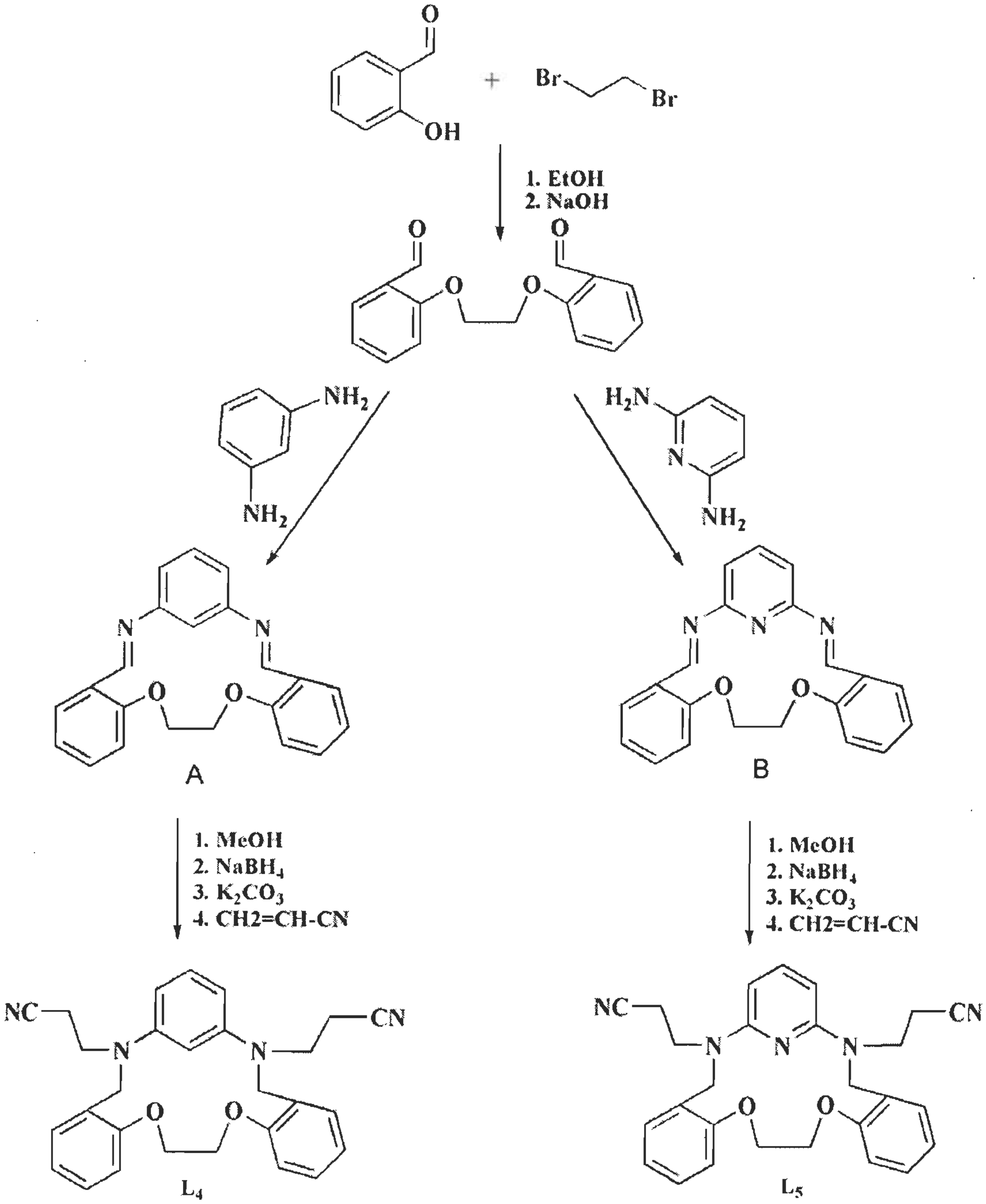


Figure 5.1: Reaction scheme for the synthesis of L_4 and L_5

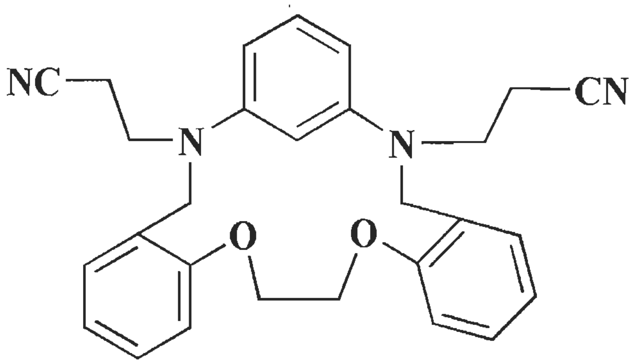
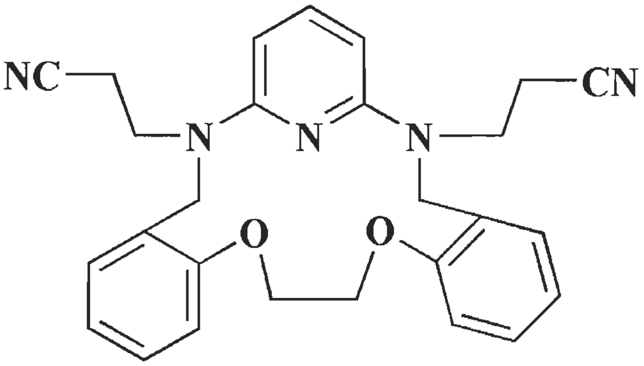


Figure 5.2: Structure of 1,5-di(cyanoethane)-2,4:7,8:13,14-tribenzo-1,5-diaza-9,12-dioxacyclopentadeca-2,7,13-triene (L_4)



Fgure 5.3: Structure of 1,5-di(cyanoethane)-2,3,4-pyridine-7,8:13,14-dibenzo-1,3,5-triaza-9,12-dioxacyclopentadeca-2,7,13-triene (L_5)

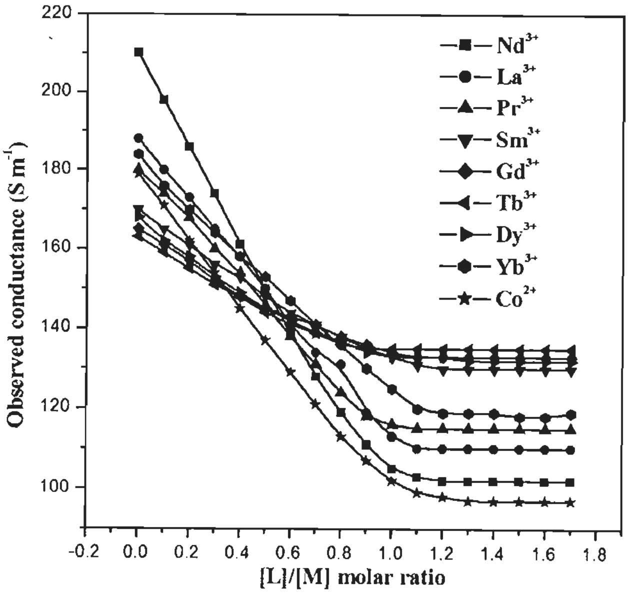


Figure 5.4: Conductometric study of various ion-ionophore complexes of L_4

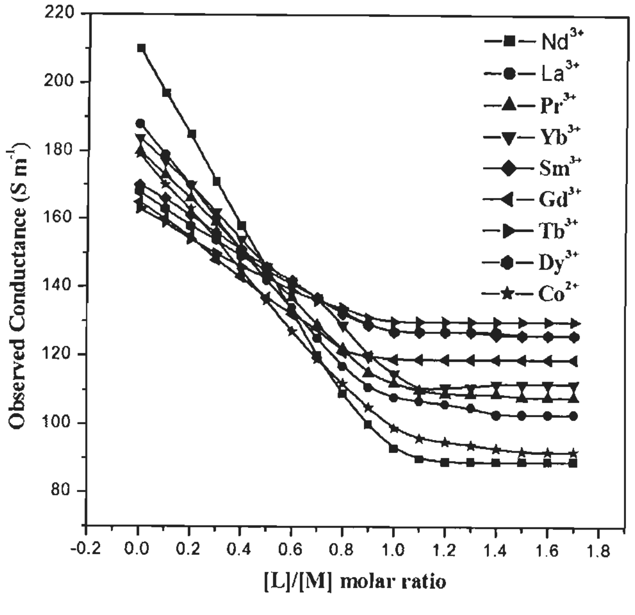


Figure 5.5: Conductometric study of various ion-ionophore complexes of L_5

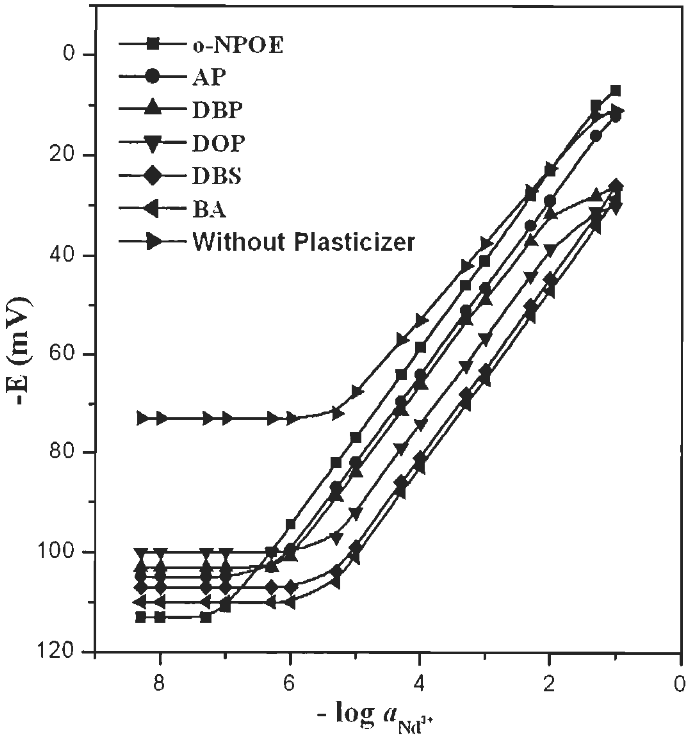


Figure 5.6: Potential responses of Nd^{3+} ion selective electrodes based on L_4 with different plasticizers

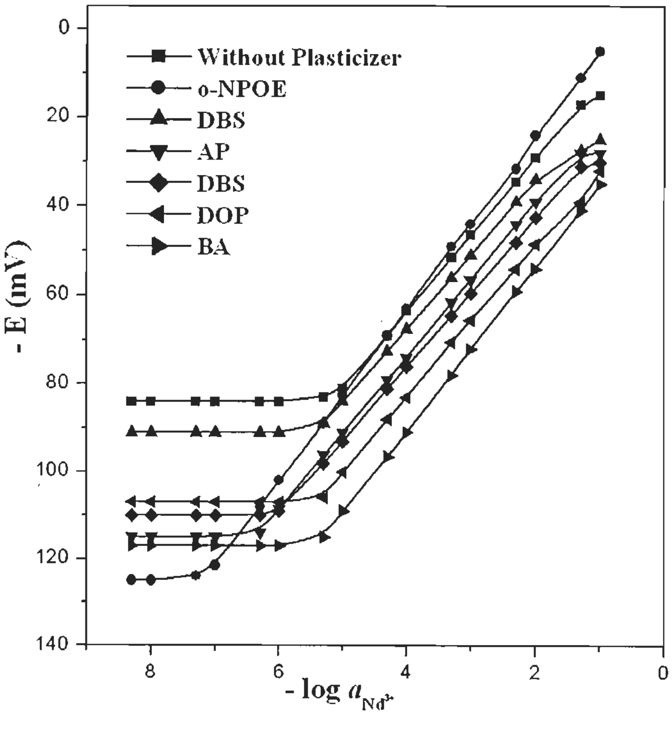


Figure 5.7: Potential responses of Nd^{3+} ion selective electrodes based on L_5 with different plasticizers

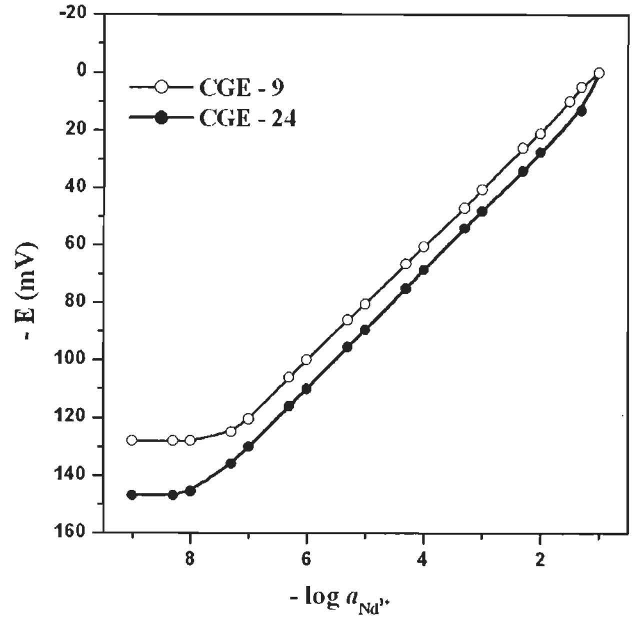


Figure 5.8: Calibration curves of Nd^{3+}-selective electrodes CGE-9 and CGE-24

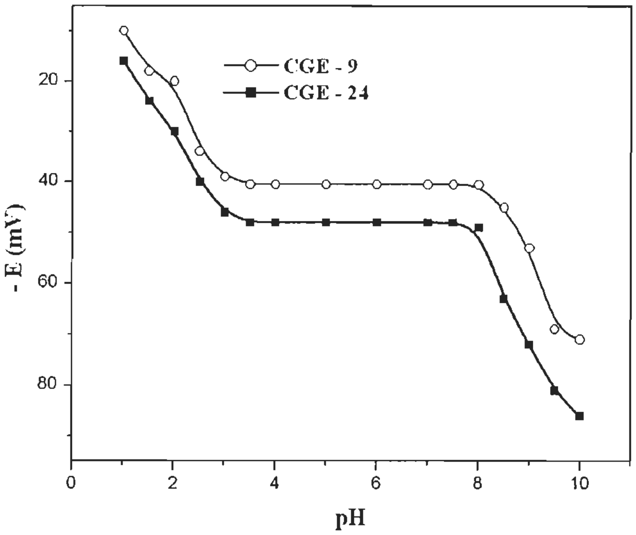


Figure 5.9: Effect of pH on the performance of CGE-9 and CGE-24 at 1.0 × 10^{-3} mol L^{-1} $NdCl_3$ solution.

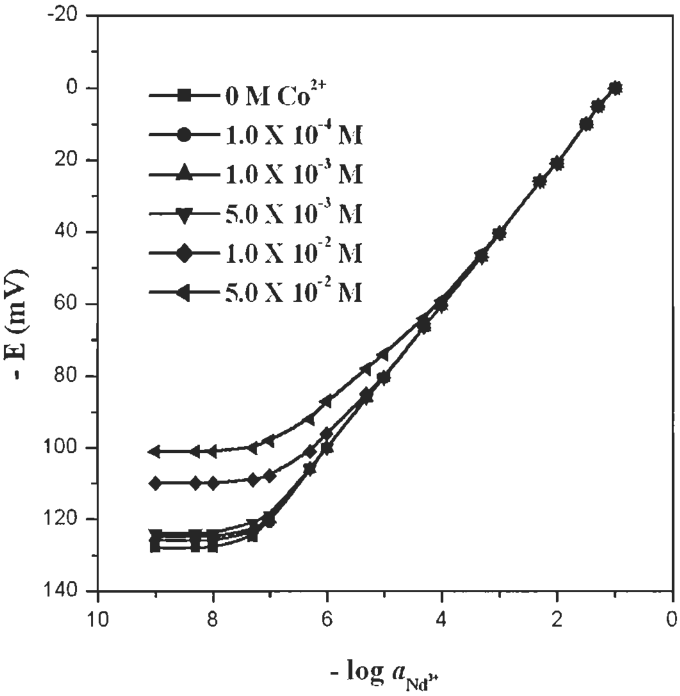


Figure 5.10: Effect of different concentrations (1.0×10^{-4}, 1.0×10^{-3}, 5.0×10^{-3}, 1.0×10^{-2}, 5.0×10^{-2} mol L^{-1}) of Co^{2+}on the performance of CGE-9

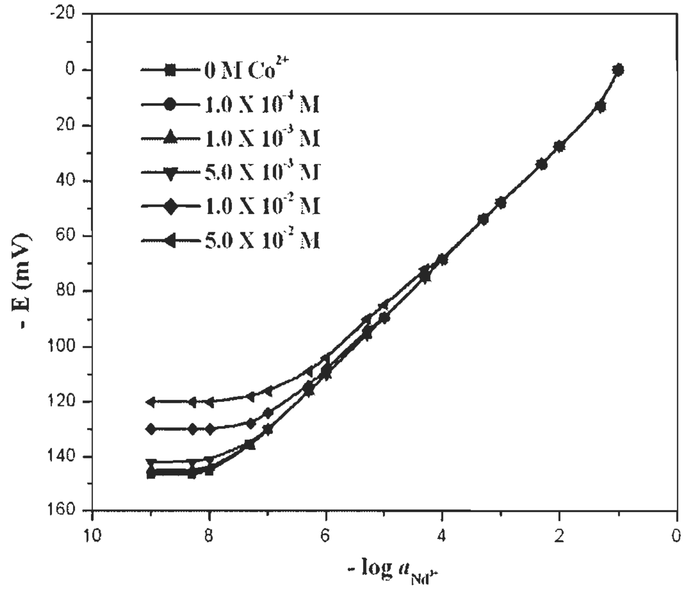


Figure 5.11: Effect of different concentrations (1.0×10^{-4}, 1.0×10^{-3}, 5.0×10^{-3}, 1.0×10^{-2}, 5.0×10^{-2} mol L^{-1}) of Co^{2+}on the performance of CGE-24

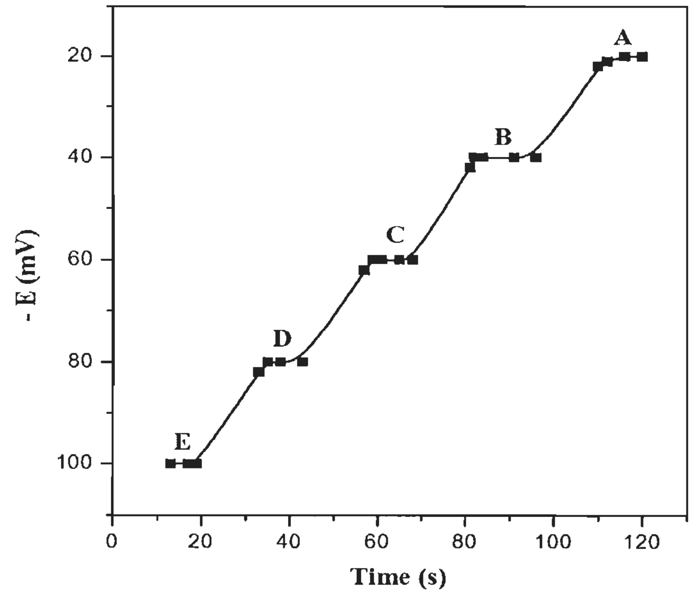


Figure 5.12: Determination of response time of CGE-9 for 10-fold step change in Cd^{2+} ion concentration varying from (A) 1.0×10^{-2} M (B) 1.0×10^{-3} M (C) 1.0×10^{-4} M (D) 1.0×10^{-5} M (E) 1.0×10^{-6} M

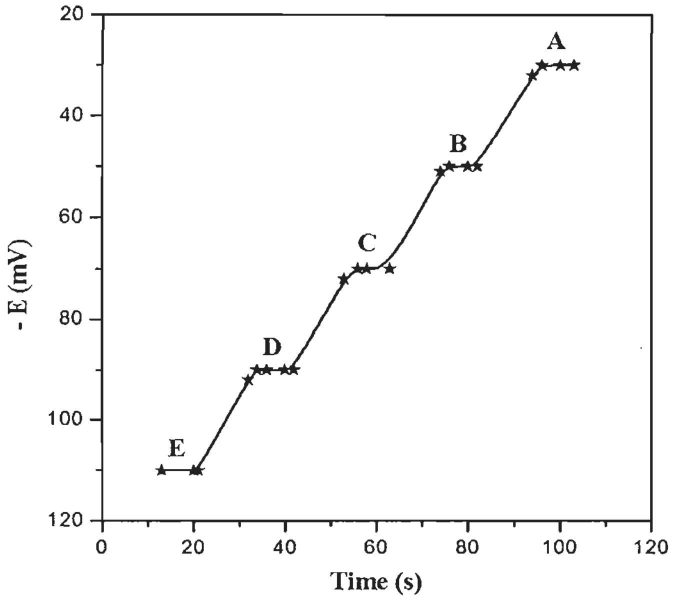


Figure 5.13: Determination of response time of CGE-9 for 10-fold step change in Cd^{2+} ion concentration varying from (A) 1.0×10^{-2} M (B) 1.0×10^{-3} M (C) 1.0×10^{-4} M (D) 1.0×10^{-5} M (E) 1.0×10^{-6} M

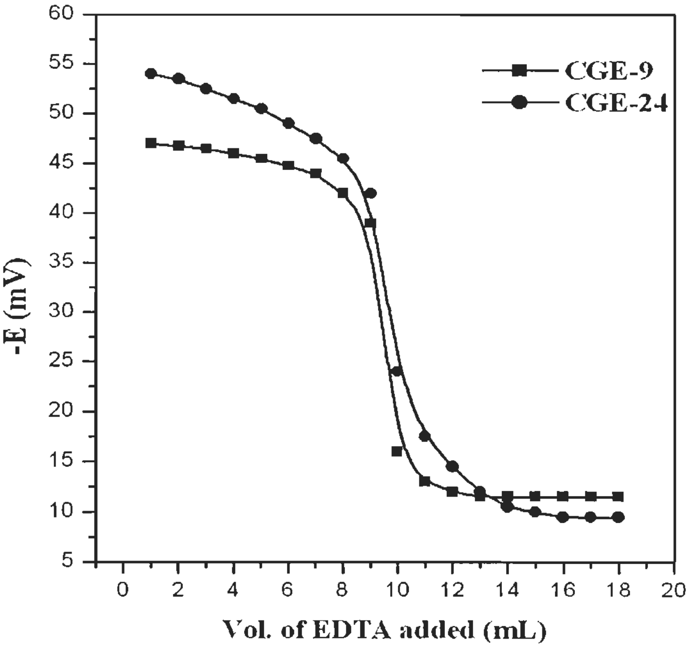


Figure 5.14: Potentiometric titration curve for 20 mL of 5.0×10^{-3} mol L^{-1} Nd^{3+} with 1.0×10^{-2} mol L^{-1} EDTA, at constant pH 5.0 using the proposed electrodes CGE-9 and CGE-24

References

1. Hirano, S. and Suzuki, K.T., "Exposure, metabolism, and toxicity of rare earths and related compounds", *Environ. Health Perspect. Suppl.*, **104**, 85 (1996).
2. Yongxing, W., Xiaorong, W. and Zichun, H., "Genotoxicity of Lanthanum (III) and Gadolinium (III) in human peripheral blood lymphocytes", *Bull. Environ. Contam. Toxicol.*, **64**, 611 (2000).
3. Yang, W.Z., Laarman, A., He, M.L. and Liu, Q., "Effect of rare earth elements on *in vitro* rumen microbial fermentation and feed digestion", *Anim. Feed Sci. Technol.*, **148**, 227 (2009).
4. Li, J., Hong, M., Yin, X. and Liu, J., "Effects of the accumulation of the rare earth elements on soil macrofauna community", *J. Rare Earth.*, **28**, 957 (2010).
5. Ozaki, T., Suzuki, Y., Nankawa, T., Yoshida, T., Ohnuki, T., Kimura, T. and Francis, A.J., "Interactions of rare earth elements with bacteria and organic ligands", *J. Alloy. Comp.*, **1334**, 408 (2006).
6. Kirk, R.E. and Othmer, D.F., "Encyclopedia of chemical technology", Wiley, New York, **19**, 851 (1982).
7. Rao, G.S.S., Upadhyay, V.K. and Jain, R.C., "Polymerization of 1,3-butadiene using neodymium chloride tripentanolate-triethyl aluminum catalyst systems", *J. Appl. Polym. Sci.*, **71**, 595 (1999).
8. Gladilovich, D.B., Kuban, V. and Sommer, L., "Determination of the sum of rare earth elements by flow-injection analysis with Arsenazo III, 4-(2-pyridylazo) resorcinol, Chrome Azurol S, and 5-bromo-2-(2-pyridylazo)-5-diethylaminophenol spectrophotometric reagents", *Talanta,* **35**, 259 (1988).
9. Hrdlicka, A., Havel, J., Moreno, C. and Valiente, M., "Micellar-enhanced highly sensitive reaction of rare earths with Xylenol Orange and surfactants. Study of reaction conditions and optimization of spectrophotometric method", *Anal. Sci.*, **7**, 925 (1991).
10. Houk, R.S., Fassel, V.A., Flesch, G.D., Svec, H.J., Gray, A.L. and Taylor, C.E., "Inductively coupled argon plasma as an ion source for mass spectrometric determination of trace elements", *Anal. Chem.*, **52**, 2283 (1980).

11. Shibata, N., Fudagawa, N. and Kubota, M., "Electrothermal vaporization using a tungsten furnace for the determination of rare-earth elements by inductively coupled plasma mass spectrometry", *Anal. Chem.*, **63**, 636 (1991).
12. Mazzucotelli, A., De Paz, F., Magi, E. and Frache, R., "Interferences of major elements in the determination of rare earth elements by inductively coupled plasma atomic emission spectroscopy", *Anal. Sci.*, **8**, 189 (1992).
13. Masuda, A., Nakamura, N. and Tanaka, T., "Fine structure of mutually normalized rare earth patterns of chondrites", *Cosmochim. Acta*, **37**, 239 (1973).
14. D'Orazio, M. and Tonarini, S., "Simultaneous determination of neodymium and samarium in silicate rocks and minerals by isotope dilution inductively coupled plasma mass spectrometry: results on twenty geochemical reference samples", *Anal. Chim. Acta*, **351**, 325 (1997).
15. Ramendik, G.I., Fatyushina, E.V. and Stepanov, A.I., "Determination of Neodymium and Ytterbium by isotope dilution laser mass spectrometry", *J. Anal. Chem.*, **58**, 152 (2003).
16. Marsh, S.F., "Separation of lanthanide fission products from nuclear fuels by extraction chromatography and cation exchange for isotope dilution mass spectrometric analysis", *Anal. Chem.*, **39**, 641 (1967).
17. McCown, J.J. and Larsen R.P., "Radiochemical determination of total rare earths by liquid-liquid extraction", *Anal. Chem.*, **33**, 1003 (1961).
18. Cornell, D.H., "Rare earths from supernova to superconductor", *Pure Appl. Chem.*, **65**, 2453 (1993).
19. Zhukov, A.F., Erne, D., Ammann, D., Güggi, 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).
20. Gadzekpo, V.P.Y. and Christian, G., "The 1, 4, 7, 10-tetraoxacyclododecane (12-crown-4) as neutral carrier for lithium ion in lithium ion selective electrode", *Anal. Lett.*, **16**, 1371 (1983).
21. 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).

22. Lee, M.H., Yoo, C., Lee, J.S., Cho, I., Kim, B.H., Cha, G.S. and Nam, H., "Tweezer-type neutral carrier-based calcium-selective membrane electrode with drastically reduced anionic interference", *Anal. Chem.*, **74**, 2603 (2002).

23. Suzuki, K., Tohda, K., Aruga, H., Matsuzoe, M., Inoue, H. and Shirai, T., "Ion-selective electrodes based on natural carboxylic polyether antibiotics", *Anal. Chem.*, **60**, 1714 (1988).

24. Singh, A.K., Gupta, V.K. and Gupta, B., "Chromium(III) selective membrane sensors based on Schiff bases as chelating ionophores", *Anal. Chim. Acta,* **585**, 171 (2007).

25. 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).

26. Cattrall, R.W. and Pui, C., "Coated wire ion selective electrodes for the determination of mercury(II)", *Anal. Chem.*, **48**, 552 (1976).

27. Gupta, V.K., Singh, A.K., Al Khayat, M. and Gupta, B., "Neutral carriers based polymeric membrane electrodes for selective determination of mercury(II)", *Anal. Chim. Acta*, **590**, 81 (2007).

28. Senkyr, J., Ammann, D., Meier, P.C., Morf, W.E., Pretsch, E. and Simon, W., "Uranyl ion selective electrode based on a new synthetic neutral carrier", *Anal. Chem.*, **51**, 786 (1979).

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

30. Gupta, V.K., Singh, A. K. and Gupta, B., "A cerium(III) selective polyvinyl 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).

31. Singh, A.K. and Singh, P., "Determination of cerium ion by polymeric membrane and coated graphite electrode based on novel pendant armed macrocycle", *Anal. Chim. Acta*, **675**, 170 (2010).

32. Bastida, R., Fenton, D.E., López-Deber, M., Macías, A., Valencia, L. and Vicente, M., "Synthesis of perchlorate metal complexes with a new tetrapyridyl pendant armed macrocyclic ligand", *Inorg. Chim. Acta*, **355**, 292 (2003).

33. Aime, S., Cravotto, G., Crich, S.G., Giovenzana, G.B., Ferrari, M., Palmisano, G. and Sisti, M., "Synthesis of the Gd(III) complex with a tetrazole-armed macrocyclic ligand as a potential MRI contrast agent", *Tetrahedron Lett.*, **43**, 783, (2002).

34. Arnold, K.A., Echegoyen, L., Fronczek, F.R., Gandour, R.D., Gatto, V.J., White, B.D. and Gokel, G.W., "Evidence for cryptand-like behavior in bibracchial lariat ether (BiBLE) complexes obtained from x-ray crystallography and solution thermodynamic studies", *J. Am. Chem. Soc.*, **109**, 3716 (1987).

35. Rothermel, G.L., Miao, 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).

36. Botta, M., "Second coordination sphere water molecules and relaxivity of gadolinium(III) complexes: implications for MRI contrast agents", *Eur. J. Inorg. Chem.,* 399 (2000).

37. Wainwright, K.P., "Applications for polyaza macrocycles with nitrogen-attached pendant arms", *Adv. Inorg. Chem.*, **52**, 293 (2001).

38. Rybak-Akimova, E.V., Nazarenko, A.Y. and Silchenko, S.S., "Unusual ligand isomerization dictated by coordination requirements of the metal ion: A double-bond shift in Cu(II)-assisted template condensation between diacetylpyridine and a tripodal tetramine", *Inorg. Chem.*, **38**, 2974 (1999).

39. Prasad, R., Gupta, V.K. and Kumar, A., "Metallo-tetraazaporphyrin based anion sensors: regulation of sensor characteristics through central metal ion coordination", *Anal. Chim. Acta*, **508**, 61 (2004).

40. Jain, A.K., Gupta, V.K., Singh, L.P. and Khurana, U., "Macrocycle based membrane sensors for the determination of cobalt(II) ions", *Analyst*, **122,** 583 (1997).

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

42. Agarwal, H. and Chandra, S., "Studies on PVC-based chelating inorganic ion exchange resin membrane sensor for neodymium(III) ion", *Indian J. Chem., Sect. A: Inorg., Bio-inorg., Phys., Theor. Anal. Chem.*, **43A**, 2361 (2004).

43. Shamsipur, M., Hosseini, M., Alizadeh, K., Mousavi, M.F., Garau, A., Lippolis, V. and Yari, A., "PVC Membrane potentiometric sensor based on 5-Pyridino-2, 8-dithia-[9](2, 9)-1, 10-phenanthroline-phane for selective determination of neodymium(III)", *Anal. Chem.*, **77**, 276 (2005).

44. Ganjali, M.R., Ahmadalinezhad, A., Norouzi, P. and Adib, M., "Nd(III)-PVC membrane sensor based on 2-{[(6-aminopyridin-2-yl)imino]methyl}phenol", *J. Appl. Electrochem.*, **36**, 931 (2006).

45. 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. Braz. Chem. Soc.*, **17**,1309 (2006).

46. Behmadi, H., Zamani, H.A., Ganjali, M.R. and Norouzi, P., "Determination of neodymium(III) ions in soil and sediment samples by a novel neodymium(III) sensor based on benzyl bisthiosemicarbazone", *Electrochim. Acta*, **53**, 1870 (2007).

47. Chandra, S. and Singh, D.R., "Polymeric membrane neodymium(III)-selective electrode based on 11,13-diaza-4,7,12-trioxo-2(3),8(9)-dibenzoyl-cyclotetridecane-1,11-diene", *Mater. Sci. Eng., A,* **A502**, 107 (2009).

48. Gupta, V.K., Goyal, R.N. and Sharma, R.A., "Comparative studies of neodymium(III)-selective PVC membrane sensors", *Anal. Chim. Acta*, **647**, 66 (2009).

49. Liu, Z., Wang, S. and Wang, L., "Development of p-toluenesulfonyl-serine-Nd(III) complex modified PVC membrane ion selective electrode for neodymium", *Yejin Fenxi*, **30**, 21 (2010).

50. Kumar, R., Sharma, H.K. and Dogra, P., "Potentiometric determination of neodymium (III) ions using tin (IV) antimonotungstate and zirconium (IV) antimonotungstate as electro-active materials", *Int. J. Environ. Anal. Chem.*, **91**, 280 (2011).

51. Menon, S.K., Modi, N.R., Patel, B. and Patel, M.B., "Azo calix[4]arene based neodymium(III)-selective PVC membrane sensor", *Talanta,* **83**, 1329 (2011).

52. Zamani, H.A., Imani, A., Arvinfar, A., Rahimi, F., Ganjali, M.R., Faridbod, F. and Meghdadi, S., ". Neodymium(III)-PVC membrane sensor based on a new four dentate ionophore", *Mater. Sci. Eng., C,* **31,** 588 (2011).

53. Simion, A., Simion, C., Kanda, T., Nagashima, S., Mitoma, Y., Yamada, T., Mimura, K. and Tashiro, M., "Synthesis of imines, diimines and macrocyclic diimines as possible ligands, in aqueous solution", *J. Chem. Soc., Perkin Trans.,* 1, 2071 (2001).

54. Singh, A.K., Singh, P., Banerjee, S. and Mehtab, S., "Development of electrochemical sensors for nano scale Tb(III) ion determination based on pendant macrocyclic ligands", *Anal. Chim. Acta,* **633,** 109 (2009).

55. Lindner, E. and Gyurcsanyi, R.E.," Quality control criteria for solid-contact, solvent polymeric membrane ion-selective electrodes", *J. solid state Electrochem.,* **13,** 51 (2009).

56. Sokalski, T., Zwickl, T., Bakker, E. and Pretsch, E., "Lowering the detection limit of solvent polymeric ion-selective electrodes. 1. modeling the influence of steady-state ion fluxes", *Anal. Chem.,* **71,** 1204 (1999).

57. Szigeti, Z., Vigassy, T., Bakker, E. and Pretsch, E., "Approaches to improving the lower detection limit of polymeric membrane ion-selective electrodes", *Electroanalysis,* **18,** 1254 (2006).

58. Eugster, R., Rosatzin, T., Rusterholz, B., Aebersold, B., Pedrazza, U., Rueegg, D., Schmid, A., Spichiger, U.E. and Simon, W., "Plasticizers for liquid polymeric membranes of ion-selective chemical sensors", *Anal. Chim. Acta,* **289,** 1 (1994).

59. Ammann, D., Pretsch, E., Simon, W., Lindner, 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).

60. Wang, W.N., Chen, Y.J. and Wu, M.T., "Complementary analytical methods for cyanide, sulfide, certain transition metals, and lanthanides in ion chromatography", *Analyst*, **109,** 281 (1984).

61. Kojima, R. and Kamata, S., "Zinc-selective membrane electrodes using tetrabutyl thiuram disulfide neutral carrier", *Anal. Sci.*, **10**, 409 (1994).

62. Lindner, E., Toth, K and Pungor, E., "Definition and determination of response time of ion selective electrodes", *Pure Appl. Chem.*, **58**, 469 (1986).

63. Dinten, O., Spichiger, U.E., Chaniotakis, N., Gehrig, P., Rusterholz, B., Morf, W.E. and Simon, W., "Lifetime of neutral-carrier-based liquid membranes in aqueous samples and blood and the lipophilicity of membrane components", *Anal. Chem.*, **63**, 596 (1991).

64. Wardak, C., Marczewska, B. and Lenik, J., "Influence of ionic and nonionic surfactants on analytical parameters of ion-selective electrodes based on chelating active substances", *Electrochim. Acta*, **51**, 2267 (2006).

Chapter 6

Cd^{2+} Ion-Selective Electrodes Based On N_4, N_2S_2 and N_2O_2 Type Chelating Ligands

6.1 Introduction

The widespread use of cadmium in electroplating and in Ni-Cd batteries has resulted in cadmium contamination of various water sources. Cadmium represents one of the important toxic metals and the effect of its acute poisoning is manifested in a variety of symptoms, including high blood pressure, kidney damage, anemia, hypertension, bone marrow disorders, respiratory problems, reproductive failure, cancer and toxicity to aquatic biota [1]. The permissible limits of cadmium discharge in wastewater and drinking water are 0.1 and 0.05 mg L^{-1}, respectively. Because of the increased industrial use of cadmium and its toxic effects to living biota, its monitoring in environment samples is increasingly important. A number of sophisticated instrumental methods [2-10] have been utilized for the detection of cadmium. Since these methods require adequate expertise and large-scale infrastructure so they are not very appropriate for on-site monitoring of cadmium in various environmental samples. Because of their low fabrication cost and easy handling, ion selective electrodes (ISEs) can be used for quantitative determination of cadmium in a number of samples.

Cd^{2+} ion-selective electrodes

In view of toxicity of cadmium, a reliable ion selective sensor for cadmium ions is of considerable importance for the protection of environment and human health. The high toxicity of cadmium and the general concern over its presence in the environment has led to the development of Cd^{2+}-selective electrodes involving a number of electroactive materials by many researchers. In early seventies, Cd^{2+}-selective electrodes based on Ag_2S/CdS mixture [11-13] were described. Later on, Cd^{2+}- selective sensors based on homogeneous polycrystalline membranes of CdS-Ag_2S [14, 15], and glass membranes of CdS-Ag_2S-As_2S_3 and CdI_2-Ag_2S-As_2S_3 [16-19]. These sensors suffered serious interferences from various cations including Ag^+, Cu^{2+}, Zn^{2+}, Hg^{2+} and Fe^{3+}. ISEs based on cadmium complexes of quinoxaline-2,3-dithiol as ion-active substances of solid membrane electrodes offered a reasonable discrimination of all alkali and alkaline earth metal ions but are poisoned by Cu^{2+}, Pd^{2+}, Pt^{2+}, Ag^+ and Hg^+ ions [20]. Jain *et al.* [21] reported cerium(IV) vanadate in polystyrene matrix as Cd^{2+} selective electrode. Another polystyrene matrix membrane electrode incorporating polyaniline zirconium (IV) tungsto-phosphate, a composite ion exchanger, as an electroactive material was prepared by Ikram *et al.* [22]. A higher discrimination of Cu^{2+} ions was reported for a cadmium selective electrode based on benzo-15-crown-5 [23]. Gupta *et al.* explored several crown ethers such as dibenzo-24-crown-8 [24], monoaza-18-crown-6 [25], dicyclohexano-18-crown-6 [26] and dicyclohexano-24-crown-8 [27] in PVC matrix for construction of Cd^{2+}-selective electrodes while Shamsipur *et al.* utilized tetrathia-12-crown-4 [28] as electroactive material for determination of cadmium. Singh and co-workers also explored different macrocyclic ionophores such as dibenzo-2,5,11,14-tetraoxo-1,6,10,15-tetraazacyclooctadecane [29], 3,4,11,12-dibenzo-1,6,9,14-tetraaza-cyclohexadecane [30] and tridentate sulfur and nitrogen containing ligands [31] for fabrication of Cd^{2+}-selective electrodes. These sensors were successfully used as indicator electrodes for the potentiometric titration of Cd^{2+} against EDTA as well as for its determination in waste waters. Ion *et al.* [32] studied Cd^{2+}-selective electrodes based on a neutral carrier *viz. N, N, N', N'*-tetradodecyl-3, 6-dioxaoctanedithioamide with detection limit down to 10^{-10} mol L^{-1}. A new sulfur containing macrocyclic diamide (1,15-diaza-3,4,12,13-dibenzo-5,11-dithia-8-oxa-1,15-(2,6-pyrido)cyclooctadecan-2,14-dione) was used by Shamsipur *et al.* [33] as an active component for fabrication of polymeric membrane electrodes for sensing Cd^{2+} ion. Khan *et al.* [34-36] synthesized organic-inorganic composite cation exchangers and explored as suitable sensing materials for the construction of cadmium ISEs. These electrodes were mechanically stable and could be used as indicator electrode in the potentiometric titration of Cd^{2+} with EDTA and for the determination of Cd^{2+} in real samples. A cadmium ion-selective membrane electrode based on strong acidic organic-inorganic composite cation-exchanger *viz.* polyaniline Ce(IV) molybdate was constructed by Nabi and co-workers [37]. PVC membrane sensors for Cd^{2+} based on 2-(3',4'-dihydroxyphenylazo-1')-1,3,4 thiadiazole and 3-(2',4'-dihydroxyphenylazo-l')-l,2,4-triazol as membrane carrier were constructed by Wardak *et al.* [38, 39]. These sensors showed good selectivity towards Cd^{2+} over zinc, nickel, cobalt, calcium, mercury, copper, barium, magnesium, manganese, potassium and sodium ions. Gupta *et al.* [40] fabricated Cd^{2+}-selective electrodes based on thiacalixarenes which showed Nernstian response over a wide concentration range. Schiff bases have also evoked considerable interest in the development of highly selective Cd^{2+}-selective electrodes by many research groups [41-43]. Neutral carriers *viz.* tetrol compound [44], *N,N'*-(4-methyl-1,2-phenylene)diquinoline-2-carboxamide [45], 4,4′-di(5-nonyl)-2,2′-bipyridine [46], N'-[1-(2-furyl)methylidene]-2-furohydrazide [47] and 1,2-bis(quinoline-2-Carboxamido)-4-chlorobenzene [48] have been reported as ionophore in PVC membrane electrode for Cd^{2+} ions. Abbas *et al.* [49] developed solid-state cadmium ISEs based on tetraiodo- and tetrabromo-ion pairs with cetylpyridinium. These electrodes showed fast response and but experienced interference from Hg^{2+} ions. Mohammadi *et al.* [50] fabricated a modified carbon paste electrode based on a tripodal ligand for the determination of Cd^{2+}. Singh *et al.* [51] synthesized and explored two different tripodal ligands potassium[hydrotris-N-(2,6-xylyl,thioimdazolyl)borate] and potassium[hydrotris(3,5-phenyl, methylpyrazolyl)borate] as highly selective ionophores for the construction of PVC-based polymeric membrane electrodes for determination of Cd^{2+} ion.

Bizerea [52] developed and characterize a new Cd^{2+}-selective potentiometric sensor with multilayer solid membrane based on selenide. Tyagi *et al.* [53] employed a highly selective electroactive material $Mo_2[(OAc)_2(H_2\text{-calix}[4]\text{arene})]$ for fabricating of Cd^{2+}-selective electrode. This electrode exhibited fast Nernstian response over the concentration range 9.9×10^{-8} to 1.0×10^{-1} mol L^{-1} with a low limit of detection 9.8×10^{-8} mol L^{-1}. Gupta *et al.* [54] studied the potential response of Cd^{2+}-selective electrode based on cyanocopolymer matrixes and 8-hydroxyquinoline as ionophore. The cyano groups of the copolymers contributed significantly to enhance the selectivity of this electrode. In spite of large amount of work has been done to develop ion-selective electrodes, for the quantitative estimation of Cd^{2+}, still investigations are called for in this direction as the reported sensors have limitations, including narrow working concentration ranges, poor selectivities, long response times and limited pH ranges.

Therefore, to improve the analytical selectivity, it is essential to search carrier compounds that would interact with cadmium ions more selectively. Keeping this in view, in present work we attempted to prepare improved versions of Cd^{2+}-selective coated graphite electrodes (CGEs) using three different derivatives of Schiff bases as neutral carriers having N_4, N_2S_2 and N_2O_2 donor sites for complexation with cadmium. These ionophores have been considered as model compounds for this particular application because they provide a coordination cavity for complexation. Hence, these chelating ligands were found to behave as potential ionophores for preparing Cd^{2+}-selective electrodes. These ionophores were coated onto graphite rods, and the resulting coated graphite electrodes were studied as Cd^{2+}-selective electrodes. The results presented here show that these electrodes are highly selective for Cd^{2+}.

6.2 Experimental

6.2.1 Reagents

Reagent grade sodium tetraphenylborate (NaTPB), potassium tetrakis-*p*-(chloro phenyl)borate (KTpClPB), benzyl acetate (BA), dioctylphthalate (DOP), *o*-nitrophenyloctylether (*o*-NPOE), dioctylsebacate (DOS), acetophenone (AP), dibutyl phosphate (DBP), tributyl phosphate (TBP), tetrahydrofuran (THF) and high molecular weight poly (vinylchloride) were purchased from E. Merck (Mumbai) and used as received. 2-pyridinecarboxaldehyde, *o*-phenylenediamine, 2-furancarboxaldehyde and 2-thiophenecarboxaldehyde were procured from Sigma Aldrich (USA). The metal chlorides/nitrates were of analytical grade and used without further purification and their solutions were prepared in doubly distilled water. The solutions were standardized wherever necessary.

6.2.2 Synthesis of chelating ligands

The pendent ligands N^1,N^2-dicyanoethyl-N^1,N^2-bis(pyridin-2-ylmethyl) benzene-1,2-diamine [L_6], N^1,N^2-dicyanoethyl-N^1,N^2-bis(thiophen-2-ylmethyl)benzene-1, 2-diamine [L_7] and N^1,N^2-dicyanoethyl-N^1,N^2-bis(furan-2-ylmethyl) benzene-1,2-diamine [L_8] are shown in Figures 6.1, 6.2 and 6.3 respectively. These chelating ligands were synthesized by following the previously published procedure [55-57].

6.2.2.1 Synthesis of N^1, N^2-dicyanoethyl-N^1, N^2-bis (pyridin-2-ylmethyl) benzene-1, 2-diamine [L_6]

2-Pyridinecarboxaldehyde (3.8 mL, 40 mmol) was dissolved in 20 mL of isopropanol and mixed into a 20 mL solution of *o*-phenylenediamine (2.16 g, 20 mmol). The resulting solution stirred for 2 h at room temperature. The dark yellow precipitate obtained was filtered and washed with cold isopropanol and then with ether. The crude Schiff base was dissolved in 50 mL methanol, and solid $NaBH_4$ (0.76 g, 20 mmol) was added in small portions, keeping the flask in an ice bath. The reaction was quenched with 50 mL of water, and the reduced ligand was extracted in dichloromethane (DCM, 4×25 mL). The extract was dried over anhydrous sodium sulfate and evaporated to yield a viscous brown compound *N^1*, *N^2*-bis(pyridin-2-ylmethyl)benzene-1, 2-diamine. This reduced product (290 mg (1 mmol)) was dissolved in 10 mL of methanol and stirred with 1.5 g K_2CO_3 for 2 h. Two milliliters of acryonitrile was added to this solution drop by drop, and the resulting solution was refluxed for 2 h. The volume of the reaction mixture was reduced to approximately 3 mL and kept on ice. Light-brown crystals of *N^1*, *N^2*-dicyanoethyl-*N^1*,*N^2*-bis(pyridin-2-ylmethyl)benzene-1,2-diamine were separated out after 2 days. The crystals were washed with water and recrystallized with ethanol.

Yield: 42%, analytically calculated. For [$C_{24}H_{24}N_6$] (%): C, 72.7; H, 6.1; N, 21.2 Observed (%): C, 71.9; H, 6.8; N, 21.3. ^{1}H NMR (DMSO, 500 MHz) δ_{ppm}: 7.4 – 8.6 (m, H-Py, 8H), 4.9 (s, -Py-CH_2-N-, 4H), 3.7 (t, -N-CH_2-C, 4H), 2.6 (t, -C-CH_2-CN-, 4H), 6.4 (m, Ar-H, 4H). Fourier transform infrared spectroscopy measurements (FT-IR; KBr, cm^{-1}): 3042 (aromatic C-H stretching); 2917 (asymmetric -CH_2 stretching); 2856 (symmetric -CH_2 stretching); 2236(-CN stretching); 1461, 1552 and 1645(Ar-ring vibration); and 1267, 1321 and 1356 (Ar-N stretching).

6.2.2.2 Synthesis of N^1, N^2-dicyanoethyl-N, N^2-bis(thiophen-2-ylmethyl)benzene-1, 2-diamine [L_7]

2-Thiophenecarboxaldehyde (2.24 g, 20 mmol) was dissolved in 25 mL of toluene and was added to a 15 mL solution of *o*-phenylenediamine (1.08 g, 10 mmol) in toluene. The reaction mixture was stirred for 15 min, and then its volume was concentrated to

5 mL of the original solution. The concentrated mixture was cooled in an ice bath for 2 days, and the light yellow crystals were separated. The crystals were filtered out and washed with cold toluene. The Schiff base was dissolved in 25 mL of methanol, and solid $NaBH_4$ (0.76 g, 20 mmol) was added in small portions, keeping the flask in an ice bath. The reaction was quenched with 25 mL of water, and the reduced ligand was extracted in DCM (4×25 mL). The extract was dried over anhydrous sodium sulfate and evaporated to dryness. The reduced product was dissolved in 10 mL of methanol and stirred with 1.5 g of K_2CO_3 for 2 h. Two milliliters of acryonitrile was added to this solution drop by drop, and the resulting solution was refluxed for 2 h. The volume of the reaction mixture was reduced to approximately 3 mL and kept on ice. After three days, the light yellow crystals of *N^1*,*N^2*-dicyanoethyl-*N^1*,*N^2*-bis(thiophen-2-ylmethyl)benzene-1,2-diamine were filtered, washed with water and recrystallized with ethanol.

Yield: 48%, analytically calculated. For [$C_{24}H_{24}N_6$] (%): C, 72.7; H, 6.1; N, 21.2 Observed (%): C, 71.9; H, 6.8 and N, 21.3. ^{1}H NMR (DMSO, 500 MHz) δ_{ppm}: 6.4 – 7.0 (m,thio-H,6H), 4.9 (s, -thio-CH_2-N-, 4H), 3.7 (t, -N-CH_2-C, 4H), 2.6 (t, -C-CH_2-CN-, 4H), 6.4 (m, Ar-H, 4H). FT-IR (KBr, cm^{-1}): 3026, 2978 (aromatic C-H stretching); 2904 (asymmetric -CH_2 stretching); 2851 (symmetric -CH_2 stretching); 2213 (-CN stretching); 1446, 1560 and 1649 (Ar-ring vibration); 1252, 1317 and 1364 (Ar-N stretching); and 1209, 1115 and 870(asymmetric -C-S-C stretching.).

6.2.2.3 Synthesis of N^1,N^2-dicyanoethyl-N^1,N^2-bis(furan-2-ylmethyl)benzene-1, 2-diamine [L_8]

Furan-2-aldehyde (3.3 mL, 40 mmol) was dissolved in 10 mL of DCM and added to a 10 mL solution of *o*-phenylenediamine (2.16 g, 20 mmol) in DCM. The resulting solution was stirred for 2 h at room temperature, and then the solvent was completely evaporated to leave a red liquid. The liquid was added to 50 mL of methanol, and solid $NaBH_4$ (0.76 g, 20 mmol) was added in small portions, keeping the flask in an ice bath. The reaction was quenched with 50 mL of water, and the reduced ligand was extracted in DCM (4×25 mL). The extract was dried over anhydrous sodium sulfate and evaporated to yield a brown solid. The solid was dissolved in 10 mL of methanol and stirred with 1.5 g K_2CO_3 for 2 h. An excess of acryonitrile (2.0 mL) was added to this solution drop by drop, and the resulting solution was refluxed for 2 h. The volume of the reaction mixture was reduced to approximately 3 mL and kept in ice for 2 days. The N-substituted reduced Schiff base N^1, N^2-dicyanoethyl-N^1, N^2-bis(furan-2-ylmethyl)benzene-1, 2-diamine was separated out as a dark brown solid that was washed with water and recrystallized with ethanol.

Yield: 35%, analytically calculated. For [$C_{24}H_{24}N_6$] (%): C, 72.7; H, 6.1; N, 21.2 Observed (%): C, 71.9; H, 6.8; N, 21.3. ^{1}H NMR (DMSO, 500 MHz) δ_{ppm}: 6.0 – 7.3 (m, fur-H, 6H), 4.5 (s, -fur-CH_2-N-, 4H), 3.7 (t, -N-CH_2-C, 4H), 2.6 (t, -C-CH_2-CN-, 4H), 6.4 (m, Ar-H, 4H). FT-IR (KBr, cm^{-1}): 3039, 2941 (aromatic C-H stretching); 2913 (asymmetric -CH_2 stretching), 2849 (symmetric -CH_2 stretching); 2228(-CN stretching); 1451, 1557 and 1652 (Ar-ring vibration); 1259, 1325 and 1359 (Ar-N stretching); and 1215, 1108 and 790 (asymmetric -C-O-C stretching).

6.2.3 Preparation of coated graphite electrodes and potential measurement

Appropriate amounts of the membrane components (ionophore, anion additives, PVC and plasticizers) were dissolved in 5 mL of THF, and the solvent was evaporated to obtain a concentrated solution. Spectroscopic-grade graphite rods (10 mm length and 5 mm diameter) with polished surfaces were dipped into the solution (up to 5 mm deep), withdrawn quickly and suspended upside-down for a few seconds to allow the THF to dry. The process was repeated several times until a uniform coating formed on the graphite surface, and the electrode was allowed to stabilize overnight. After immobilization, we obtained a scanning electron microscopy (SEM) image (Figure 6.4) of the graphite electrode surface. The membrane components and pores of varying size, which may facilitate the adsorption of ion on the electrode surface, are seen to be uniformly distributed on the graphite surface. Finally, the electrode was sealed in a glass tube with epoxy resin.

The coated electrodes were conditioned in a 1 mM $Cd(NO_3)_2$ solution for 24 h before the potentiometric measurements. The potentials were measured by varying the concentration of the $Cd(NO_3)_2$ solution in the range 1 nM to 0.1 M. Standard $Cd(NO_3)_2$ solutions were obtained by gradual dilution of a 0.1 M $Cd(NO_3)_2$ solution. The potentials were measured on a Century CP 901 digital pH meter at 25 ± 0.1°C, and the following cell was set up.

Coated graphite electrode || test solution || Hg/Hg_2Cl_2 |KCl (saturated)

The activity coefficients were calculated according to the Debye-Hückel procedure using the equation (1) given in *section 3.2.6* of Chapter 3.

6.3 Results and Discussion

6.3.1 Complexation study

In a preliminary study on the affinity of the ligands (L_6, L_7 and L_8) for different metals, a conductometric titration was conducted. 20 mL of 0.1 mM cation solution was titrated with a ligand solution of 10 mM. The conductance of the mixture was measured after each addition of ligand. Among the metals tested, the conductance of the cadmium solution showed the greatest variation upon the addition of ligands. The change in conductance of the Cd^{2+} solution as a function of the $[L]/[Cd^{2+}]$ ratio is shown in Figure 6.5. The conductance decreases with the addition of the ligand, which shows that Cd^{2+} ions are strongly interacting with the added ligand. A stage is reached when all of the metal is consumed by the ligand, 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. These breaks show that the ligands form a 1:1 complex with cadmium. The conductometric titration data was further used to calculate the stability constants of the various ion-ionophore complexes [58, 59], and the results are summarized in Table 6.1. It is clear from the stability constant values that cadmium has the maximum value, indicating that ligand-metal binding is strongest for Cd^{2+} and weaker for the others, relative to Cd^{2+}. Therefore, these ligands are good ionophores for complexing with Cd^{2+}, and their membranes may work as Cd^{2+}-selective electrodes.

6.3.2 Evolution of stability constant

The stability constants of the resulting 1:1 metal-ionophore complexes were also calculated according to the sandwich membrane method as described in *section 3.2.7* of Chapter 3. The stability constants of different complexes, calculated by the sandwich membrane method, are also given in Table 6.1. These values show that these chelating ligands form the most stable complexes with Cd^{2+} ions, having stability constants of 6.59, 7.42 and 6.21 for L_6, L_7 and L_8, respectively. The stability constant values for the other metal complexes are much smaller, indicating their weaker stability. The high stabilities of the Cd^{2+} complexes with L_6, L_7 and L_8 reflect the high affinity of these ligands for Cd^{2+} ions as compared to the other metal ions. Therefore, these ligands could be used as potential ionophores for preparing Cd^{2+}-selective electrodes.

6.3.3 Optimization of membrane composition

Various components which are usually present in membrane are binder (matrix material), ionophore, plasticizer and anion excluding additive. It is well known that the composition [60-63] of the membrane affects the performance of the electrode. The performance characteristics which render an electrode better are wide working concentration range, low response time and Nernstian slope. In terms of these parameters, various membranes were evaluated. In order to arrive at an optimum composition of the electrode performing best, membranes of various compositions were prepared and studied. For all the three ionophores, first of all blank membranes containing only PVC, ionophore and additive (NaTPB) were prepared, studied and their performance characteristics determined from potential response plots are given in Tables 6.2, 6.3 and 6.4 respectively. It is seen from these Tables that the performance of these electrodes (A1, B1 and C1) is not excellent as the slope is sub-Nernstian, detection limit is high and working concentration range is narrow. Therefore, to improve the performance of these electrodes addition of seven plasticizers *viz., o*-NPOE (ε = 24), BA (ε = 5.1), TBP (ε = 8.0), AP (ε = 17.4) DOP (ε = 5.1), DBP (ε = 6.4) and DOS (ε = 3.9) was studied and a number of coated graphite electrodes (CGEs) having plasticized membranes were prepared, studied and the performance characteristics of these electrodes determined from potential response plots are given in Tables 6.2, 6.3 and 6.4. It is seen that the addition of plasticizers improves the performance of all plasticized electrodes in terms of higher slope, wider working concentration range and low detection limit. A comparison of performance characteristics of all plasticized electrodes (A2 to A8) of ionophore L_6, in Table 6.2, show that the electrode A2 having NPOE plasticizer improves the characteristics of the electrode best as the slope becomes Nernstian (29.5 ± 0.07 mV decade^{-1} of $a_{Cd}{}^{2+}$), working concentration range is widest (2.5×10^{-7} - 1.0×10^{-1} mol L^{-1})

and the detection limit is lowest (7.8×10^{-8} mol L^{-1}). To see the effect of nature of anion excluder additives, another electrode (A9) having a different additive (KTpClPB) was prepared and studied. Its performance characteristics show that the addition of KtpClPB in place of NaTPB does not result in any improvement rather than deterioration as the working concentration range has been shortened and detection limit becomes higher. Therefore NaTPB remains a preferred anion excluding additive. Effect of varying amount of ionophore (CGE-A10, A11 and A12) and no addition of additive NaTPB (CGE-A13) was also seen. An examination of these electrodes clearly shows that the additive improves the performance and the optimum amount of ionophore required is 4 wt%. Therefore comparison of performance of all the electrodes given Table 6.2 shows that the electrode A2 based on ionophore L_6 is the best performing electrode.

Similarly from the performance characteristics of CGEs of ionophores L_7 and L_8 given in Tables 6.3 and 6.4 respectively, it is concluded that the electrode B2 of L_7 and electrode C2 of L_8 are the best performing electrodes. Further it is seen from Tables 6.2, 6.3 and 6.4 that the optimum compositions of best performing electrodes (A2, B2 and C2) are L_6:o-NPOE:NaTPB:PVC as 4:51:2.5:42.5 (wt%), L_7:o-NPOE:NaTPB:PVC as 3:52.5:1.5:43 (wt%) and L_8:o-NPOE:NaTPB:PVC as 7:49:3.5:40.5 (wt%), respectively. The observed Nernstian response of these electrodes to the Cd^{2+} ion at the membrane solution interface arises due to the adsorption of Cd^{2+} ions on the electrodes surface followed by the ion-to-electron transfer mechanism. The conducting graphite surface acts as a good transducer and helps in the electron transfer process between heterogeneous phases [64]. The potential response plots of these electrodes are shown in Figure 6.6 respectively. Further detailed investigations were done with these electrodes only.

6.3.4 Effect of pH on the performance of the electrode

The effect of pH on the performance of these electrodes was determined by measuring their potential response for a 0.1 mM Cd^{2+} ion solution at different pH values, ranging from 1.0 to 11.0. The pH was adjusted by the addition of 0.1 M HCl/NaOH, and the results are shown in Figure 6.7 respectively. The potentials do not change in the pH range 2.0 to 8.0 (CGE-A2), 2.6 to 8.0 (CGE-B2) and 3.0 to 7.5 (CGE-C2). These results established the useful working pH range for these electrodes. The change in potential at higher pH value may be due to the formation of metal hydroxide species in the system [65]. At low pH, the deviations occur due to the protonation of the ionophore [66] and the electrodes start responding to H_3O^+ ions along with the Cd^{2+} ions, leading to an increase in the potentials.

6.3.5 Potentiometric selectivity and the effect of interfering ions

The most important feature of an ISE is its selectivity, which is measured in terms of the selectivity coefficient. The potentiometric selectivity coefficients for these electrodes were determined by IUPAC recommended fixed interference method (FIM) using the expression discussed in Chapter 2. For this purpose, a fixed concentration of interfering ions (a_B =10 mM) was added to the primary Cd^{2+} ion solutions ranging from 1 nM to 10 mM, and the potentials were measured. The potential values were plotted versus the activity of the Cd^{2+} ions. The linear portions of the potential response curve were extrapolated, and the value of $a_{Cd}{}^{2+}$ was obtained from the intersection point.

Potentiometric selectivity coefficients given in Table 6.5 indicate that the electrodes are highly selective over a number of monovalent (Ag^+, Na^+ and K^+) and divalent (Hg^{2+}, Pb^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+}, Mg^{2+} and Ca^{2+}) and trivalent (Sm^{3+},

Nd^{3+}, Ce^{3+}, Gd^{3+} and La^{3+}) ions. However, the selectivity coefficients for Hg^{2+} are not very small, and it would cause some interference if present in higher concentrations. To estimate the extent of interference caused by the Hg^{2+} ions, mixed run studies were performed, and the effect of the Hg^{2+} ion concentration on the performance of these electrodes was examined. The potentials were measured in the presence of different concentrations (0.5, 1, 5, 10 and 50 mM) of Hg^{2+}, and the potential responses of the electrodes to the mixture are shown in Figure 6.8, 6.9 and 6.10 respectively. The results indicate that no significant interference is observed at the lower concentrations (up to 5 mM) of Hg^{2+} ion, and the electrodes can be used for the estimation of cadmium. However, in the presence of higher concentrations of Hg^{2+} (above 5 mM), significant interference was observed, which also shortens the linear range and leads to high detection limit.

6.3.6 Determination of the response time and lifetime

According to the I.U.P.A.C recommendations, the response time of an ion-selective electrode is defined as the length of the time between the instant at which the ISE and the reference electrode are immersed in the sample solution and the moment at which the potential of the cell reaches its steady-state value within ± 1 mV [67]. In this study, the response time was determined by the successive immersion of these electrodes in a series of cadmium ion solutions, each having a 10-fold increase in concentration from 100 nM to 10 mM. The potential was measured continuously until the steady-state potential was attained. Electrodes A2, B2 and C2 responded sharply with response times of 12, 7 and 17 s, respectively (Figures 6.11, 6.12 and 6.13).

The loss of membrane components due to chemical process at the membrane sample interface is the main cause for the limited lifetime of neutral carrier-based ISEs

[68]. To determine the shelf life of the electrodes, their performance was checked daily over a period of 12 weeks. The potential response plots were acquired daily, and the performance characteristics were measured. The results are summarized in Table 6.6. The potentiometric characteristics of electrode B2 did not change significantly over a period of six weeks. After this period, the performance of the electrode started to deteriorate, and the slope became smaller as the detection limit increased. The results also indicate that electrodes A2 and C2 worked satisfactory for four weeks without showing significant change in their performance characteristics. However, the electrodes were conditioned in a 1 mM $Cd(NO_3)_2$ solution prior to the analysis.

The reproducibility of the Cd^{2+} electrodes was also checked, and the standard deviations of ten replicate measurements at 1 mM were ± 0.01, ± 0.07 and ± 0.03 mV for electrodes A2, B2 and C2 based on ligands L_6, L_7 and L_8, respectively.

6.3.7 Effect of non-aqueous impurities on the response of electrodes

The effect of the non-aqueous content on the performance of these electrodes was determined by measuring the potentials of solutions having different concentrations (10 to 30 %, v/v) of acetonitrile, methanol and ethanol. The results are summarized in Table 6.7. The results indicate that the electrodes worked satisfactorily in the solutions containing up to 20 % (v/v) non-aqueous content. With higher non-aqueous content, the performance of the electrodes deteriorated, and the potential produced was not reproducible, which may be due to the leaching of ionophores from the membrane phase.

6.3.8 Comparisons of the proposed electrodes with reported ISEs

The potentiometric characteristics of the newly developed electrodes (A2, B2 and C2) and previously developed Cd^{2+}-selective electrodes based on various ionophores are shown in Table 6.8. A comparative study of the CGEs based on L_6, L_7 and L_8 shows that they are superior to the previously reported Cd^{2+}-selective electrodes in terms of their wider working range and lower detection limit. However, their selectivity is comparable to the reported electrodes.

6.4. ANALYTICAL APPLICATIONS

6.4.1 Potentiometric titration

A potentiometric titration of 25 mL of 1 mM Cd^{2+} ions against 10 mM EDTA at pH 5.5 was carried out using these electrodes as indicators. The titration plots obtained are sigmoidal in shapes indicating high selectivity for Cd^{2+}. The titration plots (Figure 6.14) can be used to determine the amount of cadmium present in the sample.

6.4.2 Determination of Cd^{2+} in water samples

The electrodes were used for Cd^{2+} monitoring in Ganga (Roorkee) and Yamuna (Delhi) river water as well as in the wastewater taken from the State Infrastructure and Industrial Development Corporation of Uttaranchal (SIDCUL) industrial area and the Indian Institute of Technology-Roorkee Chemistry Department. The samples were collected from different locations and treated with 1 M nitric acid. The pH of these samples was adjusted to 5.5 before the analysis. The potentiometric results are in close agreement (Table 6.9) with those obtained by ICP-MS showing the utility of the electrodes for the determination of Cd^{2+}.

6.4.3 Determination of cadmium in biological samples

The electrodes were also used successfully for the determination of cadmium in some medicinal plant and soil samples collected from Haridwar region. Two grams of dried powdered plant samples was digested with a 5:1 mixture of nitric acid (25 %, v/v) and perchloric acid, followed by controlled heating until the evolution of gases ceased.

Fifteen milliliters of deionized water was added to this mixture and filtered through into a 25 mL volumetric flask. The volume was adjusted to a final volume of 25 mL.

The soil samples were digested in a cleaned Teflon beaker by treating 2 g of each soil sample with 10 mL of nitric acid. The solution was heated until the evolution of gases was completed. A mixture (5:3:5) of nitric acid, perchloric acid and concentrated hydrofluoric acid was added, followed by controlled heating until white fumes evolved. The solution was filtered and diluted with deionized water to a final volume of 25 mL in a volumetric flask [69]. The pH of the samples was adjusted to 5.5. The results obtained by potentiometry were compared with those of ICP-MS and are given in Table 6.10.

6.5. Conclusions

Studies of CGEs of different membrane compositions have established that the compositions performing best are L_6:o-NPOE:NaTPB:PVC as 4:51:2.5:42.5 (wt%), L_7:o-NPOE:NaTPB:PVC as 3:52.5:1.5:43 (wt%) and L_8:o-NPOE:NaTPB:PVC as 7:49:3.5:40.5 (wt%). The membranes of these compositions work over widest working concentration range with low detection limit and fast response time. These electrodes are unaffected by the pH in the range 2.6-8.0 and can also work satisfactorily in the non-aqueous content up to 20 % (v/v) They also show high selectivity for Cd^{2+} over a large number of metal ions. The utility of the electrodes has been demonstrated by detecting cadmium in medicinal plants, soil and industrial waste water by direct potentiometry and also as an indicator electrode in the potentiometric titration of Cd^{2+} against EDTA. A comparison of performance characteristics with reported electrodes shows that the proposed electrodes are superior to existing electrodes in terms of wide concentration range and low detection limit and selectivity is better over most of them. Therefore, these are important addition to the existing set of cadmium selective electrodes.

Tables

Table 6.1: Stability constants of ionophores (L_6, L_7 and L_8) with different metal ions

Metal ions (M^{n+})	Sandwich membrane method			Conductivity method		
	($\log \beta_{ML1}$) ± σ	($\log \beta_{ML2}$) ± σ	($\log \beta_{ML3}$) ± σ	($\log \beta_{ML1}$) ± σ	($\log \beta_{ML2}$) ± σ	($\log \beta_{ML3}$) ± σ
Cd^{2+}	6.59 ± 0.1	7.42 ± 0.05	6.21 ± 0.09	4.11 ± 0.03	6.23 ± 0.01	4.49 ± 0.01
Hg^{2+}	3.46 ± 0.6	3.82 ± 0.02	3.38 ± 0.3	2.63 ± 0.2	3.52 ± 0.08	2.41 ± 0.05
Ag^{+}	3.25 ± 0.2	3.17 ± 0.1	3.01 ± 0.1	1.24 ± 0.04	3.04 ± 0.01	1.13 ± 0.04
Cu^{2+}	3.35 ± 0.01	2.89 ± 0.8	3.14 ± 0.04	1.66 ± 0.1	1.08 ± 0.05	1.11 ± 0.05
Pb^{2+}	2.76 ± 0.09	3.24 ± 0.02	2.91 ± 0.3	1.03 ± 0.9	1.17 ± 0.04	1.06 ± 0.07
Zn^{2+}	3.42 ± 0.6	3.53 ± 0.4	3.12 ± 0.08	1.73 ± 0.03	1.83 ± 0.4	1.09 ± 0.01
Ni^{2+}	2.14 ± 0.4	2.63 ± 0.9	2.57 ± 0.2	1.31 ± 0.05	1.35 ± 0.1	1.14 ± 0.5
Co^{2+}	2.19 ± 0.02	2.37 ± 0.2	2.48 ± 0.07	1.33 ± 0.04	1.41 ± 0.3	1.27 ± 0.8
Fe^{2+}	2.55 ± 0.7	2.06 ± 0.02	2.17 ± 0.05	1.20 ± 0.02	1.32 ± 0.07	1.03 ± 0.05
Mg^{2+}	1.86 ± 0.06	1.48 ± 0.04	1.25 ± 0.06	1.13 ± 0.04	1.26 ± 0.04	1.07 ± 0.5
Ca^{2+}	1.42 ± 0.2	1.19 ± 0.01	1.23 ± 0.02	1.16 ± 0.2	1.28 ± 0.07	1.14 ± 0.01
Sm^{3+}	2.04 ± 0.5	1.63 ± 0.05	2.29 ± 0.06	2.13 ± 0.01	2.24 ± 0.02	1.98 ± 0.5
Nd^{3+}	1.62 ± 0.1	2.27 ± 0.3	2.34 ± 0.02	1.84 ± 0.5	2.16 ± 0.06	1.69 ± 0.5
Gd^{3+}	1.76 ± 0.05	2.01 ± 0.08	1.65 ± 0.04	2.22 ± 0.1	2.48 ± 0.02	1.79 ± 0.8
Ce^{3+}	1.15 ± 0.9	1.34 ± 0.04	1.59 ± 0.1	1.93 ± 0.7	1.97 ± 0.5	1.74 ± 0.02
La^{3+}	1.31 ± 0.7	1.44 ± 0.03	1.51 ± 0.08	1.46 ± 0.4	1.58 ± 0.1	1.36 ± 0.4
Na^{+}	1.17 ± 0.06	1.01 ± 0.1	1.23 ± 0.04	1.42± 0.2	1.48 ± 0.01	1.32 ± 0.02
K^{+}	1.03 ± 0.1	0.84 ± 0.09	1.16 ± 0.07	1.15 ± 0.03	1.13 ± 0.01	1.02 ± 0.01

σ- standard deviation

Table 6.2: Membrane compositions of CGEs based on L_6 and their potentiometric response as Cadmium(II) ion-selective electrodes

CGE No.	Composition of membrane (%, w/w)				Slope (mV decade^{-1})	Linear working range (mol L^{-1})	Detection limit (mol L^{-1})
	Ionophore	Plasticizer	Additive	PVC			
A1	4		2.5,NaTPB	93.5	20.9	5.8×10^{-5} - 1.0×10^{-1}	3.2×10^{-5}
A2	4	51,NPOE	2.5,NaTPB	42.5	29.5	2.5×10^{-7} - 1.0×10^{-1}	7.8×10^{-8}
A3	4	51,AP	2.5,NaTPB	42.5	27.4	1.7×10^{-6} - 5.0×10^{-2}	9.6×10^{-7}
A4	4	51,TBP	2.5,NaTPB	42.5	24.9	3.5×10^{-6} - 1.0×10^{-1}	1.8×10^{-6}
A5	4	51,DBP	2.5,NaTPB	42.5	24.2	5.0×10^{-6} - 1.0×10^{-2}	7.8×10^{-6}
A6	4	51,BA	2.5,NaTPB	42.5	23.5	7.3×10^{-6} - 5.0×10^{-2}	4.6×10^{-6}
A7	4	51,DOP	2.5,NaTPB	42.5	23.2	4.8×10^{-6} - 5.0×10^{-2}	2.1×10^{-6}
A8	4	51,DOS	2.5,NaTPB	42.5	22.6	1.3×10^{-5} - 1.0×10^{-1}	8.4×10^{-6}
A9	4	51,NPOE	2.5,KTpClPB	42.5	28.6	1.4×10^{-6} – 1.0×10^{-1}	8.2×10^{-7}
A10	3	51,NPOE	2.5,NaTPB	43.5	25.5	8.9×10^{-6} - 1.0×10^{-2}	6.1×10^{-6}
A11	5	51,NPOE	2.5,NaTPB	41.5	29.1	7.8×10^{-7} - 1.0×10^{-1}	6.7×10^{-7}
A12	-	51,NPOE	2.5,NaTPB	46.5	10.4	6.9×10^{-4} - 1.0×10^{-2}	4.4×10^{-4}
A13	4	51,NPOE	-	45.0	26.5	5.0×10^{-6} - 1.0×10^{-2}	2.5×10^{-6}

Table 6. 3: Membrane compositions of CGEs based on L_7 and their potentiometric response as Cadmium(II) ion-selective electrodes

CGE No.	Composition of membrane (%, w/w)				Slope (mV decade^{-1})	Linear working range (mol L^{-1})	Detection limit (mol L^{-1})
	Ionophore	Plasticizer	Additive	PVC			
B1	3	-	1.5,NaTPB	95.5	21.4	1.9×10^{-5} - 1.0×10^{-2}	8.1×10^{-6}
B2	3	52.5,NPOE	1.5,NaTPB	43.0	29.6	1.7×10^{-8} - 1.0×10^{-1}	7.0×10^{-9}
B3	3	52.5,AP	1.5,NaTPB	43.0	27.5	2.0×10^{-6} - 1.0×10^{-1}	8.9×10^{-7}
B4	3	52.5,TBP	1.5,NaTPB	43.0	25.3	5.0×10^{-6} - 1.0×10^{-2}	2.5×10^{-6}
B5	3	52.5,DBP	1.5,NaTPB	43.0	23.8	6.9×10^{-6} - 1.0×10^{-2}	3.4×10^{-6}
B6	3	52.5,DOP	1.5,NaTPB	43.0	23.8	3.8×10^{-6} - 1.0×10^{-1}	1.2×10^{-6}
B7	3	52.5,BA	1.5,NaTPB	43.0	23.2	6.5×10^{-5} - 5.0×10^{-2}	3.5×10^{-6}
B8	3	52.5,DOS	1.5,NaTPB	43.0	22.5	8.7×10^{-6} - 1.0×10^{-1}	4.4×10^{-6}
B9	3	52.5,NPOE	1.5,KTpClPB	43.0	28.3	9.4×10^{-7} - 5.0×10^{-2}	5.8×10^{-7}
B10	2	52.5,NPOE	1.5,NaTPB	43.0	26.4	2.3×10^{-6} - 5.0×10^{-2}	8.3×10^{-7}
B11	4	52.5,NPOE	1.5,NaTPB	42.0	28.7	1.8×10^{-7} - 1.0×10^{-1}	9.7×10^{-8}
B12	-	52.5,NPOE	1.5,NaTPB	46.0	11.7	5.4×10^{-4} - 1.0×10^{-2}	2.0×10^{-4}
B13	3	52.5,NPOE	-	44.5	25.1	7.6×10^{-7} - 1.0×10^{-1}	4.3×10^{-7}

Table 6.4: Membrane compositions of CGEs based on L_8 and their potentiometric response as Cadmium(II) ion-selective electrodes

CGE No.	Composition of membrane (%, w/w)				Slope (mV decade^{-1})	Linear working range (mol L^{-1})	Detection limit (mol L^{-1})
	Ionophore	Plasticizer	Additive	PVC			
C1	7	-	3.5,NaTPB	89.5	20.9	4.1×10^{-4} - 5.0×10^{-2}	9.5×10^{-5}
C2	7	49,NPOE	3.5,NaTPB	40.5	29.8	4.6×10^{-7} - 5.0×10^{-2}	8.4×10^{-8}
C3	7	49,AP	3.5,NaTPB	40.5	27.3	1.8×10^{-6} - 5.0×10^{-2}	9.5×10^{-7}
C4	7	49,TBP	3.5,NaTPB	40.5	27.0	4.5×10^{-6} - 1.0×10^{-1}	1.6×10^{-6}
C5	7	49,DBP	3.5,NaTPB	40.5	24.5	9.4×10^{-6} - 1.0×10^{-1}	6.3×10^{-6}
C6	7	49,BA	3.5,NaTPB	40.5	22.8	6.7×10^{-5} - 5.0×10^{-2}	4.2×10^{-5}
C7	7	49,DOP	3.5,NaTPB	40.5	22.3	7.9×10^{-5} - 1.0×10^{-1}	5.1×10^{-5}
C8	7	49,DOS	3.5,NaTPB	40.5	21.6	8.4×10^{-5} - 1.0×10^{-1}	5.4×10^{-5}
C9	7	49,NPOE	3.5,KTpClPB	40.5	28.1	3.4×10^{-6} - 5.0×10^{-2}	1.8×10^{-6}
C10	6	49,NPOE	3.5,NaTPB	41.5	27.1	5.5×10^{-6} - 1.0×10^{-2}	3.6×10^{-6}
C11	8	49,NPOE	3.5,NaTPB	39.5	29.2	9.8×10^{-7} - 1.0×10^{-1}	4.7×10^{-7}
C12	-	49,NPOE	3.5,NaTPB	47.5	12.3	6.7×10^{-4} - 1.0×10^{-2}	4.2×10^{-4}
C13	7	49,NPOE	-	44.0	27.8	1.8×10^{-6} - 5.0×10^{-2}	9.5×10^{-7}

Table 6.5: Selectivity coefficients of Cd^{2+}-selective electrodes A2, B2 and C2 based on L_6, L_7 and L_8 respectively

Interfering Ions (B)	Selectivity Coefficients (–Log $K_{Cd^{2+},B}$)		
	CGE-A2	CGE-B2	CGE-C2
Hg^{2+}	0.3 ± 0.03	1.6 ± 0.05	0.7 ± 0.10
Pb^{2+}	2.4 ± 0.10	2.9 ± 0.04	2.2 ± 0.05
Cu^{2+}	2.1 ± 0.09	3.2 ± 0.02	2.5 ± 0.07
Zn^{2+}	2.8 ± 0.05	3.6 ± 0.10	3.3 ± 0.20
Ni^{2+}	3.0 ± 0.10	3.8 ± 0.03	3.2 ± 0.30
Fe^{2+}	3.2 ± 0.10	3.6 ± 0.20	3.4 ± 0.20
Co^{2+}	3.5 ± 0.20	3.9 ± 0.07	3.1 ± 0.30
Mg^{2+}	3.0 ± 0.10	4.2 ± 0.05	3.1 ± 0.01
Ca^{2+}	3.5 ± 0.07	3.7 ± 0.03	3.0 ± 0.20
Sm^{3+}	4.7 ± 0.10	3.9 ± 0.05	4.0 ± 0.20
Nd^{3+}	4.5 ± 0.30	4.5 ± 0.10	4.3 ± 0.04
Gd^{3+}	4.4 ± 0.05	4.0 ± 0.02	3.7 ± 0.01
Ce^{3+}	3.9 ± 0.30	3.4 ± 0.04	3.7 ± 0.20
La^{3+}	4.2 ± 0.40	3.8 ± 0.01	3.7 ± 0.07
Na^{+}	2.6 ± 0.30	3.2 ± 0.20	2.6 ± 0.03
K^{+}	2.3 ± 0.20	3.1 ± 0.40	2.0 ± 0.10
Ag^{+}	2.5 ± 0.06	2.7 ± 0.30	2.0 ± 0.09

Table 6.6: Lifetime study of coated graphite electrodes no. A2, B2, and C2

Time (weeks)	CGE-A2		CGE-B2		CGE-C2	
	Slope (mV Decade^{-1})	Detection limit (mol L^{-1})	Slope (mV Decade^{-1})	Detection limit (mol L^{-1})	Slope (mV Decade^{-1})	Detection limit (mol L^{-1})
1	29.5 ± 0.02	7.8×10^{-8}	29.6 ± 0.04	7.0×10^{-9}	29.8 ± 0.05	8.4×10^{-8}
2	29.5 ± 0.05	7.8×10^{-8}	29.6 ± 0.20	6.8×10^{-9}	29.8 ± 0.05	8.4×10^{-8}
3	29.3 ± 0.01	7.5×10^{-8}	29.6 ± 0.03	6.8×10^{-9}	29.4 ± 0.03	7.9×10^{-8}
4	29.1 ± 0.20	7.1×10^{-8}	29.4 ± 0.40	6.3×10^{-9}	29.4 ± 0.40	7.2×10^{-8}
5	28.7 ± 0.10	1.6×10^{-7}	29.4 ± 0.45	6.3×10^{-9}	28.3 ± 0.50	5.5×10^{-7}
6	28.4 ± 0.20	3.9×10^{-7}	29.2 ± 0.10	1.5×10^{-8}	27.6 ± 0.10	8.7×10^{-7}
7	27.6 ± 0.04	7.4×10^{-7}	28.8 ± 0.50	4.2×10^{-7}	26.2 ± 0.50	9.5×10^{-7}
8	27.1 ± 0.20	1.6×10^{-6}	28.5 ± 0.30	1.3×10^{-7}	25.9 ± 0.30	2.8×10^{-6}
9	26.7 ± 0.10	3.2×10^{-6}	28.2 ± 0.20	2.0×10^{-7}	25.4 ± 0.20	3.1×10^{-6}
10	26.4 ± 0.05	5.9×10^{-6}	27.5 ± 0.40	4.6×10^{-7}	25.1 ± 0.40	4.3×10^{-6}
11	26.0 ± 0.35	7.3×10^{-6}	27.6 ± 0.50	7.8×10^{-7}	24.7 ± 0.50	6.8×10^{-6}
12	25.8 ± 0.80	8.5×10^{-6}	27.1 ± 0.70	3.5×10^{-6}	23.5 ± 0.70	8.5×10^{-6}

Table 6.7: Performance of Cd^{2+} selective CGEs in presence of non-aqueous media

Non-aqueous content (%, v/v)	CGE-A2		CGE-B2		CGE-C2	
	Slope (mV decade^{-1})	Detection Limit (mol L^{-1})	Slope (mV decade^{-1})	Detection Limit (mol L^{-1})	Slope (mV decade^{-1})	Detection Limit (mol L^{-1})
0	29.5 ± 0.07	7.8×10^{-8}	29.6 ± 0.08	7.0×10^{-9}	29.8 ± 0.05	8.4×10^{-8}
Acetonitrile						
10	29.5 ± 0.04	7.8×10^{-8}	29.5 ± 0.08	7.6×10^{-9}	29.6 ± 0.03	8.7×10^{-8}
15	29.5 ± 0.05	8.3×10^{-8}	29.4 ± 0.08	8.2×10^{-9}	29.6 ± 0.1	8.7×10^{-8}
20	29.4 ± 0.07	8.9×10^{-8}	29.2 ± 0.2	8.6×10^{-9}	29.2 ± 0.04	9.3×10^{-8}
25	28.1 ± 0.1	5.6×10^{-7}	28.9 ± 0.7	9.4×10^{-8}	28.5 ± 0.3	7.8×10^{-7}
30	26.7 ± 0.5	8.8×10^{-6}	26.6 ± 0.6	8.3×10^{-7}	26.4 ± 0.2	2.4×10^{-6}
Methanol						
10	29.4 ± 0.08	8.9×10^{-8}	29.5 ± 0.3	7.6×10^{-9}	29.4 ± 0.08	8.9×10^{-8}
15	29.4 ± 0.05	8.9×10^{-8}	29.3 ± 0.06	8.5×10^{-9}	29.1 ± 0.1	9.6×10^{-8}
20	29.2 ± 0.09	8.2×10^{-8}	29.0 ± 0.03	9.4×10^{-9}	29.0 ± 0.5	1.2×10^{-7}
25	27.3 ± 0.05	4.5×10^{-7}	28.5 ± 0.6	8.7×10^{-8}	28.9 ± 0.2	7.3×10^{-6}
30	26.8 ± 0.9	3.9×10^{-6}	25.9 ± 0.8	4.2×10^{-6}	26.2 ± 0.06	1.5×10^{-6}
Ethanol						
10	29.4 ± 0.05	8.9×10^{-8}	29.5 ± 0.05	7.6×10^{-9}	29.8 ± 0.3	8.4×10^{-8}
15	29.4 ± 0.04	8.8×10^{-8}	29.5 ± 0.2	7.6×10^{-9}	29.5 ± 0.1	8.6×10^{-8}
20	29.3 ± 0.08	8.6×10^{-8}	29.2 ± 0.7	8.6×10^{-9}	29.1 ± 0.04	9.6×10^{-8}
25	28.2 ± 0.08	3.9×10^{-7}	28.9 ± 0.02	9.1×10^{-8}	28.6 ± 0.02	7.5×10^{-6}
30	26.2 ± 0.2	6.4×10^{-6}	26.4 ± 0.1	7.9×10^{-7}	26.7 ± 0.5	1.8×10^{-6}

Table 6.8: Comparison of potentiometric characteristics of coated graphite electrodes A2, B2 and C2 with the reported Cd^{2+} selective electrodes

Reference no.	Slope (mV decade^{-1})	Linear range (mol L^{-1})	pH range	Response time (s)	Selectivity coefficient ($-Log K^{Pot}_{Cd^{2+},B}$)
42	30.0	7.9×10^{-8}-1.0×10^{-1}	2.0-8.0	10	Co^{2+}(3.7), Zn^{2+}(3.4),Pb^{2+}(3.3), Ni^{2+}(3.2), Cu^{2+}(2.8), Hg^{2+}(3.6), Ca^{2+}(3.9), Ag^{+}(3.1)
43	28.0	7.5×10^{-7}-1.5×10^{-1}	3.5-9.0	~10	Co^{2+}(3.2), Zn^{2+}(2.6),Pb^{2+}(2.1), Ni^{2+}(2.6), Cu^{2+}(2.7), Hg^{2+}(2.8), Ca^{2+}(2.5)
40	29.5	3.2×10^{-6}-1.0×10^{-1}	4.5-6.5	~ 8	Co^{2+}(2.5), Zn^{2+}(2.6),Pb^{2+}(2.3), Ni^{2+}(2.4), Cu^{2+}(2.0), Hg^{2+}(2.8), Ca^{2+}(2.5), Ag^{+}(3.2)
26	29 ± 1.0	2.1×10^{-5}-1.0×10^{-1}	1.9-7.0	17	Co^{2+}(1.07), Zn^{2+}(1.2),Pb^{2+}(0.43),Cu^{2+}(1.04), Hg^{2+}(1.72), Ca^{2+}(1.29), Ag^{+}(1.14)
27	30 ± 1.0	3.0×10^{-5}-1.0×10^{-1}	2.0-5.4	23	Co^{2+}(0.63), Zn^{2+}(0.56),Pb^{2+}(0,52), Ni^{2+}(0.69), Hg^{2+}(0.52), Ca^{2+}(0.24)
25	29.0	1.0×10^{-5}-1.0×10^{-1}	5.0-7.7	<10	Co^{2+}(0.95), Zn^{2+}(0.75),Pb^{2+}(0.75), Cu^{2+}(0.95), Ca^{2+}(0.65) Fe^{3+}(0.60)
28	29 ± 1.0	4.0×10^{-7}-1.0×10^{-1}	2.5-8.5	< 10	Co^{2+}(3.0), Zn^{2+}(3.4),Pb^{2+}(0.39), Ni^{2+}(3.1), Cu^{2+}(0,69), Ca^{2+}(3.72), Ag^{+}(1.0)
24	30.0 ± 1.0	3.9×10^{-5}-1.0×10^{-1}	3.2-7.5	25	Co^{2+}(0.62), Zn^{2+}(0.69), Pb^{2+}(0.52), Ni^{2+}(0.64), Hg^{2+}(0.52),
44	27.8	1.0×10^{-5}-1.0×10^{-1}	4.0-7.0	<15	Co^{2+}(4.2), Zn^{2+}(2.3),Pb^{2+}(3.2), Ni^{2+}(3.1), Cu^{2+}(2.4), Hg^{2+}(3.4), Ca^{2+}(3.1), Ag^{+}(3.1)
50	30 ±1.0	2.16×10^{-7}-1.0×10^{-1}	5.0-7.0	50	Co^{2+}(4.2), Zn^{2+}(3.8),Pb^{2+}(3.2), Ni^{2+}(4.5), Cu^{2+}(2.3), Hg^{2+}(3.4), Ag^{+}(3.5)
45	29.9 ± 0.5	1.0×10^{-6}-1.0×10^{-1}	4.0-9.0	< 8	Co^{2+}(2.8), Zn^{2+}(1.8),Pb^{2+}(1.6), Ni^{2+}(2.5), Cu^{2+}(0.67), Ag^{+}(1.04)
49	28.5	1.0×10^{-5}-1.0×10^{-1}	4.3-8.5	~5	Co^{2+}(1.5), Zn^{2+}(1.3), Ni^{2+}(2.5), Cu^{2+}(1.4), Ca^{2+}(1.4)
CGE-A2	29.5±0.07	2.5×10^{-7}-1.0×10^{-1}	2.0-8.0	12	Co^{2+}(3.5), Zn^{2+}(2.8),Pb^{2+}(2.4), Ni^{2+}(3.0), Cu^{2+}(2.1), Hg^{2+}(0.3), Ca^{2+}(3.5), Ag^{+}(2.5)
CGE-B2	29.6±0.08	1.7×10^{-8}-1.0×10^{-1}	2.6-8.0	7	Co^{2+}(3.9), Zn^{2+}(3.6),Pb^{2+}(2.9), Ni^{2+}(3.8), Cu^{2+}(3.7), Hg^{2+}(1.6), Ca^{2+}(3.7), Ag^{+}(2.7)
CGE-C2	29.8±0.05	4.6×10^{-7}-5.0×10^{-2}	3.0-7.5	17	Co^{2+}(3.1), Zn^{2+}(3.3),Pb^{2+}(2.2), Ni^{2+}(3.2), Cu^{2+}(2.5), Hg^{2+}(0.7), Ca^{2+}(3.0), Ag^{+}(2.0)

Table 6.9:Determination of Cd^{2+} concentration (mg L^{-1}) in water samples

Samples	CGE-A2	CGE-B2	CGE-C2	ICP-MS
Ganga water	4.33±0.22	4.92±0.05	5.14±0.4	4.67±0.43
Yamuna water	8.71±0.43	9.36±0.40	9.12±0.16	9.54±0.38
Industrial water	10.95±0.33	12.83±0.29	12.32±0.11	13.17±0.30
Laboratory Waste water	9.20±0.72	9.44±0.11	9.67±0.52	10.72±0.53

Table 6.10: Determination of Cd^{2+} concentration (mg kg^{-1}) in medicinal plants and soil samples

Samples	CGE-A2	CGE-B2	CGE-C2	ICP-MS
Ocimum sanctum (Tulsi)	0.97±0.08	0.92±0.03	0.96±0.4	0.98±0.02
Withania somnifera (Ashwagandha)	1.12±0.02	1.15±0.01	1.13±0.01	1.18±0.04
Cassia fistula (Amaltas)	0.92±0.02	0.95±0.04	0.97±0.10	0.95±0.01
Adhatoda vasica (Arusa)	0.79±0.25	0.73±0.04	0.71±0.01	0.77±0.05
Soil sample 1(Haridwar)	3.41±0.11	3.42±0.05	3.36±0.27	3.40±0.36
Soil sample 2(Rishikesh)	3.30±0.14	3.34±0.07	3.21±0.09	3.20±0.10

Figures

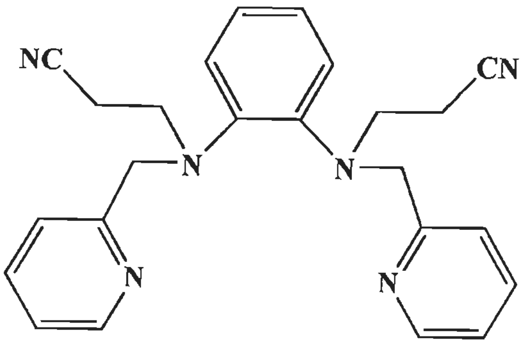


Figure 6.1: Structure of *N*^{1},*N*^{2}-dicyanoethyl-*N*^{1},*N*^{2}-bis(pyridin-2-ylmethyl) benzene-1,2-diamine [L$_6$]

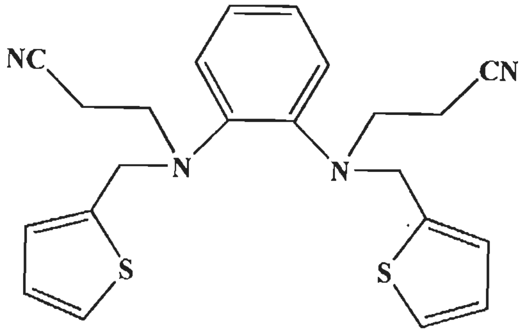


Figure 6.2: Structure of *N*^{1},*N*^{2}-dicyanoethyl-*N*^{1},*N*^{2}-bis(thiophen-2-ylmethyl)benzene-1,2-diamine [L$_7$]

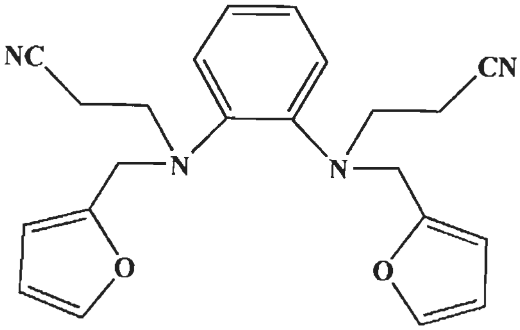


Figure 6.3: Structure of *N*^{1},*N*^{2}-dicyanoethyl-*N*^{1},*N*^{2}-bis(furan-2-ylmethyl) benzene-1,2-diamine [L$_8$]

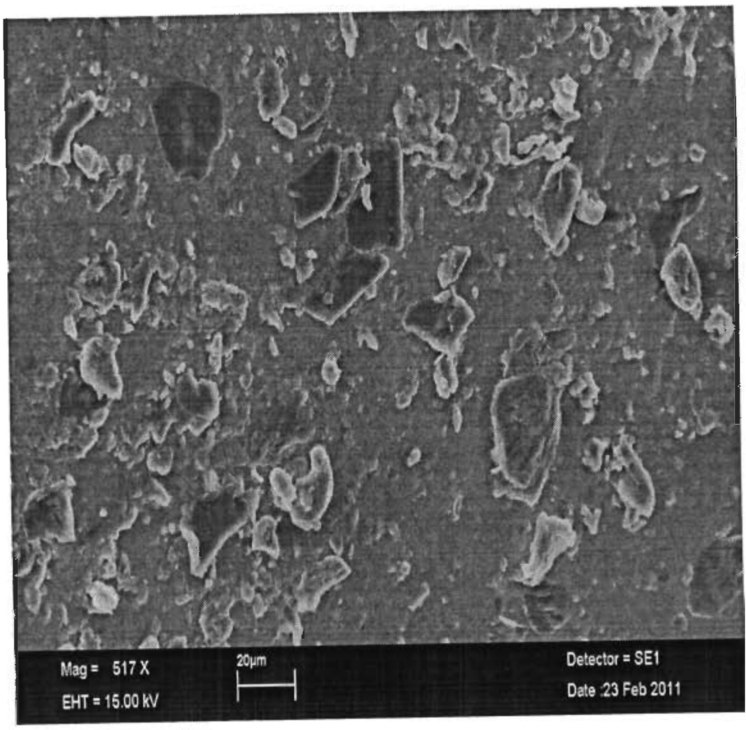


Figure 6.4: Scanning electron microscopy (SEM) image of the graphite electrode after immobilization

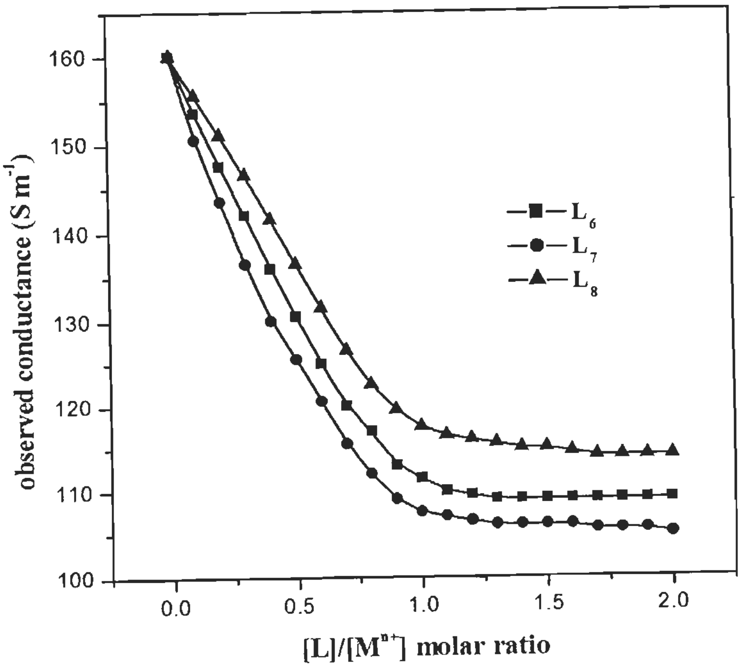


Figure 6.5: Variation in the Conductance of Cd^{2+} solution with the addition of ligands L_6, L_7 and L_8

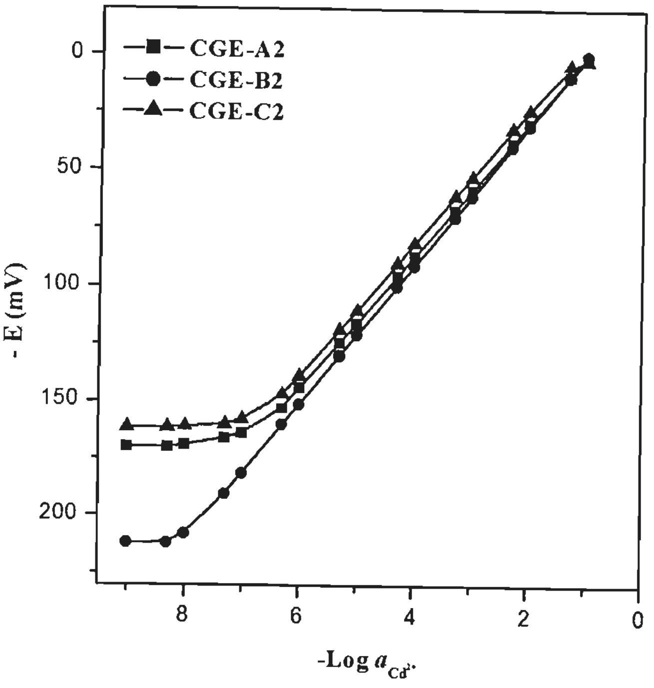


Figure 6.6: Calibration plot for Cd^{2+} selective coated graphite electrodes A2, B2 and C2

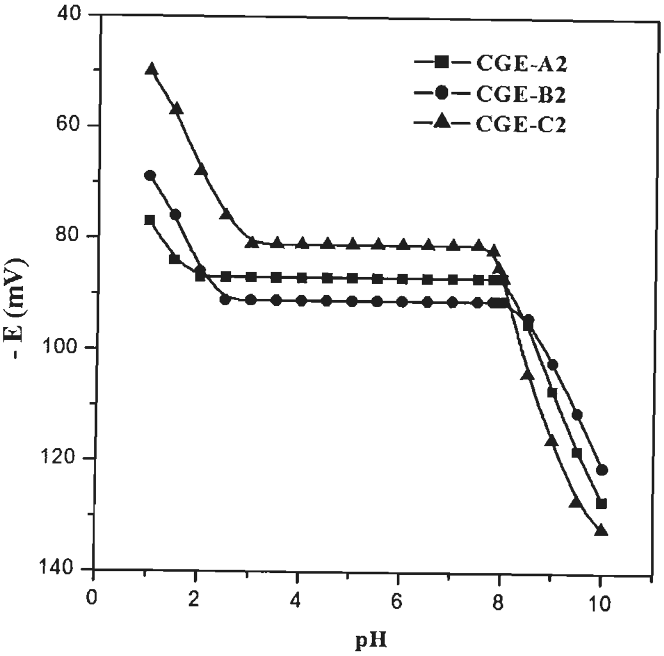


Figure 6.7: Effect of pH on the performance of CGE-A2, CGE-B2 and CGE-C2 at 1.0×10^{-4} mol L^{-1} $Cd(NO_3)_2$ solution

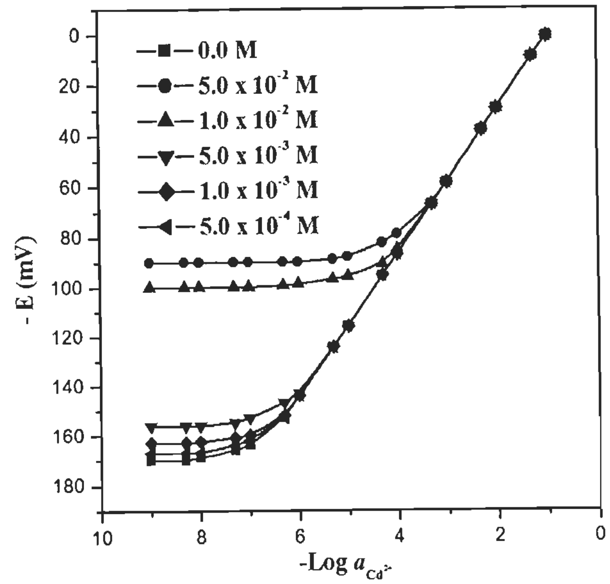


Figure 6.8: Effect of different concentrations (5.0×10^{-4}, 1.0×10^{-3}, 5.0×10^{-3}, 1.0×10^{-2}, 5.0×10^{-2} mol L^{-1}) of Hg^{2+} on the performance of CGE-A2

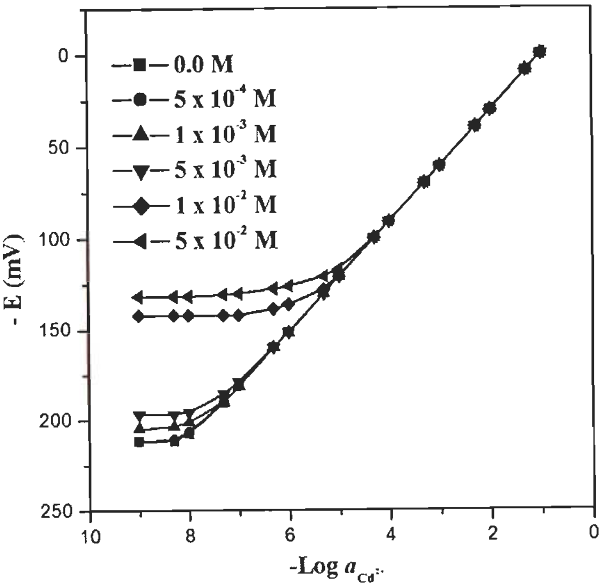


Figure 6.9: Effect of different concentrations (5.0×10^{-4}, 1.0×10^{-3}, 5.0×10^{-3}, 1.0×10^{-2}, 5.0×10^{-2} mol L^{-1}) of Hg^{2+} on the performance of CGE-B2

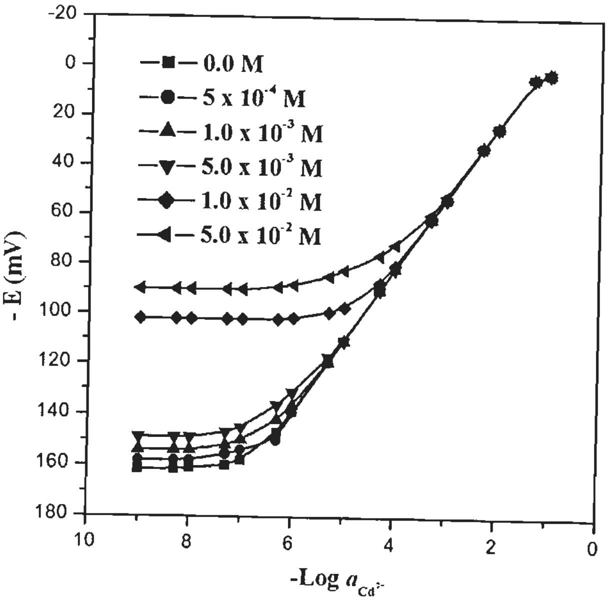


Figure 6.10: Effect of different concentrations (5.0×10^{-4}, 1.0×10^{-3}, 5.0×10^{-3}, 1.0×10^{-2}, 5.0×10^{-2} mol L^{-1}) of Hg^{2+}on the performance of CGE-C2

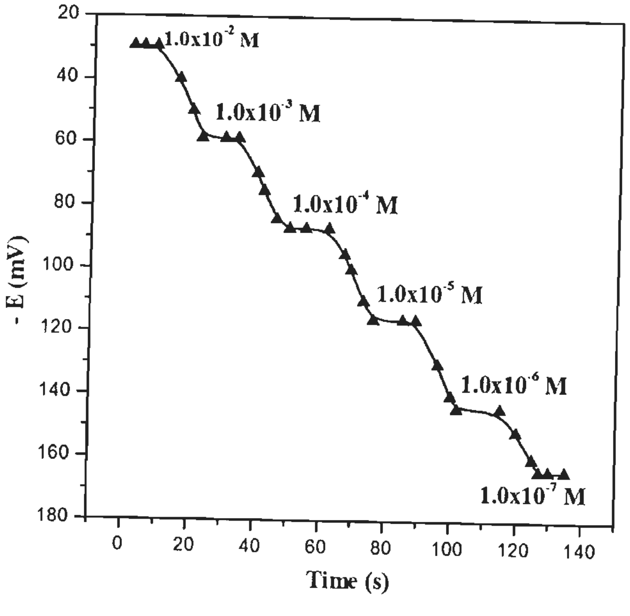


Figure 6.11: Determination of response time of CGE-A2 for ten-fold step change in Cd^{2+} ion concentration

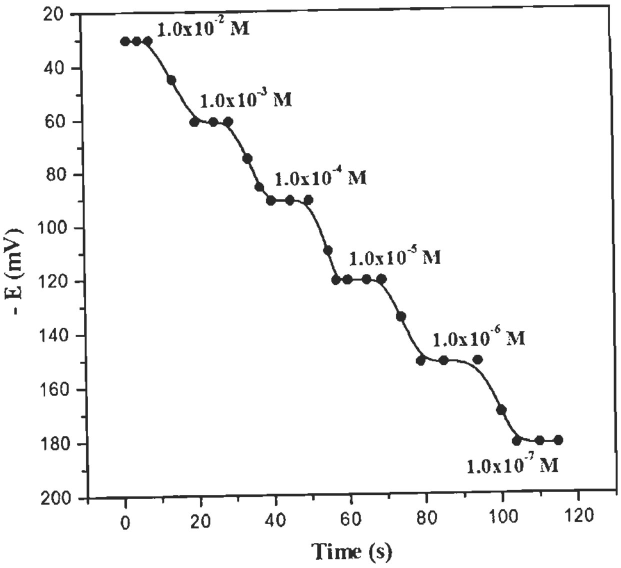


Figure 6.12: Determination of response time of CGE-B2 for ten-fold step change in Cd^{2+} ion concentration

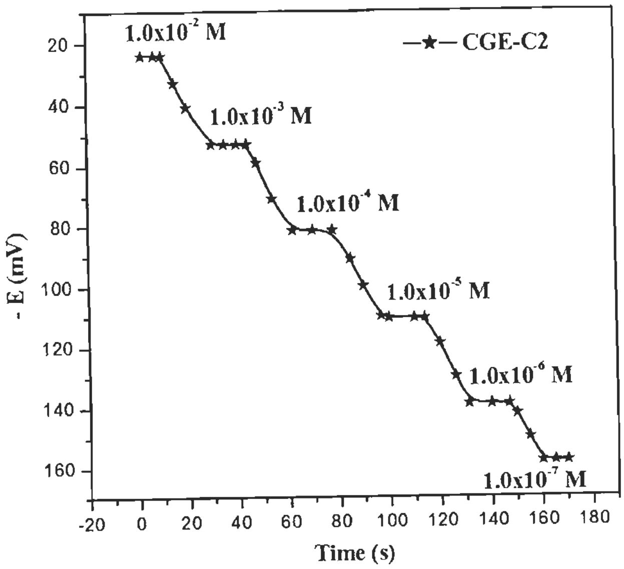


Figure 6.13: Determination of response time of CGE-C2 for ten-fold step change in Cd^{2+} ion concentration

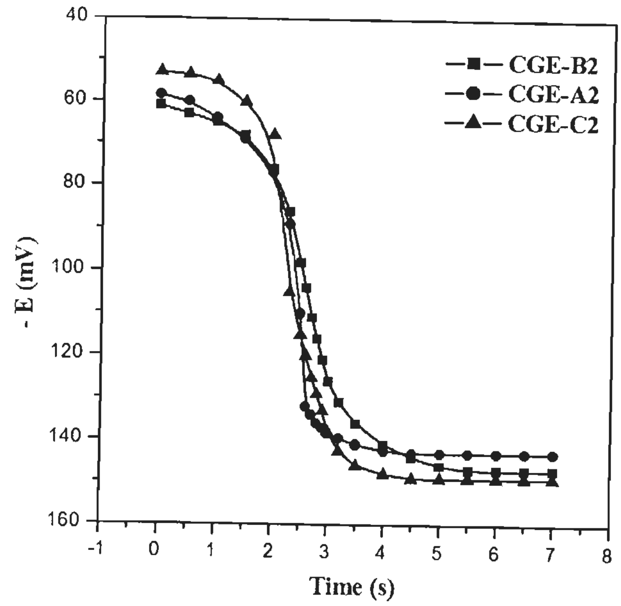


Figure 6.14: Potentiometric titration curve of CGE-A2, CGE-B2 and CGE-C2 for 25 mL of 1.0×10^{-3} mol L^{-1} Cd^{2+} ion against 1.0×10^{-2} mol L^{-1} EDTA at pH 5.5

References

1. Satarug, S., Baker, J., Urbenjapol, S., Haswell-Elkins, M., Reilly, P.E.B., Williams, D.J. and Moore, M.R., "A global perspective on cadmium pollution and toxicity in non-occupationally exposed population", *Toxicol. Lett.*, **137**, 65 (2003).
2. Li, Y., Jiang, Y., Yan, X.P., Peng, W.J. and Wu, Y.Y., "A flow injection on-line multiplexed sorption preconcentration procedure coupled with flame atomic absorption spectrometry for determination of trace lead in water, tea, and herb medicines", *Anal. Chem.*, **74**, 1075 (2002).
3. Ye, Q., Li, Y., Jiang, Y. and Yan, X., "Determination of trace cadmium in rice by flow injection on-line filterless precipitation-dissolution preconcentration coupled with flame atomic absorption spectrometry", *J. Agric. Food Chem.*, **51**, 2111 (2003).
4. Xu, Z.R., Pan, H.Y., Xu, S.K. and Fang, Z.L., "A sequential injection on-line column preconcentration system for determination of cadmium by electrothermal atomic absorption spectrometry", *Spectrochim. Acta B*, **55**, 213 (2000).
5. Tsalev, D.L., Lampugnani, L., Georgieva, R., Chakarova, K.K. and Petrov, I.I., "Electrothermal atomic absorption spectrometric determination of cadmium and lead with stabilized phosphate deposited on permanently modified platforms", *Talanta*, **58**, 331 (2002).
6. Dolan, S.P., Nortrup, D.A., Bolger, P.M. and Caper, S.G., "Analysis of dietary supliments for arsenic, cadmium, mercury, and lead using inductively coupled plasma mass spectrometry", *J. Agric. Food Chem.*, **51**, 1307 (2003).
7. Dias, L.F., Miranda, G.R., Saint'Pierre, T.D., Maia, S.M., Frescura, V.L.A. and Curtius, A.J., "Method development for the determination of cadmium, copper, lead, selenium and thallium in sediments by slurry sampling electrothermal vaporization inductively coupled plasma mass spectrometry and isotopic dilution calibration", *Spectrochim. Acta B*, **60**, 117 (2005).
8. Lu, Y.K., Sun, H.W., Yuan, C.G. and Yan, X.P., "Simultaneous determination of trace cadmium and arsenic in biological samples by hydride generation double channel atomic fluorescence spectrometry", *Anal. Chem.*, **74**, 1525 (2002).

9. Shams, E. and Torabi, R., "Determination of nanomolar concentrations of cadmium by anodic-stripping voltammetry at a carbon paste electrode modified with zirconium phosphated amorphous silica", *Sens. Actuators, B*, **117**, 86 (2006).

10. Ali, A., Shen, H. and Yin, X., "Simultaneous determination of trace amounts of nickel, copper and mercury by liquid chromatography coupled with flow-injection on-line derivatization and preconcentration", *Anal. Chim. Acta*, **369**, 215 (1998).

11. Hirata, H. and Date, K., "Cadmium and silver sulfide-impregnated silicone rubber membranes as selective electrodes for cadmium ions", *Bull. Chem. Soc. Jpn.*, **46**, 1468 (1973).

12. Mascini, M. and Liberti, A., "The preparation and analytical evaluation of a new heterogeneous membrane electrode for cadmium(II)", *Anal. Chim. Acta*, **64**, 63 (1973).

13. Linden, W.E. and Oostervink, R., "The formation and properties of mixed cadmium sulphide-silver sulphide and mixed mercury sulphide -silver sulphide membranes for electrodes selective to cadmium(II) and mercury(II)", *Anal. Chim. Acta*, **108**, 169 (1979).

14. Vlasov, Y.G., Ermolenko, Y.E. and Kolodnikov, V.V., "Cadmium-selective electrodes based on mixtures of cadmium and silver sulphides", *Zh. Anal. Khim.*, **36**, 889 (1981).

15. Ito, S., Asano, Y. and Wada, H., "Development of highly sensitive cadmium ion-selective electrodes by titration method and its application to cadmium ion determination in industrial waste water", *Talanta*, **44**, 697 (1997).

16. Vlasov, Y.G., Bychkov, E.A., Safarov, A.D., Antonov, P.P. and Miloshova, M.S., "Cadmium-selective chalcogenide glass electrodes", *Zh. Anal. Khim.*, **40**, 1438 (1985).

17. Vlasov, Y.G., Bychkov, E.A., Legin, A.V. and Miloshova, M.S., "Chalcogenide glass electrodes for lead, cadmium and iodine ions", *Zh. Anal. Khim.*, **45**, 1381 (1990).

18. Essi, M.M.M., "Characterization of cadmium (II) selective electrode based on chalcogenide glass", *Chalcogenide Lett.*, **8**, 341 (2011).

19. Vassilev, V., Radonova, M. and Boycheva, S., "Cd(II)-ion-selective electrode based on chalcogenide glasses", *J. Non-Crystalline Solids*, **355**, 2365 (2009).

20. Rejabushko, O.P., Pilipenko, A.T., Savin, Y.S. and Batkovskaya, L.A., "The complex compounds of quinoxaline-2,3-dithiol with cadmium as ion-active substances of membrane electrodes", *Ukr. Khim. Zh.*, **56**, 263 (1990).

21. Jain, A.K. and Singh, L.P., "A new polystyrene based heterogenous membrane of cerium(IV) vanadate as cadmium(II) ion-selective electrode", *Ind. J. Chem.*, **33** , 1122 (1994).

22. Ikram, S., Agarwal, H. and Gupta, A.P., "Studies on polystyrene based polyaniline-zirconium(IV) tungsto-phosphate membrane; Cd(II) selective electrode", *J. Saudi Chem. Soc.*, **6**, 107 (2002).

23. Srivastva, S.K., Gupta, V.K. and Jain, S., "A PVC-based benzo-15-crown-5 membrane sensor for cadmium", *Electroanalysis*, **8**, 938 (1996).

24. Gupta, V.K. and Kumar, P., "Cadmium(II)-selective sensors based on dibenzo-24-crown-8 in PVC matrix", *Anal. Chim. Acta*, **389**, 205 (1999).

25. Gupta, V.K., Kumar, P. and Mangla, R., "PVC based monoaza-18-crown-6 membrane potentiometric sensor for cadmium", *Electroanalysis*, **12**, 752 (2000).

26. Gupta, V.K., Chandra, S. and Mangla, R., "Dicyclohexano-18-crown-6 as active material in PVC matrix membrane for the fabrication of cadmium selective potentiometric sensor", *Electrochim. Acta*, **47**, 1579 (2002).

27. Gupta, V.K., Jain, A.K. and Kumar, P., "PVC-based membranes of dicyclohexano-24-crown-8 as Cd(II) selective sensor", *Electrochim. Acta*, **52**, 736 (2006).

28. Shamsipur, M. and Mashhadizadeh, M.H., "Cadmium ion-selective electrode based on tetrathia-12-crown-4", *Talanta*, **53**, 1065 (2001).

29. Panwar, A., Baniwal, S., Sharma, C.L. and Singh, A.K., "A polystyrene based membrane electrode for cadmium(II) ions", *Fresenius J. Anal. Chem.*, **368**, 768 (2000).

30. Singh, A.K., Saxena, P. and Singh, R., "New cadmium (II) selective electrode based on a tetraazacyclohexadeca macrocyclic ionophore", *Anal. Sci.*, **21**, 179 (2005).

31. Singh, A.K., Mehtab, S., Singh, U.P. and Aggarwal, V., "Comparative studies of tridentate sulfur and nitrogen-containing ligands as ionophores for construction of cadmium ion-selective membrane sensors", *Electroanalysis*, **19**, 1213 (2007).

32. Ion, A.C., Bakker, E. and Pretsch, E., "Potentiometric Cd^{2+} selective electrode with a detection limit in the low ppt range", *Anal. Chim. Acta*, **440**, 71 (2001).

33. Shamsipur, M., Dezaki, A.S., Akhond, M., Sharghi, H., Paziraee, Z. and Alizadeh, K., "Novel PVC-membrane potentiometric sensors based on a recently synthesized sulfur-containing macrocyclic diamide for Cd^{2+} ion. Application to flow-injection potentiometry", *J. Hazard. Mater.*, **172**, 566 (2009).

34. Khan, A.A. and Alam, M.M., "Synthesis, characterization and analytical applications of a new and novel organic-inorganic composite material as a cation exchanger and Cd(II) ion-selective membrane electrode: polyaniline Sn(IV)tungustoarsenate", *React. Funct. Polym.*, **55**, 277 (2003).

35. Khan, A.A. and Akhtar, T., "Synthesis, characterization and analytical application of nano-composite cation-exchange material, poly-o-toluidine Ce(IV) phosphate: Its application in making Cd(II) ion selective membrane electrode", *Solid State Sci.*, **13**, 559 (2011).

36. Khan, A.A. and Khan, A., "Ion-exchange studies on poly-o-anisidine Sn(IV) phosphate nano composite and its application as Cd(II) ion-sélective membrane electrode", *Cent. Eur. J. Chem.*, **8**, 396 (2010).

37. Nabi, S.A., Alam, Z. and Inamuddin., "A cadmium ion-selective membrane electrode based on strong acidic organic-inorganic composite cation-exchanger: polyaniline Ce(IV) molybdate", *Sens. Transducers J.*, **92**, 87 (2008).

38. Wardak, C., Marczewska, B. and Lenik, J., "An ion-selective electrode with a polymeric membrane containing an active chelating substance", *Desalination*, **163**, 69 (2004).

39. Wardak, C. and Marczewska, B., "Properties of cadmium ion-selective electrode containing chelating agent in polymeric membrane", *Chem. Anal.*, **49**, 497 (2004).

40. Gupta, V.K., Jain, A.K., Ludwig, R. and Maheshwari, G., "Electroanalytical studies on cadmium(II) selective potentiometric sensors based on t-butyl thiacalix[4]arene and thiacalix[4]arene in poly(vinyl chloride)", *Electrochim. Acta*, **53**, 2362 (2008).

41. Pal, M.K., Al Khayat M., Singh, A.K. and Gupta, V.K., "Nano level detection of Cd(II) using poly(vinyl chloride) based membranes of Schiff bases", *Anal. Chim. Acta*, **634**, 36 (2009).

42. Gupta, B., Gupta, V.K. and Singh, A.K., "Schiff bases as cadmium(II) selective ionophores in polymeric membrane electrodes", *Anal. Chim. Acta*, **583**, 340 (2007).

43. Mashhadizadeh, M.H., Sheikhshoaie, I. and Saeid-Nia, S., "Asymmetrical Schiff bases as carriers in PVC membrane electrodes for cadmium(II) ions", *Electroanalysis*, **17**, 648 (2005).

44. Javanbakht, M., Shabani-kia, A., Darvich, M.R., Ganjali, M.R. and Shamsipur, M., "Cadmium(II)-selective membrane electrode based on a synthesized tetrol compound", *Anal. Chim. Acta*, **408**, 75 (2000).

45. Rezaei, B., Meghdadi, S. and Zarandi, R.F., "A fast response cadmium-selective polymeric membrane electrode based on N,N′-(4-methyl-1,2-phenylene)diquinoline-2-carboxamide as a new neutral carrier", *J. Hazard. Mater.*, **153**, 179 (2008).

46. Stevens, A.C. and Freiser, H., "Coated-wire cadmium ion-selective electrode based on the bidentate neutral carrier 4,4′-di(5-nonyl)-2,2′-bipyridine", *Anal. Chim. Acta*, **248**, 315 (1991).

47. Zamani, H.A., Ganjali, M.R. and Adib, M., "Cd(II) PVC-based membrane sensor based on N'-[1-(2-furyl)methylidene]-2-furohydrazide", *Sens. Lett.*, **4**, 345 (2006).

48. Rezaei, B., Meghdadi, S. and Bagherpour, S., "Cadmium selective PVC-membranes sensor based on 1, 2-bis(quinoline-2-carboxamido)-4-chlorobenzene as a neutral carrier", *IEEE Sens. J.*, **8**, 1469 (2008).

49. Abbas, M.N. and Zahran, E., "Novel solid-state cadmium ion-selective electrodes based on its tetraiodo- and tetrabromo-ion pairs with cetylpyridinium", *J. Electroanal. Chem.*, **576**, 205 (2005).

50. Mohammadi, L., Shirzadmehr, A., Marjani, K., Khoshsafar, H., Chaloosi, M. and Abbastabar-Ahangar, H., "Ion-selective carbon paste electrode based on new tripodal ligand for determination of cadmium", *J. Incl. Phenom. Macrocycl. Chem.*, **63**, 287 (2009).

51. Singh, A.K., Mehtab, S., Singh, U.P. and Aggarwal, V., "Comparative studies of tridentate sulfur and nitrogen-containing ligands as ionophores for construction of cadmium ion-selective membrane sensors", *Electroanalysis*, **19**, 1213 (2007).

52. Bizerea-Spiridon, O., "Cd (II)-selective potentiometric sensor with multilayer solid membrane based on selenide and its applications", *J. Optoelectron. Adv. M.*, **12**, 2226 (2010).

53. Tyagi, S., Agarwal, H. and Ikram, S., "A polyvinylchloride based cadmium ion selective electrode using [$Mo_2(OAc)_2(H_2$-calix[4]arene)] as an electroactive material", *Water Sci. Tech.*, **62**, 2510 (2010).

54. 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 Cd(II) ion selective electrode", *Talanta*, **52**, 1087 (2000).

55. Mishra, D., Naskar, S., Butcher, R.J.and Chattopadhyay, S.K., "Ruthenium(II/III) mediated transformation of 1,2-bis(2'-pyridylmethyleneimino)benzene (L) to 2-(2'-benzimidazolyl)pyridine (L'H) and its in situ formed complexes with Ru(II): X-ray structure of *trans*-[$Ru(PPh_3)_2(L'H)_2](ClO_4)_2$", *Inorg. Chim. Acta*, **358**, 3115 (2005).

56. Karthikeyan, G. and Pitchaimani, P., "Synthesis, characterization and electrochemical studies of ruthenium(III) heterocyclic Schiff bases", *Trans. Met. Chem.*, **28**, 482 (2003).

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

58. Katsuta, S., Ito, Y., Kudo, Y. and Takeda, Y., "Stability and solvation of alkali metal ion complexes with dibenzo-30-crown-10", *Inorg. Chim. Acta*, **358**, 713 (2005).

59. Deep, K., Singh, K.P., Kansal, M.L. and Mohan, C., "A real coded genetic algorithm for solving integer and mixed integer optimization problems", *Appl. Math. Comput.*, **212**, 505 (2009).

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

61. Butts, W.C., Kuehneman, M. and Widdowson, G.M., "Automated method for determining serum thiocyanate to distinguish smokers from nonsmokers", *Clin. Chem.*, **20**, 1344 (1974).

62. Morf, W.E., Kahr, G. and Simon, W., "Reduction of the anion interference in neutral carrier liquid-membrane electrodes responsive to cations", *Anal. Lett.*, **7**, 9 (1974).

63. Li, G.X., Ma, L.X. and Huang, R.M., "Lead(II) ion-selective electrode based on polyaminoanthraquinone particles with intrinsic conductivity", *Talanta*, **78**, 498 (2009).

64. Bobacka, J., Ivaska, A. and Lewenstam, A., "Potentiometric ion sensors", *Chem. Rev.*, **108**, 329 (2008).

65. Rounaghi, G. and Kakhki, R.M., "Highly selective and sensitive coated-wire yttrium (III) cation selective electrode based on Kryptofix-22DD", *J. Electrochem. Soc.*, **158**, F121 (2011).

66. Abbaspour, A. and Izadyar, A., "Chromium(III) ion-selective electrode based on 4-dimethylaminoazobenzene", *Talanta*, **53**, 1009 (2001).

67. 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**, 127 (1976).

68. Oesch, U. and Simon, W., "Lifetime of neutral carrier based ion-selective liquid-membrane electrodes", *Anal. Chem.*, **52**, 692 (1980).

69. Maharia, R.S., Dutta, R.K., Acharya, R. and Reddy, A.V.R., "Heavy metal bioaccumulation in selected medicinal plants collected from Khetri copper mines and comparison with those collected from fertile soil in Haridwar, India", *J. Environ. Sci. Health, Part B*, **45**, 174 (2010).