Potentiometric Investigations on Cation-Selective Electrodes based on Macrocyclic and Acyclic Amides as Ionophores

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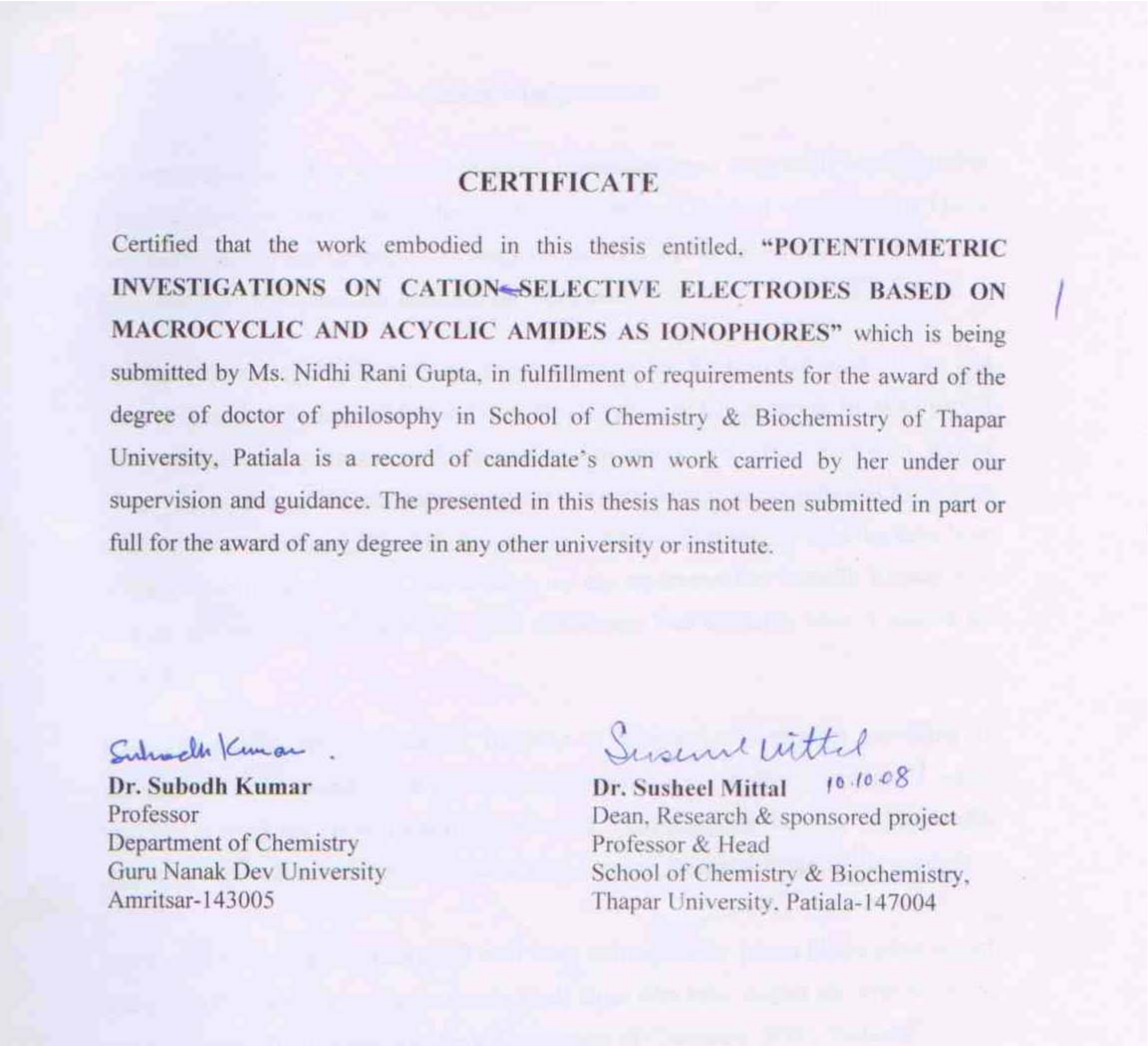

CERTIFICATE

Certified that the work embodied in this thesis entitled, **"POTENTIOMETRIC INVESTIGATIONS ON CATION-SELECTIVE ELECTRODES BASED ON MACROCYCLIC AND ACYCLIC AMIDES AS IONOPHORES"** which is being submitted by Ms. Nidhi Rani Gupta, in fulfillment of requirements for the award of the degree of doctor of philosophy in School of Chemistry & Biochemistry of Thapar University, Patiala is a record of candidate's own work carried by her under our supervision and guidance. The presented in this thesis has not been submitted in part or full for the award of any degree in any other university or institute.

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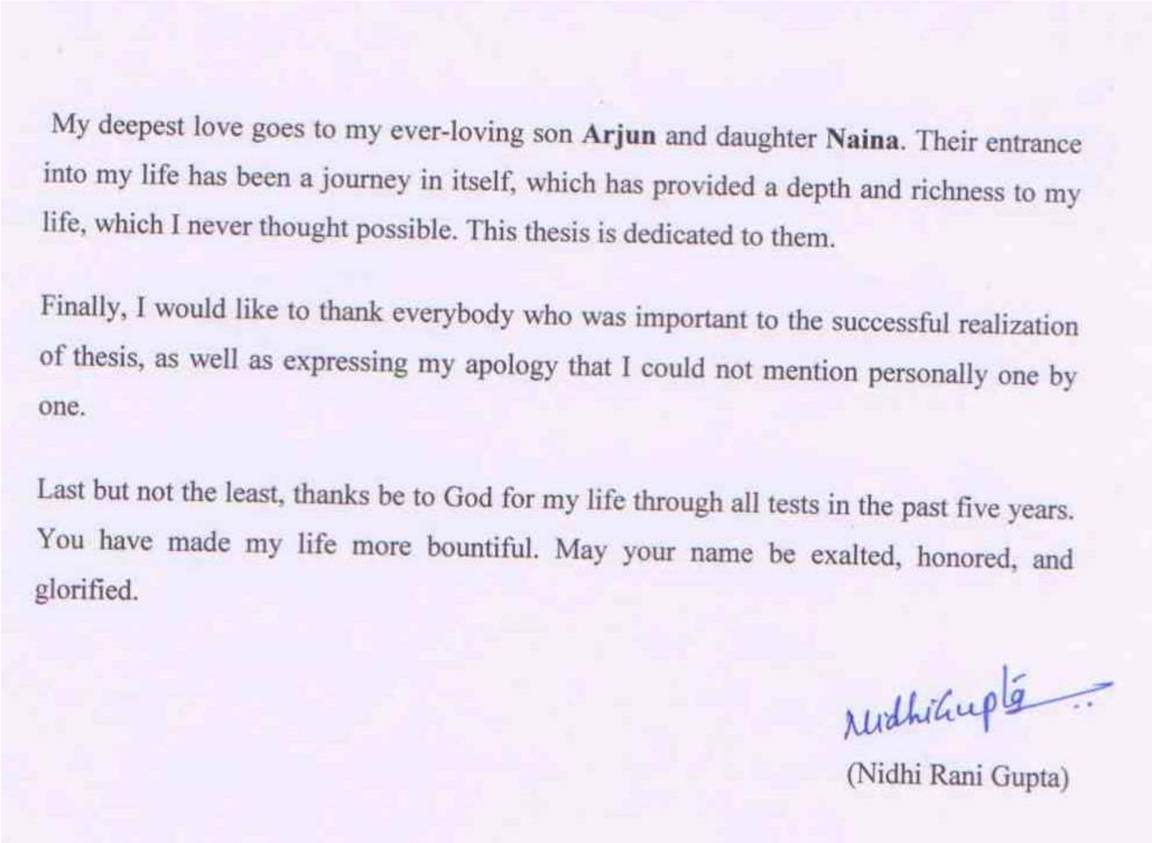

My deepest love goes to my ever-loving son **Arjun** and daughter **Naina**. Their entrance into my life has been a journey in itself, which has provided a depth and richness to my life, which I never thought possible. This thesis is dedicated to them.

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Nidhi Gupta

(Nidhi Rani Gupta)

Dedicated to
my ever loving children
Arjun & Naina

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Abbreviations

AAS	**:**Atomic Absoprtion Spectrophotometer
DBP	:Dibutylphthalate
DOP	:Dioctyl phthalate
DOS	:Bis(2-ethylhexyl)sebacate
EDTA	:Ethylene diamine teraacetic acid
FIM	:Fixed Interference Method
ISE	:Ion-Selective Electrode
KTpClPB	:Potassium tetrakis(4-chlorophenyl)borate
MPM	:Matched Potential Method
NaTPB	:Sodium tetrapheylborate
o-NOPE	:Ortho-nitrophenyl octyl ether
PVC	:Poly(vinyl chloride)
THF	:Tetrahydrofuran

Chapter –1

Introduction

Ion-selective electrodes have been the subject of rapidly increasing interest to analytical chemists over the past few decades and their development has provided new direction to the research in Analytical Chemistry. The speed at which this field has developed is a measure of the degree to which electrodes and probes meet requirements of an average analyst for rapid, accurate and inexpensive analysis. The design and synthesis of receptors with target selectivity has enabled the easy availability of materials for sensors and the ease in making devices and the low cost of equipment has further given impetus to this area. Because of their binding properties for various measured ions, ion-selective electrodes are used as important tools for environmental protection. In many frequently performed analyses electrodes and the probes are replacing the existing techniques. The term ion-selective electrode is taken to mean an electrode having an ion chelating substance or supramolecule, which is present in a membrane media, either liquid or solid membrane. Spectacular progress in the last two to three decades, including the development of ultra-microelectrodes (Edmonds et al., 1985), the design of the tailored interfaces (Murray et al., 1989) and molecular monolayers, the coupling of biological components (Diamond et al., 1998) and electrochemical transducers (Leclerc, 2001), synthesis of ionophores and receptors containing cavities of molecular size, development of voltammetry techniques of high-resolution scanning probe microscopes (Nagaka et al., 1993) and the micro fabrication of molecular devices have led to a substantial increase in the popularity of electroanalysis and to its expansion into new phases and environments. Hence, electroanalytical techniques and probes are receiving major attention in the development of chemical sensors (Adams et al., 1969).

1.1 Electroanalytical Techniques

Electroanalytical techniques are concerned with the interplay between electricity and chemistry, namely, the measurements of electrical quantities such as current, potential charge and their relationship to chemical parameters. Such use of electrical measurements for analytical purposes have found vast range of applications, including environmental monitoring, industrial quality control or biomedical analysis.

Electroanalytical methods are very useful for the characterization and determination of important parameters, like stability constant, formation constant and mobility of the coordination complexes (Martel et al., 1989). Such methods were mainly used for the consideration of structures of ligands or the coordination complexes. The most commonly used techniques for characterization insisted of either cyclic voltammetry or conductance measurement. Although potentiometry was used to some extent, unfortunately, this technique was not employed for the quantitative analysis with neutral carriers. However, with the discovery of ion selective electrodes this gap was filled.

Electrochemical sensors are the largest and oldest group of chemical sensors (Pungor et al. 1969, Rechnitz et al. 1966, Ross 1967). Many members of this have reached commercial maturity while many are still in various stages of development. They are developed by their mode of measurements into potentiometric (measurement of voltage), amperometric (measurement of current) and conductometric (measurement of conductivity) sensors. Potentiometry is of great practical importance, is a zero current technique in which the information about the sample composition is obtained from the measurement of potential established across a membrane material, possessing different ion recognition processes and have been developed to impart high selectivity. Electrochemical processes take place at the electrode solution interface. The distinction between various electrodes and analytical techniques reflects the type of electrical signal used for the quantification. The two principal types of electroanalytical measurements are potentiometric and potentiostatic measurements. Both type of measurements require at least two electrodes (Conductance) and a contacting sample (Electrolyte solution), which constitutes the electrochemical cells. The electrode surface is thus a junction between an ionic conductor and an electronic conductor. One of the two electrodes responds to the target analyte(s) and is thus termed the reference electrode, is of constant potential (i.e., independent of the properties of the solution). The resulting potentiometric probes have thus been widely used for several decades for direct monitoring of ionic species, like cations viz., alkali, alkaline earth and transition metal ions and anions viz., F, Cl^-, Br^-, I^-, CN^- etc.

1.2 Ion-Selective Electrodes

Ion-selective electrodes are well-established analytical tools, routinely used for the measurement of a wide variety of different ions selectively and directly in complex biological and environmental samples (Greenwood et al., 1984). More than 50 ISEs are commercially available and widely used (although many more have been reported in the literature). Firms such as Thermo, Corning, Beckmann, Metrohm, Radiometer produce such types of electrodes. Recent research activity has led to exciting advances in the area of ISEs, including dramatic lowering of their detection limits, identification of new ionophore systems or new membrane responding to important polyionic species (e.g., heparin) or to neutral species (such as surfactants). Depending on the nature of the membrane material used to impart the desired selectivity, ISEs can be divided mainly into these three groups:

1. Glass electrodes
2. Liquid-membrane electrodes
3. Solid-membrane electrodes

Our work is mainly focused on the liquid-membrane based ISE

1.3 Liquid-Membrane Electrodes

Liquid membrane type ion-selective electrodes based on water immiscible liquid substances impregnated in polymeric membrane are widely used for direct potentiometric measurements (Bakker et al., 1997, Bühlman et al., 1998, Harris, 1995, Skoog et al., 1997, Gadzekpo et al 1984, Linder 1988). Such ISEs are particularly important because they permit direct measurement of several mono- and polyvalent cations as well as anions (Morf, 1981, Umezawa, 1990, 1963 and 1967). Membranes are commonly prepared by dissolving the recognition element, a plasticizer (which provides properties of ligand phase) and the PVC in a solvent such as terahydrofurane (THF) Moody et al. 1988. Slow evaporation of the solvent leaves a flexible membrane of ~50-200 μm thickness, which can be cut and mounted on an electrode body. The polymeric membrane separates the test solution from the inner compartment containing a standard solution of the primary ion. Active (recognition) component in the membrane can be an ion exchanger or a neutral carrier. The selective extraction of target ion at the sample-membrane interface creates the electrochemical phase boundary potential (Morf, 1981). Selectivity coefficient or ion the discriminating ability depends not only on the nature of the recognition element including the membrane solvent, but also on the nature and content of the plasticizer. The PVC matrix provides mechanical strength and permits diffusion of analytes to the recognition site. Hydrophobic nature of the membrane prevents leaching of the membrane component in to the aqueous phase and thus extends the operational lifetime.

There are two kinds of ionophores generally used in the preparation of liquid membranes, the first one is based on charged ionophores, which are usually termed as liquid ion exchangers and another one is a neutral carrier. Table-1 shows some early reports on these categories.

TableT_1: Some Common Ion-Exchangers and Neutral Carrier Based Electrodes

Ion	Type of membrane	Electroactive material	Solvent medium
U(VI)	Solid PVC	Di(2-ethyl) phosphoric acid (Meera et al., 2002)	Diamylamyl phosphate
K^+	Solid PVC	Valinomycin (Andy et al., 1999)	Dioctyl adipate
NH_4^+	Liquid membrane	Nonactin (Ghauri, et al., 1994)	Tris(2-ethylhexyl) phosphate
Ca^{2+}	Solid PVC	ETH 1001 (Iwona et al., 2002)	*ortho*-nitrophenyloctyl ether

From 1980 onwards much efforts have been devoted to the isolation or synthesis of compounds containing cavities of molecule-sized dimensions. Such use of chemical recognition principle has made an enormous impact on the wide spread acceptance of ISEs. For example, most blood electrolyte determinations are currently being performed with ionophore based sensors, either with centralized clinical analyzer or with decentralized disposable units.

1.4 Host Guest Chemistry

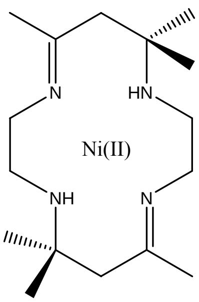
Neutral carriers can be neutral macrocyclic / acyclic molecules or they are macrocyclic and acyclic compounds containing donor atoms (N, O and S) either in the form of cyclic polyethers, thioethers, mixed ethers, amides, amines, imines, oximes, esters, etc. capable of enveloping various target ions in to their pocket. Electron donor atoms present in the polar host cavity further facilitate and influence the interaction with the target ion (Izatt et al. 1995, Stoddart, 1988). The interaction is purely reversible among them. Such binding event creates the phase boundary potential at the membrane-sample interface. To ensure the reversible binding it is essential to keep the free energy of activation of the analyte-ionophore reaction sufficiently small. Molecular modeling techniques are being used to guide the design of ionophores towards target analytes.

The pioneer work of Pederson (Pedersen, 1957 and 1988) on macrocyclic polyethers or crown ethers was chiefly concerned with oxygen containing ring system and produced a series of powerful complexing agent for alkali and alkaline earth cations. Pederson noted that the cyclic polyether called 18-crown-6 formed remarkably tight complexes with simple cations like K^+. The original observations of Pederson were brilliantly supported by other workers most notably Cram and Lehn (Lehn, 1995, 1988, 1980, Cram, 1988) and these three shared the 1987 Nobel Prize in chemistry for this work. “Host-Guest chemistry” was born with the crown ethers serving as a molecular host to the cationic guest.

Molecular recognition with the large ion-dipole components certainly gives some interesting solution to this concept. It is not surprising that one ether oxygen should interact favorably with K^+. The lone pair on oxygen or alternatively, the dipole associated with a C-O-C unit, will have a significant electrostatic attraction to a cation. The same forces are involved when a simple salt dissolves in water. What then is special about crown ethers? Consider the interaction of K^+ with the single molecule of water, the oxygen of which is similar to the oxygen of crown ether. High-pressure mass spectrometric studies established that the binding interaction is enthalpically favorable, with $\Delta H° = -18$ Kcal/mol in the gas phase. However, there is a significant entropy change for freezing out the motions of two particles, so that $\Delta S°$ is considerably negative (in this case = -22 eu). The net effect is that $\Delta G°$ is only –11.5 Kcal/mol, perhaps not as favorable. With each addition of water, $\Delta H°$ becomes strongly less favorable but the $\Delta S°$

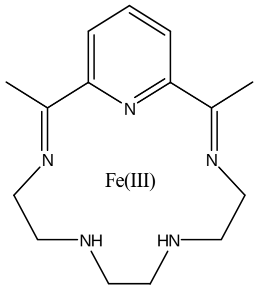
effect persists for each step. To get six ether or water oxygens around the K^+, one has to freeze out the motions of seven particles -A severe entropic effect, $K^+ + H_2O$ ---> K^+H_2O Now, consider the complexation of K^+ by 18-crown-6. These are six favorable oxygen-potassium ion interactions, but now these have to restrict the movement of two molecules. The ΔH° component has not changed substantially, while ΔS° clearly has, and hence ΔG° will be more favorable. As is always true in thermodynamics you cannot get something for nothing, then the entropy effect has to be occurring somewhere. It is occurred during the synthesis of 18-crown-6 (It is difficult to close the macrocyclic ring) instead of during the complexation process. As a result, ΔG° for the complexation is much more favorable. This is a general theme, in which the synthesis of artificial receptors involves steps that pay the entropy requirement for preorganizing a binding site, thereby making complexation more favorable. This concept made rapid development in the synthesis of neutral macrocyclic ligands capable of complexing metal ions and organic ions has stimulated research efforts in many fields of chemistry.

Development of macrocyclic chemistry in the 1960s particularly is the development of macrocyclic ligands for metal cations. Four systems of fundamental importance may be identified, prepared by the groups of Curtis et al. 1961, Busch et al. 1964, Juger et al. 1969 and Pedersen, 1967, three of which used the Schiff's base condensation reaction of an aldehyde with an amine to give an imine. Conceptually, those systems may be seen as a development of the natural macrocycles (ionophores, hemes, phthalocyanins etc.). To these may be added the work of Donald Cram (Cram, 1988) on cyclophanes (Cram, 1978) and more recently on spherands and carcerands (Lehn, 1995, 1988), the tremendous contribution by Lehn who prepared cryptands in the late 1960s and has since gone on to shape many of the recent developments in this field.



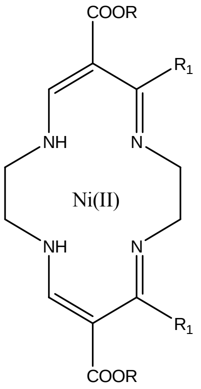
(1.1)

(Curtis 1961)



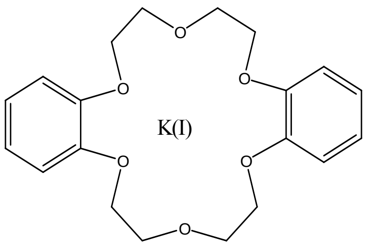
(1.2)

(Busch 1964)



(1.3)

(Jagar 1964)



(1.4)

(Pederson 1967)

1.5 Supramolecular Interactions

Supramolecular chemistry concerns monovalent bonding interactions (attractive and repulsive forces). When considering a supramolecular system it is vital to consider the interplay of all these interactions and effects relating both to the host guest as well as their surroundings (e.g., solution, crystal lattice, gas phase etc.) The major energetic contribution, which enables the formation of cation-liquid complex, is the electrostatic interactions between cation and binding sites of the ligand. As far as hard cations and ligands carrying predominantly oxygen donor atoms are concerned, the driving force to the form complex is primarily the charge-charge, charge-dipole, and/or charge-induced dipole interaction.

- Ion-ion interactions (100-350 KJ/mol)
- Ion-dipole interactions (50-200 KJ/mol)
- Dipole-dipole interactions (5-50 KJ/mol)
- Hydrogen bonding (4-120 KJ/mol)
- Cation-π interactions (5-80 KJ/mol)

- π- π stacking (0-50 KJ/mol)
- Van der Waals forces (<5 KJ/mol)

However, this is no longer realistic for the interaction between soft cations and ligands with soft donor atom(s). Typical combinations of this kind include transition or heavy metal ions with ligand carrying nitrogen or sulphur donors. Such cation/ligand combinations result in highly covalent rather than electrostatic interaction giving rise to chelate compounds. It is therefore important to discriminate the complexation behavior of the nitrogen or sulphur ligands with transition or heavy metal ions from that of the oxygen ligands.

In this context, the cation-ligand interaction may be classified as Type-I, II and IV complexes (Inoue,1990), but usually the combination of hard cation with soft donor, Type III, does not appear to from a stable complex. One might suppose that there must be intermediate or border line cases especially when the ligand possesses mixed donor atoms. However, those appear to exist a critical number of soft atoms in a ligand molecule, above which the ligand behaves as a soft ligand towards soft cations.

In addition to hard acids and hard base concept, a successful host exhibits a strong affinity for one particular guest and a much lower affinity (as measured by the binding constant) for other cations. The complex formation usually proceeds by binding of cations caused by electrostatic ion-dipole interaction between cations and negatively charged donor atoms arranged regularly in the ring. Designing of synthetic host, which will be highly selective for a given cation, is a very complicated task because the selectivity is governed by an enormous number of factors, some of the most important of which are listed below:

- The number and type of donor atoms available (more numbers give better stability)

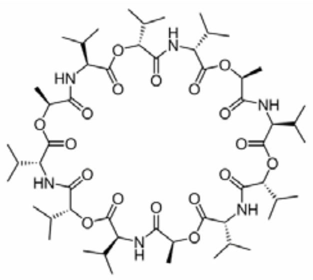
- Arrangement of donor atoms in the chelation periphery (Symmetrical arrangement gives more stability)
- Degree of host preorganisation
- Nature of the counter-anion and its interactions with solvent and the cation
- Electrostatic charge of cation (of utmost importance in stabilizing)
- Solvent (polarity, hydrogen bonding and coordinating ability)
- Nature of the counter anion and its interaction with solvent and the cation
- Basicity of donor atom
- Chelate ring size

Solvation and preorganisation also play a very important part as well as more subtle effects such as chelate ring size (Hancock 1992). Amongst these, the size match is an important and readily envisaged factor, but it is not necessarily dominant. The thermodynamic factors associated with cation complexation affinity are usually summed up in an overall binding constant *(K),* which essentially represents the equilibrium constant for the complexation reaction. Thus, selectivity may be expressed in terms of the ratio of one binding constant to another.

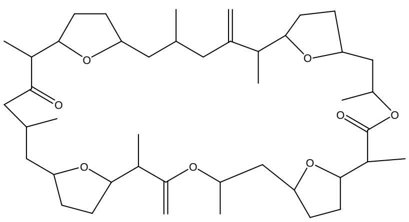
This precise description of supramolecular sciences is one of the most vigorous and fast-growing fields of chemical endeavor. Its interdisciplinary nature has brought, wide-ranging collaborations between physicists, theorists and computational modelers, crystallographers, inorganic and solid-state chemists, synthetic organic chemists, biochemists and biologists. Experimental behavior of these chemical-building blocks i.e., supramolecules, in terms of hosts and their complexes with guests, has increased enthusiasm in this area.

1.6 Ionophores

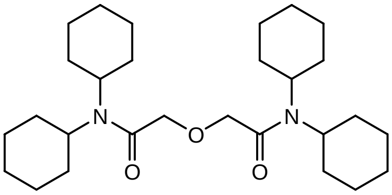
Structurally, receptors / hosts / ligands / electroactive substances for the charged species have lipophilic skeleton embedded with varied functional moieties, like ether, amine, thioethers, amide, ester, phenol, carboxylic acid, etc. functional groups. Ionophores based on their structural features have been classified into different categories viz; the acyclic and multiligating and multiarmed molecules (Podands), monocyclic molecules with O, N, S, etc. and their combinations as ligating sites (Coronands), Coronands with one or more appendages which can participate in binding with the guest (Lariats), bicyclic and polycyclic heteromacrocycles with three dimensional cavities (Cryptands) and monocyclic receptors with spherical cavities (Spherands). The common thing in all these compounds is that they act like a host for a metal ion and encapsulate the ion just like a ball is catched up in hands. The chemistry of such complexation is called as "host-guest" chemistry (Vogtle et. al., 1981). An ionophore acts like a host to receive a guest, like metals to form complexes called "host-guest" compounds.



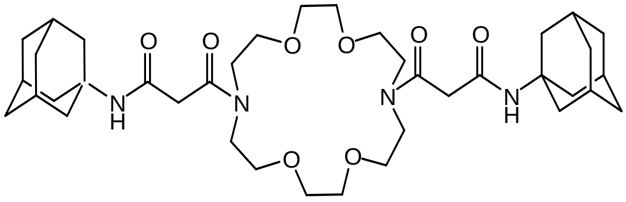
K^+ (Valinomycin)



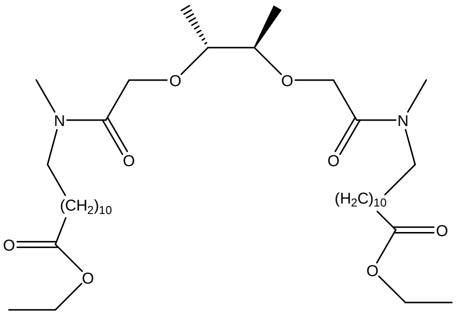
NH_4^+ (Nonactin)



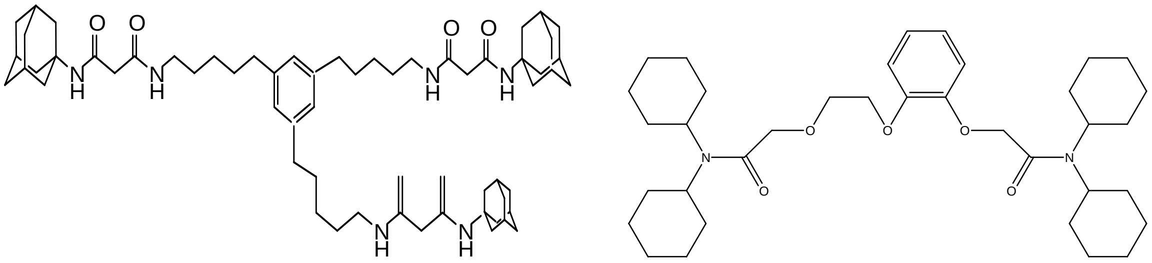
Ca^{2+} (ETH 129)



Mg^{2+} (K22B5)



Ca^{2+} (ETH 1001)



Mg^{2+} (ETH 5596) Ba^{2+} (ETH 231)

Figure 1.F$_1$: Some important reported structures of amide based ionophores for different metal ions

1.7 Structural Importance of Amide Based Ionophores

The neutrally structured nitrogen donor is wide-spread in ligands used in co-ordination chemistry. This is partly because it provides a synthetically convenient point of attachment for three other chelating groups. However, the neutral nitrogen donor displays stronger coordinating properties with many metal ions than it does the neutral oxygen donor, and it is of interest to examine coordinating properties of the neutral nitrogen donor in the form of amide, amine, imine and mixed neutral donor atoms in the macrocycle.

Nitrogen donors are not limited to sp^3-hybridized amines and vast number of macrocyclic ligands based upon imine or pyridine donors have been prepared and studied (Gooding et. al., 2001, Hassan et. al., 2005). Ligands may be neutral, anionic or cationic (less commonly). Anionic ligands may result from deprotonation of NH or other acidic groups and include the fully conjugated systems. These nitrogen macrocycles exhibit a similar coordination behavior to their open chain analogues and form complexes, which often resemble but are significantly more stable than familiar compounds with amines, imines or pyridine donors.

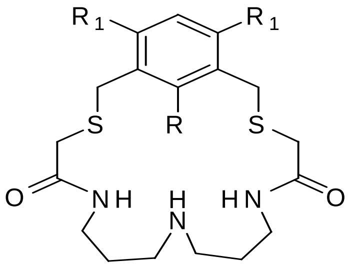
Macrocyclic ligands containing two or more different types of donor atoms are widely used. These ligands have the advantage of combining two or more different bonding preferences allowing new types of selectivity in metal ion binding. Numerous different combinations of donor atoms have been reported (Shamsipur et al., 1999, 2002, 2006). Indeed, mixed N, S-donor compounds tend to have considerable affinity for transition and most often heavy metal ions. Many types of neutral carriers e.g., cyclic amides, acyclic amides, bicyclic amide derivatives have been reported (Kumar et al., 1996 and 1998, Casnati 2001). Most of these are characterized by ether oxygen and amide groups as the binding sites in the compounds (Kim et al., 2003 and 2005, Chen et al., 2006). Nature quite generously uses the amide linkage (peptide bond) as the ligating site alongwith –S (cystine), -N (serine), -COOH (aspertate), etc. as ligating units. Amongst all these functionalities, amides have attained special status due to:

a. Highly polarized neutral oxygen of amide due to resonance of lone pair of amide nitrogen with the carbonyl group
b. The high rotation barrier around C-N bond (in amides C-N bond has ~ 40% double bond character)
c. Multiple coordinating nature

In addition to all these features, due to its rigid structure and negligible solubility in water and the existence of nitrogen atoms in the cavity, the macrocyclic / acyclic diamides seemed to be potential carrier for the soft transition and heavy metal ions in the PVC membrane electrode.

1.8 Research Problem

Over the years, a large number of amides were investigated (Kataky et al., 1993, James et al., 1993, Hisamoto et al., 1994, Yang et al., 1998, Alina et al., 2001, Qin et al., 2000, Casnati et al., 2001, Kim et al., 2003 and 2005). Variation in backbone connecting the two-amide groups and the substituents on the amide nitrogen leads to design and synthesis of new functionalized macrocyclic ligands for specific analytical applications, which is a subject of continuous interest in recent times (Shamsipur et al., 1999, 2002 and 2004). Following ionophores (Fig 1.F_2 - Fig 1.F_9) have been used for the fabrication of electrodes for metal ions. Also, nitrogen donors in the form of amines, imines, some newly synthesized and some commercially available molecules were chosen to fabricate electrodes for some transition metal ions.



L1 - L3

L1 R = R_1 = H
L2 R = R_1 = Me
L3 R = OMe, R_1 = H

Figure 1.F_2: Macrocycles possessing thioether – amide – amine combinations

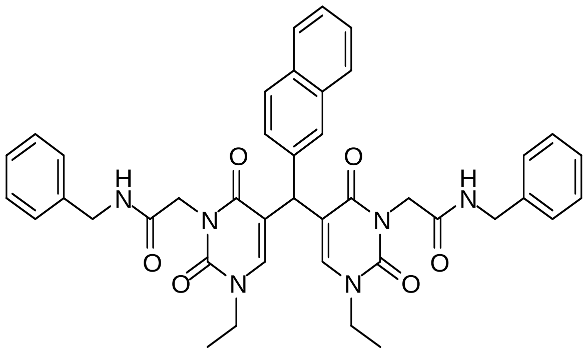


Figure 1.F_3: Uracil based acyclic amide ionophore

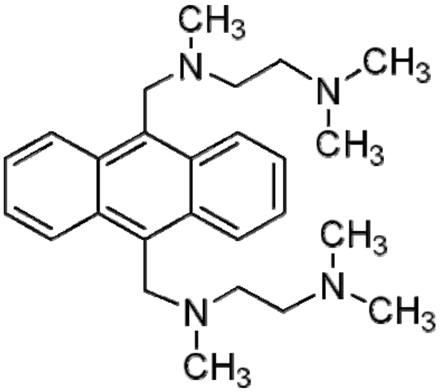


Figure1.F$_4$: N,N'-bis(2-dimethylamino ethyl)-N,N dimethyl 9,10-anthracene dimethanamine [Bis(TMEDA) anthracene]

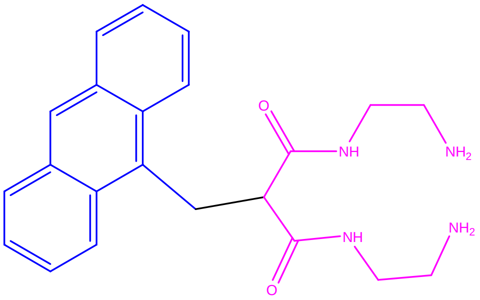


Figure 1.F$_5$: N,N'-bis(2-aminoethyl)-9-anthrylmethylmalonamide

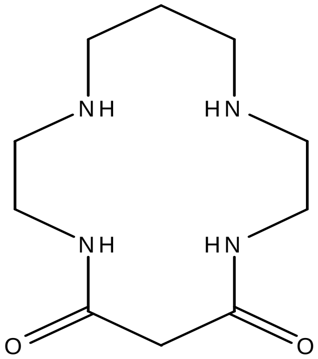


Figure 1.F$_6$: 1,4,8,11 tetraazacyclotetra decane-5,7-dione

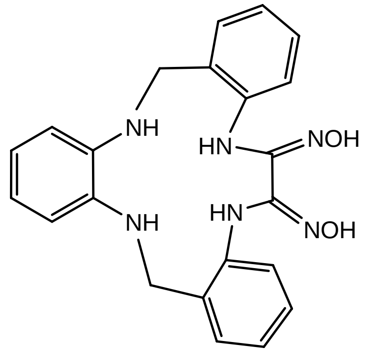


Figure1.F$_7$: Macrocycles possessing N_4 combinations

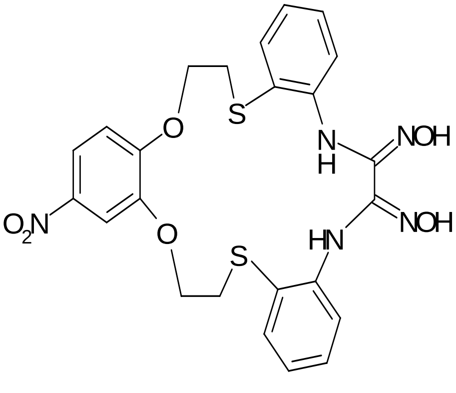


Figure 1.F$_8$: Macrocycles possessing $N_2S_2O_2$ combinations

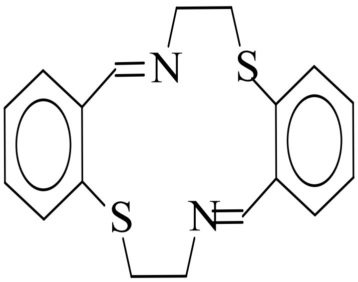


Figure1.F$_9$: Macrocycles possessing imine and thioether combinations

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Chapter –2

Literature Survey

Electroanalytical chemistry has a long history of development for quantitative analytical methods that are based upon the electrical properties of the solution of the analyte when it is made part of an electrochemical cell. Three types of electroanalytical procedures are encountered. First involves establishing the relationship between analyte concentration and such electrical quantities as current, potential, conductance, capacitance or charge. The second one involves the same electrical measurements and serves to establish the end point in a titration of the analyte. In the third, an electrical current converts the analyte to a form that can be measured gravimetrically or volumetrically. Regardless of type, the intelligent application of an electroanalytical method requires an understanding of the basic theory and practical aspects of the operation of electrochemical cells. Today, studies of single ion transfer energetics and kinetics at interfaces of insoluble ionic crystalline, mobile and fixed site plasticized polymer and immiscible liquid electrolytes are leading part of physical and electroanalytical chemistry research (Buck et al., 2001).

Synthetic membranes can be tailored to choose and transport ions with a selected charge sign or a particular ion among others of the same charge. Discoveries such as these have led to exciting opportunities for theory and experiment, including the synthesis of neutral and charged ion carriers or ionophores. Faradic ionic process membranes have also explored themselves to the development of ion-selective electrodes. This chapter is devoted largely on reported acyclic and cyclic molecules as mobile sites, ion-selective sensor materials that with appropriate mediator solvents provide improved sensor cocktails.

2.1 History of Sensing Material

Syntheses of novel organic ligands permit the quantitative analysis by complexation of elements with these ligands at trace concentrations. Although a large number of organic ligands were synthesized and characterized, unfortunately very few of them were used for the quantitative analysis of either cations or anions. The antibiotic nigercin was isolated in 1951 as the first representative natural ionophore. Natural ionophores are known to specifically transport biological guest species across a bio-membrane e.g., valinomycin transports K^+ ions with much greater efficiency than Na^+ ions, where monensin selectively transports Na^+ ions against the concentration gradient. Their molecular structure, cation binding, transport properties, physiological activities and other biochemical actions have been extensively investigated and their molecular recognition and transport functions are important topics of current chemistry.

Ionophores are organic molecules that form a specific complex with metal cations and certain hydrophilic organic cations rendering them lipophilic and providing a mean for their transport across polar barriers. They have large hydrocarbon backbone incorporating functional groups with electron donating ability. They have various molecular skeletons, donor atoms, chain lengths and ligand anologies, a distinction made between the acyclic podands, the macrocyclic crown ether and the armed macrocycles. Ionophores can be classified on the basis of structural features into three categories: neutral ionophores, charged ionophores, and channel-forming ionophores.

Neutral ionophores are those compounds, which don’t contain any ionizable groups and form complexes with metal ions due to ion-dipole interactions. The water of solvation about the cation is replaced by oxygens (six carbonyl ester oxygens in valinomycin) of the ionophore in a concerted reaction. The resulting complex assumes the charge of the cation. When the complex encounters a hydrophilic environment (e.g., at the other side of the membrane), decomplexation occurs as the reverse reaction of complexation. Among the ionophores included in this group are valinomycin, macrotetralide, nactins, synthetic polyethers and certain cyclic polypeptides.

Charged ionophores are open-chain compounds that have oxygen-containing heterocyclic aromatic rings incorporated in their structure with a terminal-charged head group and a tail capable of participating in hydrogen bonding. These molecules also contain additional functional groups for cation complexation, including ether, carbonyl, and hydroxyl moieties. The carboxylic acid group must be ionized for ionophoric activities. In the protonated form, the ionophore conducts hydrogen ions across apolar barriers. Complexation with cations requires ionophore cyclization involving head-to-tail interaction through hydrogen bonding. The cyclic structures are stabilized by the rigidity of the heterocyclic rings. In most cases, ion-pair formation appears to account for initiation of complexation followed by cyclization of the ionophore. In some instances, however, electrostatic interaction of the metal ion with the carobxylate anion does not appear to contribute to complexation. Structures of complexes are such that there is an internal compensation of the charge.

Channel forming ionophores differ from other ionophores in that way that they only complex with metal ions in the presence of a membrane. This class of ionophores is most notably represented by the gramicidins. These molecules dimerize in the lipid membrane to form a channel 25-30 Å long and about 4 Å in diameter, which act as ion-conducting channel through the membrane. The interior of these channels is lined with a series of oxygen-containing functionalities that form an electron-rich field that stabilizes cations.

The most important property of crown ethers is their selective complexing ability. They bind cations in their cavity through ion-dipole interactions between cation and donor atoms in a ring structure. Such selectivity depends upon cation size–cavity and size-relationship, number of donor atoms in crown ring, etc. The selective formation of a molecular complex with one of the analyte amongst a number of them is called molecular recognition (Pedersen 1987).

Moore et al., 1964 discovered that the antiobiotic valinomycin induces ion-selective effects in metabolic studies in liver mitochondria, and the uncoupling activity of valinomycin was measured with the polarograph in terms of the release of respiratory control of an acceptor-free rat liver mitochondrial system. Stimulation of respiration by it was dependent on K^+, and increased with increasing K^+ concentration Rb^+ and Cs^+ can be substituted for K^+ but not with Na^+ and Li^+. In 1967, Pedersen discovered cation-complexing macrocyclic polyethers (33 cyclic polyethers) derived from aromatic vicinal diols and containing from 9 to 60 atoms including 3 to 20 oxygen atoms in the ring. Many of those containing 5 to 10 oxygen atoms form stable complexes with some or all of the cations of: Li^+, Na^+, NH_4^+, RNH_3^+, K^+, Rb^+, Cs^+, Ag^+, Au^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Cd^{2+}, Hg^{2+}, Hg^{2+}, La^{3+}, Tl^+, Ce^{3+}, and Pb^{2+}. Many of these complexes can be isolated in the crystalline form depending on the anion. Pioda et al., 1969 reported a K^+-selective electrode based on valinomycin in diphenyl ether of the liquid exchanger type. The selectivity of potassium is 5000 times higher than that of sodium ion. This electrode has shown an excellent tool for investigating biological phenomena involving changes in potassium activity in the presence of a larger concentration of sodium ions. In 1969, Eisenman et al. introduced a theory of membrane potentials and conductances of neutral carrier membranes.

The key ingredient of a carrier based PVC membrane is the incorporated carrier that defines the selectivity of electrode via selective complexation formation with the cation of interest. Though charged ionophores have been successfully used for the construction of an ion-selective electrode but due to the electrical neutrality, lipophilic character capability to selectively and reversible bind metal ions, the amide/N containing (amine/imine) based ionophores have been extensively used in the construction of PVC based ion-selective electrodes. Some of the important reports are discussed critically on the basis of type of metal ions. Literature survey on ionophore based ion-selective electrodes covering the discussions on response mechanism, selectivity, detection limits, measuring range and lifetime was done and the important observations are given below.

2.2 Ionophore Based ISEs for Some Alkali Metal Ions

Zhukov et al., 1981 reported a lithium ion-selective electrode based on the lipophilic N,N,N',N',-tetraisobutylcyclohexane-cis-l,2-dicarboxylicdiamide. Selectivity coefficient values for lithium ions over other alkali and alkaline earth metal cations were greater than 100 and 1000, respectively. Shanzer et al, 1983 described the design, preparation, and properties of a new series of lipophilic lithium ion carriers. The structure of these carriers is based on an acyclic system in which a hexafunctional lipophilic envelope is formed around the metal ion in an octahedral arrangement. Sugihara et al., 1986 described a lithium-selective electrode based on non-cyclic polyether diamide carriers. Selectivity coefficients for lithium over sodium were up to 2.1 x 10^1, over potassium up to 1.4 x 10^2 and over alkaline-earth metals up to 1.5 x 10^2 M. The detection limit for lithium was 5.0 x 10^{-5} M.

Borowitz, 1989 described the syntheses of several bis-(1,2-phenylenedioxydiscetamides) with eight binding sites (four ethers, four amides). It had been anticipated that these bis-compounds would be much stronger binders for Group IIA cations. Kataky et al., 1993 did a comparative study of tripodal oxa-amides and oxa-esters as ionophores in potentiometric ion-selective electrodes for alkali and alkaline earth cations. The effects of the nature of the plasticiser bis(butylpentyl)adipate (BBPA) vs. o-nitrophenyl octyl ether (o-NPOE), the structure of the ionophore, the pH and the ionic strength of the analyte solution on the electrode response were studied. From this study it was observed that the oxa-amides gave a superior performance (slope, limits of detection) than the oxa-esters. Suzuki et al., 1993 obtained new lithium-selective ionophores by introducing a bulky “block” subunit into the ethano-bridge section of the base crown ring of dichlorophenyl amide ionophores. This modification in the structure could effectively prevent the formation of a 2:1 or 3:1 sandwich type complex consisting of the crown ether and cations larger than Li^+. Saleh, 1994 has reported a pyrimidine based neutral carrier as a rubidium ion-selective electrode.

Sugihara et al., 1996 found that 2,9-dibutyl-1,10-phenanthroline is an excellent Li^+-sensing agents for ISEs. 1,6-Bis(9-butyl-1,10-phenanthrolin-2-yl)hexane, which is one of the bridged bisphenanthrolines, exhibits high selectivity toward Li^+ among alkali and alkaline earth metal ions in a liquid membrane system. A variety of double-armed crown ethers were prepared by Tsukube et al., 1997, in which amine, amide, ester, nitrile and pyridine moieties were attached as cation-ligating side arms to diaza-12-crown-4 ring. Studies revealed that most of them exhibited Li^+ cation selectivity, though corresponding single armed lariat ethers showed Na^+ cation selectivity. Among them, amine-armed diaza-12-crown-4 derivative offered the highest Li^+ ion-selective ionophoric property. Structural aspects of ligand molecules acting as neutral ionophores in ion-selective membrane electrodes were discussed and examples of Li-selective ionophores were presented by Bocheska in 1998. The electrodes contaning o-NPOE and DBP as plasticizer gave good performance in terms of slope, limits of detection, etc., to lithium and sodium ions. The electrode plasticized with o-NPOE also exhibited near-Nernstian response to divalent ions, Ca^{2+}, Sr^{2+} and Ba^{2+}. Fouskaki et al., 2002 reported a picolinamide residue-based hydrogen-selective ISEs. Results show that the membrane composition can be adjusted for the measurement of pH at very low pH values (down to pH -0.5) and up to at least pH 10.

Choi et al., 2006 synthesized macrocyclic ionophores with four amide carbonyl ligands and investigated as lithium ion-selective electrodes. Xian et al., 1996 reported lithium ion-selective electrode based on several kinds of synthesized oligomethylene bridged bis-

1,10-phenanthroline derivatives as neutral carriers. The effects of different plasticizers and lipophilic salts on the electrode performance are discussed. The electrode with the optimal membrane composition showed a selectivity coefficient (logKij) value for sodium ions of -3.2 (1700 times more selective to lithium ion over sodium ion). Sudeshna et al., 2006 reported the synthesis of 1-methyl-1-vinyl-14-crown-5 (III) and described its PVC-based membranes selective for Na^+ ions. The response of the electrode was linear with a Nernstian slope of 55.0 mV/decade a concentration range of 3.16×10^{-6} to 1.0×10^{-1} M and a detection limit of 2.81×10^{-6} M, workable pH range of 6.5–9.5. Grady et al., 1996 has reported the performance of sodium selective electrodes based on triethylacetate and trimethylacetate monoacid derivatives of p-tert-butylcalix[4]arene. All electrodes exhibited slopes in excess of 50 mV dec^{-1} (53.5-56 mV dec^{-1}) and lifetimes of at least 35 days.

A potassium-selective silicone-rubber membrane electrode based on a neutral carrier was repoted by Pick et al., 1973. Le Blanc et al., 1976, reported potassium-selective electrodes incorporating potassium valinomycin tetraphenylborate salt in a polymeric matrix. Guggi et al., 1977 reported a barium-selective liquid membrane electrode based on a neutral carrier N,N,N',N' tetraphenyl-3,6,9-trioxaundecane diamide in a poly(vinylchloride) matrix. The sensor discriminates against alkali and alkaline earth metal cations by factors in the range of approximately 10^2-10^3 and 30-10^5, respectively. The electrode has shown an excellent emf stability (the drift is less than 0.8 mV/decade) and an operational lifetime of more than two years**.** Kim et al., 2003 (b) described a series of 1,3-alternate calix[4]aza crown ethers for which the monoaza and unsymmetrical crowned-azacrown with different side arms were examined as an ionophore for ion-selective polymeric membrane electrodes toward potassium ions. Among them, the electrode based on calix[4]crown-5-azacrown-5 with a phenyl group exhibited near Nernstian response for K^+ ions over a wide concentration range (1×10^{-5} to 1×10^{-1} M) with a limit of detection of 2×10^{-6} M.

Bereczki et al., 2006 reported novel 1,3-alternate thiacalix[4]mono- and biscrown-6 ethers as ionophores in poly(vinyl chloride) membrane electrodes. Among the ionophores, 1,3-alternate thiacalix[4] mono(crown-6) ether showed, especially high selectivity for cesium over other alkali-metal ions. Transition and heavy metal ions did not interfere seriously with the electrode response, which indicates that the bridging sulfur atoms do not take part in the ion recognition process. Peper et al., 2005 reported a Cs^+-selective electrode based on by doping ethylene glycol-functionalized cross-linked polystyrene microspheres (P-EG) into a plasticized poly(vinyl chloride) (PVC) matrix containing sodium tetrakis-[3,5-bis(trifluoromethyl)phenyl] borate (TFPB) as the ion exchanger. ISEs containing P-EG and TFPB that were plasticized with 2-nitrophenyl octyl ether (o-NPOE) yielded a linear range from 10^{-1} to 10^{-5} M Cs^+, a slope of 55.4 mV/decade, and a lower detection limit (log C) of -5.3.

Choi et al., 2004 described four thiacalix[4]biscrown ethers with 1,3-alternate conformation for the potentiometric response in poly(vinyl chloride) membrane electrodes for Cs^+. The electode exhibits near Nernstian slope of 57.6 mV per decade in the concentration range of 1.0×10^{-6} - 3.2×10^{-2} M, workable in a wide range of pH 2.5-12.5 and had a fast response time of 5 seconds. Mahajan et al., 2002 reported a cesium ion-selective PVC membrane electrode employing calix[4]crown ether–ester as an ionophore. The electrode exhibits a good response for cesium ions over a wide concentration range of 5.0×10^{-6}-1.0×10^{-1} M with a Nernstian slope of 59 mV per decade. The detection limit of the electrode is 5.0×10^{-6} M. Chen et al., 2001 (a) described two novel double flexible spacers brideged biscalix[4]arenas; 25,25',27,27'-bis(1,3-dioxypropane)-bis(5,11,17,23-p-tert-tetrabutylcalix[4]arene-26,28-diol) and 25,25',27,27'-bis(1,4-dioxybutane)-bis(5,11,17,23-p-tert-tetrabutylcalix[4]arene-26,28-diol) were used as cesium ion-selective ionophores in polymeric membrane electrodes.

The electrodes exhibited a good response of 51 mV per decade for Cs^+ in the concentration range from 1 x 10^{-5} to 1 x 10^{-1} M and good selectivity.

Oh et al., 2000 studied tetraesters of calix[6] arene and calix[6]diquinone as cesium ion-selective ionophores in poly(vinyl chloride) membrane electrodes. For an ion-selective electrode based on calix[6]arene tetraester, a linear response was reported in the Cs^+ concentration range 1 x 10^{-6}-1 x 10^{-1} M. Selectivity coefficients for cesium ions over alkali, alkaline earth and ammonium ions were determined. The detection limit (log aCs^+=-6.31) and the selectivity coefficient (log $k_{Cs+,Rb+}$pot=-1.88) were also observed magnesium-selective electrodes based on macrocycles 4,11-dimethyl-2,4,9,11-tetraethyl-1,5,8,12-tetraaza cyclotetradeca-1,8-diene (I) and 4,11-dioxa-2,9-dimethyl-1,5,8,12-tetraaza cyclotetradeca-1,8-diene (II) were prepared and investigated by Baniwal et al., 1999. The best performance was observed having the composition (II)–PVC–STB–DBP in the ratio 2:10:1:7, which works well over a wide concentration range from $1.9x10^{-6}$ to $1.0x10^{-1}$ M with a Nernstian slope of 29 mV per decade of activity between pH 2.5 and 6.5. These electrodes show a fast response time of 15 s and could be used over a period of 3 months with good reproducibility. Selectivity coefficient values indicate excellent selectivity for Mg^{2+} over a large number of cations, but an interference of anions such as Cl^- and SO_4^{2-} was also observed. The electrodes have also been used successfully in partially non-aqueous medium and as an indicator electrode in the potentiometric titration of Mg^{2+} with EDTA.

2.3 Ionophore Based ISEs for Some Alkaline Earth Metal Ions

Calcium-selective electrodes based on calcium tetra(4-chlorophenyl)borate complexes of macrocyclic polyether diamides were described by Petranek et al., 1981. Electrodes based on these complexes showed K_{ij} for calcium over barium up to 10^3, and over alkali metals up to $3x10^4$. Preparation and properties of neutral diamide ionophores for group

IIA metal cations have been described by Borowitz et al., 1984. Selectivity ratios of over 100:1 for Na^+ vs. Ca^{2+} were found for several piperidenyl amides of 1,2-phenylenedioxydiacetic acid. Incorporation of N-methylamino instead of ether oxygen groups into the basic structure gives a stronger cation binder selective for Group IIA cations. Kimura et al., 1984, reported calcium-selective electrodes based on bicyclic polyether amide derivatives showing excellent selectivity coefficients for Ca^{2+} relative to H^+, Na^+, K^+, and Mg^{2+}. Bogatsky et al., 1984 reported selectivity coefficients for liquid membranes containing 27 macrocyclic lactones and lactone-lactams with respect to alkali and alkaline-earth metal ions. It is shown that the introduction of amide and ester groups into cyclic polyethers modified the cation selectivity over a wide range. The results indicated the possibility of obtaining various highly selective membrane electrodes based on these neutral macroheterocyclic compounds.

A new Ca^{2+} ion-selective electrode based on a Nafion membrane modified by means of the new ionic carrier N-ethyl-N-(2-trimethylammoniumethyl) -N′-heptyl-N′-methyl-succinamide is described by Rondininia et al., 1995. This electrode had shown acceptable selectivity towards alkaline-metal cations, a nearly equal response to Mg^{2+} ion (which makes it suitable for water hardness determinations) and an extremely long lifetime. Another diamides having a base diazacrown ether ring with two diamide-type side chains, were designed and synthesized for Ca^{2+} and Mg^{2+} ions (Suzuki et al., 1995). These electrodes were prepared with over 20 kinds of systematically synthesized diazacrown ether derivatives. The electrodes based on the 21- and 18-membered diazacrown ether derivatives possessing a glycolic diamide and malonic diamide in their side chains exhibited excellent Ca^{2+} and Mg^{2+} selectivities, respectively. Raban et al., 1994 described mobile, ether-amide as calcium ionophore and less effective complexation was demonstrated for magnesium and potassium ions. The complexing ability of a range of 19 symmetrical, unsymmetrical and bridged calix[4]arene derivatives having ester, ketone, amide, amine and thioether functionalities were determined by the picrate extraction method (O'Connor et al., 1994). On incorporating these calix[4]arene derivatives as neutral carrier ionophores in sodium-selective poly (vinyl chloride) membrane electrodes the performance was assessed on the basis of the sensitivity and selectivity over the alkali, alkaline earth metals and hydrogen and ammonium ions. The temperature dependence, response time and lifetimes were also determined and observed well.

A Ca^{2+}-selective electrode derived from calix[4]arene-diamide was developed by Kim et al., 2003 (a). The pH-sensitive chromogenic behavior of the compound suggests that the compound can be used as a sensitive pH indicator around pH 6.5. Strontium ion-selective electrodes were developed by Qian et al., 1998, using three lipophilic diamides containing pyridine ring as ionophores. The Sr^{2+}-selective electrode based on N,N,N′,N′-tetracyclohexyl-2,6-pyridine-bis(methyleneoxy acetamide) as neutral carrier, potassium tetrakis(p-chlorophenyl)borate (KTpClPB) as additive, and o-nitrophenyloctyl ether (o-NPOE) as plasticizing solvent exhibited excellent properties with a Nernstian slope of 29 mV/decade and a linear range of 2×10^{-5} to 1×10^{-2} M at 25°C. Shamsipur et al., 1999 (a) synthesized eight different macrocyclic diamides and incorporated them as strontium ion carriers in PVC- membrane electrodes. The electrodes exhibited Nernstian response for Sr^{2+} ions over a wide concentration range of 1.0×10^{-1} - 3.2×10^{-5} M with a detection limit of 8.0×10^{-6} M. The response time of the sensor is ~10 s, and the membrane can be used for more than three months without observing any deviation. Some monopodal and oligopodal Mg^{2+}-selective ionophores were characterized by their selectivity coefficients in plasticized poly(vinyl chloride) (PVC) membranes for Mg^{2+} ion by Zhang et al., 2000.

Casnati et al., 2001 reported synthesis, complexation, and extraction properties of new efficient calixarene amide ionophores for the selective removal of strontium ions from nuclear waste. High efficiency and high divalent/monovalent selectivity were found in metal ion extraction experiments for the new octamide ligands. Yan, 2002 synthesized, a tripodal compound, 1,1,1-tris(N-ethyl-N-phenylamino-carboxylmethoxymethyl) propane which has been evaluated as an ionophore in a PVC-membrane electrode for the analysis of alkali and alkaline earth metal cations. Another strontium(II)-selective electrode based on a macrocyclic tetraamide named 5,7,12,14-dibenzo-2,3,9,10-tetraoxa-1,4,8,11-tetraazacyclotetradecane was fabricated and investigated by Singh et al., 2006 (a). The best performance was exhibited by the membrane having composition 8: 200: 4: 120 (I: o-NPOE: NaTPB: PVC). The electrode exhibited a Nernstian response for strontium ions over a wide concentration range $3.98x10^{-6}$ to $1.0x10^{-1}$ M with a slope of 29.0 ± 0.1 mV/decade of concentration and a detection limit of 2.82×10^{-6} M. The observed response time and lifetime was of less than 10 s and 3 months, respectively. Zamani et al., 2008 used 2-[(2-mercaptophenylimino)methyl]phenol (MPMP) as an ionophore in the construction of a PVC-based membrane sensor for Sr^{2+} ions. The best performance was obtained with a membrane composition of 30% poly(vinyl chloride), 62% nitrobenzene (NB), 5.5% MPMP and 2.5% sodium tetraphenyl borate (NaTBP). The proposed sensor exhibits a Nernstian behavior (with a slope of 29.6 ± 0.3 mV per decade) for the concentration range of ($1.0x10^{-6}$–$1.0x10^{-1}$ M) with a detection limit of $5.5x10^{-7}$ M. It illustrates a relatively fast response time in the whole concentration range (<10 s) and it can be used for at least 10 weeks in a pH range of 2.8–9.6.

2.4 Ionophore Based ISEs for Some Transition Metal Ions

Singh et al., 2007(a) reported chromium chelates of Schiff bases, N-(acetoacetanilide)-1,2-diaminoethane (L1) and N,N′-bis(acetoacetanilide)-triethylenetetraammine (L2), as neutral ionophores. The best performance was obtained for the membrane sensor having a composition of L1: PVC: DBP: NaTPB in the ratio 5: 150: 250: 3 (w/w). The sensor exhibits Nernstian response in the concentration range $8.9 \text{ x } 10^{-8}$ to $1.0 \text{ x } 10^{-1}$ M Cr^{3+} with a limit of detection 5.6×10^{-8} M. Zamani et al., 2006 reported a poly vinyl chloride membrane sensor for Cr^{3+} ions based on 4-amino-3-hydrazino-6-methyl-1,2,4-triazin-5-one (AHMTO) as a membrane carrier. The sensor has a linear dynamic range of $1.0x10^{-6}$

to $1.0x10^{-1}$ M, with a Nernstian slope of 19.7 ± 0.3 mV $decade^{-1}$, and a detection limit of 5.8×10^{-7}M and could be used in a pH range of 2.7–6.6. Gupta et al., 2006 (a) reported Tri-o-thymotide (I) as an electroactive material. The optimum ratio 5: 1: 75: 100 (w/w) exhibits a working concentration range of 4.0 x 10^{-6} to 1.0 x 10^{-1} M with a Nernstian slope of 20.0 ± 0.1 mV/decade of activity in the pH range of 2.8–5.1. The detection limit of this sensor is 2.0 x 10^{-7} M. The electrode exhibits a fast response time of 15 s. Gholivand et al., 2003(a) discussed poly(vinyl chloride) membrane based on glyoxal bis(2-hydroxyanil) as membrane carrier prepared and investigated as a Cr^{3+}-selective electrode. The electrode has a linear dynamic range of 3.0 x 10^{-6}–1.0 x 10^{-2} M, with a Nernstian slope of 19.8 mV per decade and a detection limit of 6.3 x 10^{-7} M. Abbaspour et al., 2001 reported a PVC-based membrane of 4-dimethylaminoazobenzene with a Nernstian potentiometric response (with slope of 19.5±0.6 mV/decade) for Cr^{3+} over a wide concentration range (1.66 x 10^{-6}–1.0 x 10^{-2} M). The potential of this electrode is independent of pH in the range of 3.0–5.5. It has a fast response time of about 10 s and was used for a period of 3 months with good reproducibility. The detection limits of this membrane electrode was 8 x 10^{-7} M. Lu et al., 2002 prepared a lead ion-selective electrode based on a calixarene derivative containing carboxyphenyl azo groups. The electrode gave good Nernstian responses of 29.4 mV per decade for lead in the activity range 10^{-6}–10^{-2} M. The limit of detection reached $10^{-6.1}$ M. Three recently synthesized Schiff's bases were studied to characterize their ability as Cr^{3+} ion carrier in PVC-membrane electrodes (Shamsipur et al.**,** 2005(a)). The polymeric membrane (PME) and coated glassy carbon (CGCE) electrodes based on 2-hydroxybenzaldehyde-O,O-(1,2-dioxetane-1,2-diyl) oxime (L1) exhibited Nernstian responses for Cr^{3+} ion over wide concentration ranges (1.5 x 10^{-6}-8.0 x 10^{-3} M for PME and 4.0 x 10^{-7}-3.0 x 10^{-3} M for CGCE) and very low limits of detection (1.0 x 10^{-6} M for PME and 2.0 x 10^{-7} M for CGCE). The potentiometric responses of the electrodes are independent of pH of the test solution in the pH range 3.0-6.0. The electrodes were successfully applied to determine chromium(III) in water samples.

Ekmekci et al., 2007 reported a membrane electrode selective to Fe^{3+}. The electrode consisted of trans-dinitro-dibenzo-18-crown -6 ether as a neutral carrier. An analytically useful potential change occurs in the $1x10^{-6}$ to $1x10^{-1}$ M concentration range. The slope of linear portion ($1x10^{-4}$ to 10^{-1} M) is 57.4 mV/10-fold concentration changes in Fe^{3+}. Sil et al., 2005 described the determination of Fe^{3+} by ion-selective potentiometry using a coated-wire ion-selective electrode (CWISE) based on iron–cyclam complex. Linear Nernstian response for this electrode was obtained over the total Fe^{3+} concentration range of $1x10^{-6}$ to $1x10^{-2}$ M. Working pH range of the electrode was found to be 1.3–3.5. Selectivity coefficients of some mono- and divalent metal ions were determined. Mashhadizadeh et al., 2004 reported a membrane based potentiometric sensor that is highly selective to Fe^{3+} ions and was prepared by using 2-[(2-hydroxy-1-propenyl-buta-1,3-dienylimino)-methyl]-4-p-tolylazo-phenol [HPDTP] as a suitable carrier. The electrode exhibits a linear response for Fe^{3+} ions over a wide concentration range ($3.5x10^{-6}$ to $4.0x10^{-2}$ M) with a super Nernstian slope of 28.5 (±0.5) per decade. The electrode can be used in the pH range from 4.5 to 6.5.

Singh et al., 2007 (b) reported membrane electrode for trace level determination of Co^{2+} ions based on 5-amino-3-methylisothiazole as an ionophore. The electrode exhibits a Nernstian slope of 29.5 ± 0.2 mV/decade in a linear range of $1.0x10^{-1}$ to $6.3x10^{-7}$ M for Co^{2+} ions. The detection limit of this electrode is $3.9x10^{-7}$ M. It has a fast response time of 12 s and can be used for a period of 4 months without any divergence in potentials. Gupta et al., 2006 (b) reported a membrane electrode for Co^{2+} based on N,N′-bis(salicylidene)-3,4-diaminotoluene as a neutral carrier. The electrode exhibits a linear potential response in the concentration range of $7.9x10^{-8}$ to $1.0x10^{-1}$ M with a slope of 30 ± 0.2 mV per decade. The detection limit of the proposed sensor is $5.0x10^{-8}$ M and it can be used over a period of 5 months and could be used in the pH range of 2.0–9.0. Singh et al., 2006 (b) fabricated a Co^{2+} ion-selective membrane sensor based on 2,3,4-pyridine-

1,3,5,8,11,14-hexaazacyclohexadeca-2-ene as a neutral carrier. The electrode exhibits a Nernstian response over a wide concentration range ($6.3x10^{-6}$ to $1.0x10^{-1}$ M) between pH 2.5 and 6.5. The response time of the sensor is about 15 s and it can be used over a period of 4 months without any divergence in potential. Mashhadizadeh et al., 2002(a) reported a membrane electrode for Co^{2+} ions based on (2-mercapto-4-methylphenyl)-2-benzamido-3-phenyl-thiopropenoate as a neutral carrier. The electrode exhibits a Nernstian response for Co^{2+} ions over a wide concentration range ($1.0x10^{-7}$ to $4.0x10^{-2}$ M) with a slope of 30 ± 1 mV per decade. The limit of detection is $1.0x10^{-7}$ M. It has a fast response time of <5 s and very high lifetime, it can be used for at least 6 months and in the pH range 5.0–8.0.

Gupta et al., 2007(a) discussed PVC-based membranes of meso-tetrakis-{4-[tris-(4-allyldimethylsilyl-phenyl)-silyl]-phenyl}porphyrin (I) and $(sal)_2$trien (II) as electroactive material used to act as Ni^{2+}-selective sensor. The sensor exhibits Nernstian response in the activity range $2.5x10^{-6}$ to $1.0x10^{-1}$ M, performs satisfactorily over wide pH range (2–5.5) with a fast response time (8 s) and could be used over a period of 4 months. Singh et al., 2007(c) discussed an ISE based on dibenzo[e,k]-2,3,8,9-tetraphenyl-1,4,7,10-tetraazacyclododeca-1,3,5,7,9,11-hexaene used for determination of Ni^{2+} ions. The electrode worked well in a wide concentration range of $3.98x10^{-6}$ to $1.0x10^{-1}$ M with a Nernstian slope of 29.5 mV per decade of activity between pH 2.5 and 7.7. The electrode exhibited a detection limit of $2.98x10^{-6}$ M and a fast response time of 8 s, and was used over a period of 4 months. Gupta et al., 2007(b) fabricated membranes containing neutral carrier dibenzo-18-crown-6 as electroactive material, for Ni(II) ions. The membrane having the composition of crown ether:NaTPB:TEHP:PVC in the ratio 10:1:200:200 (w/w) exhibits best results with linear potential response in the concentration range of 1.0×10^{-5} to 1.0×10^{-1} M and a Nernstian slope of 29.5 mV/decade of activity between 2.6 and 6.8. Yari et al., 2006 described a dioxime derivative, (2E, 3E)-2H-1,4-benzothiazine-2,3(4H)-dione dioxime as a neutral ionophore for the preparation of a PVC-membrane electrode for Ni(II) ions. It can be used for at least 4 months without any considerable divergence in potentials and it has a relatively fast response of <10 s. The prepared membrane exhibits a near Nernstian response for Ni^{2+} ions over a wide concentration range (1.0×10^{-6} to $1.0x10^{-1}$M) with a detection limit of 1.6×10^{-6} M. At a working pH range of 2.0–6.5. Mashhadizadeh et al., 2003 (a) reported a Ni^{2+} selective electrode using N,N′-bis-(4-dimethylamino-benzylidene)-benzene-1,2-diamine. The sensor exhibits a Nernstian response for nickel ions over a wide concentration range (1.0×10^{-2} to 2.0×10^{-7} M) with a slope of 30±1 mV per decade. It has a response time of <10 s and can be used for at least 2 months without any measurable divergence in potential. The electrode can be used in the pH range from 4.5 to 9.0. Mashhadizadeh et al., 2003 (b) used a mercapto compound as an ionophore for Ni^{2+} ions. The electrode exhibits a Nernstian slope of 28–30 mV per concentration decade at wide concentration range of (1.0×10^{-7} M–1.0×10^{-2} M). It has a fast response time of <15 s and can be used for at least 4 weeks. The potentiometric response is independent of the pH of the test solution in the pH range 5–8.5.

Mazloum et al., 2002 reported 1,3,7,9,13,15,19,21-Octaazapentacyclooctacosane (pentacyclooctaaza) as a neutral ionophore for Ni(II) ion. The electrode exhibited a near-Nernstian response in the concentration range of 1×10^{-6} to 1×10^{-1} M Ni(II). The limit of detection, as determined from intersection of the extrapolated linear segments of the calibration graph, was 6×10^{-7} M. It has a response time between 5 and 40 s for nickel concentrations ranging from 1×10^{-6} M -1×10^{-1} M. Mousavi et al., 2000 reported 1,10-dibenzyl-1,10-diaza-18-crown-6 (DBzDA18C6) as a neutral carrier. The sensor exhibits a Nernstian response for Ni(II) ions over a wide concentration range (5.5×10^{-3}–2.0×10^{-5} M). The electrode life time can be used for 6 months and is working over a pH range of 4.0–8.0. Jain et al., 1997 used a series of membranes of 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene diperchlorate (I) and 3,5,7,7,10,12,14, 14-octamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene diperchlorate (II) in PVC and polystyrene medium. The electrode exhibited near-Nernstian response in the concentration range ≈ 10^{-5}-10^{-1} M, while polystyrene based membranes exhibit linearity in the concentration range 10^{-6}-10^{-1}M. These membranes have response times as fast as 15 s and can be used over a period of six months. The electrodes work in the pH range 1.7–5.4. Gholivand et al., 2007 fabricated a membrane electrode based on Bis(2-hydroxyaceto phenone)butane-2,3-dihydrazone (BHAB) for Cu(II) sensor. The electrode exhibits a Nernstian behavior (with slope of 29.6 mV per decade) over a very wide concentration range (5.0×10^{-8} to 1.0×10^{-2} M) with a detection limit of $3.0\text{x}10^{-8}$ M (2.56 ng mL^{-1}). It shows a relatively fast response time in the whole concentration range (<15 s), and can be used for at least 12 weeks in the pH range of 2.8–5.8.

Mittal et al., 2007 reported a PVC-membrane ion-selective electrode based on 1,3,5-Tris(8-quinolinoxymethyl)-2,4,6-trimethylbenzene (MO8HQ). The basic sensing material belongs to the group of tripodal ionophores. Also their derivatives were prepared by placing suitable substitutents at fifth position of 8-oxine moiety. Among all the four electrodes, MO8HQ and HYD-8HQ ionophores based electrodes show excellent response towards Cu (II) ions. The electrode exhibits Nernstian response to Cu (II) ions in the range of 1.0×10^{-6} to 1×10^{-1} M. The electrode shows a reasonably fast response time of 15 s. Gupta et al., 2006 (c) reported $Cu2^{+}$- selective sensors that have been fabricated from polyvinyl chloride (PVC) matrix membranes containing neutral carrier porphyrin (A and B) ionophores. The membrane of composition B:PVC:NaTPB:DOP in the ratio 5:150:2:150 shows a linear potential response for Cu^{2+} over a wide concentration range 4.4×10^{-6} to 1.0×10^{-1} M with a Nernstian compliance (29.3 mV per decade of activity) between pH 2.8 and 7.9 and a fast response time of 8 s. Singh et al., 2006 (c) described 3-(2-pyridinyl)-2H-pyrido[1,2,-a]-1,3,5-triazine-2,4(3H)-dithione (L1) and acetoacetanilide (L2) as Cu^{2+}-selective sensor. It works satisfactorily in the concentration range 5.0×10^{-8} to 1.0×10^{-2} M (detection limit 4.0×10^{-8} M) with a Nernstian slope of 29.5 mV $decade^{-1}$ of activity. Wide pH range (3.0–9.5), fast response time (12 s), non-aqueous tolerance (up to 20%) and adequate shelf life (4 months) indicate the vital utility of the proposed sensor.

Ocypa et al., 2006 described the electrochemical properties of poly(3,4-ethylenedioxythiophene) doped with hexacyanoferrate(II,III) ions (PEDOT(HCF)) in the presence of Cu^{2+} ions. The lower detection limit of the potentiometric response range was reaching under optimised conditions $1x10^{-7}$M $CuSO_4$. Gupta et al., 2005 (a) described bis(acetylacetone)propylenediimine (I) as Cu^{2+} sensor. The composition is 5:100:200:6 (I:PVC:DBBP:NaTPB) (w/w; mg), where the electrode had a Nernstian response (30.0 mV/decade) to Cu^{2+} within the concentration range 1.0×10^{-5} to 1.0×10^{-1} M and a detection limit of 0.5 ppm. The operational pH range of the electrode was 3.3–7.0. Chai et al., 2005 described on N,N′-bis-(benzaldehyde)-glycine metallic complexes of Cu(II), Ni(II), Zn(II) and Co(II) as neutral carriers. The results showed that the electrode based on the N,N′-bis-(benzaldehyde)-glycine copper(II) complex [Cu(II)-BBAG] had a near-Nernstian response to the thiocyanate ion ranging from 1.0×10^{-1} to 9.0×10^{-7} M in a phosphate buffer solution of pH 4.0 with a detection limit of 7.0×10^{-7} M and a slope of −57.6 mV/decade at 25 °C. Acetylacetone, ethylacetoacetate and salicyldehyde are reported to form chelates with copper of high stability as compared to other metals (Jain et al., 2005). The membrane lead a composition of ionophore (1%): PVC (33%): TBP (65%): NaTPB (1%). The sensor shows a linear potential response to Cu(II) over a wide concentration range from 2.0×10^{-6} to 1.0×10^{-1} M (detection limit 0.1 ppm) with a Nernstian compliance (29.3 mV $decade^{-1}$ of activity) between pH 2.6 and 6.0 with a fast response time of 9 s.

Singh et al., 2004 (a) reported copper selective electode using Schiff’s base, which is derived from 2,3-diaminopyridine and o-vanilin. Optimum performance was observed with Schiff’s base (B) having a membrane composition of B(1%):PVC(33%):DOP(65%):NaTPB(1%). The sensor works satisfactorily in the concentration range 5.0×10^{-6} to 1.0×10^{-1} M (detection limit 0.3 ppm) with a Nernstian slope of 29.6 mV per decade of activity, a wide pH range (1.9–5.2), fast response time (<30 s), high non-aqueous tolerance (up to 20%) and an adequate shelf life (>4 months). Gupta et al., 2003 (a) used a copper(II) complex of ethambutol (I) in the fabrication of a Cu^{2+}-selective ISE membrane. The membrane having Cu(II)–ethambutol complex (I) as electroactive material, along with sodium tetraphenylborate (NaTPB) as anion discriminator, dioctylphthalate (DOP) as plasticizer in poly(vinyl chloride) (PVC) matrix in the percentage ratio 6:2:190:200 (I:NaTPB:DOP:PVC) (w/w), gave a linear response in the concentration range 7.94 x 10^{-6} to 1.0 x 10^{-1} M of Cu^{2+} with a slope of 29.9 ± 0.2 mV per decade of activity and a fast response time of 11 s. Mashhadizadeh et al., 2002 (b) reported a 3,6, 9,14-tetrathiabicyclo[9.2.1]tetradeca-11,13-diene based Cu^{2+}-selective electrode. The electrode exhibits a Nernstian slope of 28 ± 1 mV per decade at 25 °C for Cu^{2+} ions over a wide concentration range (6.3 x 10^{-7} to 2.5 x 10^{-1} M) with a detection limit of 3.2×10^{-7} M.

Abbaspour et al., 2002 prepared 1,3-dithiane,2-(4-methoxy phenyl) as ionophore. The electrode exhibits a Nernstian slope of 29.5±1 mV per decade in a linear range of 3.0×10^{-6} to 5.0×10^{-2} M for Cu^{2+} ions. The detection limit of this electrode is 1.0×10^{-6} M. This sensor has a very short response time of about 5 s and could be used in a pH range of 4.0–7.0. Shamsipur et al., 2001(a) synthesized three different mixed aza-thioether crowns containing a 1,10-phenanthroline sub-unit and investigated these as to copper(II) ion carriers. The electrode exhibited a Nernstian response for Cu^{2+} ions over a wide concentration range (2×10^{-1} to 1×10^{-5} M) with a limit of detection of 8.0×10^{-6} M. The response time of sensor is 15 s, and the membrane can be used for more than 3 months without observing any deviation and could be used in a pH range of 2.5–5.5. Park et al., 2001 prepared five novel 1,3-alternate calix[4]azacrown ethers having 2-picolyl, 3-picolyl and benzyl unit on the nitrogen atom and 2-picolyl armed 1,3-alternate calix [4] azacrown ether, exhibiting a Nernstian response towards copper (II) ions over a concentration range $10^{-4.5}$ M–$10^{-2.5}$ M.

Ganjali et al., 2001 used 2-thiophenal propanediamine (TPDA) coated directly on graphite as ISE for Cu^{2+} over a very wide concentration range (1.0×10^{-1} to 6.0×10^{-8} M) with a detection limit of 3.0×10^{-8} M that can be used in the pH range of 3.0–7.0. Gholivand et al., 2001 reported a 2,2′-dithiodianiline based electrode for Cu(II) ions. The electrode worked over a concentration range 5.0×10^{-2}–7.0×10^{-7} M with a Nernstian slope of 30 ± 1 mV per decade. The response time of the electrode is 10 s. Shamsipur et al., 1999(b) synthesized 23-member macrocyclic diamide to prepare a Cu^{2+}-selective polymeric membrane electrode. The electrode exhibits a Nernstian response for copper(II) ions over a wide concentration range (1.0×10^{-1} to 3.2×10^{-5} M), with a limit of detection of 1.2×10^{-5} M. It has a response time <20 s. Gismera et al., 1999 reported carbon paste ion-selective electrodes based on complexes of copper with the macrocyclic 3,4,10,11-tetraphenyl-1,2,5,8,9,12,13-octaaza-cyclotetra-deca-7,14-dithizone-2,4,9,11-tetraene, L1, and benzilbisthiosemicarbazone, L2, for the copper determination. The calibration graphs were linear for a wide concentration range (1×10^{-5}–1×10^{-2} M).

Kamata et al., 1988 developed, Poly(vinyl chloride)-membrane Cu^{2+} ion-selective electrodes by using neutral carriers such as tetraethyl-, tetrabutyl-, and dimethyldioctadecylthluram disulfide. The electrodes exhibit a Nemstian slope of 30-31 mV per concentration decade at 25 °C. Saad et al., 2005 reported two novel potentiometric copper(II)-selective membrane sensors based on cyclic tetrapeptide derivatives as neutral ionophores. The sensors exhibit a fast and stable near-Nernstian response over the concentration range 1.0×10^{-6} M -1.0×10^{-2} M Cu^{2+} with a cationic slope of 30.2–25.9 mV per decade at pH 4.5–7 with a lower detection limit of 0.05–0.13 μg ml^{-1}. Gupta et al., 2006 (d) prepared 4-tert-butylcalix[4]arene (I) as an electroactive material to fabricate a zinc-selective sensor. The sensor works well in the concentration range 9.8×10^{-6} to 1.0×10^{-1} M with a near-Nernstian slope of 28.0 ± 1.0 mV/decade of activity. The detection limit is down to 5.0×10^{-7} M. The working pH range of this sensor is 2.5–4.3. Gupta et al., 2006 (e) reported N,N′-bis(acetylacetone)ethylenediimine (I) for a Zn^{2+}-selective electrode. The electrode had a Nernstian response (30.0 mV/decade of Zn^{2+} activity) to Zn^{2+} within the concentration range of 1.0×10^{-6} to 1.0×10^{-1} M. The operational pH range of the electrode was 3.2–7.1. Gupta et al., 2005 (b) prepared dibenzo-24-crown-8 (I) as an ion-active material for zinc(II)-selective sensors. The electrode gave the best results with a wide working concentration range of 9.2×10^{-5} to 1.0×10^{-1} M, a Nernstian slope of 29.0 ± 0.5 mV/decade of activity, a fast response time of 12 s and a good selectivity over a number of mono-, bi-, and trivalent cations. The sensor works well in a pH range 4.8–6.2. Gholivand et al., 2003 (b) reported a membrane electrode based on bis(2-nitrophenyl)disulfide for Zn^{2+} in a wide concentration range (from 2.9×10^{-7} M to 3.2×10^{-2} M) with a slope of 29.9±0.4 mV per decade of Zn^{2+} concentration. The response time of the sensor is about 10 s and the membrane can be used for more than 3 months and can be used in a wide pH range (2–9). Fakhari et al., 2002 prepared a membrane electrode for Zn^{2+} ions using tetra(2-aminophenyl) porphyrin (TAPP) as membrane carrier. The sensor exhibits a linear stable response over a wide concentration range (5.0×10^{-5} to 1.0×10^{-1} M) with a slope of 26.5 mV/decade and a limit of detection 3.0×10^{-5} M. It has a response time of about l0 s and can be used for at least 8 months without any divergence in potential and can be used in pH range of 3.0–6.0. Shamsipur et al., 1999 (c) prepared benzo-substituted macrocyclic diamide (1,13-diaza-2,3;11,12;15,18-tribenzo-4,7,10-trioxacyclononaoctane-14,19-dione) as membrane carrier. The sensor exhibits a Nernstian response for Zn^{2+} over a wide concentration range (9.0×10^{-5} M -1.0×10^{-1} M). It has a response time of about 20 s and can be used for at least 3 months without any divergence. It can be used in a pH range of 3.0–7.0. Gupta et al., 1998 reported bis(2,4,4-trimethylpentyl) dithiophosphinic acid for the preparation of PVC-based Zn^{2+}-selective electrodes. The electrode exhibited a working concentration range of 2.8×10^{-5}–1.0×10^{-1} M, with a slope of 30.1 mV per decade of activity and a fast response time of 15 s. The valid pH range for the membrane sensor is 2.1–6.9.

Ulla et al., 1979 prepared several polymeric membranes for zinc ion-selective electrodes. A PVC membrane containing the zinc salt of di(2-ethylhexyl)phosphoric acid dissolved in tri(2-ethylhexyl)phosphate was the first ion-selective electrode which responds primarily to zinc. The sensor, which has a lifetime of at least two months, is characterized by a rapid response, potential stability and good sensitivity caused by a super-Nernstian slope (43.8mV/p Zn); the detection limit is 4.5±0.1 pZn. Cattrall et al., 1976 discussed the potentiometric determination of zinc in chloride solutions with a coated-wire electrode.The electroactive membrane contains the chlorozincate(II) salt of Aliquat 336S in poly (vinyl chloride). The electrode shows a useful response over the range 10^{-5} M–10^{-1} M zinc(II) in 3 M total chloride solutions in the pH range 1.5 –6.0. Evtugyn et al., 2007 fabricated potentiometric sensor based on glassy carbon electrode covered with polyaniline and a neutral carrier, e.g. thiacalix[4]arene containing pyridine fragments in the substituents in the lower rim has been developed and applied for determination of Ag^+ ions in the range from 1.0×10^{-2} to 5.0×10^{-7} M with a response time of 12 s.

Yan et al., 2007 prepared six new bis(dialkyldithiocarbamates) as neutral ionophore for the application of silver ions. The electrode works well over a wide range of concentration (1.0×10^{-6} to 1.0×10^{-3} M) with Nernstian slope. The present silver ISEs display a very good selectivity for Ag^+ ions against an interferent, Hg^{2+} ion, and the values are around −3.0. Mousavi et al., 2006 prepared glassy carbon electrodes using 3, 4-ethylenedioxythiophene. The electrodes showed a selective response to Ag^+ compared to several alkali, alkaline-earth, and transition-metal cations. Mashhadizadeh et al., 2006 reported a carbon paste electrode (CPE) and a coated-wire PVC-membrane electrode (CWE) based on Schiff's base of [bis 5-(4-nitrophenyl azo) salisylaldimine] 1,8-diamino, 3,6-dioxo octan (BNSAO) as a suitable carrier for Ag^+ ions. The electrodes exhibit a

Nernstian slope of 56.2 ± 0.7 (CWE) and 58.4 ± 0.3 (CPE) mV per decade for Ag^+ ions over a wide concentration range from 3.1 x 10^{-2} to 9.0 x 10^{-7} M for CPE and 2.7 x 10^{-2} to 1.9×10^{-6} M Ag^+ for CWE respectively. The lower detection limits are 4.2 x 10^{-7} M Ag^+ for CPE and 7.8 x 10^{-7} M Ag^+ for CWE electrode respectively. Kim et al., 2005 reported tweezer-type and non-tweezer-type ionophores containing dithiocarbamoyl groups on a 7-deoxycholic amide.

Amini et al., 2003 prepared silver ion-selective electrodes based on methyl-2-pyridyl ketone oxime (MPKO), phenyl-2-pyridyl ketone oxime (PPKO) and bis[2-(o-carboxythiophenoxy)methyl]-4-bromo-1-methoxybenzene (CMBMB) carriers. The electrodes exhibited linear responses with Nernstian slopes of 59.8–60.5 mV per decade within the range of 1 x 10^{-6} M to 1 x 10^{-1} M silver ions. The response times of the electrodes were <10 s over the concentration range of 1 x 10^{-2} M to 1 x 10^{-4} M and they did not show a considerable divergence in their potential response over a period of 3 months. The electrodes based on MPKO and PPKO carriers can be used in a wide pH range of 2.5–8.5 and the one based on CMBMB is suitable in the pH range of 3.0–6.5. Mahajan et al., 2003 discussed the potentiometric response characteristics and selectivity properties of poly(vinylchloride) (PVC) matrix membrane ion-selective electrodes for silver(I) ions, based on Schiff's base p-tert-butyl calix[4]arene derivatives containing N and O as binding sites. These electrodes work well over a wide range of concentration (1.0 x 10^{-5} to 1.0 x 10^{-1} M) with a Nernstian slope. The electrodes have a fast response time of 20 s and operate in a wide pH range. Liu et al., 2000 reported poly(vinyl chloride) (PVC) membrane electrodes based on bis(dialkyldithiophosphates) carriers tested for the selective detection of silver ions. A PVC membrane with 5% bis(diethyldithiophosphates) ionophore and 65% o-NPOE plasticizer satisfies these requirements. This electrode exhibits a linear response over a concentration range of 10^{-1}–10^{-6} M Ag^+ with a slope of 57.3 mV/dec. Wróblewski et al., 1995 reported membrane silver-selective electrodes based on lipophilic acyclic thioethers. The potentiometric selectivities and Ag^+ responses of these membranes are based on macrocyclic thioethers. Hasse et al., 1994 discussed pyridinophanes as a new class of macrocyclic neutral carriers as ionophores in PVC-based membrane electrodes. After adding a lipohilic salt as an anion blocker to the membrane, they succeeded in suppressing the anion interference, developing ion-selective electrodes for silver with excellent electrode characteristics

Gupta et al., 2007 (c) constructed polymeric membrane electrodes based on N,N′-[bis(pyridin-2-yl)formylidene]butane-1,4-diamine (S1) and N-(2-pyridinylmethylene)-1,2-benzenediamine (S2) for the quantification of cadmium ions. The best performance was obtained with the electrode having a membrane composition (w/w) of (S1) (2.15%):PVC (32.2%):o-NPOE (64.5%):KTpClPB (1.07%). The proposed electrode exhibits a Nernstian response in the concentration range of 7.9 x 10^{-8} to 1.0 x 10^{-1} M Cd^{2+} with a limit of detection 5.0 x 10^{-8} M. It performs satisfactorily over a wide pH range (2.0–8.0) with a fast response time (10 s). Gupta et al., 2007(d) reported dicyclohexano-24-crown-8 (I) as an ion-selective compound for cadmium(II)-selective sensors. It was observed that the membrane having the composition I: NaTPB:DBBP:PVC in the ratio 10:1:100:100 exhibited the best performance with a wide working concentration range of 3.0 x 10^{-5} to 1.0 x 10^{-1} M, a Nernstian slope of 30.0±1.0 mV/decade of activity with a response time of 23 s. It was found selective to cadmium ions over a number of mono-, bi- and trivalent cations. The sensor works satisfactorily in the pH range of 2.0–5.4.

Plaza et al., 2005 research on heavy metals, and especially on transport of Cd^{2+}, has attracted much interest during the past decade. An optimized Cd^{2+}-selective electrode for the continuous potentiometric monitoring of Cd^{2+} fluxes in biological systems is presented. The selectivity of the electrode for Cd^{2+} was further improved, and it now has a very good long-term stability. Abbas et al., 2005 prepared cadmium solid-state ion-selective electrodes by coating the surface of a graphite rod electrode directly with a tetrahydrofuran solution containing PVC, cetylpyridinium–tetraiodocadmate (I) or cetylpyridinium–tetrabromocadmate (II), dioctyl phthalate and sodium tetraphenyl borate. The two sensors exhibit near-Nernstian anionic slopes of −29.8 and −25.1 mV/concentration decade, independently of pH over a wide range with a very fast response time of 3 and 7 s, respectively. Tetraiodocadmate (TIC) and tetrabromocadmate (TBC) electrodes posses linear ranges of 1.5×10^{-6} to 1×10^{-1} and 1.0×10^{-6} to1×10^{-1} M and lower detection limits (LDL) of 6×10^{-7} and 8×10^{-7} M, respectively. The effects of membrane composition, type of plasticizer and pH of the sample solution were investigated thoroughly. The TBC electrode is shown to be free of all interferences that is common for most of the reported cadmium ISEs except for that of Hg^{2+} ions. The two electrodes were applied for the determination of cadmium in some alloys and polluted water. Gupta et al., 2002 released a PVC based membrane containing dicyclohexano-18-crown-6 (I) as active material along with sodium tetraphenyl borate (NaTPB) as an anion excluder and dibutyl phthalate as solvent mediator in the ratio 20:4:150:150 (w/w) (I–NaTPB–DBP–PVC) exhibiting good properties with a Nernstian response of 29.0 ± 1.0 mV per decade of activity of Zn^{2+} and a working concentration range of 2.1×10^{-5}–1.0×10^{-1} M. The working pH range of the sensor is 1.9–7.0. It exhibits a fast response time as fast as 17 s and has a lifetime of about 6 months.

Shamsipur et al., 2001(b) discussed a polyvinylchloride membrane sensor for Cd^{2+} ions based on tetrathia-12-crown-4 as an ionophore. The sensor exhibits a Nernstian response for cadmium ions over a wide concentration range (4.0×10^{-7} to 1.0×10^{-1} M) with a slope of 29±1 mV decade^{-1}. The limit of detection is 1.0×10^{-7} M (0.01 ppm). It has a fast response time of <10 s and can be used for at least 6 weeks without any divergence in potential. The electrode can be used in the pH range from 2.5 to 8.5. Gupta et al., 2000 (a) reported a cadmium (II) ion-selective electrode based on cyanocopolymer matrices and 8-hydroxyquinoline. The electrodes prepared with 2.38×10^{-2} molkg^{-1} of ionophore,

1.23×10^{-2} $moldm^{-3}$ of plasticizer and 2.0 g of cyanocopolymer (molecular wt., 59365) have shown a Nernstian slope of 29.00±0.001 mV per decade activities of Cd^{2+} ions with a response time of 12 s. The electrodes have shown an appreciable selectivity for Cd^{2+} ions in the presence of alkali and alkaline earth metal ions and could be used in a pH range of 2.5–6.5. Javanbakht et al., 2000 described a PVC-membrane electrode for Cd^{2+} ions based on [1,1′-bicyclohexyl]-1,1′, 2,2′-tetrol as membrane carrier. The electrode exhibits a Nernstian response for Cd^{2+} over a wide concentration range (1.0×10^{-1}–1.0×10^{-5} M) with a slope of 27.8 mV $decade^{-1}$. The limit of detection is 9.0×10^{-6} M (1.0 μg ml^{-1}). The electrode has a response time of <15 s and a useful working pH range of 4.0–7.0. Gupta et al., 1999 discussed cadmium(II)-selective sensors containing a neutral carrier, dibenzo-24-crown-8 as ionophore. This membrane gives a linear potential response in the concentration range 3.9×10^{-5}–1.0×10^{-1} M with a Nernstian slope of 30 mV/decade between pH 3.2 and 7.5.

Gupta et al., 2007 (d) prepared mercury ion-selective membrane electrodes based on 2-amino-6-purinethiol (I1) and 5-amino-1, 3, 4-thiadiazole-2-thiol (I2). The best performance was obtained with the electrode having a membrane composition (w/w) of (I1) (3.17%): PVC (31.7%): DOP (dioctylpthalate) (63.4%): NaTPB (sodium tetraphenylborate) (1.58%). The proposed electrode reveals a Nernstian response over Hg^{2+} ions in the concentration range of 7.0×10^{-8}–1.0×10^{-1} M with a limit of detection of 4.4×10^{-8} M. Yu et al., 2007 reported a membrane electrode based on 4-(4-N,N-dimethylphenyl)-2,6-diphenylpyrilium tetrafluoroborate as ionophore. The electrode indicates a good linear response for mercury(II) over a wide concentration range from 1.0×10^{-8} to 1.0×10^{-3} M, with a near-Nernstian slope of 34 mV per decade and the detection limit is 1.0×10^{-8} M. This membrane electrode operates well in the pH range of 2.5–7.0 and can be used for at least 30 days without observing any considerable deviation. Khan et al., 2006 prepared a polyaniline Sn(IV) phosphate an ‘organic–inorganic’ composite material via sol–gel mixing of the organic polymer polyaniline into the matrices of the inorganic precipitate of Sn(IV) phosphate. The ion-exchange capacity and distribution coefficients with respect to various metal ions were determined on the column of polyaniline Sn(IV) phosphate. The membrane electrode was mechanically stable with a quick response time and could be operated over a wide pH range with a slope of 30 mV per decade change in a linear concentration range of 1×10^{-1} to 1×10^{-6} M.

Singh et al., 2004 (b) reported a polystyrene based membrane of 2,3,4,9,10,11-dipyridine-3,10-diaza-1,5,8,12-tetrathiacyclotetradeca-2,9-diene as Hg(II)-selective electrode. The best performance was observed with the membrane having the ligand–polystyrene–DBP–STB composition 1:4:1:1 with a Nernstian slope of 30.0 mV per decade of concentration between pH 2.5 and 5.0. Mashhadizadeh et al., 2003 (c) described a membrane electrode for Hg(II) ions using bis[5-((4-nitrophenyl)azo salicylaldehyde)] (BNAS) as a suitable neutral carrier. The sensor exhibits a Nernstian response for mercury ions over a wide concentration range (7.0×10^{-7}M - 5.0×10^{-2}) with a slope of 30±1 mV per decade. It has a response time of <10 s and can be used for at least 3 months without any measurable divergence in potential. The electrode can be used in the pH range from 1.0 to 3.5. Lu et al., 2003 discussed a mercury ion-selective electrode (ISE) with a polymeric membrane based on a calixarene derivative containing a thiazole azo group as the ionophore.The ISE gave two kinds of response slope for Hg^{2+}. One, which has twice the Nernstian response for Hg^{2+}, is obtained at pH 6.5 with a slope of 61.1 mV per decade in the concentration range of 7.5×10^{-6}–5×10^{-2} M.

Mahajan et al., 2003 reported an electrode based on salicylaldehyde thiosemicarbazone as an ionophore as sensor for mercury(II) ions. The electrode shows excellent potentiometric response characteristics and displays a linear log[Hg^{2+}] versus EMF response over a wide concentration range of 1.7×10^{-6}–1.0×10^{-1} M with a Nernstian slope of 29 mV per decade with the detection limit of 1.0×10^{-6} M. The response time of the electrode is less than 30 s and the membrane electrode operates well in the pH range of 1.0–3.0. The lifetime of the sensor is about 2 months. Mazloum et al., 2000 described coated-wire mercury(II)-selective electrodes based on 2-mercaptobenzimidazole (MBIM), 2-mercaptobenzothiazole (MBTH), and hexathiacyclooctadecane (HT18C6) carriers in plasticized poly(vinyl chloride) (PVC) matrix. The electrodes exhibit near-Nernstian responses for Hg^{2+} ions over a wide concentration range (4 to 5 decades of concentration), and a detection limit of about 6×10^{-7} M (for the electrode based on MBTH). The response time of the electrodes is between 20 and 100 s, depending on the concentration of mercury, and they can be used for about 2 months. Chen et al., 2006 (a) discussed a number of double-armed calix[4]arene amide derivatives for lead ion-selective electrodes. The electrodes based on ionophores with dioctyl phthalate (DOP) as a plasticizer exhibit a close theoretical Nernstian response for Pb^{2+} over a relatively wide concentration range (1×10^{-6} –1×10^{-1} M), a fast response time (<15 s), at least two months lifetime and a good selectivity towards alkali, alkaline earth and some common transition metal ions.

Ardakani et al., 2005 discussed a sol–gel electrode and coated-wire ion-selective electrode (CWISE) based on Schiff's base as a neutral carrier. It was successfully developed for the detection of Pb(II) in aqueous solution.The sol–gel and CWISE exhibited linear response with Nernstian slope of 29.1 and 28.9 mV/decade, respectively, within the concentration ranges of 5.0×10^{-6} to 1.0×10^{-1} M lead ion for the sol–gel and coated ion selective electrode, respectively. The sol–gel and CWISE have shown detection limits of 3.0×10^{-6} and 5.0×10^{-6} M, respectively. The electrodes are suitable for use in aqueous solutions in a wide pH range of 4.0–8.2. Jeong et al., 2005 reported membrane electrodes for lead ion based on N,N'-bis(salicylidene)-2,6-pyridinediamine. The electrode exhibits a Nernstian response (29.4 mV/decade) and the limit of detection of $-\log a$ (M) = 6.04 of Pb^{2+}. It has a rapid response time within 10 s over the entire concentration range. Lee et al., 2004 reported PVC- membrane electrodes for lead ions based on meso-tetrakis(2-hydroxy-1-naphthyl)porphyrin (THNP: I) and meso-tetrakis(2-

methoxy-1-naphthyl)porphyrin (TMNP: II) as membrane carriers. The electrode exhibits a Nernstian response (29.2 ± 0.3 mV/decade) to Pb^{2+} in $Pb(NO_3)_2$ solutions over the linear range of 3.2×10^{-5} to 1×10^{-1} M at room temperature. The limit of detection was 3.5×10^{-6} M. Bhat et al., 2004 described a coated-wire lead ion-selective electrode (ISE) using 5,11,17,23,29,35-hexa-tert-butyl-37,38,39,40,41,42-hexahydroxycalix[6]arene as a neutral carrier in a poly(vinyl chloride) matrix. The sensor exhibited a linear Nernstian response over the range 1×10^{-6} to 1×10^{-1} M with a slope of 30±1 mV per decade change and a detection limit of 6×10^{-7} M. The working pH range of the sensor is 1.5–6.0 and it shows a good selectivity for Pb(II) ions over other mono-, bi- and trivalent cations.

Ganjali et al., 2002 discussed a membrane electrode for the determination of a trace amount of lead. The PVC membrane containing N,N′-dimethylcyanodiaza-18-crown-6 (DMCDA18C6) directly coated on a graphite electrode, exhibits a Nernstian response for Pb^{2+} ions over a very wide concentration range (from 1.0×10^{-2} to 1.0×10^{-7} M) with a limit of detection of 7.0×10^{-8} M (14.5 ppb). Susan et al., 2002 described an ion-selective electrode (ISE) for lead based on piroxicam. The electrode responds to Pb^{2+} in a linear range from 1.0×10^{-5} to 1.0×10^{-1} M with a slope of 30±0.2 mV per decade and a detection limit of 4.0×10^{-6} M. The proposed electrode could be used in a pH range of 4.0–8.0. Szymaska et al., 2001 reported potentiometric responses towards lead ions of liquid membrane electrodes containing 1,4-bis[2-(3,4,5-trimethoxyphenyl)ethenyl]benzene(1),2,5-dimethoxy-1,4-bis[2-(3,4,5trimethoxyphenyl) ethenyl]benzene(2),1,4-bis[2-(3,4,5-trimethoxyphenyl)ethyl]benzene (3) and 2,5-dimethoxy-1,4-bis[2-(3,4,5-trimethoxyphenyl)ethyl]benzene (4). All ligands strongly respond to lead ions in the activity range 10^{-6}–10^{-3} M and they show a high selectivity against common interfering mono- and doubly charged cations. The new ligands demonstrate a low affinity for protonation. Addition of 1 mol% of potassium tetrakis(p-chlorophenyl)borate as a lipophilic anionic salt significantly increases the selectivity of ligands 2, 3 and 4. The ligands show a potential as sensory elements of liquid-membrane electrodes destined for the determination of lead ions. Mousavi et al., 2001 studied four different fatty acids (C7, C10, C14, and C18) to characterize their abilities as lead(II) ion carrier in PVC-membrane electrodes. The electrode based on capric acid [CH3(CH2)8COOH] shows a good Nernestian response for Pb^{2+} ions. The electrode exhibits a Nernstian slope of 29 mV per decade for Pb^{2+} over a wide concentration range (1.0×10^{-5}–1.0×10^{-2}). It can be used for a period of 3 months without any considerable divergence in potentials. The proposed electrode revealed good selectivities for Pb^{2+} over a wide variety of other metal ions and could be used in the pH range of 4.5–7. It shows a good stability, good reproducibility and a fast response time.

Ohki et al., 1997 designed 12 kinds of lipophilic acyclic dibenzopolyether diamides and used them to prepare solvent polymeric membrane Pb^{2+} ion-selective electrodes. These ISEs exhibit remarkably high selectivities for Pb^{2+} relative to heavy metal cations, such as Cu^{2+}, Fe^{2+} and Ni^{2+} ions. Ceresa et al., 1999 did the determination of formal complex formation constants of various Pb^{2+} ionophores in the sensor membrane phase. To this purpose, potentiometric selectivities of the target ions relative to tetramethylammonium are compared for ion-exchanger- and ionophore-based ion-selective electrode membranes. The results show that ionophores having thioamide are less efficient in coordinating Pb^{2+} than corresponding ones with oxamide.

Malinowska et al., 2000 reported macrocyclic amides as ionophores for lead-selective membrane electrodes. Zeng et al., 2000 prepared silver ion-selective electrodes using novel 1,3-bis(2-benzothiazolyl)thioalkoxy-p-tert-butylcalix[4]arenas as electroactive material. All electrodes exhibited excellent properties with a Nernstian slope and linearity range. In the year 2002 the same group (Zeng et al.) had discussed the syntheses and properties of benzothiazolylthiaalkoxy functionalized calix[4]arenes based Ag^{+}-selective electrode. Selectivity against most of the interfering cations examined, except for Hg^{2+}, having a very weak interference. Beltramello et al., 2001 developed a new chemosensor for the Cu(II) ion by connecting via an amido bond an anthracenyl residue to the all cis 2,4,6-triamino-1,3,5-trihydroxycyclohexane ligand (TACI). This sensor is able to detect micromolar concentrations of Cu(II) ions in water at pH 7 without interference with many other divalent transition metal ions. Chen et al., 2001(b) prepared silver ion-selective electrodes (ISEs) by incorporating four novel calix[4]arene derivatives substituted by benzothiazolyl units, as the neutral carrier into the plasticized polymeric membranes. The better results were obtained with membranes containing bis(2-benzothiazolyl) groups with dibutyl phosphate (DBP) as a plasticizer. The electrodes show good Nernstian response to Ag^+ over a wide concentration range (5×10^{-6} to 1×10^{-1} M) and an excellent selectivity against alkali, alkaline earth and some transition metal ions. Gupta et al., 2006 prepared Pb(II)-selective sensor based on N,N′-dibenzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane. The sensor exhibits a Nernstian response for lead ions over a wide concentration range of 8.2×10^{-6} to 1.0×10^{-1} M with a slope of 30 mV/decade of activity. The electrode can be used in the pH range 2.0–6.8. The proposed sensor shows fairly good discriminating ability towards lead ions in comparison with some alkali, alkaline earth, transition and heavy metal ions. Another PVC-based membranes of N,N′-dibenzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane as Pb(II)-selective sensor was prepared by Gupta et al., in 2006 (f). The sensor exhibited a Nernstian response for lead ions over a wide concentration range of 8.2×10^{-6} to 1.0×10^{-1} M with a slope of 30 mV/decade of activity. The electrode had shown a fast response time of about 10 s and a lifetime of at least 3 months in the pH range 2.0–6.8. In an another case, a comparative study of Pb^{2+}-selective sensors based on derivatized tetrapyrazole and calix[4]arene receptors was done by the same group (Jain et al., 2006), in which two neutral ionophores, 2,12-dimethyl-7,17-diphenyltetrapyrazole (I) and 5,11-dibromo-25,27-dipropoxycalix[4]arene (II), have been explored for preparing PVC based membrane sensors selective to Pb^{2+}. The best performance was obtained with the sensor having a membrane of composition (w/w) of (I) (1%):PVC (33%):TBP (65%):NaTPB (1%). The sensor exhibits Nernstian response in the concentration range 2.5×10^{-6} to

5.0×10^{-2} M Pb^{2+}, performs satisfactorily over a wide pH range (1.6–6.0) with a fast response time (10 s). The sensor could be used over a period of 5 months.

2.5 Ion-Selective Electrode for some Inner-Transition Metal Ions

The binding properties of 5-pyridino-2,8-dithia[9](2,9)-1,10-phenanthrolinephane(L) towards La^{3+}, Sm^{3+}, Gd^{3+}, Yb^{3+}, and Nd^{3+} in methanol solution by Shamsipur et al., 2005 (b) revealed the occurrence of both 1:1 and 2:1(ligand/metal) complexation with a stability order of $Nd^{3+} > Yb^{3+} > Gd^{3+} > Sm^{3+} > La^{3+}$. Consequently, L was used as a suitable neutral ionophore for the preparation of a novel polymeric membrane-selective electrode for Nd^{3+} ions. The electrode exhibited a Nernstian response over a wide concentration range ($1.0\text{x}10^{-6}$-$1.0\text{x}10^{-2}$ M) with a low limit of detection of $7.9 \text{ x } 10^{-7}$ M. The electrode possesses a fast response time of <5 s and can be used for at least 9 weeks without observing any considerable deviation. The potentiometric response of the electrode is independent of the pH of test solution in the pH range 4.0-6.5. Shamsipur et al., 2003 did solution studies on the binding properties of 4,5,6,7- tetrathiocino[1,2-b:3,4-b]diimidazolyl-1,3,8,10-tetraethyl- 2,9-dithione (Et4todit) towards some lanthanide ions. The electrodes exhibit a Nernstian behavior for Sm^{3+} ions over a wide concentration range ($1.0\text{x}10^{-5}$ - $1.0\text{x}10^{-1}$ M for PME and $1.0\text{x}10^{-7}$- $1.0\text{x}10^{-1}$ M for CGE) and very low limits of detection ($8.0\text{x}10^{-6}$ M for PME and $1.6\text{x}10^{-8}$ M for CGE). The potentiometric responses of the electrodes are independent of the pH of the test solution in the pH range 4.0-6.5. La^{3+}-selective sensors have been fabricated by Gupta et al., 2003 (b), from poly(vinyl chloride) (PVC) matrix membranes containing a neutral carrier, monoaza-12-crown-4 as ionophore. Best performance was exhibited by the membrane having a composition crown: PVC: NaTPB: DBBP in the ratio 7: 48: 8: 37 (w/w). This membrane works well over a wide concentration range of 3.16×10^{-5} to 1.0×10^{-1} M of La^{3+} with a Nernstian slope of 20.5 ± 1.0 mV per decade of La^{3+} activity. The response time of the sensor is <15 s and the membrane can be used over a period of 5 months with good reproducibility. The proposed electrode can be used in a wide pH range from 3.0 to 7.0 and demonstrates a good discriminating power over a number of monovalent, divalent, and trivalent cations. In an another work, a novel gadolinium membrane sensor based on new S–N Schiff's base (2-[{3-[(2-sulfanylphenyl)imino)-1-methylbutylidene}amino]phenyl hydrosulfide (SMPH) is presented by Ganjali et al., 2003 (a) . The sensor displays a linear dynamic range between 1.0×10^{-1} and 1.0×10^{-5} M, with a Nernstian slope of 19.8±0.3 mV per decade and a detection limit of 3.0×10^{-6} M. The best performance was obtained with a membrane composition of 33% poly(vinyl chloride), 61% benzyl acetate, 2% sodium tetraphenyl borate and 5% SMPH. The potentiometric response of the sensor is independent of the pH of the solution in the pH range of 4.0–8.0. Solution studies have been done by Ganjali et al., 2005 (a), on the binding properties of N-2,4-dimethylphenyl-N′-ethylformamidine towards nine lanthanide ions including lanthanum, cerium, neodium, samarium, europium, gadolinium, terbium, dysprosium, ytterbium and some other transition and heavy metal ions such as copper, lead, cobalt, nickel ions. It showed a selective 1:1 complexation between amitraz and lanthanum ions. Consequently, it was applied as an ion carrier in construction of a novel poly(vinyl chloride) membrane sensor for La(III). The sensor has a linear dynamic range of $1.0\text{x}10^{-1}$ to $1.0\text{x}10^{-7}$ M with a Nernstian slope of 19.8 ±0.2 mV per decade and a detection limit of $8.0\text{x}10^{-8}$ M. The proposed sensor displays a fast response time (<8 s), and can be used for at least 2 months without any considerable divergences in the potentials. It could be used in a pH range of 3.0–9.0. Mittal et al, 2004 developed a sensor for La^{3+} ion-selective using dicyclohexano-18-crown-6 (DC18C6) as neutral carrier.The electrode comprises of dicyclohexano-18-crown-6 (6%), PVC (33%), and ortho-nitrophenyl octyl ether (o-NPOE) (61%). The electrode shows a linear dynamic response in the concentration range of 10^{-6} to 10^{-1} M with a Nernstian slope of 19 mV per decade and a detection limit of 5×10^{-7} M. It has a response time of <30 s and can be used for at least 5 months without any significant divergence in potentials. The membrane is successfully applied in partially non-aqueous medium. It can be used in the pH range 4–

9. A PVC-based sensor for La^{3+} ions based on N-[hexahydrocyclopentapyrol-2((1H)yl)amino]carbonyl]-4-methyl benzene sulfonamide (gliclazide) as a novel carrier was prepared by Ganjali et al., 2003 (b). The electrode exhibits a Nernstian response for La^{3+} over a wide concentration range (1.0×10^{-1} – 1.0×10^{-6} M) with a slope of 20.1 mV per decade. The limit of detection is 8.0×10^{-7} M. The sensor has a very short response time (<15 s) and a useful working pH range of 4.0–8.0. Ganjali et al., 2003 (c) used N-[2-[4-[[[(cyclohexyl amino)carbonyl]amino]sulfonyl] phenyl]ethyl]-5-methyl pyrazine carboxamide (glipizid) as an excellent ionophore to make a novel Sm^{3+}-selective membrane sensor. The electrode based on glipizid, containing sodium teraphenyl borate as lipophilic salt and benzyl acetate as a plasticiser, gave the best performance. The electrode exhibits a good Nernstian response towards Sm^{3+} ions in the range of 1.0×10^{-1} to 1.0×10^{-6} M with a slope of 19.8 mV per decade. A Tb^{3+}-selective solvent polymeric membrane sensor based on N,N,-bis(pyrrolidene) benzene-1,2-diamine, poly(vinyl chloride) (PVC), benzylacetate (BA) plasticizer, and an anionic additive was described by Ganjali et al., 2005 (b). At a pH range of 3.5–7.7, this sensor responds to dysprosium in a linear range from $1.0x10^{-5}$ to $1.0x10^{-1}$ M, with a slope of 19.8 mV per decade and a detection limit of $7.0x10^{-6}$ M. It has a fast response time of <20 s in the whole concentration range, and can be used for at least 2 months without any considerable divergences in the potentials. Ganjali et al., 2004 described a novel La^{3+} sensor based on bis(thiophenal)phenylen-1,3-diamine (TPD). The sensor was prepared by incorporating the TPD into plasticized PVC membrane. The effect of membrane composition and pH and influence of additive anionic on the response properties were investigated. The sensor with 35% PVC, 54% solvent mediator, 8% ionophore and 3% anionic additive shows the best potentiometric response characteristics. It displays a Nernstian behavior (19.6 mV per decade) over the concentration range $1.0x10^{-7}$ to $1.0x10^{-1}$ M. The detection limit of the electrode is $2.0x10^{-8}$ M (3.0 ng/ml). The response time of the electrode is very fast (10 s) in the whole concentration range. The sensor can be used in the pH range 3.5–9.5 for at least 2 months.

In an another work Ganjali et al., 2005 (c) described the construction, performance and applications of a novel Tm^{3+} sensor that is based on thiophene-2-carbaldehyde-(7-methyl-1,3-benzothiazol-2-yl)hydrazone (TCMH), which acts as an excellent carrier, when used in a plasticized poly (vinyl chloride) PVC matrix. The Sensor reveled a lower detection limit of $8.0 \text{x} 10^{-6}$ M, the sensor response for Tm^{3+} ion is Nernstian over a wide concentration range of three decades of concentration ($1.0 \text{x} 10^{-5}$-$1.0 \text{x} 10^{-2}$ M). The response time of the electrodes is less than 7 s, depending on the concentration of Tm^{3+} ions. The lifetime was found to be about 7 weeks. The optimum responses were found with a membrane composition of 30% PVC, 58% nitrobenzene (NB) as solvent mediator, 7% TCMH, and 5% sodium tetraphenyl borate (NaTPB). The construction, performance and applications of a novel Yb^{3+} sensor based on N-(2-pyridyl)-N-(2-methoxyphenyl)-thiourea (PMT), as an excellent carrier, in plasticized poly(vinyl chloride) PVC matrix, was described by Ganjali et al., 2005 (d). The sensor exhibits a Nernstian response for Yb^{3+} ions over a wide concentration range of four decades of concentration (1.0×10^{-6} - 1.0×10^{-2} M), and a detection limit of 5.0×10^{-7} M. The response time of the electrodes is between 8 and 10 s, depending on the concentration of Yb^{3+} ions. The proposed sensor can be used for about 8 weeks without any considerable divergence in potential. The sensor revealed very good selectivity for Yb^{3+} in the presence of several metal ions. The best performance was observed for the membrane containing 30% PVC, 59% o-nitrophenyloctyl ether (o-NPOE) as solvent mediator, 7% PMT and 4% sodium tetraphenyl borate (NaTPB). Akhond et al., 2004, have reported a new Ce^{3+}-selective membrane electrode based on 2-aminobenzothiazole. The electrode exhibits a Nernstian slope of 19.6 ± 1.0 mV per decade over wide Ce^{3+} ion concentration range from $2.0 \text{x} 10^{-6}$-$2.0 \text{x} 10^{-2}$ M and low detection limit $1.8 \text{x} 10^{-6}$ M. The electrode possesses a fast response time of 13 s and a relatively long lifetime (at least 3 months). The electrode could be used in a pH range of 4.1–7.3.

The comprenshive literature survey shows that amide, amine and some N_2S_2 mixed donor type of neutral carrier have not been used for fabrication of liquid-membrane electrodes.

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Chapter -3

Methodology

Ion-selective electrodes are miniaturized devices, which consist of an ion-selective membrane as a key component. These sensors are able to give information about the desired ionic species in presence of various interfering ions from the sample. Today, electrochemical sensors are tightly integrated and hyphenated with sampling, fluid handling, separation and other detection principles. Recent years can be treated as revolutionary period for the well-established field of potentiometric electrodes. Among various class of chemical sensors, ion-selective electrodes (ISE) are one of the most frequently used potentiometric sensors during laboratory analysis as well as industrial, process control, physiological measurements and environmental monitoring.

The ion-selective electrode is a system in which two solutions containing electrolyte are separated by a membrane, which is freely permeable to ionic species of interest. Ideally, potentiometric sensors detect the ion activity in the sample. To make measurements with an ion-selective electrode, the electrochemical concentration cell is established the cell consists of mainly three components a reference electrode, the sample and the ion-selective electrode (ISE).

3.1 Reagents and Apparatus

PVC of high relative molecular weight, plasticizers viz., dibutyl phthalate (DBP), dioctyl phthalate (DOP), Bis-2-ethyl sebacate (BES), ortho-Nitrophenyloctylether (o-NPOE) and all metal salts were obtained from Aldrich Chemical Company, USA. All solvents used in investigations were of analytical reagent grade. All aqueous solutions were prepared with deionized, distilled water and standardized by suitable chemical methods. pH adjustments were made with dilute nitric acid or sodium hydroxide solutions as required. All potentials were measured with a digital potentiometer (EQ-602 Equiptronics, India, accuracy, ±0.1 mV) and pH measurements were carried out on an ISFET pH meter (Delta Track, USA) at room temperature (25 ± 0.1 ^{0}C) in stirred solutions.

3.2 Stability Constant Determination of Metal–Ionophore Interaction

Conductivity measurements were carried out with a conductivity meter (Equiptronics, India). A dip-type conductivity cell made of platinum black, with a cell constant of 1.02 cm^{-1} was used. In all measurements, the cell was thermostated at the desired temperature 25 ± 0.5 ^{0}C. In typical experiments, 50 mL of metal nitrate solution (1x10^{-4} M) was placed and a solution of titrant ligand (1x10^{-3} M) was added from the burette. Conductivity of the solution was measured after each addition. Addition of ligand continued until the desired ligand-to-metal ion mole ratio was achieved. The 1:1 binding of the metal ions with ligand can be expressed by the following equilibrium (Shamsipur et al., 2000).

$$M^{n+} + L \leftrightarrow ML^{n+} \qquad \text{-----------------3.2.1}$$

The corresponding equilbrium constant, K_f is given by

$$K_f = \frac{[ML^{n+}]}{[M^{n+}][L]} X \frac{f_{ML^{n+}}}{f_{M^{n+}} f_L} \qquad \text{-----------------3.2.2}$$

where [ML^{n+}], [M^{n+}], [L] and ‘f’ represent the equilibrium molar concentration of complexes, free cation, free ligand and the activity co-efficient of the species indicated, respectively. The complex formation constant in terms of the molar conductance Λ can be expressed as

$$K_f = \frac{[ML^{n+}]}{[M^{n+}][L]} = \frac{\Lambda_M - \Lambda_{obs}}{(\Lambda_{obs} - \Lambda_{ML})[L]} \quad \text{------------------3.2.3}$$

where,

$$[L] = C_L - C_{M^{n+}} \frac{\Lambda_M - \Lambda_{obs}}{(\Lambda_{obs} - \Lambda_{ML})} \quad \text{-----------------3.2.4}$$

3.3 Picrate Extraction Studies

Extraction experiments were performed according to a standard procedure (Lamb et al., 1981). Metal picrates were prepared by mixing metal nitrates (1x10^{-3} M) with picric acid (1x10^{-3} M) and the solution was stirred for about 1 hour. A chloroform solution (5 mL) of the ligand (1x10^{-3} M) and 5 mL of the aqueous solution (1x10^{-3} M) of metal picrate were placed in a stoppered flask and shaken for 1 hour at 25 ± 0.5 °C. This period of shaking was enough to establish equilibrium between the two phases. Resulting mixtures were allowed to stand for least 2 hour at that temperature in order to complete the phase separation. The concentration of picrate ion remaining in the aqueous phase was then determined spectrophotometrically at 355 nm. Blank experiments showed that no picrate extraction occurred in the absence of the ligand. Extraction of the metal ions was determined on the basis of absorbance measurement of picrate ions in the aqueous solution. The extraction was calculated from the equation (Lamb et al., 1981)

$$E = \frac{(A_0 - A)}{A_0} X100 \quad \text{----------------3.3.1}$$

where A_0 is absorbance in the absence of ligand. A denotes absorbance in aqueous phase after extraction.

3.4 Mole Ratio Method

Composition of the complexes was also determined by applying the mole ratio method (Yoe et al., 1948). A series of solutions were prepared with a constant concentration of the metal ion ($1x10^{-3}$ M) and variable concentration of the ligand ($1x10^{-3}$ M). Absorbance was measured at λ_{max} of the ligand.

3.5 Fabrication of Ion-Selective Electrode

All liquid membranes were prepared by the standard procedure given by Craggs et al., 1974. Different membranes were prepared by dissolving 200 mg of a mixture of ionophore, plasticizer and PVC in 2-3 mL of THF. The amount of ionophore was varied from 1% to 6%. Different plasticizers viz; o-NPOE, DBP, DOP and BES were also added to get membranes of different characteristics. The membrane cocktail was then poured in a glass ring of 30 mm diameter placed on a pyrex glass plate and allowed to evaporate at room temperature for about 24 hours. The membrane was then removed from the glass ring and circular pieces of 1.25 cm diameter were cut and mounted on pyrex glass tubes with suitable adhesive and conditioned with desired metal ion solution for 24 hours. The ratio of ionophore and different additives in the membrane was optimized so that it should give good response in terms of Nernstian slope, working range, detection limit, etc. The membrane should also give reproducible and stable potentials.

3.6 Measurements of Potential

All EMF were measured using either of the following cell assembies depending upon the metal ion of interest:

SCE // 0.1 M M^{n+} / membrane / M^{n+} (test solution) // SCE
Ag /AgCl, $Cl^{-}_{(satd.)}$ // 0.1 M M^{n+} / membrane / M^{n+} (test solution) // $Cl^{-}_{(satd.)}$, AgCl /Ag

Variations in emf were recorded after stabilization and the value was plotted as a function of the logarithm of the M^{n+} ion activity. Activity coefficients were calculated by the Debye-Huckel approximation (Kielland, 1937). The response time of electrodes was obtained by measuring the time required to achieve a steady state potential (within ±1 mV) when the electrodes were inserted in M^{n+} solutions of different concentrations under stirring. For proper ionic contact, salt bridges were used which were prepared using agar-agar and KNO_3 for Ag^+ determination while agar-agar and KCl mixture for other metal ions.

3.7 Working Principle of an Ion-Selective Electrode

Ion-selective electrode membranes are typically investigated under zero-current conditions in a galvanic cell. The electromotive force (emf) across the cell is the sum of all individual potential contributions. Many of these are sample-independent and the measured emf can usually be described as (Bakker et al., 1997)

$$emf = E_{const} + E_J + E_M \qquad \text{..................3.7.1}$$

where,

E_M = Membrane potential

E_J = Liquid-junction potential at the sample/bridge electrolyte interface

Since the membrane is usually interposed between the sample and an inner reference electrolyte, it is common to divide the membrane potential E_M into three separate potential contributions, namely the phase boundary potential at both interfaces and the diffusion potential within the ion-selective membrane. For ion-selective electrodes that show a Nernstian response, the membrane internal diffusion potential is zero if no ion-concentration gradient occurs. It is, therefore, postulated:

$$E_M = E_{const} + E_{PB} \qquad \text{............3.7.2}$$

Here,

E_{PB} = Phase Boundary potential at the membrane-sample interface.

The electrochemical potential, is formulated for the aqueous phase

$$\begin{aligned}\mu(aq) &= \mu(aq) + zF\phi(aq) \\ &= \mu^0 + RT\ln a_I(aq) + zF\phi(aq)\end{aligned} \qquad \text{…………..3.7.3}$$

and for the contacting organic phase

$$\begin{aligned}\mu(org) &= \mu(org) + zF\phi(org) \\ &= \mu^0(org) + RT\ln a_I(org) + zF\phi(org)\end{aligned} \qquad \text{…………….3.7.4}$$

where,

μ = Chemical potential

μ° = Chemical potential under standard conditions,

z = valency

a_I = activity of the uncomplexed ion I,

ø = electrical potential, and

R, T and F are the universal gas constant, the absolute temperature and the Faraday constant.

It is assumed that the interfacial ion transfer and complexation processes are relatively fast. Therefore, equilibrium holds at the interface so that the electrochemical potentials for both phases (aqueous as well as organic) are equal. This leads to a simple expression for the phase boundary potential:

$$E = \Delta\phi = -\frac{\mu^0(org) - \mu^0(aq)}{zF} + \frac{RT}{zF}\ln\frac{a_I(aq)}{a_I(org)} \qquad \text{……………3.7.5}$$

By combining equations 3.7.5 and 3.7.2 one obtains,

$$\begin{aligned}E_M = E_{const} + E_{PB} = E - \frac{\mu^0(org) - \mu^0(aq)}{zF} - \\ \frac{RT}{zF}\ln a_I(org) + \frac{RT}{zF}\ln a_I(aq)\end{aligned} \qquad \text{……………………3.7.6}$$

Under the condition that a_I(org) remains unaltered, it can be included in one term (E_0) and equation 3.7.6 reduces to the well-known "**Nernst equation"**

$$E_M = E^0 + \frac{RT}{zF} \ln a_I (aq) \qquad \text{.............................. 3.7.7}$$

where

E = Experimentally observed emf of a cell (at zero current)

E° = Standard electrode potential of cell (constant potential contribution that often includes the liquid junction potential at the reference electrode)

R = Gas constant, 8.314 $JK^{-1}mol^{-1}$

T = Absolute temperature

F = Faraday constant, 9.648 x 10^4 Coulombs

a_A = Activity of primary ion A

z = Charge no. of ion A

The sign in the equation is positive when z is a cation and negative when it is an anion.

3.8 General Terminology of Ion-Selective Electrodes

Primary Ion: It is the ion which the electrode is designed to measure and is termed as primary ion. It doesn't mean that electrode is most responsive to the primary ion, since nearly all sodium electrodes, e.g., respond to hydrogen and silver ions more strongly than to sodium ions.

Interferent Ion: Any species other than the primary ion, to which the electrode responds is defined as an interferent. The presence of significant concentration of interferents in a sample leads to the apparent concentration of primary ion being erroneously high.

Calibration Graph: A calibration graph of the ion-selective electrode is defined as a plot of the potential difference between the ion-selective electrode and a reference electrode against the logarithm of its activity or concentration of the primary ion in the measurement cell. For a primary ion A, the logarithm of its activity or concentration is usually plotted along the abscissa of the graph pA (= $-\log_{10} a_A$ or $-\log_{10}$ [A] as appropriate) and the cell potential is plotted along the ordinate.

Nernstian Response: Nernstian response occurs when an ion-selective electrode responds to "local" thermodynamic equilibrium over a given range of activity (or concentration). Nernstian response is revealed when a plot of potential difference of the ISE cell (electrode, with an outer reference electrode) vs. the logarithm of the ionic activity of a given species (a_A) is linear with a slope of 2.303 RT/Z_AF (59.16/z_A mV per unit change of pa_A at 298.15 K). Nernstian response implies ideal sensitivity, but not necessarily ideal selectivity since interfering ions may also give Nernstian response when present as the sole potential determining species.

Slope: According to the Nernst equation the theroretical value of the slope is 59.16 mV per decade at 298 K for a single charged ion or 59.16/2 = 29.58 mV per decade for a double charged ion or 59.16/3= 19.72 mV per decade for a triple charged ion. However, in certain applications the value of the electrode slope is not very critical and a not-so-good value does not exclude its usefulness.

Linear Range: The linear range of ion-selective electrode is defined as the activity ratio of upper and lower detection limits and approximately corresponds to the range where the electrode responds according to the Nernst equation.

Detection Limit: Every ion-selective electrode has a lower and upper detection limit where the response starts to deviate significantly from a Nernstian electrode slope. According to the IUPAC recommendation of 1976, the detection limit is defined by cross section of the two interpolated inner calibration curves.

Response Time: According to the IUPAC recommendations, it is defined as the time taken for the potential of the cell containing the electrode to reach a value of 1 mV from the final equilibrium potential after a supposedly instantaneous change in determinand activity. The response time is extremely dependent on the experimental conditions such as stirring rate, determinand's activity etc.

Selectivity Coefficients: The potentiometric selectivity coefficient is a measure of the selectivity of an electrode for the primary ion ‘A’ in the presence of an interferent ‘B’. The smaller the value of selectivity coefficient, the more selective is electrode for the primary ion in presence of the interferent. Selectivity coefficient has also been called as selectivity constant and selectivity factor. It is well established now that the Nicolsky-Eisenman (N-E) equation is not valid in the activity range where the primary and the interfering ion significantly contribute to the potential. Despite this deficiency of the Nicolsky-Eisenman equation, the potentiometric selectivity factor is the best possible measure to quantify interferences because it corresponds to the ion-exchange selectivity of the membrane. Different methods of the selectivity determination can be found in the literature (Buck et al., 1994 and Umezawa et al., 1995). The separate Solution Method (SSM), Fixed Interference Method (FIM) and Matched Potential Method (MPM) are methods suggested by the IUPAC. Each of these methods possesses their own advantages and drawbacks. There are no general rules pointing which method gives the true result. Methods proposed by IUPAC with several precautions will give meaningful data.

Fixed Interference Method (FIM): In this method, a solution of constant activity of interfering ion a_B, and varying activity of primary ion a_A is taken and the emf is measured. These emf values are plotted against the log of the activity of the primary ion a_A. The intersection of extrapolation of this plot indicates the value of a_A and is used to calculate the selectivity coeffcient from the Nicolsky-Eisenman equation;

$$-\log K_{AB} = \frac{E_A - E_B}{S} \qquad \text{--------------------3.8.1}$$

Separate Solution Method (SSM): This method involves measuring the emf of two separate solutions, containing the ion A of activity a_A (but not B), while the other solutions containing the ion B of same activity $a_A = a_B$ (but not A). If the measured emf values are E_A and E_B, respectively, the value of selectivity coeffiecients can be calculated from this equation:

$$\log K_{A,B}^{pot} = \frac{(E_B - E_A)Z_A F}{2.303RT} + \left[1 - \frac{Z_A}{Z_B}\right]\log a_A$$

------------ 3.8.2

Limitations of Nicolsky-Eisenman equation: This equation is not accurate for the determination of selectivity coefficient, when the charges of ions are different. It assumes Nernstian behavior of primary as well as interfering ions.

Matched Potential Method (MPM): This method is independent of the Nicolsky-Eisenman equation for the determination the selectivity coefficient. In this method, primary ions (A) of a specified activity (concentration) are added into a reference solution, and the potential is measured. In a separate experiment, interfering ions (B) are successively added to an identical reference solution until the measured potential matches with that obtained before adding the primary ions. In the matched potential method, the selectivity coefficient $K_{A,B}$ is then given by the ratio of the resulting activities (concentrations) of primary ions versus interfering ions. The selectivity coefficient, K_{AB}, is determined as below

$$K_{A,B}^{pot} = \frac{a'_A - a_A}{a_B}$$

---------------------------3.8.3

where

a'_A = activity of reference solution containing primary ion A

a_B = activity of interfering ion B in the presence of reference solution a'_A

Characteristics of MPM method

- Charge number of the primary and interfering ions need not to be taken into consideration.
- Nernstian responses are assumed neither to primary nor interfering ions.
- The power-term problem for ions of unequal charges disappears.
- This method is widely applicable, even to non-Nernstian interfering ions.

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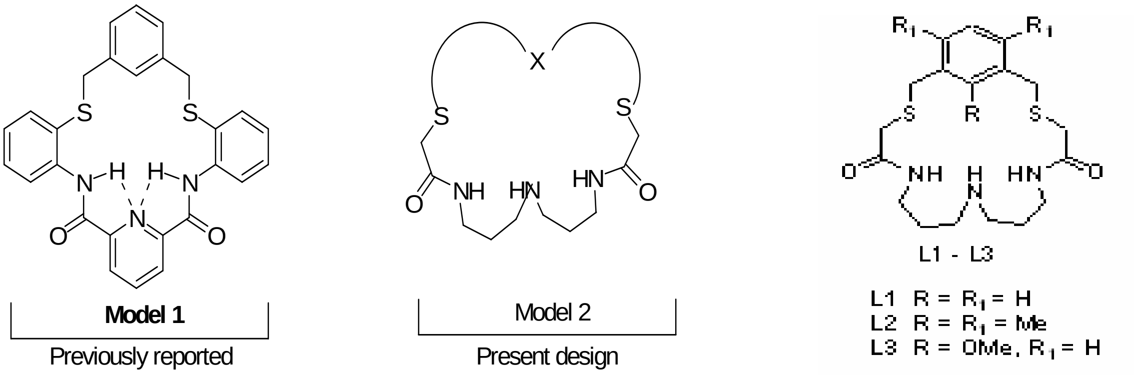
Chapter -4

Amide-Amine Ionophore Based Chemical Sensors

4a. Silver (I)-Selective Membrane Electrodes Based on Macrocycles Possessing Thioether – Amide – Amine Combinations

Introduction

The quick estimation, removal, separation techniques and application of Ag^+ complexes in industry, biological, medical and daily analysis (Seiler et al., 1994, Forstner et al., 1979, Oue et al., 1998, Brzozka et al., 1993, Wroblewski et al., 1915, Siswanta et al., 1996) requires a fast and efficient method of Ag^+ determination. The ability of the Ag^+ to form stable bidentate complexes and occasionally tridentate or higher coordinate complexes in comparison with stabilization of octahedral complexes by other competing metal ions has been successfully used to design and synthesize highly Ag^+-selective receptors. So, in addition to the presence of 2-4 appropriately placed soft ligating sites, the number of other structural features, like the minimal incorporation of hard ligating sites (ether, etc.), the induction of conformational and stereochemical restrictions to avoid 2:1 complexation towards interfering metal ions, etc. have been used by us to design Ag^+-selective ionophores. In order to attain appropriate cavity size and to restrict the coordination number < 4, the noncoordinating ester and amide based spacers have been used. We had earlier reported that in case of o-aminothiophenol based cyclic diamide macrocycles due to rigidity and steric reasons, the amide -NH units fill the cavity and due to reorganization of ligating sites during complexation, their binding capacity is lowered. Now we have designed new cyclic ionophores, which possess two thioether - one amine - two amide units as the common structural feature. We envisaged that the presence of three carbon spacers between nitrogen atoms and replacement of o-aminothiophenol group with alkylthioether moiety would create desired flexibility in the resulting receptors.



Model 1
Previously reported

Model 2
Present design

L1 - L3

L1 R = R1 = H
L2 R = R1 = Me
L3 R = OMe, R1 = H

Figure 4a.F$_1$: Structure of macrocycles possessing thioether – amide – amine combinations

The receptors of model-2 have been synthesized through aminolysis of diesters with respective diamines. These receptors, in their extraction experiments, show remarkably enhanced extraction of Ag^+ and Ag^+ / Pb^{2+} selectivity in comparison with the earlier model-1. In order to study their application in estimation of Ag^+, liquid-membrane based ion-selective electrodes have been prepared. These electrodes exhibit good selectivity with respect to Ag^+ ions. Some of the reports show serious interference of mercury ions (Mashhadizadeh et al., 1999, Chen et al., 2000) in determination of Ag^+ but here Hg^{2+} is interfering very systematically and their presence makes suitable protecting shield for other metal ion interferences (Table 4a.T$_5$).

Reagents, Preparation of Electrodes and Potential Measurements

A number of liquid-membrane based electrodes were prepared according to the previously reported method and potential measurements as discussed in chapter 3.

Results and Discussion

Optimization of the Membrane Composition

Membrane composition does influenc the sensitivity and selectivity of an electrode. Optimum concentration of the ionophore was achieved by changing its content from 2% to 6% (by weight) with increments of 1% each time (Table 4a.T_1). Membranes having PVC: DBP: Ionophore compositions as 33: 63: 4 (wt%) for L1 and L3 and composition 33: 64: 3 (wt%) for L2 showed the best responses in terms of both slope and measuring range concentration. Electrodes based on o-NPOE as plasticizer show slopes between 43-46 mV/decade (entries 19 - 21, Table 4a.T_1) and are defined as E1, E2 and E3 for further studies.

Effect of pH

Effect of pH on the electrode response was studied at 2 x 10^{-2} M $AgNO_3$ solution. pH was adjusted with 0.1 N HNO_3 and 0.1 N NaOH solutions as per requirement. As it is seen from Figure 4a.F_2, the potential response for E1, E2 and E3 remains uniform between the pH ranges 3.5 - 8.0, 4.0 - 8.0 and 4.0 – 7.5, respectively. At pH below this range, the emf gets altered probably due to protonation of the ionophore and above this pH range due to formation of AgOH and Ag_2O.

Calibration Curve, Response Time and Lifetime of Ag(I) Selective Electrode

Calibration curves were drawn for the electrodes E1-E3 over a concentration range 10^{-6} - 10^{-1} M with an inner filling solution of Ag^+ ($1x10^{-1}$M) that show reproducible slopes of 45, 43, and 46 mV/decade, respectively. For five repeated experiments, the standard deviation of the slope is ± 0.5 mV. Representative calibration curves are shown in Figure 4a.F_3. The workable concentration range for all the electrodes is $1x10^{-4}$ to 10^{-1} M for Ag^+

ions. The limit of detection was calculated according to IUPAC recommendations (Buck et al., 1994) from the intersection of the two extrapolated linear portions of the curves.

Detection limits were also determined by potentiometric titrations of Ag^+ against KI. Potentiometric titrations of Ag^+ (10^{-2}, 10^{-3}, 10^{-4}, 10^{-5} M) ions against KI (10^{-1}, 10^{-2}, 10^{-3} and10^{-4} M) were carried out using the proposed Ag-ISE as an indicator electrode. The potential break is usually poor in dilute solutions near the end point, probably due to weak ionophore–metal ion interactions. Detection limits were determined from potentiometric titration curves. A sharp change in slope of the curve represents the equivalence point of the titration. Titration curves for the solution more dilute than the detection limit of an electrode shall not show a sharp change in a slope at the equivalence point. Hence, the concentration of the primary ion below which a typical potentiometric titration curve is not obtained indicates the level of detection limit by the electrode. Such detection limits are more accurate than those obtained by conventional methods because absolute values of emf are not required for these type of determinations. They are more reliable and accurate than those obtained by applying the calibration curve method, which exhibits an irregular curve at lower concentrations. If the electrode is not sensitive at lower concentrations there will be no change in the emf observed in the equivalence point region and the titration curve goes parallel to the X-axis of the curve (Figure 4a.F_{4a}, 4a.F_{4b} and 4a.F_{4c}). The response time of the electrodes E1-E3 is <15 seconds and remains unchanged on the measuring potentials from low to high concentrations. However, for concentrations beyond the lower detection limit, the response time increases to > 60 seconds. The lifetime for electrodes E1-E3 is about four months. During this time the detection limits of the electrodes remain almost constant and the slope of the calibration curve varies between ± 2 mV of the original value. Electrodes were stored in distilled water when not in use for a short period. For long period storage (like for a month and so), the electrode is required to be immersed in 0.1 M solution of the primary ion.

Potentiometric Selectivity Coefficient

The selectivity coefficients were determined by fixed interference and matched potential methods. In fixed interference method, a 1x10^{-3} M concentration of interfering ions was used for calculating the selectivity coefficient values. In the matched potential method, selectivity coefficients are defined as ratio of the primary ion concentration to the interfering ion concentration that gives the same potential change with a reference solution. The change in potential must be produced in a constant initial background reference solution of the primary ion (10^{-4} M) and must be the same in both cases.

It is seen from Table 4a.T_2 that the L2 based electrode shows better values of selectivity coefficients for almost all the interfering ions (by MPM). Further, the L1 based electrode shows better selectivity for Ag^+ than the L3 based electrode. The selectivity coefficient values by FIM do not represent a regular trend for the choice of ionophore. So, MPM is a better technique to determine the selectivity coefficients. Mercury is known to interfere in the determination of Ag^+ ions. In these proposed electrodes, the level of interference of Hg^{2+} is the same as that of other bivalent ions, like Cd^{2+}, Zn^{2+} and Pb^{2+}. Moreover, the interference of Hg^{2+} is the least for the L2 based electrode in comparison of other two derivatives. Selectivity data indicate that values are of the order, of 10^{-2} for divalent and trivalent metal ions (except Na^+, and K^+). Therefore, the electrode can be used for the determination of Ag^+ ions in the presence of certain interfering ions.

Effect of Electrode Response in Mixed Solvent Medium

The working nature of the electrode was also studied in mixed solvent media using methanol-water, acetone-water and acetonitrile-water mixtures. The membrane showed satisfactory response to Ag^+ ions in mixed solvent medium containing up to 30% (V/V) non-aqueous content (Table 4a.T_3). The working range of concentration (10^{-4} to 10^{-1} M) is observed in aqueous medium while the slope has considerably improved values and shows a Nernstian behavior. This is due to the changed sheath of solvent around the primary ion Ag^+. In the aqueous medium H_2O molecules form a stable complex with Ag^+ ions, while in mixed solvent media, the solvent sheath includes solvent molecules as well, thereby, reducing the resistance due to a decreased dielectric constant of the solvent mixture while reaching the ionophore. The best results are observed for 20% non-aqueous content.

Potentiometric Titration

Potentiometric titrations are among the most accurate methods because the potential follows the actual change in activity and therefore, the end point will often coincide directly with the equivalence point. A large potential break will occur at the equivalence point. Since we are interested only in the potential change, the correct potential of the indicating electrode need not be known.

Direct and Reverse Titration of Ag^+ Ions

Known concentrations of Ag^+ ions solution were titrated against a standard solution of iodide ions. Figure 4a.F_{5a}, 4a.F_{5b} and 4a.F_{5c} show the observed potential break at an 1:1 complex formation between the metal ions and I^- ions. The same observations were made during the reverse titration.

Potentiometric Titrations of Binary and Ternary Mixtures of Ions

50 mL of solution containing $1x10^{-3}$ M Ag^+ ions in binary, ternary and multi-ion mixtures was titrated against standard solution of KI (Figures 4a.F_{7a}, and 4a.F_{7b}). In each titration only one break in EMF corresponding to AgI complex formation was observed. The titration shows an equivalence point corresponding to the formation of 1:1 complexes with I^- ions. No break in titration was observed corresponding to the complex formation with Hg^{2+} ions. It indicates that the electrode does not respond to Hg^{2+} ions.

These results show that mercury is either not interfering or the extent of interference is too small to be measured in silver determination.

Binary Titrations (with Hg^{2+} ions)

Equimolar mixture of Ag^{+} and Hg^{2+} ions were titrated against I^{-} ions and the Figure $4a.F_{6a}$ shows the equivalence point corresponding to 1:3 equivalents of iodide ions. It is clearly indicated that 1/3 rd (1 equivalent) of the reagent is used up in precipitating the Ag^{+} ions and 2/3rd (2 equivalents) is used up for precipitating the Hg^{2+} ions. However, the extent of Hg^{2+} of interference is quite predictable because the inflection in the curve is obtained corresponding to the 1:3 equivalence point.

Further, titrations were done by taking different amounts of Hg^{2+} ions (Figures $4a.F_{6a}$, $_{6b}$ and $_{6c}$). When it is taken in concentration less than that of Ag^{+} ions, no interference is observed and the titration curve obtained is exactly the same to that as if Hg^{2+} is not present at all. This is due to its high selectivity for silver ions. This is further established from the titration curve where the emf remains stable in the pre-equivalence region of the curve and does not change even when the stoichiometric amount of Hg^{2+} is completely precipitated and Ag^{+} starts forming precipitates with iodide ions. During this part of titration, first Hg^{2+} is precipitated because of its lower (Ksp $Hg_2I_2 = 10^{-51}$) value than Ag^{+} ions (Ksp $AgI = 10^{-48}$). This indicates that the ionophore is not able to distinguish between Hg^{2+} and Ag^{+} ions when concentration of Hg^{2+} and Ag^{+} are the same. As the concentration of interfering ion is decreased (i.e., Hg^{2+} is at lower concentration than Ag^{+} ions) the inflexion point of titration is obtained only for the concentration corresponding to silver ions. This shows that the presence of Hg^{2+} ions in the solution is not detected and measured by the electrode. It establishes the great selectivity of the Ag^{+}-selective electrode in presence of Hg^{2+} ions.

Ternary and Quaternary Titrations

Silver ions were also titrated against iodide ions in presence of Cu^{2+}, Hg^{2+} and Pb^{2+} ions as binary, ternary and quaternary mixtures (Figures 4a.F_{7a}, and 4a.F_{7b}). During potentiometric titrations in presence of Hg^{2+} ions, equivalence points were observed corresponding to the iodide ion concentration. The iodide required for Ag^+ is one equivalent and Hg^{2+} ions 2 equivalents as reported above in binary titrations. This shows that there is interference only due to the presence of Hg^{2+} and no interference of Cu^{2+} and Pb^{2+} ions was observed. These electrodes behave in a highly selective manner for Ag^+ ion determinations.

Potentiometric Determinations of CN^- and SCN^-

The proposed electrodes can be used as probe for the determination of anions, like SCN^- and CN^- ions with which Ag^+ forms very stable complexes. Titration curves were plotted and are shown in Figures 4a.F_{8a} and 4a.F_{8b}. The difference of these titrations from those with I^- ions was that the curves were half-sigmoid in shape and not true sigmoid. These curves were, however, good enough to locate the equivalence point of the titration. The break in slopes was corresponding to the 1:1 complex formation. All the three ionophores show a similar behavior during the potentiometric titrations. 50 mL of $1x10^{-3}$ M of each anion solution was titrated separately against $1x10^{-2}$ M Ag^+ solution. The potential break was observed at the 1:1 complex formation of metal anion interactions.

Potentiometric Determinations of Cl^-, Br^- and I^- Contents in a Mixture

50 mL of a mixture of halides each having $1x10^{-3}$ M concentration was titrated against $AgNO_3$ solution of $1x10^{-2}$ M. Figure 4a.F_9 shows three breaks in the curve corresponding to precipitation of Ag^+ with each ion in the ratio 1:1. The first break is for I^-, the second and third breaks in curve are for Br^- and Cl^-, respectively. This trend can be explained on

the basis of the solubility product. The K_{sp} values are in the order $I^- < Br^- < Cl^-$. Iodide ions precipitate first and then, bromide and chloride ions follow.

Table 4a.T$_1$: Optimization of membrane ingredients

Sl. No	Ionophore/ Electrode	PVC, (Wt%)	Plasticizer (Wt%)	Ligand (Wt%)	Slope (mV/ decade)	Detection limit [M]
1	L1	33	66	1	7	1.5×10^{-4}
2		33	65	2	10	1.0×10^{-4}
3		33	64	3	23	6.3×10^{-5}
4		33	63 (DBP)	4	35	3.9×10^{-5}
5		33	62	5	19	1.5×10^{-4}
6		33	61	6	16	1.2×10^{-4}
7	L2	33	66	1	8	1.0×10^{-4}
8		33	65	2	12	1.0×10^{-4}
9		33	64 (DBP)	3	36	2.5×10^{-4}
10		33	63	4	24	1.0×10^{-5}
11		33	62	5	22	1.2×10^{-4}
12		33	61	6	20	3.9×10^{-4}
13	L3	33	66	1	25	1.2×10^{-5}
14		33	65	2	29	1.6×10^{-4}
15		33	64	3	32	1.2×10^{-4}
16		33	63 (DBP)	4	40	5.0×10^{-5}
17		33	62	5	34	1.0×10^{-4}
18		33	61	6	30	6.3×10^{-5}
19	E1	33	63 (NPOE)	4	45	6.0×10^{-5}
20	E2	33	64 (NPOE)	3	43	1.0×10^{-4}
21	E3	33	64 (NPOE)	4	46	1.0×10^{-4}

Table 4a.T$_2$: Potentiometric selectivity coefficient by FIM and MPM

Interfering ions	$\log K^{Pot}_{Ag^+,M^{n+}}$					
	L1		**L2**		**L3**	
	FIM	**MPM**	**FIM**	**MPM**	**FIM**	**MPM**
Na$^+$	-1.2	-1.3	-1.4	-1.7	-1.0	-1.1
K$^+$	-1.1	-1.4	-1.0	-1.9.	-1.0	-1.2
Mg^{2+}	-1.8	-2.0	-2.0	-2.1	-1.9	-1.7
Ca^{2+}	-2.4	-1.9	-1.9	-2.1	-2.1	-1.8
Sr^{2+}	-2.1	-2.0	-2.4	-2.1	-2.0	-1.9
Co^{2+}	-2.3	-2.0	-2.4	-2.2	-2.0	-1.9
Ni^{2+}	-2.3	-2.0	-2.1	-2.2	-2.1	-1.8
Cu2+	-2.3	-1.9	-2.4	-2.2	-2.2	-1.9
Cd^{2+}	-2.5	-1.9	-2.5	-2.2	-2.0	-2.0
Zn^{2+}	-2.5	-2.2	-2.5	-2.2	-2.0	-2.0
Pb^{2+}	-2.3	-1.8	-2.5	-2.2	-2.3	-1.7
Hg^{2+}	-2.5	-1.9	-2.5	-2.2	-2.5	-1.8
Fe^{3+}	-2.9	-2.0	-2.5	-2.3	-2.8	-2.1

(FIM: Primary ion concentration varied from 1x10^{-1}M to 1x10^{-6}M, interfering ion concentration is 1x10^{-2}M

MPM: Primary ion concentration 1x10^{-2} –1x10^{-4}M, reference solution, 1x10^{-4}M and interfering ion concentration added is 1x10^{-2}M)

Table 4a.T$_3$: Effect of mixed solvent media on the electrode response

Mixed solvent	**Percentage (v/v) in water**	**Slope, mV/decade**			**Detection limit [M]**		
		L1	**L2**	**L3**	**L1**	**L2**	**L3**
Methanol	10	52	44	50	$4x10^{-5}$	$4x10^{-5}$	$1x10^{-4}$
	20	54	47	55	$5x10^{-5}$	$5x10^{-5}$	$1x10^{-4}$
	30	49	46	52	$5x10^{-5}$	$6x10^{-5}$	$6x10^{-5}$
Acetonitrile	10	55	48	58	$1x10^{-4}$	$8x10^{-5}$	$5x10^{-5}$
	20	52	55	48	$5x10^{-5}$	$6x10^{-5}$	$1x10^{-4}$
	30	47	49	44	$1x10^{-4}$	$6x10^{-5}$	$1x10^{-4}$
Acetone	10	53	53	49	$4x10^{-5}$	$4x10^{-5}$	$4x10^{-5}$
	20	60	54	54	$5x10^{-5}$	$5x10^{-5}$	$6x10^{-5}$
	30	52	48	46	$6x10^{-5}$	$8x10^{-5}$	$1x10^{-4}$

Table 4a.T$_4$: Comparison of the behaviour of various silver selective supramolecules with proposed ligands

Sl No	Measuring range [M]	Slope mV/ decade	pH range	Lifetime (months)	log $K^{Pot}_{Ag+,B}$	Method of detection limit determination	Used for anion determination	References
1	10^{-5}-10^{-1}	Nernstian	1 – 6	6	sufficiently selective	From calibration curve	NR	(Mahajan et al., 2002)
2	5×10^{-6}-10^{-1}	Nernstian	2.5–6.5	NM	highly selective	From calibration curve	NR	(Chen et al., 2000)
3	2.7×10^{-2} – 1.9×10^{-6}	near-Nernstian	2.5 – 7	NM	sufficiently selective	From calibration curve	NR	(Mashhadizadeh et al., 2006)
4	10^{-4} –10^{-1}	Nernstian	--	NM	sufficiently selective	From calibration curve	NR	(Kimura et al., 2000)
5	10^{-6} – 10^{-1}	Nernstian	2.5–8.5	3	highly selective	From calibration curve	NR	(Amini et al., 2003)
6	10^{-5} – 10^{-1}	Nernstian	1- 10	NM	sufficiently selective	From calibration curve	NR	(Mahajan et al., 2003)
7	1×10^{-6} - 1×10^{-2}	near-Nernstian	2.8-12	NM	sufficiently selective	From calibration curve	NR	(Lim et al., 2002)
8	$1x10^{-5}$ – $1x10^{-1}$	pseudo-Nernstian	4.5-8.0	4-5	highly selective	Calibration curve and Potentiometric titration method	Cl^-, Br^-, I^-,CN^-, SCN^-	Proposed work

NM: not mentioned, NR: not reported

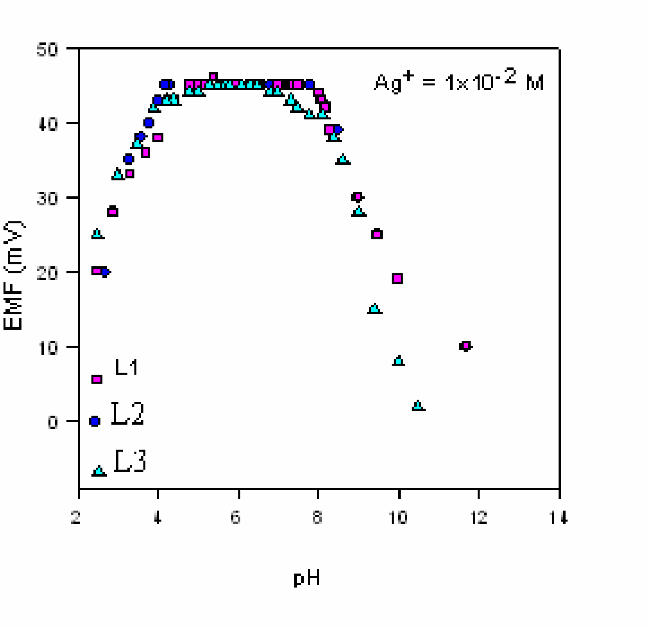


Figure 4a.F$_2$: Effect of pH on the potential response of E1, E2 and E3 electrodes

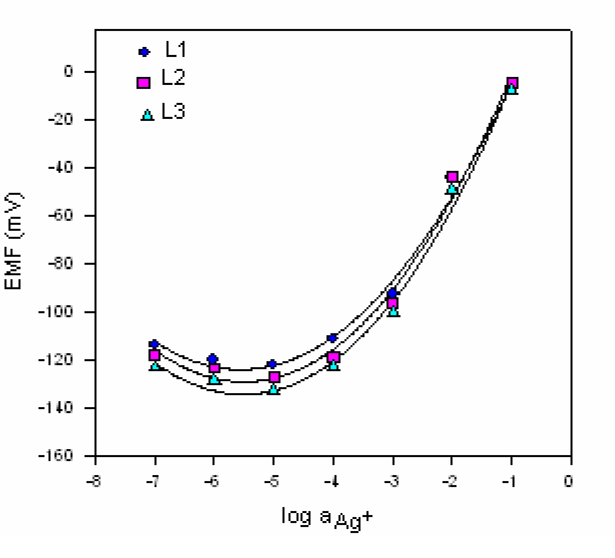


Figure 4a.F$_3$: Calibration curves for E1, E2 and E3 electrodes

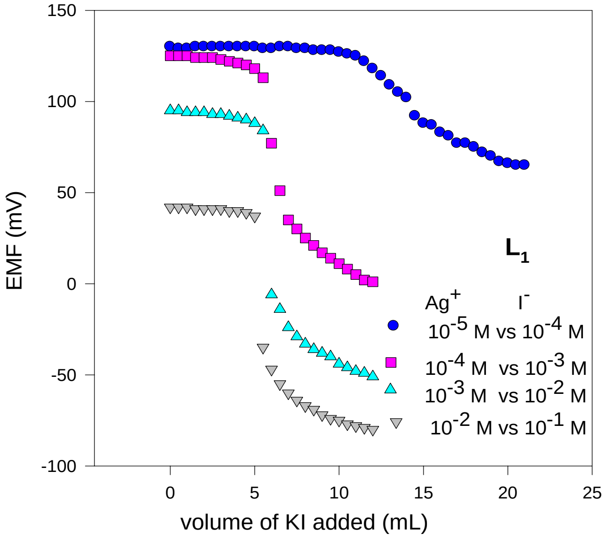


Figure 4a.F$_{4a}$: Sensitivity of potentiometric titrations using E1 and their detection limits

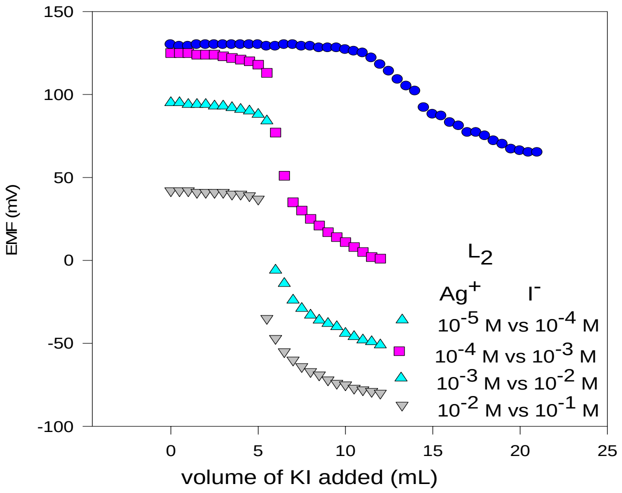


Figure 4a.F$_{4b}$: Sensitivity of potentiometric titrations using E2 and their detection limits

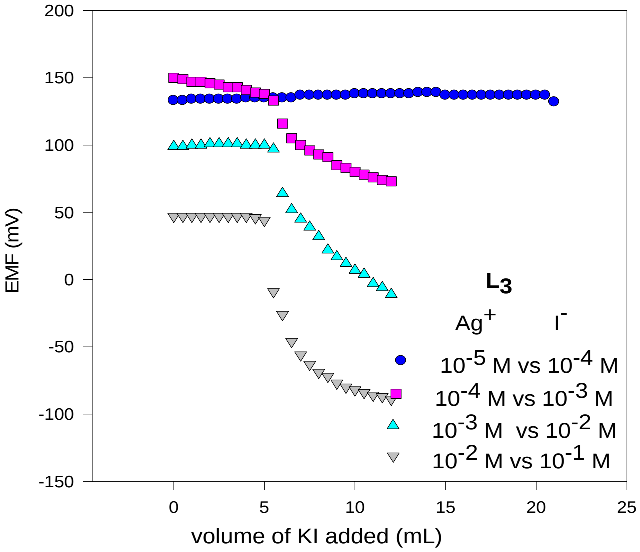


Figure 4a.F$_{4c}$: Sensitivity of potentiometric titrations using E3 and their detection limits

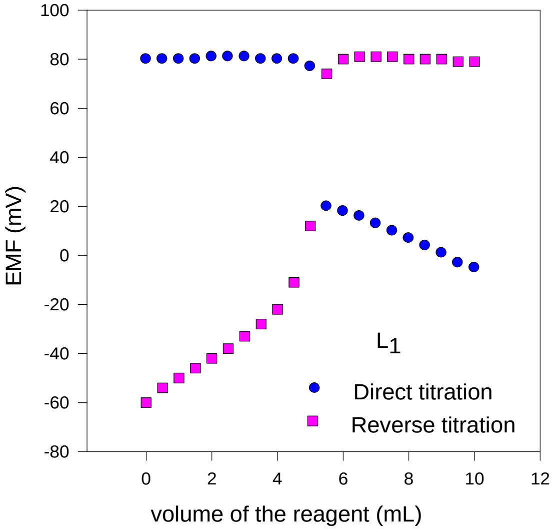


Figure 4a.F$_{5a}$: Potentiometric titrations (direct and reverse) of Ag^+ ions versus Cl^- ions using E1 electrode

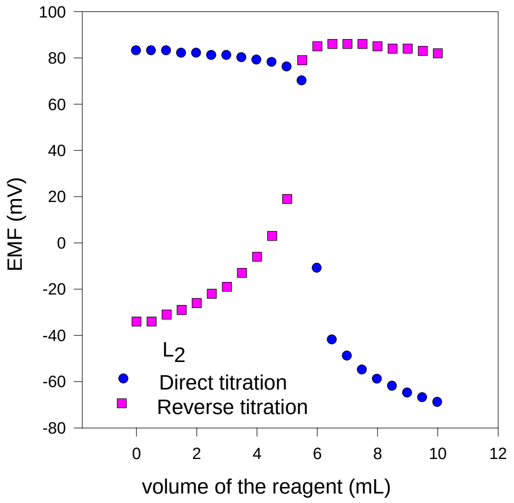


Figure 4a.F$_{5b}$: Potentiometric titrations (direct and reverse) of Ag^+ ions versus Cl^- ions using E2 electrode

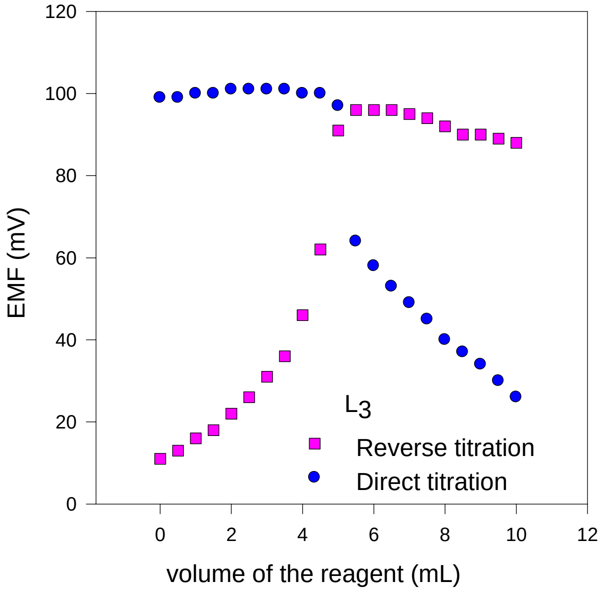


Figure 4a.F$_{5c}$: Potentiometric titrations (direct and reverse) of Ag^+ ions versus Cl^- ions using E3 electrode

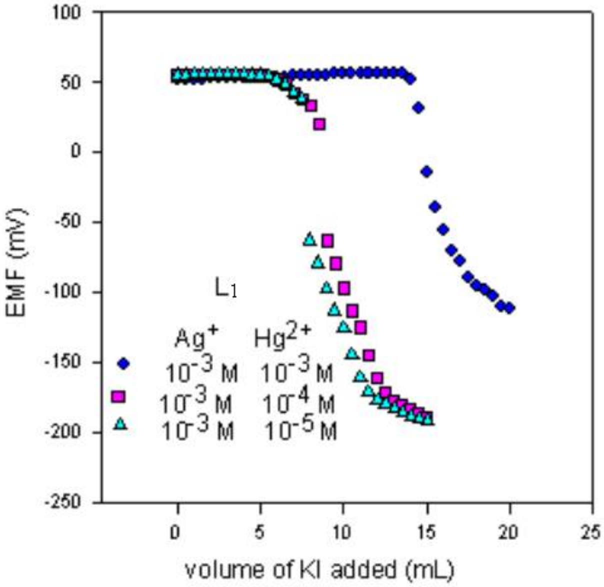


Figure 4a.F$_{6a}$: Potentiometric titration of Ag^+ ions with I^- ions in presence of Hg^{2+} ions using E1 electrode

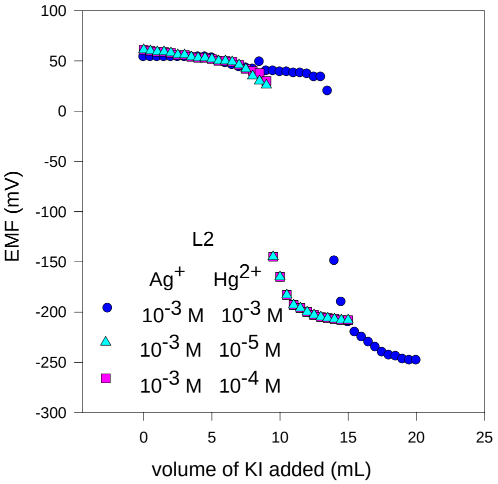


Figure 4a.F$_{6b}$: Potentiometric titration of Ag^+ ions with I^- ions in the presence of Hg^{2+} ions using E2 electrode

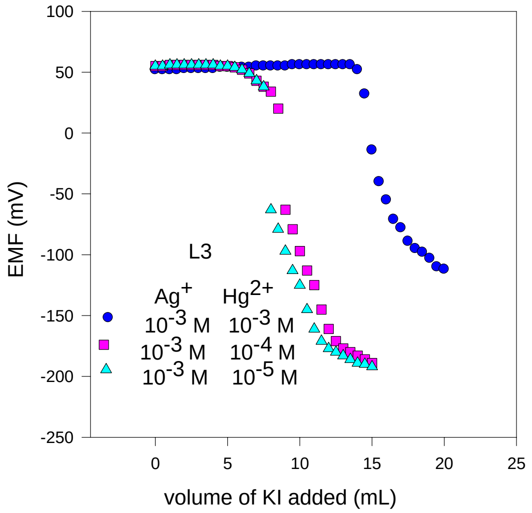


Figure 4a.F$_{6c}$: Potentiometric titration of Ag$^+$ ions with I$^-$ ions in the presence of Hg^{2+} ions using E3 electrode

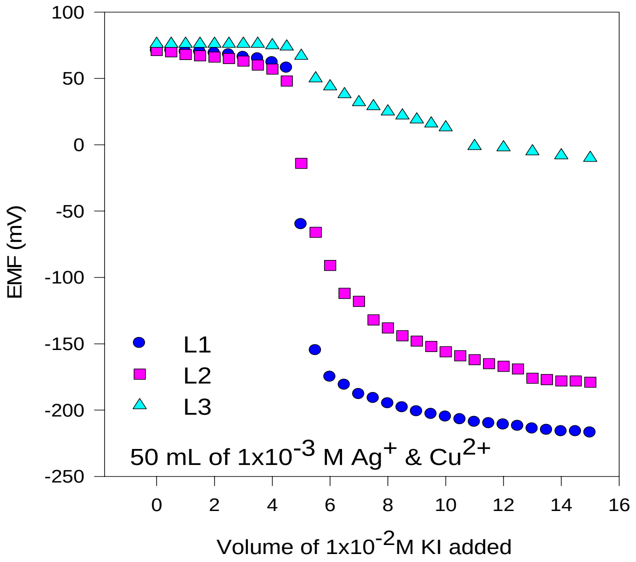


Figure 4a.F$_{7a}$: Potentiometric titrations of Ag$^+$ ions with I$^-$ ions in the presence of Cu^{2+} ions (interfering ions) using E1, E2 and E3 electrodes

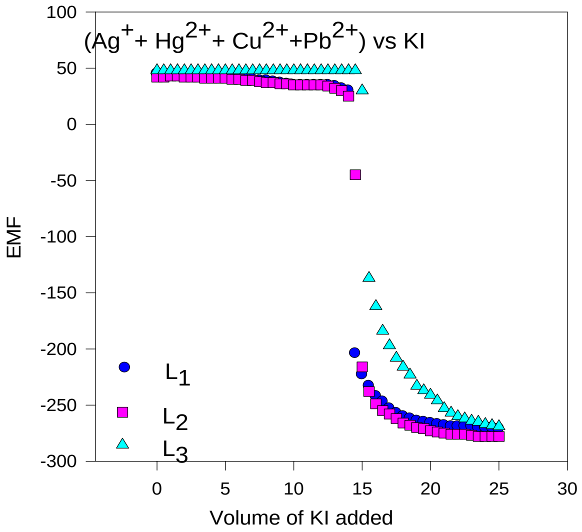


Figure 4a.F$_{7b}$: Potentiometric titrations of Ag^+ ions with I^- in the presence of interfering metal ions ($Cu^{2+,}$ Hg^{2+}, Pb^{2+} ions) using E1, E2 and E3 electrodes

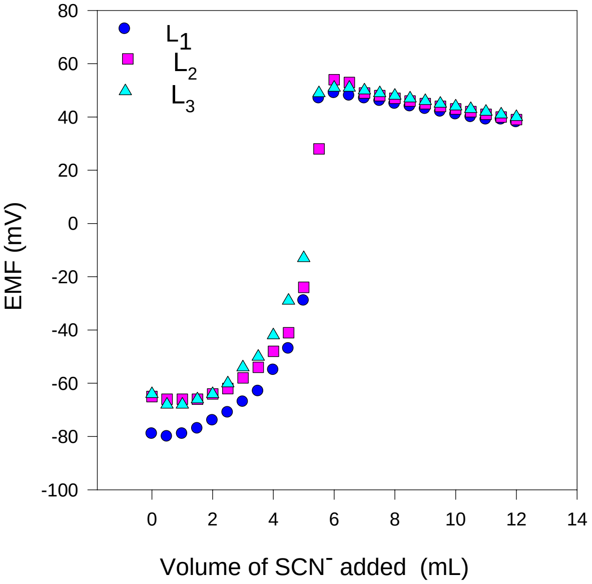


Figure 4a.F$_{8a}$: Potentiometric titrations of Ag^+ ions ($1x10^{-2}$ M) with SCN^- ions ($1x10^{-3}$ M) using E1, E2 and E3 electrodes

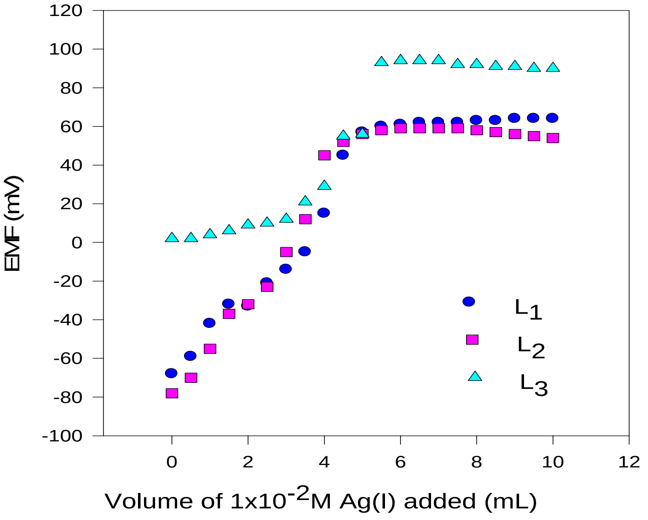


Figure 4a.F$_{8b}$: Potentiometric titrations of Ag$^+$ (1x10^{-2} M) ions with CN$^-$ (1x10^{-3} M) using E1, E2 and E3 electrodes

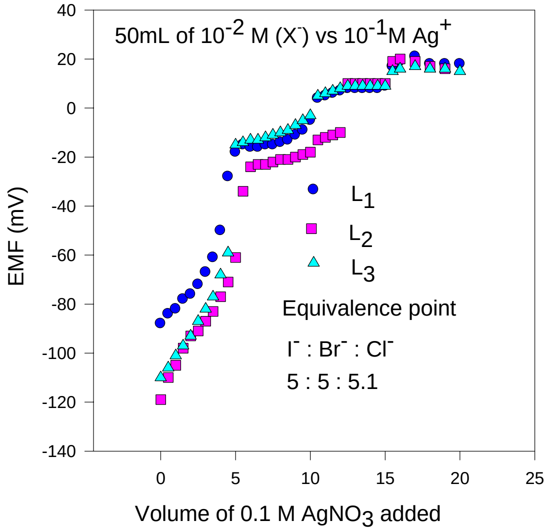


Figure 4a.F$_9$: Potentiometric titrations of a mixture of halide ions with Ag$^+$ ions using E1, E2 and E3 electrodes

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4b. Liquid-Membrane Based Electrode Containing an Electroactive Material Selective for Cobalt (II) Ions

Introduction

Cobalt in trace amounts is essential for human life. Cobalt has also been used in treatment for anemia because it causes red blood cells to be produced. Toxicity of cobalt is quite low compared to many other metals in soil. Exposure to very high levels of cobalt can cause health effects. Cobalt is widely distributed in the environment and the average abundance of cobalt in earth crust is 29 ppm, 1.0 to 14 ppm in soil, 0.2 ppm streams, 1 to10 ppm in ground water (Greenwood et al., 1984). Cobalt is considered essential for algae, some bacteria and for animals. Occupational toxicology of cobalt, hygienic and epidemiologic aspects, and monitoring of cobalt poisoning are also topics of special interest. Cobalt is a metal with marked allergenic potential. Asthma, interstitial lung disease and combined asthma and alveolitis have been described as occupational health hazards. EDTA, DTPA, and N-acetyl-L-cysteine have been suggested as possible antidotes in cobalt intoxication (ATSDR ToxFAQs). Because of increased use of Co^{2+} and its hazardous effects on plants and humans its determination in the environment is important.

The available methods of the low-level determination of Co^{2+} ions in solution include ICP-MS, ICP-AES spectrofluorometer, isotope dilution mass spectrometer, and neutron activation analysis, etc., (Chao et al., 2003, Matsuoka et al., 2006, Steffan et al., 1993, Kiado et al., 1991, Beer et al., 1993) are also used in some laboratories. These methods are either time-consuming involving multiple sample analysis or too much expensive for most analytical laboratories.

Potentiometric ion-selective electrode are known for many metal ions and as a low-cost tool for the selective, sensitive and rapid determination of a vast variety of analytes in different fields of application. This has led to an increasing interest in the development of the sensors for several ionic species, increasing the number of available electrodes and microelectrodes over the last few years. The following neutral carrier type ISEs have been used for Co^{2+} determination such as Singh et al., 2006 reported 2,3,4-pyridine-1,3,5,8,11,14-hexaazacyclohexadeca-2-ene and 5-amino-3-methylisothiazole, (Gupta et al., 2006), *N,N′*-bis(salicylidene)-3,4-diaminotoluene (Mashhadizadeh et al., 2002) (2-mercapto-4-methylphenyl)-2-benzamido-3-phenyl-thiopropenoate.

The aim of this study is the design of a highly sensitive and selective membrane electrode for Co^{2+} determination using 14-membered dioxo-cyclam derivative (Figure 4b. F_1).

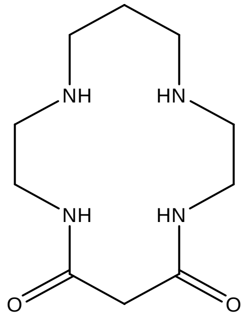

Figure 4b.F_1: Structure of the ionophore for a Co^{2+} ISE

Experimental

Reagents, Preparation of Electrodes and Potential Measurements

A number of liquid-membrane based electrodes were prepared according to the previously reported method and potential measurements as discussed in chapter 3 methodology.

Results and Discussion

Investigation of Complexation

Three different experiments have been done to monitor the interaction between the metal ion and neutral molecule as well as their complexation. Due to the rigid structure of the 14-membered dioxo-cyclam derivative (I) and the presence of four nitrogen atoms in the cavity, macrocyclic diamide seemed to be selective for soft transition and heavy metal ions. Thus, before proceeding for any potentiometric studies, photometric and conductometric studies were done to determine the complexation behavior of the metal/ligand system. In this context, picrate extraction studies show a maximum ligand complexation with Co^{2+}ions ($Co^{2+} > Cu^{2+} > Pb^{2+} > Ni^{2+} > Ag^{+}$). Log K_f values obtained by conductometric method also confirm this trend of complexation.

In order to estimate the complex stoichiometry of the metal-ionophore, the mole ratio method was applied (Obradovic et al, 2005). A series of solution was prepared with a constant concentration/volume of Co^{2+} ($1x10^{-3}$ M) and a variable concentration of the ligand. The curve of UV absorbance change vs ligand/metal ion ratio at a ligand concentration of $1x10^{-3}$ M confirms the 1:1 complex formation. The trend of this curve (after 1:1, a continuous increase of the absorbance of the complex with increasing ligand concentration) also indicates that a complex of lower stability is formed. According to Prestch et al., in 1974, the stability of the complex between the complex and metal ion should be intermediate and not necessarily the highest one. Further, picrate extraction was done by taking a dichloromethane solution (5 mL) of ligand ($1x10^{-3}$ M) and 5 mL aqueous solution containing ($1x10^{-3}$ M) metal picrate, placed in a stoppered flask and shaken for around 1 hour at 25 ºC ±1 ºC (Nazarenko et al., 1994). The resulting mixture was allowed to stand for over night to complete the phase separation. The concentration of picrate ion remaining in the aqueous phase was then determined by spectrophotometer at 355 nm. Blank experiments have shown that no picrate extraction occurred in the absence of the ligand. The percentage of extraction of Co^{2+} and Cu^{2+} ions are 93% and 69%, respectively.

Calibration Curve

The ion-selective electrode was examined potentiometrically after proper conditioning in a 1.0 x 10^{-1} M solution of Co^{2+}. It is well understood that the sensitivity, linearity and selectivity obtained for a given ionophore depend significantly on the membrane composition and nature and amount of additive used (Amman et al., 1983, Moody et al., 1988, Ying et al., 1997, Badr et al., 1995, Bakker et al., 1994, Kim et al., 1998). The calibration curve was plotted for different concentrations of Co^{2+} and was varying from 1.0x10^{-10} M to 1.0x10^{-1} M (Figure 4b.F_2). From the Table 4b.T_1, it is clear that the electrode containing PVC, (I), plasticizer and lipophilic additive in the ratio of 33:1:65:1, exhibits good response characteristics in terms of slope, detection limit, working concentration range and response time. Electrode E-4 (Table 4b.T_1) shows reproducible Nerstian response with a slope 30 mV/decade (± 0.5 mV standard deviation for 5 sets of measurements) in the concentration range from 1.0 x 10^{-5} M to 1.0 x 10^{-1} M of Co^{2+} with a detection limit of 5.0 x 10^{-7} M and a response time of ~15 seconds.

Effect of Membrane Solvent and Lipophilic Additive

Any membrane electrode, based on the principle of concentration cell, imparts some potential for different concentrations of the electrolyte solution. But to enhance their electrode characteristics the membrane solvent plays a very important role. Thus, taking different aspects of plasticizer into the consideration, the amount of plastisizer was optimized. The potentiometric response of the membrane ion-selective electrode based on neutral ionophores is greatly influenced by the polarity of the membrane medium, which is defined by the dielectric constants of the major membrane components (Bakker et al., 1997, Ammann et al., 1985, Yang et al., 1987, Morf, 1981). The influence of the nature of plasticizer on the Co^{2+} response was studied on electrodes containing three types of plasticizers having different dielectric constants, namely, DBP, DOP and o-NPOE. As shown in Table 4b.T_1, o-NPOE with the highest dielectric constant in the series resulted in the best sensitivity of the potential responses. It should be noted that nature of the plasticizer affects not only the dielectric constant of the membrane phase but also the mobility of ionophore molecules and the state of ligands (Bakker et al., 1997, Ammann et al., 1985, Yang et al., 1987, Morf, 1981).

The use of lipophilic additives as membrane constituent also significantly influences the performance characteristics of a membrane electrode (Bakker et al., 1997, Ammann et al., 1985, Masoda et al., 1998, Lindner et al., 1988, Rosatzin et al., 1993, Schaller et al., 1994). It is clear from Table 4b.T_1 that the membrane electrode incorporating KTClPB as a liphophillic additive improves the sensitivity of the Co^{2+} electrode considerably (with a slope of 30 mV/decade). Whereas, in the absence of a proper additive, the sensitivity of the PVC- membrane based ISE on (I) is quite low. As it is obvious from Table 4b.T_1, 4b.E_{14} with a PVC: (I):NPOE:KTClPB percent ratio of 33:1:65:1 resulted in Nernstian behavior of the membrane electrode over a wide concentration range.

Effect of pH

The influence of pH on the electrode response was studied at two different concentrations, $1x10^{-2}$ M and $1x10^{-3}$ M of Co^{2+} ions. The pH was adjusted with HNO_3 0.1 N and NaOH 0.1 N solutions as per requirement. As it is seen from Figure 4b.F_3, the potential response remains constant between the pH range 5.0 - 8.0, beyond which the potential changed considerably. At a pH below this range, the emf gets altered probably due to protonation of the ionophore and above this pH range, due to the formation of some hydroxyl complexes of Co^{2+} ions in the solution.

Potentiometric Selectivity Coefficients

The effect of metal ions other than the primary ion on the response behavior of the electrode is measured in terms of potentiometric selectivity coefficients. In this work, the selectivity coefficients were determined by fixed interference (FIM) and matched potential (MPM) methods (Buck et al., 1994, Umezawa et al., 1995). The results are summarized in Table 4b.T_2. For almost all interfering ions, selectivity coefficients obtained by both methods are in close agreements. As seen from Table 4b.T_2, the negative sign of each value implies a better selectivity of the electrode for the primary ion in the presence of other interfering ions in the solution. Table 4b.T_2 shows that, for all divalent ions, the selectivity coefficients are in the order of 10^{-2} or smaller, indicating that they would not significantly interfere in the determination of the Co^{2+} ion-selective electrode.

Effect of Mixed Solvent Medium

The working nature of the electrode was also studied in mixed solvent media using methanol-water, acetone-water and acetonitrile-water mixtures. The membrane showed a satisfactory response to Co^{2+} ions in partially non-aqueous medium containing upto 30% (V/V) non-aqueous content. The results are summerized in Table 4b.T_3. The best results are observed at 30% non-aqueous medium.

Analytical Applications

Potentiometric Titration with EDTA

The electrode was used as an indicator electrode in the potentiometric titration of Co^{2+} solution. 30 mL of 1.0×10^{-2} M Co^{2+} solution was titrated against 1.0×10^{-1} M EDTA solution (Figure, 4b.F_4). The pH of the medium is between 5-8 during the titrations. A very good inflection point, corresponding to Co^{2+}-EDTA stoichiometry, was observed which shows that this electrode can be used as an indicator electrode for the determination of Co^{2+} ions.

Table 4b.T$_1$:Optimization of membrane ingredients in the Co^{2+} ISE

E.N	**Components of the membrane (% w/w)**				**Slope (mV/decade)**	**Working concentration range (M)**	**Detection limit (M)**
	(I)	**PVC**	**Plasticizer**	**Anion-excluder**			
1	-	33	-	-	--	--	--
2	-	33	67	-	15	$1x10^{-3}$ –$1x10^{-1}$	$1x10^{-3}$
3	1	33	66	-	31	$1x10^{-5}$ – $1x10^{-1}$	$1x10^{-5}$
4	2	33	65	-	32	$1x10^{-6}$ – $1x10^{-1}$	$5x10^{-6}$
5	3	33	64	-	34	$1x10^{-6}$ – $1x10^{-1}$	$4x10^{-6}$
6	4	33	63	-	36	$5x10^{-6}$ – $1x10^{-1}$	$6.3x10^{-6}$
7	5	33	62	-	35	$1x10^{-5}$ – $1x10^{-1}$	$4x10^{-6}$
8	2	33	132	-	20	$1x10^{-5}$ – $1x10^{-1}$	$5x10^{-5}$
9	3	33	192	-	21	$1x10^{-5}$ – $1x10^{-1}$	$5x10^{-5}$
10	1	33	66	-	14	$1x10^{-5}$ – $1x10^{-1}$	$1x10^{-5}$
11	1	33	66	-	23	$5x10^{-5}$ – $1x10^{-1}$	$1x10^{-4}$
12	1	33	66	-	26	$5x10^{-5}$ – $1x10^{-1}$	$5x10^{-5}$
13	1	33	65.5	0.5	31	$5x10^{-6}$ – $1x10^{-1}$	$5x10^{-6}$
14	**1**	**33**	**65**	**1.0**	**30**	**$1x10^{-6}$ – $1x10^{-1}$**	**$5x10^{-7}$**
15	1	33	64.5	1.5	22	$1x10^{-5}$ – $1x10^{-1}$	$5x10^{-5}$
16	1	33	64	2.0	18	$5x10^{-5}$ –$1x10^{-1}$	$5x10^{-5}$

Table 4b.T_2: Selectivity coefficients for interfering ions by FIM and MPM on the Co^{2+} ISE

Interfering ions (B)	$\log K_{A,B}$	
	FIM	MPM
Na^+	-2.1	-2.0
K^+	-1.9	-2.0
Mg^{2+}	-2.0	-2.1
Ca^{2+}	-2.1	-2.2
Sr^{2+}	-2.2	-2.2
Pb^{2+}	-2.3	-2.4
Cu^{2+}	-2.1	-2.2
Ni^{2+}	-2.1	-2.2
Zn^{2+}	-2.0	-2.3
Cd^{2+}	-2.0	-2.2
Hg^{2+}	-2.1	-2.2
Fe^{3+}	-2.2	-2.2

Table 4b.T_3: Effect of mixed solvent media on the electrode response

Mixed solvent medium	Percentage (V/V)	Slope (mV/decade)	Detection limit (M)
water	--	31.0	5.0×10^{-7}
methanol:water	10:90	30.0	3.0×10^{-6}
	20:80	31.0	1.9×10^{-5}
	30:70	33.0	3.4×10^{-5}
	40:80	37.0	7.9×10^{-5}
acetone:water	10:90	31.5	6.3×10^{-6}
	20:80	32	3.1×10^{-5}
	30:70	31	5.0×10^{-5}
	40:60	35	7.9×10^{-5}
acetonitril:water	10:90	30	1.0×10^{-5}
	20:80	31.5	3.1×10^{-5}
	30:70	33	5.0×10^{-5}
	40:60	36	8.0×10^{-5}

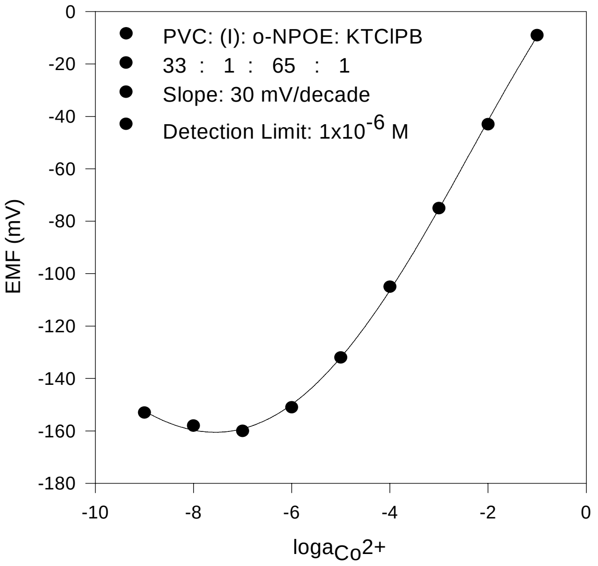

Figure 4b.F$_2$: Calibration curve of the Co^{2+} ISE

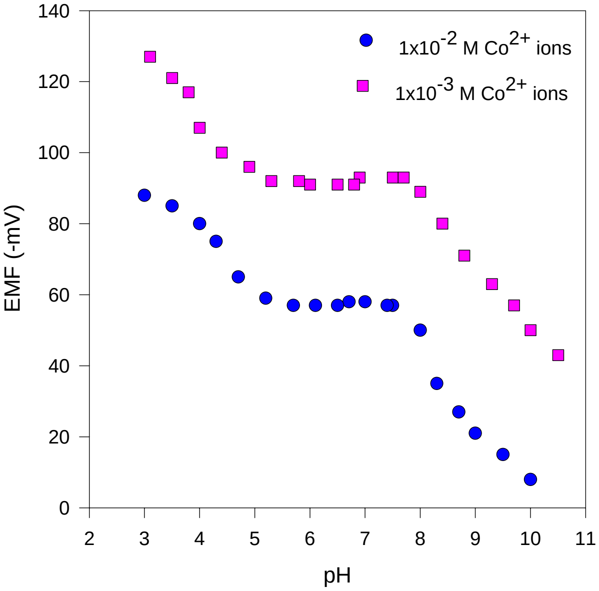

Figure 4b.F$_3$: Effect of pH on the Co^{2+} ISE

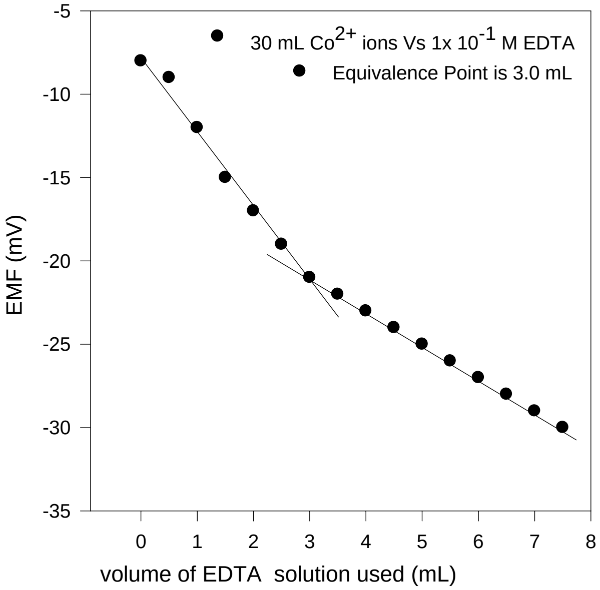

Figure 4b.F$_4$: Potentiometric titration of Co^{2+} ions (1x10^{-2} M) against EDTA (1x10^{-1} M) using Co^{2+} ISE

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4c. Liquid-Membrane Based Electrode for Copper Ions Incorporating *N,N'*-Bis(2-aminoethyl)-9-anthrylmethylmalonamide as Neutral Carrier

Introduction

Copper is essential to all living things and plays an important role in modern technology. Our bodies depend on copper for neurological activity, for creating our own internal heat, and for communication between and among cells. The recommended daily requirement of dietary copper is 1-2 mg L^{-1} (Greenwood et al., 1984). In fact, a deficiency in copper is one factor leading to an increased risk of high cholesterol and coronary heart disease (Prego et al., 2003, Manzoori et al., 2002, Kenduzler et al., 2003). On the other hand, copper toxicity in humans takes the form of stomach upset, nausea, and diarrhea. So, the copper levels should always be monitored, for environmental pollution control and industrial applications.

Trace level determination of copper is important. Most of the available methods require expensive equipment and manpower. Potentiometric determination of copper ions is inexpensive, provided a suitable ionophore is available that the can selectively detect copper ions. A number of electrodes selective for copper ions are available but most of them suffer from poor selectivity and chemical stability. Neutral ionophores contaning amide functional groups are found effective for the selective coordination for alkaline earth metal ions and some transitions metal ions (Craggs et al., 1997, Choi et al., 2006, Chen et al., 2006, Kim et al., 2005, Kim et al., 2003, Kataky et al., 1993, Shamsipur et al., 1999). The side arms possessing amide linkage offer suitable coordination sites for metal ions (Figure 4c.F_1). The distance between amide groups is also an important factor for ion selectivity, because the carbonyl oxygens and amine nitrogens in the amide groups as coordination sites in the side arms produce a specific configuration together with the spacer of the ionophore (O'Donnell et al., 1993, Borowitz et al., 1984, Erne et al., 1994, Zhukov et al., 1981, Erne et al., 1980, Güggi et al., 1977).

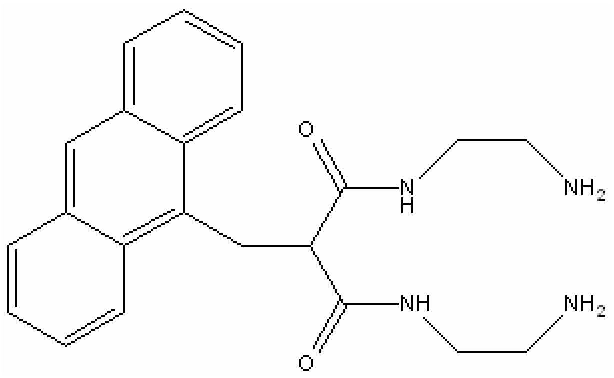

Figure 4c.F$_1$: Structure of the ionophore for Cu^{2+} ISE

Experimental

Reagents, Preparation of Electrodes and Potential Measurements

A number of liquid membrane based electrodes were prepared according to a previously reported method and potential measurements as discussed in chapter 3.

Results and Discussion

Membrane Characteristics

Composition of membranes based on *N,N'*-Bis(2-aminoethyl)-9-anthrylmethyl malonamide (I) in PVC matrix was optimized by varying the amount of ionophore and also by varying the nature of plasticizer so as to get a membrane which gives the reproducible response in terms of Nernstian slope, detection limit and working measuring range. It was found that the composition 33:2:64.5:0.5 (PVC:I:o-NPOE:NaTPB) exhibits Nernstian response (29.0 ± 1.7 mV per decade, standard deviation for 5 sets of measurements) over the concentration range $3.9x10^{-6}$ to $1.0x10^{-1}$ M of Cu^{2+} and a response time of 15 s (Electrode E_2 in Table 4c.T_1).

Calibration Curve, Response Time and Detection Limit

The electrode shows a linear response towards Cu^{2+} ions over a wide concentration range from $3.9x10^{-6}$ to $1.0x10^{-1}$M. The calibration curve has a slope of 29 mV/decade with a detection limit of $2.5x10^{-6}$ M, which was obtained from the intersection of two straight-line portions of the curve (Figure 4c.F_2). The increase in emf may be due to the possibility of interference from the anions due to failure of Donnan exclusion phenomenon at very low concentrations (Bakker et al., 1997). The response time is measured by recording the emf of the electrode as a function of time, when it is immersed in the solution to be studied. The estimated response time to get a stable potential was 10 s. The effect of inner solution concentration was also studied on the response behavior of the electrode. It was found that the variation in the concentration of the internal solution did not cause any significant difference in the emf, except for an expected change in the intercept of the resulting plots. $1.0x10^{-1}$ M internal solution concentration of copper nitrate was used for further studies.

Effect of pH and Mixed Solvent Media

The pH dependence was studied in the range of 2–12 by using two different concentrations ($1.0x10^{-2}$ and $1.0x10^{-3}$ M) of Cu^{2+} solutions. The pH value was adjusted by diluted hydrochloric acid (0.1 M) or sodium hydroxide (0.1 M), drop-wise as per requirment. It was observed that the electrode gave a steady response over a pH range of 3.0 to 7.5 (Figure 4c.F_3). The variation above and below this range is due to the formation of some hydroxy complexes of Cu^{2+} at higher pH values and interference from excess H^+ ions at lower pH values.

Electrode characteristics were also investigated in mixed solvent medium using methanol-water, acetone-water and acetonitril-water mixtures (Table 4c.T_2). It was found that the membrane electrode worked well up to 20% (v/v) non-aqueous content without showing any significant change in the working concentration range or slope.

Potentiometric Selectivity Coefficient

The most desirable quality of an ion-selective electrode is to detect the primary ion in the presence of other ions in the same solution. This quality of electrode is termed as the selectivity coefficient. Selectivity coefficients were evaluated by two different methods viz., fixed interference method (FIM) and matched potential method (MPM) (Buck et al., 1994 and Umezawa et al., 1995). The interfering ion concentration was fixed at $1x10^{-2}$ M in case of FIM. In case of MPM a specified amount of primary ions is added to a reference solution and the membrane potential is measured. In a separate experiment, interfering ions are successively added to an identical reference solution until the membrane potential matches with that one obtained before with the primary ions. The MPM based selectivity coefficient is then defined by the ratio of the primary to interfering ion activities. From results presented in Table 4c.T_3 it is clear that there are no serious interferences from the common ions in both cases.

Analytical Applications

Potentiometric Titration with EDTA

A direct titration of a Cu^{2+} solution (10 mL of $1x10^{-2}$ M) against EDTA ($1x10^{-1}$M) was carried out and the emf is plotted in Figure 4c.F_4. The equivalence point confirms 1:1 stoichiometry of the chemical reaction taking place in the solution and this electrode can be used as an indicator electrode for the determination of Cu^{2+} potentiometrically under laboratory conditions.

Determination of Cu^{2+} in Real Life Samples

The electrode was applied for the direct determination of Cu^{2+} in brass and tea leaves samples. The tea leaves sample was prepared as per procedure given by Ganjali et al., 2001. The results obtained show a satisfactory agreement with those obtained by AAS. This good agreement shows that the proposed membrane electrode may be used for Cu^{2+} determination in real life samples.

Table 4c.T$_1$: Optimization of membrane ingredients in the Cu^{2+} ISE

E. No.	Composition (%)			Slope (mV/dec)	Concentration range (M)	Detection limit (M)
	PVC	Plasticizer	Ionophore (I)			
E-1	33	66 (NPOE)	1	23.5	$3.1x10^{-4}$ to $1.0x10^{-1}$	$1.5x10^{-4}$
E-2	33	65 (NPOE)	2	29.0	$3.9x10^{-6}$ to $1.0x10^{-1}$	$2.5x10^{-6}$
E-3	33	64 (NPOE)	3	26.0	$6.3x10^{-5}$ to $1.0x10^{-1}$	$3.1x10^{-5}$
E-4	33	63 (NPOE)	4	20.5	$3.1x10^{-4}$ to $1.0x10^{-1}$	$1.9x10^{-4}$
E-5	33	62 (DBP)	2	22.0	$3.1x10^{-4}$ to $1.0x10^{-1}$	$1.5x10^{-4}$
E-6	33	62 (BES)	2	10.0	$1.0x10^{-4}$ to $1.0x10^{-1}$	$1.0x10^{-4}$
E-7	33	62 (DOP)	2	8.0	$1.0x10^{-3}$ to $1.0x10^{-1}$	$1.0x10^{3}$

Table 4c.T$_2$: Potentiometric selectivity coefficients for the Cu^{2+} ISE

Interfering ions	Selectivity coefficients, - $\log K^{pot}_{A,B}$	
	MPM	FIM
Li^+	2.1	1.5
Na^+	1.8	1.6
K^+	1.9	1.8
Ca^{2+}	1.6	2.1
Mg^{2+}	1.8	2.2
Sr^{2+}	1.8	2.0
Ag^+	1.5	1.9
Hg^{2+}	3.9	1.8
Ni^{2+}	2.1	2.1
Cd^{2+}	1.9	2.0
Co^{2+}	2.0	2.2
Zn^{2+}	2.0	2.3
Pb^{2+}	1.3	1.8
Fe^{3+}	2.0	2.1
Al^{3+}	2.4	2.0

Table 4c.T_3: Effect of mixed solvent media on the electrode response

Mixed solvent medium	**Mixed solvent content (%V/V)**	**Slope (±1mV/dec)**	**Working concentration range (M)**
Methanol: water	10:90	37.5	6.3×10^{-5} to 1.0×10^{-1}
	20:80	40.0	1.2×10^{-4} to 1.0×10^{-1}
	30:70	42.0	1.9×10^{-4} to 1.0×10^{-1}
Acetone: water	10:90	40.5	7.9×10^{-5} to 1.0×10^{-1}
	20:80	49.0	1.5×10^{-4} to 1.0×10^{-1}
	30:70	45.0	1.9×10^{-4} to 1.0×10^{-1}
Acetonitril: water	10:90	35.5	6.3×10^{-5} to 1.0×10^{-1}
	20:80	35.0	2.5×10^{-4} to 1.0×10^{-1}
	30:70	40.0	3.9×10^{-4} to 1.0×10^{-1}

Table 4c.T_4: Analysis of Cu^{2+} ions in real life samples

Name of the sample	**Proposed electrode (mgL^{-1})**	**Determined by AAS (mgL^{-1})**
Brass	794 (±4)	789 (±2)
Tea leaves	2.0 (±0.5)	2.3 (±0.3)

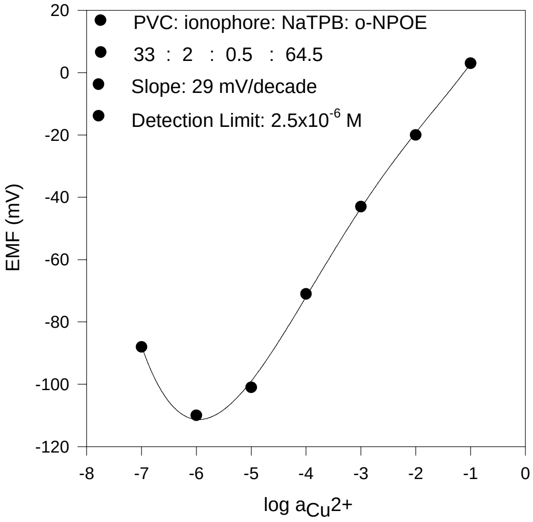

Figure 4c.F$_2$: Calibration curve for the Cu^{2+} ISE

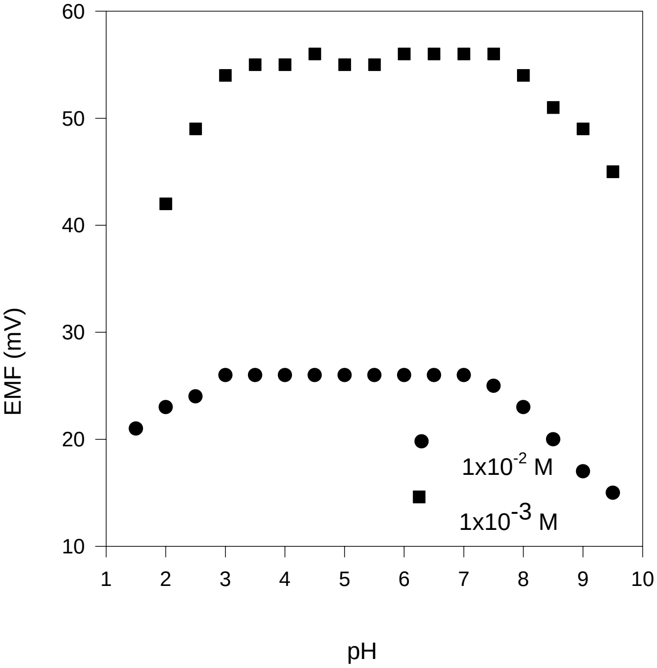

Figure 4c.F$_3$: Effect of pH on the Cu^{2+} ISE

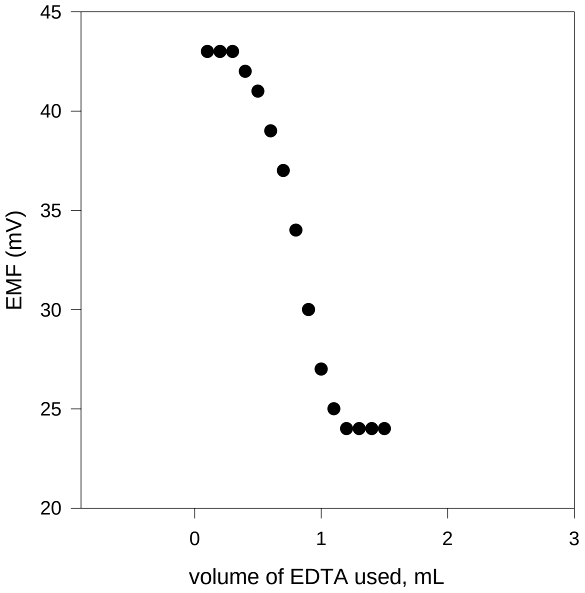

Figure 4c.F$_4$: Potentiometric titration of Cu^{2+} ions ($1.0x10^{-2}$ M) against EDTA ($1.0x10^{-1}$ M) using Cu^{2+} ISE

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4d. Potentiometric Studies of N,N’-Bis(2-dimethylaminoethyl)-N,N'-dimethyl-9,10 anthracenedimethanamine as a Chemical Sensing Material for Zn(II) Ions

Introduction

Ion-selective electrodes have been the subjects of rapidly increasing interest for analytical chemists over the past few decades (Bakker et al., 1997, Buhlmann et al., 1998). The growth of ion-selective electrodes is partly due to their low costs, good selectivity and convenience in application. Zinc ions are present in the effluent of industries such as electroplating, pharmaceutical, rubber, dye, batteries, etc. These ions are toxic to human being when present in concentrations beyond 124 mg/m^3 i.e., its TLV (www.carolina.com). Hence, there is an urgent need for the selective potentiometric determination of minute amounts of zinc ions, especially in food, biological and environmental samples. In this respect, many compounds have been employed as ionophores in the construction of ISEs for zinc ions (Gupta et al., 2005, Gupta et al., 2006, Fakhari et al., 2002, Gupta et al., 2001, Jain et al., 2002, Gupta et al., 2001b, Gholivand et al., 2003, Saleh et al., 2001, Ganjali et al., 2004, Ganjali et al., 2005, Gupta et al., 2006, Gupta et al., 1998).

Nitrogen ligands coordinate with transition metal ions as exclusive donor atoms. In this respect, macrocyclic and non-cyclic compounds containing nitrogen donors have attracted wide-spread attention, owing to their unique properties (Ammann et al., 1991). In aqueous solution, little reaction occurs between nitrogen ligands and either alkali or alkaline earth metal ions but the stability of complexes with transition metal ions is markedly enhanced (Ganjali et al., 2005, Ganjali et al., 2003, Ganjali et al., 2006). Detailed literature survey shows that the reported zinc-selective electrodes are suffering from following properties, like poor sensitivity, poor selectivity towards zinc ions in presence of Cu^{2+}, Cd^{2+}, Pb^{2+}, etc., stability, long response time and life time (Gorton et al., 1977, Uchida et al., 1978, Lebedeva et al., 1987, Rocheleau et al., 1990, Hirata et al., 1972, Kojima et al., 1994, Srivastava et al., 1995). These difficulties promoted us to find an ionophore suitable to function as a receptor for a zinc-selective electrode. Therefore, the behavior of N,N'-Bis(2-dimethylaminoethyl)-N,N'-dimethyl-9,10 anthracene dimethanamine, [Bis(TMEDA) anthracene] (Figure 4d.F1) with two donating nitrogen atoms on both sides of TMEDA was investigated as a neutral carrier in the construction of PVC based membrane for the estimation of zinc ions.

Recently, 9,10,Bis-(2-aminophenylthiomethyl)anthracene has been reported as silver-selective electrode (Mittal et al., 2007) in which two nitrogen and two sulphur atoms are involved in bonding with the metal ion. In the proposed work, we are reporting Bis(TMEDA) anthracene (I) as a novel neutral ionophore for monitoring of zinc in various samples. Huston et al. in 1986 synthesised this compound and since then it has not been used as an ion-sensing material. The fluorescence emission intensity of (Bis(TMEDA) anthracene) increases over 1000 folds in the presence of Zn^{2+} indicating a strong affinity for these ions (Nanjappan et al., 1987, Huston et al., 1988).

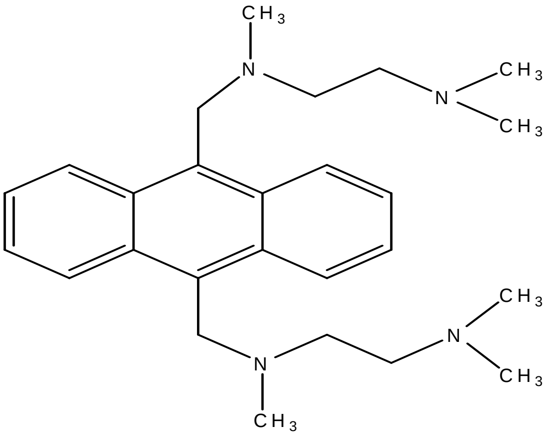

Figure 4d.F$_1$: Structure of the ionophore for Zn^{2+} ISE

Further, stability constants have been determined for a number of metal ions by conductometric method at 25 ^{0}C (Shamsipur et al., 2000). The observed log K_f values for Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+} and Ag^+ are 4.22 ±0.2, 3.0 ±0.3, 3.14 ±0.3, 3.0 ±0.3 and 3.46 ±0.2, respectively, which show the highest stability for zinc ions as compared to other ions. Complexation occurs between zinc ions and nitrogen atoms of the ligand, and resulting complexes are highly stable and selective for zinc ions. These lipophilic ligands, when incorporated into membranes, behave as sensing material for zinc ions.

Experimental

Reagents, Preparation of Electrodes and Potential Measurements

A number of liquid-membrane based electrodes were prepared according to a previously reported method and potential measurements as discussed in chapter 3.

Results and Discussion

Membrane Characteristics

The electrode that gave Nernstian slope with low detection limits and good working range was opted for further studies. Table-4d.T_1 shows results of slope, detection limit, working concentration range and response time of each membrane electrode. The potentials were obtained by varying the Zn^{2+} ion concentration from 1.0×10^{-8} to 1.0×10^{-1} M. The membrane having 2% ionophore (w/w) exhibited the best results (E-2, Table 4d.T_1). This composition gave a reproducible response in terms of Nernstian response (slope 30.0 mV/ decade, ± 0.5 mV, standard deviation for 5 sets of measurements) in the concentration range from 1.0×10^{-5} to 1.0×10^{-1} M of Zn^{2+} and a response time of 15 seconds. The optimized composition PVC:(I):o-NPOE (33:2:65) was chosen for all further studies.

Effect of Plasticizer and Inner Solution Concentration

The dielectric constant of a plasticizer plays a very important role in response characterictics of any electrode. In order to find the best membrane solvent, different plasticizers o-NPOE, DBP, DOP and BES were used. In case of the plasticizers DOP and BES (E-7, E-8, Table 4d.T_1) the potential remains linear only in a small concentration range of 3.9 x 10^{-3} to 1.0 x 10^{-1} M and 7.9 x 10^{-3} to 1.0 x 10^{-1} M, respectively. The detection limits with these two plastcizers were also not appreciable. However, the use of the DBP plasticizer shows a detection limit of 1.5 x 10^{-5} M, but it did not show Nernstian response. With a more polar plasticizer, divalent ions are preferred over monovalent ones (Buhlmann et al., 1997) that is why E-2, containing o-NPOE, enhances the detection limit to 1.5 x 10^{-6} M and the slope to 30 mV/decade. The working concentration range also improved remarkably to 1.0 x 10^{-5} - 1.0 x 10^{-1} M in the presence of the o-NPOE plasticizer.

The internal solution concentration also affects the response behavior of ion-selective electrodes. It has been observed by performing the experiment of calibration curve using three different concentrations of inner solution ranging from 1.0 x 10^{-3} M to 1.0 x 10^{-1} M. Variation in the concentration of the internal solution did not cause any significant difference in the emf, except for an expected change in the intercept of the resulting plots. A 1.0 x 10^{-1} M internal solution concentration of zinc nitrate was used for further studies. The electrode shows a linear response towards Zn^{2+} ions over a wide concentration range from 1.0 x 10^{-5} M to 1.0 x 10^{-1} M. The calibration curve has a slope 30 mV/decade with a detection limit of 1.5 x 10^{-6} M, which was obtained from the intersection of two straight-line portions of the curve in Figure 4d.F_2. Further, the response behavior did not change up to three months. It gave a reproducible curve without observing any change in the slope, detection limit, and working concentration range. The electrode was kept in double-distilled water when not in use.

Effect of pH and Effect of Mixed Solvent Media

Effect of pH on the membrane electrode was observed by using two different concentrations (1.0×10^{-2} and 1.0×10^{-3} M) of Zn^{2+} solutions over a pH range 1 to 12. To find the optimum pH range of the membrane electrode, the pH was adjusted by diluted hydrochloric acid (0.1 M) and/or sodium hydroxide (0.1 M) drop-wise. As shown in Figure 4d.F_3, the electrode E-2 gave a useful pH range of 3.0 to 7.5. Beyond this pH, a drift in potential is observed which is due to the formation of some hydroxy complexes of Zn^{2+} at higher pH while at lower pH (<3), the membrane may respond to the presence of hydrogen ions, which results in a loss of their complexing ability with the metal ion. Thus, the working pH range of the proposed assembly may be taken from 3.0-7.5.

Functioning of the electrode was also investigated in mixed solvent medium using methanol-water, acetone-water and acetonitril-water mixtures (Table 4d.T_2). It was found that the membrane electrode worked well up to 20% (v/v) non-aqueous content without showing any appreciable change in the working concentration range or slope.

Potentiometric Selectivity Coefficient

Selectivity is the most important parameter to assess the working ability of an electrode. It is most often used as characteristic of an electrode, which determines whether a reliable measurement in the target sample is possible. Potentiometric selectivity coefficients $\log K^{Pot}_{Zn^{2+},M}$ were determined by using the matched potential method (MPM) and fixed interference method (FIM) (Umezawa et al., 2000, Umezawa et al., 1995). In case of FIM, the interfering concentration used was 1×10^{-2} M and in MPM, a specified activity (concentration) of primary ions (A, 1×10^{-2} molL^{-1} of zinc ions) was added to a reference solution (1×10^{-3} mol L^{-1} of zinc ions) and the potential was measured. In a separate experiment, interfering ions (B, 1×10^{-2} mol L^{-1}) were successively added to an identical reference solution, until the measured potential matches the one obtained before adding primary ions. The matched potential method selectivity coefficient, $K_{Zn^{2+},M}^{Pot}$, is then given by the resulting primary ion to the interfering ion activity (concentration) ratio, $K^{\mathrm{MPM}} = a_{\mathrm{A}}/a_{\mathrm{B}}$. As can be seen from Table 4d.T_3, the potentiometric selectivity coeffcient values are of the order of 10^{-2} for bivalent and trivalent metal ions from both methods. Table 4d.T_3 shows that the proposed electrode is superior to the reported zinc-selective electrodes Table 4d.T_4 in terms of selectivity behavior.

Analytical Applications

Potentiometric Titration with EDTA

The electrode was used as an indicator electrode in the potentiometric titration of Zn^{2+} solution. 50 mL of 1.0 x 10^{-2} M Zn^{2+} solution was titrated against 1.0 x 10^{-1} M EDTA solution (Figure, 4d.F_4) at a pH 4-5. A very good inflection point, corresponding to 1:1 Zn^{2+}-EDTA stoichiometry, was observed which shows that this electrode can be used as an indicator electrode for the determination of Zn^{2+} ions.

Analysis of Zinc in Brass, Dry Cell and Tobacco Leaves Samples Using the Proposed Electrode

The electrode was also applied for the direct determination of zinc in brass, dry cell and tobacco leaves samples. The zinc content in all samples was extracted by acid digestion (HNO_3) followed by evaporation of excess acid and pH adjustment to range 4-5. The concentration of zinc in the extracted sample was determined with the proposed electrode and atomic absorption spectrometry (AAS) as well (Table 4d.T_5). The results show a satisfactory agreement with those obtained by AAS.

Table 4d.T$_1$: Optimization of membrane ingredients in the Zn^{2+} ISE

E. No.	Components of the membrane (% w/w)			Slope, (mV/decade)	Detection limit (M)	Working concentration range (M)
	Ionophore	PVC	Plasticizer			
E-1	1	33	66 (NPOE)	24.0 ±0.8	1.2×10^{-5}	5.0×10^{-5} - 1.0×10^{-1}
E-**2**	**2**	**33**	**65 (NPOE)**	**30.0±0.5**	**1.5×10^{-6}**	**1.0×10^{-5} - 1.0×10^{-1}**
E-3	3	33	64 (NPOE)	34.0 ±0.7	1.0×10^{-4}	7.9×10^{-5} - 1.0×10^{-1}
E-4	4	33	63 (NPOE)	36.0 ±0.8	6.3×10^{-4}	5.0×10^{-4} - 1.0×10^{-1}
E-5	5	33	62 (NPOE)	40.0 ±0.8	1.0×10^{-4}	5.0×10^{-4} - 1.0×10^{-1}
E-6	2	33	65 (DBP)	35.0 ±0.6	1.5×10^{-5}	2.5×10^{-5} - 1.0×10^{-1}
E-7	2	33	65 (DOP)	20.0 ±0.7	3.1×10^{-4}	3.9×10^{-3} - 1.0×10^{-1}
E-8	2	33	65 (BES)	25.0 ±0.8	5.0×10^{-4}	7.9×10^{-3} - 1.0×10^{-1}

Table 4d.T$_2$: Effect of mixed solvent media on the electrode response

Mixed solvent content	Volume/Volume (%)	Slope (mV/decade)	Working concentration range (M)
Nil	-	30.0 ±0.5	1.0×10^{-5} to 1.0×10^{-1}
Methanol: water	10:90	28.5 ±0.7	1.0×10^{-5} to 1.0×10^{-1}
	20:80	30.0 ±0.9	3.1×10^{-5} to 1.0×10^{-1}
	30:70	24.5 ±1.5	1.0×10^{-4} to 1.0×10^{-1}
Acetone:water	10:90	30.0 ±0.3	1.5×10^{-5} to 1.0×10^{-1}
	20:80	27.0 ±0.3	7.9×10^{-5} to 1.0×10^{-1}
	30:70	23.5 ±0.6	6.3×10^{-4} to 1.0×10^{-1}
Acetonitril:water	10:90	29.5 ±0.5	1.3×10^{-5} to 1.0×10^{-1}
	20:80	28.0 ±0.6	1.4×10^{-5} to 1.0×10^{-1}
	30:70	22.0 ±0.7	1.6×10^{-4} to 1.0×10^{-1}

Table 4d.T_3: Potentiometric selectivity coefficient for the Zn^{2+} ISE

Interfering ion (B)	**Selectivity coefficient log $K^{Pot}_{Zn^{2+},M}$**	
	Fixed interference method	**Matched potential method**
Na^+	-1.8	-2.2
K^+	-2.1	-2.1
Mg^{2+}	-2.5	-2.1
Sr^{2+}	-2.2	-2.0
Co^{2+}	-2.3	-2.1
Ni^{2+}	-2.3	-2.1
Cu^{2+}	-2.1	-2.1
Fe^{3+}	-2.3	-2.0
Cd^{2+}	-2.0	-2.0
Pb^{2+}	-2.4	-2.8
Hg^{2+}	-1.2	-0.2
Ag^+	-2.2	-2.8

Table 4d.T_4: Comparison of general performance characteristics of the Zn^{2+} ISE with some reported electrodes

Ionophore (References)	**Range(M)**	**Slope (mV/decade)**	**Detection limit (M)**	**Interferent ($-\log K^{Pot}_{Zn^{2+},M}$)**
Zn-bis(2,4,4-trimethyl-pentyl)dithiophosphinic acid (Gupta et al., 1998)	10^{-5}-10^{-1}	30.1	5.0×10^{-6}	Na^+ (1.5), Ca^{2+} (1.47), Cu^{2+} (0.4), Cd^{2+} (1.17), Pb^{2+} (1.15)
Zn-di-n-octylphenyl phosphoric acid (Gorton et al., 1977)	10^{-5}-10^{-1}	25.7	1.0×10^{-6}	Na^+(2.0), Ca^{2+}(3.2), Cu^{2+}(0.6), Cd^{2+}(0.0), Pb^{2+}(1.1)
Carbon supported zinc orthophosphateand zinc mercuricthiocyanate(Rocheleau et al., 1990)	10^{-5} 10^{-2}	Nernstian response	1.0×10^{-5}	Cu^{2+} (0.0), Cd^{2+} (0.95), Pb^{2+} (1.0)
2,2,2-Cryptand (Srivastava et al., 1996)	10^{-4}-10^{-1}	22.0	1.0×10^{-5}	Na^+(1.3),Ca^{2+}(0.67), Cu^{2+}(0.76), Cd^{2+} (0.70), Pb^{2+}(0.78)
Di(2-ethylhexyl) phosphoric acid-Zn(II) (Fiedler et al., 1979)	10^{-4}-10^{-1}	43.8	3.16×10^{-5}	---
Proposed electrode	10^{-5}- 10^{-1}	30.0	1.5×10^{-6}	Ca^{2+} (2.1), Mg^{2+} (2.1), Sr^{2+} (2.0), Ni^{2+}(2.1), Co^{2+}(2.1), Cd^{2+} (2.0), Cu^{2+}(2.1), Pb^{2+}(2.8), Fe^{3+}(2.0),Hg^{2+}(0.2), Ag^+(2.8)

Table 4d.T_5: Analysis of Zn^{2+} ions present in real life samples using the Zn^{2+} ISE

Name of the sample	**Proposed electrode** (mg mL^{-1})	**Determined by AAS** (mg mL^{-1})
Brass	0.345 (±0.001)	0.348 (±0.002)
Dry cell - 1	1.015 (±0.001)	1.013 (±0.002)
Vitamin tonic	0.420 (±0.003)	0.419 (±0.002)
Tobacco leaves	0.003 (±0.0004)	0.0026 (±0.0002)

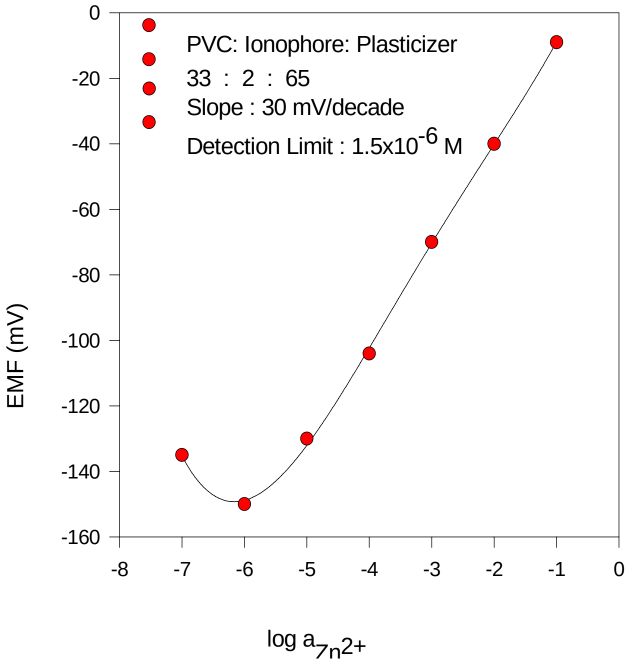

Figure 4d.F$_2$: Calibration curve for the Zn^{2+} ISE

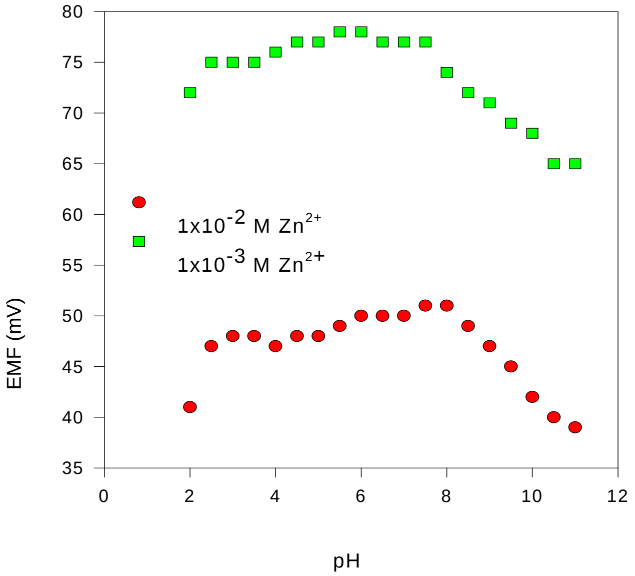

Figure 4d.F$_3$: Effect of pH on the Zn^{2+} ISE

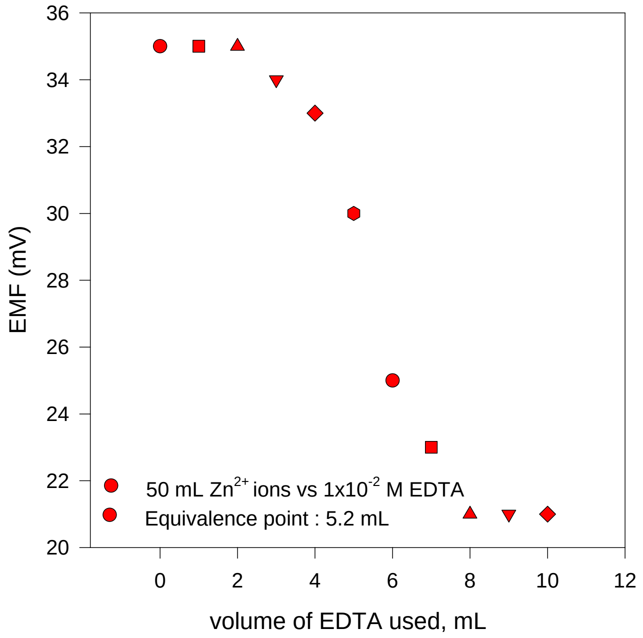

Figure 4d.F$_4$: Potentiometric titration of Zn^{2+} ions (1.0 x 10^{-2} M) against EDTA (1.0 x 10^{-1} M) using the Zn^{2+} ISE

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4e. Copper-Selective Electrode Based on Ionophore Containing Acyclic Amide Linkage

Introduction

Trace heavy metal analysis is an important part of environmental pollution studies. Researchers have continuously performed determination of copper metal contents of various environmental, industrial and medical fields. Copper is essentially required in the formation of hemoglobin, red blood cells as well as bones. A lack of copper may also lead to increased blood fat levels. It is also necessary for the manufacture of the neurotransmitter noradrenaline as well as for the pigmentation of hair. Copper is essential for maintaining the strength of the skin, blood vessels, and epithelial and connective tissue throughout the body. Deficiencies of copper can result in hernias, aneurysms, and blood vessel breakage manifesting as bruising or nosebleeds (Ruegger et al, 1995).

Potentiometric sensors are widely used for the determination of copper ion concentration in a wide variety of samples (Gupta et al., 2006, Singh et al., 2006, Marques de Oliveira et al., 2006, Gupta et al., 2005, Chai et al., 2005, Jain et al., 2005, Szigeti et al., 2005, Bakker et al., 2005). A very few reports are available based on ionophores containing amide linkage as the ligating site alongwith, –S- (cystine), -N (Uracil), -COOH (aspertate), etc., as ligating units. These molecules have the ability to modulate the metal binding affinity (Figure 4e.F_1)**,** which is essential and an important characteristic of such peptide-based sensors over a wide metal ion concentration range (Kazmierski et al, 1995, Gilbertson et al, 1994 and Imperiali et al, 1991). Some recent reports such as Chang et al., 1996 have used polypeptide molecules (biomolecules) for metal ions recognition and in particular to design fluorescent chemical sensors sensitive to nano-molar concentrations of Cu^{2+} in water at pH 7. Here, we are proposing a metal-binding ionophore containing two amide linkages as a sensing material for Cu^{2+} ions.

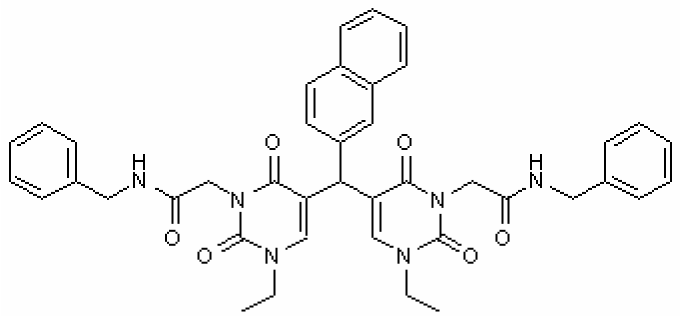

Figure 4e.F$_1$: Structure of the ionophore for Cu^{2+} ISE

Experimental

Reagents, Preparation of Electrodes and Potential Measurements

A number of liquid-membrane based electrodes were prepared according to a previously reported method and potential measurements were taken as discussed in chapter 3.

Results and Discussion

Membrane Characteristics (Calibration Curve, Response Time and Detection Limit)

Ligands having sufficiently high lipophilicity and rigidity are expected to be selective for both transition as well as heavy metal ions. Thus, in order to check the characteristics of ligands as ion-sensing material in the preliminary experiments, it was used to prepare PVC based membrane electrodes with different ratios of membrane components, like PVC, plasticizer, ionophore, etc. The response behavior of each electrode has been measured. It was found that the composition 33:2:64 (PVC:I:o-NPOE) exhibits a relatively good response in terms of Nernstian slope (29.0 ± 0.5 mV per decade, standard deviation for 5 sets of measurements) over the concentration range $3.0\text{x}10^{-5}$-$1.0\text{x}10^{-1}$ M of Cu^{2+} and a response time of 15 seconds (Table 4e.T$_1$). The calibration curve shows a detection limit of $1.0\text{x}10^{-5}$ M, which was obtained from the intersection of two straight-line portions of the curve (Figure 4e.F$_2$). The influence of the inner solution concentration on the working of the Cu^{2+}-selective electrode was also studied and it was found that an internal solution from $1x10^{-2}$ M to $1x10^{-4}$ M not causes any significant change in the response behavior of electrodes. A $1x10^{-1}$ M internal solution concentration has found to be more suitable for the smooth working of electrodes.

Effect of pH and Mixed Solvent Media

The influence of pH of the test solution on the potential response of the electrode was tested in the pH range of 2.0–11.0 and the results are shown in Figure 4e.F_3. It is observed that the electrode can be suitably used over a pH range of 3.0 to 7.0. The variation above and below this range may be due to the formation of some hydroxy complexes of Cu^{2+} at higher pH and interference from excess H^+ ions at lower pH, respectively.

The electrode characteristics were also investigated in mixed solvent medium using methanol-water, acetone-water and acetonitrile-water mixtures (Table 4e.T_2). It was found that the membrane electrode worked well up to 20% (v/v) non-aqueous content without showing any significant change in the working concentration range or slope of the calibration curve.

Potentiometric Selectivity Coefficient

The potentiometric selectivity coefficient, which reflects the relative response of the membrane electrode for the primary ion over other ions, present in the solution, is the most important characteristic of any ion-selective electrode. In this work, the potential of responses of the Cu^{2+} ion-selective electrode were measured for thirteen cations by means of fixed interference method (FIM) as well as matched potential method (MPM) (Buck et al., 1994, Umezawa et al., 1995). The selectivity coefficient values are given in Table 4e.T_3. It is clear from results that there is no serious interference from common ions in both cases.

Analytical Applications

Potentiometric Titration with Na_2S

A direct titration of Cu^{2+} (100 mL of $1x10^{-2}$ M) against Na_2S ($1x10^{-1}$ M) was carried out and the emf is plotted in Figure 4e.F_4. The equivalence point confirms a 1:1 stoichiometry of the chemical reaction taking place in the solution. This electrode can be used as an indicator electrode for the determination of Cu^{2+} ions under laboratory conditions.

Table 4e.T$_1$: Optimization of membrane ingredients for the Cu^{2+} ISE

E. No.	Components of the membrane (% w/w)			Slope, (mV/decade)	Detection limit (M)	Working concentration range (M)
	Ionophore (I)	PVC	Plasticizer			
1.	1	33	66	18.0	$1.5x10^{-4}$	$1.0x10^{-4}$-$1.0x10^{-1}$
2.	2	33	65	26.0	$1.0x10^{-4}$	$1.0x10^{-4}$-$1.0x10^{-1}$
3.	**3**	**33**	**64**	**29.0**	**$1.0x10^{-5}$**	**$3.0x10^{-5}$-$1.0x10^{-1}$**
4.	4	33	63	24.0	$3.9x10^{-5}$	$1.0x10^{-4}$-$1.0x10^{-1}$
5.	5	33	62	19.0	$1.5x10^{-4}$	$1.0x10^{-4}$-$1.0x10^{-1}$
6.	6	33	61	16.0	$1.2x10^{-4}$	$1.0x10^{-4}$-$1.0x10^{-1}$

Table 4e.T$_2$: Effect of mixed solvent media on the electrode response

Non-aqueous Content	Volume/volume (%)	Slope (mV/decade)	Working concentration range (M)
Nil	-	28.0	$1x10^{-5}$-$1x10^{-1}$
Methanol: water	10:90	30.5	7.9×10^{-5} to 1.0×10^{-1}
	20:80	31.0	5.0×10^{-5} to 1.0×10^{-1}
	30:70	34.0	6.9×10^{-4} to 1.0×10^{-1}
Acetone:water	10:90	31.0	6.5×10^{-5} to 1.0×10^{-1}
	20:80	30.0	7.9×10^{-5} to 1.0×10^{-1}
	30:70	33.0	4.3×10^{-4} to 1.0×10^{-1}
Acetonitril:water	10:90	29.5	6.3×10^{-5} to 1.0×10^{-1}
	20:80	31.0	5.5×10^{-5} to 1.0×10^{-1}
	30:70	36.0	1.0×10^{-4} to 1.0×10^{-1}

Table 4e.T_3: Potentiometric selectivity coefficient by FIM and MPM

Interfering ions (B)	**Selectivity coefficient log $K^{Pot}_{Zn^{2+},M}$**	
	Fixed interference method (FIM)	**Matched potential method (MPM)**
Na^+	-1.4	-1.6
K^+	-1.1	-1.4
Mg^{2+}	-2.0	-2.2
Sr^{2+}	-2.2	-2.2
Co^{2+}	-1.9	-1.8
Ni^{2+}	-2.2	-2.1
Ca^{2+}	-1.9	-2.0
Fe^{3+}	-2.2	-2.0
Cd^{2+}	-2.5	-2.3
Pb^{2+}	-2.2	-2.1
Hg^{2+}	-2.0	-2.1
Ag^+	-1.8	-2.0

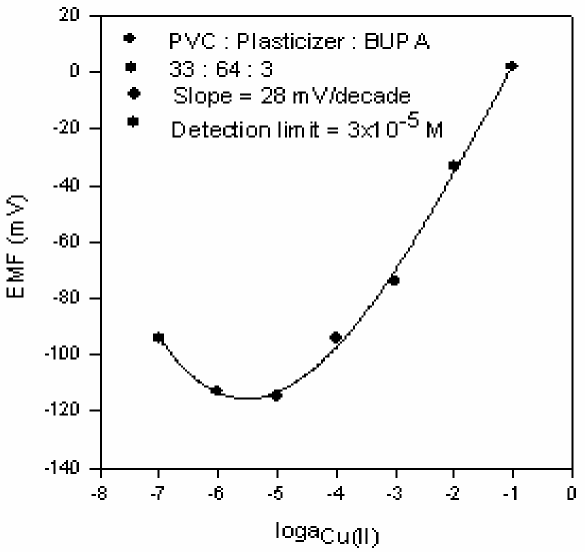

Figure 4e.F$_2$: Calibration curve for the Cu^{2+} ISE

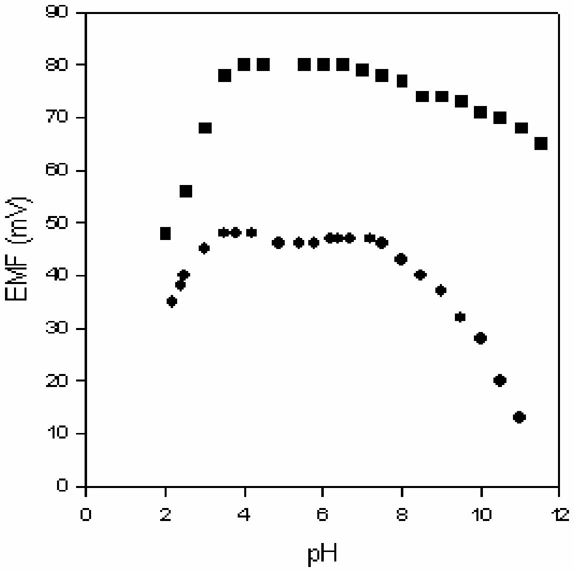

Figure 4e.F$_3$: Effect of pH on the Cu^{2+} ISE

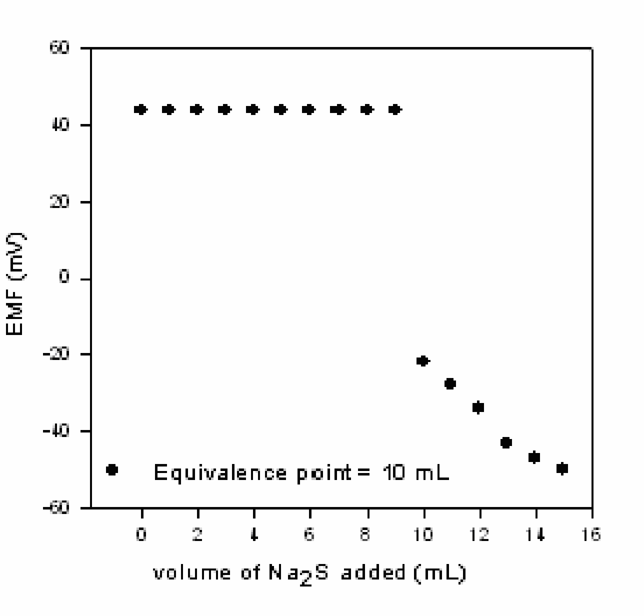

Figure 4e.T$_4$: Potentiometric titration of Cu^{2+} (1x10^{-2} M) ions with Na$_2$S (1x10^{-1}M)

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Chapter -5

Heteroatoms (N, O, S) Containing Ionophore Based Chemical Sensors

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5a. Silver (I)-Selective Membrane Electrodes Based on Macrocycles Possessing Imine and Thioether Combinations

Introduction

The need for selective and sensitive sensors which are able to monitor the concentration of analytes of biological, clinical, and environmental interest is nowadays generally accepted (Wygladacz et al., 2005, Chakrapani et al., 2001, Pu et al., 1998, Shamsipur et al., 2003, Hisamoto et al., 1995, Lerchi et al., 1994). Various kinds of sensors are now available but liquid-membrane based electrodes are still standing at the peak position of electrode systems, due to advantages, like high sensitivity and selectivity. In this context, special interest has been devoted to the development of liquid-membrane electrodes for soft metal ions, since some of them are present in biological systems in trace amounts and at the same time, they all can represent an environmental concern when present in uncontrolled amounts. In recent years, a relatively large number of ion-selective electrodes (Mashhadizadeh et al., 1999, Liu et al., 2000, Zhang et al., 2006, Mahajan et al., 2001, Sil et al., 2001, Shamsipur et al., 2002, Shamsipur et al., 2002) including calix[4]arene derivatives (Kimura et al., 2000, Chen et al., 2001, Ceresa et al., 2002) crown ether derivatives (Casabo et al., 1995, Su et al., 2001, Goldcamp et al., 2005) and tweezer-type compounds (Kim et al., 2005) have been reported. However, these electrodes generally exhibit a long response time, a narrow working concentration range or a moderate selectivity. Mercury ion interference is the main reason for a continued search for new silver-selective sensors for the past few years. Searching for new ionophores with high selectivity for silver ions with less interference from mercury ions is still a challenge for the analytical research efforts. To improve the analytical selectivity, it is essential to search novel carrier compounds that would react with silver ions with high selectivity.

Based on donor atom type, macrocyclic ligands can be divided into two extreme categories. The first category incorporates donor atoms such as N and S. These macrocycles tend to have considerable affinity for transition and most other heavy metals. The enhanced stability of metal ion complexes formed with macrocyclic ligands compared to those formed with analogous open-chain species has been termed as "macrocyclic effect" and has sparked much interest in the study of cyclic ligand complexes. The second category constitutes polycrown ethers for alkalies and alkaline earth metal ions. However, many macrocycles lying on these extremes have been reported. The series of N_2S_2 macrocycles incorporating cis and trans arrangements of the hetroatoms has been synthesized by high dilution technique and their complexes have been isolated (Adam et al., 1992, Siegfried et al., 1984, Lean et al., 1980, Westerby et al., 1991).

14-membered N_2S_2 quardidentate macrocycle was chosen as a ligand in the membrane electrode (Figure 5a.F_1). It was designed and synthesized to exhibit complexation properties with Cu^+ ions by Martin et al., 1987. This property of the ionophore made it suitable for making a chemical sensor for Ag^+ and Cu^+ ions because they follow the singular co-ordination system of d^{10} configuration. However, the present report deals with its characteristics as an Ag^+-selective ionophore.

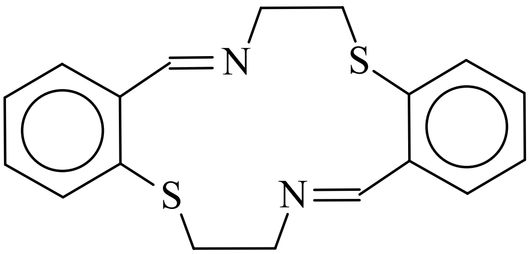

Figure 5a.F$_1$: Structure of the ionophore for Ag$^+$ ISE

Experimental

Reagents, Apparatus, Preparation of Electrodes and EMF Measurements

A number of liquid-membrane based electrodes were prepared according to a previously reported method and potential measurements were taken as discussed in chapter 3.

Results and Discussion

Choice of Ligand

Crown ethers with an oxygen donor show good selectivity for alkali and earth alkaline metal cation in aqueous and organic solutions. However, the affinity of crown ethers for transition metal cations can be enhanced by replacing oxygen atoms with softer donor atoms such as nitrogen or sulfur (Beer et al., 1999). Therefore, we have decided to use a macrocycle containing nitrogen and sulfur donor atoms. The preliminary picrate extraction studies (Ocak et al., 2006) based on N_2S_2 macrocycle show the maximum extraction for silver. Due to its steriochemical structure, high lipophilicty and existence of trans-disposed pairs of imine-N and thioether-S donors, the (I) forms a cavity and the N_2S_2 macrocycle acts as a potential carrier for silver ions (Ocak et al., 2006) in the PVC-membrane electrodes. Further, the pattern of response behavior of the ion-selective electrode varies significantly with the composition of the membrane, especially the type and amount of electro-active material, and the type and amount of the plasticizer. The electrode membranes based on (I), were studied for all these important characteristics.

Stability constants have been determined for a number of complexes of some metal ions with N_2S_2 macrocycle by conductometric method at 25 °C using acetonitrile as a solvent. The calculated log K_f values for Ag^+, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+} are 3.9 ± 0.2, 3.3 ± 0.3, 3.0 ± 0.3, 3.4 ± 0.3 and 3.2 ± 0.2, respectively, which show highest stability for silver ions as compared to other ions. Complexation occurs between silver ions and imine nitrogen and sulphur atoms of the macrocycle and the resulting complexes are highly stable and selective for silver ions. These lipophilic ligands, when incorporated into membranes, behave as sensing materials for silver ions.

Effect of Membrane Composition and Response Time

The potentiometric response of ion-selective electrodes based on neutral carrier ionophores is known to depend not only on the nature of the ionophore but also on the composition, nature and amount of the plasticizer used, which may result in the highest degree of complexation between the metal ion and the ionophore. Electrostatic forces between complexes and the surrounding membrane solvents result in the stability of the carried complexes in the membrane since the dielectric constant of a plasticizer also plays a very important role in the response characteristics of any electrode (Su et al., 2001, O'Connor et al., 1992, Bakker et al., 1997). As seen from the Figure 5a.F_1, the response of plasticized-PVC membranes containing o-NPOE as plasticizer is superior to other plasticizers like DBP, TOP and BES. In all other cases except of o-NPOE, the slope of the corresponding potential is not Nernstian. The potential responses obtained for different ion-selective electrodes are shown in Table 5a.T_1. The optimized composition of membrane constituents PVC: (I): o-NPOE (66:10:124), which gave a Nernstian response (slope 59.0 mV/decade ± 0.5 mV), and a wide dynamic range of 1.0 x 10^{-5} to 1.0 x 10^{-1} M of Ag^+. A lower detection limit of 3.0×10^{-6} M and a fast response time of 15 s were observed with this composition. As the ionophore content in the membrane medium is increased up to 5%, the electrode response also increases with a Nernstian response, but beyond this amount a decrease in the electrode properties is observed. This is probably due to the saturation of ligand in the medium. The electrode could be used over a period of 4 months without any significant change in the response behavior. Membrane electrodes were re-conditioned time to time in 0.1 M $AgNO_3$ solutions for good lifetime and response characteristics.

Effect of pH and Non-aqueous Media

The effect of pH on the response of the membrane electrode was tested over a pH range 2 to 11 using two different concentrations 1.0×10^{-3} M and 1.0×10^{-4} M of silver ions, respectively. It is clear from Figure 5a.F_2, that the potentials were almost constant in the pH range 3.0 to 7.5. Above and below this pH range gradual changes in the EMF were observed, which attributed to the fact that the excess of H^+/OH^- ions in the medium react with the ionophore and/or Ag^+ ions. As a result of this, the Ag^+-ionophore complex dissociates.

The electrode also functioned well in the presence of mixed solvent media using methanol-water, acetone-water and acetonitril-water mixtures (Table 5a.T_2). It was found that the membrane electrode worked satisfactorily well up to 30% (v/v) non-aqueous content without showing any appreciable change in the working concentration range or slope.

Potentiometric Selectivity Behavior of the Electrode

The most important output of a membrane electrode is its ability to sense the primary ion in presence of other interfering metal ions. This important characteristic was monitored in terms of selectivity coefficients by two different methods, FIM as well as MPM

(Umezawa et al., 1995, Gadzekpo et al., 1984). Different alkali, alkaline-earth, transition and heavy metal ions were used as interfering ions. The results obtained are illustrated in the Table 5a.T_3. In case of FIM the electrode based on ionophore (I) is highly Ag^+-selective against alkali, alkaline earth, transition and heavy metal ions. In this electrode, there is some interference observed by a soft metal ion, mercury (II).

Potentiometric Titration

The proposed Ag^+ membrane electrode was found to work well under laboratory conditions. The electrode has been used as an indicator electrode in the potentiometric titration of Ag^+ with KI (Figure 5a.F_3) and vice versa. A 50 mL aliquot of $1x10^{-2}$ M Ag^+ ions was titrated with $1x10^{-1}$ M of KI solution for the direct measurement of Ag^+ ions. The equivalence point of reverse titration is observed sharp at the same position to that for the forward titration and it confirms 1:1 stoichiometry as well as fast kinetics of the reaction at the electrode surface. Further, titrations were done by taking different amounts of Hg^{2+} ions. When it is taken in concentration less than that of Ag^+ ions, no interference is observed and the titration curve obtained is exactly the same to that as if Hg^{2+} is not present at all (Figure 5a.F_4). This is due to the reason that Ag^+ and $Hg^{2+}$are isoelectronic and both of these have d^{10} electronic configuration in their respective penultimate sub shells. Moreover, the ionic radii of both of these are also comparable (Ag^+=1.12 A^0, Hg^{2+}=1.02 A^0).

Potentiometric titration of a mixture of halide ions containing equal concentrations of Cl^-, Br^- and I^- ions was carried out against $AgNO_3$. The titration curve shows three inflexion points corresponding to the precipitation of I^-, Br^-, and Cl^- in the sequence. Inflexion points are well defined for each part of the curve. Also, the electrode was used in the determination of SCN^- and CN^- ions. These applications establish that the electrode is a suitable chemical sensor for the determination of Ag^+ ions as well as the anions forming stable complexes or precipitates with Ag^+ ions.

The proposed electrode is used for determining silver contents in photographic effluents (Amini, 2003) and chloride contents present in drinking water, both in boiled and natural conditions. The silver and chloride contents determined by these methods (Figure 5a.F_5) were compared with those measured using an Orion ion-selective electrode for Ag^+ and Cl^- ions. The results shown in Table 5a.T_4 are comparable to each other, and indicate a satisfactory application of the proposed sensor for their determination.

The Ag^+-ISE is good in terms of a fast response time, Nernstian slope, wide concentration range, and low detection limit. The proposed electrode shows reproducibility over a good lifetime of 5 months, wide pH range, and significant selectivity for the target ion over a number of alkali, alkaline earth and transition metal ions. The comparison data between some reported silver-selective electrodes with the proposed electrode in terms of their response behavior revealed that our electrode characteristics are quite comparable and good with those of reported ones (Table 5a.T_5).

Moreover, this proposed Ag^+ ion-selective electrode could be used to determine Ag^+ ions by direct as well as reverse potentiometric titrations and can be successfully used in mixed solvent media. This report also suggests that the developed electrode can be applied for the direct measurements of Ag^+ ions and some anions, too.

Table 5a.T_1: Optimization of membrane ingredients

E. N.	Composition (%)(w/w)			Slope (mV/decade)	Working concentration range (M)	Detection limit (M)
	PVC	Plasticizer	5.I			
1	33	66 (o-NPOE)	1	42.5	3.9×10^{-5} to1.0×10^{-1}	3.1×10^{-5}
2	33	65 (o-NPOE)	2	48.5	1.0×10^{-4} to 1.0×10^{-1}	7.9×10^{-5}
3	33	64 (o-NPOE)	3	54.0	1.0×10^{-4} to 1.0×10^{-1}	6.3×10^{-5}
4	33	63 (o-NPOE)	4	57.0	1.0×10^{-4} to 1.0×10^{-1}	1.0×10^{-5}
5	33	62 (o-NPOE)	5	59.0	1.0×10^{-5} to 1.0×10^{-1}	3.0×10^{-6}
6	33	61 (NPOE)	6	54.0	1.0×10^{-4} to 1.0×10^{-1}	7.9×10^{-6}
7	33	62 (DBP)	5	52.5	5.0×10^{-4} to 1.0×10^{-1}	3.1×10^{-4}
8	33	62 (BES)	5	47.5	1.0×10^{-5} to 1.0×10^{-1}	1.0×10^{-5}
9	33	62 (TOP)	5	49.0	1.0×10^{-4} to 1.0×10^{-1}	1.0×10^{-4}

Table 5a.T_2: Effect of mixed solvent media on the electrode response

Non-aqueous medium:water	Percentage (V/V)	Slope (mV/decade)	Lower detection limit (M)
water	--	59.0	$3.1\text{x}10^{-6}$
methanol:water	10:90	52.5	$3.0\text{x}10^{-5}$
	20:80	54.0	$1.9\text{x}10^{-5}$
	30:70	56.0	$3.4\text{x}10^{-5}$
	40:80	57.0	$7.9\text{x}10^{-5}$
acetone:water	10:90	53.5	$6.3\text{x}10^{-5}$
	20:80	56.0	$3.1\text{x}10^{-5}$
	30:70	58.5	$5.0\text{x}10^{-5}$
	40:60	60.0	$7.9\text{x}10^{-5}$
acetonitril:water	10:90	49.5	$1.0\text{x}10^{-5}$
	20:80	53.5	$3.1\text{x}10^{-5}$
	30:70	56.0	$5.0\text{x}10^{-5}$
	40:60	60.5	$8.0\text{x}10^{-5}$

Table 5a.T$_3$: Potentiometric selectivity coefficients for the Ag$^+$ ISE

Interfering ion (B)	$\log K_{Ag,B}^{Pot}$	
	FIM	**MPM**
Na$^+$	-1.4	-1.2
K$^+$	-1.5	-1.6
Mg^{2+}	-2.0	-2.2
Ca^{2+}	-2.2	-2.1
Sr^{2+}	-2.2	-2.1
Pb^{2+}	-1.8	-2.2
Cu^{2+}	-1.2	-1.6
Co^{2+}	-2.1	-2.2
Ni^{2+}	-2.0	-2.2
Zn^{2+}	-1.9	-2.4
Cd^{2+}	-1.8	-2.3
Hg^{2+}	-1.7	-2.1
Fe^{3+}	-2.1	-2.3

Table 5a.T$_4$: Determination of silver and chloride contents in real life samples

Sl. No.	Name of sample	Contents	Orion electrode (Ag$^+$-ISE) (mgL^{-1})	Proposed selective electrode (mgL^{-1})
1	Photographic effluent	Silver ions	50.0±4	55.0±6
2	Tap water	Chloride ions	8.0±3	10.0±4

Table 5a.T_5: Comparison of various Ag^+ ISE with the proposed electrode

Sl No.	Name of ionophore	Slope (mV/ decade)	Measuring range (M)	pH range	Lifetime (months)	log $K^{Pot}_{Ag+,B}$
1	Polystyrene-based Me6(14) diene:$2HClO_4$ (Gupta et al., 2002)	53	5×10^{-6} -10^{-1}	2.5 - 9.5	4	-4.5
2	Schiff-base–p-tert butylcalix[4]arene derivative (Mahajan et al., 2002)	58	10^{-5} -10^{-1}	1 - 6	6	-2.0
3	Two calix [4] arene derivatives functionalized by two hydroxy and two benzo thiazolylthioethoxygroups, (Chen et al., 2000)	58	5×10^{-6}-10^{-1}	2.5 - 6.5	--	-2.6
4	Schiff base of [bis 5-(4-nitrophenyl azo)salisylaldimine] 1,8-diamino, 3,6-dioxo octan (BNSAO) (Mashhadizadeh et al., 2006)	56	2.7×10^{-2} - 1.9×10^{-6}	2.5 - 7	Long life time	2.3
5	2-[(2-{2-[(2-Carboxy phenyl) sulfanyl] ethoxy}ethyl)sulfanyl]benzoic acid (Abbaspour et al., 2004)	59	2.0×10^{-8}- 1×10^{-2}	2.5 - 8.7	--	-1.79
6	*tert*-butylcalix[4]arene tetra(allyl ether) (Kimura et al., 2000)	58	10^{-4} -10^{-1}	--	--	-2.2
7	Schiff base p-tert-butyl calix[4]arene derivatives containing N and O as binding sites (Mahajan et al., 2003)	60	10^{-5} - 10^{-1}	1 - 10		-2.3 - 3.3
8	Calix[2]furano[2]pyrrole (Lim et al., 2002)	57.1	1×10^{-6} - 1×10^{-2}	2.8 - 12	-	-1.7
9	9,10,Bis-(2-aminophenylthiomethyl)anthracene (Mittal et al., 2007)	60.0	10^{-4} -10^{-1}	3.3 -8.0	6	-2.3
10	6,7,15,16-tetrahydtodibenzo[f,m][1,8,4,11] dithiadiazacyclotetradecine (Proposed)	59.0	10^{-5}- 10^{-1}	5-8	5	-2.1

*B= Interfering ion (Hg^{2+})

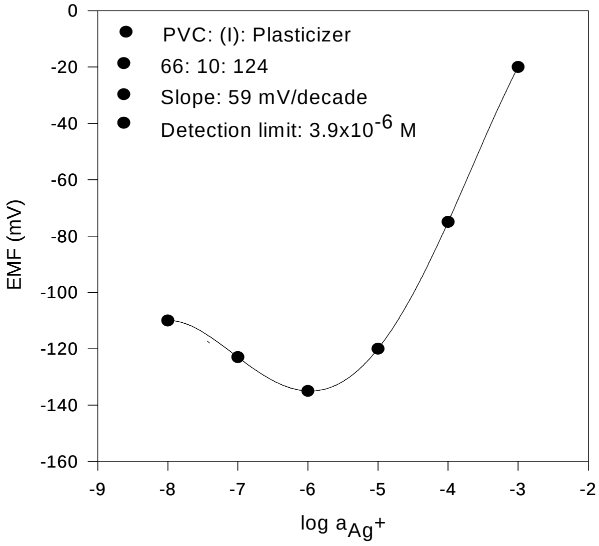

Figure 5a.F$_1$: Calibration curve of the Ag$^+$ ISE

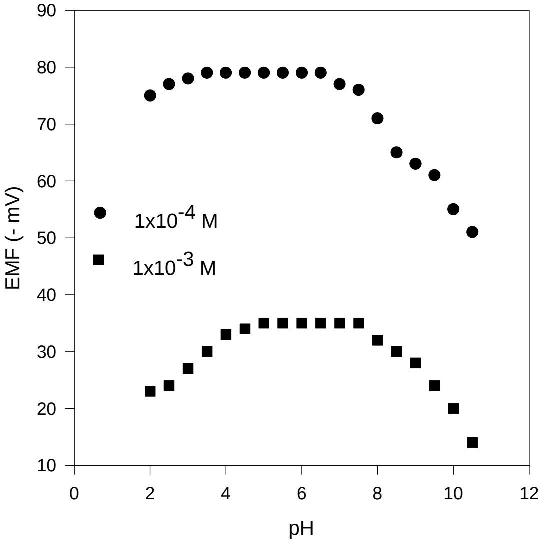

Figure 5a.F$_2$: Effect of pH on the Ag$^+$ ISE

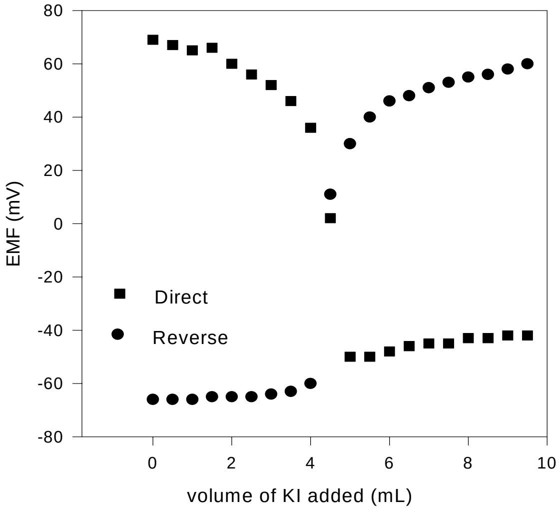

Figure 5a.F$_3$: Potentiometric titrations (direct and reverse) of Ag^+ ions with I^- ions using the Ag^+ ISE

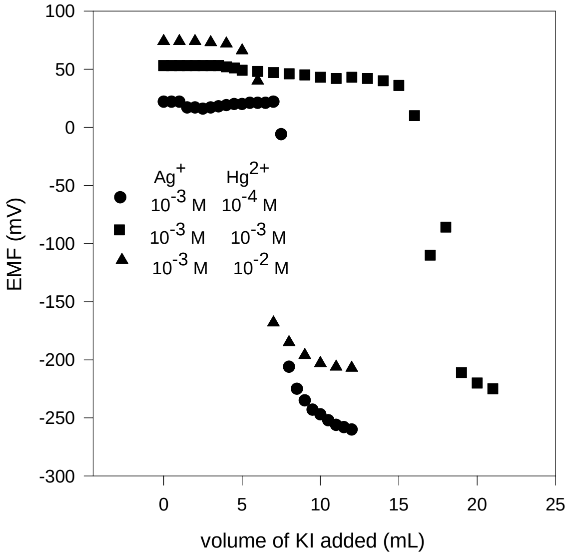

Figure 5a.F$_4$: Effect of various concentrations of Hg^{2+} ions on the response of the Ag^+ ISE by titration method

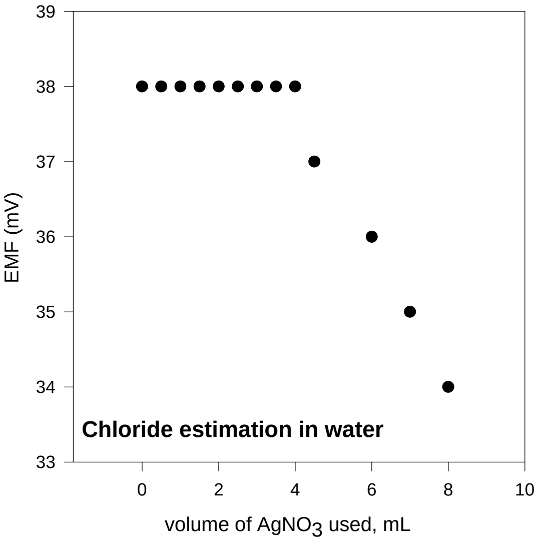

Figure 5a.F$_5$: Determination of chloride in boiled tap water using the Ag^+ ISE

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5b. Nickel-Selective Electrode Based on Liquid Membrane Containing N_4 Macrocycle as Ionophore

Introduction

There has been a considerable effort in recent years towards the preparation of new materials containing polyfunctional units, like oximes which can bind metallic ions and form stable complexes. These ionophores are suitable electrode material to design new systems selective to some specific metal ions. These materials could be applied in different areas such as electrochemistry, bioinorganic, catalysis, metallic deactivators, separation processes and environmental chemistry, among others. Several structural features of ligands have been considered to be important in their selectivity toward nickel, such as the type and geometrical arrangement of the donor atoms and its ability to coordinate with the nickel ions. The presence of mildly acidic hydroxyl groups and slightly basic nitrogen atoms make vic-dioximes amphoteric ligands which form corrin-type square-planar, square-pyramidal and octahedral complexes with transition metal ions such as Ni^{2+}, Cu^{2+}, Fe^{3+} and Co^{2+} as central atoms (Gok et al., 1993). The incorporation of amine linkages shifts the preference towards transition metal ions (Dejong et al., 1981).

The determination of nickel assumes importance due to its toxic nature, widespread use in catalytic processes and its presence in various effluents. The toxicity of nickel can cause dermatitis, asthma and disorder of central nervous system (Ganjali et al., 2002). The first nickel-selective electrode was reported by Pungor and co-workers using a nickel-dimethylglyoxime complex (Pungor et al., 1966). It is present at low concentrations in milk, milk products, chocolate, hydrogenated edible oil and wastewater of nickel electroplating industries. Despite of urgent need of Ni^{2+} ion-selective electrodes there have been only few reports in the literature (Firooz et al., 2002, Singh et al., 2001, Singh et al., 2007, Rezaei et al., 2007, Gupta et al., 2007, Yari et al., 2006, Zamani et al., 2006, Asghari, et al., 2003, Mashhadizadeh et al., 2003, Mashhadizadeh b et al., 2003, Mazloum et al., 2002, Gupta et al., 2000, Gupta et al., 1997, Jain et al., 1997, Saad et al., 1994, Hadjiioannou et al., 1981, Al-Daher et al., 1980, Gupta et al., 2007).

Due to their simple, durable and inexpensive nature and reliable response over a wide concentration range, these types of electrodes have been of a great concern nowadays. Here, we are reporting a new PVC-membrane ion-selective electrode based on ionophore containing four nitrogen atoms in the macrocycle (Figure 5b.F_1), which is selective and sensitive for nickel ions.

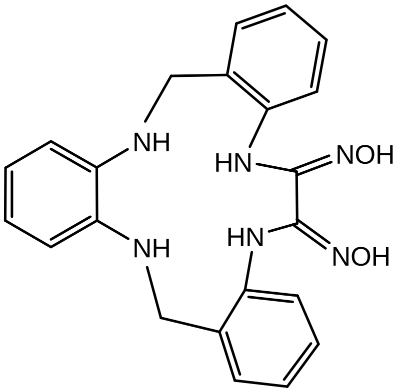

Figure 5b.F_1: Structure of the ionophore for Ni^{2+} ISE

Experimental

Reagents and Apparatus, Preparation of electrodes and EMF measurements

A number of liquid-membrane based electrodes were prepared according to a previously reported method and potential measurements were made as discussed in chapter 3.

Results and Discussion

Effect of Membrane Composition and Solvent Mediator

In this study, three plasticizers, DBP, o-NPOE and DOP were used to examine the optimized proportion of the plasticizer with PVC and of the electroactive compounds. The typical potential responses of the electrodes constructed with three plasticizers were given in Table 5b.T_1 and Figure 5b.F_4. As shown in this table, the o-NPOE-PVC electrodes were superior to DBP- and DOP- PVC electrodes with regard to the potential response, slope and linear concentration range. So, o-NPOE was selected as the plasticizer for the liquid-membrane electrode. The best membrane composition of PVC, o-NPOE and ionophore was 33:63:4 and used further in this study (Table 5b.T_1). Electrodes of this composition gave Nernstian response in terms of slope 29 mV/decade (the standard deviations of measuring the emf for 5 replicate measurements is ±1mV) over a wide concentration range of $1.5x10^{-5}$ M to $1.0x10^{-1}$M with a detection limit of $3.1x10^{-6}$ M (Figure 5b.F_2). The response properties of the proposed electrode did not change after the use of the electrode for around three months.

Effect of pH

Effects of pH on the response of the electrode were examined by measuring the potential variation in the emf over a pH range of 2.0-11.0 and results are shown in Figure 5b.F_3. It is clear from the figure that potentials were almost constant in the pH range 3.5 to 8.5. As can be seen, beyond this pH range changes in potentials occurred which might be due to the excess of H^+/OH^- ions in the medium react with the ionophore and/or Ni^{2+} ions, respectively.

Effect of Non-aqueous Media

The electrode response was also examined in the presence of mixed solvent media using methanol-water, acetone-water and acetonitrile-water mixtures. Table 5b.T_2 shows that the membrane electrode worked well up to 20% (v/v) non-aqueous content without showing any appreciable change in the working concentration range or slope.

Selectivity Behavior of the Proposed Electrode

The selectivity of the electrode was investigated by the Matched Potential Method (MPM) and the potentiometric selective coefficients were calculated by the equation as described in chapter 3. Results are summarized in Table 5b.T_3 and show that the electrode based on ionophore (I) is highly selective against various alkali, alkaline earth, transition and heavy metal ions.

Analytical Applications

Potentiometric Titration with EDTA

The electrode was used as an indicator electrode in the potentiometric titration of Ni^{2+} solution. 50 mL of 1.0 x 10^{-2} M Ni^{2+} solution was titrated against 1.0 x 10^{-1} M EDTA solution. Figure 5b.F_5 shows that the curve obtained was not perfectly sigmoid but the inflection point can be easily detected. At this point, 1:1 stoichiometry was observed which shows that this electrode can be used as an indicator electrode for the determination of Ni^{2+} ions.

Determination of Nickel in Chocolate Sample

Chocolate samples were weighed into a porcelain crucible and heated on a sand bath until fuming ceased. Then, the crucible was transferred into a furnace and heated at ~ 400 to 450 ºC for 120 minutes to ash the sample. After cooling the crucible, the residue was treated with 2 mL of 1:1 nitric acid solution and gently heated on the sand bath to dryness. The crucible was kept again into the furnace further to remove traces of black residues. Then, it was treated with 2-3 mL of 1:1 nitric acid solution and heated to dissolve the residue. The resulting solution was cooled, filtered and made up to 25 mL in a volumetric flask. The determination of nickel contents was determined by using the proposed electrode as well as by atomic absorption spectrophotometery. Results are compiled in Table 5b.T_4, which show that values by both methods are comparable.

Table 5b.T_1: Optimization of membrane ingredients

E. No.	Composition (%)			Slope (mV/dec)	Detection limit (M)	Working concentration range (M)
	PVC	Plasticizer	Ionophore 5.I			
1	33	66 (NPOE)	1	20	$3.9x10^{-5}$	$1.5x10^{-4}$ - $1x10^{-1}$
2	33	65 (NPOE)	2	23	$5.0x10^{-5}$	$7.9x10^{-4}$ - $1x10^{-1}$
3	33	64 (NPOE)	3	25	$7.9x10^{-5}$	$3.1x10^{-5}$ - $1x10^{-1}$
4	**33**	**63 (NPOE)**	**4**	**29**	**$3.1x10^{-6}$**	**$1.5x10^{-5}$ - $1x10^{-1}$**
5	33	62 (NPOE)	5	37	$6.3x10^{-5}$	$1.0x10^{-4}$ - $1x10^{-1}$
6	33	61 (NPOE)	6	35	$2.5x10^{-4}$	$1.2x10^{-3}$ - $1x10^{-1}$
7	33	63 (DBP)	4	25	$7.9x10^{-6}$	$5.0 x10^{-5}$ - $1x10^{-1}$
8	33	63 (BES)	4	22	$4.0x10^{-5}$	$9.0x10^{-5}$ - $1x10^{-1}$
9	33	63 (DOP)	4	21	$6.0x10^{-5}$	$7.1x10^{-5}$ - $1x10^{-1}$

Table 5b.T_2: Effect of mixed solvent media on the electrode response

Non-aqueous content	Mixing ratio (%v/v)	Slope (mV/decade)	Working concentration range (M)
Nil	-	29.0 ±0.5	1.5×10^{-5} to 1.0×10^{-1}
Methanol:water	10:90	27.5 ±0.9	3.1×10^{-5} to 1.0×10^{-1}
	20:80	31.0 ±0.5	3.9×10^{-5} to 1.0×10^{-1}
	30:70	34.5 ±0.9	1.5×10^{-5} to 1.0×10^{-1}
Acetone:water	10:90	30.0 ±0.5	5.0×10^{-5} to 1.0×10^{-1}
	20:80	30.0 ±0.9	2.5×10^{-5} to 1.0×10^{-1}
	30:70	33.5 ±0.5	6.3×10^{-5} to 1.0×10^{-1}
Acetonitril:water	10:90	29.5 ±0.7	1.9×10^{-5} to 1.0×10^{-1}
	20:80	30.0 ±0.6	7.9×10^{-5} to 1.0×10^{-1}
	30:70	34.0 ±0.3	1.0×10^{-4} to 1.0×10^{-1}

Table 5b.T_3: Potentiometric selectivity coefficients for the Ni^{2+} ISE

Interfering ion (B)	Selectivity coefficient log K	
	Fixed Interference Method (FIM)	**Matched Potential Method (MPM)**
Na^+	-1.8	-2.0
K^+	-1.9	-2.2
Mg^{2+}	-2.4	-2.2
Sr^{2+}	-1.8	-2.0
Co^{2+}	-2.0	-1.8
Zn^{2+}	-2.1	-1.8
Cu^{2+}	-2.2	-1.8
Fe^{3+}	-2.1	-2.2
Cd^{2+}	-2.4	-2.4
Pb^{2+}	-2.2	-2.4
Hg^{2+}	-1.6	-1.2
Ag^+	-1.8	-2.2

Table 5b.T_4: Analysis of Ni^{2+} ions present in chocolate samples

Name of the chocolate sample	**Proposed electrode** (mg L^{-1})	**Determined by AAS** (mg L^{-1})
Cadbury, Dairy Milk	1.41 (±0.03)	1.45 (±0.01)
Cadbury, 5-Star	0.44 (±0.04)	0.46 (±0.02)

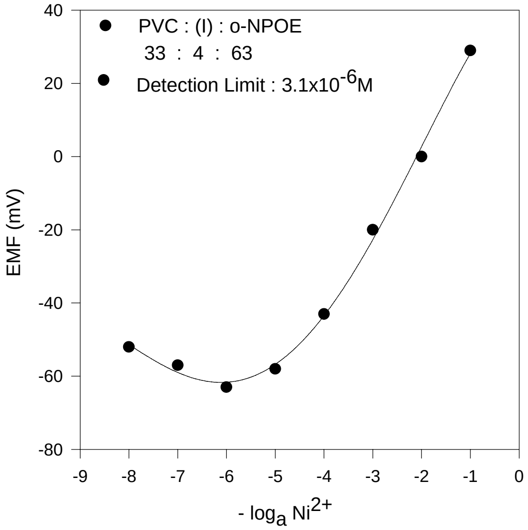

Figure 5b.F$_2$: Calibration curve for the Ni^{2+} ISE

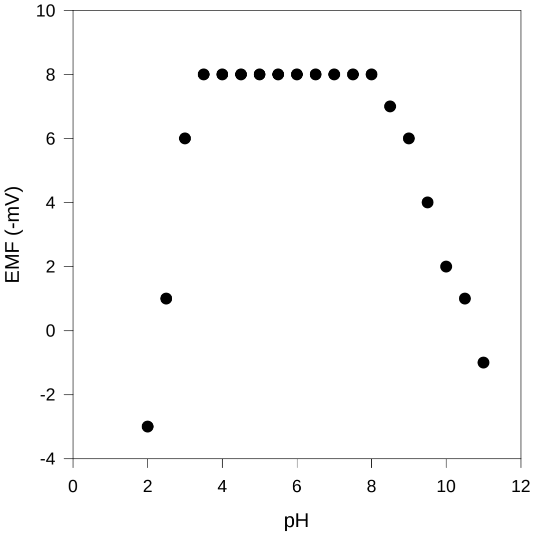

Figure 5b.F$_3$: Effect of pH for the Ni^{2+} ISE

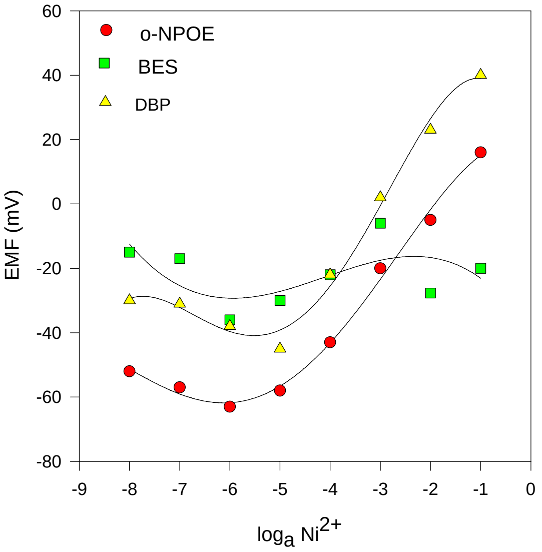

Figure 5b.F$_4$: Effect of plasticizer on the working of the Ni^{2+} ISE

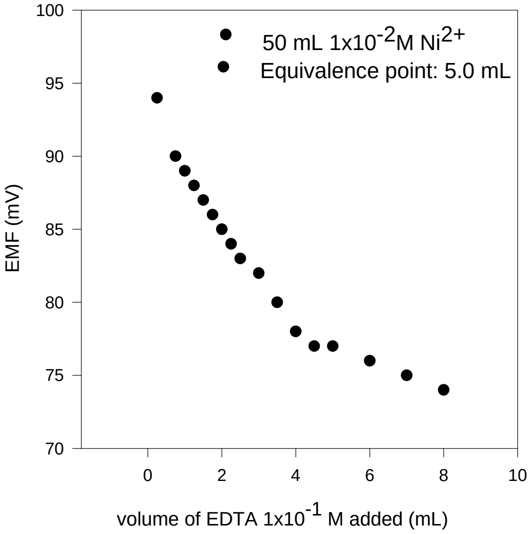

Figure 5b.F$_5$: Potentiometric titration of Ni^{2+} ions ($1x10^{-2}$ M) against EDTA ($1x10^{-1}$M) using the Ni^{2+} ISE

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5c. Silver-Selective Electrode Based on Liquid Membrane Containing $N_2S_2O_2$ Macrocycle as Ionophore

Introduction

The chemistry of mixed donor macrocyclic multidentante ligands with cation complexing ability has been explored extensively in the past (Bradshaw et al., 1993). The design and synthesis of macropolycyclic molecules, containing more than one recognition site for binding several guest species is of considerable interest in chemical literature (Chambron et al., 1986, Rebek Jr et al., 1979, Boyce et al., 1984, Hamilton et al., 1985, Beer et al., 1986). The hard, ether-oxygen containing macrocycles show binding preference towards alkali metal or alkaline earth cations, but incorporation of soft sulfide or amine linkages shifts preference towards soft transition metal ions (De Jong et al., 1981). The coordination chemistry of mixed nitrogen and sulfur donor macrocycles offer coordination of both hard sigma-donor N-ligands (with respect to S atom) and soft sigma-donor and potential pi acceptor S-ligands (Murray, S.G et al. 1984, Blake, A.J. 1989).

Macrocyclic multidentate ligands with an appropriate combination of ring size, identity and placement of donor atoms exhibit good extraction selectivity for desired metal ions such as, Filippoa et al., 2005, used mixed donor phenanthroline-containing macrocycles for the Ag^+ determination. Adam et al., 1994, used a dibenzo-substituted, 17-membered ring structure containing $S_2N_2S_2$ type to discriminate between silver(I) and lead(II). Effendy et al., 2004, prepared N-benzyl-substituted, 15- and 16-membered, macrocyclic ligands incorporating N_2O_3- and N_3O_3- donor sets attached to $CH_2CH_2NCH_2C_6H_5$ pendant arm were used for making complexes with Ag^+ and Ni^{2+} ions. Alp et al. (2007) synthesized an N_2S_4-donor macrocycle, and an N_2S_5-donor macrocycle for solvent extraction of Ag^+ and Hg^{2+} ions (Figure 5c.F_1). These compounds have been used successfully for diverse processes such as separation of ions by transport through artificial and natural membranes, liquid-liquid phase-transfer reactions, preparation of ion-selective electrodes, isotope separation (Lehn et al., 1985, Parham et al., 1994, Aguilar et al., 2001, Mousavi et al., 2000, Su et al., 2001) etc.

The detailed literature supports that the $N_2S_2O_2$ type macrocycle is not being reported as chemical sensor for silver metal ions. In the proposed work, this type of molecule is used as the sensing material in the fabrication of a liquid-membrane based silver ion-selective electrode.

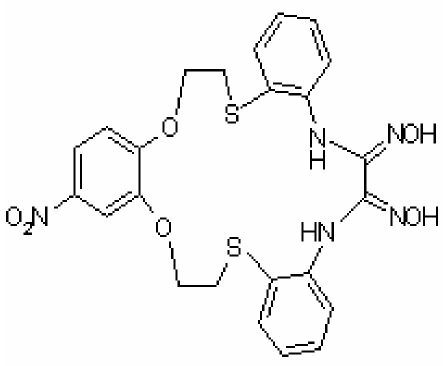

Figure 5c.F1: Structure of the ionophore for Ag^+ ISE

Experimental

Reagents, Apparatus, Preparation of Electrodes and EMF Measurements

A number of liquid-membrane based electrodes were prepared according to a previously reported method and potential measurements were taken as discussed in chapter 3.

Results and Discussion

Due to the lipophilic nature and the presence of two sulphur and two nitrogen atoms in its structure, the ionophore was expected to be selective for some special transition metal ions of proper size and charge. Thus, in the preliminary experiments conductometric titrations (Shamsipur et al., 2000) were done for the determination of the stability constant for different metal ions. Results of K_f values are in the following order $Ag^+ > Ni^{2+} > Hg^{2+} > Cd^{2+} > Zn^{2+} > Pb^{2+}$. According to this study, the ionophore (Figure 5c.F_1) tends to be more selective for Ag^+ ions in comparison to others.

Effect of Membrane Ingredients and Their Composition

The potential response of the Ag^+-selective electrode is shown in Figure 5c.F_2. As it can be seen, the PVC-membrane based on ionophore 5.II shows Nernstian response in the working range of 2.5×10^{-5} to 1.0×10^{-1} M with a detection limit of 7.9×10^{-6} M. For this response of the membrane electrode, PVC, plasticizer and ionophore were taken in the ratio of 33:65:2 (wt. %). This optimized composition, the electrode gives a Nernstian slope (58.5 mV/decade) is well known fact that not only the nature of ionophore or membrane composition affects the sensitivity and selectivity of the ion-selective electrode, but the properties of plasticizer used also affects significantly the response characteristics of the liquid-membrane based chemical sensors (Kamata et al., 1988, Bakker et al., 1997). Thus, the effect of plasticizer and influence of membrane composition on the response characteristics were also measured and the results are summerized in Table 5c.T_1. As can be seen from the Table 5c.T_1, among the three different plasticizers used, o-NPOE shows the best results in terms of slope, concentration range and detection limit. The electrodes were stored in 0.1 M Ag^+ solution when not in use.

Effect of pH and Effect of Non-Aqueous Media

The pH response for the proposed electrode was also examined using 1×10^{-3} M Ag^+ concentration. The pH value was adjusted either with 0.1 N HNO_3 or 0.1 N NaOH solution as per requirement. It is clear from Figure 5c.F_3, pH 5 to 9 was observed as the best pH range in which the electrode response is not affected by the change in pH.

Beyond this pH range, drift on both the sides was observed which might be due to the protonation of the ionophore at lower pH, and above this pH range, due to the formation of AgOH and Ag_2O beyond the pH range, respectively. The electrode response was also examined in the presence of non-aqueous media using methanol-water, acetone-water and acetonitril-water mixtures. The membrane electrode worked well up to 30% (v/v) non-aqueous content without showing any appreciable change in the working concentration range or slope.

Potentiometric Selectivity Coefficient

Potentiometric selectivity coefficient values were determined by MPM as well as by FIM method are presented in Table 5c.T_2. As it can be seen from the table, the selectivity coefficients are in the order of 10^{-2} or smaller, indicating that interfering ions will not significantly disturb the functioning of the Ag^+ ion-selective electrode.

Potentiometric Titrations

Potentiometric titrations were done by taking known concentrations of $AgNO_3$ solution against standard solution of KI. As depicted from Figure 5c.F_4, the potential break observed at 5 mL of titrant used, shows the 1:1 complex formation between the metal and I^- ions. The same equivalence point was observed during reverse titration.

Simultaneous Determinations of Halides in a Mixture

A known volume of halide mixture (each having $1x10^{-3}$ M concentration) was titrated against a standard solution of Ag^+ ions. Figure 5c.F_5 shows three breaks in the curve for I^-, Br^- and Cl^-, respectively. Each break in the curve shows the precipitation of Ag^+ with each ion in the ratio of 1:1 on the basis of the solubility product. The K_{sp} values are in the order $I^- < Br^- < Cl^-$. Iodide ions precipitate first and then, bromide and chloride ions follow.

Sensitivity of Potentiometric Titrations of Electrode

The sensitivity of the proposed electrode was also examined by potentiometric titration method. For this purpose, titrations of Ag^+ (10^{-2}, 10^{-3}, 10^{-4}, 10^{-5} M) ions against KI (10^{-1}, 10^{-2}, 10^{-3} and 10^{-4} M) were carried out using the proposed Ag-ISE as indicator electrode. Figure 5c.F_6 shows the curves obtained of these titrations. This titration is more sensitive and than the direct method of measurement. In the direct measurement, the liquid-junction potential and inner solution concentration affect the change in the total emf of the electrode. In the titration method these observations are relative and cancel each other. More explanation about this method is discussed in the previous section 5a and 5c.

Determination of Ag^+ in Presence of Hg^{2+} by Potentiometric Titration Using KI

An equimolar mixture of Ag^+ and Hg^{2+} ions were titrated against I^- ions and Figure 5c.F_7 shows the equivalence point corresponding to 1:3 equivalents of iodide ions. It is clearly indicated that 1/3 (1 equivalent) of the reagent is used up in precipitating the Ag^+ ions and 2/3 (2 equivalents) are used up for precipitating the Hg^{2+} ions. However, the extent of Hg^{2+} of interference is quite predictable because the inflection in the curve is obtained corresponding to the 1:3 equivalence point. The type of interaction of Ag^+ and Hg^{2+} ions when they alone and inmixed form in solution, is discussed in chapter 4a.

Analytical Applications

Determination of Chloride in Vitamin B_{12} Sample and Boiled Tap Water

50 mL of $1x10^{-2}$ M Vitamin B_{12} solution was titrated against standard solution of Ag^+ ions. As it is clear from Figure 5c.F_8, a sharp equivalence point is observed at 10 mL. This shows that vitamin B_{12} contains 2 moles of chloride ions. Chloride contents were also determined in tap water in normal and boiled conditions both (Figure 5c.F_9). The results coincide well with the observations made using the 798 MPT Titrino Auto titrator and chloride electrode.

Table 5c.T$_1$: Optimization of membrane ingredients for the Ag$^+$ ISE

E. No.	Composition (%)			Slope (mV/dec)	Working concentration range (M)	Detection limit (M)
	PVC	Plasticizer	(I)			
1	33	66	1	55.5	$1.0x10^{-4}$ to $1.0x10^{-1}$	$1.5x10^{-5}$
2	33	65	2	58.5	$2.5x10^{-5}$ to $1.0x10^{-1}$	$7.9x10^{-6}$
3	33	64	3	50.5	$7.9x10^{-5}$ to $1.0x10^{-1}$	$3.1x10^{-5}$
4	33	63	4	30.0	$1.0x10^{-3}$ to $1.0x10^{-1}$	$1.0x10^{-4}$
5	33	62	2	25.0	$3.1x10^{-3}$ to $1.0x10^{-1}$	$1.5x10^{-3}$
6	33	65 (DBP)	2	55.0	$3.9x10^{-4}$ to $1.0x10^{-1}$	$3.1x10^{-5}$
7	33	65 (BES)	2	40.0	$5.0x10^{-3}$ to $1.0x10^{-1}$	$5.0x10^{-3}$

Table 5c.T$_2$: Potentiometric selectivity coefficients for the Ag$^+$ ISE

Interfering ions	Selectivity coefficients, - $\log K^{pot}_{A,B}$	
	MPM	FIM
Li$^+$	2.0	1.9
Na$^+$	2.0	1.8
K$^+$	2.1	2.0
Ca^{2+}	1.8	2.0
Mg^{2+}	2.0	2.1
Sr^{2+}	1.9	2.1
Ag$^+$	1.8	1.9
Hg^{2+}	1.5	1.8
Ni^{2+}	2.1	2.1
Cd^{2+}	2.0	2.1
Co^{2+}	2.0	2.1
Zn^{2+}	2.0	2.2
Pb^{2+}	1.5	1.8
Fe^{3+}	2.2	2.1
Al^{3+}	2.4	2.3

Table 5c.T$_3$: Determination of Cl$^-$ ions in Vitamin B$_{11}$ and tap water samples

Sr. No.	Name of the sample	798 MPT Titrino Auto titrator and 6.0430.100 Ag titrode)	Proposed selective electrode (mgL^{-1})
1	Vitamin B$_1$	712.0 ±3	710.0±5
2	Tap water	425.0±4	426.0±5

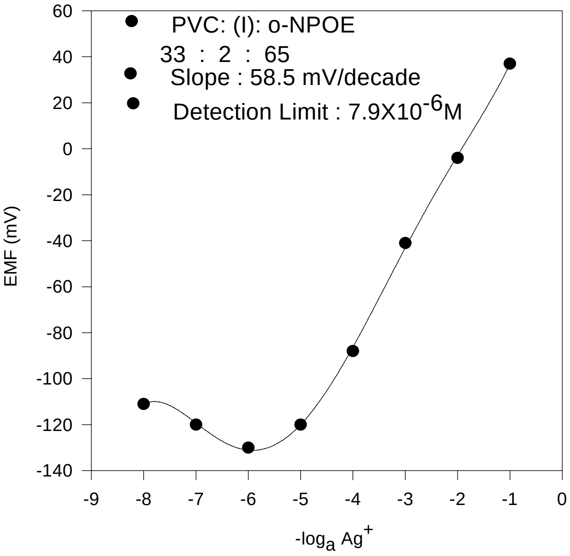

Figure 5c.F$_2$: Calibration curve for the Ag$^+$ ISE

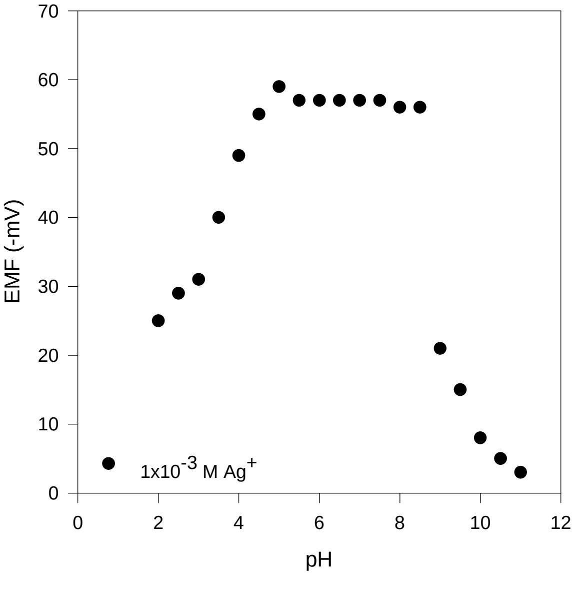

Figure 5c.F$_3$: Effect of pH for the Ag$^+$ ISE

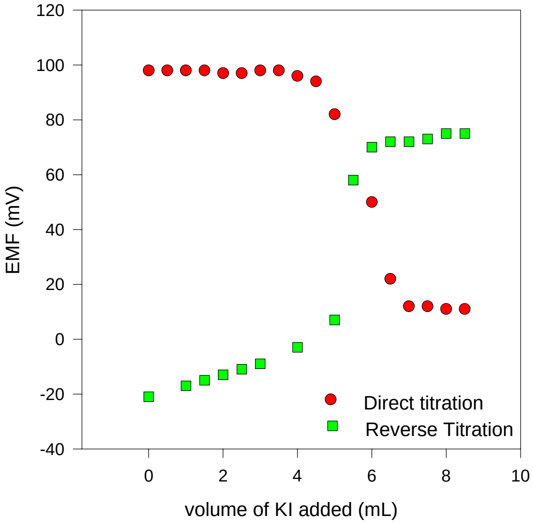

Figure 5c.F$_4$: Potentiometric titrations (direct and reverse) of Ag$^+$ ions with I$^-$ ions using the Ag$^+$ ISE

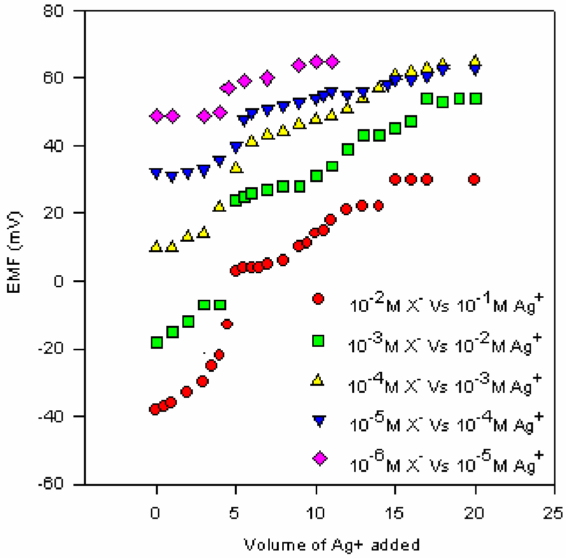

Figure 5c.F$_5$: Simultaneous determinations of halides in a mixture by using the Ag$^+$ ISE

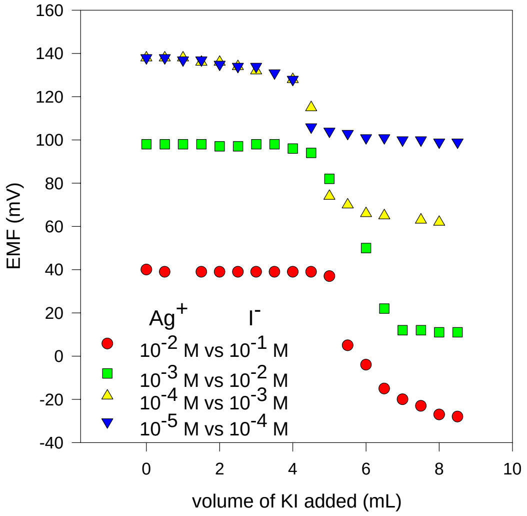

Figure 5c.F$_6$: Sensitivity of the Ag^+ ISE by using the potentiometric titration method

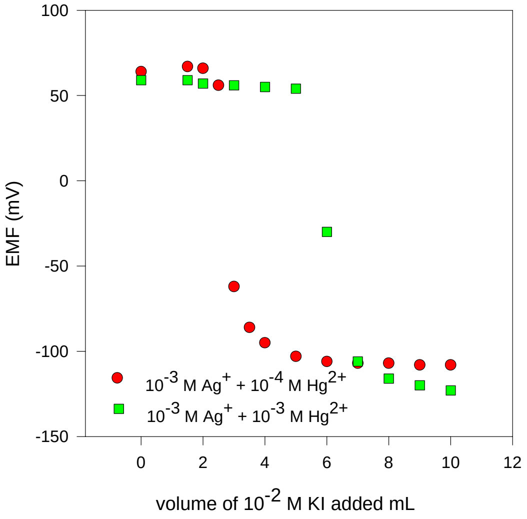

Figure 5c.F$_7$: Determination of Ag^+ in the presence of Hg^{2+} by potentiometric method

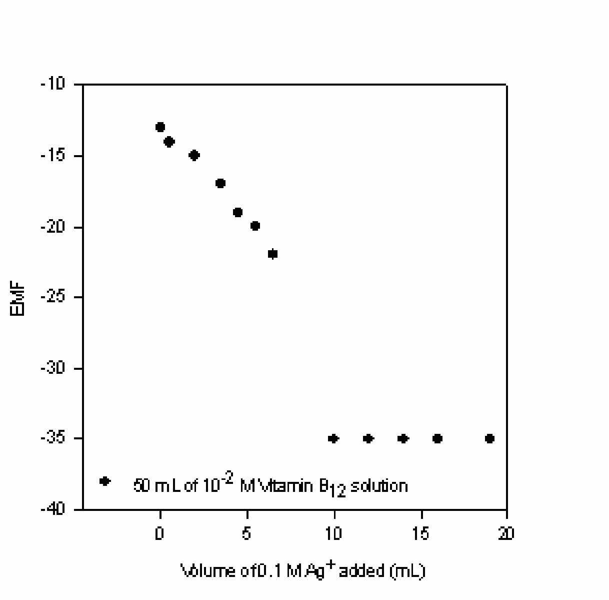

Figure 5c.F$_8$: Determination of chloride in Vitamin B$_{11}$ using KI by titration using Ag$^+$ ISE

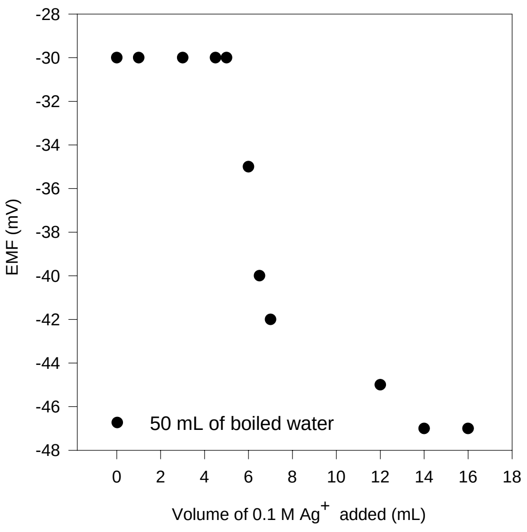

Figure 5c.F$_9$: Determination of chloride in boiled tap water samples

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Conclusion and Future Prospects

Cyclic ionophores (L1, L2 and L3) which possess two thioether - one amine - two amide units along with alkyl thioether as the common structural feature have been designed. These groups create desired flexibility in the resulting receptors. These receptors have been used for preparing Ag^+ ion-selective electrodes. L1, L2 and L3 ionophores exhibit linear responses with pseudo-Nernstian slopes between 43-46 mV/decade in the concentration range of 1 x 10^{-5} to 1 x 10^{-1} M of Ag^+ ions for macrocycle L1, and 1 x 10^{-4} to 1 x 10^{-1} M for macrocycles L2, L3, respectively. The lower detection limit of 6 x 10^{-5} M is observed for electrodes based on L1 and 6 x 10^{-5} M for L2 and L3 based electrodes. These electrodes can perform well over a wide pH range of 4.5 to 8.0. The observed response time is <15 sec. These electrodes exhibit a good selectivity for Ag^+ with respect to other interfering ions, like alkali, alkaline earth, some transition metal ions and heavy metal ions. The electrodes can be used for at least four months without any considerable divergence in their performance and as indicator electrodes in the potentiometric determination of Ag^+ ions, and to estimate anions, like Cl^-, Br^-, I^-, SCN^- and CN^-.

Spectrophotometric and conductometric studies on the binding properties of 1,4,8,11-tetraazacyclotetradecane-5,7-dione (I) toward Co^{2+} and some other metal ions revealed the occurrence of 1:1 (ligand/metal) complexation with a stability order of $Co^{2+} > Cu^{2+} > Pb^{2+} > Ni^{2+} > Ag^+$. Consequently, (I) was also used as a neutral carrier for the preparation of a novel liquid-membrane based electrode selective for Co^{2+}ions. The electrode exhibited a Nernstian slope of 29 mV/decade over a wide concentration range (1.0 x 10^{-6}- 1.0 x 10^{-1} M) and a detection limit of 1.0 x 10^{-6} M. It shows a response time of <10 sec and can be used over a pH range of 5.0-8.0. The electrode possesses a fast response time and can be used for at least 4 months without observing any considerable deviation in the response behaviour and selectivity. Infact, the electrode shows a very good selectivity for Co(II) over a number of alkali, alkaline earth and heavy metal ions. The proposed electrode was successfully applied as an indicator electrode, in the potentiometric titration of Co(II) ions.

N,*N'*-Bis(2-aminoethyl)-9-anthrylmethylmalonamide (I) was used as an ionophore in a liquid- membrane based electrode in PVC-matrix for the determination of Cu^{2+} ions. The membrane electrode with composition 33:2:64:1 (PVC:I:o-NPOE:NaTPB) exhibits a Nernstian response towards Cu^{2+} ions with a slope of 29.0 ± 1.7 mV per decade over the concentration range 3.9×10^{-6} to 1.0×10^{-1} M, and the potential response remains almost unchanged over pH range 3.1–6.3. The electrode shows a fast response time of 15 ± 2 s and a lifetime of five months. It shows selectivity for Cu^{2+} ions over some other mono-, di- and trivalent cations. In partially non-aqueous medium this electrode response is found to be satisfactory. The electrode can also be used as an indicator electrode in the potentiometric titration of Cu^{2+} with EDTA and its determination in real life samples.

A liquid-membrane based Zn^{2+} ion-selective electrode containing N,N'-Bis(2-dimethylaminoethyl)-N,N'-dimethyl-9,10 anthracenedimethanamine as ionophore has been prepared and characterized. DBP, DOP, BES and o-NPOE were tried as plasicizers in the preparation of the PVC based membrane, o-NPOE was selected for further studies. The membrane comprises of PVC, ionophore and plasticizer in the ratio of 33:2:65, respectively. It showed the best response in terms of detection limit (1.5×10^{-6} M) and working concentration range (1.0×10^{-5} M to 1.0×10^{-1} M) with a Nernstian response towards Zn^{2+} ions. The electrode responds within 15 seconds of coming in contact with the solution. The potential response remains almost unchanged over a pH range 3.0 to 7.5. The electrode can be used for at least three months without any considerable alteration in its response behaviour. The proposed electrode revealed a good selectivity towards Zn^{2+} ions over a number of alkali, alkaline earth, transition metals and some other heavy metal ions. The electrode has been used as an indicator electrode in the potentiometric titration of Zn^{2+} with EDTA. The proposed electrode was also used to detect Zn^{2+} ions from some real life samples.

A new PVC-membrane electrode selective to Cu (II) ions was prepared by using uracil containing acyclic amide linkage as a suitable neutral carrier. The electrode exhibits a Nernstian slope of 28 mV per decade at 25 °C for Cu^{2+} ions over a wide concentration range ($5 \times 10^{-5} - 1 \times 10^{-1}$ M). It has a response time of <20 s and a detection limit of 3.0×10^{-5} M. The proposed electrode revealed good selectivity over a wide variety of other cations including alkali, alkaline earth and transition metal ions and could be used for at least 4 months without any divergence in potential. It was applied for the direct determination and potentiometric titration of copper ions.

A new electrode based on a synthesized ionophore named N_2S_2 macrocyclic Schiff's base as an ionophore has been developed. This PVC-membrane based silver ion-selective electrode gave a Nernstian response for silver ions in the concentration range of $1 \times 10^{-5} - 1 \times 10^{-1}$ M. The limit of detection was 5×10^{-6} M. This electrode displayed a very good selectivity for Ag^+ ions against alkali, alkaline earth and some transition metal ions. Overall, the performance of the present silver ion-selective electrode based on the proposed ionophore is comparable to that of reported electrodes based on a neutral carrier. The proposed silver-selective electrode could be used in a pH range of 5.0-8.0. It was used as an indicator electrode in potentiometric titration of Ag^+ with I^-. Applications of the electrode in potentiometric titrations and determination of the Ag^+ concentration in some synthetically prepared sample solutions are also reported.

A new PVC membrane ion-selective electrode for nickel ions has been constructed using a neutral ionophore contaning four secondary amine groups inside the cavity. Effect of various plasticizers, viz. o-nitrophenyloctyl ether (o-NPOE), dibutylphthalate (DBP), and bis 2-ethyl sebacate (BES) was studied. The electrode was prepared with an optimized composition as 4% ionophore, 63% o-NPOE (as plasticizer) and 33% PVC. The electrode gave a Nernstian slope (29 mV/decade) over the concentration range of 1.5 x 10^{-5} M to 1.0 x 10^{-1} M and a workable pH range of 3.5–8.5. The lower limit of detection was 3.1 x 10^{-6} M. It has a response time of <20 s and can be used for at least three months without any divergence in potential. The proposed electrode shows a good discrimination of Ni^{2+} ions from several cations. The effect of aprotic solvents on the electrode response was examined. The results show that this electrode can be used in mixed solvent media contaning up to 20%(v/v) aprotic solvent with a Nernstian slope. The electrode can be used as an indicator electrode and successfully applied for the determination of Ni^{2+} ions in chocolate samples.

Plasticized membranes using an $N_2S_2O_2$ based molecule as an ionophore are explored as Ag^+ ion-selective sensor materials. An optimum performance was noted with the membrane of the neutral carrier ionophore having a composition of PVC, plasticizer and ionophore in the ratio of 33:65:2 (wt.%). Stability constants for the ionophore with different metal ions were determined by conductometric titrations. The sensor works satisfactorily in the concentration range from 2.5 x 10^{-5} - 1.0 x 10^{-1} M (detection limit 7.9 x 10^{-6} M) with a Nernstian slope of 58.5 mV/decade. A wide pH range (5.0–9.0), fast response time (15 s), non-aqueous tolerance (up to 30%) and adequate shelf life (3 months) indicate the vital utility of the proposed sensor. The proposed electrode comparatively shows a good selectivity for Ag^+ ions with respect to alkali, alkaline earth, transition and rare earth metals ions and can be used for the determination in binary mixtures. The electrode can also be used for the determination of halides in a mixture. Determinations of chloride in Vitamin B_{12} and boiled tap water samples were also made by using the proposed electrode as an indicator electrode.

The proposed set of electrodes provides new chemical sensors based on neutral carrier ionophores. These electrodes are based on easily available ionophores as sensing molecules, and the operation protocol is simple. There is a lot of scope for improvment of lower detection limit, response time and shelf life. Selectivity coefficients are reasonably good for a number of metal ions, which are likely to interfere e.g., the presence of Hg^{2+} ions can be calculated. Novelty of the work lies in the methodology of detection limit by potentiometric titration. This technique is used for silver ion-selectivie electrodes.

List of Publications

Journals

1. **Nidhi Rani Gupta**, Susheel Mittal, Subodh Kumar, Ashok Kumar S.K, Potentiometric studies of N,N′-Bis(2-dimethylaminoethyl)-N,N′-dimethyl-9,10 anthracenedimethanamine as a chemical sensing material for Zn(II) ions, Materials Science and Engineering C, 28(2008)1025.

2. **Nidhi Rani Gupta**, Susheel Mittal, Subodh Kumar, Ashok Kumar S.K, A liquid membrane based electrode containing an electroactive chelating substance selective for cobalt (II) ions, Analytical Chemistry, An Indian Journal, 7(4), 2008.

3. **Nidhi Rani Gupta**, Susheel Mittal, Ashok Kumar S.K, Mirac Ocak, Ummuhan Ocak, Silver (I)-selective membrane electrodes based on macrocycles possessing imine and thioether combinations, Analytical Chemistry, An Indian Journal, 7(4), 2008.

4. **Nidhi Rani Gupta**, Susheel Mittal, Ashok Kumar S.K, Mirac Ocak, Ummuhan Ocak, Silver selective electrode based on liquid membrane containing $N_2S_2O_2$ macrocycle as ionophore, Journal of Indian Chemistry, 47A(2008)1676.