INVESTIGATIONS ON SOME IONOPHORE BASED CHEMICAL SENSORS

By

S. K. ASHOK KUMAR

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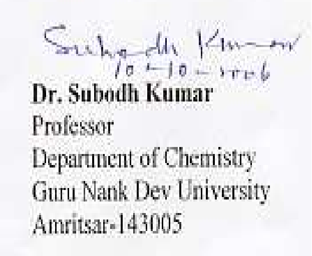
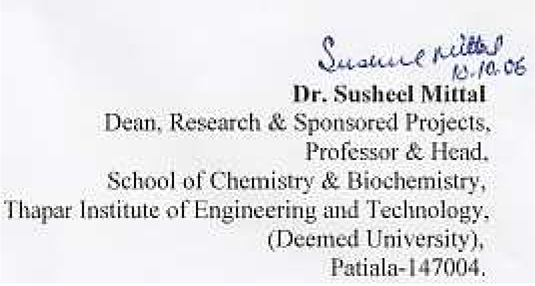
Certificate

Certified that the work embodied in this thesis entitled, “INVESTIGATIONS ON SOME IONOPHORE BASED-BASED CHEMICAL SENSORS” which is being submitted by Mr. S.K. Ashok Kumar, in fulfillment of requirements for the award of the degree of Doctor of Philosophy in School of Chemistry & Biochemistry of Thapar Institute of Engineering and Technology (Deemed University), Patiala is a record of candidate’s own work carried out by him under our supervision and guidance. The matter presented in this thesis has not been submitted in part or full for the award of any degree in any other University or Institute.



Subodh Kumar
10-10-2006
Dr. Subodh Kumar
Professor
Department of Chemistry
Guru Nank Dev University
Amritsar-143005



Susheel Mittal
10.10.06
Dr. Susheel Mittal
Dean, Research & Sponsored Projects,
Professor & Head,
School of Chemistry & Biochemistry,
Thapar Institute of Engineering and Technology,
(Deemed University),
Patiala-147004.

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LIST OF ABBREVIATIONS

ABBREVIATED WORD	FULL FORM
DB18C6	Dibenzo-18-Crown-6
DC18C6	Dicyclohexano-18-Crown-6
DB2C8	Dibenzo-24-Crown-8
MO8HQ	1,3,5-tris(8-quinolinoxymethyl)-2,4,6-trimethylbenzene
5CHQ	1,3,5-tris(5-chloro-8-quinolinoxymethyl)-2,4,6-trimethylbenzene
5BHQ	1,3,5-tris(5-benzoyl-8-quinolinoxymethyl)-2,4,6-trimethylbenzene
5HYD-8HQ	1,3,5-tris [(5-(phenylhydoxymethylene)-8-quinolinoxymethyl)-2,4,6-trimethylbenzene
Diantha	9,10-bis-(2-aminophenylthiomethyl)anthracene
EDTA	Ethylene Diammine Tetraacetic Acid
EMF	Electromotive Force
FIM	Fixed Interference Method
HPIC	High Performance Ion Chromatography
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectrometry
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ISE	Ion-selective electrode
MPM	Matched Potential Method
PVC	Polyvinyl Chloride
REE	Rare Earth Element
THF	Tetrahydrofuran

Chapter -1

INTRODUCTION

Analytical Chemistry

Analytical chemistry is concerned with the theory and practice of methods used to determine the composition of matter. In developing methods of analysis, the analytical chemist feels free to draw upon principles from any field of science - chemistry, physics, biology, engineering, computer science, etc. For example, instruments developed by physicists such as the mass spectrometer, the X-ray dispersive spectrometer and the infrared spectrophotometer have found wide applications in solving analytical problems.

Today, there are many new techniques available for application to analytical problems, and for this reason the analytical chemist needs to have a good knowledge of a number of scientific fields. The explosion of technological developments in recent years has created analytical problems, which demand increasingly sophisticated instrumentation and knowledge for their solution. Typical examples of such problems are trace level determination of metal ions. The solutions to a host of problems such as these have been developed by research workers with the most diverse backgrounds. Workers in many fields are constantly confronted by analytical problems, and in many cases they work out their own solutions.

What distinguishes the analytical chemist from other workers is an interest in the methods and techniques in their own right. Workers in other fields often need to develop new analytical methods for their own purposes. Analytical chemists, developing methods is the challenging part of the research. Analytical chemists deal with real, practical systems and much of their effort is expended in an attempt to apply sound theory to actual chemical situations.

Sensors

These are devices, which sense the target species present in the system. We have at least five of these i.e., nose, tongue, ear, eye and skin. They represent main types of a sensor. In a laboratory, one of the best types of sensor is the litmus paper test for acids and alkalies, which gives a qualitative indication, by means of a colour reaction, of the presence or absence of an acid. A more precise method of indicating the degree of acidity is measurement of pH, either by the extended use of colour reactions in special indicatior solutions, or even by simple pH papers. However, the best method of measuring acidity is the use of the pH meter, which is an electrochemical device giving an electrical response, which can be read by a needle moving on a scale or on a digital read-out device or input to a microprocessor.

In such methods, the sensor that responds to the degree of acidity is either a chemical, the dye in litmus or a more complex mixture of chemical dyes in pH indicator solutions or the glass membrane electrode in the pH meter. The chemical or the electrical response then, has to be converted into a signal that we can observe. In the case of the pH meter, the electrical response (a voltage change) has to be converted i.e., transduced (= led through), into an observable response-movement of a meter needle or a digital display. The part of the device that carries out this conversion is called a transducer.

We can divide sensors into three types, namely:

(a) Physical sensors for measuring distance, mass, temperature, pressure, etc.,

(b) chemical sensors which measure chemical substances by chemical or physical responses, and

(c) biosensors, which measure chemical substances by using a biological sensing element. All of these devices have to be connected to a transducer of some sort, so that a visibly observable response occurs. Chemical sensors and biosensors are generally concerned with sensing and measuring particular chemicals which may (or many not) be biological themselves. Biosensors are really a sub-set of chemical sensors, but are often treated as a topic in their own right. A biosensor can be defined as a device incorporating a biological sensing element connected to a transducer. The analyte that this sensor detects and measures may be purely chemical (even inorganic), although biological components may be the target analyte. The key difference is that the recognition element is biological in nature.

Aspects of Sensors

Recognition Elements

Recognition elements are the key component of any sensor device. They impart the selectivity that enables the sensor to respond selectively to a particular analyte or group of analytes, thus avoiding interferences from other substances. Methods of analysis for specific ions have been available for a long time using ion-selective electrodes, which usually contain a membrane selective for the analyte of choice.

Transducers - the Detector Device

Analytical methods in chemistry have mainly been based on photometric transducers, as in spectroscopic and colorimetric methods. However, most sensors have been developed around electrochemical transducers, because of simplicity of construction and cost. With electron-driven microprocessors, the directness of an electrical device will tend to have a maximum appeal. In addition, the use of micro-mass-controlled devices, based mainly on piezo-electric crystals, may become competitive in the near future.

Transducers can be subdivided into the following four main types.

A. Electrochemical Transducers

1. Potentiometric: These involve the measurement of the emf (potential) of a cell at zero current. The emf is proportional to the logarithm of the concentration of the substance being determined.
2. Conductometric: Most reactions involve a change in the composition of the solution. This will normally result in a change in the electrical conductivity of the solution, which can be measured electrically.
3. Voltammetric: An increasing (decreasing) potential is applied to the cell until oxidation (reduction) of the substance to be analyzed occurs and there is a sharp rise (fall) in the current to give a peak current. The height of the peak current is directly proportional to the concentration of the electroactive material. If the appropriate oxidation (reduction) potential is known, one may step the potential directly to that value and observe the current. This mode is known as amperometric.
4. FET-based sensors: Miniaturisation can sometimes be achieved by constructing one of the above types of electrochemical transducers on a silicon chip-based field-effect transistor. This has mainly been used with potentiometric sensors, but could also be used with voltammetric or conductometric sensors.

B. Optical Transducers

These have taken a new lease of life with the development of the fibre optics, thus allowing greater flexibity and miniaturisation. The techniques used include absorption spectroscopy, fluorescence spectroscopy, luminescence spectroscopy, internal reflection spectroscopy, surface plasma spectroscopy and light scattering.

C. Piezo-Electric Devices

These devices involve the generation of electric currents from a vibrating crystal. The frequency of vibration is affected by the mass of material adsorbed on its surface, which could be related to changes in a reaction. Surface acoustic wave (SAW) devices are a related system.

D. Thermal Sensors

All chemical and biochemical processes involve the production or absorption of heat. This can be measured by sensitive thermistors and hence, be related to the amount of substance to be analysed.

Supra-molecular Chemistry

To achieve a ligand 'tailored' for a particular metal-ion binding application, the system needs to be designed such that it is able to read the information encoded in the metal ion of interest and differentiate it from that for other metals that might be also present (1-3). Clearly, nature has learnt to do this superbly in a wide range of biochemical systems. In contrast, the success achieved with synthetic systems has tended to be somewhat more modest. This is perhaps surprising in view of the fact that we are now around a century on from Alfred Werner's time. Thus, although metal ion recognition is inherent to many processes in nature, the factors influencing such behavior are often difficult to elucidate. This is especially the case when mixed donor sets are present and or heavy metal ions are involved.

For a particular polydenate ligand, metal ion recognition may involve contributions from some or all of the following:

(a) The number and type of donor atoms available.
(b) Their relative positions in terms of both their spacing and sequence within the ligand.
(c) The electronic and structural nature of the ligand's backbone.
(d) The formal charge and or the presence or absence of dipoles (both permanent and induced) on the bound ligand.
(e) The number and size of the chelate rings formed on metal binding.
(f) The changes in salvation of the ligand and metal ion on complex formation.

Further, for transition metal ions, crystal field effects may also contribute to a decrease in free energy for complex formation. In the case of macrocyclic ligand systems, macrocyclic ring size is another factor that will influence complex stability.

The ability of a given ligand to recognize a metal in the presence of others will normally reflect a subtle mix of factors on the type just mentioned (although, it is noted that, in some cases one factor, such as the donor set type, may appear to dominate the process). The situation is further complicated by the fact that several of the factors listed above are not independent of each other. However, in general terms, recognition for a particular metal ion of interest will occur when the properties of the ligand best match the steric and electronic nature of the metal ions, relative to those of the other metal ions present.

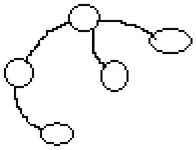
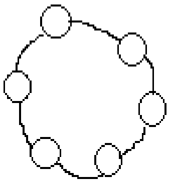
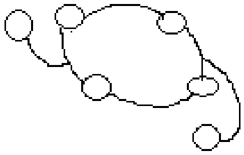
It needs to be kept in mind that metal ion selectivity depends on achieving a difference in the binding constants for the respective cations. That is the difference in the constants rather than their absolute magnitude, which is usually of prime concern. Of course, high absolute values may also be desirable since, for example, the latter may commonly be associated with enhanced kinetic stabilities.

In a typical metal-ion recognition investigation, the procedure has been to choose a cyclic or an acyclic ligand which, based on analogy with known systems, might be expected to show preference for the ion of interest. After synthesis of the ligand, an investigation of its metal coordination chemistry is then carried out. Such a study has always incorporated the determination of stability constants for the respective 1:1 complexes coupled with a range of other studies. An assessment of the possible factors influencing any observed metal-ion recognition behavior is then made and, on this basis, a decision is taken as to what structural modification might be carried out to tune up this behavior. The required ligand modification is then made and the cycle is repeated. In this manner, it is usually possible to modify a ligand type progressively, using a trial and error approach, such that enhanced metal ion discrimination is induced.

Since the antibiotic nigericin was isolated in 1951 as the first representative, natural ionophores have attracted wide attention and been the subject of numerous investigations. They are known to specifically transport biological guest species across a bio-membrane. For example, valinomycin transports the K^+ ion with much greater efficiency than the Na^+ ion, whereas monensin selectively transports the Na^+ ion against its concentration gradient. Their molecular structures, 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.

Numerous structurally diverse compounds have been found to act as ionophores in many biological membrane systems. Although they have various molecular skeletons, donor atoms, chain lengths and ligand topologies, a distinction is made between the acyclic podands, the macrocyclic crown ethers and the armed macrocycles. The minimum number of donor atoms and chain segments of each class of natural and synthetic ionophores is shown in Table 1.1. This topological classification is widely accepted for the synthetic crown ether compounds and can also be applied with some discretion to the natural ionophores.

Table 1.1: Classification and topology of ionophores

Classification	**Podand (Acyclic)**	**Crown Ether (Cyclic)**	**Armed Macrocycle (Acyclic + Cyclic) Lariat ethers**
Topology			
Natural Ionophore	Monensin Nigericin	Valinomycin Enniatinand	Enterobactin Ferrichrome
Synthetic Ionophore	Polyglyme Dipod,Tripod, and Tetrapod	18-Crown-6 Cyclam	Double-Armed Crown Ether

There are several important differences in coordination chemistry of synthetic and natural ionophores. In particular, natural ionophores form three-dimensional complexes with cations. Typically, valinomycin is the most famous ionophore specific for the K^+ ion, which has a 32-member ring of the crown ether type. Monensin is a more flexible podand-type natural ionophore, but shows greater stability constants for several metal cations than synthetic crown ethers and podands. Crystallographic studies of the Ag^+ complex clearly reveal that a stable complexation comes from the characteristic pseudo-cyclic conformation. The ends of the chain are linked by intramolecular head-to-tail hydrogen bonds involving the carboxylate anion and suitably placed –OH groups. Thus, the guest cation is located at the centre of pseudo-cavity and tightly coordinated by six oxygen atoms.

Rapid development in the synthesis of neutral macrocyclic ligands capable of complexing with anions and cations has stimulated research efforts in many fields of chemistry. The pioneering work of Pedersen on macrocyclic polyethers or crown ethers (4-6) was chiefly concerned with oxygen-containing ring systems and produced a series of powerful complexing agents for alkali and alkaline earth cations. Subsequent investigations led to macrocycles with nitrogen and sulfur atoms as binding sites in addition to oxygen and often as part of a subheterocyclic structure such as a pyridine, thiophene, and furan ring. More powerful cation complexing ligands, notably polyaza-polyoxa macropolycycles or cryptands were developed by Lehn and his co-workers (7-9). Some of these ligands have been designed to form binuclear cation inclusion complexes such as the cylindrical macro tricycles in which two macrocyclic rings are linked by two bridges. Further, Lehn et al. developed the bis-tren macobicyclic ligands, in which two cations are held inside a large intra-molecular cavity. With the proper design such a binuclear cryptate may be used to activate substrates by inserting them between the two cations. An interesting class of neutral acyclic ligands coined “podands” and developed recently by Vogtle and Weber (10-15) have properties similar to those of crown ethers and cryptands and can also form crystalline alkali ion complexes or extract alkali salts from an aqueous into an organic phase. In addition to carriers for group 1A and 2A cations, ionophores for transition metals and for their enantiometric salts have also been developed. Electrically neutral, lipophilic ion-complexing agents of rather small relative molar mass are known to behave as ionophores or ion carriers, having the capability to selectively extract ions from aqueous solutions into a hydrophobic membrane phase and to transport these ions across such barriers by carrier translocation.

Structural Features

Thousands of different macrocycles (16-17) that fall under the general description “crown ether” are now known. It is, therefore, impossible to define the structural features beyond the presence of a macrocyclic ring (generally, but not always, considered to be $\geq$ 12 members), in which heteroatoms (generally $\geq$ 4) are separated by a carbon-containing unit of two or more atoms. Oxygen is probably the predominant heteroatom in macrocycles intended to bind alkali metals. Nitrogen is often incorporated into these structures and may predominate when binding to transition metals is the object. Likewise, crowns-containing sulfur atoms in the donor array favor transition over alkali metal ions.

The two-carbon unit that separates heteroatoms may be part of an aromatic system (e.g., benzene, naphthalene and pyridine). In the case of a heteroaromatic component such as furan or pyridine, the subcyclic unit may contribute a heteroatom to the donor array. In aliphatic crown ethers, the preference for ethyleneoxy units (OCH_2CH_2) results from chemical and practical considerations. Repeating ethyleneoxy units are readily available by polymerization of ethylene oxide (oxirane). Construction of a crown from such a simple and readily available starting material is economical. Use of the ethyleneoxy unit also means that every third atom is a donor, so the macrocycle's interior void is electron rich. A higher concentration of donors would be possible if methyleneoxy (OCH_2) chains were used, but the acetal (OCH_2O) linkage is hydrolytically unstable. Fewer donors would be available in the same size of macroring if propyleneoxy ($OCH_2CH_2CH_2$) units were used for construction of the macrocycle. A problem in the latter case is that unfavorable conformational interactions would occur. Rotation about the ethylene linkage is facile when oxygens occupy the 1,2-positions (i.e., $O\text{-}CH_2CH_2\text{-}O$). The corresponding $O\text{-}CH_2CH_2CH_2$ interaction is energetically less favorable. The conformation problem increases with the number of carbons between the heteroatoms.

A ligand that behaves as an ionophore must meet the following requirements:

1. The carrier molecule should be composed of polar and nonpolar groups.
2. The carrier should be able to assume a stable conformation that provides a cavity, surrounded by the polar groups, suitable for the uptake of a cation, while the nonpolar groups form a lipophilic shell around the co-ordination sphere. These groups must ensure sufficiently large lipid solubility for ligand and complex.
3. Among the polar groups of the ligand sphere, there should be preferbly 5 to 8, but not more than 12, co-ordinating sites such as oxygen atoms.
4. High selectivites are achevied by locking the coordinating sites into a rigid arrangement around the cavity. Such rigidity can be enhanced by the presence of bridged structures, e.g. hydrogen bonds. Within one group of the periodic sytem, the cation that fits into the offered cavity is preferred. Ideally, all cations should be forced into accepting the same given number of coordinating groups.
5. Notwithstanding requirement 4, the ligand should be flexible enough to allow a suffcienctly fast ion exchange. This is possible only with a stepwise substitution of the solvent molecules by the ligand groups. Thus a compromise between stability (4) and exchange rate (5) has to be found.
6. To guarantee adequate mobility, the overall dimensions of a carrier should be rather small but still compatible with high lipid solubility.

Analytical Techniques

Quantitative measurement of an analyte will depend on a number of factors. Many available techniques possess varying degrees of selectivity, sensitivity, accuracy and precision, cost and rapidity. Gravimetric analysis usually involves the selective separation of the analyte by precipitation, followed by the very non-selective measurement of mass. In volumetric analysis, the analyte reacts with a measured volume of reagent of known concentration, in a process called titration. A change in some physical or chemical property signals the completion of the reaction. Gravimetric and volumetric analyses can provide results accurate and precise to a few parts per thousand or better. But they require relatively large quantities of analyte and are well suited for the measurement of major constituents.

Instrumental techniques are used for many analyses (Table 1.2) and constitute the discipline of instrumental analysis. They are based on the measurement of a physical property of the sample, for example, an electrical property or the absorption of electromagnetic radiation. Examples are spectrophotometry (ultraviolet, visible, or infrared), fluorimetry, atomic spectroscopy (absorption, emission), mass spectrometry, nuclear magnetic resonance spectrometry (NMR), X-ray spectroscopy, electroanalytical chemistry (potentiometric, voltammetric, electrolytic), chromatography (gas, liquid), and radiochemistry. Instrumental techniques are generally more sensitive and selective than the classical techniques but are less precise, on the order of 1 to 5% or so. These techniques are usually much more expensive. But depending on the numbers of anlyses, they may be less expensive when the analysis is done in bulk. They are usually more rapid, may be automated, and may be capable of measuring more than one analyte at a time. Chromatographic techniques are particularly powerful for analyzing complex mixtures. They perform the separation and measurement step simultaneously. Constituents are separated as they are washed down a column of appropriate material that interacts with the analytes to varying degrees, and the analytes are sensed with an appropriate detector as they emerge from the column, to give a transient peak signal, in proportion to the amount of analyte.

Table 1.2: Various analytical methods with respect to sensitivity, precision, selectivity, speed and cost

Method	**Approx. Range (mol/L)**	**Approx. Precision (%)**	**Selectivity**	**Speed**	**Cost**	**Applications**
Gravimetry	10^{-1}-10^{-2}	0.1	Poor-moderate	Slow	Low	Inorg.
Titrimetry	10^{-1}-10^{-4}	0.1-1	Poor-moderate	Moderate	Low	Inorg., org
Potentiometry	10^{-1}-10^{-6}	2	Good	Fast	Low	Inorg.
Electrogravimetry	10^{-1}-10^{-4}	0.01-2	Moderate	Slow-moderate	Moderate	Inorg., org.
Volammetry	10^{-3}-10^{-10}	2-5	Good	Moderate	Moderate	Inorg. , org
Spectrophotmetry	10^{-3}-10^{-6}	2	Good-moderate	Fast moderate	Low-moderate	Inorg., org

Fluorometry	10^{-6}-10^{-9}	2-5	Moderate	Moderate	Moderate	Org.
Atomic spectroscopy	10^{-3}-10^{-9}	2-10	Good	Fast	Moderate-high	Inorg. multielement
Chromatorgaphy	10^{-3}-10^{-9}	2-5	Good	Fast moderate	Moderate high	Inorg., multicomponent
Kinetic methods	10^{-2}-10^{-10}	2-10	Good-moderate	Fast moderate	Moderate	Inorg. enzymes

In direct determinations, the ion-selective electrode (ISE) and a reference electrode are immersed in a stirred sample and the resultant cell potential related to the determinand activity or concentration by means of a calibration graph: the expected accuracy and precision for such a straightforward method should be comparable to those of a pH measurement. The 'glass electrode' is the best-behaved of all ion-selective electrodes, yet measurements of pH to better than ± 0.001 pH is equivalent to ±0.6 mV or in terms of hydrogen ion activity, ± 2% is not known. Thus, using other electrodes an uncertainty of ± 2% or even down to ± 0.5% may only be obtained with care; this may be good in comparison with other techniques at the 10^{-5} M level but is often poor at 10^{-2} M. The accuracy and precision may be improved by resorting to a more elaborate technique involving several potential measurements. Consequently, a balance must be struck between accuracy and convenience in the choice of technique. A corollary of this is that the sensors are more suited to the relatively imprecise analysis of samples containing the determinand in a wide range of activity than to precise analysis of samples containing the determinand in a narrow range.

One of the most attractive features of the electrodes and probes is the speed with which they permit a sample to be analyzed, and the ease with which the methods may be made semi-automatic or fully automatic. If samples are measured by a direct method, all that has to be done is to pre-treat the sample by addition of an pretreatment reagent, stir the sample and put the ISE and reference electrode into it; the equilibrium cell potential may be read usually within about a minute and the answer is obtained.

Other advantages of analyses by electrodes are that the methods may be non-destructive and are adaptable to very small sample volumes. Fluoride samples have been analyzed with volumes down to 10 µL. Also analyses may be made without difficulty of highly colored, viscous samples containing a high concentration of suspended solids. However, problems do arise in the analysis of some non-aqueous and partially non-aqueous samples.

There are three basic electrochemical processes that are useful in transducers for sensor applications:

1. Potentiometry, the measurement of a cell potential at zero current.
2. Conductometry, where the conductance of the cell is measured by an alternating current bridge method.
3. Voltammetry, in which an oxidizing (or reducing) potential is applied between the cell electrodes and the cell current is measured.

The potential benefits of electrochemical monitoring, using the potentiometric measurement in an environmental context, are:

1. The choice of electrode material can lead to selectivity, particularly in ion-selective electrodes.
2. There is the possibility of furnishing not only the results but also treated data in real time or close to real time, using computerized control and particularly in flow systems for on-line monitoring.
3. Portable sensors with dedicated instrumentation, possibly battery-powered, that can be used outside the laboratory.
4. Miniaturized sensors, for application in situations where other probes may not be usable.

General Sensor Design Criteria

A useful electrochemical sensor (based on potentiometry) must obey a number of experimental design criteria, many of which are linked to its potential benefits. Among the most important are:

1. For potentiometric sensors, there is an adequate electrode material, free from interferences.
2. The concentration of electroactive species can be determined with sufficient accuracy and precision.
3. The measurements are sufficiently reliable and repeatable.
4. The response time of the sensor is sufficiently fast.
5. The drift or diminution of sensor response with time owing to electrode degradation or surface fouling is sufficiently small.
6. Calibration is simple and easy to perform, or not necessary.
7. The detection limit is sufficiently low for the purpose envisaged.

The relative importance of these factors depends on the monitoring necessities as well as on the technique employed and the electrode and cell configuration.

Recent tendencies in development of potentiometric sensors for monitoring have been the production of sensors that are more robust, more reliable (i.e., needing less calibration with smaller potential drift) and can be used in an ever-wider range of situations with low maintenance. Potentiometric sensors based on plasticized PVC membranes doped with neutral carriers have been extensively developed for many ions (18-22). For example, crown and bis-crown ether ionophores can be incorporated into polymer membranes, the recognition coming from the size of the host cavity or through specific metal–ligand interactions; an alternative with similar properties is calixarenes derivatized to bind metal ions. There is much effort in improving selectivity relative to interfering species through chemical recognition principles.

Ion-selective electrodes ideally respond to species according to the Nernst equation. For example for an X- selective electrode the Nernst equation may be written as:

$$E = E° \pm \frac{RT}{ZF} \ln a_X \qquad (1.1)$$

Here,
E is the potential,
E^0 is the standard potential of cell,
R is the gas constant,
T is the absolute temperature,
F is the Faraday constant,
a_X is the activity of ion X_a, and
z is the number of charges on X.
The sign in the equation is positive when X is a cation and negative when it is an anion.

Ion-Selective Electrodes

An ISE is an electrode, designed to respond to one particular ion more than others. This is a potentiometric device, i.e. the potential of the electrode, measured against an appropriate reference electrode, is proportional to the logarithm of the activity of the ion being tested. Such a device usually responds rapidly, with a linear range of about 10^{-6} to 10^{-1} M for most ISEs. It operates on the principle of a concentration cell (23-28), in that it contains a selective membrane, which develops a potential if there is a concentration difference across the membrane of the ion being tested.

Components of the PVC-based Polymeric Ion-Selective Electrode

The ion-sensitive polymeric membrane is ideally a water-immiscible liquid of high viscosity containing the components listed below.

Polymeric Matrix

The polymeric matrix provides mechanical stability to the membrane. In ideal cases it is inert and has no chemical interaction with the sensed ions. Polymeric ISE-membranes are commonly prepared with poly (vinyl chloride).

Membrane Solvent

The membrane solvent reduces the viscosity and ensures a relatively high mobility of the membrane constituents. In order to provide a homogeneity of the organic phase it must be compatible with the other membrane components and acts as a plasticizer characteristics of the membrane and, as a consequence, the selectivity. The plasticizers that are usually used in ISE-membranes are orthonitrophenyloctyl ether (o-NPOE, polar) or bis(2-ethylhexyl)sebacate (2BS, apolar).

Lipophilic Ion

The prerequisite for a theoretical Nernstian response of the ISE is that no significant amount of primary ions may be co-extracted together with counter ions (ions with opposite charge sign of the measuring ion) from the sample into the membrane phase. This means that the membrane is permeable only for ions with the same charge sign of the measuring ion. This membrane characteristic is called permselectivity or Donnan exclusion. The presence in the membrane phase of non-exchangeable lipophilic ions guarantees the operation of the ISE by keeping the total concentration of measuring ions in the membrane much higher than the co extracted amount, i.e. constant. Cation-selective ISE-membranes contain normally a tetraphenylborate derivative as a lipophilic site, whereas anion-selective membranes, a tetraalklylammonium salt for this purpose.

Ionophore

The ionophore or ion carrier or ligand, has the main influence on the selectivity of the ISE membrane. It ideally forms relatively strong, selective and reversible complexes only with the target ion, so that in the membrane no ion-exchange occurs between primary and interfering ions, i.e. no interference occurs. Additionally, the ionophore structure must contain numerous lipophilic groups in order to keep its leaching rate from the membrane to the sample phase as low as possible.

Lipophilic Salt

The addition of a lipophilc salt without ion-exchanger properties reduces the electrical resistance of the membrane.

Response Mechanism

An electrochemical-measuring cell consists of two galvanic half-cells: the ion-selective electrode and the reference electrode. The total potential difference (electromotive force, EMF) measured under zero-current conditions between the two electrodes is the sum of local potential differences, arising at each electrochemical interface. Membranes of ionophore-based ISEs normally consist of a plasticized polymeric phase, typically with poly vinylchloride as polymeric matrix, lipophilic ion-exchanger sites, and a lipophilic or covalently immobilized ionophore. Such membranes are placed between two aqueous solutions, one being the sample and the other, the so-called inner electrolyte. The response of ISEs has been described by using three models; the kinetic model, the phase boundary potential model and the membrane surface model (29-33).

According to the kinetic model, ion-transport through the membrane is essential, and selectivities are related to mobilities. The phase-boundary potential model describes the potential emerging at the interface of the aqueous and organic membrane phases by using thermodynamic equilibria and the electroneutrality condition within each phase and by assuming kinetic processes being fast between the two phases. It directly relates the spontaneous equilibrium partitioning of ions across the sample membrane interface to the phase-boundary potential. The third model assumes that only the membrane surface processes are relevant for the potential, emphasizing that the phase-boundary potential across the sample-membrane interface is the result of ion-selective charge separation at that interface. In most cases of practical significance, the response of ISEs can be described by the phase-boundary potential, E_{PB}, because all other contributions of the emf of the potentiometric cell are sufficiently constant:

$$E_{PB} = E^0 \pm \frac{RT}{zF} \ln \frac{a_1(aq)}{a_1(org)} \tag{1.2}$$

with R, T, and F having usual meaning, z being the charge, and;

$$E^0 = \frac{\mu^0(aq) - \mu^0(org)}{zF}$$

μ° and a_1 being the standard potentials and the ion activity in the respective phases.

The phase-boundary potential model has been used for many different cases to calculate the activity of the uncomplexed ion, a_1(org), in the membrane based on mass and charge balances and complex formation equilibria. If a_1 (org) does not depend on a_1(aq), the ISE response has a Nernstian slope of 59/x mV/decade. Apparent deviations from this slope can be described by changes of a_1(org) with a_1(aq) or by differences between a_1(aq) at the membrane surface and in bulk of the sample. The influence of an interfering ion was first described with the still widely used empirical Nicolskii-Eisenman equation, which is an extension of the Nernst equation:

$$E = E_I^0 + \frac{RT}{z_I F} \ln(a_{Ii}(aq) + K_{I,J}^{pot} a_I(aq)^{z_I / z_J}) \tag{1.3}$$

Selectivity and Interference

It is well established now that for $z_I \neq z_J$ the Nicolskii-Eisenman equation is not valid in the activity range where the primary and the interfering ion significantly contribute to the potential. However, it is valid in the linear ranges of the response curve, $a_I <$ and $a_I >$. Despite this deficiency of the Nicolskii-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.

Research Work

Podal ionophores and macrocyclic compounds are gaining increasing interest as tools for the analysis and separation of metal ions as well as for many biological and other applications. To monitor these neutral carriers we have prepared PVC-membrane electrodes as analytical tools for the monitoring of a variety of different metal ions in various simple ways.

Some commercially available crown ethers and some novel synthetic podands synthesized by our groups (35,36) were used as ionophores in preparing liquid membrane electrodes.

Crown Ethers:

- Dibenzo-18-Crown-6,
- Dicyclohexano-18-Crown-6,
- Dibenzo-24-Crown-8.

8-Hydroxyquinoline-based Ionophores:

- 1,3,5-Tris(8-quinolinoxymethyl)-2,4,6-trimethylbenzene,
- 1,3,5-Tris(5-chloro-8-quinolinoxymethyl)-2,4,6-trimethylbenzene,
- 1,3,5-Tris(5-benzoyl-8-quinolinoxymethyl)-2,4,6-trimethylbenzene,
- 1,3,5-Tris[(5-phenylhydroxymethylene)-8-quinolinoxymethyl]-2,4,6-trimethylbenzene,
- 1, 2, 4, 5-Tetrakis[8-hydroxyquinolinoxymethyl]benzene.

2-Aminothiophenol-based Ionophores:

- 9,10-Bis(2-aminophenylthiomethyl)anthracene,
- 1,3,5-Tris(2-aminophenylthiomethyl)-2,4,6-trimethylbenzene.

Ethylenediaminotetraacetic acid

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Chapter -2

The thermodynamics of any two species that combine to form one species in a reversible equilibrium: acid + base, metal + ligand, Lewis acid + Lewis base one needs to study the Lewis octet theory. A Lewis base was originally described as a species with an available (reactive) pair of electrons and a Lewis acid as an electron pair acceptor species. In the 1960s Klopman updated this idea and suggested that a Lewis base is a species which reacts via its highest occupied molecular orbital or HOMO, and a Lewis acid is a species which reacts via its lowest unoccupied molecular orbital or LUMO (see Fig. 2.1).

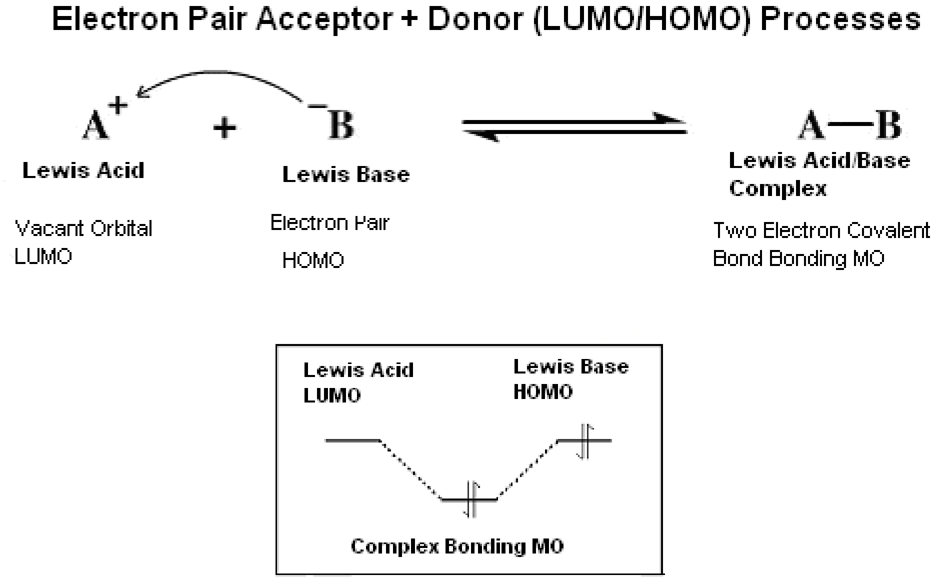

Figure 2.1: Lewis acid/base MO interaction diagram

Ionophores are organic molecules that form specific complexes with metal cations and certain hydrophilic organic cations, rendering them lipophilic and providing a means for their transport across polar barriers. Ionophores are structurally diverse molecules with certain common characteristics. They have a large hydrocarbon backbone incorporating functional groups (e.g., oxygen-containing moieties) with electron-donating ability. The neutral oxygens complex with cations through ion-dipole interactions and perturb the ionophore conformation. The cation is centrally located, and the polar nucleophilic moieties are oriented towards the interior of the resulting complex, creating a hydrophilic, electron-rich environment; the hydrocarbon is exposed to the exterior. Complexation appears to take place by concerted exchange of the hydration shell of the cation with the ionophoric nucleophilic system.

Ionophores can be classified on the basis of structural features, which in turn determine the mechanism by which they facilitate ion conductance as:

(a) neutral,
(b) charged, and
(c) channel-forming ionophores.

Neutral ionophores contain no ionizable groups. The complex that forms between such compounds and metal ions results from ion-dipole interactions when the cation encounters an apolar medium containing the ionophore. 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.

The 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. The structures of the complexes are such that there is an internal compensation of the charge.

Channel forming ionophores differ from other ionophores in 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 channels 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 neutral ionophores based on their structural features have been further classified into different categories viz:

Podands : The acyclic and multiligating and multiarmed molecules.

Coronands : Monocyclic molecules with O, N, S, etc. and their combinations as ligating sites.
Lariats : Coronands with one or more appendages which can participate in binding with the guest.
Cryptands : Bicyclic and polycyclic heteromacrocycles with three-dimensional cavities.
Spherands : The monocyclic receptors with spherical cavities.

The common thing in all these compounds is that they have a cavity (or hole) in their structure. Further, if the hole is matched with the ionic size of the cation then it is capable of forming complexes. The chemistry of such complexation is called as "host-guest" chemistry (1, 2). Ionophore acts like host to receive guest-like metals to form complexes called "host-guest" compounds.

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 ring structure. Such selectivity depends upon cation size–cavity size- relationship, number of donor atoms in crown ring, etc. The selective formation of a molecular complex wih one of the analyte amongst a number of them is called molecular recognition (3).

Development of Ion-Selective Electrodes

Ion-selective electrodes are only a small part of the much broader electroanalytical technique termed potentiometry. As its name implies, the method is based on the measurement of an electrode potential that is formed at the interface between a solution and an electrode surface, the aim of the potentiometric technique being to assay the quantity or activity of an analyte in that solution. The need to quantify the degree of acidity became more pressing as chemistry, physiology, and brewing grew in scope during the early years of 20th century. In thirtees, the formula for successful introduction of ISE technology was worked out through:

(i) Cooperation between academe and industry aiming at the development of a new technology.
(ii) Integration of concepts of solution chemistry (pH buffers), electrochemistry (the electrode), and electronics (the meter).

The era of ISEs was initiated through the theoretical work of Nikolski and Schultz (4), which was further expanded by Eisenman (5). Indeed, the Eisenman-Nikolski equation is the basis of ISE theory and of the selectivity concept. Eisenman demonstrated the link between the (troublesome) sodium error of the pH electrode and the central role of the ion exchange mechanism, thus focusing on the mechanism of the charge transfer process across the membrane surface (6). This work opened the field to a rational search for new electrode materials, and its importance can be appreciated against the background of previous largely unsuccessful attempts to create potentiometric devices that would measure ionic species selectively.

The pioneering work of Tendeloo (7*)* and Kolthoff (8) and even later attempts by Pungor (9) to produce halide-selective electrodes are often quoted as examples of early attempts to make ISEs work. Yet, in this context it is only fair to point out that silver wires covered by AgCl, AgBr, AgI, or Ag_2S had been used routinely as both indicator and reference electrodes since the early ’30s. Also, silver wires covered with sulfur-containing organic compounds were at that time used as indicator electrodes in potentiometric titrations (10) and for direct potential measurements to estimate solubility products (11).

The breakthrough came in the ’60s when Ross, working for the newly founded Orion Company (12), invented an entirely new concept of the liquid membrane electrode, and the calcium electrode (13, 14) attracted immediate attention. Ross and Frant’s work on the fluoride electrode (15), shortly followed by other liquid membrane ISEs and a variety of gas sensors, had an electrifying effect on both academe and industry, albeit for different. The opening of an unexpected new avenue of research attracted immediate attention. Indeed, in following decades, academic centers of electrochemical research such as the schools founded by Heyrovsky (Czechoslovakia), Shikata (Japan), Kemula (Poland) and Pungor (Hungary) yielded a considerable output on the theme of ISE, comprising a large number of papers and meetings dealing with both theory and practice. The combined intellectual and economic challenge provided an impetus that created a vigorous, exciting research field, in which major advances were achieved during the ’60s. It blossomed further in the ’70s, when the largest numbers of papers were published, numerous national and international meetings were held, and major monographs were authored by leading workers from the field (16–19).

During the ’70s, two very important developments take place. Moody and and Thomas invented a practical support for liquid membrane electrodes of the PVC membrane (20). This advancement alone made all liquid membranes practical and demonstrated that polymerizable materials can indeed serve as a reliable backbone for ISE membranes. Prior to their work, the only polymerizable material of some utility was silicone rubber (21), which never quite fulfilled the expected function. The continuing work of Thomas (22) led to a wide use of home-made as well industrially produced ISEs, thus allowing extensive use of these devices worldwide. In this way, ISE technology and research became widely practiced, an important aspect of training and education in instrumental analysis. Introduction of PVC as a membrane material led to further simplifiy the ISE construction.

H. Freiser proposed the “coated-wire electrode” (CWE) comprising a Pt wire coated by a PVC layer that served as a membrane. This bold approach disposed of both the inner reference solution and the reference electrode and was consequently subjected to criticism because CWEs were subject to drift. Further development of the CWE, however, led to the introduction of inner redox solid.

The second important development took place in Switzerland, where Simon discovered the suitability of polypeptides as electroactive materials and successfully pursued research on this entirely new group of electroactive ligands, the so-called neutral carriers. His initial work with Stefanec (23, 24) was focused on naturally occurring materials, nonactins that were known to facilitate the transport of alkali metal ions across the lipid membranes. This work led to discovery of the valinomycin electrode for potassium, the ISE of unprecedented selectivity.

The topic of ISE selectivity was discussed and published by IUPAC commissions twice: in 1976 and in 1995 (25). Initially, a view was taken that the entire problem of selectivity can be neatly described by applying a strictly theoretical approach using Nikolski– Eisenman (N-E). The first complication occurred when ions of different charges had to be considered. At that stage Buck proposed a more complex equation (26, 27), which, however, assumes a Nernstian response for both primary and interfering ions. At that point, the IUPAC commission adopted a pragmatic approach, concluding that a method for establishing selectivity was needed that would be independent of the N-E equation. It finally adapted the so-called "matched potential" method, originally suggested by Gadzekpo and Christian (28). In this method, the selectivity coefficient is defined as the activity (concentration) ratio of the primary ion and the interfering ion, which gives the same potential change in a reference solution. Thus, the value of the selectivity coefficient is not based on the Nernstian slope, and the charges of ions involved need not be considered. Although 100 years old, many aspects of membrane-based potentiometry, especially its response–selectivity function, are still not fully understood. It is therefore, encouraging that novel theoretical insights are being advanced (29) and that new neutral carriers are being synthesized and used by the research team led by Buck (30) and Janata (31). Table 2.1 gives a summary of neutral carrier-based ion-selective electrodes.

Table 2.1: Important Contributions to the Development, Applications and Response Mechanism of Neutral Carrier-based Ion-selective Electrodes

Moore and Pressman (32)	1964	Discovery that the antiobiotic valinomycin induces ion-selective effects in metabolic studies in liver mitochondria
Stefanac and Simon (33-35)	1966	First report on the action of antibiotics as neutral complexing agents, as carriers
Pedersen (36)	1967	Discovery of cation-complexing macrocyclic polyether (crown compounds)
Pioda et al. (37)	1969	K$^+$-selective electrode based on valinomycin in diphenyl ether
Simon (38)	1969	First patents on valinomycin and other antiobiotics as components for ISEs issue
Eisenman et al. (39)	1969	Theory of membrane potentials and conductances of neutral carrier membranes
Moody et al. (40)	1970	Standard procedure for the preparation of the ISE-PVC membranes

Morf and Simon (41)	1971	Analysis of molecular aspects of cation selectivity of neutral carriers
Ammann et al. (42)	1972	Ca(II)-selective electrode based on the first tailored synthetic neutral carrier
Morf et al. (43)	1972	Reports on PVC-membrane electrodes based on valinomycin
Ryba et al. (44)	1973	K^+-selective electrode based on crown ethers
Morf et al. (45)	1973	Analysis of the parameters affecting the monovalent/ divalent ion selectivity of neutral carriers in membrane electrodes
Morf et al. (46)	1974	Studies of the anion interference in cation-selective neutral carrier-based electrodes
Freiser (47)	1974	First coated-wire electrode based on valinomycin
Simon et al. (48)	1975	Recent developments in the field of ion-selective electrodes
Simon (49)	1976	Microelectrode for potassium ions based on a neutral carrier and comparison of
Pretsch et al. (50)	1977	Lipophilic complexing agents designed for use in ion-selective liquid membrane electrodes
Takamatsu et al. (51)	1978	Determination of stability constants of metal-humic acid complexes by potentiometric titration and ion-selective electrodes
Koryta (52)	1979	Theory and applications of ion-selective electrodes
Horvai (53)	1980	Comparative study on the precision of potentiometric techniques applied with ion-selective electrodes. III. Potentiometric titrations
Lindner (54)	1981	Dynamic characteristics of ion-selective electrodes
Pungor (55)	1982	Limits of applicability of ion-selective electrodes
Covington (56)	1983	Reference electrodes and liquid-junction effects in ion-selective-electrode potentiometry
Pretsch (57)	1984	Design and application of neutral-carrier-based ion-selective electrodes
Morf (58)	1985	Neutral carriers for anions
Koryta (59)	1986	Theory and applications of ion-selective electrodes
Zhang (60)	1987	Developments of ion-selective electrodes in rare-earth analysis
Pretsch (61)	1988	Design features of ionophores for ion-selective electrodes
Moody (62)	1989	Studies on bis(crown ether)-based ion-selective electrodes for the potentiometric determination of sodium and potassium in serum
Aomi (63)	1990	Ion-selective electrodes and their application to analytical

		instruments
Ma (64)	1991	Ion-selective micro-electrodes and their application in biomedicine
Nikolskii (65)	1992	Development of the theory and practice of ionometry
Pungor (66)	1993	Ion-selective electrodes: Surface studies
Buck (67)	1994	Selectivity coefficients for ion-selective electrodes IUPAC commission to establish standard procedure
Buhlmann (68)	1995	Studies on the phase boundaries and the significance of ionic sites of liquid membrane ion-selective electrodes
Bakker (69)	1996	Origin of anion response of solvent polymeric membrane based silver ion-selective electrodes
Pretsch (70)	1997	Chemical sensors and computer-aided analytical chemistry
Pretsch (71)	1998	Ion-selective electrodes based on two competitative ionophores for determining effective stability constants of ion-carrier complexes in solvent polymeric membranes
Pretsch (72)	1999	Lowering the detection limit of solvent polymeric ion-selective membrane electrodes. 2. Influence of composition of sample and internal electrolyte solution
Pretsch (73)	2000	Improved detection limits and unbiased selectivity coefficients obtained by using ion-exchange resins in the inner reference solution of ion-selective polymeric membrane electrodes
Bakker (74)	2001	Highly improved detection limits and sensitivities of potentiometric titrations
Bakker (75)	2002	New design and use of ion-selective electrodes in two important areas: Assessment of the true selectivity of an electrode, and the design and measurement technique to lower the limits of detection
Pretsch (76)	2003	Influence of incorporated lipophilic particles on ion fluxes through polymeric ion-selective membranes
Bakker (77)	2004	The phase-boundary potential model
Toth (78)	2005	Covalent attachment of the ionophore to the polymeric backbone has been expected to improve the detection limit of the respective ion-selective sensors
Bakker (79)	2006	Approaches to improve the lower detection limit of polymeric membrane ion-se

Pederson's synthesis of 18-crown-6 and its derivatives and their ability to dissolve the metal ions in organic solvents and subsequent rational design of variety of receptors for alkali metal ions, alkaline earth metal ions and organic cations of biological significance by D.J. Cram and J.M. Lehn has lead to the new era of “Host-Guest” chemistry. Their area has developed by leaps and bounds to be termed as supramolecular chemistry.

Carrier-based PVC-membrane sensors 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 (80-83). The key ingredient of such plastisized PVC-membrane is the incorporated carrier that defines the selectivity of the electrodes via selective complex formation with cation of interest. Due to their electrical neutrality, lipophilic character and capability to selectively and reversibly bind metal ions (84), these compounds have attracted the attention of analytical scientists.

Ionophore-based ISEs for some alkali metal ions

Zhukov et al. (85) prepared a lithium ion-selective electrode based on lipophilic diamide, N,N^1,N,N^1-tetraisobutylcyclohexane–cis-1,2-dicarboxylic diamide, while, Sugihara et al. (86) reported a lithium-selective electrode based on non-cyclic polyether diamides. These electrodes are reported to exhibit excellent selectivities over other alkali and alkaline earth metal ions. Suzuki et al. (87) 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 (88) has reported a pyrimidine based neutral carrier as a rubidium ion-selective electrode.

S. Chander (89) reported 1-methyl-1-vinyl-14-crown-5 as Na^+-selective electrode with a slope of 55.0 mV/decade over a concentration range of $3.16\times10^{\bullet 6}$ to $1.0\times10^{\bullet 1}$ M and a detection limit of $2.81\times10^{\bullet 6}$ M, and the electrode is suitable for use within the pH range of 6.5–9.5. The selectivity relative to alkali, alkaline earth and transition heavy metal ions is good. S. Peper (90) reported a Cs^+-selective electrode which was developed by doping ethylene glycol-functionalized cross-linked polystyrene microspheres (PEG) into a plasticized poly(vinylchloride)(PVC) matrix containing sodium tetrakis-[3,5-bis (trifluoromethyl) phenyl]borate (TFPB) as the ion exchanger. ISEs containing PEG and TFPB show a linear range from $10^{\bullet 1}$ to $10^{\bullet 5}$ M Cs^+, a slope of 55.4 mV/decade and a lower detection limit ($\log a_{Cs}$) of • 5.3. J.S. Kim (91) described thiacalix[4]biscrown ethers with 1,3-alternate conformation that were examined for cesium over potassium. The electrode exhibited a linear response with a near Nernstian slope of 57.6 mV/decade in the concentration range of $1.0\times10^{\bullet 6}$ to $3.2\times10^{\bullet 2}$ M and wide range of pH 2.5–12.5. S. Jeon (92) reported that new lipophilic tetraesters of calix[6]arene and calix[6]diquinone were studied as Cs^+ ion-selective ionophores. For ISE based on calix[6]arene tetraester, the linear response is $1\text{x}10^{-6}$ to $1\text{x}10^{-1}$M of Cs^+ concentration. The selectivity coefficients for Cs^+ ion over alkali, alkaline earth and ammonium ions are determined. The detection limit, $\log a_{Cs+}$ is -6.3, the selectivity coefficient $\log K_{(Cs+,Rb+)}$ is -1.88 and was obtained for a polymeric membrane electrode configuration calix[6]arene tetraester. Xing et al. (93) has reported that two new pendant-armed calix[4]arene derivatives that showed excellent selectivity to Cs^+ ions and exhibited linear, near-Nernstian response characteristics with a slope of 56.4 mV/decade in the concentration range of 10^{-4} - 10^{-1} mol/L, and a selectivity coefficient $\log K_{Cs.Na}^{Pot}$ of -3.39. R.K. Mahajan (94) used calix[4]crown ether-ester as an ionophore for Cs^+ ions and the electrode exhibited a linear response for cesium ion over a wide concentration range of $5.0\times10^{\bullet 6}$–$1.0\times10^{\bullet 1}$ M with a Nernstian slope of 59 mV/decade. The detection limit of the electrode is $5.0\times10^{\bullet 6}$ M. The response time of the electrode is less than 20 s.

Ionophore-based ISEs for some Alkaline Earth Metal Ions

The most important ionophores are the ones that are selective for biologically important metal ions. A lot of interest is seen in the development of alkaline earth metal ion- sensitive electrodes. The selective ionophoric properties of calix[4]arene-diamide have been very well investigated for the recognition of Ca^{2+} ions (95). A latest addition in this class of ionophores is that of calix[4]arene-diamide frame-work having benzothiozolium ion moieties (96). This ionophore shows a significant selectivity for calcium in the presence of other physiologically important ions, like Na^+, K^+, Mg^{2+}, etc. Other latest additions in the category of calcium-selective electrodes include the work of A.K. Covington et al. (97) (based on polyimide polymeric matrix). Some of the work done in the 90's include the reported references of Bouklouze et al. (98), Kataky et al. (99), Donell et al. (100), Vander wal et al. (101), Shamsipur et al. (102) and Suzuki et al. (103).

A.K. Singh (104) used 5,7,12,14-dibenzo-2,3,9,10-tetraoxa-1,4,8,11-tetraazacyclotetra decane as an ion carrier for Sr^{2+} over a wide concentration range from $3.98\times10^{\bullet 6}$ to $1.0\times10^{\bullet 1}$ M with a slope of 29 mV/decade of concentration and a detection limit of $2.82\times10^{\bullet 6}$ M. The electrode can be used in the pH range of 2.5–10.5. Also, he has (105) reported 2,3,4-pyridine-1,3,5,7,12-pentaazacyclo pentadeca-3-ene as a Ba(II)-selective electrode which worked well over a wide concentration range $1.41\times10^{\bullet 6}$–$1.0\times10^{\bullet 1}$ $molL^{\bullet 1}$ with a Nernstian slope of 30.0 mV/decade of activity between pH 2.5 and 7.0. The selectivity coefficient for mono-, di- and trivalent cation indicates an excellent selectivity for Ba^{2+} ions over a large number of cations. V.K. Gupta (106) reported benzo-15-crown-5 as an ionophore for Mg^{2+} ions. This membrane worked well over a wide concentration range from$1.0\times10^{\bullet 5}$ to $1.0\times10^{\bullet 1}$ M of Mg^{2+} with a Nernstian slope and can be used over a period of 4 months. The proposed electrode works well in a wide pH range 2.2–9.8 and demonstrates a good discriminating power over a number of mono-, di-, and trivalent cations. S.K. Mittal et al. (107) reported a PVC-based membrane using dibenzo-18-crown-6 for an ionophore as a calcium ion-selective electrode. The electrode shows a linear dynamic response in the concentration range from $1\times10^{\bullet 5}$ M to $1\times10^{\bullet 1}$ M with a Nernstian slope of 28.0 mV/decade and a detection limit of $4\times10^{\bullet 6}$ 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 proposed sensor shows a reasonably good selectivity with respect to alkali, alkaline earth and transition metal ions. It can be used in the pH range 3–11.

Ionophore-based ISEs for some Transition Metal Ions

Amongst the transition metals most of the literature available is regarding copper- selective electrodes. Abbaspour (108) has reported a PVC-membrane electrode for copper ion based on 1,3-dithane, 2-(4-methoxy phenyl) as an ionophore. The electrode exhibits a Nernstian slope of 29 mV/decade in a linear range from $3.0\text{x}10^{-6}$ to $5.0\text{x}10^{-2}$ M for Cu^{2+} ions. The detection limit of this electrode is $1\text{x}10^{-6}$ mol/L and can be used in a pH-range of 4.0 to 7.0. M. Shamsipur et al (109) has reported three different mixed aza-thioether crowns containing 1,10 phenanthroline as a sub unit. The electrode based on the ionophore exhibited a Nernstian response for Cu^{2+} ions over a wide concentration range ($2\text{x}10^{-1}$ to $1\text{x}10^{-5}$M) with a limit of detection $8\text{x}10^{-6}$M and a reponse time of 15 s. M.R. Ganjali (110) reported 2-(1’-(4’-(1’’-hydroxy-2’-naphthyl)methyleneamino)butylimino methyl)-1-napthol as copper sensor. The electrode exhibited a Nernstian response for Cu^{2+} ions over a wide concentration range ($10^{\bullet 1}$ to $10^{\bullet 6}$ M). The response time of the sensor is 15 s, and the membrane can be used for more than 3 months without observing any deviation. The electrode revealed comparatively good selectivities with respect to many alkali, alkaline earth, transition and heavy metal ions and could be used in a pH range of 3.5–7.0. S. Park et al. (111) has reported that five novel 1,3 alternate calix (4) aza crown ether having 2-picolyl, 3-picolyl and benzyl unit on the nitrogen atom were used as ionophores for transition metal-selective polymeric membrane electrodes. The electrodes based on 2-picolyl armed 1,3 alternate calix (4) azacrown ether exhibited a Nernstian response toward Cu^{2+} ion over a concentration range of $10^{-4.5}$ M to $10^{-2.5}$ M, and selectivity coefficients for possible interfering cations are reported. Ganjali (112) has reported that a PVC-membrane electrode based on bis-2-thiophenol propanediamine (TPDA) was coated directly on graphite. The electrode exhibited Nernstian response for Cu^{2+} over a very wide range of concentration ($1.0\text{x}10^{-1}$ to $6.0\text{x}10^{-8}$ M) with a detection limit of $3\text{x}10^{-8}$ M. M. Gholivand et al. (113) has reported that a PVC-membrane electrode that is highly selective and sensitive to Cu^{2+} ions, was developed by using 2,2' dithiodianiline as a carrier and dibutyl phthalate as a plasticizer. The electrode exhibits a good potentiometric response for Cu^{2+} over a wide concentration range $5.0\text{x}10^{-2}$ to 10^{-7} mol/L with a Nernstian slope of 30 mV/decade. It exhibits good selectivity towards Cu^{2+} in comparison to alkali, alkaline earth, transition and heavy metal ions with no interference caused by Pb^{2+}, Cd^{2+} and Fe^{2+}, which are known to interfere with many other copper electrodes. K.C. Gupta (114) has reported a copper ion-selective electrode based on Cu^{2+} salicylaniline Schiff's base complex in a styrene-co-acrylonitrile co-polymer. The SAN-based membrane electrode containing Cu^{2+}-Schiff's base complex, exhibited a linear response with a Nerstaian slope of 30 mV/decade within the concentration range of 10^{-6}-10^{-2} mol/L. M. Jesus Gismera et al. (115) has reported that carbon paste ion-selective electrodes based on complexes of copper with macrocycle 3,4,10,11, tetraphenyl 1,2,5,8,9,12,13-octaaza-cyclo-tera-decca-7,14,-dithi-zone-2,4,9,11 tetrane and benzil bis thio semicarbazone were constructed for copper determination. The calibration graphs were linear for a wide concentration range from $1\text{x}10^{-5}$ to $1\text{x}10^{-2}$ mol/L. Wygladucz et al. (116) has reported that 13-membered azothia and azoxy thiacrown ethers were applied as ion carriers in ion-selective membrane electrodes. The membrane doped with the azoxy thiacrown ether shows a higher affinity towards Pb^{2+} than Cu^{2+} ($\log K^{Pot}_{Cu,Pb}$ is 1.7), whereas membranes with the azothiacrown ether are more selective towards Cu^{2+} than Pb^{2+} ($\log K^{Pot}_{Cu.Pb}$ is -2.4). The discrimination of alkali and alkaline earth cations is greater for first than for second. Electrodes with both ionophores suffered from a strong interference by Ag^{+} and Hg^{2+} ions.

V.K. Gupta (117) reported Cu^{2+}-selective electrodes based on bis(acetylacetone) propylenediimine. The electrode had a Nernstian response of 30.0 mV/decade to Cu^{2+} within the concentration range from $1.0x10^{\bullet 5}$ to $1.0x10^{\bullet 1}$ M and a detection limit of 0.5 ppm. The operational pH range of the electrode was 3.3–7.0. V.K. Gupta (118) reported a Cu^{2+}-selective sensor using neutral carrier porphyrin ionophores. The sensor shows a linear potential response for Cu^{2+} over a wide concentration range from $4.4x10^{\bullet 6}$ to $1.0x10^{\bullet 1}$ M with a Nernstian compliance of 29.3 mV/decade of activity between pH 2.8 and 7.9 and a fast response time of 8 s. A.K. Jain (119) reported that bis[acetylacetonato]-Cu^{2+} bis[ethylacetoacetate]-Cu^{2+} and bis[salicyldehyde]-Cu^{2+} have been investigated as Cu^{2+}-selective sensors. The sensor showed a linear potential response to Cu^{2+} over a wide concentration range from $2.0\times10^{\bullet 6}$ to $1.0\times10^{\bullet 1}$ M with a Nernstian compliance (29.3 mV/decade of activity) between pH 2.6 and 6.0 with a fast response time of 9 s and excellent potentiometric selectivity coefficient values. M.J. Gismera (120) reported that Tetraethyl thiuram disulfide was chosen as a chemical modifier in a carbon paste electrode for the potentiometric determination of Cu^{2+} and Hg^{2+} ions. The electrode has wide linear response ranges and rapid response times. The pH influence on the potentiometric response is studied. The limits of detection are $10^{\bullet 7.4}$ and $10^{\bullet 7.6}$ M for Cu^{2+} and Hg^{2+} activity, respectively. L.P. Singh (121) used Schiff base complexes, derived from 2,3-diaminopyridine and o-vanilin as Cu(II)-selective sensors. The sensor worked satisfactorily in the concentration range from $5.0\times10^{\bullet 6}$ to $1.0\times10^{\bullet 1}$ M (detection limit 0.3 ppm) with a Nernstian slope of 29.6 mV per decade of activity over a wide pH range (1.9–5.2) and fast response time (<30 s). S.J. Park (122) reported that five novel 1,3-alternate calix[4]azacrown ethers having 2-picolyl, 3-picolyl, and a benzyl unit on the nitrogen atom were synthesized and used as ionophores for transition metal-selective polymeric membrane electrodes. The electrode based on 2-picolyl armed 1,3-alternate calix [4] azacrown ether exhibited a Nernstian response toward copper (II) ions over a concentration range $10^{\bullet 4.5}$ M to$10^{\bullet 2.5}$ M. The detection limit was determined as $10^{\bullet 5}$ M in pH 7 and the selectivity coefficients for possible interfering cations were evaluated. Anions in the sample solution strongly affected the electrode response. M.B. Gholivand (123) reported a poly(vinyl chloride) membrane electrode, that is highly selective and sensitive to Cu^{2+} ions. It was developed by using 2,2•-dithiodianiline. The electrode exhibits a good potentiometric response for Cu(II) over a wide concentration range ($5.0\times10^{\bullet 2}$–$7.0\times10^{\bullet 7}$ mol/L) with Nernstian slope of 30.0 mV per decade. The response time of the electrode is 10 s and exhibited a good selectivity towards Cu^{2+} in comparison to alkali, alkaline earth, transition and heavy metal ions, with no interference caused by Pb^{2+}, Cd^{2+} and Fe^{2+}. K.C. Gupta (124) reported a Cu^{2+} ion-selective electrode based on Cu^{2+}-salicylaniline Schiff's base complex in styrene-co-acrylonitrile copolymer (SAN) that has been developed, it exhibits a linear response with a Nerstian slope of 30 mV/decade within the concentration range $10^{\bullet 6}$ to$10^{\bullet 2}$ mol/L of Cu^{2+} ions. The electrode has shown a detection limit of $10^{\bullet 7}$ M of Cu^{2+} ion with an average lifetime of 6 months. The electrode was suitable for use within the pH range of 2.0–7.0 at $1.0x10^{\bullet 3}$ mol/L of Cu^{2+} ion.

K. Toth et al. reported that a range of acyclic compounds based on 1,3-dithiole-2-thione-4,5-dithiolate (DMIT)(125) have shown an excellent selectivity for Ag^+ ions with Nernstian response in the range from 10^{-6} to 10^{-1} M. Selectivity coefficients were in the range of 10^{-4} M. Amini (126) reported that 2-quinolyl-2-phenylglyoxal-2-oxime was directly coated on the surface of a platinum-wire electrode as a neutral carrier for Cu^{2+} ions. The response of the electrode was linear with a near-Nernstian slope of 28.2 mV/decade in a concentration range $1x10^{-6}$-$1x10^{-1}$ mol/L. The response time of the electrode was between 10 and 50 s, and the electrode worked in the pH range of 3 to 6.5. Selectivity relative to several alkali, alkaline earth, transition, and heavy metal ions was good and the electrode could be used for at least two months.

Calix[4]arene derivatives (127) are also reported to be selective for Ag^+ ions with a linear slope of 50 mV/decade, in the concentration range from 10^{-5} to 10^{-1} mol/L. R.K. Mahajan (128) has reported a PVC-membrane electrode for silver(I) ions based on Schiff's base-tert-butyl calix[4]arene. The electrode worked well over a wide range of concentration ($1.0x10^{-5}$ to $1.0x10^{-1}$ moles/litre) with a Nernstian slope of 59.7 mV/decade. The electrode showed a fast response time of 20 s and worked well in pH range 1.0-5.6. Z.Z. Zhang et al. (129) has reported that 25,27,-bis(6-hydroxymethyl-2-pyridylmethoxyl)-26,28-dispropoxy-5,11,17,23-tetra-tert-butylcalix[4]arene-6 has shown an excellent selectivity for Ag^+ ions against other alkali metal, alkaline earth-metal, Pb^{+2}, NH_4^+ ions and some transition metal ions using the mixed solutions method. C.L.Xing et al. (130) have reported that thioether-substituting calix[4]arene derivatives show an excellent selectivity and a linear response of 50 mV/decade for Ag^+ ions in the range of 10^{-5} to 10^{-1} mol/L. M. Mazlouma (131) reported a membrane electrode based on 2,c-8,c-14,c-20-tetrabutyl-4,6,10,12,16,18,22,24-octaacetyl-resorc[4]arene, as a neutral carrier for detection of Ag(I) in aqueous solution. The electrode exhibited a linear response with a Nernstian slope of 58 mV/decade within the concentration range $1x10^{-5}$ -$1x10^{-1}$ M silver ion. The limit of detection was $3x10^{-6}$ M. The electrode exhibited good selectivities for Ag(I) with respect to alkali, alkaline earth and several heavy metal ions. The response time of the electrode was 20 s over the entire concentration range and could be used for at least two months without a considerable divergence in its potential. The electrode is suitable for use in aqueous solutions in a wide pH range of 1.5 - 6.0. K. Kimura (132) reported calix[4]arene derivatives incorporating π-coordinate substituents such as allyl, benzyl, and propyl groups as soft neutral carriers for silver ion sensors. Most of all, *tert*-butylcalix[4]arenetetra(allylether) is an excellent neutral carrier for plasticized poly(vinyl chloride) membrane silver ion-selective electrodes. A. Ceresa (133) reported that submicromolar to picomolar lower detection limits were obtained with various polymer membrane ion-selective electrodes by minimizing biases due to ion fluxes through the membrane. As an application of the proposed general recipe, a silver-selective electrode is developed on the basis of the ionophore O,O’-bis[2-(methylthio)ethyl]-tert-butylcalix[4]arene. With the predicted optimal composition of the inner electrolyte, its lower detection limit is found to be 10^{-9} M or 100 ppt Ag^+ with an ionic background of 10^{-5}M $LiNO_3$, which is very close to the expected value. S.M. Golabi (134) reported that a new wire-coated silver ion-selective electrode with a wider concentration range (10^{-7}M-10^{-1}M) was developed using 2-mercaptobenzothiazole (MBT). M.M.Ardakani (135) reported that the performance of silver metal complexes with meso-tetraphenylporphyrin as ionophores for ion-selective electrodes was studied. The electrode exhibited a Nernstian slope of 59.2 mV/decade within the concentration range of 1.0×10^{-7} - 1.0×10^{-1} M silver ions with the response time of <10 s. The silver-selective electrode exhibited a good selectivity for Ag(I) with respect to alkali, alkaline earth and heavy metal ion and a working pH range of 3.0 - 9.0.

T. Shinohara (136) reported that the performance of an octahydroxycalix[4]arene derivative was used as a neutral carrier for a silver-polymeric membrane electrode. The sensor gave a good Nernstian response of 58 mV/decade for silver ions in the activity range 3.3×10^{-6} to 3.3×10^{-2}M. The limit of detection reached 2.1×10^{-6} M Ag^+ and exhibited a high selectivity for silver ion against the alkali, alkaline earth and transition metal ions. The sensor can be used in a wide pH range from 1.5 to 6.5. H.R. Zare (137) reported a novel membrane-coated platinum-wire electrode (MCPWE) based on N,N•-bis(2-thienylmethylene)-1,2-diaminobenzene (BTMD) for a highly selective determination of Ag^+ ions over the concentration range from 1.0×10^{-6} to 1.0×10^{-1} M with a lower detection limit of 6.0×10^{-7} M. These electrodes worked in the pH range of 5.0-9.0. The electrode possesses a Nernstian slope of 59.7 mV/decade. R.K. Mahajan (138) reported a silver ion-selective electrode incorporating 2,6-bis-methylsulfanyl-[1,3,5]thiadiazine-4-thione as an ionophore. The electrode exhibited a slope of 52 mV/decade over a linear concentration range of 1.0×10^{-5}-1.0×10^{-1} M with a lower detection limit of 9.77×10^{-6} M and a pH range 1.77 - 7.13. The response time of the electrode was less than 20 s. M. Ueda (139) examined three kinds of tridentate ligands and compared them with the similar quadridentate ligand as the silver ionophore. Among the Schiff base derivatives tested, 3-(2-pyridylethylimino)-2-butanoneoxime, having one oxime and a pyridine substituent, was found to be the best ionophore for a silver-ion electrode. The electrode based on this derivative exhibited a good silver-ion selectivity, -log $K_{Ag,K}$ = 3.8, comparable to that of a quadridentate Schiff base, N,N•-bis(2•-hydroxyimino-1•-phenylpropyleden)-1,3-propanediamine, reported previously, except for a pseudo-Nernstian response (35.6 mV per decade) over a wide activity range from 5.0×10^{-7} to 7.9×10^{-2} M A. Sil (140) reported a coated-wire ion-selective electrode (ISE) based on cyclam (1,4,8,11-tetraaza cyclotetradecane) that was studied as a neutral carrier and exhibited a linear Nernstian response over the range 1×10^{-1} to 1×10^{-7} M with a slope of 59 ± 2 mV per decade change and a detection limit of 5×10^{-8} M. The selectivity coefficients of these cations are in the range of 10^{-4} to 10^{-2}. R.K. Mahajan (141) preapared a membrane using Schiff base p-tert-butyl calix[4]arene derivatives containing N and O as binding sites. These

electrodes worked well over a concentration from $1.0\times10^{\bullet 5}$ to $1.0\times10^{\bullet 1}$ M with a Nernstian slope. The electrodes have a fast response time of 20 s and operate in a wide pH range. These calix[4]arene derivatives showed excellent selectivities in ISE-membrane electrodes with log K_{Ag+} • 4.5 against some of the alkali, alkaline and transition metals. Even against the strongest interferent, Hg^{2+} ions, the value was around • 3.0. Kimura et al. (142) reported that calixarene derivatives incorporating ω-unsaturated alkenyl groups or saturated alkyl groups and their monomeric analogues were used as π-cordinate neutral carriers for ISEs of soft metals (silver and thallium(I)] ions. Chen (143) prepared electrode based on calixarene derivatives containing nitrogen atoms used as a neutral carrier for a silver-polymeric membrane electrode. The faster transport rates were found by the soft heavy metal ions such as Ag^+, Hg^{2+} in the bulk liquid membrane system. The silver ion-selective electrode based on calixarene derivative gave a good Nernstian response of 57 mV per decade for silver in the activity range $5\times10^{\bullet 6}$-$10^{\bullet 2}$ M, the limit of detection reached $10^{\bullet 5.3}$. Y. Liu (144) reported a novel calix[4]arene derivative (5,11,17,23-tetra-tert-butyl-25,27-bis(3-pyridinecarboxylate)-26,28-dihydroxycalix[4] arene) bearing two nicotinic moieties which show excellent cation selectivities for Ag^+ and Hg^{2+} ions over other alkali, alkaline earth, transition metals, and ammonium ions. The higher cation selectivity is attributed mainly to the host-guest interaction which occurs between the cations and the derivatives of calix[4] arene. D. Liu (145) reported a poly(vinyl chloride) (PVC) membrane electrodes based on bis (dialkyldithiophosphates) carriers for the selective detection of silver ions. This electrode exhibited a linear response over a concentration range of $10^{\bullet 6}$-$10^{\bullet 1}$M Ag^+ with a slope of 57.3 mV/decade. Silver ion-selective electrodes were prepared with polymeric membranes (146) based on nitrogen-containing calixarene derivatives. The electrodes gave a good Nernstian response of 49-53 mV per decade for silver in the activity range $5\times10^{\bullet 6}$-$5\times10^{\bullet 2}$ M, with a limit of detection $10^{\bullet 5.6}$. A PVC-membrane based on bis-pyridine tetramide macrocycle (147) exhibited a good response for silver ions over a wide concentration range ($4.0\times10^{\bullet 5}$-$1.0\times10^{\bullet 1}$mol $L^{\bullet 1}$). Two sym-dibenzo-16-crown-5 ethers with sidearms were synthesized and fabricated as ion-selective (PVC) membrane electrodes by Chia-Ching Su (148). Among these two ion-selective electrodes (ISEs), 3-butenyl sym-dibenzo-16-crown-5 ether gave the best Ag^+ selectivity and 2•methoxyethoxyl sym-dibenzo-16-crown-5 ether the best selectivity for Pb^{2+} ions.
These two membrane electrodes show Nernstain response toward silver and lead over a wide concentration range from $5\times10^{\bullet 5}$ to $5\times10^{\bullet 1}$ M. The detection limit for Ag^+ and Pb^{2+} ions were estimated as $1\times10^{\bullet 6}$ M. The response time was less than 30 s and a good reproducibility over a period of 3 months was observed. O,O,O-tris(2-ethylhexyl) phosphorothioate and O,O,O-tributyl phosphorothioate with a thiophosphoryl (P=S) (149) group are reported as simple and effective ionophores to make Ag^+-selective membrane electrodes. The electrode based on O,O,O-tris(2-ethylhexyl) phosphorothioate exhibited a near-Nernstian response to Ag^+ in the concentration range from $5\times10^{\bullet 6}$ to $1\times10^{\bullet 2}$ M with a slope of 56 mV per decade and could be used over a pH range of 3-8.5. The performance of calix[2]furano[2]pyrrole and related compounds used as neutral carriers for a silver-selective polymeric membrane electrode was investigated by Seon Mook Lim (150). The silver ion-selective electrode based on calix[2]furano[2]pyrroles gave a good Nernstian response of 57.1 mV

per decade for silver ions in the activity range $1\times10^{\bullet 6}$ to $1\times10^{\bullet 2}$ M. A series of benzothiazolylthiaalkoxy functionalized calix[4]arenes showed excellent Ag^+ selectivities, log $K_{Ag,M}$ • • 4.0, against most of the interfering cations examined, except for Hg^{2+} having a very weak interference (151). A. Jiménez-Morales (152) reported a new electrode based on a selective complexing agent for Ag^+ ions, the 6-oxa-3, 9-dithiabicycle[9.3.1]pentadeca-1(15),11,13-triene (MAO). Novel polymeric membrane (PME) and coated graphite (CGE) silver-selective electrodes based on two recently synthesized mixed azathioether crowns containing a 1, 10-phenanthroline sub-unit were reported (153). The electrodes reveal a Nernstian behavior over quite wide Ag^+ ion concentration ranges with a very low limit of detection down to $1.0\times10^{\bullet 8}$ M. The potentiometric responses are independent of the pH of the test solution in the pH range 3.0–7.0. M.K. Amini (154) reported silver ion-selective electrode 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/decade within the range of $1\times10^{\bullet 6}$ M to $1\times10^{\bullet 1}$ M silver ion. The response times of the electrodes were <10 s and did not show a considerable divergence in their potential response over a period of 3 months. The electrodes exhibited good selectivities toward silver ions with respect to alkali, alkaline earth and several transition and heavy metal ions. A new silver solid-state ion-selective electrode has been prepared by directly coating the surface of a glassy carbon electrode with a tetrahydrofuran solution containing PVC, 25, 27-dihydroxy-26, 28-bis[5-(4-methyl-6-hydroxypurimidine) thiaamyloxy] calix[4]arene, with a good Nernstian slope of 61.4 mV/decade over an Ag^+ ion concentration range of $5\times10^{\bullet 8}$-$1x10^{\bullet 1}$ M and a detection limit of $1\times10^{\bullet 8}$ M (155). The response time was between 5 and 10 s, and the electrode is suitable for use within the pH range of 3-7. The selectivity relative to several alkali, alkaline earth, transition and heavy metal ions was good. The electrode could be used for at least one month without a considerable alteration in its potential. The utility of carbon as a new component in a highly selective and sensitive coated-wire electrode (CWE) for silver ions using 2-[(2- 2-[(2-carboxyphenyl)sulfanyl]ethoxy ethyl)sulfanyl]benzoic acid as ionophore is demonstrated (156). This CWE exhibited a good Nernstian slope of 59 mV/decade in a wide linear concentration range from $2.0\times10^{\bullet 8}$ to $1.0\times10^{\bullet 2}$ M for $AgNO_3$. This sensor had a short response time of about 10 s and could be used in a pH range of 2.5–8.7. H. Nam (157) reported tweezer-type and non-tweezer-type ionophores containing dithiocarbamoyl groups on a 7-deoxycholic amide or cholane derivatives used in the potentiometric evaluation of poly(vinyl chloride) (PVC) membranes containing those deoxycholic amides/cholanes linked with tweezer-type dithiocarbamoyl moieties that showed excellent affinity and selectivity to Ag^+ ions over alkali, alkaline earth and other transition metal cations.

It has been pointed out that molecules contining three heteroatoms (N, S & O), like hexathia-18-crown-6-tetraone (158) dithiazone (159), 2-mercaptobenzimidazole (160), were used as potential-selective agents for Hg^{2+}-PVC-membrane electrodes having a good Nernstian response and high selectivity. L.P. Marin (161) has reported 1,3-diphenylthiourea as a neutral carrier for Hg^{2+} ions. The electrode exhibited 58.6 mV/decade over a concentration range from $6x10^{-6}$ to $5x10^{-4}$ mol/L. Javanbakht et al. [162] has reported that a PVC-based membrane of dibenzo-diazo thia-18-crown-6-dione reveals a Nernstian potentiometric response for Hg^{2+} over a wide concentration range from 10^{-6} to 10^{-2} mol/L. It has a response time of 10 s and can be used for at least 3 months without any divergence. The proposed electrode revealed a very good selectivity of Hg^{2+} over a wide variety of alkali, alkaline earth, transition and heavy metal ions. V.K. Gupta (163) reported $(H_2NCHMeCH_2NH_2)(H_2O)2HgCl_2$ as potentiometric sensor for Hg^{2+} metal ions showing a linear response to Hg^{2+} ions in a concentration range from $1.25\times10^{\bullet 5}$ to $1.0\times10^{\bullet 1}$ M having a detection limit of $8.9\times10^{\bullet 6}$ with a slope of 25 mV/decade over the pH range 6.6–9.3. The electrode was highly selective for Hg^{2+} ions over a large number of mono-, bi- and trivalent cations. Normal interferents, like Ag^{+} and Cd^{2+}, do not interfere. R.K. Mahajan (164) reported a membrane electrode based on salicylaldehyde thiosemicarbazone as an ionophore developed successfully as a sensor for mercury(II) ions. The electrode showed an excellent potentiometric response characteristic and displayed a linear log[Hg^{2+}] versus EMF response over a wide concentration range from $1.778\times10^{\bullet 6}$ to $1.0\times10^{\bullet 1}$ M with a Nernstian slope of 29 mV/decade and a detection limit of $1.0\times10^{\bullet 6}$ M. The response time of the electrode is less than 30 s and the membrane electrode operated well in the pH range of 1.0–3.0. The lifetime of the sensor was about 2 months. The electrode showed a better selectivity towards Hg^{2+} ions in comparison with the alkali, alkaline and some heavy metal ions; most of these metal ions did not show a significant interference. X. He (165) reported a mercury ion-selective electrode based on a calixarene derivative containing a thiazole azo group as the ionophore. The ISE gave two kinds of slope for Hg^{2+} at different pH values of 6.5 and 4, respectively. The slopes of these electrodes are reported to be 61.1 mV/decade and 28.7 mV/decade, respectively. A polystyrene-based membrane of 2,3,4,9,10,11-dipyridine-3,10-diaza-1,5,8,12-tetrathiacyclotetradeca-2,9-diene a showed Nernstian slope and adequate stability with a response time of 18 s and was used over a period of 120 days. The potentiometric selectivity coefficient values indicate that the membrane sensor was highly selective for Hg(II) ions over a number of monovalent, divalent and trivalent cations (166). A new polyvinyl chloride (PVC) membrane electrode that is highly selective to Hg(II) ions was prepared by using bis[5-((4-nitrophenyl)azo salicylaldehyde)] (BNAS) as a suitable neutral carrier (167). The sensor exhibited a Nernstian response for mercury ions over a wide concentration range ($7.0\times10^{\bullet 7}$-$5.0\times10^{\bullet 2}$ M) with a slope of 30 mV/decade. It had a response time of <10 s and could be used in the pH range 1 to 3.5, and for at least 3 months without any measurable divergence in potential. The proposed sensor showed a fairly good discriminating ability towards Hg^{2+} ions in comparison with some hard and soft metals.

Pb^{2+} is another heavy metal ion that has attracted attention of analytical chemists. A number of groups are working for the development of lead-selective electrodes e.g., Ohki et al. (168) have reported acyclic dibenzopolyether diamide selective for Pb^{2+} with a measuring range $1x10^{-6}$-$3x10^{-2}$ M. The electrode showed a good selectivity with respect to Cu^{2+}, Fe^{2+}, Ni^{2+}, etc. Oh et al. (169) have reported that bis-crown ethers containing 18-crown-6 moiety showed excellent selectivity for lead ions with a detection limit of $<10^{-6}$ M. Malinowska et al. (170) prepared a series of ionophores based on diaza 18-crown-6 units possessing amide and sulfonamide functional groups selective for lead ions. Their complexing properties were investigated in solvent polymeric membrane electrodes. Hassan et al. (171) have reported a new Pb^{+2}-selective membrane potentiometric sensor based on chiral 2,6–bis–pyridinecarboximide derivatives. The sensor exhibited significantly enhanced response towards Pb^{2+} ions over the concentration range $4x10^{-6}$-$1x10^{-2}$ $molL^{-1}$ with a lower detection limit of 0.4-3.7 $\mu g\ mL^{-1}$. Shamsipur [172] reported a PVC-based membrane electrode for Pb^{2+} ions based on hexa thia-18-crown-6 tetraone as neutral carrier. The electrode showed a Nernstian response over a lead concentration range from $1x10^{-6}$ M to $8.0x10^{-3}$ M at 25 ^{o}C. Jabar et al. (173) have introduced liquid-ion-exchange membranes incorporating tetraphenylborate salts of non-ionic surfactant polyoxylates for the preparation of a Pb^{2+}-ISE. A.K. Jain (174) reported that two neutral ionophores, 2,12-dimethyl-7,17-diphenyltetrapyrazole and 5,11-dibromo-25,27-dipropoxycalix[4]arene were used as membrane sensors for Pb^{2+} ions. The sensors exhibited Nernstian response in the concentration range from $2.5\times10^{\bullet 6}$ to $5.0\times10^{\bullet 2}$M. It performed satisfactorily over a wide pH range (1.6–6.0) with a fast response time (10 s) and could be used over a period of 5 months. Potentiometric selectivity coefficients indicated excellent selectivity for Pb^{2+} ions. A.K. Srivastava (175) reported a coated-wire lead ion-selective electrode (ISE) constructed 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 $1\times10^{\bullet 6}$ to $1\times10^{\bullet 1}$ M with a slope of 30 mV/decade and a detection limit of $6\times10^{\bullet 7}$ M. The working pH range of the sensor was 1.5–6.0 and it showed good selectivity for Pb (II) ions over other mono-, bi- and trivalent cations. The selectivity coefficients for these ions being in the range of $10^{\bullet 4}$-$10^{\bullet 2}$ M. Ardakany (176) reported a sensor based on a dispersion of N, N•-bis(5-methyl salicylidene)-p-diphenylene methane diamine particles into a polymeric membrane using a coated-wire configuration. The response time of <15 s was displayed. The sensor could be used for more than 3 months and the electrode showed a very good selectivity for Pb(II) over a wide variety of metal ions and the signal was constant in the pH range 1.7–6.0. R. Ganjali (177) reported the determination of an ultra-trace amount of lead using N,N•-dimethylcyanodiaza-18-crown-6 coated on a graphite electrode, exhibiting a Nernstian response for Pb^{2+} ions over a very wide concentration range (from $1.0\times10^{\bullet 7}$ to $1.0\times10^{\bullet 2}$ M) with a limit of detection of $7.0\times10^{\bullet 8}$ M (14.5 ppb). It had a fast response time of 10 s and could be used for at least 2 months without any major deviation in the potential. The electrode revealed a very good selectivity with respect to all common alkali, alkaline earth, transition and heavy metal ions. Susan (178) described an ion-selective electrode (ISE) for lead based on piroxicam as a suitable ionophore. The electrode responded to Pb^{2+} in a linear range from $1.0\times10^{\bullet 5}$ to $1.0\times10^{\bullet 1}$ mol/L with a slope of 30 mV/decade and a detection limit of $4.0\times10^{\bullet 6}$ mol/L. The proposed electrode could be used in a pH range of 4.0–8.0.

V.K. Gupta (179) reported some zinc-based ion-selective electrodes. N,N•-bis (acetylacetone) ethylenediimine was used as a neutral carrier for Zn^{2+} and the electrode showed Nernstian response. The pH range of the electrode was 3.2–7.1. Selectivity characteristics of the proposed electrode were also assessed by the fixed interference method. He has also reported (180) 4-tert-butylcalix[4]aren as a zinc-selective sensor. The sensor worked well in a concentration range from 9.8×10^{-6} to 1.0×10^{-1} mol/L with a near-Nernstian slope of 28.0±1.0 mV/decade of activity and a detection limit down to 5.0×10^{-7} mol/L. The working pH range of this sensor was 2.5–4.3. It exhibited a fast response time of 30 s and could be used for more than four months without any considerable change in the response characteristics. It showed an excellent selectivity for Zn(II) over other mono-, bi- and trivalent cations. Further, same group described (181) dibenzo-24-crown-8 as an ion-active material in a poly (vinylchloride) PVC-based matrix for zinc (II)-selective sensors working with a concentration range from 9.2×10^{-5} to 1.0×10^{-1} M, a Nernstian slope of 29.0 ± 0.5 mV/decade of activity fast response time of 12 s and a good selectivity over a number of mono-, bi-, and trivalent cations. The sensor worked well in a pH range 4.8–6.2. A PVC-based membrane containing dimethyl-8,13-divinyl-3,7,12,17-tetramethyl-21H, 23H-porphine-2,18-dipropionate as active material along with sodium tetraphenyl borate (NaTPB) as anion excluder exhibited a working concentration range from 1.5×10^{-5} to 1.0×10^{-1} M, with a slope of 29.0±1.0 mV/decade of activity and a fast response time (10 s) (182). The working pH range of the sensor was 2.1-4.0 and the sensor had a life time of more than 5 months. It exhibited a good selectivity over a number of cations. A zinc complex of the organic ion exchanger, bis(2,4,4-trimethylpentyl) dithiophosphinic acid, was used as an electroactive material for the preparation of PVC-based Zn^{2+}-selective electrodes (183) and a working concentration range from 2.8×10^{-5} to 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 was 2.1-6.9 A.R. Fakhari (184) showed tetra (2-aminophenyl) porphyrin (TAPP) as membrane carrier for Zn^{2+} ions. The sensor exhibited 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 had a response time of about l0 s and could be used for at least 8 months without any divergence in potential. The membrane revealed a good selectivity for Zn^{2+} over a wide variety of other metal ions and could be used in a pH range of 3.0–6.0. Shamsipur (185) reported a benzo-substituted macrocyclic diamide (1,13-diaza-2,3,11,12,15,18-tribenzo-4,7,10-trioxacyclononaoctane-14,19-dione) as a membrane carrier for Zn^{2+} ions. The sensor exhibited a Nernstian response for Zn^{2+} over a wide concentration range (1.0×10^{-1} to 9.0×10^{-5} M). It had a response time of about 20 s and could be used for at least 3 months without any divergence. The proposed membrane sensor revealed good selectivities for Zn^{2+} over a wide variety of other metal ions and could be used in a pH range of 3.0-7.0.

V.K. Gupta (186) reported dicyclohexano-18-crown-6 as active material for $Cd^{2+}$and a working concentration range from 2.1×10^{-5} to 1.0×10^{-1} M with a Nernstian response of 29 mV/decade of activity. The working pH range of the sensor is 1.9-7.0. It exhibited a fast response time as fast as 17 s and had a lifetime of about 6 months. The proposed sensor had a good selectivity for cadmium over alkali, alkaline earth, some transition and heavy metal ions. Also, the same group described (187) dibenzo-24-crown-8 as ionophore for Cd^{2+} ions. The working concentration range is 3.9×10^{-5} to 1.0×10^{-1} M with a Nernstian slope of 30.0±1.0 mV/decade between pH 3.2 and 7.5. It had a fast response time of 25 s. The membrane could be used over a period of five months with a good reproducibility. It is selective over a number of mono, bi- and trivalent cations. M. Shamsipur (188) explored tetrathia-12-crown-4 as an ionophore for Cd^{2+} ions. The sensor exhibited 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 per decade. The limit of detection is 1.0×10^{-7} M (0.01 ppm). It had a fast response time of <10 s and could be used for at least 6 weeks without any divergence in potential. K.C. Gupta (189) worked on cyanocopolymer matrices and 8-hydroxyquinoline as ionophore for Cd^{2+} and showed a Nernstian slope of 29 mV/decade activities of Cd^{2+} ions with a response time of 12 s. 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. The cyano groups of the copolymers contributed significantly to enhance the selectivity of the electrode. The electrode had an appreciable average life of 6 months. A new PVC-membrane electrode for Cd^{2+} ions based on [1,1′-bicyclohexyl]-1,1′, 2,2′-tetrol as membrane carrier was prepared by Ganjali (190). The electrode exhibited a Nernstian response for Cd^{2+} over a wide concentration range (1.0×10^{-5}-1.0×10^{-1}M) with a slope of 27.8 mV/decade. The limit of detection is 9.0×10^{-6} M. The electrode had a response time of <15 s and a useful working pH range of 4.0-7.0. The proposed membrane sensor showed an excellent discriminating ability towards Cd^{2+} ions with regard to several alkali, alkaline earth, transition and heavy metal ions. H. Freiser (191) prepared a coated-wire ion-selective electrode (CWE) based on the bidentate neutral carrier 4,4′-di(5-nonyl)-2,2′-bipyridine (DNBP) for the determination of cadmium ions. The CWE exhibited a Nernstian response, and a detection limit of $1\text{x}10^{-6}$M.

Nickle is another industrially important metal and monitoring of Ni^{2+} ions is very important. A.Yari (192) reported the suitability of 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 could be used for at least 4 months without any considerable divergence in potentials and it had a relatively fast response of <10 s. The prepared membrane exhibited a near-Nernstian response for Ni^{2+} ions over a wide concentration range (1.0×10^{-6} to $1\text{x}10^{-1}$ M) with a detection limit of 1.6×10^{-6} M. At a working pH range of 2.0-6.5 the proposed membrane electrode revealed a very good selectivity for Ni^{2+} ions over a wide variety of other cations. Mashhadizadeh (193) reported N,N′-bis-(4-dimethylamino-benzylidene)-benzene-1,2-diamine as a suitable neutral carrier for Ni(II). The sensor exhibited a Nernstian response for nickel ions over a wide concentration range (2.0×10^{-7} to 1.0×10^{-2} M) with a slope of 30±1 mV per decade. It had a response time of <10 s and could be used in the pH range from 4.5 to 9.0 for at least 2 months without any measurable divergence in potential. The proposed sensor showed a fairly good discriminating ability towards Ni^{2+} ions in comparison to some hard and soft metals. M.K. Amini (194) reported 1,3,7,9,13,15,19,21-octaazapenta- cyclooctacosane as a neutral ionophore for Ni(II). The electrode exhibited a near-Nernstian response in the concentration range from 1×10^{-6} to 1×10^{-1} M Ni(II). It had a response time between 5 and 40 s for nickel concentrations ranging 1×10^{-6}-1×10^{-1}M. The electrode revealed moderate selectivities over a number of alkali, alkaline earth and several transition and heavy metal ions. The electrode is suitable for use in aqueous solutions in a wide pH range of 3-6. A PVC-membrane nickel(II) ion-selective electrode was constructed using 1,10-dibenzyl-1,10-diaza-18-crown-6 (DBzDA18C6) as a neutral carrier (195). The sensor exhibited a Nernstian response for Ni(II) ions over a wide concentration range ($2.0\times10^{\bullet\,5}$-$5.5\times10^{\bullet\,3}$ M). It had a relatively fast response time and could be used for at least 6 weeks without any considerable divergence in potentials. The proposed sensor revealed relatively good selectivity for Ni(II) over a wide variety of other metal ions, and could be used in a pH range of 4.0-8.0.

Chromium is another transition metal ion for which a number of ISEs are reported. To monitor these ions many techniques are available and the ion-selective electrode is one of the most economical modes of determination. V.K. Gupta (196) reported tri-o-thymotide as an electroactive material for the fabrication of a chromium(III)-selective sensor, exhibiting a working concentration range from $4.0\times10^{\bullet\,6}$ to $1.0\times10^{\bullet\,1}$ M with a Nernstian slope of 20±0.1 mV/decade of activity in the pH range of 2.8–5.1. The detection limit of this sensor was $2.0\times10^{\bullet\,7}$ M. The electrode exhibited a fast response time of 15 s, showed a good selectivity towards Cr^{3+} over a number of mono-, bi- and trivalent cations. M.R. Ganjali (197) reported 4-amino-3-hydrazino-6-methyl-1,2,4-triazin-5-one (AHMTO) as a neutral ionophore for Cr(VI). The sensor had a linear dynamic range from $1.0\times10^{\bullet\,6}$ to $1.0\times10^{\bullet\,1}$ M, with a Nernstian slope of 19.7±0.3 mV per decade, and a detection limit of $5.8\times10^{\bullet\,7}$ M. It had a fast response time of <10 s and could be used for at least 3 months in a pH range of 2.7-6.6. Moon (198) described that N,N,N,N-tetrakis(3-aminopropyl)-1,4-butane- diamine exhibited the highest Cr(VI) ion selectivity in both extraction and potentiometry experiments. A reproducible response of Cr(VI) was attained within a response time of 1 s in the range from $2.16\times10^{\bullet\,6}$ to 0.1 M. Gholivand (199) used glyoxal bis(2-hydroxyanil) as as a Cr(III)-selective electrode. The electrode had a linear dynamic range of $3.0\times10^{\bullet\,6}$ to $1.0\times10^{\bullet\,2}$ mol/L with a Nernstian slope of 19.8±0.5 mV per decade and a detection limit of $6.3\times10^{\bullet\,7}$ mol/L. It had a fast response time of <20 s and could be used for at least 3 months without any considerable divergence in potential. The proposed electrode revealed good sensitivities for Cr(III) over a wide variety of metal ions and could be used in a pH range of 2.7-6.5.

A.K. Srivastava (200) described an iron-cyclam complex as an ion-active material for Fe(III). It exhibited a Nernstian response over a concentration range of $1\times10^{\bullet\,6}$-$1\times10^{\bullet\,2}$. The working pH range of the electrode was found to be 1.3-3.5. Selectivity coefficients of some mono- and divalent metal ions were also determined.

Ionophore-based ISEs for some Rare Earth Metal Ions

A cerium (III) sensor was reported by Shamsipur et al. (201) using 1,3,5-trithiane as an ionophore. It showed a linear response in the range $5.0\text{x}10^{-5}$ M-$1.0\text{x}10^{-1}$ M with a Nernstian slope of ~19.4 mV/decade. It was used as an indicator electrode in potentiometric titration of oxalate and fluoride ions and in the determination of F^- ions in some mouthwash preparations. Another coated graphite electrode (202) for cerium (III) ions was reported by Shamsipur using 1,3,5-trithiane as an ionophore. It showed a detection limit of $2.0\text{x}10^{-8}$ M. Karami et al. (203) reported a cerium-selective electrode based on N-[(Z)-2-chloro-2-(1-hydroxy-1,1,1-triphenyl phosphoranyl)-1-ethenyl]-4-ethyl-1-benzene sulfonamide which had a detection limit of $2.3\text{x}10^{-7}$ M. This sensor was used for measurement of the cerium content in stainless steel samples. Recently, a new PVC-membrane electrode based on 2-aminobenzothiazole has been reported by Akhond et al. (204) for Ce(III) ions. Ogata et al. (205,206) reported a samarium (III)-selective electrode constructed using bis (alkylxanthato) alkanes and bis (thiaalkylxanthato) alkanes as ion carriers. Acceptable selectivity was obtained for Sm (III) determination against many of the transition, alkali, alkaline-earth and some lighter rare-earth metal ions. Ganjali et al. (207) prepared a samarium (III)-selective membrane sensor based on glipizid. The electrode had an average lifetime of only two months and was successfully used as an indicator electrode in potentiometric titration of Sm (III) ions with EDTA. An ytterbium(III)-selective membrane electrode based on cefixime had been reported by Ganjali et al. (208). It had a detection limit of $7.0\text{x}10^{-7}$ M. A new S-N Schiff's base, 2-[{3-[(2-sulfanylphenyl) imino)-1-methylbutylidene} amino] Phenyl hydrosulfide was reported as a gadolinium(III) sensor (209). It had a detection limit of $3.0\text{x}10^{-6}$ M and had been used for the determination of Gd(III) in a urine sample. Recently, a PVC-membrane containing zirconium (IV) selenomolybdate inorganic ion exchanger as dysprosium (III) ion-selective electrode has been reported by Gupta et al. (210). It had a detection limit of $3.8\text{x}10^{-5}$ M. The electrode could be used in a mixed solvent medium and for the direct determination of Dy (III) in metaborate rock with an experimental error 2-4%.

Mohamed B. Saleh (211) reported [4-(4•-nitrobenzyl)-1-phenyl-3,5-pyrazolidinedion)] as a cerium sensor. This electrode had a wide linear dynamic range from $2.5\times10^{\bullet 6}$ to $1\text{x}10^{\bullet 1}$ mol/L with a Nernstian slope of 19.5±0.2 mV per decade and a low detection limit of $1.6\times10^{\bullet 6}$ mol/L. It had a fast response time (<10 s) and good selectivity with respect to different metal ions. The NBPP-based electrode was suitable for aqueous solutions of pH range from 4.0 to 8.0. It could be used for about 3 months without any considerable divergence in potential. M.R. Ganjali (212) describing a novel Pr(III)-selective membrane sensor based on N•-(pyridin-2-ylmethylene) benzohydrazide (PBA), exhibiting a Nernstian response for Pr(III) ions over a relatively wide concentration range ($1.0\times10^{\bullet 6}$-$1.0\times10^{\bullet 2}$ M) with a limit of detection of $8.0\times10^{\bullet 7}$ M (115 ppb). It had a fast response time of 20 s and could be used for at least 6 weeks without observing any major deviation. The sensor revealed a very good selectivity with respect to common alkali, alkaline earth, and especially lanthanide metal ions. The response of the proposed sensor was independent on pH in the range 3.5-8. M.R. Ganjali (213) showed 4-methyl-2-hydrazinobenzothiazole (MHBT) as an ionophore for La(III) in the working range $1.0\times10^{\bullet 7}$ to $1.0\times10^{\bullet 1}$ M of La^{3+}. The sensor exhibited a Nernstian slope of 19.8 mV per decade in La^{3+} activity. The detection limit of the sensor was $2.5\times10^{\bullet 8}$ M. Ganjali (214) reported a highly sensitive ytterbium(III) sensor based on 3-hydroxy-N•-[(2-hydroxyphenyl)methylene]-2-naphtho- hydrazide (HPMN). This sensor responded to the Yb(III) activity in a linear range from 1.0×10^{-7} to 1.0×10^{-2} M, with a slope of 19.2±0.2 mV per decade and a detection limit of 4.0×10^{-8} M at a pH range of 3.0-8.5. It had a very fast response time of <6 s in the whole concentration range, and can be used for at least 6 weeks without any considerable divergences in its potentials. Ganjali (215) reported a Tb(III)-selective sensor based on N,N,-bis(pyrrolidene) benzene-1,2-diamine in a pH range of 3.5-7.7. This sensor responded to dysprosium in a linear concetration range from 1.0×10^{-5} to 1.0×10^{-1} M, with a slope of 19.8 mV per decade and a detection limit of 7.0×10^{-6} M. It had a fast response time of <20 s and a comparatively good selectivity with respect to common alkali, alkaline earth, transition and heavy metal ions. Morteza Akhond (216) studied a PVC-membrane sensor for La^{3+} ions based on 2,2′-dithiodipyridine as an ion carrier. The electrode exhibited a Nernstian slope of 20.0±1.0 mV per decade of La^{3+} over a concentration range from 7.1×10^{-6} to 2.2×10^{-2} M of La^{3+} in the pH range 3.3-8.0. The response time was about 7 s and the detection limit was 3.1×10^{-6} M. The electrode could be used for at least 2 months without a considerable divergence in potential. Morteza Akhond (217) developed electrode based on 2-aminobenzothiazole, which was highly selective for the determination of Ce^{3+} ion. The electrode exhibited a Nernstian slope of 19.6±1.0 mV per decade over a wide Ce^{3+} ion concentration range from 2.0×10^{-6} to 2.0×10^{-2} M and a low detection limit of 1.8×10^{-6} M. The electrode possessed a fast response time of 13 s and a lifetime of at least 3 months. The proposed electrode revealed an excellent selectivity for Ce^{3+} over a wide variety of alkali, alkaline earth, some transitions, and heavy metal ions. The electrode could be used in a pH range of 4.1-7.3. S.K. Mittal (218) reported dicyclohexano-18-crown-6 (DC18C6) as a neutral carrier for lanthanum (III) ions. The electrode showed a linear dynamic response in the concentration range from 10^{-6} to 10^{-1} M with a Nernstian slope of 19 mV per decade and a detection limit as 5×10^{-7} M. It had a response time of <30 s and could be used for at least 5 months without any significant divergence in potentials. Selectivity coefficients for mono-, di-, and trivalent cations indicated a good selectivity for La(III) ions over a large number of interfering cations. It could be used in the pH range 4-9. Mohammad Reza Ganjali (219) described S–N Schiff,s base (2-[{3-[(2-sulfanylphenyl) imino)-1-methylbutylidene} amino]phenyl hydrosulfide (SMPH) as gadolinium sensor. The sensor displays a linear dynamic range between 1.0×10^{-5} and 1.0×10^{-1} M, with a Nernstian slope of 19.8±0.3 mV per decade and a detection limit of 3.0×10^{-6} M. The sensor was independent of the pH in a range of 4.0-8.0, had a very fast response time and very good selectivity towards a large number of cations such as Sm(III), Ce(III), La(III), Cu(II), Pb(II) and Hg(II). The electrode could be used for at least 9 weeks without any considerable divergence in the potentials. V.K. Gupta (220) reported monoaza-12-crown-4 as an ionophore for a lanthanum(III) sensor that works well over a wide concentration range from 3.16×10^{-5} to 1.00×10^{-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 a good reproducibility. The proposed electrode could be used in a wide pH range from 3.0 to 7.0 and demonstrated a good discriminating power over a number of monovalent, divalent, and trivalent cations. Shamsipur (221) described a polymeric membrane (PME) and coated graphite (CGE) samarium(III)-selective electrode based on isopropyl 2-[(isopropoxycarbothioyl) disulfanyl] ethanethioate. The electrodes exhibited Nernstian slopes for Sm^{3+} ions over a wide concentration range (1.0×10^{-5} to 1.0×10^{-1} M for PME and 1.0×10^{-6} to 1.0×10^{-1} M for CGE). The PME and CGE have limits of detection of 3.1×10^{-6} and 5.0×10^{-7} M, respectively, and response times of about 20 s. The potentiometric responses are independent of the pH of the test solution in the pH range 4.0-7.0. Ganjali (222) prepared a sensor for La(III) ions based on N-[hexahydrocyclo- pentapyrol-2((1H)yl)amino]carbonyl]-4-methyl benzene sulfonamide (gliclazide) as a novel carrier. The electrode exhibited a Nernstian response for La(III) over a wide concentration range (1.0×10^{-1} to 1.0×10^{-6} M) with a slope of 20.1 mV/decade. The limit of detection is 8.0×10^{-7} M. The sensor had a very short response time (<15 s) and a useful working pH range of 4.0–8.0. Ganjali (223) discovered that the antibiotic cefixime (CFI) could be used as a suitable ionophore in PVC membranes having interesting response characteristics for Yb(III) ions. The selective complexation behavior of cefixime with Yb^{3+} over different metal ions was studied in DMSO solution. The negligible water solubility of cefixime and the increased stability and selectivity of its Yb(III) complex made the antibiotic an attractive ionophore for use in potentiometric poly (vinyl chloride) membrane electrodes for Yb(III). The results revealed a Nernstian response to Yb(III) over a concentration range 1.0×10^{-2}-1.0×10^{-6} M as well as an improved selectivity against a wide range of common interferences. The sensor possessed a detection limit of 7.0×10^{-7} M and could be used in a pH range 3.0-8.0 for at least 8 weeks.

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Chapter -3

METHODOLOGY

Ion-selective Electrodes (ISE) are probes that respond selectively to certain ions in the presence of others. These include probes that measure specific ions in solution. The most commonly used ISE is the pH probe. Other ions that can be measured include fluoride, bromide, cadmium, etc., in solution.

Ion-selective Electrodes work on the basic principle of the galvanic cell (1-3). By measuring the electric potential generated across a membrane by "selected" ions, and comparing it to a reference electrode, a net charge is determined. The strength of this charge is directly proportional to the concentration of the selected ion.

The use of Ion-selective Electrodes in environmental analysis offers several advantages over other methods of analysis. First, the cost of the initial setup to make analysis is relatively low. The basic ISE setup includes a meter (capable of reading millivolts up to an accuracy of ±0.1 mV), a probe (selective for each analyte of interest) and various consumables used for pH or ionic strength adjustments. The expense is considerably less than other methods such as Atomic Adsorption Spectrophotometry or Ion Chromatography. ISE determinations are not subjected to interferences such as color in the sample. There are few matrix modifications needed to conduct these analyses. A large number of indicator electrodes with good selectivity for specific ions are based on the measurement of the potential generated across a membrane. Electrodes of this type are referred to as ion-selective electrodes. The membrane is usually attached to the end of a tube that contains an internal reference electrode. This membrane electrode and an external reference electrode are then immersed in the solution of interest. Since the potentials of the two reference electrodes are constant, any change in the cell potential is due to a change in potential across the membrane.

Calibration

Direct - The electric potentials are determined for a series of standards and a standard curve is developed. Additional analyses are fit to the standard curve in order to determine their concentration. Direct calibration is the most common and easiest way to measure concentrations.

Titrations - ISEs have also been used as indicator electrodes for titrations. Titration methods use a titrant which will complex or react with the ion to be analyzed. Concentration of the ion in the sample is back calculated from the volume of the titrant used.

Membranes - Nature of the membrane determines the selectivity of the electrode. A membrane is considered to be any material that separates two solutions. It is across this membrane that the charge develops.

Polymer membrane electrodes consist of various ion-exchange materials incorporated into an inert matrix such as PVC, polyethylene or silicone rubber. After a membrane is formed, it is sealed to one end of a PVC-tube. The potential developed at the membrane surface is related to the concentration of the species of interest.

Preparation of the Electrode and EMF Measurements

Membranes of ~ 0.2 mm thickness were obtained (4) by pouring a solution of the membrane components of PVC 33%, ligand 2-6%, and o-nitro phenyl octyl ether 63% dissolved in 2-3 mL of tetrahydrofurane (THF). The viscous solution of polymer thus, obtained was poured in a glass ring of 30mm diameter placed on a dust free Pyrex glass plate. The solvent was allowed to evaporate slowly for about 24 h at room temperature. To obtain membranes with similar characteristics, viscosity of the casting solution and the rate of solvent evaporation were controlled so that thickness and morphology of membranes remained almost unchanged. Membranes were then removed from the glass ring and circular pieces of 1.25 cm diameter were cut and mounted on the ground end of a Pyrex glass tube with araldite and conditioned with the metal ion solution for 24 h.

EMF Measurements

All the emf measurements were carried out using the following cell assembly:

$$\textbf{SCE} \,|\,|\, \textbf{0.1M M}^{n+} \,|\, \textbf{membrane} \,|\, \textbf{M}^{n+} \textbf{ test soln} \,|\,|\, \textbf{SCE}$$

Salt bridges containing KNO_3 were used to provide electrical links between KCl and Ag^+ solutions on both sides of the membrane. A digital potentiometer having a sensitivity of 0.1 mV (Equiptronics EQ602, India) was used for the potential measurements at 25±0.1 °C. Activities were calculated according to the Debye-Hückle equation (5). Standard metal nitrates solutions were obtained by gradual dilution of a 0.1 M metal salt solution, and their emf measurements were performed.

Temperature - It is important that temperature be controlled as variation in this parameter can lead to significant measurement errors. A single degree (C) change in sample temperature can lead to measurement errors greater than 4%. The experimental set up was placed in an thermostata temperature of which was maintained up to ±0.1 °C.

Agitation - When carrying out selective ion measurements, it is important to have a good agitation. This allows a fresh supply of ions to be exposed to the sensing portion of the ISE. An agitation of the solution was done by stirring it using a telfon-coated magnetic bead and a magnetic stirrer at a moderate speed.

Response Time - ISEs require a much longer time for the reading to stabilize. Sufficient time was allowed for equilibrium to be established while measuring standard solutions. The response time was measured when the mV reading remained stable for about 30 seconds.

Rinsing - It is necessary to rinse the ISE between measurements to insure accurate readings. A steady stream of deionized or distilled water was used. The electrode was wiped off the excess water by shaking it gently.

Conditioning - The ISE needs to remain moist at all times even when not in use. It was kept immersed in standard solution of primary ion when not in use.

Slope - It is the linear part of the calibration curve of the electrode. The theoretical value according to the Nernst equation is: 59.16 [mV/log(a_x)]at 298 K for a single charged ion or 59.16/2 = 29.58 [mV perdecade] for a double charged ion.

Range of Linear Response - At high and very low target ion activities there are deviations from linearity. Typically, the electrode calibration curve exhibits linear response in a range between 10^{-5}M and 10^{-1}M.

Detection Limit - According the IUPAC recommendations (6-7) the detection limit is defined by the cross-section of the two extrapolated linear parts of the ion-selective calibration curve. Detection limit of the order of 10^{-5}-10^{-6}M was measured for most of ion-selective electrodes.

Selectivity

Selectivity is one of the most important characteristics of an electrode, as it often determines whether a reliable measurement in the sample is possible or not. The selectivity coefficient (K_{xy}) has been introduced in the Nikolski-Eisenman equation. Negative values indicate a preference for the target ion relative to the interfering ion. Positive values of log K_{xy} indicate a preference of the electrode for an interfering ion. The experimental selectivity coefficients depend on the activity and the method of their determination. Different methods of the selectivity determination can be found in the literature. The IUPAC suggests two methods (6-7): separate solution method (SSM) and fixed interference method (FIM). There is also an alternative method of the selectivity determination called matched potential method (MPM). Each of them has got advantages and drawbacks, and there are not general rules pointing, which method gives the true result. Selectivity coefficients were determined by using SSM, FIM & MPM methods.

Separate Solution Method - In this method, calibration curves are prepared for each ion being tested.

Parallel curves should result, with the potentials for the primary ion (if a cation) being more positive. The selectivity ratio can be related to the difference in potential between the two curves (3.1). The more selective the electrode is for ion A, the larger will be the potentials difference (the smaller will be the potential for ion B). For two monovalent ions:

$$-\log K_{AB} = \frac{E_A -}{S} \qquad (3.1)$$

Mixed Solution Method - There are various measurement methods using mixed solutions of the two ions. The fixed interference method is commonly used. The emf of a cell comprising an ion-selective electrode and a reference electrode is measured with solutions of constant activity of interfering ion, a_B , and varying activity of the primary ion. The emf values obtained are plotted against the logarithm of the activity of the primary ion a_A. The intersection of the extrapolation of the linear portions of this plot indicates the value of a_A which is to be used to calculate K_{AB} from the Nikolski- Eisenman equation (3.2).

$$K_{AB} = \frac{a_A}{a_B^{z_A/z_B}} \qquad (3.2)$$

Matched Potential Method - This method involves measuring potentials of a pure solution of the primary ion, E_A and of a mixed solution containing the primary and interfering ions, E_{A+B}. Activities of the primary ion are the same in both solutions. And the selectivity co-efficient is calculated by inserting the values of potential difference, $\Delta E = (E_{A+B} - E_A)$, a_A and a_B into the following equation (3.3):

$$K_{AB}^{pot} = \frac{a_A(10^{\Delta E z_A F/2.303})}{a_B^{z_A/z_B}} - 1 \qquad (3.3)$$

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 (3.4):

$$K_{AB} = \Delta A / a_B \qquad (3.4)$$

Here **$\Delta A = a^{\bullet}_{A} \bullet a_{A}$; a_{A}** is the initial activity of primary ions A and $a^{\bullet}_{B}$ is the activity of A in the presence of interfering ions at $\mathbf{a}_B$.

Limitation in Interpretation of Selectivity Coefficients

There are several IUPAC approved methods that are used concurrently by researchers. Selectivities for a given ionophore are only valid for the matrix and plasticizer composition in which they are tested. In addition, each method will generate different selectivity coefficients. Due to many limitations and dependencies on the empirical determination of selectivity coefficients, only the ratios of selectivity coefficients can be used to evaluate (compare) ionophores from different research groups. The fixed interference method is amongst the most commonly employed for its good mix of realism and simplicity. One can consider the interference coefficient (as determined by the fixed interference method) to mean the at which the uncertainty of the measurement of the analyte matches the deviation due to the interfering ion. In this way, the interference point is not only dependent upon the ionophore selectivity to other ions, but also the uncertainty of the measurement for a given concentration. The fixed interference concentration is commonly set to 0.1 or 0.01 M, for systems with good selectivity and lower concentrations (0.001 or 0.0001 M) for systems that demonstrate poorer selectivity.

The advantages and drawbacks of the three described methods (SSM, FIM, MPM) are summerised subsequently.

Separate Solution Method

Advantages:

- speed and ease of determination,
- can determine a large array of interfering ion-selectivity coefficients very quickly,
- is used for simple flow-injection potentiometry applications (simple and well defined systems).

Disadvantages:

- does not account for any error due to multiple ion interaction,
- overly simplistic method for real solutions, often giving very different coefficients than other methods.

Fixed (Constant) Interference Method

Advantages:

- accurate for a larger variety of systems than separate solutions,
- relatively simple to perform for a reasonable set of potential interfering ions of interest,
- more accurate than separate solutions,
- method gives good (reasonable) data for most real world systems,

- coefficients translate fairly well to many observed application selectivity performance.

Disadvantages:

- does not account for all multiple ion-ion interactions, only interfering ion analyte interference.

Mixed Solutions Method

Advantages:

- accurate for almost all stable systems, even if complex,
- more accurate than fixed interference solutions,
- method gives very good data for complex systems.

Disadvantages:

- very cumbersome to perform if the system has any variance of the ionic background,
- laboratory technique and uncertainties of measurement are of great importance.

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Chapter -4

CYCLIC PODANDS AS SENSING MATERIALS

(4a) PVC-based Dicyclohexano-18-Crown-6 Sensor for La(III) Ions

Introduction

Lanthanum is found in rare-earth minerals such as cerite, monazite, allanite, and bastnasite. Pure lanthanum has very few applications being almost limited to the scientific research. In spite of this, the metallurgical industry is the only commercial domain where the metal finds application (1). Some rare-earth chlorides, such as lanthanum chloride ($LaCl_3$), are known by their anticoagulant properties although they should be used with very care. Lanthanum salts are generally considered to have low or moderate toxicity (2). Attempts were made to promote germination of neutral rice seed by treating them with lanthanum nitrate (3). Thus, because of the increasing industrial use of lanthanum compounds as well as their enhanced discharge and its useful and harmful biological activity, the determination of lanthanum has been of a recent increasing concern.

Available methods for low-level determination of rare-earth ions in solution include spectrophotometry (5), ICP-AES (6), isotope dilution mass spectrometry (7), neutron activation analysis (8), X-ray fluorescence spectrometry (9), etc. These methods are either time consuming, involving multiple analysis or too expensive for most analytical laboratories.

Trivalent lanthanides are expected to form stable complexes with various macrocyclic ligands similarly to alkali and alkaline earth metals because of the similarity of radii between lanthanides and Na^+ or Ca^{2+} ions. In fact, it was mentioned in the first report on crown ethers by Pedersen (1967) (10) that some crown ethers formed complexes with La(III) and Ce(III) in solution. The formation of La(III) complexes with DC18C6 was reported in the original paper of Pedersen (1967) but details are not available. However, some detailed studies are available in the following references (11-13).

Potentiometric sensors can offer an inexpensive and convenient method for the analysis of rare-earth metal ions in solution; provided acceptable sensitivity and selectivity are achieved. In spite of successful progress in the design of highly selective ionophores for various metal ions, there are only a limited number of reports on the development of selective ionophores for lanthanum (14-18)

Bis (2-mercaptoanil) diacetyl (BMDA) by M.R. Ganjali et al. (19), Monoaza-12-crown-4 , by V.K.

Gupta et al. (20) , 1,3,5-trithiacyclohexane by M. Shamsipur (21), 4-methyl-2- hydrazinobenzothiazole (MHBT) by M.R. Ganjali et al. (22), 2, 2-dithiodipyridine, by M. Akhond, et al. (23), *N*-[hexahydrocyclopentapyrol-2((1H)yl)amino]carbonyl]-4-methyl benzene sulfonamide (gliclazide), by M.R. Ganjali et al. (24), *N*,*N*′-adipylbis(5-phenylazo salicylaldehyde hydrazone), by M. Shamsipur et al. (25) group of ionophores for La(III) determination showed good preference for La(III) over other ions, However, lifetime of some of electrodes is very poor. The detailed performances of the electrodes are consolidated in Table 4.4(a).

The main objective this work is to introduce a selective and sensitive electrode for lanthanum ions for the potentiometric monitoring of trace amounts of La(III) by using DC18C6.

Experimental

Reagents

Reagents, like dicyclohexano-18-crown-6 (DC18C6), o-nitro phenyl octyl ether (o-NPOE), dibutylpthalate (DBP), bis-2-ethylsebacate(2BES) were procured from Sigma-Aldrich. All other chemicals were of analytical reagent grade. Double distilled deionized water was used throughout the experiments.

Electrode Preparation

Membranes of ~0.2 mm thickness were obtained by pouring a solution of the membrane components: PVC, 33%; DC18C6, 6%; 2-nitro phenyl octyl ether, 61% dissolved in 2-3 mL of THF at room temperature as per procedure of JDR Thomas (26). The viscous solution of polymer, thus obtained was poured in a glass ring of 30mm diameter placed on a dust free Pyrex glass plate. Solvent was allowed to evaporate slowly for about 24 hours at room temperature. To obtain membranes with similar characteristics, viscosity of the casting solution and the rate of solvent evaporation were controlled so that thickness and morphology of the membranes remain almost unchanged. The prepared membranes were removed from the glass plate and circular pieces of 1.25 mm diameter were cut and mounted on the ground end of the Pyrex glass tube with araldite. Membranes were conditioned with $La(NO_3)_3$ solution of ($1x10^{-1}$M) for 24 hours.

EMF Measurements

All the emf measurements were carried out using the following cell assembly:

SCE│0.1 M La(III)││ membrane ││test solution│SCE

A digital potentiometer (Equiptronics EQ-602, India) was used for the potential measurements at 25±0.1 °C. Activities were calculated according to the Debye-Huckle equation. Standard solutions of $La(NO_3)_3$

were obtained by gradual dilution of 0.1 M $La(NO_3)_3$ solution and their potential measurements were performed in unbuffered solutions.

Results and Discussion

The trivalent lanthanide ion has an outer shell electronic configuration as $4f^7 5s^2 5p^6$. The bonds between the lanthanum ion and the macrocycle DC18C6 are mainly ion-dipole and non-directional, and are similar to those between alkali metal ions and crown ethers, since the 4f electrons are effectively shielded. DC18C6 forms a stable complex with lanthanum (La(III)) ions as supported by a high stability constant value. This means that the stability of the complexes might be unusually sensitive to the size of the lanthanide ion primarily because of the electrostatic and steric effects. So, a unique selectivity for La (III) ions is expected with a DC18C6 ligand.

Optimization of the Membrane Composition

Membrane composition and the nature of plasticizer influence the sensitivity and selectivity of an electrode (27-29). The effect of composition on the response of the electrode was investigated. For this purpose, the performance characteristics, like slope of the calibration curve, measurement range and detection limit were studied [Table 4.1(a)]. The results show that the electrode with the ratio PVC: 2-NPOE: DC18C6; 33%: 61%: 6%, exhibit the best response with a slope of 19 mV per decade. As it is obvious from Table 4.1(a), 2-NPOE is a more effective solvent medium than DBP in preparing the La^{3+}ion-selective electrode. The quantity of ion carrier DC18C6 was also found to affect the sensitivity of the membrane electrode. The sensitivity of the electrode response increases with increasing ionophore content until a value of 6% (w/w) is reached. Further addition of ionophore results in a decreased slope of the electrode.

Effect of Internal Solution Concentration

The influence of concentration of the internal solution on the response of the La (III) ion-selective electrode was studied (18). Results shown in Table 4.2(a) indicate that the variation in the concentration ($1x10^{-4}$ M-$1x10^{-1}$ M) of the internal solution changes the slope. A $1x10^{-4}$ M concentration of internal solution is quite appropriate for a smooth functioning of the electrode system.

Effect of pH

The influence of pH of the test solution on the electrode response of the electrode was studied at 3 different concentrations; $1x10^{-2}$ M, $1x10^{-3}$ M and $1x10^{-4}$ M over the pH range 2-12. The pH was adjusted by introducing small drops of HNO_3 (0.1 M) or NaOH (0.1 M) as per requirement and the results are shown in Figure 4.1 (a). The EMF is independent of pH in the range 4-9. Therefore, this range can be chosen as the working pH range for the electrode assembly. However, variations above and below this pH range may be due to a formation of La $(OH)_3$ and protonation of oxygen atoms of the DC18C6, respectively.

Detection Limit, Response Time, Reproducibility and Lifetime

Working concentration ranges and slopes for all the membrane electrodes are given in Table 4.1(a). The electrode composition PVC:DC18C6:2-NPOE, 33:6:61 (wt%) shows linearity in the concentration range $1x10^{-6}$M to $1x10^{-1}$M with a slope of 19 mV/decade. However, the addition of KTpClB did not lead to a significant improvement in the working concentration range. Hence, this membrane was studied in detail as a La(III)-selective electrode and all further studies were carried out on this membrane. Repeated monitoring of potentials (five identical measurements) on the same portion of the concentration range gave a standard deviation of ±1 mV. To obtain better electrode properties, solvent mediators such as 2-NPOE, DBP and 2BES were tested. The membrane based on 2-NPOE exhibits a Nernstian slope of 19 mV/decade over a wide concentration range from $1x10^{-6}$ M to $1x10^{-1}$ M, while in the same concentration range, the plasticisers DBP and 2BES showed slopes as 17 mV/decade and 14 mV/decade, respectively. Further, the electrode based on 2-NPOE had a better electrode response than the other two mediators. The limit of detection ($1x10^{-6}$M) was calculated according to IUPAC recommendation (30,31) from the intersection of the two extrapolated linear portions of the curve Figure 4.2(a). The response time of the electrode is at least for the electrode No.7, i.e. 25 seconds, and for all other electrodes it is greater than 30 seconds. The sensing behavior of the membrane remains unchanged when the potentials are recorded either from low to high or high to low concentrations. This membrane electrode could be used for at least five months without any measurable divergence. The electrodes were stored in 0.1 M $La(NO_3)_3$ when not in use to avoid any change in the lanthanum ion concentration in the membrane phase.

Selectivity Coefficients and Analytical Properties of Lanthanum-selective Electrode

Selectivity is perhaps the single most important characteristic of any electrode, which defines the nature of the device and the extent to which it may be employed in the determination of a particular ion in presence of other interfering ions. Potentiometric selectivity coefficients of the lanthanum membrane electrodes were evaluated by Fixed Interference Method (FIM) (30,31) at $1x10^{-3}$ M concentration of the interfering ions and Matched Potential Method (MPM) (30,31). MPM is recommended by IUPAC to overcome the difficulties associated with the methods based on the Nicolski-Eisensenman equation. According to this method, the specified activity of the primary ion (A) is added to a reference solution, and the potential is measured. In a separate experiment, the interfering ion (B) is successively added to an identical reference (containing primary ion) solution until the measured potential matches to that obtained only with the primary ions. Table 4.3(a) shows the potentiometric selectivity coefficients of a DB18C6-based on lanthanum-selective electrode. The selectivity data indicate that $K^{Pot}_{La,M}$ values are of the order 10^{-2} for trivalent metal ions. Therefore, the electrode can be used for the determination of La

(III) ions in the presence of certain interfering ions.

Effect of Mixed Solvent Media on the Working of La(III) Electrode

The proposed sensor was investigated in partially non-aqueous media using methanol, ethanol and acetone mixtures with water. Table 4.5(a) indicates that the slope is decreased with the addition of non-aqueous solvents from 19 mV/decade to 17 mV/decade. An increase beyond 30% in non-aqueous content causes a significant interference in slope. In a water-acetone medium, a significant change in potential, stable slope, measuring range, detection limit is observed Figure 4.3(a). This may be due the dynamic complex formation and decomplexation between DC18C6 and La(III) in the water-acetone mixture.

Potentiometric Titration

Potentiometric titrations were performed by using the proposed electrode as an indicator electrode for the titration of 25 mL of 1x10^{-4} M La(III) ions against 1x10^{-3} M EDTA. The pH of the solution was adjusted to 7-8 using dilute ammonia solution. The titration curve is shown in Figure 4.4(a). The curve shows a sharp inflexion point at the titrant volume corresponding to the formation of an 1:1 complex of lanthanum ions with EDTA.

Table 4.1(a): Optimization of membrane ingredients in La(III)-selective electrode

No.	PVC, Wt%	Plasticizer, (Wt%)	DC18C6, (Wt%)	KTpClB, Wt%	Slope, mV/ decade	Linear range, (M)	Detection limit, (M)
1	33	67 (NPOE)	--	--	5.0	1x10^{-4}-1x10^{-1}	5x10^{-3}
2	33	65 (NPOE)	--	2	8.0	1x10^{-4}-1x10^{-1}	5x10^{-3}
3	33	65 (NPOE)	2	--	10.0	1x10^{-4}-1x10^{-1}	1x10^{-3}
4	33	64 (NPOE)	3	--	12.0	1x10^{-4}-1x10^{-1}	1x10^{-3}
5	33	63 (NPOE)	4	--	15.0	1x10^{-4}-1x10^{-1}	1x10^{-4}

6	33	62 (NPOE)	5	--	17.0	1x10^{-5}- 1x10^{-1}	3x10^{-5}
7	**33**	**61 (NPOE)**	**6**	**--**	**19.0**	**1x10^{-6}- 1x10^{-1}**	**1x10^{-6}**
8	33	60 (NPOE)	7	--	18.5	1x10^{-6}- 1x10^{-1}	1x10^{-5}
9	33	59 (NPOE)	8	--	14.0	1x10^{-6}- 1x10^{-1}	1x10^{-5}
10	33	61(DBP)	6	--	17.0	1x10^{-6}- 1x10^{-1}	1x10^{-5}
11	33	61(2-BES)	6	--	14.0	1x10^{-4}- 1x10^{-1}	1x10^{-3}
12	33	58 (NPOE)	6	2	18.0	1x10^{-6}- 1x10^{-1}	1x10^{-6}
13	33	57 (NPOE)	6	3	18.0	1x10^{-6}- 1x10^{-1}	1x10^{-6}

Table 4.2 (a): Effect of internal solution concentration on the membrane electrode

Electrode Composition	Internal solution concentration, M	Slope (mV/decade)	Detection limit, M
Electrode No. 7	1x10^{-1}	16	6.3x10^{-6}
	1x10^{-2}	17	1.0x10^{-6}
	1x10^{-3}	19	1.0x10^{-6}
	1x10^{-4}	19	1.0x10^{-6}

Table 4.3(a): Selectivity co-efficient values of La(III)-selective electrode by fixed interference method and matched potential method

Interfering ions (B)	$\log K^{Pot}_{La^{3+},M^{n+}}$		**Interfering ions (B)**	$\log K^{Pot}_{La^{3+},M^{n+}}$	
	FIM	**MPM**		**FIM**	**MPM**
Ce^{3+}	**-1.6**	-1.9	Fe^{3+}	**-2.3**	**-2.7**
Nd^{3+}	**-1.5**	-1.8	Mg^{2+}	**-2.5**	**-2.8**
Sm^{3+}	**-1.6**	-1.8	Ca^{2+}	**-2.3**	**-2.7**
Eu^{3+}	**-1.5**	-1.9	Cu^{2+}	**-2.3**	**-2.5**
Pr^{3+}	**-1.6**	-1.7	Pb^{2+}	**-2.0**	**-2.7**
Tb^{3+}	**-1.7**	-1.9	Hg^{2+}	**-2.6**	**-2.8**
Dy^{3+}	**-1.7**	-1.8	K^{+}	**-1.9**	**-2.5**
Yb^{3+}	**-1.8**	-1.9	Ag^{+}	**-2.3**	**-2.8**

Experimental conditions for matched potential method: Primary ion lanthanum nitrate solution ($1x10^{-7}$ to $1x10^{-1}$M), Reference solutions lanthanum nitrate of $1x10^{-5}$M and interfering ion concentrations ($1x10^{-5}$ to 10^{-2} M)

Table 4.4(a): Comparison of various La(III)-selective electrodes with the proposed electrode

Sl No	Type of the ionophore	Slope, mV/ decade	Measuring range (M)	pH range	Lifetime (months)
1	M.R. Ganjali et al. (19)	Nernstian	10^{-6} -10^{-1}	4 -8	-
2	V.K. Gupta et al. (20)	20.5	$10^{\bullet 5}$ -$10^{\bullet 1}$	3-7	5
3	M. Shamsipur (21)	Nernstian	10^{-6} - 10^{-2}	5-8	5
4	M.R. Ganjali et al. (22)	19.8	$10^{\bullet 7}$ -$10^{\bullet 1}$	3-10	2
5	M. Akhond, et al. (23)	20.1	$10^{\bullet 6}$ -$10^{\bullet 2}$	3.3-8	2
6	M.R. Ganjali et al.(24)	20.1	$10^{\bullet 1}$ -$10^{\bullet 6}$	4-8	-
7	M. Shamsipur et al.(25)	19.4	10^{-6} -10^{-2}	4 - 8	3

Table 4.5 (a): Effect of mixed solvent medium on the working of La (III) electrode

Solvent Mixture	Contents % v/v	Slope, mV/decade	Working range, $1\text{x}10^{-1}$ (**M) to**
Methanol	0:100	19	$1.0\text{x}10^{-6}$
	10:90	18	$3.16\text{x}10^{-6}$
	20:80	18	$3.16\text{x}10^{-6}$
	30:70	17	$5.0\text{x}10^{-6}$
Ethanol	0:100	19	$1.0\text{x}10^{-6}$
	10:90	18	$1.99\text{x}10^{-6}$
	20:80	18	$1.99\text{x}10^{-6}$
	30:70	17	$4.3\text{x}10^{-6}$
Acetone	0:100	19	$1.0\text{x}10^{-6}$
	10:90	19	$1.0\text{x}10^{-6}$
	20:80	19	$5.0\text{x}10^{-7}$
	30:70	19	$2.3\text{x}10^{-6}$

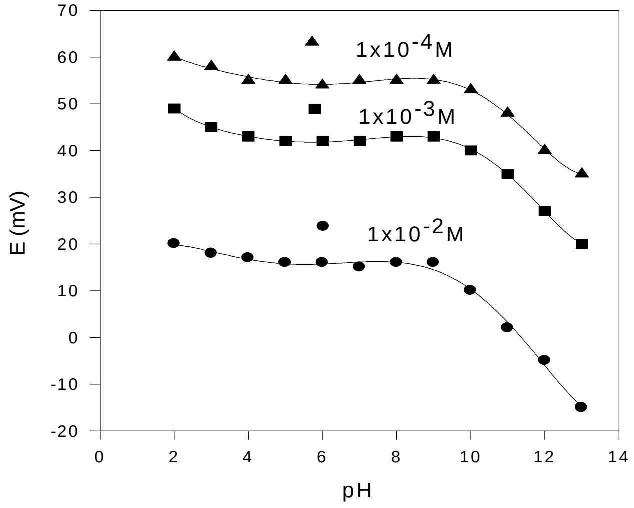

Figure 4.1(a): Effect of pH on the response of La(III) ion-selective electrode at different La(III) ion concentrations.

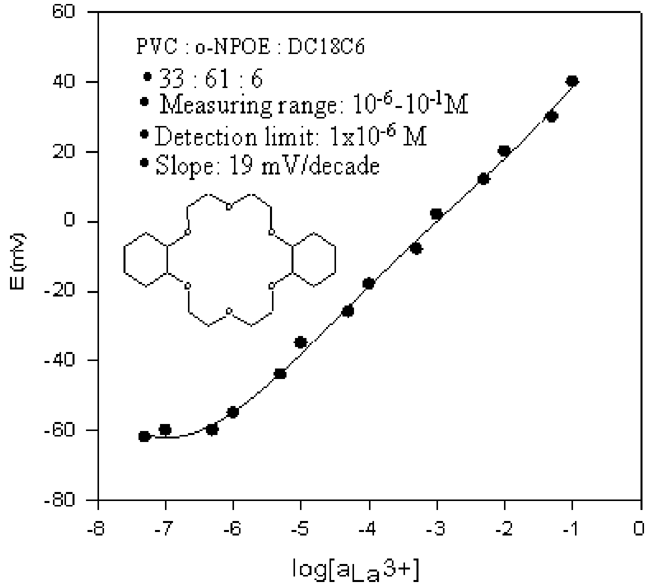

Figure 4.2 (a): Calibration curve for the La(III) ion-selective electrode

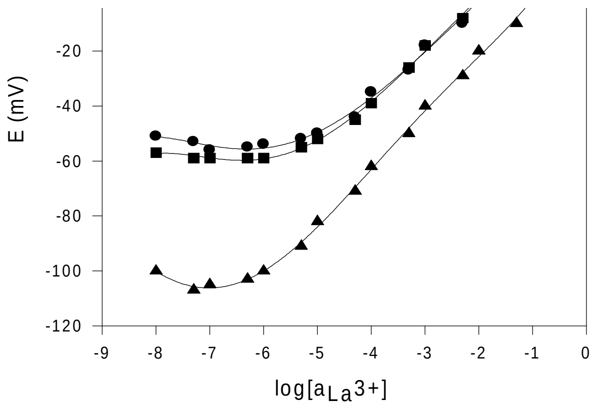

Figure 4.3(a): Effect of mixed solvent medium on EMF of the electrode

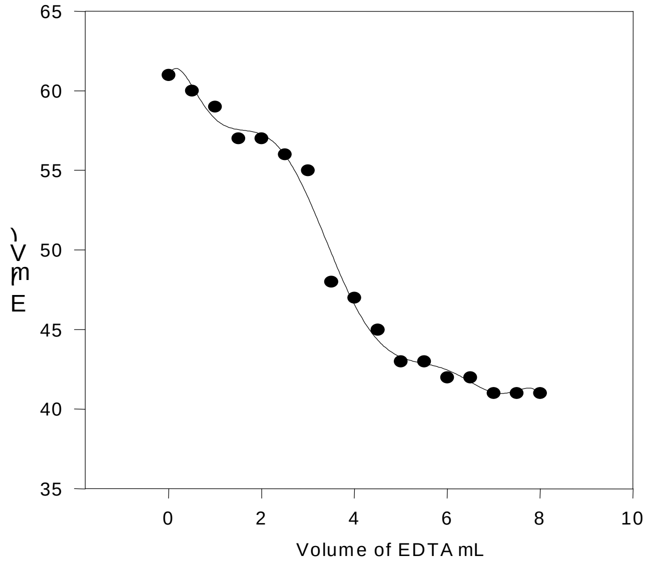

Figure 4.4(a): Titration curve of La(III) solution with EDTA solution using La(III)-selective electrode

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(4b) PVC-based Dibenzo-24-Crown-8 Sensor for Ce(III) Ions

Introduction

The advantages of ion-selective electrodes (ISE) over many other methods (1-9) for cation and anion detection are their easy handling, non-destructive analysis and inexpensive sample preparation. The function of a crown ether as an electro-active material for ion-selective electrodes is based on such diverse parameters as the structure and cavity size of the ligand, the stability and selectivity of its metal ion complex, its solubility and the ability to extract the metal ion into the membrane phase.

Cerium is a member of the lanthanum group of elements and the most abundant of them. It is found in monazite, ceric bastnaesite and silicate rocks. It is widely used in production of ductile iron, cast iron and some stainless steels (10). The use of cerium is still growing due to the fact that it is suited to produce catalysts and to polish glasses.

Cerium is mostly dangerous in the working environment due to the fact that damps and gases can be inhaled with air. This can cause lung embolisms, especially during long-term exposure. Cerium can be a threat to liver when it accumulates in body. It is noteworthy that despite the urgent need for a cerium (III) sensor for the potentiometric monitoring of cerium in many industrial, geological and chemical samples (11,12), there are only a few reports (13-15) of cerium (III)-selective electrodes in literature.

Lanthanides are expected to form stable complexes with various macrocyclic ligands, similar to alkali and alkaline earth metals, because of the similarity of radii between lanthanides and Na^+ or Ca^{2+} ions. In fact, it was mentioned in the first report on crown ethers by Pedersen (1967) (16) that some crown ethers formed complexes with La(III) and Ce(III) in solution. However, attention has been focused, mainly on complexes of alkali and alkaline earth metal ions.

In this chapter, we report the determination of Ce(III) ions based on dibenzo-24-crown-8 (DB24C8) as a neutral carrier to construct a PVC-based membrane electrode.

Experimental

Reagents

Reagents, like dibenzo-24-crown-8 (DB24C8) and 2-nitro phenyl octyl ether (2-NPOE), were procured from Sigma-Aldrich. Cerium chloride and other rare earth chlorides were purchased from Indian Rare Earth Chemicals Ltd., India. Since all the chemicals were of analytical grade, these were used as such.

All stock solutions of rare earth metal ions were standardized with EDTA using xylenol orange as an indicator. Double distilled deionized water was used throughout the experiments.

Instruments Used

ISFET 701 pocket pH meter (Delta TRAK, INC., USA Model 24003) was used to measure pH of the solutions. Emf measurements were made using a digital potentiometer (Equiptronics EQ-602, Mumbai, India) with an accuracy of ±0.1 mV.

Preparation of PVC-membrane

A homogenized mixture of about 1 g with components: PVC, 33%; DB24C8, 4.5%; 2-NPOE, 62.5% was dissolved in 2-3 mL of THF at room temperature. The viscous solution, thus obtained was poured in a glass ring of 30 mm diameter placed on a dust free Pyrex glass plate (17). The solvent was allowed to evaporate slowly for about 24 hours at room temperature. To obtain membranes with similar characteristics, viscosity of the casting solution and the rate of solvent evaporation were controlled so that the thickness and morphology of membranes remain almost unchanged. The prepared membranes were removed from the glass plate and circular pieces of 2.0 cm diameter were cut.

EMF Measurements

Membranes were fixed to one end of the glass tube of 1.8 cm (internal diameter) using an epoxy resin as adhesive. These were then equilibrated with a Ce^{3+} solution (0.1 M) for 12 hours. The tube was filled 1/4th with cerium (III) chloride solution (0.1 M) and immersed in a beaker containing the test solution of varying concentration of Ce^{3+} keeping the level of inner filling solution higher than the level of the test solution to avoid any reverse diffusion of the electrolyte. All the emf measurements were carried out using the following cell assembly:

$$\textbf{SCE} \mid \textbf{Ce}^{3+}\ \textbf{(0.1 M)} \parallel \textbf{Membrane} \parallel \textbf{Ce}^{3+}\ \textbf{(test solution)} \mid \textbf{SCE}$$

Potentiometric measurements were made using a digital potentiometer (Equiptronics EQ-602, India), at 25±0.1 ºC. Activities were calculated according to Debye-Huckel equation (18). Test solutions were obtained by gradual dilution of the stock solution. Potential measurements were made in unbuffered solutions to avoid interference from any foreign ion.

Storage of Electrodes

DB24C8-based electrodes were stored in distilled water when not in use for more than one day. These were activated with Ce(III) solution (0.1 M) by keeping immersed in the solution for two hours, before use, to compensate for any loss of metal ions in the membrane phase that might have taken place due to a long storage in distilled water. Electrodes were then washed thoroughly with distilled water before use.

Result and Discussion

Ion-selective electrodes work on the principle of measurements at zero current. The membranes are fixed in the electrode assembly and all measurements are made in a concentration cell. Concentration of the electrolyte on the inner side of the membrane is fixed at 0.1 M of Ce(III) ions while on the other side of the membrane it varies from 10^{-8} M to 10^{-1} M. The potential difference can be measured between two identical reference electrodes placed in the two phases. No ionic strength adjustment buffer was used to avoid any unwanted foreign ions from the buffer. Moreover, the ionic strength does not change much during the study as experiments are done in dilute solutions only in the major part of the measuring range of the electrode (i.e., 10^{-6} M -10^{-1} M).

Optimization of Membrane Ingredients

The effect of membrane composition on the response of the electrode was investigated. For this purpose, performance characteristics, like slope of the calibration curve, measurement range and detection limit, were studied. The results are shown in Table 4.1(b). It is evident from this table that the electrode 6 with the ratio PVC:2-NPOE: DB24C8 as 33%:62.5%:4.5%, shows the best performance with a near-Nernstian slope of 19.0 mV per decade. This electrode is used for the subsequent studies.

Calibration Curve

Experiments were conducted a number of times to check the reproducibility of the results. EMFs were plotted against log of activities of cerium ions and calibration curves were drawn for five sets of experiments. A standard deviation of ±0.9 mV was observed. A representative calibration curve using the electrode 6 is shown in Figure 4.1(b). The limit of detection ($3x10^{-5}$ M) was calculated according to IUPAC recommendations from the intersection of the two extrapolated linear portions of the curve (19, 20).

The electrode response was quite reproducible over the lifetime of the electrode. The sensing behavior of the membrane remains unchanged when potentials are measured from low to high or high to low concentrations. The electrode could be used for at least four months without any significant divergence. The electrode was kept in water, when not in use, and was equilibrated with 0.1 M Ce^{3+} solution for 2 hours before use.

Influence of the Concentration of Internal Solution

Electrode responses were measured by changing the internal filling solution from $1x10^{-1}$ M to $1x10^{-3}$ M, Figure 4.2(b). It was found that the variation in the concentration of the internal solution does not cause any significant difference in the potential response, except for an expected change in the intercept of the resulting curve. The concentration of the internal solution as $1x10^{-1}$ M is quite appropriate for the functioning of the electrode system.

pH dependence of the Electrode

It is very important to find out the pH range where the electrode can work without interference from hydrogen ions present in aqueous solutions. The pH dependence of the sensor was tested by using 1.0 x

10^{-2} M and 1.0 x 10^{-3} M Ce^{3+} solutions over a pH range of 2.0 to 11.0, Figure 4.3(b). The pH was adjusted by the addition of small drops of hydrochloric acid (0.1 M) or sodium hydroxide (0.1 M), as required. It is clear from the Fig. that the emf remains constant from pH 4.0 to 8.0 and 3.5 to 7.5 for $1x10^{-2}$ M and $1x10^{-3}$ M Ce^{3+} ion concentrations, respectively. Beyond this pH, a drift in emf is observed which may be due to the formation of hydroxy complexes of Ce^{3+} at higher pH and due to protonation of oxygen atoms of DB24C8 at lower pH.

Effect of Mixed Solvent Media

Functioning of the electrode was also investigated in mixed solvent media using methanol-water, acetone-water and DMSO-water mixtures. It was found that the assembly works well up to 20% non-aqueous content without showing any appreciable change in the working concentration range or slope, Figure 4.4(b). In acetone medium, a significant change in emf, slope, measuring range and detection limit is observed. This may be due to the dynamic complex formation and decomplexation between DB24C8 and Ce (III) in the water-acetone mixture.

Potentiometric Selectivity

One of the most important characteristics of a membrane sensor is its response for the primary ion in presence of other ions, which is measured in terms of the potentiometric selectivity coefficient $(K_{A,B}^{Pot})$. The fixed interference method (FIM) at the interfering ion concentration $1x10^{-3}$ M is adopted in the present case to determine the selectivity coefficient data. According to this method, a calibration curve is drawn for the varying primary ion concentration in a constant background of the interfering ion. The linear (i.e., Nernstian) response curve of the electrode is a function of the primary ion activity and is extrapolated until at the lower detection limit, it intersects with the observed potential for the background alone. The selectivity coefficient is calculated from these two extrapolated linear segments of the calibration curve. Following expression (4.1) is used for this purpose:

$$K_{A,B}^{Pot} = \frac{a_A}{(a_B)^{z_A/z_B}} \tag{4.1}$$

Here, a_A is the activity of the primary ion and a_B the activity of the interfering ion. z_A and z_B are their respective charges.

The resulting log $(K_{A,B}^{Pot})$ values for the proposed Ce(III)-selective electrode are summarized in Table 4.2 (b). Selectivity coefficients for the previously reported cerium-selective electrodes (4-7) are also included in Table 4.2(b). It can be seen from that, the electrode has a reasonably good selectivity for Ce^{3+} ions in the presence of other rare earth metal ions, some alkali, alkaline earth and transition metal ions, which are present with cerium (III) in its ores. The selectivity is good in the sense that all the rare earth metal ions have identical sizes and properties. Moreover, a comparison between the selectivity coefficients of the proposed electrode with those previously reported for the cerium (III) reveals that the proposed electrode shows almost comparable selectivity, in some cases, to foreign ions.

Potentiometric Titration

The analytical applicability of the sensor was tested by using it as an indicator electrode in the potentiometric titration of Ce^{3+} ion solution. 50.0 mL of Ce^{3+} solution ($1x10^{-3}$ M) was titrated against oxalic acid solution ($1x10^{-2}$ M). The curve is not a standard sigmoid shaped Figure 4.5(b). However, a very good inflection point corresponding to Ce-oxalate stoichiometry is observed which shows that this sensor can be used for the determination of Ce^{3+} ions potentiometrically.

Lifetime of Electrode

The proposed sensor can be used for at least four months without any significant divergence in results.

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Table 4.1(b): Optimization of membrane ingredients in Ce(III)-selective electrode

Sl. No.	PVC Wt%	Plasticizer Wt%	Ionophore Wt%	Slope mV/decade	Working range, M	Detection Limit, M
1	33	67	0	10	$1x10^{-4}$-$1x10^{-1}$	$8x10^{-4}$
2	33	66	1	17	$1x10^{-4}$-$1x10^{-1}$	$3x10^{-4}$
3	33	65	2	20	$1x10^{-4}$-$1x10^{-1}$	$2x10^{-4}$
4	33	64	3	20	$1x10^{-4}$ $1x10^{-1}$	$8x10^{-5}$
5	**33**	**63**	**4**	**20**	**$1x10^{-4}$-$1x10^{-1}$**	**$5x10^{-5}$**
6	33	62.5	4.5	21	$1x10^{-4}$-$1x10^{-1}$	$3x10^{-5}$
7	33	62	5	39	$5x10^{-4}$-$1x10^{-1}$	$5x10^{-5}$
8	33	61	6	34	$5x10^{-4}$-$1x10^{-1}$	$5x10^{-5}$

9	33	63	7	35	5×10^{-4}- 1×10^{-1}	5×10^{-5}
10	33	63	8	36	5×10^{-4}- 1×10^{-1}	8×10^{-5}

Table 4.2 (b): Selectivity coefficient values for Ce(III)-selective electrode by fixed interference method

Interfering ion (B)	**Selectivity Coefficient values log $(K^{Pot}_{A,B})$**				
	Present study	**Previous reports**			
		[4]	**[5]**	**[6]**	**[7]**
Nd^{3+}	-0.4	-	-	-	-
Sm^{3+}	-0.6	-	-	-	-
Eu^{3+}	-0.6	-	-	-	-
Pr^{3+}	-0.7	-	-	-	-
Tb^{3+}	-0.8	-	-	-	-
Dy^{3+}	-0.7	-	-	-	-
Yb^{3+}	-1.2	-	-	-	-
La^{3+}	-0.3	-1.3	-2.4	-1.4	-2.5
Fe^{3+}	-0.3	-	-	-	-
Mg^{2+}	-0.4	-2.5	-	-2.4	-6.0
Ca^{2+}	-0.6	-1.6	-	-2.3	-6.0
Cu^{2+}	-0.6	-1.4	-4.2	-2.3	-2.4
Pb^{2+}	-0.7	-1.9	-2.0	-2.3	-2.6
Hg^{2+}	-0.8	-4.0	-4.1	-2.3	-2.7
K^{+}	-0.7	-	-	-	-
Ag^{+}	-1.2	-1.5	-3.9	-4.0	-2.8

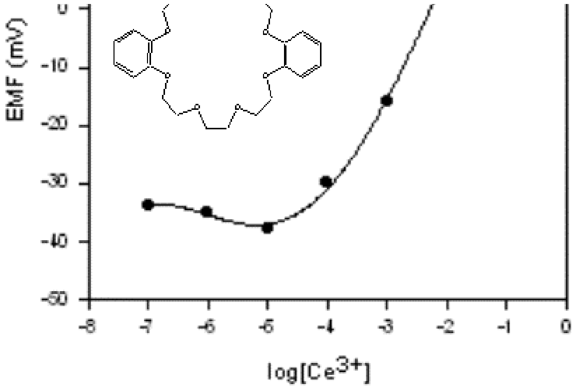

Figure 4.1(b): Calibration curve for Ce(III) ion selective electrode

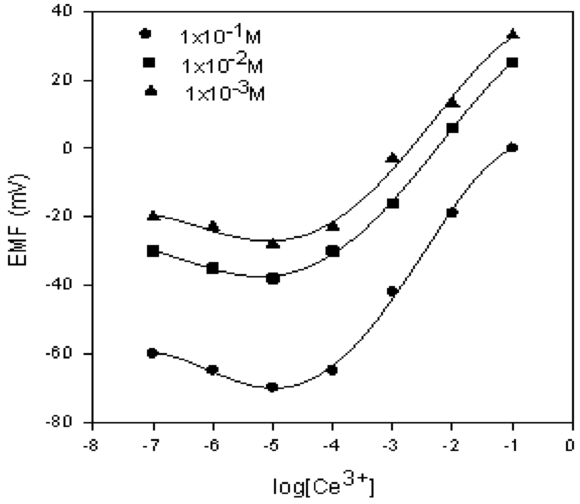

Figure 4.2(b): Effect of internal solution on potential response of the Ce(III)-selective electrode

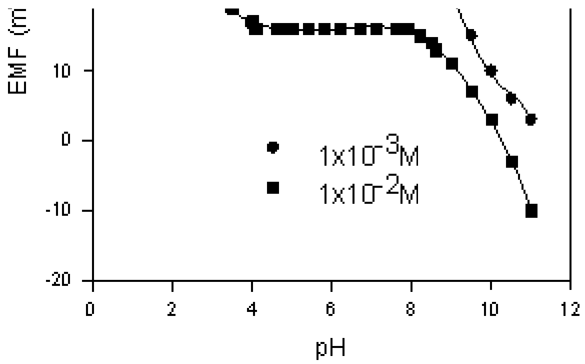

Figure 4.3(b): Effect of pH on the response of Ce(III)-selective electrode

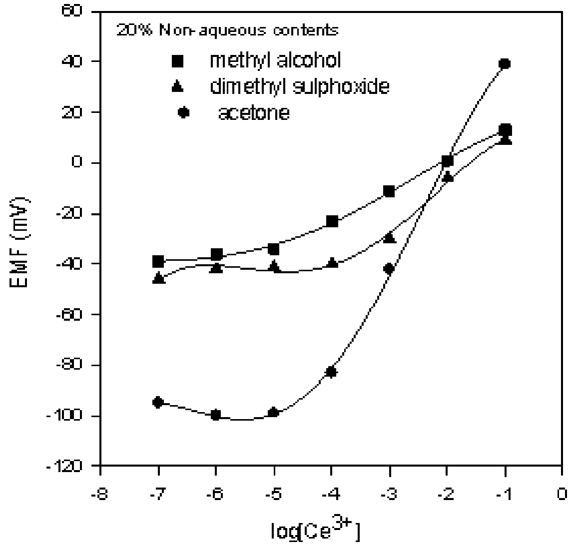

Figure 4.4(b): Effect of mixed solvent medium on EMF of the electrode.

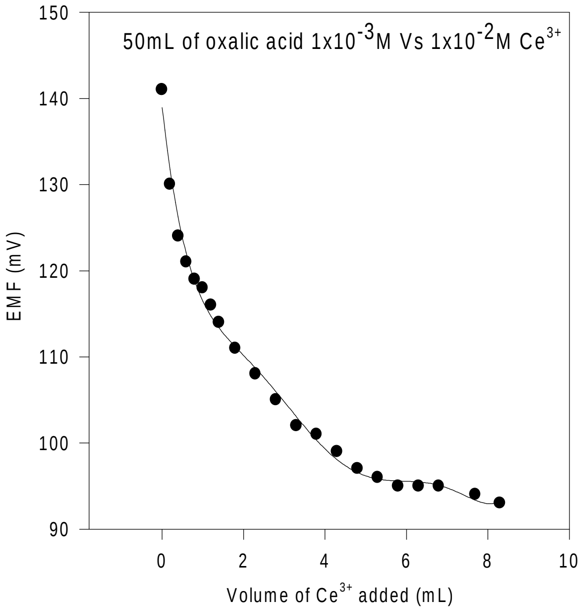

Figure 4.5(b): Titration curve of Ce(III) solutions with oxalic acid solution using Ce (III)-selective electrode

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(4c) PVC-based Dibenzo-18-Crown-6 Electrode for Ca(II) Ions

Introduction

Since the investigations relating to ionophore-based ISEs in 1970s, an increasing number of papers are being published because of the simple operation and good selectivity characteristics. Ca^{2+}-sensitive electrodes were among the first commercially available ISEs (1-4). Clinical situations in which the in-vivo monitoring of Ca^{2+} are of interest include, for example, organo-transplantations, heme-dialysis or exchange transfusion, during which rapid changes in the concentration of the ionized calcium may occur. Such applications have made Ca^{2+} ions one of the analyst's top interests in ion-selective potentiometry. Important industrial applications are: Ca^{2+}-ion measurements in boiler water, soils and fertilizers.

Electrically neutral lipophilic ligands containing an appropriate number of binding sites of high solvating ability can behave as ionophores for alkali and alkaline earth cations. The macrocyclic polyethers have cavities that can take up alkali and alkaline earth cations (5-6). Complexation occurs between cation and the ethereal oxygen of the crown ether, and the resulting complexes are highly stable and selective. These lipophilic ethers when incorporated into membranes behave as ionophore-based ion-selective electrodes for alkali and alkaline earth cations. Very few studies are available in literature on the old crown ethers that were used as ion-selective electrodes. Gahan and co-workers have investigated the interaction of monoaza-polyoxa-crown ethers with Pb^{2+}, Hg^{2+}, Cd^{2+} and Zn^{2+} by potentiometry (7-9). Nakamura and Rechnitz prepared a Ba^{2+}-selective electrode using dibenzo-18-crown-6 as the neutral carrier. But this electrode had very poor selectivity and suffered from interferences from Na^+, K^+, Mg^{2+} and Ca^{2+}. Dibenzo-10-crown-4 has been used for a Li^+-selective electrode (10). Benzo-18-crown–6 has been reported as a neutral carrier in K^+-selective electrodes (11).

Reviews on macrocyclic ethers (12-14) provide a good comprehensive survey of the literature. It shows that DB18C6 has not been used as an ionophore in making a Ca^{2+}-selective electrode

Experimental

Reagents

Reagents, like dibenzo-18-crown-6 (DB18C6), dibutyl pthalate (DBP), bis-2-ethyl sebacate (2-BES) were procured from Sigma-Aldrich. All other chemicals were of analytical reagent grade. Double distilled deionized water was used throughout the experiments.

Electrode Preparation

120 mg of powdered PVC, 10 mg of plasticizer, 10 mg of DB18C6 were mixed thoroughly and dissolved in about 5 mL of THF. The mixture was put in a glass ring of 30 mm diameter. The solvent

was allowed to evaporate slowly at room temperature. The resulting membrane was attached to a glass tube (4 mm, i.d.) with an epoxy resin adhesive (Araldite) used as a binder. The membrane was conditioned for 72 hours in a 0.1 M solution of Ca^{2+} ions.

EMF Measurements

All emf measurements were carried out with the following cell assembly:

$$\textbf{SCE} \,|\, \textbf{0.1 M Ca}^{2+} \,||\, \textbf{membrane} \,||\, \textbf{test solution} \,|\, \textbf{SCE}$$

Equiptronics(India) potentiometer (±0.1mv) was used for the potential measurements at 27±0.1 ^{0}C.

pH Adjustment

pH of the test solution was adjusted by using 0.1 N HCl or 0.1 N NaOH, as per requirement, added in small increments to make the desired pH. Buffer solutions were not used to avoid the unnecessary increase in ionic strength and the presence of metal ions from buffer.

Selectivity Coefficient Measurements

Selectivity coefficients for seventeen metal ions were determined by the fixed interference method (FIM) (15-16). Appropriate volumes of a fixed concentration of the interfering ion (10^{-2} M) were added to all the solutions of the primary ion and plotted calibration curves. Extrapolated calibration curves were used to find the detection limits, which were further applied in Nikolski-Eisenmann equation (17) to find the $K_{A,B}$ values.

$$K_{A,B} = \frac{a_A}{a_B^{z_A/z_B}} \qquad (4.2)$$

Here, a_A is the activity of the primary ion A and a_B is the activity of the interfering ion, B.

Results and Discussion

DB18C6 is a coplanar, symmetrical, polyether with a strong charged cavity (18) with a diameter of 4 Å and can accommodate only the nonsolvated metal cation. If calcium is being solvated in aqueous medium, the diameter (7 Å) is too large to be accommodated in the cavity. A high charge on the oxygen atoms of DB18C6 makes the oxygen atoms as hard donors. Calcium ions are also hard acids. So, there is a reasonably good interaction (ion-dipole) (19-22) between six oxygen atoms and the Ca^{2+} ion. This much of interaction is sufficient to make the complex of metal ion with the crown ether. The complexation is not in the cavity but a little above or below the cavity. Moreover, for a complex to be electroactive in an ion-selective membrane, it is essential for the complexing species to have reasonable flexibility for decomplexation as well. This property is very much required for the application of crown ether as an ion-selective electrode. The process of complexation of calcium ion with DB18C6 is supported by the work of Kim et al. (19), who determined K_{ML} values for DB18C6 with alkaline earth metal ions and found the values to be in the order $Ca^{2+} < Sr^{2+} < Ba^{2+}$ in any solvent. These results indicate that DB18C6 does form the complex with the Ca^{2+} ions.

Selection of Plasticizer

Commonly used plasticisers are dibutyl pthalate (DBP) and bis-2-ethyl sebacate (BES). All of these were used in preparation of the membranes. Results with BES were very poor, so these are not reported. DBP was used in membranes for detailed studies.

Membrane Composition

The recommended composition (23) (by weight ratio) is ionophore:PVC:plasticiser as 1:12:1.

Calibration Curves for the Electrode

A PVC-based membrane containing DB18C6 was equilibrated with 0.1 M calcium salt ($Ca(NO_3)_2{:}4H_2O$) solutions for 3 days so as to completely saturate the cavities in the crown ether with calcium ions. These calcium ions forming a reversible complex with DB18C6 develop a potential with the calcium ion solution on the other side of the membrane. The potentiometric response of the electrode was studied over a concentration range from $1x10^{-7}$ M to $1x10^{-1}$ M of Ca^{2+} ions. The ISE exhibits a linear response for Ca^{2+} ions in the concentration range from $1x10^{-5}$ M to $1x10^{-1}$ M with a Nernstian slope of 28.0 mV/decade shown in Figure 4.1(c). At concentrations lower than this, the response deviates from the linear behaviour. Experiments were repeated 5 times to check the reproducibility of the electrode system. Standard deviation of the calibration is observed as ±0.5 mV.

Effect of pH

The effect of pH on the response of the sensor was studied over two different concentrations ($1x10^{-3}$M and $1x10^{-4}$ M) of Ca^{2+}ions. Studies were carried out over a pH range of 1-12. Introducing HCl or NaOH drop wise adjusted the pH, and the results are shown in Figure 4.2(c). The potential difference is independent of pH in the range 3 to 11. Therefore, this can be taken as the working pH range for the proposed electrode system. Since at pH value lower than 4, a decrease in potential is observed, probably the electrode starts responding to H^+ ions. At pH greater than 12, the deviation can be assigned to the formation of $Ca(OH)_2$ precipitates.

Interference Studies

Selectivity coefficients for the membrane electrode were measured by the fixed interference ion method (FIM) with a fixed concentration of the interfering ion ($1x10^{-2}$ M, $1x10^{-3}$ M and $1x10^{-4}$ M) and varying the amounts of primary ions (Ca^{2+}). The emf values are plotted against the logarithm of the primary ion activity. Calcium ion concentrations corresponding to the intersection of the extrapolated linear portions of the plots are used to calculate $K_{A,B}^{Pot}$ from the equation (4.2). $K_{A,B}^{Pot}$ values indicate that the electrode is quite selective for Ca^{2+} ions in the presence of a large number of interfering ions particularly, Al^{3+}, Fe^{3+}, Ni^{2+} and Cu^{2+}. The electrode shows a better selectivity at the fixed interfering ion concentration of 10^{-2} M. It is observed from the Table 4.1(c) that the degree of selectivity decreases with a decrease in concentration of the interfering ion. The electrode is highly useful for Ca^{2+} ion determination when the interfering ions are present in an approximate concentration of 10^{-2} M.

Potentiometric Titration

Potentiometric titrations were performed by using the proposed electrode as an indicator electrode for the titration of 25 mL of $1x10^{-2}$ M Ca^{2+} ions against $1x10^{-1}$ M EDTA. The pH of the solution was adjusted to 9-10 by using an appropriate volume of ammonium chloride and ammonia buffer. The titration curve is shown in Figure 4.3(c). The curve shows a sharp inflexion point at the titrant volume corresponding to the formation of an 1:1 complex of calcium ions with EDTA.

Table 4.1(c): Selectivity coefficients values for Ca(II)-selective electrode by fixed interference method

Interfering ions (B)	**log $K_{Ca,B}^{Pot}$**					
Reference	**24**	**25**	**26**	**27**	**28**	**This work**
Method	**SSM**	**SSM**	**FIM**	**FIM**	**FIM**	**FIM**
Li^+	-0.3	-1.3	-1.7		-0.8	-0.4
Na^+	+0.5	-0.8	-1.1	-1.2	-0.2	-0.2
K^+	+1.4	+0.2	+0.6	-2.1	-0.2	-0.1
Mg^{2+}	-	-0.4	-0.5	-1.5	-1.3	-0.4
Sr^{2+}	-	+0.1	+0.2	-	-0.8	-0.2
Ba^{2+}	-	+0.4	+0.5	-	-1.0	-0.2
Pb^{2+}	-	-	-	-	-	-0.4
Ag^+	-	-	-	-	-	-0.1
Co^{2+}	-	-	-	-	-	-0.6
Ni^{2+}	-	-	-	-	-	-1.5
Zn^{2+}	-	-	-	-	-	-0.4
Cd^{2+}	-	-	-	-	-	-0.1
Hg^{2+}	-	-	-	-	-	-1.8
Al^{3+}	-	-	-	-	-	-1.9
Fe^{3+}	-	-	-	-	-	-1.6
Rb^+	+1.9	+0.7	-0.4	-	-	-
H^+	+2.1	-	-	-	-	-
Cs^+	+2.0	+1.4	-0.2	-	-	-

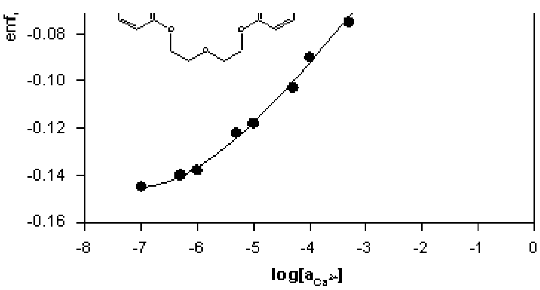

Figure 4.1(c): Calibration curve for Ca(II) ion-selective electrode

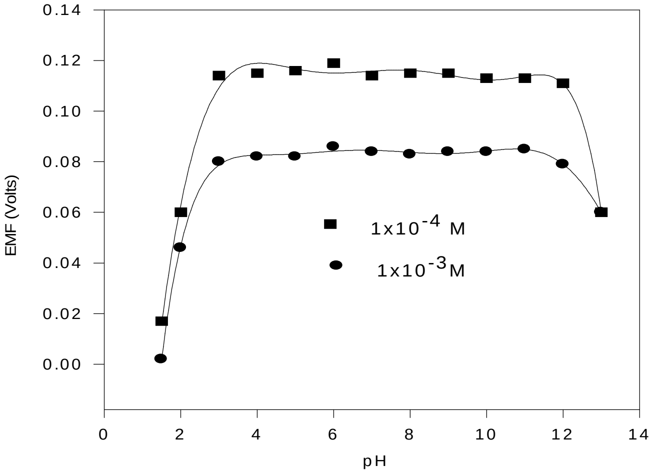

Figure 4.2(c): Effect of pH on the response of Ca(II)-selective electrode

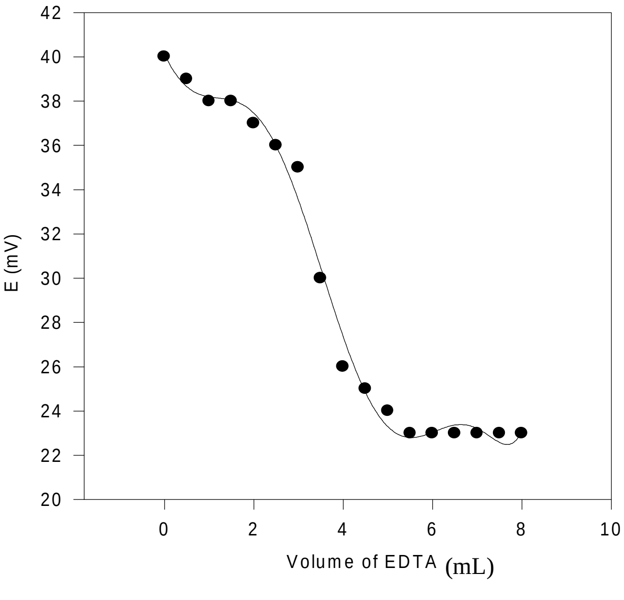

Figure 4.3(c): Titration curve of Ca(II) solution with EDTA solution using Ca(II)-selective electrode

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Chapter -5

ACYCLIC PODANDS AS SENSING MATERIALS

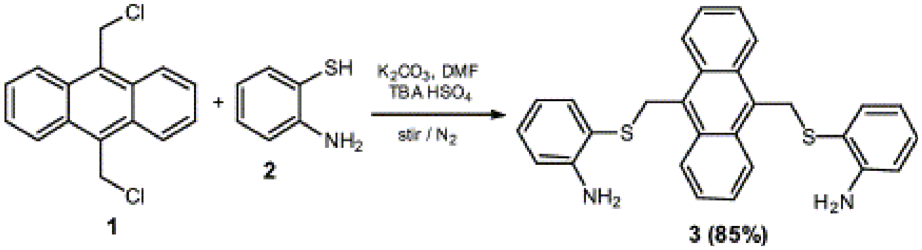
5(a) Potentiometric Performance of 2-Aminothiophenol-based Dipodal Ionophore as a Silver Sensing Material

Introduction

One of the greatest applications of neutral carriers in analytical chemistry is their use for separations, enrichment and analyses of ionic species (1-3). In particular, ion-selective electrodes are the most important analytical tools for detection of the target ions. Concentrations of certain ionic species can be determined selectively in solutions containing various species by ion-selective electrode methods. Ion-selective electrodes are simple, handy and inexpensive as compared with other analytical instruments. Neutral carrier type ion-selective electrodes have been extensively studied and neutral ionophores like thiacrown ethers (4, 5), acyclic dithioethers (6) and calixarenes-containing sulfur binding sites (7, 8), podand-type (9), dithiocarbamoyl moieties on steroid backbones (10) are being used as active components in electrode membranes (11-18).

9,10,Bis-(2-aminophenylthiomethyl)anthracene was chosen as a ligand in the membrane electrode. It was designed to exhibit complexation properties with Ag^+ and Cu^{2+} ions and synthesized by our co-workers (19). This property of the ionophore made it suitable for making a chemical sensor for Ag^+ and Cu^{2+} ions. However, the present report deals with its characteristics as a Ag(I)-selective ionophore.

In molecules, like rusticyanin having two N and two S bonding sites, aromatic rings provide an additional stability. With these structural features in mind, an acyclic fluroionophore-3) having 2-aminothiophenol units as ligating sites placed on 9,10-bis (methylene) anthracene was synthesized. Here, the anthrancene moiety is a part of the main skeleton of the ionophore, and is placed perpendicular to the ligating site. So, the anthrancene unit would face the cavity of the ionophore and is expected to provide a much-needed hydrophobic environment and high complex stability. The possible cation-π interactions in the cavity provide sensitivity towards the metal ions:



Preliminary studies (19) show that the ionophore is fluoresence active and show fluorescence quenching with Cu^{2+} and Ag^+ ions only in the presence of 500 mM of these metal ions. Other metal ions, like Ni^{2+}, Cd^{2+}, Zn^{2+}, Hg^{2+}, Pb^{2+}, alkali and alkaline earth metal ions do not affect the fluorescence of (3). Therefore, (see above figure, 3) shows selective fluorescence quenching with Cu^{2+} and Ag^+ and may be used for their quantitative estimation.

Moreover, the equilibrium constant of complex (3)-Ag^+ gives logK = 3.7±0.1, while the values for other metal ions are very less (19). The ionophore (3) was studied by UV-visible spectroscopy to see the effect of other transition metal ions and to understand the role of π-cation interactions. A 20 μM amount of cations, like Ni^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+} do not affect the absorption spectrum of the ionophore taken at the same concentration (20 μM).

Sensitive qualitative assessment of binding strengths in a metal-ionophore complex is necessary for useful comparisons of binding ligands. A chemosensor is a molecular device that senses and reports its binding towards the molecular target. The chemosensor device that we describe here is containing a binding pocket comprised of two 2-aminothiophenol arms attached to 9, 10 positions of the anthrancene core which changes its configuration upon analyte binding. Complexation occurs between the cations and nitrogen atoms and sulphur atoms of thioether of the ligand, and the resulting complexes are highly stable and selective for silver ions. These lipophilic ligands, when incorporated into membranes, behave as neutral carrier membranes.

Recent reviews on ionophore-based chemical sensors and research papers (20-32) provide an intensive survey of literature. It shows that 9,10,bis-(2-aminophenylthio)methylene anthracene has not been used as an ionophore in making Ag^+-selective electrodes.

Experimental

Reagents

Reagents, like dibutyl pthalate (DBP), 2-nitrophenyloctyl ether (2-NPOE), bis-2-ethyl sebacate (BES) and potassium salt of tetrachlorophenyl borate (KTClPB) were procuded from Sigma-Aldrich. All other chemicals were of analytical reagent grade. Double distilled deionized water was used throughout the experiments.

Electrode Preparation

Membranes of ~ 0.2 mm thickness were obtained by pouring a solution of the membrane components of PVC 33%, ligand 2-6%, and 2-nitro phenyl octyl ether 63% dissolved in 2-3 mL of tetrahydrofurane (THF). The viscous solution of polymer, thus obtained was poured in a glass ring of 30 mm diameter placed on a dust free Pyrex glass plate. The solvent was allowed to evaporate slowly for about 24 h at room temperature. To obtain membranes with similar characteristics, viscosity of the casting solution and the rate of solvent evaporation were controlled so that the thickness and morphology of the membranes remained almost unchanged and the appearance of the film looked like pale yellow color. The membranes were then, removed from the glass ring and circular pieces of 1.25 cm diameter were cut and mounted on the ground end of a pyrex glass tube with araldite and conditioned with a $AgNO_3$ solution (0.1 M) for 24 h.

EMF Measurements

All the emf measurements were carried out using the following cell assembly:

$$\mathbf{SCE \,|\,|\, 0.1\ M\ Ag^{+} \,|\, membrane \,|\, Ag^{+}\ test\ soln \,|\,|\, SCE}$$

Salt bridges containing KNO_3 were used to provide electrical links between KCl and Ag^+ solutions on both sides of the membrane. A digital potentiometer having a sensitivity of 0.1 mV (Equiptronics EQ602, India) was used for the potential measurements at 25±0.1 °C. Activities were calculated according to the Debye-Hückel equation (33). Standard $AgNO_3$ solutions were obtained by gradual dilution of a 0.1 M $AgNO_3$ solution and their potential measurements were performed.

Results and Discussion

The membrane material is a plastic, polyvinyl chloride (PVC) that is highly hydrophobic and impermeable to any ions. It is plasticized (softened) by addition of a similarly hydrophobic solvent, e.g. o-NPOE (ortho nitrophenyl octyl ether). In order to reduce the resistance, it is usual to add a lipophilic salt, e.g. K-TClPB. So far, the membrane is just a flexible piece of plastic, which acts as a near perfect barrier to ions. To make it ion-selective, a neutral ligand, which is selective for the analyte and is lipophilic in nature, is added.

Optimization of the Membrane Composition

The sensitivity and selectivity of an electrode are significantly affected by the nature of plasticizer, the composition of ionophore, internal solution (34-37), etc. So, for optimization of the membrane, the effect of the composition on the response characteristics of the electrode, like the slope of the calibration curve, measurement range and detection limit were studied The electrode with the ratio PVC:2-NPOE:DIANTH =33%:62%:5%, exhibits the best response with a slope of 60 mV per decade. Table 5.1 (a) shows that 2-NPOE is a more effective solvent medium than BES and DBP in preparing the Ag^+ ion-selective electrode. The amount of ion carrier DIANTH (figure 3) affects the sensitivity. Sensitivity of the electrode increases with increasing ionophore content until a value of 6% (w/w) is reached. A further increase in percentage of ionophore results in a decrease in slope of the electrode. This may be due to the reason that equilibration of the ionophore with the metal ions is maximum at this composition.

Addition of potassium salt of tetrakis(4-chloro-phenyl) borate (KTPClB) is known to increase the sensitivity of the membrane as it reduces the anionic interference. It is observed that the addition of this lipophilic cation does not affect the working electrode response.

Effect of pH

The pH was studied in the range of 2 to 12 using 2×10^{-2} M and 2×10^{-3} M Ag^+ concentration. The pH was adjusted by addition of dilute nitric acid or sodium hydroxide, as appropriate. It was observed that the electrode responses were independent of pH over a range 3.3-8.0 as shown in Figure 5.1(a). The variation above and below this range is due to the interference from excess H^+ ions and hydrolysis of Ag^+ to form silver hydroxide.

Calibration Curve, Response Time and Detection Limit

The electrode shows a linear response towards Ag^+ ions over a wide concentration range from 10^{-4} M to 10^{-1} M. The calibration curve has a slope 60 mV/decade with a detection limit of 3×10^{-5} M, which was obtained from the intersection of two straight-line portions of the curve in Figure 5.2(a). The slow decrease in emf beyond 10^{-5} M is due to the release of silver nitrate, which was continuously co-extracted from the inner electrolyte and transported across the membrane, and hence, leads to deviations from the normal electrode response. The increase in emf may also be due to the possibility of interference from the anions due to failure of Donnan exclusion phenomenon at very low concentrations. 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 time to get a stable potential was 10 s.

The influence of concentration of the internal solution on the electrode potential was also studied. The Ag^+ ion concentration was varied from 1.0×10^{-4} M to 1.0×10^{-1} M and an emf *vs.* -log $[Ag^+]$ plot was obtained. 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. A 1.0×10^{-1} M concentration of silver nitrate was used for further studies.

Potentiometric Titrations to find Detection Limit

Further, the detection limit was evaluated by another method based on potentiometric titrations. Figure 5.3(a) of different concentrations of silver ions against the KI solution. During each titration the concentration of potassium iodide is about 10-fold to Ag^+ ions. The plots between emf and volume of KI are a perfect sigmoid curve and exhibit the 1:1 stoichiometry of the metal-ligand complex up to a concentration of 1×10^{-4} M of the metal ion. At 1×10^{-5} M, it shows an 1:2 stoichiometry, probably due to anion interference. Beyond this (lower than 10^{-5} M) concentration, the sigmoid curve becomes parallel to the X-axis. This shows that the detection limit can be taken as 1×10^{-5} M, i.e. the point beyond which the curve becomes parallel to the abscissa. This method is better than the conventional method, in which the detection limit is taken as the point of intersection of two straight-line portions of the curve.

The main advantage is that there is no effect of a liquid junction potential in our proposed method, as only the relative emf is plotted against the volume of the reagent and actual values of the emf are not required in the potentiometric titrations. Hence, potentiometric titrations are always considered more accurate than direct potentiometry (38).

Potentiometric Selectivity Coefficient

Ion-selective electrodes are rarely ion-specific. The ability of an ion-selective electrode to distinguish between different ions in the same solution is expressed as the selectivity coefficient -log $K_{Ag+,B}^{Pot}$. The selectivity coefficient is not always constant and depends on several factors including the concentration of both ions, the total ionic strength of the solution and the temperature. All electrodes are sensitive to some or the other ions, to some extent. For many applications these interferences are insignificant and can often be ignored. In some extreme cases, however, the electrode is far more sensitive to the interfering ions than to the primary ions and can only be used if the interfering ions are only present in trace quantities.

Selectivity coefficients were evaluated by the fixed interference method (FIM) (39) (interfering ion concentration was fixed at 1×10^{-2} M). From the data of Table 5.2(a) it is clear that there are no serious interfering ions. In case of the matched potential method (MPM) (39), 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 data it is obvious that there is no serious interference from common ions. The proposed sensing material is suitable for preparing silver-selective electrodes and is excellent in its response to Ag^+ ions in the presence of potential interferants, like Hg^{2+}, Cu^{2+} and Pb^{2+} when compared with other electrodes (see Table 5.5(a)).

Effect of Mixed Solvent Medium on the Electrode Response

Functioning of the membrane sensor was also investigated in mixed solvent media using methanol-water, acetone-water and acetonitrile-water (see Table 5.3(a)). The membrane worked satisfactorily in these media up to a maximum of 30% (v/v) content of methanol, acetonitrile and acetone. In these mixtures, the working concentration range and slope are reported in Figure 5.4(a). However, a 20% non-aqueous content showed the best response in all the media.

Direct Titration and Reverse Titration

A direct titration of $AgNO_3$ solution (taken in titration vessel) with the reagent KI (taken in a burette) was carried out and the emf is plotted in Figure 5.5(a). A reverse titration was also carried out by taking KI in the vessel and $AgNO_3$ is added from a burette. The equivalence point for the reverse titration is obtained at the same position as that in the forward titration. It confirms the 1:1 stoichiometry of the chemical reaction taking place in the solution and fast kinetics of the reaction at the electrode.

Determination of Ag^+ in Presence of Interfering Ions

Mixtures of Ag^+ with some probable interfering ions, like Hg^{2+}, Cu^{2+} and Pb^{2+} were taken in different proportions and titrated with KI. The inflection points of these titration curves were used to estimate the extent of interferences shown, if any. Synthetic samples were prepared by taking into consideration the alloys of silver with these metals. Solutions of mixtures of Ag^+ (1×10^{-3} M) with each of the interfering other ions (1×10^{-3} M) were titrated separately with KI (1×10^{-2} M), as shown in Figure 5.6(a). The plots in this Figure show that there is no interference from Cu^{2+} and Pb^{2+} ions. Hg^{2+} interferes in such a way that the extent of interference can be easily predicted. However, its presence does not alter the equivalence point of Ag^+. Hence, Hg^{2+} is a systematic interfering ion. Many reports are indicating that it is a seriously interfering ion (40-44). Even though the proposed electrode shows moderate values of selectivity coefficient by interference determination methods, like FIM and MPM, the potentiometric titration method reported here shows that there is no interference from any metal ions. Hence, the application of a proper experimental procedure brings the electrode close to the ion-specific electrode for Ag^+ ions in the presence of Hg^{2+}.

A very interesting observation is noticed when Hg^{2+} is studied as an interfering ion. Experiments were carried out for the potentiometric titration of $AgNO_3$ with KI. In an equimolar mixture of Ag^+ and Hg^{2+} ions, the equivalence point corresponds to the 3 equivalents of iodide ions (being 2 equivalents for divalent mercury and 1 equivalent for univalent silver ion). It is clearly indicated that a third (1 equivalent) of the reagent is used up in precipitating the Ag^+ ions and the two-thirds (2 equivalents) are used up for precipitating the Hg^{2+} ions. Fortunately, the extent of interference of Hg^{2+} is quite predictable because the equivalence point is obtained at the expected point at Figure 5.6(a), corresponding to the 3-equivalents point, thereby supporting the hypothesis (i.e, 2 units reagent was used for Hg^{2+} ions and one unit reagent for Ag^+ ion) proposed here.

Further, the titrations were carried out by taking different amounts of Hg^{2+} ions. When it was taken in a concentration less than that of Ag^+ ions, no interferences was observed and the titration curve obtained was exactly the same as that as if Hg^{2+} was not present at all. The similar responses of the electrode towards Ag^+ and Hg^{2+} are due to the reason that Ag^+ and Hg^{2+} are isoelectronic and have the d^{10} electronic configuration in their respective penultimate shells. This was further established from the titration curve, where the emf remained stable in the pre-equivalence region of the curve and did not change even when the stoichiometric amount of Hg^{2+} was completely precipitated and Ag^+ started forming precipitation with iodide ions. During this part of titration, first Hg^{2+} is precipitated as Hg_2I_2 because of its lower K_{SP} value than that of AgI. After the complete precipitation of Hg^{2+} as Hg_2I_2, the precipitation of Ag^+ as AgI begins. This indicates that the ionophore is not able to distinguish between Hg^{2+} and Ag^+ ions when the concentration of Hg^{2+} is larger than that of Ag^+. As the concentration of interfering ions decreases, the inflexion point of titration is not shifted from the equivalence point of Ag^+, indicating clearly that there is no interference by Hg^{2+} ions in Figure 5.7(a).

Determination of Sulphate, Thiocynate, Cynaide, and Iodide Contents Present in Spiked Sample Solution

Silver ions form stable complexes with species, like SCN^-, CN^- SO_4^{2-} and S^{2-} in a stoichiometric way. To determine these species, there is hardly any need to find their electrodes. The cation-selective electrode (like that of Ag^+ ions) can be used for the quantitative determination of anions (that for insoluble salts with the said cation) as well.

The potentiometric titration for sulphide ions was carried out by taking a solution of silver ions in a vessel and sodium sulphide is added from a burette. The potentiometric titration curve is shown in Figure 5.8a(i). While, in case of cyanide and thiocynate, the anion solutions were taken in vessels and a silver ion solution was added from a burette, because of the severely hazardous nature of the CN^- and SCN^- solution. The results are shown in Figure 5.8a(ii) and Figure 5.8a(iii), respectively. The inflexion points of the titration curves for S^{2-} and SCN^- are sigmoidal in nature and that for CN^- is semi-sigmoidal. All the curves shown here are sharp enough to calculate the inflexion points accurately. So, the method can be applied for a quantitative determination of the reported anions.

Simultaneous Determination of Halides from a Mixture

To establish the applicability of the proposed chemical sensor for Ag^+ ions, potentiometric titration of a mixture of halide ions containing equal concentrations of Cl^-, Br^- and I^- ions was carried out with $AgNO_3$. The proposed chemical sensor based on the ionophore was used as an indicator electrode. The titration curve shows three inflexion points corresponding to the precipitation of I^-, Br^- and Cl^- in the given sequence in Figure 5.9(a). Inflexion points are well defined for each part of the curve. A little deviation near the end of the titration for Cl^- may be due to the relatively high solubility product value of AgCl (1×10^{-10} M) as compared to AgBr (4×10^{-13} M) and AgI (1×10^{-16} M).

This application establishes that the electrode is a versatile chemical sensor for the determination of Ag^+ ions as well as the anions forming stable complexes or precipitates with Ag^+ ions.

Determination of Chloride Contents in Tap Water

The proposed electrode is used for determining the chloride contents present in drinking water, both in boiled and natural conditions. The equivalence point is determined by using Gran's plots as shown in Figures 5.10(a) and 5.11(a). Chloride contents determined by these methods were comparable with those measured using an Orion ion-selective electrode (940016) for Cl^- ions. The results shown in Table 5.4(a) are comparable to each other, and indicate the satisfactory application of the proposed sensor for Cl^- ion determination.

Table 5.1(a): Optimization of membrane ingredients

Sl. No	PVC (wt%)	Plasticizers (wt%)	Ligand (wt%)	KTClPB (wt%)	Slope (mV/decade)	Detection limit [M]
1	33	65 (2-NPOE)	2	-	50	1×10^{-4}
2	33	64 (2-NPOE)	3	-	52	1×10^{-4}
3	33	63 (2-NPOE)	4	-	57	5×10^{-4}
4	33	62 (2-NPOE)	5	-	60	6×10^{-5}
5	33	61 (2-NPOE)	6	-	60	6.3×10^{-5}
6	33	60 (2-NPOE)	7	-	65	5×10^{-4}
7	33	59 (2-NPOE)	8	-	50	1×10^{-4}
8	33	61 (DBP)	6	-	62	5×10^{-5}
9	33	61 (BES)	6	-	51	5×10^{-5}
10	33	60 (2-NPOE)	6	1	60	5×10^{-5}
11	33	59 (2-NPOE)	6	2	52	5×10^{-5}
12	33	58 (2-NPOE)	6	3	40	1×10^{-4}

Table 5.2(a): Potentiometric selectivity coefficients for interfering ions by FIM & MPM

Interfering ions (B)	$\log K^{Pot}_{Ag+,B}$	
	FIM	**MPM**
Na^+	-1.9	-2.1

K^{+}	-1.8	-2.1
Mg^{2+}	-2.5	-2.1
Ca^{2+}	-2.5	-2.3
Sr^{2+}	-2.3	-2.5
Pb^{2+}	-2.1	-2.7
Cu^{2+}	-2.2	-1.7
Co^{2+}	-3.0	-2.4
Ni^{2+}	-2.1	-2.6
Zn^{2+}	-2.2	-2.6
Cd^{2+}	-3.0	-2.6
Hg^{2+}	-2.3	-2.3
Fe^{3+}	-2.2	-2.5

FIM: Primary ion concentration varied from 1×10^{-6} M to 1×10^{-1} M, interfering ion concentration is 1×10^{-2} M.
MPM: Primary ion concentration is 1×10^{-4} M-1×10^{-2}, reference solution is 1×10^{-4} M and interfering ion concentration added is 1×10^{-2} M.

Table 5.3(a): Electrode response in mixed solvent media

Mixed solvent	Percentage, [V/V]	Slope, mV/decade	Detection limit, [M]
Methanol: Water	10 : 90	50	2.5×10^{-5}
	20 : 80	51	4.0×10^{-5}
	30 : 70	46	5×10^{-5}
Acetonitrile:	10 : 90	54	5×10^{-5}

Water	20 : 80	58	5×10^{-5}
	30 : 70	50	3.1×10^{-5}
Acetone: Water	10 : 90	60	3.1×10^{-5}
	20 : 80	60	5×10^{-5}
	30 : 70	62	5×10^{-5}

Table 5.4(a): Comparison of chloride content in water samples determined by the proposed chemical sensor and Orion (941600) Electrode

Sr. No.	**Sample**	**Chloride contents in ppm**	
		Proposed electrode	**Orion Cl^--selective electrode**
1.	Natural water	(i) 7.1 (ii) 6.9 (iii) 7.1	(i) 6.8 (ii) 6.8 (iii) 6.8
2.	Boiled water	(i) 149 (ii) 147 (iii) 148	(i) 150 (ii) 150 (iii) 151

Table 5.5(a): Comparison of various silver-selective electrodes with the proposed electrode

Sl No.	Ionophore	Slope mV/ decade	Measuring range [M]	pH range	Lifetime (months)	$\log K^{Pot}_{Ag+,B}$	Referenc
1	Polystyrene-based Me6(14) diene:$2HClO_4$	53	5×10^{-6} -10^{-1}	2.5 - 9.5	4	-4.5	45
2	Schiff-base–p-tert butylcalix[4] arene derivative	58	10^{-5} -10^{-1}	1 - 6	6	-2.0	46
3	Two calix [4] arene derivatives functiona- lized by two hydroxy and two benzo thiazolylthioethoxygroups,	58	5×10^{-6}-10^{-1}	2.5 - 6.5	--	-2.6	47
4	Schiff base of [bis 5-(4-nitrophenyl azo)salisylaldimine] 1,8-diamino, 3,6-dioxo octan (BNSAO)	56	$2.7\times10^{\bullet 2}$ - $1.9\times10^{\bullet 6}$	2.5 - 7	Long life time	2.3	48
5	Tweezer-type and non-tweezer-type ionophores containing dithiocarbamoyl groups on a 7-deoxy cholic amide or cholane derivatives	60	10^{-9} -10^{-3}	--	--	3.6	49
6	2-[(2-{2-[(2-Carboxy phenyl) sulfanyl] ethoxy}ethyl)sulfanyl] benzoic acid	59	2.0×10^{-8}- $1\times10^{\bullet 2}$	2.5 - 8.7	--	-1.79	50
7	*tert*-butylcalix[4]arene tetra(allyl ether)	58	10^{-4} -10^{-1}	--	--	-2.2	51
8	25,27-dihydroxy- 26,28-bis[5-(4-methyl-6hydroxypurimidine) thia amyl oxy] calix[4]arene	61.4	5×10^{-8} - 1×10^{-1}	3 - 7	1	-3	52
9	Methyl-2-pyridyl ketone oxime (MPKO), phenyl-2-pyridyl ketone oxime (PPKO) and bis[2-(ocarboxythiophenoxy) methyl]-4-bromo-1-methoxybenzene	59.8 and 60.5	$10^{\bullet 6}$ - $10^{\bullet 1}$	2.5 - 8.5	3	-3.5	53
10.	Schiff base p-tert-butyl calix[4] arene derivatives containing N and O as binding sites	60	10^{-5} - 10^{-1}	1 - 10		-2.3 - 3.3	54
11.	6-oxa-3,9 dithiabicicle [9.3.1] pentadeca-1(15),11,13-triene (MAO)	43	5×10^{-8} -10^{-2}	--	6	--	55
12.	Calix[2]furano[2]pyrrole	57.1	$1\times10^{\bullet 6}$ - $1\times10^{\bullet 2}$	2.8 - 12	-	-1.7 at pH 5 -3.5 at pH 2.5	56
13.	2,2'-dithiobis(benzo thiazole)	60.3	8.3×10^{-7} - 0.094	2 - 7.5	--	-3.0	57
14.	9,10,Bis-(2-aminophenylthiomethyl) anthracene	60.0	10^{-4} -10^{-1}	3.3 -8.0	6	2.3	in pres

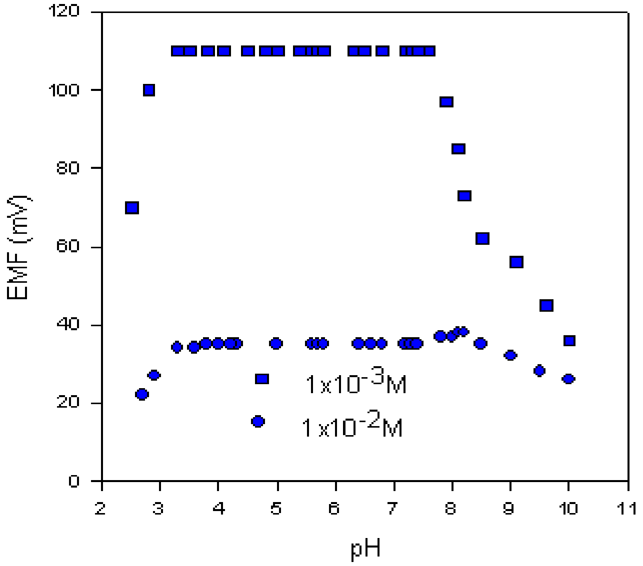


Figure 5.1(a): Effect of pH on the potential response of Ag-ISE based on dipodal ionophore

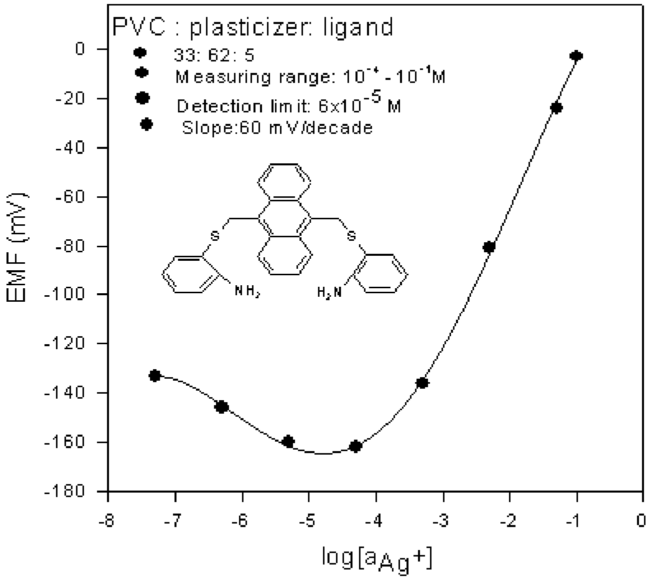


Figure 5.2(a): Calibration curve for Ag-ISE based on dipodal ionophore

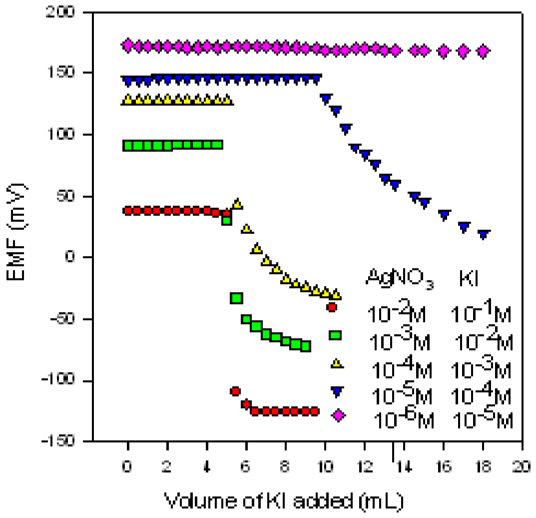


Figure 5.3(a): Sensitivity of potentiometric titration to predict the detection limit

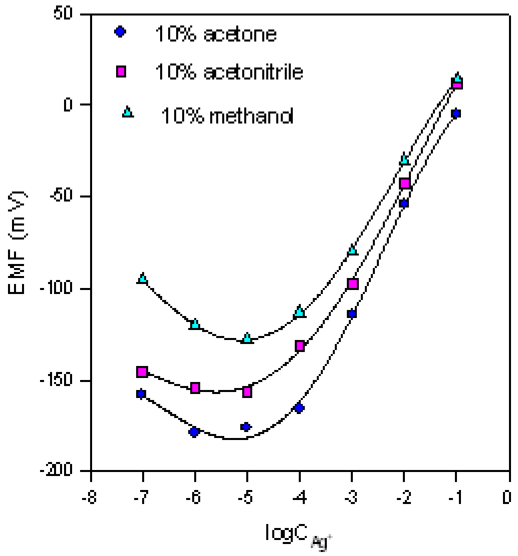


Figure 5.4(a): Calibration graphs of Ag-ISE in mixed solvent media

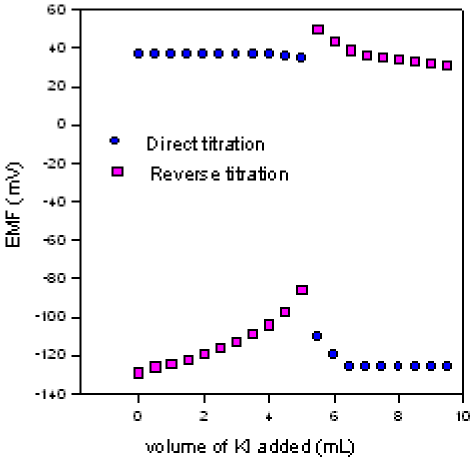


Figure 5.5(a): Potentiometric titration (direct and reverse) on Ag-selective electrode

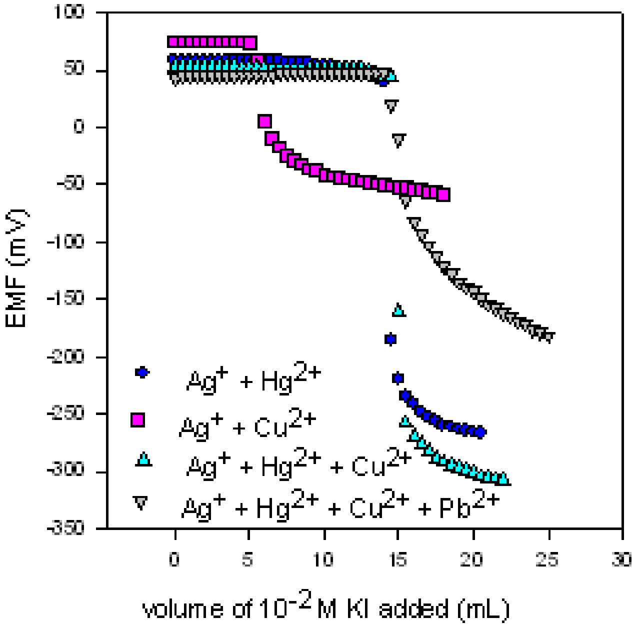


Figure 5.6(a): Determination of silver contents in the presence of interfering metal ions Cu^{2+}, Hg^{2+} and Pb^{2+}

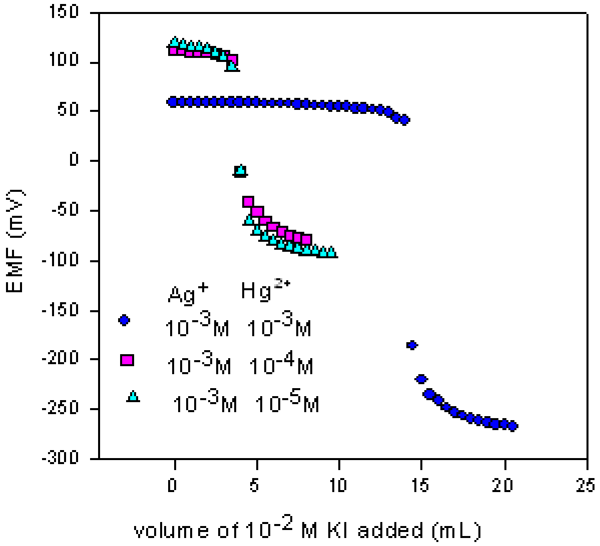


Figure 5.7(a): Determination of silver contents in the presence of various concentrations of Hg^{2+} ions

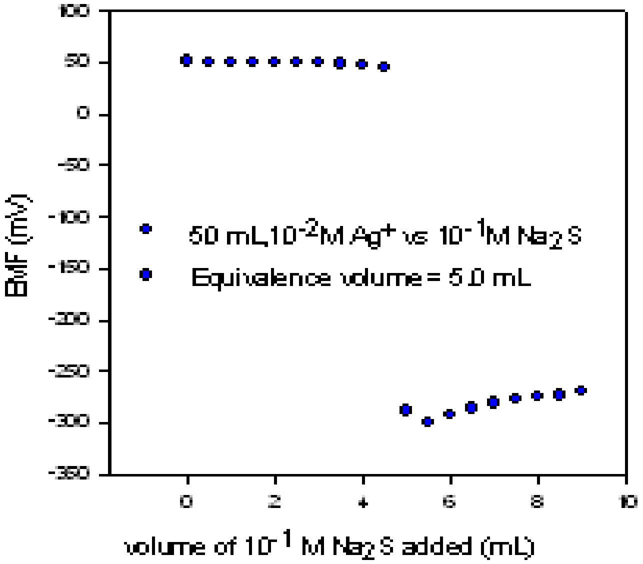
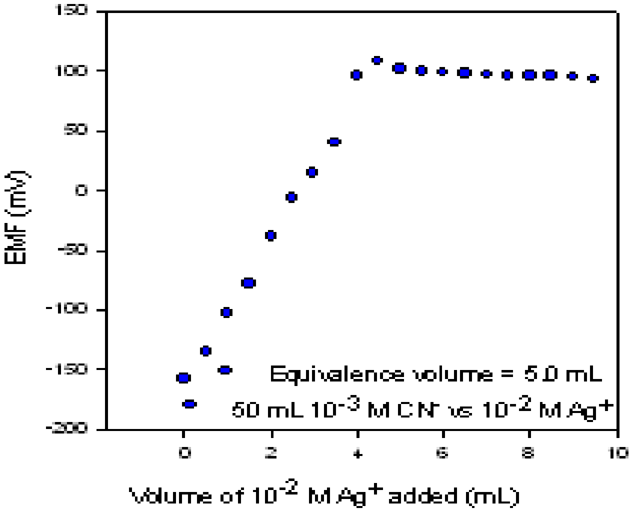
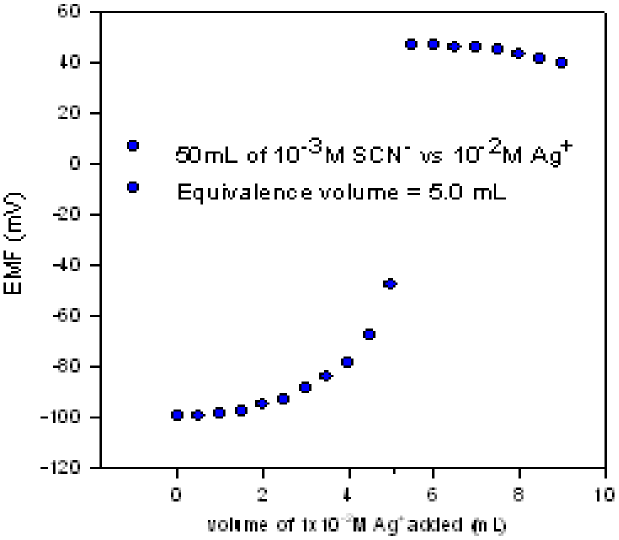


Figure 5.8a(i): Determination of S^{2-} contents present in the sample



5.8 a (ii)



5.8 a (iii)

Figure 5.8(a)[ii & iii]: Determination of (ii) CN^- and (iii) SCN^- contents present in the sample

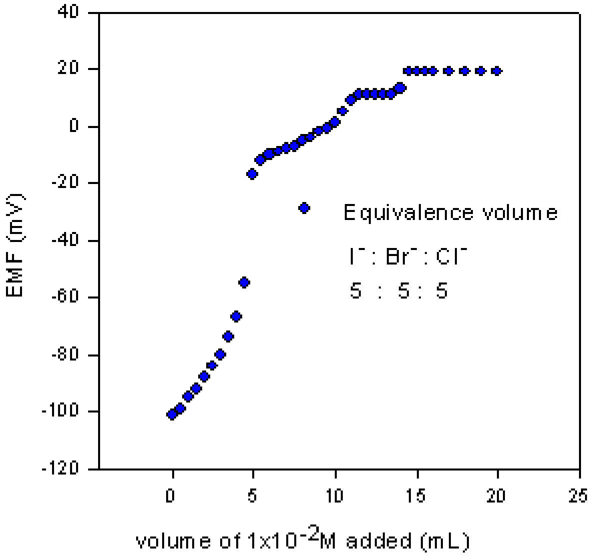


Figure 5.9(a): Simultaneous determination of halide mixtures present in a sample solution of mixture of halides

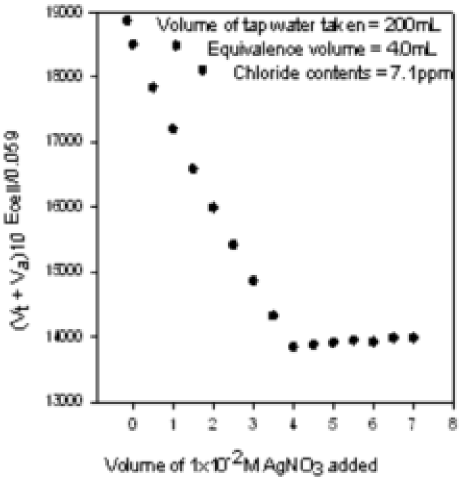


Figure 5.10(a): Gran’s plot for the determination of chloride contents present in a drinking water

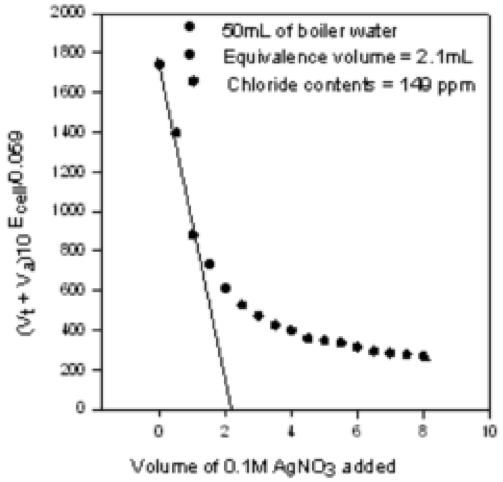


Figure 5.11(a): Grans’s plot for the determination of chloride contents present in a boiled water sample

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(5b) Potentiometric Performance of 2-Aminothiophenol-based Tripodal Ionophore as a Silver Sensing Material

Introduction

The need for selective and sensitive sensors able to monitor in real-time and real-space the concentration of analytes of biological, clinical, and environmental interest is nowadays generally accepted (1-6). Various kinds of sensors are now available but liquid membrane-based electrodes are still standing at the peak position of electrode systems, due to its their 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 (7–13) including calix[4]arene derivatives (14–16), crown ether derivatives (17–19) and tweezer-type compounds (20) 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.

Tripodal ionophores have a special structure due to their three flexible donor-atom-containing chains. Due to this, they can form complexes with many cations from alkali and alkaline earth metals to transition metals (21-25). By chemical modification of the arms (e.g. changing the chain length or the donor-atom) and under certain experimental conditions, a tripodal ionophore can carry metal ions selectively. In an attempt to find selective metal ion carriers our coworkers have designed and synthesized 2,4,6-tris(2-aminophenylthio methyl)-1,3,5-trimethylbenzene as tripodal ionophore and examined it for silver metal ions.

Experimental

Reagents

Reagents, like dibutyl phthalate (DBP), 2-nitrophenyl octyl ether (2-NPOE), were procured from Sigma-Aldrich. All other chemicals were of analytical reagent grade. Double distilled deionized water was used throughout the experiments.

Electrode Preparation and EMF Measurements

The procedure for membrane preparation is same as in the previous section 5(a) with Poly(vinyl chloride) PVC (33 %), ortho-Nitrophenyloctylether o-NPOE (63) and tripodal ionophore (4%). Discs of

1.25 cm in diameter were cut from the PVC-membrane and incorporated into a glass tube tube tip with adeshive glue (Araldite). The electrode was conditioned by soaking in 0.1 M aqueous solution of $AgNO_3$ for 24 h.

All emf measurement were carried out with the following electrochemical cell assembly:

SCE | 0.1 M Ag^+ || membrane || Ag^+ test solution | SCE

A digital potentiometer (Equip-tronics, EQ-602, India) was used for the potential measurements at 25±0.1° C. Activities were calculated according to the Debye-Huckel quation (28). $AgNO_3$ solutions for calibration of the electrode were obtained by gradual dilution of 0.1 M $AgNO_3$ solution. The salt bridge used here was Agar-Agar-KNO_3.

Results and Discussion

The principle of ISE chemistry involves permselective transport of analyte ions from adjacent aqueous sample solutions into ionophore-incorporated in the organic liquid membrane. This process leads to an ion-selective charge separation at the aqueous/organic interface, and the change in boundary potentials becomes a measure for the analyte ion concentrations (activities). The development of the liquid-membrane ISEs makes much to the progress of supramolecular chemistry and has played an important role in bridging supramolecular chemistry with analytical chemistry.

Optimization of the Membrane Composition

The nature and amount of membrane ingredients affect the sensitivity and selectivity of the ionophore (29-30). The characteristics of several membranes having different compositions are shown in the Table 5.1(b) as seen in the table, the increasing ligand concentration improves the performance of the electrode in slope and detection limit. At 1-3% of the ionophore the electrode exhibits a sub-Nernstian slope. At 4% content of ionophore, the slope becomes Nernstian and a subsequent increase in the ionophore concentration shifts the electrode response to the sub-sub-Nernstian range. Results are shown in Table 5.1(b). The reason for this trend could not be ascertained easily. Among the three different plasticizers 2-NPOE, DBP and BES, 2-NPOE is the best plasticizer (due to its high dielectric constant makes the ionophore in free movement and fast exchange in complexation and decomplexation between ionophore and silver ions).

On the basis of the response characteristics of the proposed sensing material, following point is worth considering: The tripodal ionophore undergoes a series of Nernstian responses starting with sub-Nernstian at lower concentration of the ionophore to Nernstian at optimized concentration and then to sub-sub-Nernstian at higher concentration. This shows at 4% a dynamic complexation between ionophore and silver ions.

Calibration Curve and Internal Solution Concentration

The potential responses of the Ag electrode at different concentrations of Ag^+ ions show a linear response to the concentration of Ag^+ ions in the range from 10^{-4} M to 10^{-1} M. The slope of calibration curve is 56 mV/decade while the detection limit is $3x10^{-5}$ M obtained from the intersection of the two extra-plotted curves of the calibration graph in Figure 5.2(b). Further, the detection limited is evaluated from another method based on potentiometric titration of different concentration of silver ions vs different concentrations of KI solution. During each titration, the concentrations of potassium iodide are maintanied 10 at a fold more concentrated than the Ag^+ ions. The graph between emf and volume of KI is shown as a perfect sigmoid curve and exhibited an 1:1 complexation up to a concentration of $1x10^{-4}$ M. At $1x10^{-5}$ M it shows an 1:2 complexation and beyond this concentration, the sigmoid curve becomes constant along the X-axis [see Figure 5.3(b)]. This shows that the detection limit can be taken as $1x10^{-5}$ M. The response time is measured by recording the emf of the electrode as a function of time, when it is immersed in solution to be studied. The estimated time to get stable potential was 10 seconds.

Effect of pH

The pH was studied in the range from 2 to 12 using $1x10^{-3}$ M Ag^+ concentration. The pH was adjusted by addition of dilute nitric acid or sodium hydroxide, as appropriate. It was observed that the potential responses were independent of pH over the range of 2.5-8.5 in Figure 5.1(b). Below and above the variation, the change in emf is due to interference from excess H^+ ions and hydrolysis of Ag^+ and formation of silver hydroxide.

Potentiometric Selectivity Coefficient

In the fixed interference method, a $1x10^{-3}$ M concentration of interfering ions was used for calculating the selectivity coefficient values (32). In the matched potential method, a constant initial background of the primary ion (10^{-4} M) was used. The electrodes already reported in literature, generally suffer from strong interference by mercury ions (33-35), but the proposed electrode system shows a good selectivity for silver ions even in the presence of these ions [see Table 5.2(b)]. Selectivity coefficients were also determined using the titration method for a binary mixture of all the interfering with Ag^+ ions. The results indicate that the equivalence point is observed at the stoichiometric point of an 1:1 complex formation. It shows that the presence of mercury ions along with silver ions does not alter the selectivity coefficient of silver.

Effect of Electrode Response in Mixed Solvent Medium

The working nature of the sensor was also studied in mixed solvents medium using methanol-water, acetone-water and acetonitrile-water mixtures. The membrane showed a satisfactory response in the medium upto 30% (V/V) non-aqueous content [see Table 5.3(b) and Figure 5.4(b)]. The working concentration range (10^{-4} to 10^{-1} M) remains the same while the slope varies in a narrow range. The best results are observed at 20% non-aqueous medium.

Potentiometric Titration

Potentiometric titrations are among the most accurate because the potential follows the actual change in activity and therefore, the end point will often coincide directly with the equivalence point. The membrane electrodes were immersed in the analyte solution (I^-, SCN^-, CN^-, $1x10^{-3}$ M etc.) and the initial EMF was recorded. The titrant (Ag^+, $1x10^{-2}$ M) was added in the incremental amounts of 0.5 mL on the titration vessel fitted with a magnetic stirrer system. With each addition a new EMF was observed and it was recorded. The readings of EMF values were plotted as a function of volume of the reagent added from the burette.

Direct and Reverse Titration of Ag^+ Ions

50 mL of Ag^+ ions, $1x10^{-3}$ M solution, was titrated against KI solution of $1x10^{-2}$ M. The potential break was observed at an 1:1 complex formation of the metal-ionophore and metal ion and I^- ions interaction, and the same observation was made during the reverse titration also [see Figure 5.5(b)].

Potentiometric Titrations of Binary, Ternary and Several Mixtures of Ions

50 mL of solution containing some binary and some ternary mixtures of Ag^+ ions ($1x10^{-3}$ M) with interfering ions was titrated against KI solution of $1x10^{-2}$ M. In each titration only one break in EMF corresponding to the AgI complex formation was observed. The titrations show an equivalence point corresponding to the formation of 1:1 and 1:2 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 responed to Hg^{2+} ions. These results show that mercury is not interfering in silver determination as shown in Figure 5.6(b).

Low Level Potentiometric Determinations of CN^-, SCN^- and SO_4^{2-}

The proposed sensor can be used as a probe for the determination of anions, like SCN^-, SO_4^{2-}, CN^- with which Ag^+ forms very stable soluble complexes. The proposed electrode was used as an indicator electrode for the determination of these ions. The titration curves were plotted and shown in Figure 5.7 (b). 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 slope was corresponding to an 1:1 complex formation. All the three ionophores show the similar behavior during the potentiometric titrations. 50 mL of the $1x10^{-3}$ M anion solution mixture was titrated against 1x10^{-2} M Ag^+ solution. The potential break was observed at an 1:1 complex formation of the silver-anion complex.

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

50 mL of the halide mixture of 1x10^{-3} M was titrated against $AgNO_3$ solution (1x10^{-2} M) The titration [Figure 5.8(b)] shows three breaks corresponding to an 1:1 complex formation of Ag^+ ions with I^-, 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.

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Table 5.1(b): Optimization of membrane ingredients

Sl.No	PVC (Wt%)	Plasticizers (Wt%)	Ligand (Wt%)	NaTPB (Wt%)	Slope (mV/ decade)	Detection limit (M)
1	33	66(2NPOE)	1	-	25	$5.0x10^{-5}$
2	33	65(2NPOE)	2	-	27	$5.0x10^{-5}$
3	33	64(2NPOE)	3	-	28	$6.3x10^{-5}$
4	33	63(2NPOE)	4	-	56	$3.1x10^{-5}$
5	33	62(2NPOE)	5	-	16	$1.0x10^{-4}$
6	33	61(2NPOE)	6	-	17	$1.0x10^{-4}$
7	33	60(2NPOE)	7	-	19	$1.0x10^{-4}$
10	33	63(DOP)	4	-	46	$5.0x10^{-5}$
11	33	63(BES)	4	-	40	$5.0x10^{-5}$
12	33	61(2NPOE)	4	1	58	$5.0x10^{-5}$
13	33	59(2NPOE)	6	2	52	$5.0x10^{-5}$
14	33	58(2NPOE)	6	3	40	$1.0x10^{-4}$

Table 5.2(b): Potentiometric selectivity coefficient by FIM and MPM

$\log K_{Ag,B}^{Pot}$

Interfering Ions (B)		
	FIM	**MPM**
Na^+	-1.4	-1.7
K^+	-1.0	-1.9.
Mg^{2+}	-2.0	-2.2
Ca^{2+}	-1.9	-2.1
Sr^{2+}	-2.4	-2.1
Pb^{2+}	-2.4	-2.2
Cu^{2+}	-2.1	-2.2
Co^{2+}	-2.4	-2.2
Ni^{2+}	-2.5	-2.2
Zn^{2+}	-2.5	-2.4
Cd^{2+}	-2.5	-2.3
Hg^{2+}	-2.5	-2.2
Fe^{3+}	-2.5	-2.3

(FIM: Primary ion concentration varied from 1×10^{-6} M to 1×10^{-1} M, interfering ion concentration is 1×10^{-2} M. MPM: Primary ion concentration is 1×10^{-4} M-1×10^{-2}, reference solution is 1×10^{-4} M and interfering ion concentration added is 1×10^{-2} M)

Table 5.3(b): Electrode response in mixed solvent medium

Mixed Solvent	Mixed solvent, (% V/V)	Slope, mV/decade	Detection Limit, [M]
Methanol: water	10:90	48	$5x10^{-5}$
	20:80	53	$2x10^{-4}$
	30:70	56	$1x10^{-4}$
Acetonitrile: water	10:90	54	$1x10^{-4}$
	20:80	52	$4x10^{-5}$
	30:70	52	$4x10^{-5}$
Acetone: water	10:90	54	$3x10^{-5}$
	20:80	55	$3x10^{-5}$
	30:70	54	$2x10^{-5}$

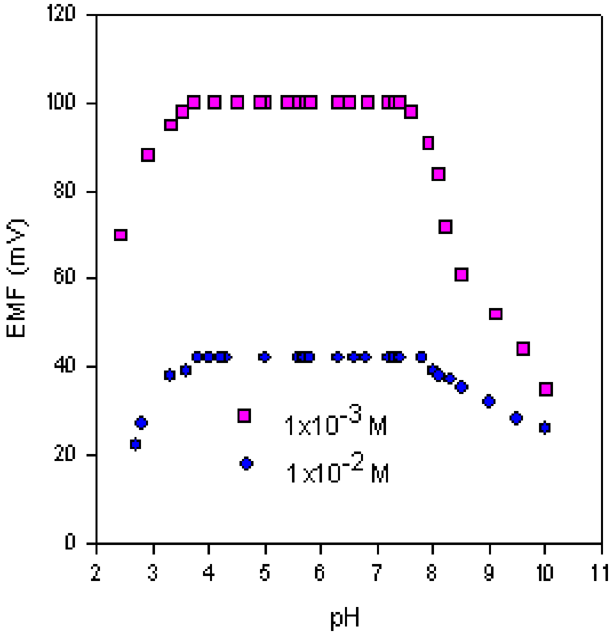


Figure 5.1(b): Effect of pH on the potential response of Ag-ISE based on tripodal ionophore

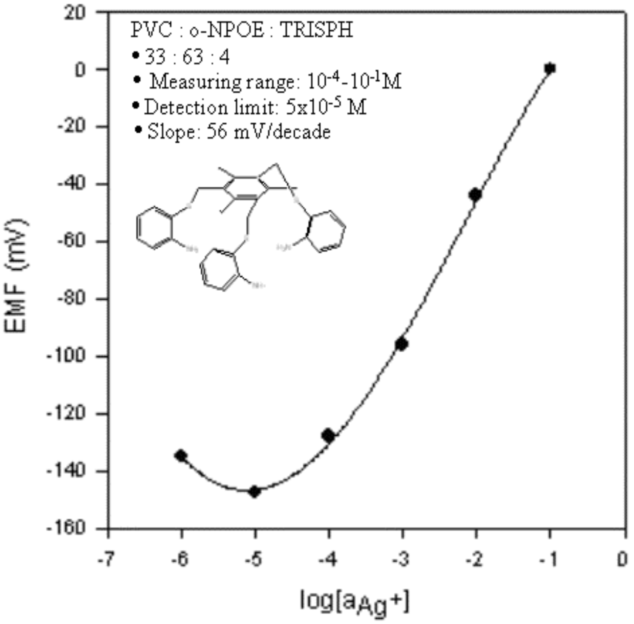


Figure 5.2(b): Calibration curve for Ag-ISE based on tripodal ionophore

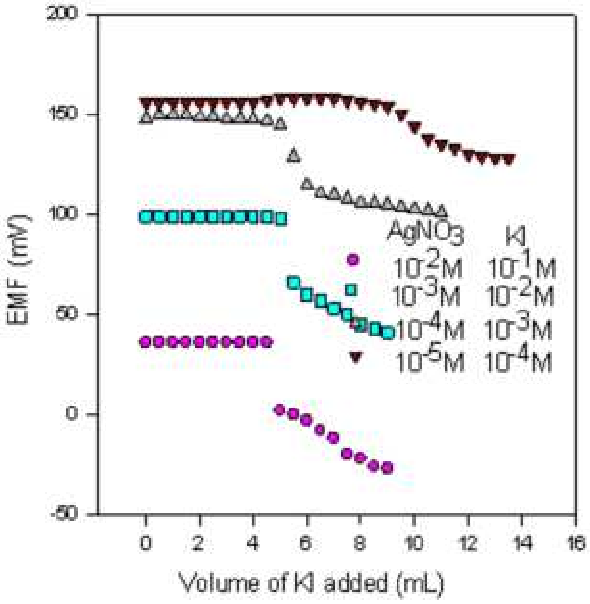


Figure 5.3(b): Sensitivity of potentiometric titration to predict its detection limit

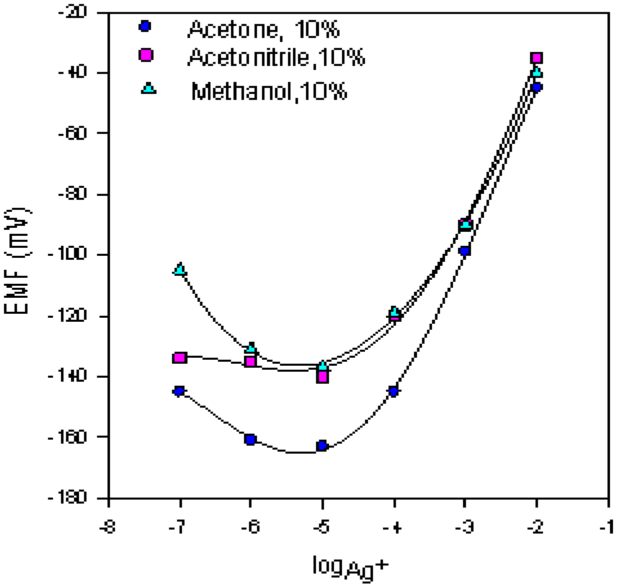


Figure 5.4(b): Calibration graphs of Ag-ISE in mixed solvent media

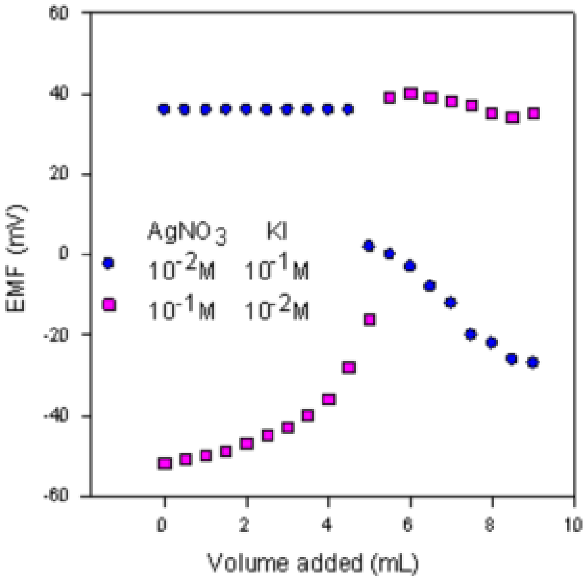


Figure 5.5(b): Potentiometric titration of Ag^+ ions against I^- ions (direct & reverse)

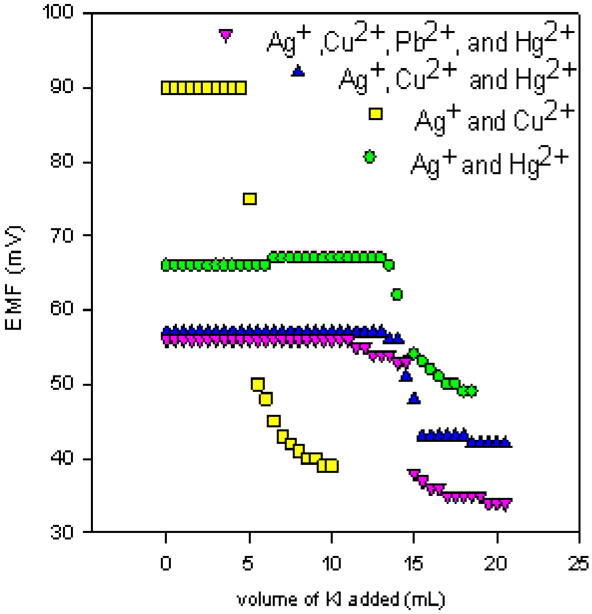
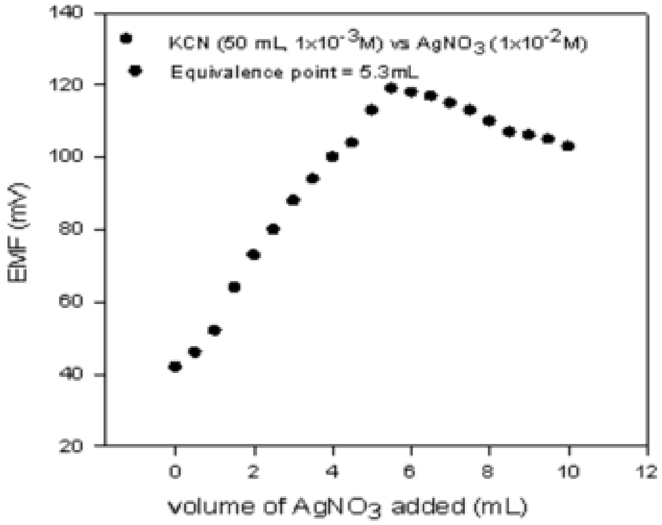
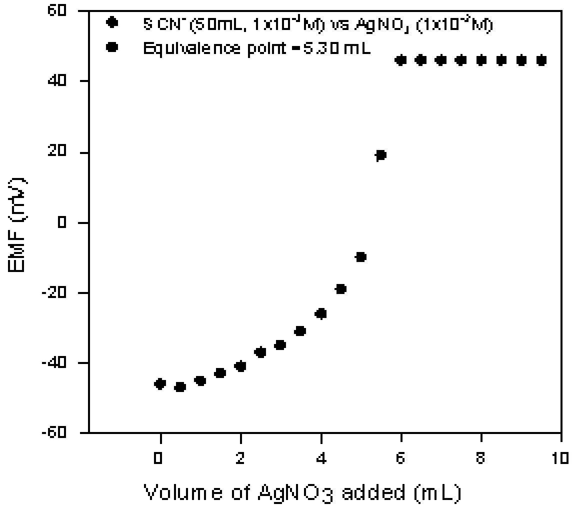


Figure 5.6(b): Determination of silver contents in the presence of interfering metal ions Cu^{2+}, Hg^{2+} and Pb^{2+}

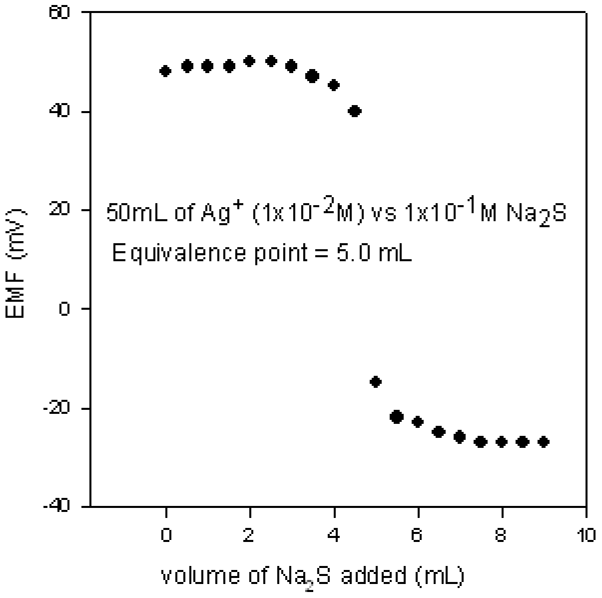


b(i)



b(ii)

Figure 5.7(b)[i & ii]: Determination of CN^- and SCN^- contents present in the sample



b(iii)

Figure 5.7(b)(iii): Determination of SCN$^-$ contents present in the sample

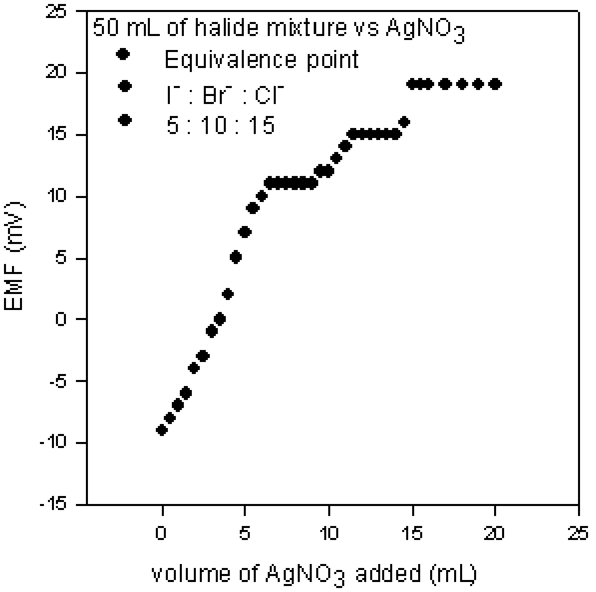


Figure 5.8(b): Simultaneous determination of halide ions present in a mixture by potentiometric titrations

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5(c) Potentiometric Performance of 8-hydroxyquiniline-based Tetrapodal Ionophore as a Silver Sensing Material

Introduction

A considerable attention has been given on the design of the molecular architecture at the electrode–

solution interface and the utilization of supramolecular interactions in making chemical sensors (1-2). Electrically neutral, lipophilic ion-complexing agents of relatively small molar mass are known to act as ion carriers having the capability to selectively sense the ions in aqueous phase. Transport of these ions across the lipophilic membrane barriers by carrier translocation is used in preparing ion-selective electrodes (3-6). In this chapter, the interaction of ions with ligands in water and water-like media are focused using tetrapodal ionophores as chemical sensing material and established that these type of molecules are excellent in preparing silver ion-selective electrodes.

Due to the continuous usage of silver-based salts and their compounds in daily usage, like photography, dentistry, electronic industry and medicine, monitoring of silver ions at the site level is the real challenge in analytical laboratories (7-18). Determination of silver ions in presence of Hg^{2+} ions is a difficult task. Due to their d^{10} electronic configuration, the system follows singular coordination characteristics (19). Many reports showed that Hg^{2+} is a serious interfering ion (20-25), but our report in the determination of Ag^+ ions claims that this ion is interfering systematically and its prediction is very accurate by the proposed method.

Experimental

Reagents

Reagents, like dibutyl phthalate (DBP), 2-nitrophenyl octyl ether(2-NPOE), were procured from Sigma-Aldrich. All other chemicals were of analytical reagent grade. Double distilled deionized water was used throughout the experiments.

Electrode Preparation and EMF Measurements

Procedure for the membrane preparation (26) is same as in previous sections of this chapter. The electrodes were prepared by taking Poly(vinylchloride) (PVC) (33%), ortho-nitrophenyloctylether, o-NPOE (61%), tetrapodal ionophore (5%) in 5-6 mL of THF. The electrodes were conditioned by soaking in 0.1 M aqueous solution of $AgNO_3$ for 24 h.

All emf measurements were carried out with the following electrochemical cell assembly:

$$\textbf{SCE} \,|\, \textbf{0.1 M Ag}^{+} \,||\, \textbf{membrane} \,||\, \textbf{Ag}^{+} \textbf{ test solution} \,|\, \textbf{SCE}$$

A digital potentiometer (accuracy, ±0.1 mV, Equip-tronics, EQ-602, India) was used for the potential measurements at 25±0.1 °C. Activities were calculated according to the Debye-Huckel equation (27). $AgNO_3$ solutions for calibration of the electrode were obtained by gradual dilution of 0.1 M $AgNO_3$ solution. The salt bridge used here was Agar-Agar-KNO_3.

Results and Discussion

In practice no ion-selective electrode has ideal selectivity for one particular ion (28) and under most conditions, there is more than one ion present in the sample solution and the contribution of EMF by interfering ion is also to be considered.

Optimization of the Membrane Composition

Nature and amount of the membrane ingredients affect the sensitivity and selectivity of the electrode (29-31). Performance characteristics of several membranes having different compositions are shown in Table 5.1(c). Increasing the ligand concentration improves the performance of the electrode in slope and detection limit and attained the best response at 5% of it. Membrane at Sr. No. 4 in Table 5.1(c) giving Nernstian slope was selected for further studies. Among the three different plasticizers, 2-NPOE, DBP and BES, 2-NPOE is the best plasticizer. Its high dielectric constant helps the ionophore in free movement and fast exchange in complexation and decomplexation between the ionophore and the silver ions.

Calibration Curve and Effect of Internal Solution Concentration

The electrode shows a linear response towards Ag^+ ions over a wide concentration range from 10^{-4} M to 10^{-1} M. The calibration curve has a slope of 60 mV/decade with a detection limit of $3x10^{-5}$ M obtained from the intersection of two straight-line portions of the curve in Figure 5.1(c). Further, the detection limit is evaluated by another method based on the potentiometric titration of different concentrations of silver ions against KI solution. During each titration, the concentration of potassium iodide is about 10-fold to Ag^+ ions. The plots between emf and volume of KI are a perfect sigmoid curve and exhibit an 1:1 stoichiometry complexation up to a concentration of $1x10^{-4}$ M. At $1x10^{-5}$ M, it shows an 1:2 stoichiometry complexation. Beyond this concentration, the sigmoid curve becomes parallel to the X-axis. This shows that the detection limit can be taken as $1x10^{-5}$ M in Figure 5.2(c). This method is better than the conventional method in which the detection limit is taken as the point of intersection of the two straight-line portions of the curve.

The response time is measured by recording the emf of the electrode as a function of time, when it is immersed in solution to be studied. The estimated time to get a stable potential was 10 seconds.

The influence of the concentration of the internal solution on the electrode potential was also studied. The Ag^+ ion concentration was varied from 1.0×10^{-4} M to 1.0×10^{-1} M and emf vs -log $[Ag^+]$ plot was obtained. 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. A 1.0×10^{-1} M concentration of silver nitrate was used for further studies.

Effect of pH

Electrode response was studied by varying pH in the range 2 to 12 using a Ag^+ concentration of $1x10^{-3}$ M. It was observed that the potential responses were independent of pH over the range of 2.5-8.5 for the electrodes in Figure 5.3(c). Below and above this range the variation is due to the interference from excess H^+ ions and hydrolysis of Ag^+ ions.

Potentiometric Selectivity Coefficients

Selectivity of any ion-selective sensor is clearly one of its most important characteristics as this property often determines whether a sensor may be used reliably for the target sample or not. It is evaluated by the fixed interference method (32) (interfering ion concentration was fixed at $1x10^{-2}$ M and matched potential method (33)). From the data in Table 5.2(c) it is obvious that there is no serious interference from the common ions.

Effect of Electrode Response in Mixed Solvent Media

Functioning of the membrane sensors was also investigated in mixed solvent media using methanol-water, acetone-water and acetonitrile-water. The membrane worked satisfactorily in partially non-aqueous media up to a maximum of 30% (v/v) content of methanol, acetonitrile and acetone, Table 5.3 (c) and Figure 5.4(c). In these mixtures, the working concentration range and slope remained almost constant. However, a 10% non-aqueous content showed the best response in all the media.

Direct Titration and Reverse Titration

Potentiometric titrations are more reliable than most of other modes of titrations because relative emf is plotted against activity. The end point often coincides directly with the equivalence point. A large potential break will occur at the equivalence point. Titration is also carried out in the reverse order, i.e. KI is taken in the titration vessel and is titrated against $AgNO_3$, taken in a burette. The equivalence point is observed at the same position to that of the forward titration (see Figure 5.5(c)). It confirms the 1:1 stoichiometry and fast kinetics of the reaction at the electrode surface.

Determination of Ag^+ in Presence of Interfering Ions

Mixtures of Ag^+ with interfering ions, like Hg^{2+}, Cu^{2+}, Pb^{2+} were taken in different proportions and titrated against KI using the Ag-ISE based on the tetrapodal ionophore. The inflection points of these titration curves were similar to those obtained using an Ag-ISE based in DIANTH, discussed in chapter 5(a). The trends of titration curves in Figure 5.6(c) and Figure 5.7(c) were also similar to those reported in chapter 5(a) with the tripodal ionophore-based ISE. It is once again established that Hg^{2+} is interfering (20-25) in the Ag^+ ion determination in a systematic way.

Simultaneous Determination of Halides from a Mixture

To establish the applicability of the proposed tetrapodal ionophore-based chemical sensor for Ag^+ ions, a potentiometric titration of a mixture of equal concentrations of Cl^-, Br^- and I^- ions was carried out against $AgNO_3$. The titration curves in Figure 5.8(c) show three inflexion points corresponding to the precipitation of I^-, Br^- and Cl^- in the given sequence.

This application establishes that the electrode is a versatile chemical sensor and can be used as an indicator electrode in potentiometric titration for the determination of Ag^+ ions as well as anions forming stable complexes or precipitates with Ag^+ ions.

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Table 5.1(c): Optimization of membrane ingredients

Sl.No	PVC, (Wt%)	Plasticizer, (Wt%)	Ionophore, (Wt%)	NaTPB, (Wt%)	Slope, (mV/ decade)	Detection limit, [M]
1	33	65(2-NPOE)	2	-	50	$1x10^{-4}$
2	33	64(2-NPOE)	3	-	52	$1x10^{-4}$
3	33	63(2-NPOE)	4	-	57	$5x10^{-4}$
4	**33**	**62(2-NPOE)**	**5**	-	**60**	**$3x10^{-5}$**
5	33	61(2-NPOE)	6	-	65	$5x10^{-4}$
6	33	60(2-NPOE)	7	-	60	$6.3x10^{-5}$
7	33	59(2-NPOE)	8	-	50	$1x10^{-4}$
8	33	61(DBP)	6	-	62	$5x10^{-5}$
9	33	61(BES)	6	-	51	$5x10^{-5}$
10	33	60(2-NPOE)	6	1	60	$5x10^{-5}$
11	33	59(2-NPOE)	6	2	40	$1x10^{-4}$
12	33	58(2-NPOE)	6	3	52	$5x10^{-5}$

Table 5.2(c): Potentiometric selectivity coefficient by FIM and MPM

$\log K_{Ag,B}^{Pot}$

Interfering ions		
	FIM	MPM
Na^+	-1.4	-1.6
K^+	-1.8	-1.9
Mg^{2+}	-2.4	-2.2
Ca^{2+}	-2.2	-2.2
Sr^{2+}	-2.6	-2.5
Pb^{2+}	-2.5	-2.3
Cu^{2+}	-2.5	-2.3
Co^{2+}	-2.5	-2.3
Ni^{2+}	-2.0	-2.4
Zn^{2+}	-2.3	-2.5
Cd^{2+}	-2.0	-2.2
Hg^{2+}	-1.9	-2.2
Fe^{3+}	-2.5	-2.7

(FIM: Primary ion concentration of varied from 1×10^{-6} M to 1×10^{-1} M, interfering ion concentration of 1×10^{-2} M. MPM: Primary ion concentration is 1×10^{-4} M-1×10^{-2}, reference solution is 1×10^{-4} M and interfering ion concentration added is 1×10^{-2} M)

Table 5.3(c): Effect of Ag^+-selective electrode in mixed solvent media

Mixed Solvent	Solvent:water	Slope, mV/decade	Detection Limit, [M]
Methanol: water	10: 90	54	$2.0x10^{-5}$
	20: 80	51	$4.0x10^{-5}$
	30: 70	50	$5.0x10^{-5}$
Acetonitrile: water	10: 90	60	$3.0x10^{-5}$
	20: 80	60	$6.3x10^{-5}$
	30: 70	57	$5.0x10^{-5}$
Acetone: water	10: 90	59	$2.5x10^{-5}$
	20: 80	56	$2.5x10^{-5}$
	30: 70	55	$4.0x10^{-5}$

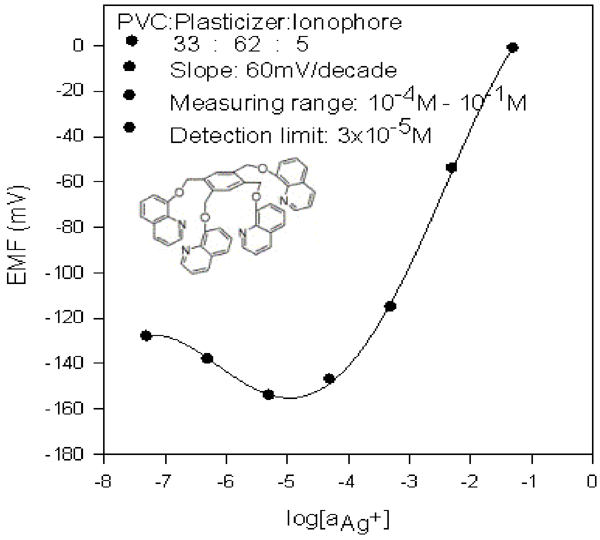

Figure 5.1(c): Calibration curve for Ag-ISE based on tetrapodal ionophore

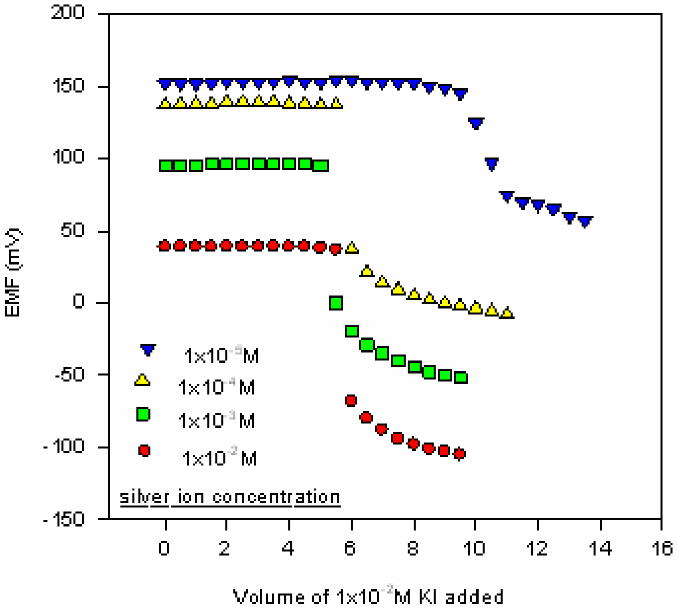

Figure 5.2(c): Sensitivity of potentiometric titration to predict the detection limit

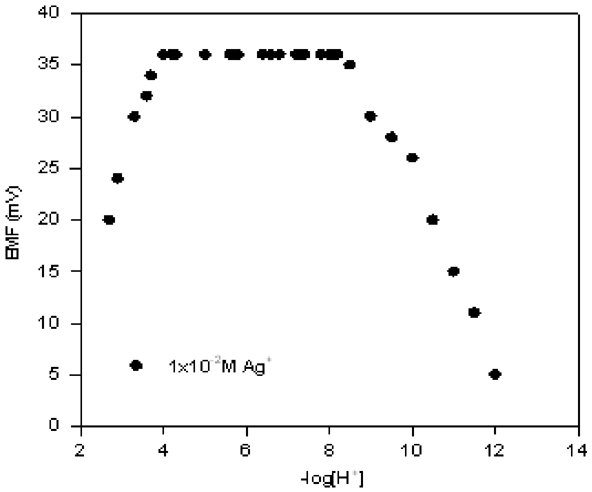

Figure 5.3(c): Effect of pH on the response of Ag-ISE

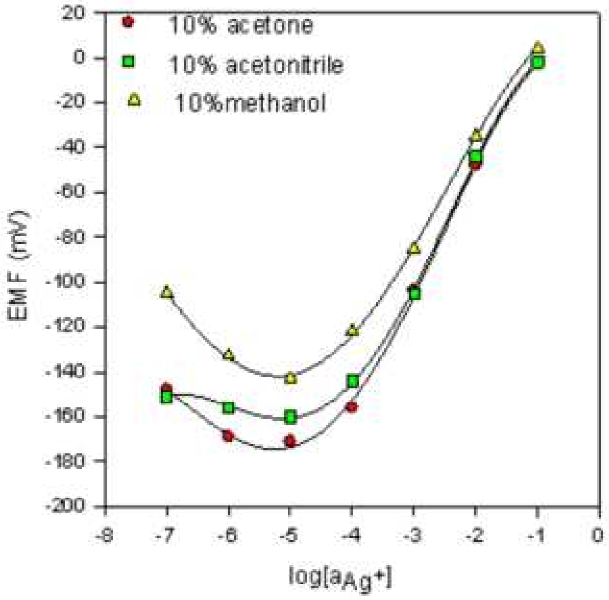

Figure 5.4(c): Calibration curves of Ag-ISE in mixed solvent media

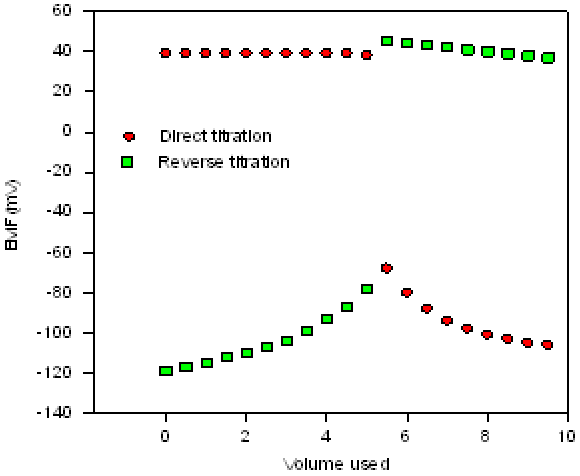

Figure 5.5(c): Potentiometric titration of Ag^+ ions against I^- ions (direct and reverse)

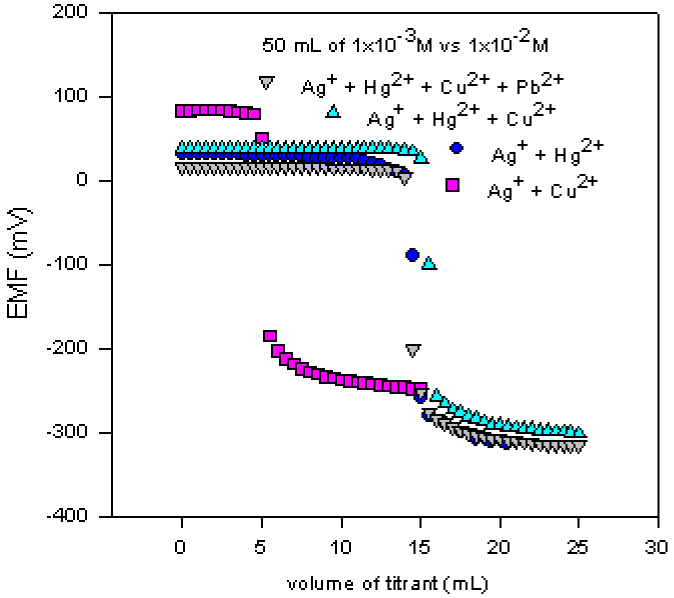

Figure 5.6(c): Potentiometric titrations of Ag^+ ions against I^- ions in presence of interfering metal ions Cu^{2+}, Hg^{2+} and Pb^{2+}

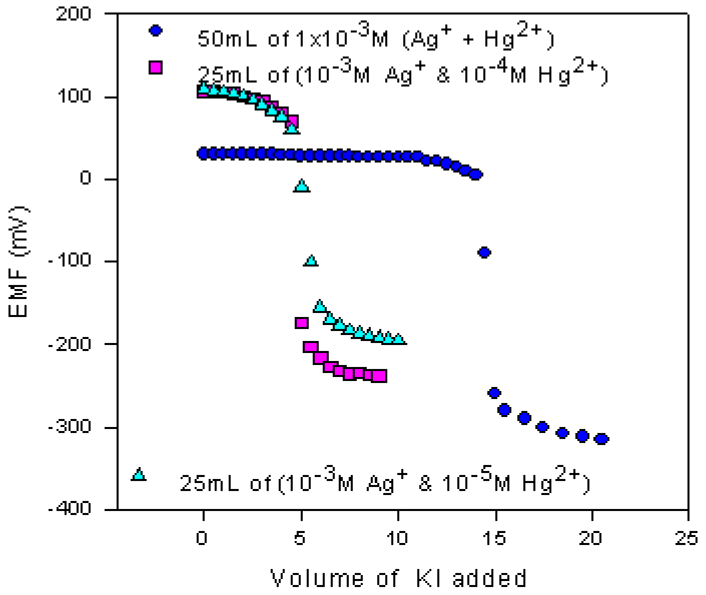

Figure 5.7(c): Potentiometric titration of Ag^+ ions against I^- ions in presence of different concentrations of Hg^{2+} ion

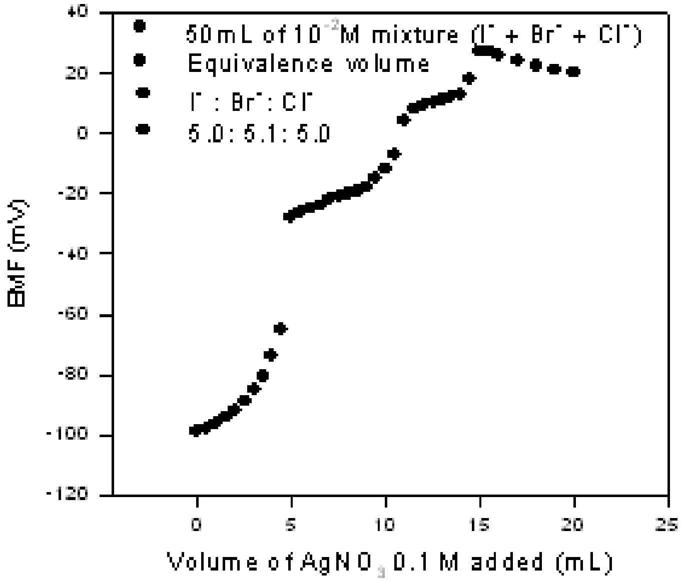

Figure 5.8(c): Simultaneous determinations of halide ions by potentiometric titration against Ag^+ ions

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5(d) Potentiometric Performance of 8-hydroxyquinolinol-based Tetrapodal Ionophore as Coated-wire Electrode for Silver (I) Ions

Introduction

Coated-wire electrodes (CWEs) were first introduced in the mid of 1970's by Freiser (1-3). In the classical CWE design, a conductor is directly coated with an appropriate ion-selective polymer membrane (PVC) to form an electrode system that is sensitive to electrolyte concentrations. The CWE response is similar to that of classical ISEs, with regard to detecting ability and range of concentration. The great advantage is that it eliminates the need for an internal reference electrode, resulting in benefits during the desire to miniaturise and mass fabricate sensors. This has led to the development of potentiometric solid-state sensors with new sensing systems, namely solid contact electrodes (SCEs) (4) such as solid crystal membranes and coated-wire electrodes (CWEs) (5-9). The substrate in the wire-type electrodes is usually a platinum wire, but silver, copper and graphite rods have also been used. CWEs are manufactured by dipping a metal wire into a solution of the membrane mixture. This is particularly useful for the *in- vitro* and *in-vivo* biomedical and clinical monitoring of different kinds of analytes.

Out of seven possible quinolinols, only 8-quinolinol forms chelate compounds with metal ions (10). On the basis of stability regularities two classes of divalent metal oxinates have been distinguished: those in which the metal ion reacts primarily with the negatively charged oxygen (zinc, cadmium, magnesium) and those in which the primary reaction may be possible with the covalent nitrogen (cobalt, copper, nickel) of the ionophore.

The recent reports (11-21) and reviews (22-23) show that a lot of improvement in the performances of coated-wire electrodes is still required to be made.

Experimental

Reagents

Reagents, like dibutyl phthalate (DBP), 2-nitrophenyl octyl ether (2-NPOE), were procured from Sigma-Aldrich. All other chemicals were of analytical reagent grade. Double distilled deionized water was used throughout the experiments.

Ionophore and its Special Features

The phenomenon of recognition depends primarily on multiple host–guest interactions. Locking for conformations of both the host and the guest makes negative contributions to the total free energies of the system. So, in addition to the complementarity of binding sites, the spatial placement of subunits constitutes the major criteria for designing new receptors (24-27). Synthetic receptor molecules that selectively complex with charged guest molecules can be used to transport salts through liquid membranes and to transduce chemical information into electronic signals. In both cases, the receptor molecules are present in thin membranes in contact with aqueous solutions. Extreme lipophilicity of the receptor molecules is therefore required. 8-Hydroxyquinoline and its derivatives are known to be the best chelators after EDTA and its derivatives, due to their guest- modulated chromogenic and fluorescent behaviour. Accordingly, they have attained prime significance and have been used in metal ion extraction and detection by various methods. It was designed to exhibit complexation properties with Ag^+ ions and has been synthesized by our co-workers (28).

Electrode Preparation and EMF Measurements

The procedure for the membrane preparation (29) is as follows: Poly(vinylchloride) (PVC) (33%), 2-nitrophenyloctylether (2-NPOE) (62%), 1,2,4,5-tetrakis(8-hydroxyquinolin oxymethyl)benzene (4%) were dissolved in 5-6 mL of THF. The solution was reduced to 2-3 mL by evaporation. To prepare an electrode, a platinum strip of 0.25 cm^2 was dipped in a highly viscous solution for several times. A membrane was formed on the platinum surface and it was allowed to evaporate in air for 5-6 hours. The electrode was conditioned by soaking in 0.1 M aqueous solution of $AgNO_3$ for 24 hours.

All emf measurements were carried out with the following electrochemical cell assembly:

$$\textbf{SCE} \,||\, \textbf{Ag}^+ \textbf{ test solution} \,|\, \textbf{ionophore membrane} \,|\, \textbf{Pt}$$

A digital potentiometer (accuracy, ±0.1 mV, Equip-tronics, EQ-602, India) was used for the potential measurements at 25±0.1 °C. Activities were calculated according to the Debye-Huckel equation. $AgNO_3$ solutions for the calibration of the electrode were obtained by gradual dilution of 0.1 M $AgNO_3$ solution. The salt bridge used was made from Agar-Agar and KNO_3.

Results and Discussion

An interesting application of the Ag^+ ionophore is also the incorporation of Ag^+ complexes of such ionophores into membranes that directly contact a Pt surface. The reversible Ag^+/ionophore couple gives a well-defined phase boundary potential at the membrane-solid interface, eliminating the need of an internal solution (1). The ideal relationship between the electrode output (mV) and the activity a_i of the ion of interest is given by the Nernst equation. In practice no ion-selective electrode has an ideal selectivity for one particular ion and under most conditions, there is more than one ion present in the sample solution and the contribution to the emf by the interfering ion is also to be considered. The modified form of the Nernst equation, i.e. The Nicolski-Eisenman equation is used for calculating the selectivity of the electrode by fixed interference method (FIM).

The soft heavy metal ions such as Ag^+, $Pb^{2+}$and Hg^{2+} have a great affinity to soft coordination centers, like nitrogen and sulfur atoms (29-32). The proposed tetrapodal ionophore is free from sulphur donor atoms on the principle of "Hard Soft Acid Base" concept and it is expected less interfering from Hg^{2+} ions. Four nitrogen atoms, which act as donor atoms and coordinate effectively with silver ions, make the ionophore more suitable for Ag^+ ions. The structural features of ligands containing only nitrogen donor atoms is likely to select only Ag^+ but not mercury ions, otherwise mercury is a serious interference in all silver ion-selective electrodes due to their common d^{10} system.

Optimization of the Membrane Composition

Nature and amount of the membrane ingredients affect the sensitivity and selectivity of the electrode (33-36). Performance characteristics of several membranes having different compositions are shown in Table 5.1(d). Increasing the ligand concentration improves the performance of the electrode in slope and detection limit and attained the best response at 4% of it. Membrane at Sr. No. 3 giving a Nernstian slope was selected for further studies. Among the three different plasticizers, 2-NPOE, DBP and BES, 2-NPOE is the best plasticizer. Its high dielectric constant helps the ionophore in free movement and fast exchange in complexation and decomplexation between ionophore and silver ions.

Calibration Curve

The electrode shows a linear response towards Ag^+ ions over a wide concentration range from 10^{-5} M to 10^{-1} M. The calibration curve has a slope of 60 mV/decade with a detection limit of $1x10^{-6}$ M obtained from the intersection of the two straight-line portions of the curve. The calibration curve was drawn 5 times and the representative curve is shown in Figure 5.1(d).

Detection Limit by Potentiometric Titration Method

Further, the detection limit is evaluated by another method based on potentiometric titration of different concentrations of silver ions against KI solution. During each titration, the concentration of potassium iodide is about 10 fold of Ag^+ ions. The plots between emf and volume of KI are a perfect sigmoidal curve and exhibit an 1:1 stoichiometry of AgI precipitation up to a concentration of $1x10^{-4}$ M. At $1x10^{-5}$ M and $1x10^{-6}$ M it shows a semi-sigmoidal curve but is good enough to indicate 1:1 stoichiometry of the reaction in Figure 5.2(d) and exhibits an 1:1 complexation. Beyond this concentration, the sigmoid curve becomes parallel to the X-axis. This shows that the detection limit can be taken as $1x10^{-6}$ M. This method is better than the conventional method in which the detection limit is taken as the point of intersection of the two straight-line portions of the curve. The main advantage here is that there is no consideration of a liquid junction potential in our proposed method as only the relative emf is plotted against the volume of the reagent, and absolute values of the emf are not required. Moreover, potentiometric titrations are always more accurate than direct potentiometry.

Effect of pH

The electrode response was studied by varying the pH in the range from 2 to 12 using an Ag^+ concentration of $2X10^{-3}$ M. The pH was adjusted by the addition of the required amount of nitric acid or sodium hydroxide solution, as appropriate. It was observed that the membrane electrode response was independent of pH over the range of 3.5-8.0. Below and above this range in Figure 5.3d(i), the variation is due to interferences from excess H^+ ions and hydrolysis of Ag^+ and formation of silver hydroxide.

Further, the pH effect on the emf was studied in presence of other interfering ions, like Hg^{2+}, Cu^{2+} and Pb^{2+}. In case of Ag^+ and Cu^{2+}, the emf decreased with increase in pH up to pH=6, after this when pH is lowered to pH=5, the emf is increased by about 30 mV. It remains constant at this level up to pH=8 and above this value, the emf decreases sharply due to the formation of Ag^+ hydroxide.

In presence of Hg^{2+}, the initial pH of the Ag^+ solution was about 1.5. It was raised by the addition of sodium hydroxide solution and corresponding emf measurements were done. Plots between pH *vs* emf show that there is a stable emf up to pH=3.5, thereafter, the emf decreases sharply upto pH=4 again it becomes constant up to pH=8.2. This trend may be done due to precipitation of Hg^{2+} ions with OH^- ions to form $Hg(OH)_2$ up to pH=3, while Ag^+ is still not precipitated and give a stable emf up to pH=8. Above this pH, a sharp decrease in emf indicates the precipitation of AgOH (see Figure 5.3d(ii)).

In case of ternary mixtures of Ag^+, Hg^{2+} and Cu^{2+} and four component mixtures of Ag^+, Hg^{2+}, Cu^{2+} and Pb^{2+} (each metal ion taken in equal concentration) it shows two emf trends one in the range of 1.5 to 3.5 and the other one from 4.0 to 8.0. These are due to the precipitation of Hg^{2+} and Ag^+ ions, respectively. It may be due to the reason that at pH=6, copper hydroxide formation starts and continues up to pH=7. Hence, during this process, the interference from copper ions was removed and the emf rises again (due to Ag^+ ions only). The pH effect studies support the selectivity behaviour of the ionophore towards silver ions as in the presence of interfering ions the emf response changes as a function of pH.

Potentiometric Selectivity Coefficients

The selectivity of any chemical sensor is clearly one of its most important characteristics as this property often determines whether the sensor can be used reliably for the target sample or not. It was evaluated by fixed interference method (37) as well as matched potential method. Interfering ion concentration was fixed at $1x10^{-2}$ M during $K_{i,j}$ determination by FIM.

From the data in Table 5.2(d) we can find that there is no serious interference from common ions, like

Hg^{2+} and Pb^{2+}. The reported logK values are in the range of -2.0 to -2.5. These values show a high selectivity of the proposed electrode system in presence of the interfering ions having similar chemical properties. At the same time, the limits indicate that alkali metal ions have more tendency to interfere. More interference from alkali metal ions as seen in FIM method can be associated to the limitations of the FIM as it depends on charge on the ion.

Direct Titration and Reverse Titration

Potentiometric titrations were carried out in the forwarded direction by taking Ag^+ ions in the titration vessel and iodide ion solution added from the burette. The plots are between emf drawn between emf and volume of the reagent added. Titration was also carried out in the reverse order, i.e. KI is taken in the titration vessel and is titrated against $AgNO_3$. The equivalence point of reverse titration is observed at the same position to that for the forward titration the 1:1 stoichiometry is confirmed as well as fast kinetics of the reaction at the electrode surface (see Figure 5.4(d)).

Determination of Ag^+ in Presence of Interfering Ions

Mixtures of Ag^+ with interfering ions, like Hg^{2+}, Cu^{2+}, Pb^{2+} were taken in different proportions and titrated against KI. The inflection points of these titration curves were used to estimate the extent of interferences shown, if any. Synthetic samples were prepared by taking into consideration the alloys of silver with these metals. Solutions of mixtures of Ag^+ ($1x10^{-3}$ M) with each of the interfering ion ($1x10^{-3}$ M) were titrated separately against KI ($1x10^{-2}$ M). The plots show that there is no interference from Cu^{2+} and Pb^{2+} ions, as the equivalence point is obtained corresponding to an 1:1 stoichimetry. A very interesting observation is noticed when Hg^{2+} is studied as an interfering ion. Experiments were performed for potentiometric titration of $AgNO_3$ against KI in the presence of Hg^{2+} ions. In an equimolar mixture of Ag^+ and Hg^{2+} ions, the equivalence point corresponds to 3 equivalents of iodide ions. It is clearly indicated that 1/3rd (1-equivalent) of the reagent is used up in precipitating the Ag^+ ions and 2/3rd (2-equivalents) are used up for precipitating the Hg^{2+} ions. Fortunately, the extent of Hg^{2+} of interference is quite predictable because the equivalence point is obtained at the expected point of equivalence. Hg^{2+} interferes in such a way that the extent of interference can be easily predicted. However, its presence doesn't alter the equivalence point of Ag^+. Hence, Hg^{2+} is a systematic interfering ion. Many reports (38-42) indicate that Hg^{2+} is a serious interfering ion. Even though the proposed electrode shows moderate values of selectivity coefficient for mercury, the potentiometric titration values show that there is a calculated interference from mercury ions. Hence, the usage of a proper experimental procedure brings the electrode close to the ion-specific electrode for Ag^+ ion in presence of Hg^{2+}.

Further, the 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. This is due to the reason that Ag^+ and $Hg^{2+}$are isoelectronic and both of these have a 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}). 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 Ag^{+} is completely precipitated and Hg^{2+} starts forming precipitation with iodide ions. During this part of titration, first Hg^{2+} is precipitated with iodide ions because of its lower K_{sp} value ($5x10^{-29}$) than AgI ($K_{SP}=1x10^{-16}$). After the complete precipitation of Hg^{2+} as Hg_2I_2, the precipitates of AgI begin. This indicates that the ionophore is not able to distinguish between Hg^{2+} and Ag^{+} ions. As the concentration of interfering ions is decreased from

10^{-3} M to 10^{-4} M, the inflexion point of titration is remaining the same as if no Hg^{2+} ions are present, clearly that there is no interference by the Hg^{2+} ions (see Figure 5.5(d)) at the concentration less than 10^{-3} M of Hg^{2+} ions. The conclusion of this observation is that the proposed electrode is behaving like an OFF and ON with respect to an interference of Hg^{2+} at certain concentration levels.

Determination of SCN^{-}, CN^{-}, and IO_3^{-} Contents Present in Spiked Samples

Silver forms complexes with species, like SCN^{-}, CN^{-}, IO_3^{-}, etc., in a stoichiometric way. Potentiometric titration for sulphide ions was carried out by taking a solution of silver ions in the vessel, and sodium sulphide is added from the burette. The potentiometric titration curve is shown in Figure 5.6d(i). While in case of cyanide, thiocynate and iodate the anion solution was taken in the titration vessels and silver ion solution was added from the burette, because of the severly hazardous nature of the CN^{-} and SCN^{-} solutions. Titration curves are shown in Figure 5.6d(ii) and Figure 5.6d(iii), respectively. The inflexion points of titrations for the IO_3^{-} and SCN^{-} curves are sigmoid in nature and that for the CN^{-} is semi-sigmoidal. All the curves shown here are sharp enough to calculate the inflexion points accurately. So, the method can be applied for a quantitative determination of the reported anions.

Simultaneous Determination of Halides from a Mixture

To establish the applicability of the proposed chemical sensor for Ag^{+} ions, potentiometric titration of a mixture of halide ions containing equal concentrations of F^{-}, Cl^{-}, Br^{-} and I^{-} ions was carried out against $AgNO_3$. The proposed chemical sensor based on the ionophore was used as an indicator electrode. The titration curve shows four inflexion points corresponding to the precipitation of I^{-}, Br^{-}, Cl^{-} and F^{-} in the given sequence in Figure 5.7(d). The inflexion points are well defined for each part of the curve. A little deviation near the end of the titration for the F^{-} ion may be due to the relatively high solubility product value of AgF as compared to AgCl ($1x10^{-10}$ M), AgBr ($4x10^{-13}$ M) and AgI ($1x10^{-16}$ M).

This application establishes that the electrode is a versatile chemical sensor for the determination of Ag^{+} ions as well as the anions forming stable complexes or precipitates with Ag^{+} ions.

Determination of Chloride Contents in Tap Water

The proposed electrode was used for determing the chloride contents present in drinking water, both in boiled and natural conditions. The chloride contents determined by these methods were compared with those measured using the Orion Ion-Selective Electrode for Cl^- ions (941600). The results are comparable and shown in Table 5.3(d). The results indicate a satisfactory application of the proposed sensor for the Cl^- ion determination.

***

Table 5.1(d): Optimization of membrane ingredients for tertrapodal-based Ag-ISE

Sl. No	PVC, (Wt%)	Plasticizer, (Wt%)	Ionophore, (Wt%)	NaTPB, (Wt%)	Slope, (mV/ decade)	Detection limit, [M]
1	33	65	2	-	70	$1x10^{-4}$
2	33	64	3	-	62	$6x10^{-5}$
3	33	63	4	-	60	$1x10^{-6}$
4	33	62	5	-	60	$3x10^{-6}$
5	33	61	6	-	56	$5x10^{-5}$
6	33	60	7	-	51	$6.3x10^{-5}$
7	33	59	8	-	47	$1x10^{-4}$
8	33	63	4(DBP)	-	62	$5x10^{-5}$
9	33	63	4(BES)	-	51	$5x10^{-5}$
10	33	62	4	1	60	$1x10^{-5}$
11	33	61	4	2	40	$1x10^{-5}$
12	33	60	4	3	52	$5x10^{-5}$

Table 5.2(d): Potentiometric selectivity coefficient by FIM and MPM for tetrapodal-based Ag-ISE

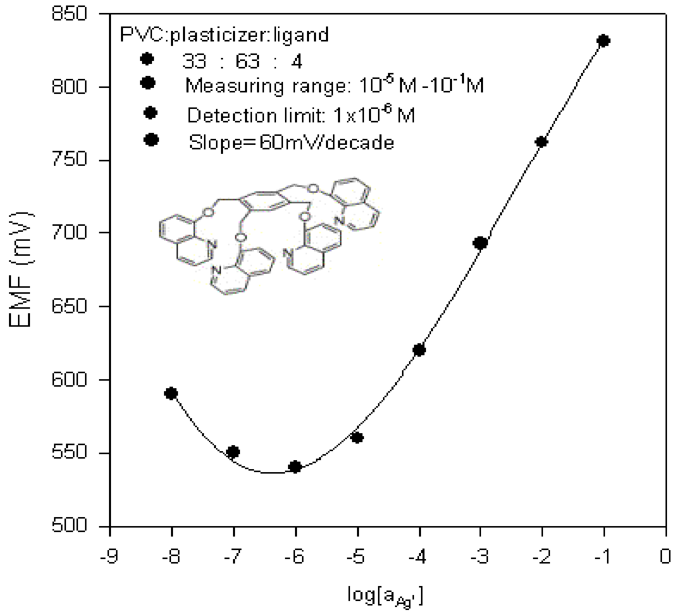
$\log K_{Ag,B}^{Pot}$

Interfering Ions (B)		
	FIM	**MPM**
Na^+	-1.1	-1.6
K^+	-1.5	-1.8
Mg^{2+}	-2.2	-2.2
Ca^{2+}	-2.2	-2.2
Sr^{2+}	-2.6	-2.5
Pb^{2+}	-2.5	-2.3
Cu^{2+}	-2.6	-2.3
Co^{2+}	-2.5	-2.3
Ni^{2+}	-2.0	-2.2
Zn^{2+}	-2.3	-2.3
Cd^{2+}	-2.0	-2.2
Hg^{2+}	-1.9	-2.1
Fe^{3+}	-2.5	-2.3

(FIM: Primary ion concentration varied from $1x10^{-1}$ M to $1x10^{-6}$ M, Interfering ion concentration is $1x10^{-2}$ M, MPM: Primary ion concentration is $1x10^{-2}$ M-$1x10^{-4}$ M, reference solution is $1x10^{-4}$ M and interfering ion concentration added is $1x10^{-2}$ M)

Table 5.3(d): Comparison of chloride content in water samples determined by Tetrapodal-based Ag-ISE and Orion chloride-selective electrode

Sr. No.	Sample	Chloride contents in sample water (ppm)	
		Proposed electrode	Cl^--selective electrode (Orion 941600)
1	Natural water	(i) 7.0 (ii) 6.9 (iii) 7.1	(i) 6.8 (ii) 6.8 (iii) 6.8
2	Boiled water	(i)149 (ii) 149 (iii) 149	(i)150 (ii)150 (iii)151



rapodal ionophore

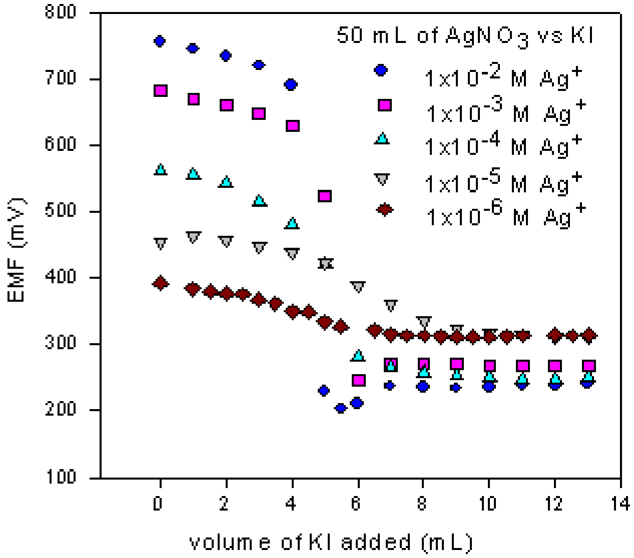


Figure 5.2(d): Potentiometric titrations of different concentrations of $AgNO_3$ against KI for Ag-ISE based on tetrapodal ionophore

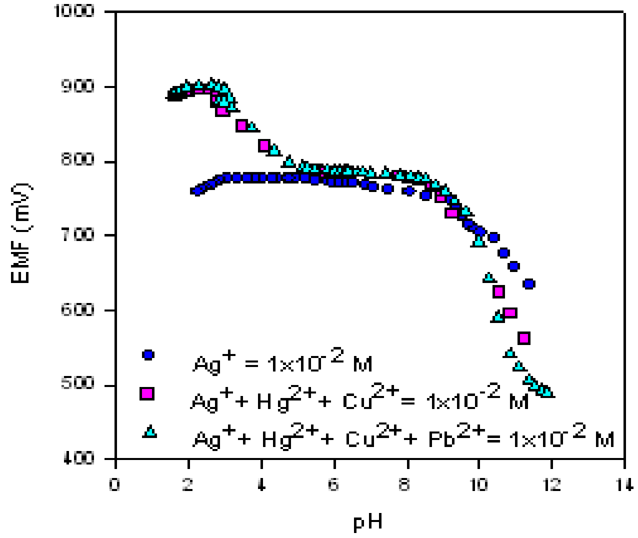


Figure 5.3d(i)

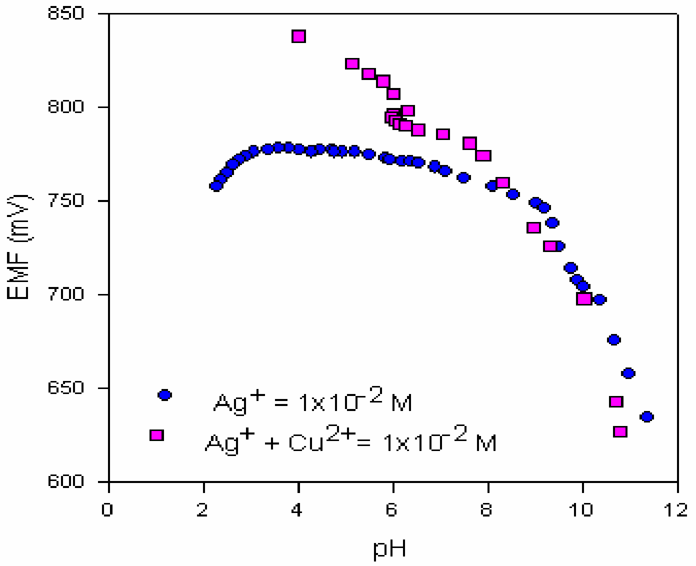


Figure 5.3d(ii)

Figure 5.3(d): Effect of pH on the response of Ag-ISE based on tetrapodal ionophore in presence of

(i) Ag^+ ions and Ag^+ and Cu^{2+} ions
(ii) Ag^+ ions; Ag^+, Cu^{2+} and Hg^{2+} ions; Ag^+, Cu^{2+}, $Hg^{2+}$and Pb^{2+} ions

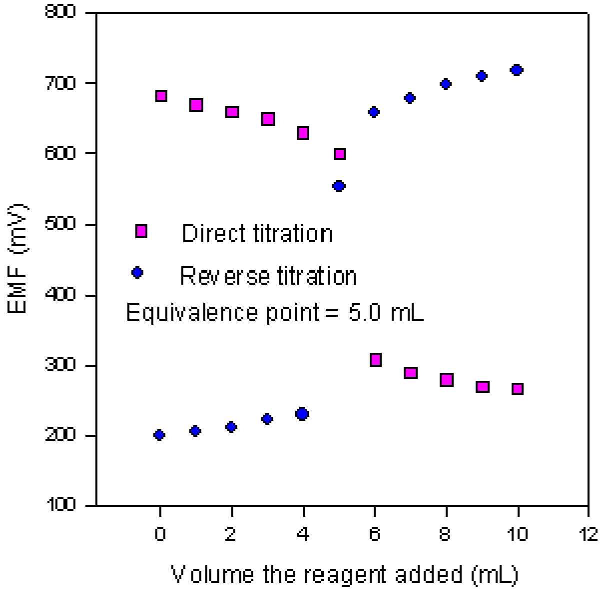


Figure 5.4(d): Potentiometric titration of Ag^+ ions against I^- ions (direct and reverse) using Ag-ISE based on tetrapodal ionophore

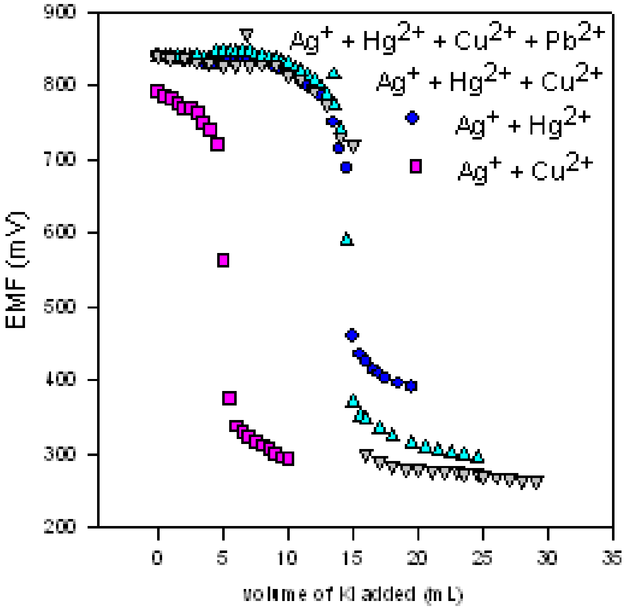
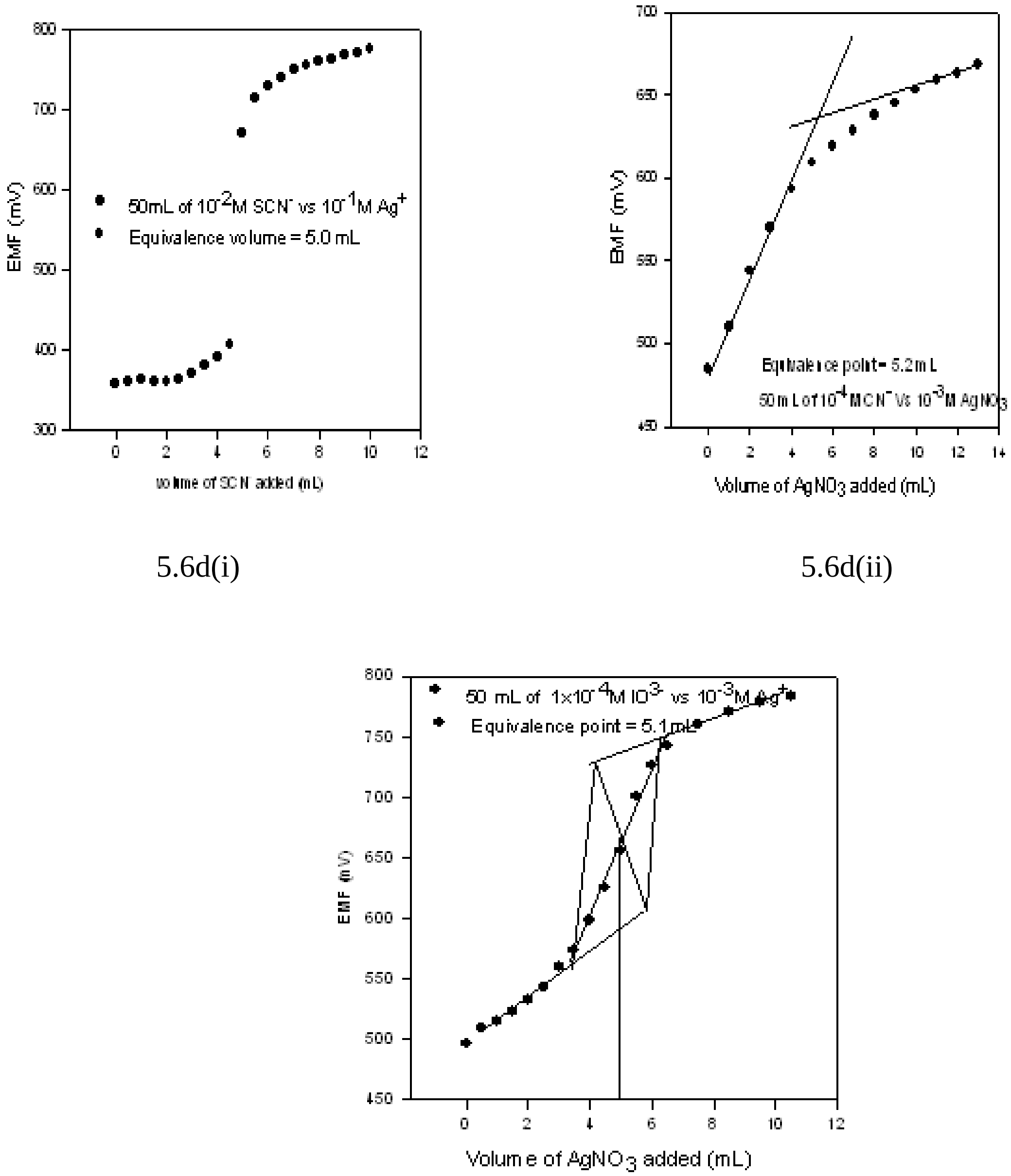


Figure 5.5(d): Potentiometric titrations using binary, ternary and quaternary mixtures of silver and interfering ions



5.6d(i) 5.6d(ii)

5.6d(iii)

Figure 5.6(d)[i, ii and iii]: Determination of SCN, CN$^-$ and IO$_3^-$ contents present in the sample by potentiometric titration against AgNO$_3$ solution using Ag-ISE based on tetrapodal ionophore

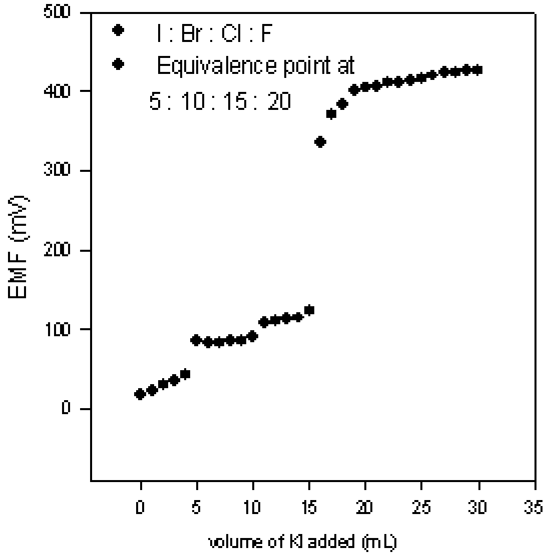


Figure 5.7(d): Simultaneous determinations of halide ions by potentiometric titration against Ag$^+$ ions using Ag-ISE based on tetrapodal ionophore

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5(e) 8-Hydroxyquinoline-based Neutral Tripodal Ionophore as a Copper (II)-selective Electrode and the Effect of Remote Substitutents on Electrode Properties

Introduction

8-Hydroxyquinoline is the name, most frequently used in the analytical chemistry; the common name oxine is very convenient, particularly for the description of the chelate compounds, which may be oxinates. Out of seven possible quinolinols only 8-quinolinol forms chelate compounds with metal ions. The uses of these chelate compounds for the determination of the metals, particularly magnesium and aluminium have been the subject of more than five hundred research articles since 1927, as well as of several reviews. On the basis of stability two classes of divalent metal oxinates have been distinguished: those in which the metal ion reacts primarily with the negatively charged oxygen (zinc, cadmium, magnesium) and those in which primary reaction may be possible with the covalent nitrogen (cobalt, copper and nickel) (1).

8-Hydroxyquinoline and its derivatives have found extensive applications as analytical reagents in absorption spectrophotometry, fluorometry, solvent extraction and partition chromatography because of their ability to form complexes with many metal ions. 8-Hydroxyquinoline and its derivatives are also used as fungicides, amoebicides, bactericides and insecticides (2).

In view of the design, synthesis and potentiometric characterization of new ionophores that are either more selective than those of previous reported or can recognize additional ionic species, still remains an important topic of research. Carrier-based PVC-membrane electrodes are routinely used as analytical tools for the monitoring of a wide variety of different ions in various samples (3-6).

Tripodal ionophores (7-12) are gaining increasing interest as tools for their analysis and separation of metal ions as well as for many biological and other applications. A novel 8-Hydroxyquinoline based tripodal ionophore (13) has been synthesized by our coworkers and characterized as a neutral carrier ionophore selective for Cu(II) ions. Due to three flexible donor atoms (N atoms) containing 8-oxine ligands it selectively forms a complex with Cu(II) ions over a large number of other ions.

Cu(II) is the third in abundance [after Fe(II) and Zn(II)] amongst the essential heavy metal ions in human body and plays an important role in various biological processes. Cu(II) is also a significant metal pollutant due to its widespread use. The Cu(II) toxicity for humans is although low compared to other heavy metals but certain microorganisms are affected by even a submicromolar concentration of Cu(II). Though average concentration of Cu(II) in earth crust is nearly 50 ppm, but a concentration as high as 2000 ppm has been found near copper production facilities and in soil near to copper industries disposed off sites.

Due to the vital importance of copper in many biological systems (14,15) and industry (16) and the need for a copper-selective electrode for the potentiometric monitoring of Cu^{2+} in trace concentrations in different industrial, medicinal and environmental samples, a variety of ion carriers have been used in the construction of copper (II)- selective electrodes. However, poor detection limit and serious interference of metal ions, like Fe^{3+}, Na^{+}, Sr^{2+}, Co^{2+}, Ni^{2+}, K^{+}, Hg^{2+} and Ag^{+} in estimation of Cu(II) has necessitated the development of new Cu(II) potentiometric electrodes. Atomic absorption spectrometery and spectroscopic methods are also used for the estimation of Cu(II). However, due to their expensive analytical approach, simpler and economical methods are required. In recent years, the ion-selective electrodes commonly based on ionophores have provided simpler and economical approaches for estimation of various metal ions.

A number of potentometric sensors based on different ionophores have been reported. In these, some of the copper sensors are - alkyl thioglycolic acid ($RSCH_2COOH$, R= C_{9-11}) (17,18), thia crown ethers (19,20), calixarenes (21,22), Schiff's bases (23,24) and noncyclic neutral ionophores (25,26). In addition, some solid-state electrodes based on CuS-Ag_2S are also well established (27,28), but cations such as Hg^{2+}, Hg_2^{2+}, Ag^{+} and Fe^{3+} present serious interferences (29, 30). Reviews on carrier-based ion-selective electrodes (31-35) and recent reports (36-41) provide a good comprehensive survey of the literature.

It shows that no mesitylene-based carrier is used in making a membrane electrode. So, we report 2,4,6-Tris(8-quinoloxymethyl)1,3,5-trimethylbenzene [MOH8Q], 2,4,6-Tris(5-chloro-8-quinoloxy)1,3,5-trimethylbenzene [5CHQ], 2,4,6-Tris(5-benzoyl-8-quinoloxy methyl)1,3,5-trimethylbenzene [5BHQ] and 2,4,6-Tris(5-benzohydroxy-8-quinoloxy- methyl)1,3,5-trimethylbenzene [HYD-8HQ] ionophores as Cu^{2+}-selective membrane materials. Mesitylene provides a platform and 8-oxine groups are acting as ligands. Mesitylene substituted at 2, 4, 6 positions by 8-oxine provide the ionophore and dibutyl phthalate is applied as a plasticizer. Tetrahydrofuran (THF) is used as a solvent mediator for casting the membrane.

Experimental

Reagents

Reagents, like dibutyl pthalate (DBP), 2-nitrophenyloctyl ether (2-NPOE), bis-2-ethyl sebacate (BES) and potassium salt of tetrakis(4-chloro-phenyl) borate (KTPClB) were procured from Sigma-Aldrich. All other chemicals were of analytical reagent grade. Double distilled deionized water was used throughout the experiments.

Electrode Preparation

Membranes of 0.2 mm thicknesses were obtained by pouring a solution of the membrane components: PVC, 33%; ligand, 2-6%; dibutyl phthalate, 63% dissolved in 2-3 mL of THF. The viscous solution of polymer, thus obtained was poured in a glass ring and transformed into a membrane as explained in previous sections of this chapter. The prepared membranes were removed from the glass ring and circular pieces of 1.25 cm diameter were cut and mounted on the ground end of a Pyrex glass tube with araldite and conditioned with $Cu(NO_3)_2$ solution (0.1 M) for 24 hours.

EMF Measurements

All the emf measurements were carried out using the following cell assembly:

$$\mathbf{SCE \mid 0.1\ M\ Cu^{2+} \mid\mid membrane \mid\mid Cu^{2+} test\ soln \mid SCE}$$

A digital potentiometer (Equiptronics EQ602, India) was used for the potential measurements at 25±0.1 °C. Activities were calculated according to the Debye-Huckel equation (42). Standard $Cu(NO_3)_2$ solutions were obtained by gradual dilution of 0.1 M $Cu(NO_3)_2$ solution and their potential measurements were performed in unbuffered solutions.

Results and Discussion

Potential Response and Selectivity of the Electrode

An electric potential is developed across the membrane when electrolyte solutions of different activities of Cu(II) ions are placed on either side of it. Its magnitude depends on the activities of the ions aswellas the characteristics of the membrane components and their relative ratios. Selectivity of the membrane represents a special attraction for that ion in presence of other similar ions. Selectivity is a function of free energy change resulting from complexation and decomplexation of the ionophore with Cu(II) ions. As the water uptake capacity of such membranes changes with the amounts of plasticizer, the amount of plasticizer is also known to influence the magnitude of potential. In our study, electrodes with different amounts of the ionophore and plasticiser are evaluated. The fabricated electrodes are tested by observing parameters, like slope, detection limit and response time repeatedly to check the reproducibility for each membrane electrode. The response is consistent in slope of the calibration curve as well as the detection limit. The optimum concentration of the ionophore was selected by changing the ionophore content from 2% to 6 % (by weight) with increments of 1% each time [seeTable 5.1(e)]. Selectivity coefficients were determined by Fixed Interference Method (FIM), in which a fixed concentration of the interfering ion ($1x10^{-3}$ M) was mixed with the copper ion solutions ranging from 10^{-8} M to 10^{-1} M. Selectivity co-efficients are calculated from the detection limit of the extrapolated calibration curves. This experiment was done for a number of metal ions, like Na^+, K^+, Cd^{2+}, Pb^{2+}, etc., as interfering ions, by using the same concentration. From the results, it is observed that the electrode recognizes the primary ion [Cu^{2+}] reasonably well even when some other ion is present. The log $K^{Pot}_{Cu,M}$ values lie in the range of -1 to -3 for most of the metal ions indicating an excellent selectivity of the membrane for Cu(II) ions that is shown in Tables 5.2(e) and 5.3(e).

Optimization of the Membrane Composition

Sensitivity and selectivity of an electrode are significantly affected by the nature of plasticizer (43, 44), composition of the membrane (45), internal solution (46,47), etc. The effect of composition on the response characteristics of the electrode, like slope of the calibration curve, measurement range and detection limit were studied. The electrode with the ratio PVC:DBP:MHO8Q ; 33%:63%:4%, exhibited the best response with a slope of 30 mV per decade. As it is obvious from Table 5.1(e), DBP is a more effective solvent medium than 2-NPOE in preparing the Cu^{2+} ion-selective electrode. Sensitivity of the electrode is affected by the amount of the ionophore MO8HQ. It increases with increasing ionophore content until a value of 4% (w/w) is reached. A number of composition with varying amounts of the ionophore and the plasticizer content were tried for the substituted ionophores-based membranes, like 5CHQ, 5BHQ and HYD-8HQ. Membranes of 5CHQ, 5BHQ and HYD-8HQ having compositions of PVC:DBP:ionophore as 33:61:6 9 wt% show the best responses as regards the slope and the measuring range concentrations. These electrodes were selected for further studies. A further increase of the amount of ionophore resulted in a decrease in the slope of the electrode. This may be due to the reason that equilibration of the ionophore with the metal ion is maximum at this composition.

The addition of potassium salt of tetrakis(4-chloro-phenyl) borate (KTPClB) is known to increase the sensitivity of the membrane (48) as it reduces the anionic interference. It is observed that the addition of a lipophilic cation (KTPClB) does not affect the working electrode response and hence, is not used in the membrane preparation.

Effect of pH

The influence of pH on the response of the membrane electrode (MO8HQ, 5CHQ, 5BHQ and HYD-8HQ) was studied at 2 different concentrations, i.e. $1x10^{-3}$ M and $1x10^{-4}$ M, over a pH range 1-12. The pH was adjusted by introducing small drops of HNO_3 (0.1 M) or NaOH (0.1 M) as per requirement and the results are shown in Figure 5.2(e). The emf is independent of pH in the range of pH= 4-7 for MO8HQ while for 5CHQ and 5BHQ the pH range with stable electrode potential was 3-7 and HYD-8HQ pH was 3-9. The variations above and below this pH range may be due to the formation of $Cu(OH)_2$ and protonation of the nitrogen atoms of the ligand, respectively.

Effect of Internal Solution Concentration

The influence of the concentration of internal solution on the emf response of all Cu^{2+} ion-selective electrodes was studied and the results show that a variation in the concentration (1x10^{-1} M-1x10^{-4} M) of the internal solution does not significantly change the electrode response of slope while parameters, like measuring range and detection limit changed to considerable extent (Table 5.2(e)). A 1x10^{-3} M concentration of internal solution gave the best response in Figure 5.1(e) and was chosen for further studies.

Inhibition to the primary ion flux from the inner reference solution to the membrane phase is probably due to the sudden decrease in extraction of the anions due to “Donnan Exclusion Phenomenon”, e.g.[NO_3^-] from the inner reference solution to the membrane phase. This activity is possible due to the presence of donor nitrogen atoms of the ionophore in the membrane phase. However, the ratio of primary ion concentrations across the membrane changes with the change in concentration of the primary ion from the other side of the membrane. Another test to confirm that no actual transport of primary ion is taking place across the membrane is that the potential difference doesn’t change with time and remains stable up to five minutes, on keeping the electrode in a sample solution of very dilute concentration. This phenomenon is true and holds good for all primary ion concentrations in the test solution. It confirms that Donnan exclusion of the membrane is well established.

Calibration Curve, Detection Limit, Response Time and Lifetime

Calibration curves were drawn for all the electrodes (Electrode Nos. 4,16,21 and 26, respectively, for MO8HQ, 5CHQ, 5BHQ and HYD-8HQ) over a concentration range from 10^{-6} M to 10^{-1} M with an internal filling solution of Cu^{2+} (1x10^{-3} M) ions. All the electrodes showed reproducible slopes of 30 mV/decade. For five repeated experiments the standard deviations of the slopes were approximately ±0.5 mV. Representative curves are shown in Figure 5.3(e). The workable concentration range for MO8HQ, 5CHQ, 5BHQ and HYD-8HQ was found to be 1x10^{-6} to 10^{-1} M for Cu(II) ions. The workable concntration ranges for all the electrodes are comparable to each other and are all in the range 1x10^{-6} M. However, the detection limits, as calculated according to IUPAC recommendation [49], are 5x10^{-7} M for MO8HQ, 5x10^{-6} M for 5CHQ, 5x10^{-7} M for 5BHQ and 1.6x10^{-7} M for HYD-8HQ.

The membrane electrodes could be used for at least 4-5 months without any measurable divergence of emf. During this time detection limits of the sensors remained almost constant and slopes of the sensors varied ±2 mV of the reported value. After this time, the electrode behavior gradually decreased. Electrodes were stored in 1.0x10^{-3} M $Cu(NO_3)_2$ when not in use to avoid any change in the copper ion concentration in the membrane phase.

The contact time and concentration of equilibrating solution was also optimized so that the electrode generated stable and reproducible emfs at a relatively short response time. It is found that an equilibrating solution of 1x10^{-3} M and contact time of only five hours was appropriate for a smooth functioning of the electrodes. Once saturated, the electrodes get equilibrated within 1 hour after their reuse.

Response time is an important factor for any ion-selective electrode. In this study, the response time was recorded by changing the Cu^{2+} concentration over a concentration range from $1x10^{-8}$ M to $1.0x10^{-1}$ M. The response of the electrodes is stable within 20 seconds over a concentration from 10^{-6} M to 10^{-2} M. The response time increased up to 30 seconds when the concentration was reduced further to 10^{-8} M. This is due to the fast exchange kinetics of the metal-ligand complexation-decomplexation of the membrane interface at concentrations $\geq 10^{-6}$ M.

Selectivity Coefficients and Analytical Applications of Cu(II)-selective Electrode

Selectivity is perhaps the single most important characteristic of any electrode, which defines the nature of the device and the extent to which it may be employed in the determination of a particular ion in presence of other interfering ions. This is measured in terms of potentiometric selectivity coefficients (log $K^{Pot}_{Cu,M}$), which has been measured using the Fixed Interference Method (FIM) at $1x10^{-3}$ M concentration of interfering ions. The potentiometric selectivity coefficient is a measure of the response of the electrode for the primary ion in the presence of foreign ions. Table 5.3(e) shows log $K^{Pot}_{Cu,M}$ values for the MO8HQ-based copper-selective electrode that are compared with those reported for other Cu(II)-selective electrodes reported in literature. The selectivity coefficient data indicate that the $K^{Pot}_{Cu,M}$ values are in the order of 10^{-2} for divalent and trivalent metal ions (except Na^+, K^+, Mg^{2+}, Ag^+ and Pb^{2+}). Therefore, the electrode can be used for the determination of Cu^{2+} ions in the presence of certain interfering ions. The electrodes already reported in literature (50-54) generally suffer from a strong interference by mercury ions, but the proposed electrode system shows a good selectivity for copper ions even in the presence of these ions. Potentiometric selectivity coefficients of the copper- membrane electrodes were evaluated by the Fixed Interference Method (FIM) (48) at $1x10^{-3}$ M concentration of interfering ions.

Selectivity co-efficients for the substituted ionophore-based membrane electrodes are summarized in Table 5.4(e) for a number of interfering ions. It can be seen from the Table that the selectivity coefficient values are poorer when the –Cl group is the substituent at 5 position of the 8-hydroxy quionline as it decreases the lipophilicity of the ionophore. However, the ionophore substituted with benzoyl and hyrdroxy benzoyl groups (5BHQ and HYD-8HQ, respectivily) shows a better selectivity, as it is able to provide an appreciable lipophilic character to the ionophore. It is clearly seen from Tables 5.3(e) and 5.4(e) that selectivity coefficients are much better for HYD-8HQ, because of its relative bulkier size. Also, it helps in creating a strong charged anionic environment in the ligand so that there is probable no interference due to anions, as well. On the basis of the results, it is concluded that mesitylene substituted at the 2, 4, 6 position by 5-benzoyl-8-quinoline responds for Cu (II) ions in presence of a large number of common interfering ions, like Zn^{2+}, Hg^{2+}, Fe^{3+} etc., with a reasonably good degree of sensitivity and selectivity. This may be due to the dynamic complexing ability of the HYD-8HQ towards Cu(II) and consequently,the potential response of the electrode.

Effect of Electrode Response in Mixed Solvent Media

The working nature of the sensor was also studied using methanol-water, acetone-water and acetonitrile-water mixtures. The membranes showed a satisfactory response in a medium with non-aqueous content up to 40% (V/V). The working concentration range and slope remained almost the same except for a slight change in slope of about 2 mV/decade compared to that in the aqueous medium [see Table 5.5(e)]. However, the best response was observed at 20% non-aqueous content.

Potentiometric Titration

Potentiometric titrations were performed by using the proposed electrodes as indicator electrodes for the titration of 25 mL of $1x10^{-2}$ M Cu^{2+} ions against $1x10^{-1}$ M EDTA. pH of the solution was adjusted to 4.5-5.0 by using an appropriate volume of 0.1 M HNO_3. The titration curves are shown in Figure 5.4(e). The curves show sharp inflexion points at the titrant volume corresponding to the formation of an 1:1 complex of copper ions with EDTA.

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Table 5.1(e): Optimization of membrane ingredients for Cu-ISE based on tripodal ionophore

Sl. No	Ionophore	PVC, (Wt%)	Plasticizers (Wt%)	Ligand, (Wt%)	KTPClB	Slope, (mV/ decade)	Detection limit, [M]
1	MO8HQ	33	67	0		19	2.0x10^{-5}
2	MO8HQ	33	65	2		21	3.2x10^{-5}
3	MO8HQ	33	64	3		25	2.5x10^{-5}
4	**MO8HQ**	**33**	**63**	**4**		**30**	**6.3x10^{-6}**
5	MO8HQ	33	62	5		24	3.2x10^{-5}
6	MO8HQ	33	61	6		19	1.2x10^{-6}
7	MO8HQ	33	63(NPOE)	4		23	6.3x10^{-6}
8	MO8HQ	33	63(2BS)	4		27	7.9x10^{-6}
9	MO8HQ	33	61	4	2	31	1.6x10^{-6}
10	MO8HQ	33	60	4	3	21	1.2x10^{-6}
11	MO8HQ	33	59	4	4	21	3.2x10^{-6}
12	5CHQ	33	65	2		19	1.0x10^{-6}
13	5CHQ	33	64	3		23	1.0x10^{-6}
14	5CHQ	33	63	4		25	1.0x10^{-6}
15	5CHQ	33	62	5		27	1.0x10^{-6}
16	**5CHQ**	**33**	**61**	**6**		**30**	**1.0x10^{-6}**
17	5BHQ	33	65	2		25	1.0x10^{-6}
18	5BHQ	33	64	3		26	1.0x10^{-6}
19	5BHQ	33	63	4		27	1.0x10^{-6}
20	5BHQ	33	62	5		28	1.0x10^{-6}
21	**5BHQ**	**33**	**61**	**6**		**30**	**1.0x10^{-7}**
22	HYD-8HQ	33	65	2		26	1.0x10^{-6}
23	HYD-8HQ	33	64	3		26	1.0x10^{-6}
24	HYD-8HQ	33	63	4		27	1.0x10^{-6}
25	HYD-8HQ	33	62	5		28	1.0x10^{-6}
26	**HYD-8HQ**	**33**	**61**	**6**		**30**	**1.0x10^{-7}**
27	5CHQ	33	61 (NPOE)	6		26	1.0x10^{-6}
28	5BHQ	33	61(NPOE)	6		27	1.0x10^{-6}
29	HYD-8HQ	33	61(NPOE)	6		28	1.0x10^{-6}
30	5CHQ	33	61(sebcate)	6		21	5.0x10^{-5}
31	5BHQ	33	61(sebcate)	6		23	4.3x10^{-5}
32	HYD-8HQ	33	61(sebcate)	6		24	1.0x10^{-5}

Table 5.2(e): Effect of internal solution concentration on the membrane electrode

Electrode Composition	Internal solution concentration, M	Slope, (mV/decade)	Detection limit, M
MO8HQ	$1x10^{-1}$	30	$6.3x10^{-6}$
	$1x10^{-2}$	30	$1.0x10^{-6}$
	$1x10^{-3}$	30	$1.6x10^{-7}$
	$1x10^{-4}$	31	$1.6x10^{-7}$
5CHQ	$1x10^{-1}$	30	$1.6x10^{-5}$
	$1x10^{-2}$	30	$2.5x10^{-6}$
	$1x10^{-3}$	30	$3.0x10^{-6}$
	$1x10^{-4}$	31	$3.16x10^{-6}$
5BHQ	$1x10^{-1}$	30	$3.2x10^{-6}$
	$1x10^{-2}$	30	$3.9x10^{-6}$
	$1x10^{-3}$	30	$7.9x10^{-7}$
	$1x10^{-4}$	30	$2.5x10^{-7}$
HYD-8HQ	$1x10^{-1}$	30	$1.0x10^{-7}$
	$1x10^{-2}$	30	$7.9x10^{-8}$
	$1x10^{-3}$	30	$7.9x10^{-8}$
	$1x10^{-4}$	31	$7.9x10^{-8}$

Table 5.3(e): Selectivity coefficients of various interfering ions

Interfering ions (B)	**log $K_{Cu,B}^{Pot}$**								
Reference	**24**	**25**	**50**	**51**	**52**	**53**	**54**	**55**	**This work**
Na^+	+1.7	-3.8	-2.5	-	-1.0	-	-2.2	-2.1	-0.9
K^+	-	-3.8	-2.0	interfere	-	-	-2.	-2.0	-1.4
Mg^{2+}	-	-2.3	-2.7	-	-	-2.8	-3.4	-2.5	-1.8
Ca^{2+}	-	-2.6	-3.0	-1.9	-	-3.3	-3.4	-3.5	-2.2
Sr^{2+}	-	-2.8	-2.8	-	-	-	-	-3.9	-2.5
Ba^{2+}	-	-	-	-	-	-	-	-4.0	-2.3
Pb^{2+}	+0.8	-3.4	-0.9	-1.7	-	-	-	-3.8	-1.8
Ag^+	-	-	-	-	-	-	-1.6	-1.7	-1.4
Co^{2+}	0.0	-3.6	-3.2	-	-1.0	-1.9	-3.3	-2.8	-2.8
Ni^{2+}	+0.4	-2.6	-3.2	-	-	-3.0	-5.0	-2.8	-2.0
Zn^{2+}	-2.2	-1.5	-2.3	-	-	-	-3.3	-2.9	-2.3
Cd^{2+}	+0.6	-2.6	-2.8	-2.1	-	-2.1	-2.6	-3.3	-1.5
Hg^{2+}	-	-	-	-	-	-	-2.9	--	-0.8
Al^{3+}	-	-	-	-	-	-	--	-4.5	-3.0
Fe^{3+}	-	-	-	-	-	-	-3.5	-4.8	-2.2

Table 5.4(e): Selectivity coefficient values ($\log K^{Pot}_{Cu^{2+},M^{n+}}$) of different ionophore-based electrodes for a number of interfering metal ions by FID and MPM

Interfering ions	$\log K^{Pot}_{Cu^{2+},M^{n+}}$					
	5CHQ		**5BHQ**		**HYD-8HQ**	
	FID	**MPM**	**FID**	**MPM**	**FID**	**MPM**
Na^{+}	-0.2	-1.1	-0.9	-1.5	-1.9	-2.5
K^{+}	-0.5	-1.2	-1.1	-1.8	-1.8	-2.6
Ag^{+}	-0.7	-1.1	-1.2	-2.0	-1.3	-2.2
Mg^{2+}	-0.8	-1.0	-1.3	-1.5	-2.0	-2.3
Ca^{2+}	-0.8	-1.2	-1.3	-1.6	-1.7	-2.0
Sr^{2+}	-1.4	-1.5	-1.4	-1.7	-1.9	-2.0
Ba^{2+}	1.7	-2.0	-1.5	-2.0	-2.2	-2.5
Co^{2+}	-1.3	-1.6	-1.9	-2.3	-2.5	-2.5
Ni^{2+}	-1.5	-1.9	-1.8	-2.1	-2.5	-2.6
Cd^{2+}	-1.6	-1.8	-1.6	-2.1	-2.5	-2.7
Zn^{2+}	-1.7	-2.0	-1.9	-2.4	-2.9	-3.0
Pb^{2+}	-1.3	-1.8	-1.4	-1.7	-1.6	-2.6
Hg^{2+}	-1.0	-1.5	-1.2	-1.5	-2.3	-2.4
Fe^{3+}	-1.1	-1.6	-1.3	-2.0	-2.4	-2.6
Al^{3+}	-0.9	-1.4	-1.6	-2.0	-2.2	-2.8

(Experimental conditions for matched potential method: Primary ion is copper nitrate solution ($1x10^{-7}$ to $1x10^{-1}$ M), reference solution is copper nitrate of $1x10^{-6}$ M, interfering ion concentrations are $1x10^{-5}$ to 10^{-2} M)

Table 5.5(e): Electrode response in mixed solvent media

e of lvent	Mixed solvent (%)	Slope, mV/decade				Detection Limit, (M)			
		MO8HQ	**5CHQ**	**5BHQ**	**HYD-8HQ**	**MO8HQ**	**5CHQ**	**5BHQ**	**HYD-8HQ**
nol	10	33	25	32	33	$3x10^{-6}$	$6x10^{-5}$	$4x10^{-5}$	$2x10^{-5}$
	20	30	25	32	32	$3x10^{-6}$	$2x10^{-5}$	$1x10^{-5}$	$2x10^{-6}$
	30	32	25	33	32	$3x10^{-6}$	$2x10^{-5}$	$3x10^{-5}$	$5x10^{-6}$
	40	32	25	27	32	$5x10^{-6}$	$5x10^{-5}$	$2x10^{-5}$	$4x10^{-6}$
itrile	10	31	22	26	33	$3x10^{-6}$	$1x10^{-5}$	$2x10^{-5}$	$1x10^{-5}$
	20	32	22	31	35	$2x10^{-6}$	$2x10^{-5}$	$2x10^{-5}$	$5x10^{-5}$
	30	33	25	31	41	$3x10^{-6}$	$1x10^{-5}$	$2x10^{-5}$	$1x10^{-5}$
	40	32	41	33	42	$5x10^{-6}$	$2x10^{-5}$	$1x10^{-5}$	$1x10^{-5}$
ne	10	46	34	41	32	$2x10^{-6}$	$3x10^{-5}$	$2x10^{-5}$	$5x10^{-6}$
	20	35	36	41	32	$3x10^{-6}$	$5x10^{-5}$	$2x10^{-5}$	$3x10^{-6}$
	30	28	36	40	35	$2x10^{-6}$	$6x10^{-5}$	$3x10^{-5}$	$3x10^{-6}$
	40	32	40	40	37	$3x10^{-6}$	$5x10^{-5}$	$2x10^{-5}$	$5x10^{-6}$

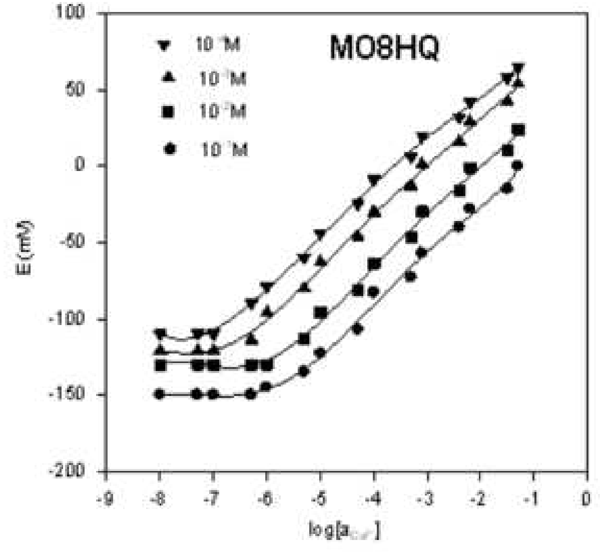

Figure 5.1(e): Effect of internal solution concentration on the membrane electrode (MO8HQ)

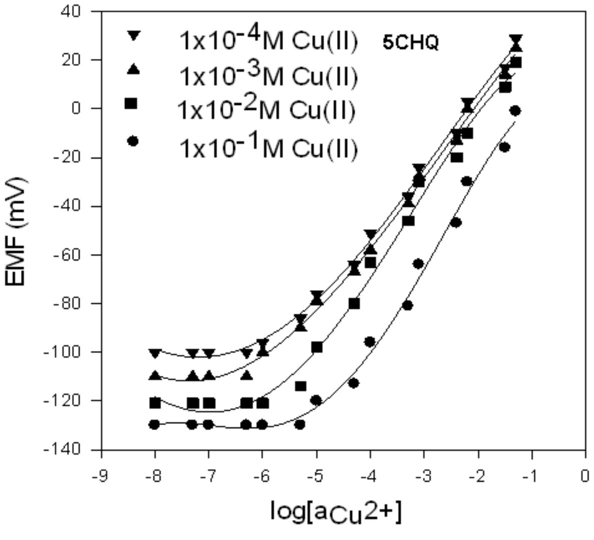

Figure 5.1(e): Effect of internal solution concentration on the membrane electrode (5CHQ)

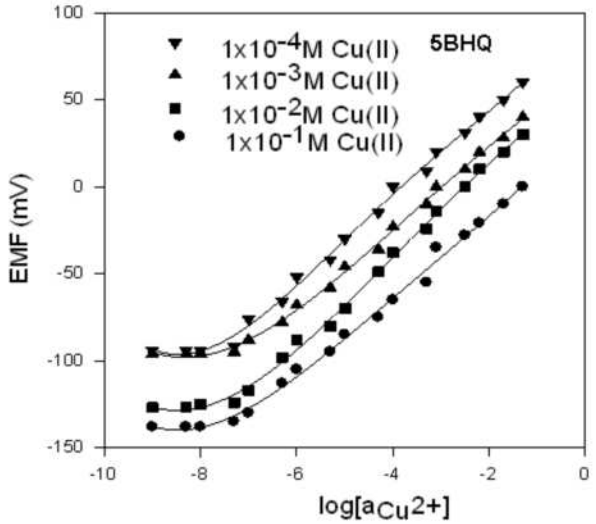

Figure 5.1(e): Effect of internal solution concentration on the membrane electrode (5BHQ)

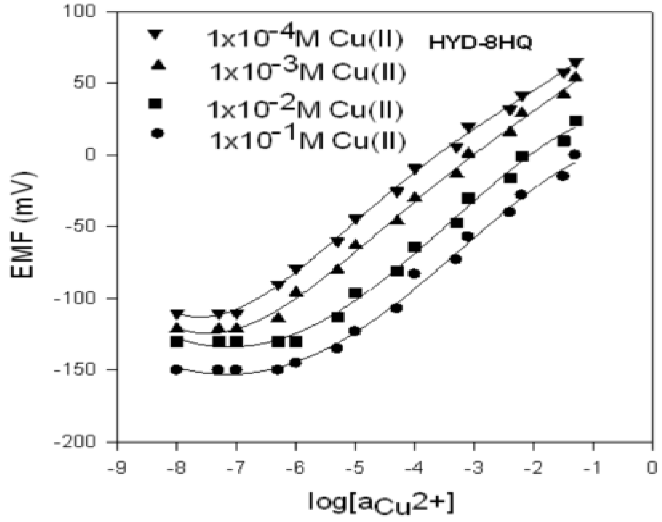

Figure 5.1(e): Effect of internal solution concentration on the membrane electrode (HYD-8HQ)

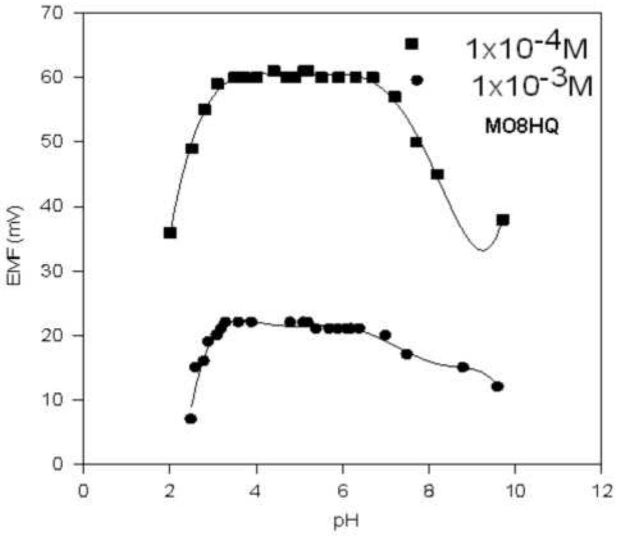

Figure 5.2(e): Effect of pH on the response of Cu(II) ISE (MO8HQ)

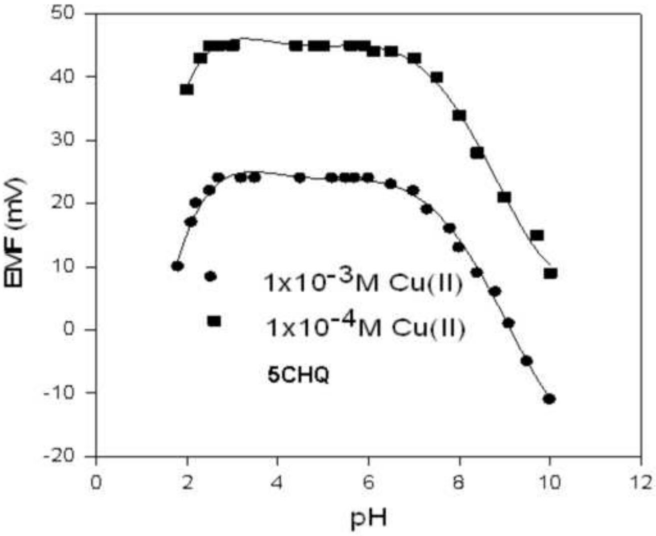

Figure 5.2(e): Effect of pH on the response of Cu(II) ISE (5CHQ)

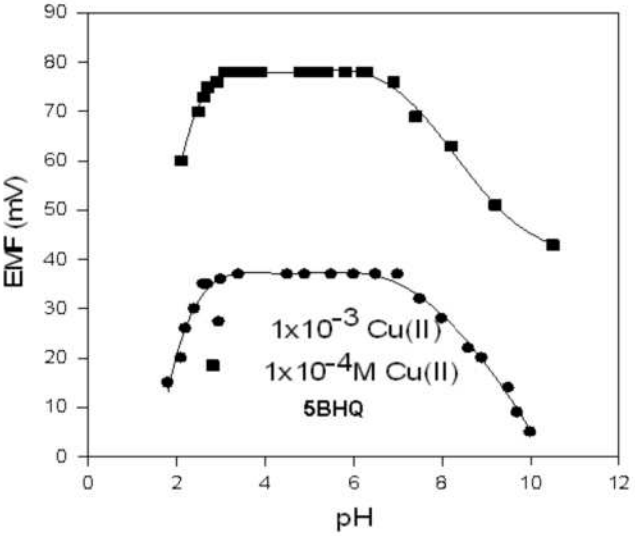

Figure 5.2(e): Effect of pH on the response of Cu(II) ISE (5BHQ)

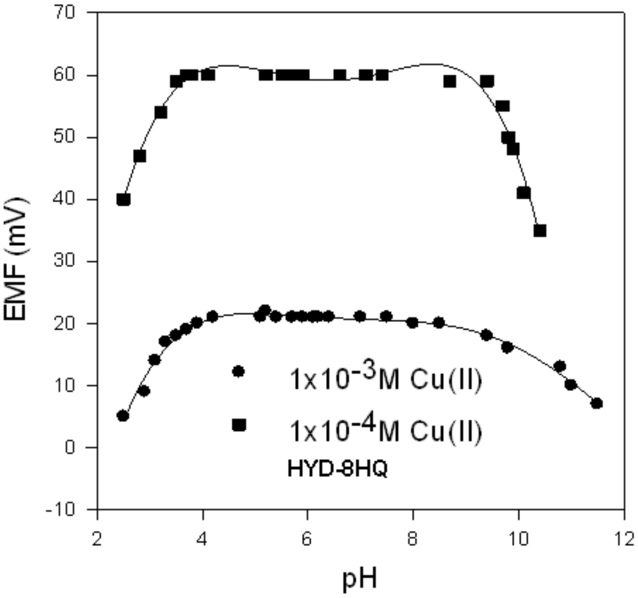

Figure 5.2(e): Effect of pH on the response of Cu(II) ISE (HYD-8HQ)

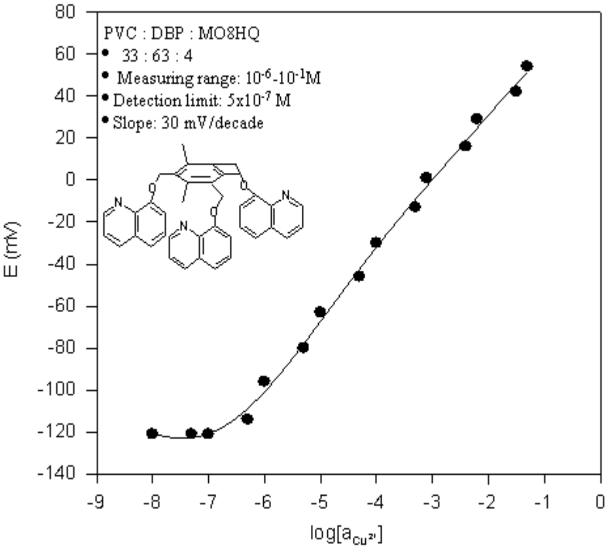

Figure 5.3(e): Calibration curve for the copper (II) ion selective electrode (MO8HQ)

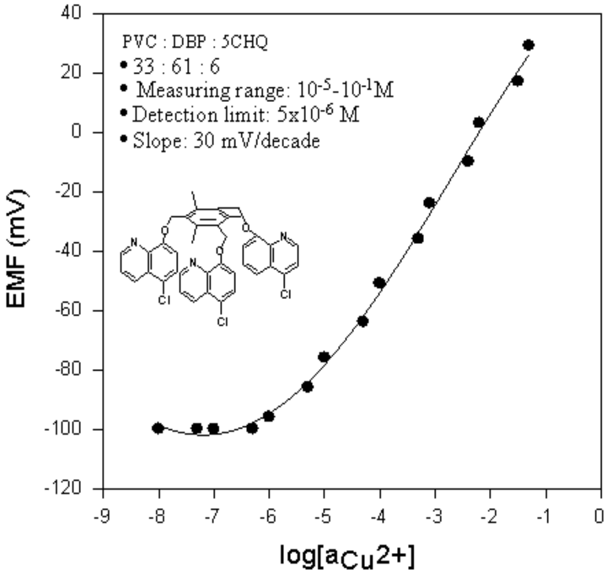

Figure 5.3(e): Calibration curve for the copper (II) ion selective electrode (5CHQ)

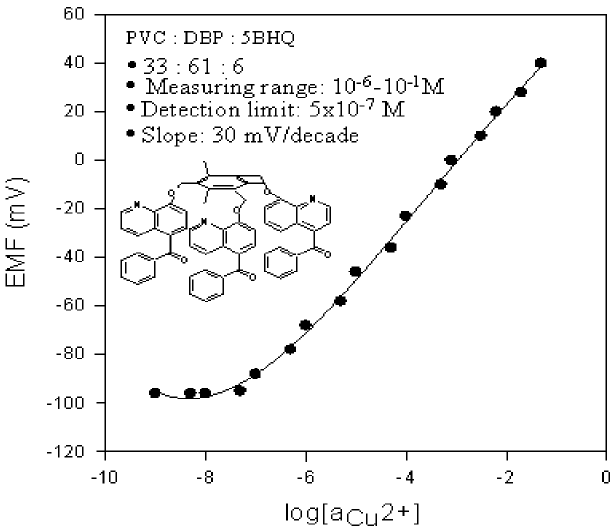

Figure 5.3(e): C **e (5BHQ)**

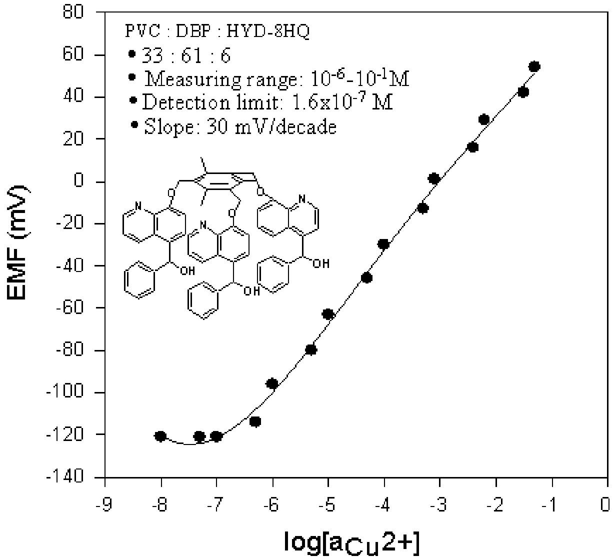

Figure 5.3(e): C **le**
(HYD-8HQ)

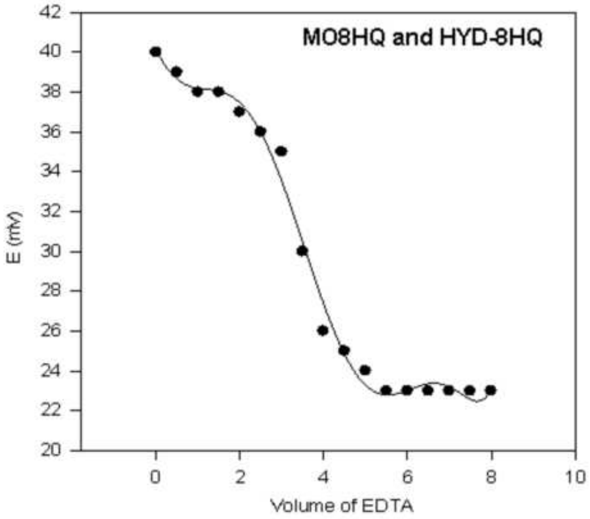

Figure 5.4(e):Titration curve for Cu(II) solution with EDTA solution (MO8HQ and HYD-8HQ)

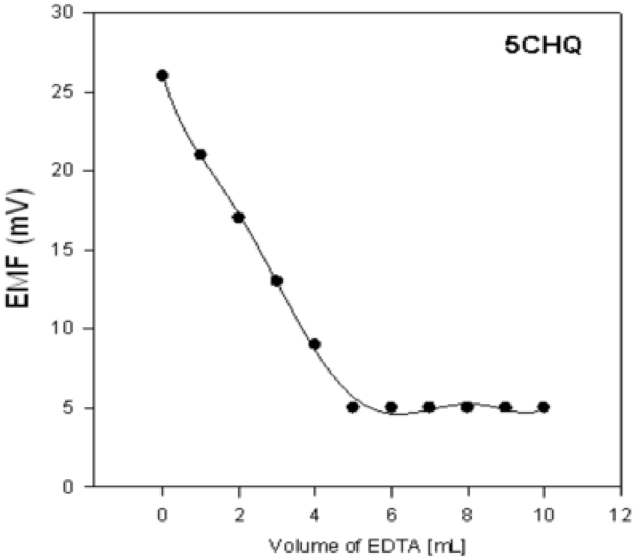

Figure 5.4(e): Titration curve for Cu(II) solution with EDTA solution (5CHQ)

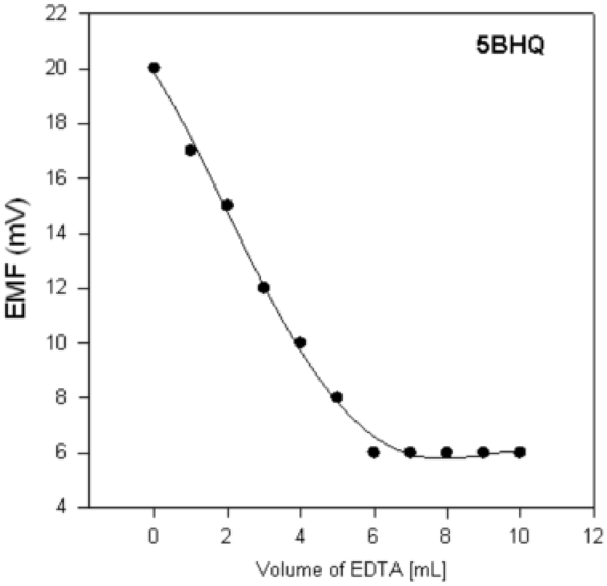

Figure 5.4(e): Titration curve for Cu(II) solution with EDTA solution (5BHQ))

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5(f) Copper(II) Ion-selective Electrode: A Study of 9,10 Bis-(2-amino-phenylthiomethyl)anthracene as an Ionophore

Introduction

The quick determination of minute quantities of copper(II) ion species by simple methods is of great importance in analytical chemistry. Potentiometric detection based on ion- selective electrodes is the simplest of all and offers great advantages such as speed and ease of electrode preparation and simple procedures, wide dynamic range and low cost (1-3). These characteristics have inevitably led to sensors for several ionic species and the list of available electrodes has grown substantially over decades (4-10). The stable soluble form of copper, namely Cu(II) is toxic at elevated concentration. Its reactivity and biological uptake is largely influenced by the free ion concentration that is controlled by the extent of copper complexation with ligands of many analytical methods available for the determination of copper, using direct potentiometry with the Cu(II) ion-selective electrode that has enabled the in-situ measurement of the free copper(II) concentration without perturbing the natural speciation. In view of this fact, researches in the speciation filed have attempted to develop sensors for its determination with high selectivity.

In order to obtain a better selectivity, membrane electrodes based on thiacrown ether, pyridine-based macrocycles containing N, O and S atoms, non-cyclic neutral ionophores with dithiocarbamate groups, calixarenes, Schiff base and macrocyclic diamides have been developed. Most of the ion-selective electrodes suffer from interfering effects from Co^{2+}, Ni^{2+}, Cd^{2+}, Hg^{2+} and Ag^{+} ions as well as a limited range of concentration. Acyclic neutral ionophores as the one type of supramolecules have been taken as the receptors to recognize a wide variety of ions and guest molecules. The complexing efficiency and selectivity in ion and molecular binding depends only on the nature of binding groups attached (14-16). The synthesis of ionophores with various side arms, combinations of varying donor atom types of side arms have provided a high degree of selectivity. The quantification of these effects is gradually allowing new ionophores to be designed with particular selectivity and other properties in mind.

By keeping above concepts in mind, we are reporting the usefulness of a variety of acyclic receptors using 2-aminothiophenol as a ligating site for some transition metal ions. In this paper, we report a highly selective copper electrode using a 9,10 bis-(2-aminophenylthio methyl) anthracene as a neutral carrier for the potentiometric monitoring of copper ions.

Experimental

All potentiometric measurements were made at 25±.0.1 °C with a potentiometer (Equiptronics, EQ-602, accuracy ±0.1 mV). An ISFET pH meter (Delta Track, USA) was used for all pH measurements.

Reagents and Materials

Analytical grade 2-nitrophenyloctyl ether (2-NPOE), DBP, BES, high molecular weight PVC, potassium tetrachlorophenyl borate (KTClPB) were purchased from Sigma Aldrich. Analytical grade nitrate salts of cations (Aldrich) were used without any purification. Double distilled deionised water was used throught the experiment.

Electrode Preparation

The membrane was prepared by dissolving 66 mg of PVC, 126 mg of NPOE as plasticizer and 8 mg of DIANTH as ionophore in 2-3 mL THF. The viscous solution so obtained was cast into a membrane as described in the previous chapter 5. The membrane was pasted on one end of the Pyrex glass tube with araldite. The tube was filled with an internal reference solution of $1x10^{-1}$ M with Cu(II) solution. The membrane was equilibrated for 24 hours and the potential for measured by direct potentiometry at 25 ^{0}C using the following cell assembly:

$$\textbf{SCE} \mid \textbf{0.1 M Cu}^{2+} \mid\mid \textbf{membrane} \mid\mid \textbf{test solution} \mid \textbf{SCE}$$

Activities were calculated according to the Debye-Huckel equation (17).

Results and Discussion

Due to its sufficient insolubility in water, low molecular weight, and flexible structure and especially, the presence of three nitrogen and three sulfur donor atoms in its structure, DIANTH is expected to act as a suitable ion carrier in the PVC-membrane with respect to the special transition of heavy metal ions of proper size and charge. This is the first report showing the usefulness of 2-aminothiophenol as good ligating site for transition metal ions. At the 9, 10 positions of anthrancene, two bonding sites are attached as they have bonding affinities with soft metal ions such as Cu(II) and Ag(I). During complexation and decomplexation with metal ions both nitrogen atoms of amino part and sulphur atom of thioether linkage were involved. The resulting complexes are highly stable, reversible and selective with respect to metal ions. These lipophilic ligands, when incorporated into membranes, behave as ionophore selective for Cu(II) ions.

Optimization of Membrane Ingredients

To obtain better electrode properties, like higher sensitivity, good selectivity and a wider working range, the optimization of membrane ingredients is the most necessary part (18-19). Solvent mediators such as NPOE, DBP and BES were tested. The copper ion- selective electrode based on NPOE exhibited a good Nernstian slope 29 mV/decade over a concentration range from $1x10^{-5}$ M to $1x10^{-1}$ M, while in this concentration range with DBP and sebacate as plasticizer the slopes are 31 mV/decade and 20 mV/decade, respectively, as shown in Table 5.1(f). This is due to less dielectric constant of solvent mediators.

Effect of Internal Solution Concentration on the Response of Electrode

The effect of internal solution concentration was changed from $1x10^{-4}$ M to $1x10^{-1}$ M and the potential responses of the Cu(II) ion-selective electrode were measured. It was found that the variation of the concentration of the internal solution doesn't cause any significant differences in the potential response and except for a slight variation in the Nernstian slope, the detection limit remains unaltered. A concentration of $1x10^{-2}$ M is quite appropriate for the functioning of the electrode (see Table 5.1(f) and Table 5.2(f) and Fig. 5.1(f)).

Effect of pH

The effect of pH on the electrode response was studied at $2x10^{-3}$ M and $2x10^{-2}$ M of Cu $(NO_3)_2$ solution. The pH was adjusted with 0.1 M HNO_3 and 0.1 M NaOH solution. As can be seen from Figure 5.2(f), the potential response remains same in the pH range 3.5-7, below and above of the range the potential get altered due to protonation of the ionophore and formation of $Cu(OH)_2$.

Calibration Curve, Response Time and Lifetime of the Cu(II)-selective Electrode

Calibration curves were drawn for the electrode no. 5 over a concentration range from

10^{-6} to 10^{-1} M with an internal filling solution of Cu(II) ($1x10^{-2}$ M) ions. The electrode shows a reproducible slope of 30 mV/decade. For five repeated experiments, the standard deviation of the slope is ±0.5 mV. A representative curve is shown in Figure 5.3(f). The workable concentration range is $1x10^{-5}$ to 10^{-1} M for Cu(II) ions. The limit of detection ($6.3x10^{-6}$ M) was calculated according to IUPAC recommendation (20) from the intersection of the two extrapolated linear portions of the curve. The response time of the electrode is 15 seconds for electrode no. 5, and for all other electrodes it is greater than 15 seconds. The sensing behavior of the membrane remains unchanged when the potentials are recorded either from low to high or high to low concentrations. The lifetime of the electrode was also studied by measuring the slope and detection limit after every one month. The results showed that the lifetime of the present electrode was about four months. During this time, the detection limit of the sensor remained almost constant and the slope of the sensor varied ±2 mV of the reported value. The contact time and concentration of equilibrating solution were also optimized so that the sensor generated stable and reproducible potentials at relatively short response time. It is found that an equilibrating solution of $1x10^{-1}$ M and contact time of only five hours was appropriate for a smooth functioning of the electrode. The electrodes were stored in $1x10^{-1}$ M $Cu(NO)_3$ solution when not in use.

Potentiometric Selectivity Coefficient Values by Fixed Interference Method

The influence of interfering ions on the response behavior of the ion-selective membrane is usually described in terms of the selectivity coefficients, $K_{A,B.}$ The methods based on the Nicolski-Eisenman equation was used for the determination of potentiometric selectivity coefficients (the fixed interference method). Results indicate that the common metal ions do not interfere the proposed electrode shown in Table 5.3(f).

Effect of Electrode Response in Mixed Solvent Media

The working nature of the sensor was also studied in partially non-aqueous medium using methanol-water, acetone-water and acetonitrile-water mixtures. The membrane showed a satisfactory response in a medium with non-aqueous content up to 40%(V/V). The working concentration range and slope remains almost the same except for a slight change in the slope of about 2 mV/decade compared to that in aqueous medium. However, the best response is observed at 20% non-aqueous content [see Table 5.4(f) and Figure 5.4(f)].

Potentiometric Titration

Potentiometric titrations were performed by using the proposed electrode as an indicator electrode for the titration of 25 mL of $1x10^{-3}$ M Cu^{2+} ions against $1x10^{-2}$ M EDTA. The titration curve is shown in Figure 5.5(f). The curve shows a sharp inflexion point at the titrant volume corresponding to the formation of an 1:1 complex of copper ions with EDTA.

Analysis of copper in brass and tea leaves samples using tripodal- and dipodal-based Cu-ISEs

The electrode was also applied for the direct determination of copper in black tea and brass samples. The copper content tea sample was extracted as described elsewhere [21]. The concentration of copper in the extracted sample is determined with the proposed electrode and atomic absorption spectrometry (AAS) [Table 5.5(f)]. The results obtained show a satisfactory agreement with those obtained by AAS.

Table 5.1(f): Optimization of membrane ingredients for DIANTH-based Cu-ISE

Sr.No.	PVC (Wt%)	Plasticizer (Wt%)	Ligand (Wt%)	Slope (mV/decade) e	Detection Limit, (M)
1	33	67(2-NPOE)	0	19	$5x10^{-4}$
2	33	66(2-NPOE)	1	20	$7x10^{-4}$
3	33	65(2-NPOE)	2	24	$2x10^{-4}$
4	33	64(2-NPOE)	3	29	$8x10^{-6}$
5	33	63(2-NPOE)	4	29	$5x10^{-6}$
6	33	62(2-NPOE)	5	27	$1x10^{-5}$
7	33	61(2-NPOE)	6	26	$1x10^{-5}$
8	33	63 (DBP)	4	31	$6.3x10^{-6}$
9	33	63(BES)	4	20	$8x10^{-5}$

Table 5.2(f): Internal solution concentration studies on DIANTH-based Cu-ISE

Internal Concentration, (M)	Slope, mV/decade	Detection limit, (M)	Response time (Seconds)
$1x10^{-1}$	31	$6.3x10^{-6}$	15
$1x10^{-2}$	28	$2.5x10^{-6}$	15
$1x10^{-3}$	28	$2.0x10^{-6}$	15
$1x10^{-4}$	26	$2.0x10^{-6}$	15

Table 5.3(f): Potentiometric selectivity coefficient on DIANTH-based Cu-ISE

Interfering metal B	-log $K_{A,B}$	Interfering metal B	-log $K_{A,B}$
Na^+	-1.5	Co^{2+}	-0.7
K^+	-1.3	Ni^{2+}	-1.0
Ag^+	-0.4	Hg^{2+}	-1.0
Mg^{2+}	-1.8	Cd^{2+}	-0.3
Ca^{2+}	-0.5	Zn^{2+}	-1.8
Sr^{2+}	-0.7	Pb^{2+}	-1.0
Ba^{2+}	-1.5	Fe^{3+}	-0.5

Table 5.4(f): Electrode response in mixed solvent media on DIANTH-based Cu- ISE

Mixed solvent	Volume Percentage	Slope mV/decade	Detection Limit, (M)
Methanol: Water	10	26	$2x10^{-6}$
	20	28	$3x10^{-6}$
	30	26	$6.3x10^{-6}$
	40	25	$3x10^{-5}$
Acetonitrile: Water	10	23	$1x10^{-5}$
	20	25	$1x10^{-5}$
	30	27	$2.5x10^{-5}$
	40	33	$2x10^{-5}$
Acetone: Water	10	22	$2.5x10^{-6}$
	20	24	$1x10^{-6}$
	30	27	$5x10^{-5}$
	40	29	$5x10^{-5}$

Table 5.5(f): Analysis of copper in brass and tea leave sample using DIANTH-based Cu-ISE

Name of the ionophore	Found by copper-selective electrode		Found by AAS	
	Brass sample (grams/litre)	Tea leaves (mg/litre)	Brass sample (grams/litre)	Tea leaves (mg/litre)
Tripodal ionophore MO8HQ	4.40	52.00	4.20	50.00
Dipodal ionophore DIANTH	4.50	54.00		

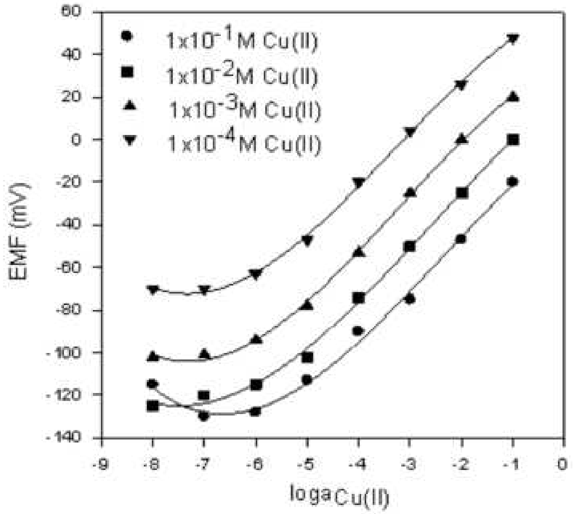

Figure 5.1(f): Effect of concentration of internal solution on the membrane electrode using DIANTH-based Cu-ISE

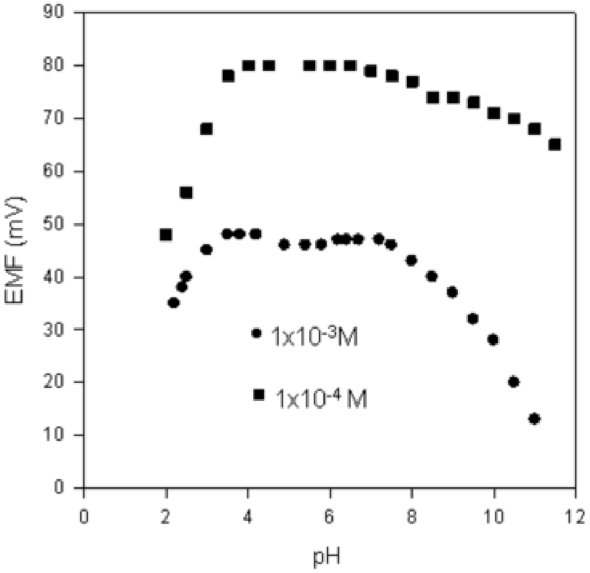

Figure 5.2(f): Effect of pH on the response of Cu(II) ISE

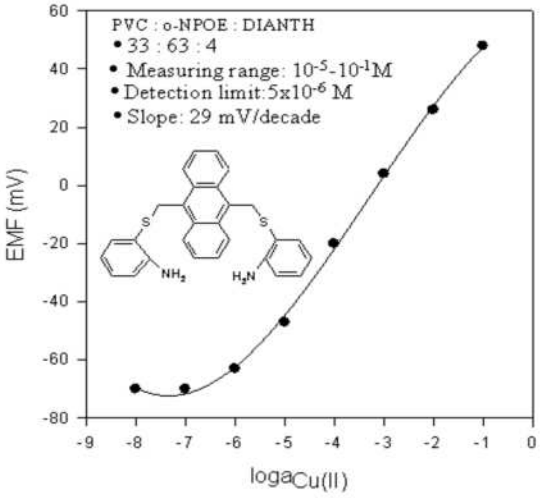

Figure 5.3(f): Calibration curve for the copper (II) ion selective electrode

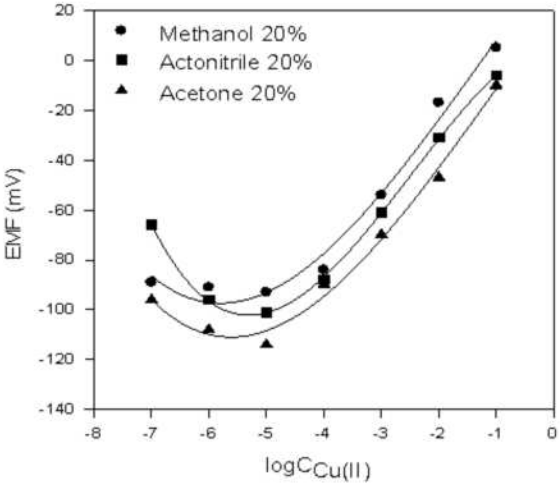

Figure 5.4(f): Calibration graphs of Cu(II) ISE in mixed solvent medium

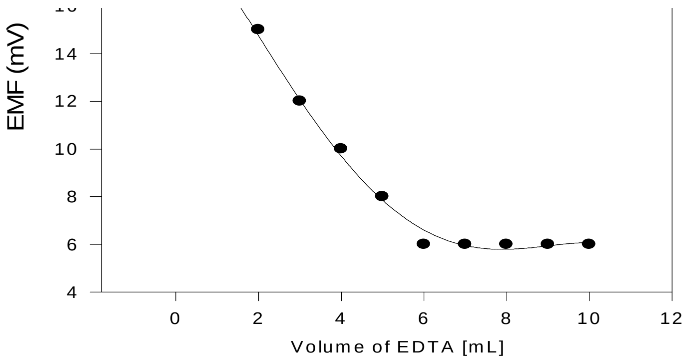

Figure 5.5(f): Titration curve for Cu(II) solution with EDTA solution using DIANTH-based Cu-ISE

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Chapter -6

EDTA AS A SENSING MATERIAL FOR RARE EARTH METAL IONS

Introduction

The most widely used of all the polyaminocarboxylic acids is ethylenediaminetetracetic acid (EDTA or H_4Y). It is used as a complexing agent for most of the alkaline earth metal ions, transition metal ions and rare earth metal ions. Due to its high complexing ability it has a variety of applications in analytical chemistry, nuclear medicine, chelation therapy and in many biological systems (1-4).

The quick determination of rare earth metal ion species by simple methods is of great importance in analytical chemistry. The available methods for low-level determination of rare-earth ions in solution include spectrophotometry (5-8), ICP-AES (9), isotope dilution mass spectrometry (10), neutron activation analysis (11) and X-ray fluorescence spectrometry (12). These methods are either time-consuming, involving multiple analysis or too expensive for most analytical laboratories. Conductometric titration is the simplest of all and offers great advantages such as speed, easy procedures and low cost. These characteristics have inspired us to conduct experiments in our lab. In our knowledge this is the first report of determination of rare earth metal ions using EDTA as a complexing agent by conductometric titration method.

Experimental

All measurements were done at 25 ± 0.1 °C using a conductivity meter (accuracy ± 0.1 mS, Elico, CM180, India) with a cell constant of 1.0 cm^{-1}.

Reagents

Solutions of metal ions were prepared by direct weighining of AnalaR grade metal nitrates (CDH, India) in double distilled deionised water having conductivity 5 μSm^{-1}. EDTA (disodium salt) (Aldrich, USA) is used as received.

Procedure for Specific Conductance Measurement

The rare earth metal nitrate solution (50 mL of $1x10^{-3}$ M) was placed in a titration vessel and the conductivity was measured. EDTA solution ($1x10^{-2}$ M) was added to the vessel in 0.5 mL increments and measured the conductivity until EDTA added was sufficiently larger than the 1:2 metal:EDTA stoichiometry. The plots of conductometry versus volume of EDTA added were drawn and the equivalence point is measured as the sharp inflexion point of the titration curves.

Results and Discussion

Measuring Range and Detection Limit

The conductivity is measured over a concentration range from $1x10^{-8}$ to $1x10^{-1}$ equivalents/liter of dissolved salts. Conductivity values ranged from 15 to 16,000 microSiemens. In order to plot these wide ranges we used log/log plots. The plots show that a relationship between concentration and conductivity is linear as shown Figs. 6.1 and 6.2 (13). The point of intersection of two straight-line portions of the calibration curve was taken as the detection limit. The detection limit for rare earth metal ions is found to be $3x10^{-6}$ M.

Effect of pH

Conductivity measurements for the titration of dysprosium with EDTA were also done in presence of buffer (sodium acetate-acetic acid buffer solution, pH= 4), but no effect of the buffer was noticed on the equivalence point because the initial pH of the lanthanide solution (pH = 4.5) is just suitable for a stable complex formation with EDTA and all along the titration pH changes only up to 4.0 due the release of H^+ ions on complex formation with EDTA. However, there is a change in the magnitude of conductivity values that did not cause any significant difference in the equivalence point. Hence, buffer solution was not used in subsequent studies.

Conductometric Titration Curves: Characterization

All the titration curves are of one kind. Curves show two distinct features, a regular increase in conductivity of the solution up to the equivalence point and after that, a slow decrease in conductivity is noticed. Conductometric titrations were carried out between a number of lanthanide metal ion solutions against EDTA. Plots were drawn and titration curves were obtained. Figs. 6.3 to 6.14 show that specific conductance (Λ) values increase with an increase of EDTA-metal ratio for all systems involving the rare earth metal ions. This can be explained on the basis of the solvation sphere. Trivalent metal ions have a high charge to radius ratio, hence they are highly solvated. On complexation, EDTA replaces the solvent sheath around the metal ion and as a result, the moving entity becomes less bulky and more mobile. Also, during complexation, there is a release of H^+ ions at each step till a suitable stoichiometry of metal-EDTA complex is achieved. At the equivalence point, slopes of the curves change very sharply and after the equivalence point, the conductance decreases. This is due to the undissociated EDTA, which is a bulky molecule and does not contribute much to the conductivity.

Titrations of Lanthanides and their Binary Mixtures with Dysprosium Metal Ion

Conductometric titrations of each metal ion were done against EDTA to study their complexation behaviour (Figs. 6.3-6.11). The titrations indicate that La^{3+}, Ce^{3+}, Pr^{3+}, Sm^{3+} and Dy^{3+} form 1:1 complexes with EDTA (Figs. 6.3-6.7), while Nd^{3+}, Eu^{3+}, Tb^{3+} form 1:2 complexes (Figs. 6.8–6.10). Above procedure is also followed for the binary mixtures of rare earth metal ions. When two lanthanides of different concentrations are titrated against EDTA, separate end points corresponding to each of the metal ions were observed. The metal-forming more stable complex shows the first equivalence point (The stability constant values (14) of 1:1 EDTA and rare earth metal ions are shown in the Table 6.1). Dysprosium was selected as a representative element for the study of binary mixtures. Conductometric titrations of binary mixture of lanthanide and dysprosium ions were studied. Since the stability constant of Dy-EDTA has a high value, it is formed first followed by other rare earth metal ions. Conductometric titrations of Nd^{3+}, Eu^{3+} and Tb^{3+} with EDTA show a complex formation in a 1:2 ratio (Figs. 6.8, 6.9 and 6.10). The reason for this trend could not be ascertained easily.

Titrations of Binary Mixtures of Dy(III) ion and Interfering Ions against EDTA

Conductometric titrations of a mixture of Dy(III) solution (25 mL, $1x10^{-3}$ M) and an equal concentration of the interfering lanthanide ion (25 mL, $1x10^{-3}$ M) were carried out against EDTA ($1x10^{-2}$ M). The dysprosium ion was selected for the study as it lies almost in the centre of the lanthanide series in the periodic table. The increase in conductivity till the equivalence point is due to the successive release of H^+ ions from EDTA. This feature is supported by the decrease in pH when Dy^{3+} is titrated against EDTA. After the equivalence point, the conductivity decreases, as no more complexation is possible and the incremental amounts of EDTA remain as such in the solution. Being high molecular and a big molecule, it does not contribute towards the conductivity of the solution.

Titration curves were obtained as expected and the inflexion point was corresponding to the formation of an 1:1 complex (Dy^{3+}-EDTA). The titration curves are not affected by the presence of an equimolar concentration of the interfering ions, like Ag^+, Na^+, Ca^{2+} and Zn^{2+}. Although formation constants of Ca^{2+}-EDTA and Zn^{2+}-EDTA complexes are comparable, there is hardly any interference. This may be due to the reason that Ca^{2+} forms complexes with EDTA at pH 9-10 and Zn^{2+} forms a complex at pH 5-6, while the pH of the medium is only 4-5 and suitable only for a Dy^{3+}-EDTA complexation. Conductometric titration in presence of Al^{3+} as interfering ion shows two inflexion points corresponding to the formation of Dy^{3+}-EDTA and Al^{3+}-EDTA complexes, respectively. It was observed that after the first inflexion point for Dy^{3+}-EDTA, the reading took a very long time (about 5 min) to stabilize, probably because of the poor kinetics of Al^{3+}-EDTA complexation.

In case of Hg^{2+} as an interfering ion, a special change in the shape of the curve is noticed in the equivalence point region (Figure 6.17). A curvature in the equivalence point region is obtained instead of a regular slope of the straight-line portions. A lower conductivity is noticed which is due to the likely interference of mercury ions that form a complex with EDTA, where a suitable pH (lowered due to release of H^+ ions) is available in the medium (Hg^{2+}-EDTA complex is formed at pH=2.0 due to the release of H^+ ions from the EDTA as well as the acidic character of the mercury solution). So, it can be concluded that the presence of Hg^{2+} ions interfere only to the extent that it changes the shape of the curve and does not alter the equivalence point of the titration.

In case of Fe^{3+} and Th^{4+}, the equivalence point is obtained corresponding to the sum of the metal ion concentrations present, i.e. Dy^{3+} and Fe^{3+}, Dy^{3+} and Th^{4+}, respectively. It is due to the reason that the stability constants of these ions are very high and the complexation of Dy^{3+} with EDTA cannot be distinguished from that of Fe^{3+}-EDTA and Th^{4+}- EDTA. However, a sharp inflexion point corresponding to the sum of the metal ions is obtained. Th^{4+} and Fe^{3+} form complexes with EDTA in the range of pH 2-3, while Dy^{3+} forms a complex at pH 4.0-4.5. Initially, the titration of Dy^{3+} with EDTA takes place and the pH of the solution is lowered with a successive release of H^+ ions from EDTA. When whole of the Dy^{3+} is complexed, the resulting pH of the solution becomes suitable for the complexation of Fe^{3+} and Th^{4+} with EDTA.

Table 6.1: Stability constant values for lanthanide – EDTA complexes (14)

Metal ions	**log K_{MY}**	**Metal ions**	**log K_{MY}**	**Metal ions**	**log K_{MY}**
La^{3+}	15.5	Dy^{3+}	18.3	Ca^{2+}	10.9
Ce^{3+}	15.98	Ho^{3+}	18.05	Zn^{2+}	16.5
Pr^{3+}	16.4	Er^{3+}	18.38	Hg^{2+}	21.80
Nd^{3+}	16.11	Tm^{3+}	18.62	Fe^{3+}	25.10
Sm^{3+}	16.7	Yb^{3+}	18.88	Th^{4+}	23.20
Eu^{3+}	17.3	Lu^{3+}	19.65	Al^{3+}	16.13
Gd^{3+}	17.0	Na^{+}	1.66		
Tb^{3+}	17.81	Ag^{+}	7.32		

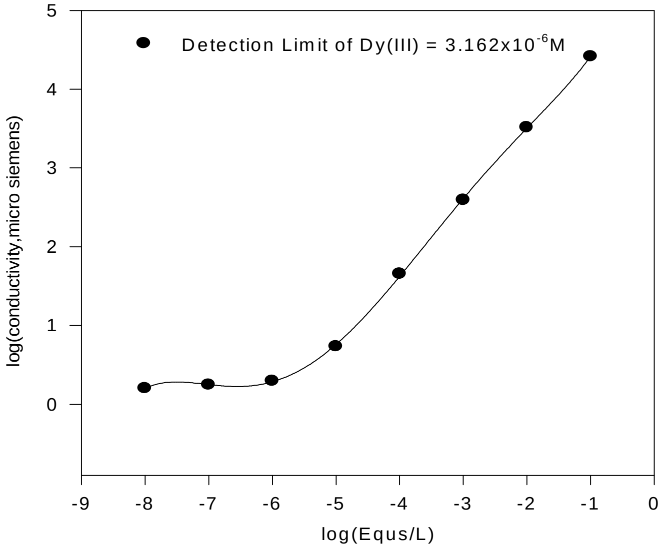

Figure 6.1: Plots of log concentrations vs. log conductivity of Dy^{3+} ions

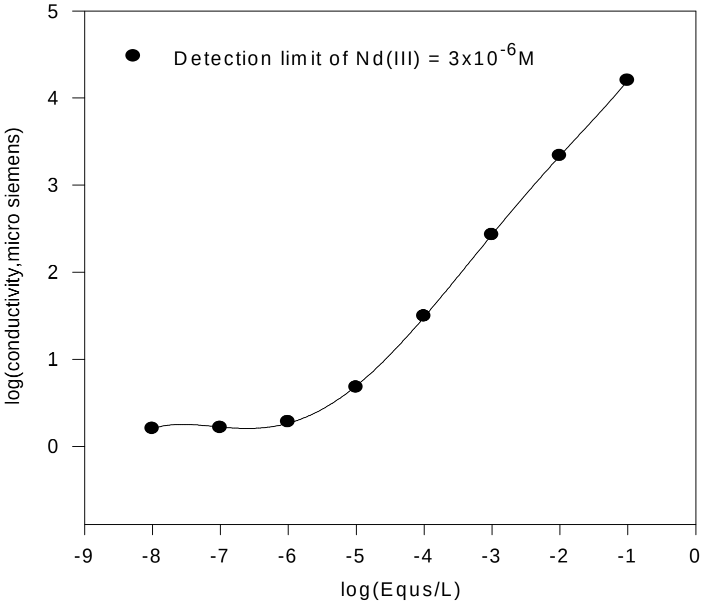

Figure 6.2: Plots of log concentrations vs. log conductivity of Nd^{3+} ions

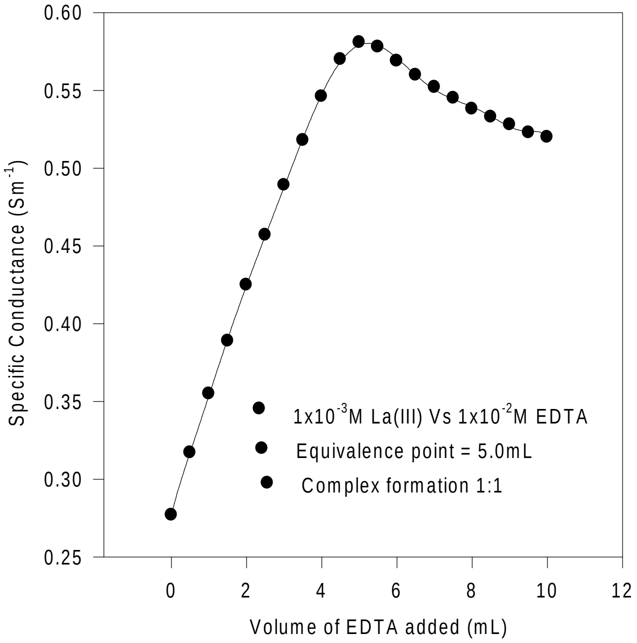

Figure 6.3: Titration curve for La(III) with EDTA

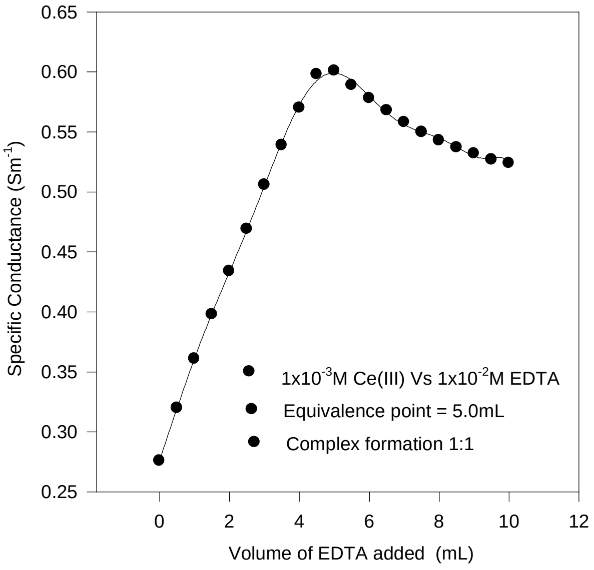

Figure 6.4: Titration curve for Ce(III) with EDTA

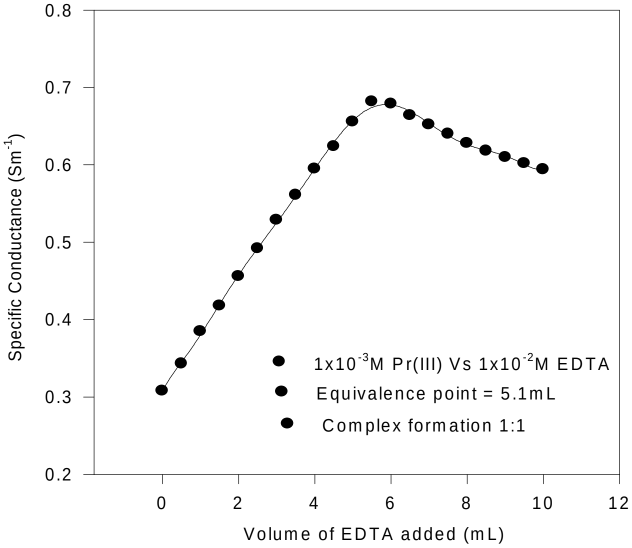

Figure 6.5: Titration curve for Pr(III) with EDTA

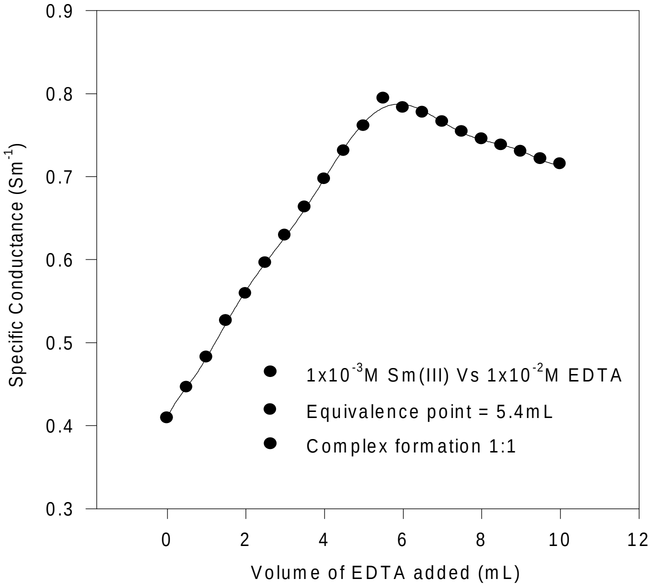

Figure 6.6: Titration curve for Sm(III) with EDTA

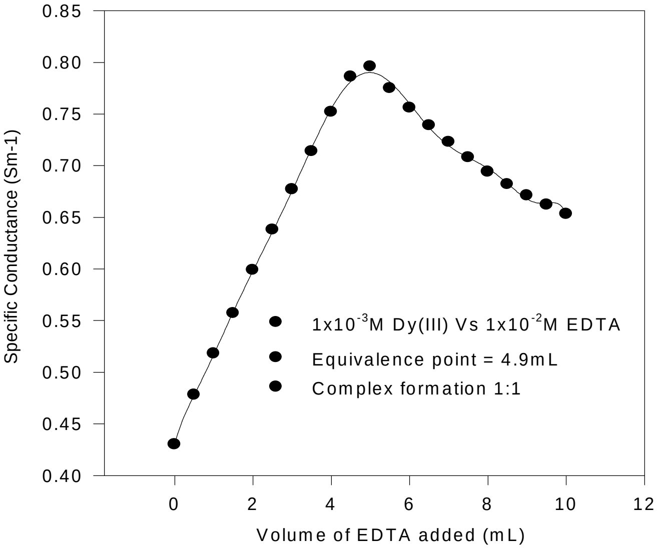

Figure 6.7: Titration curve for Dy(III) with EDTA

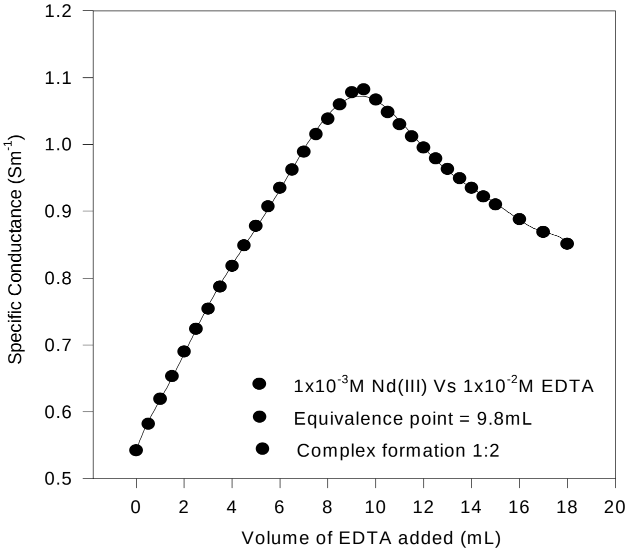

Figure 6.8: Titration curve for Nd(III) with EDTA

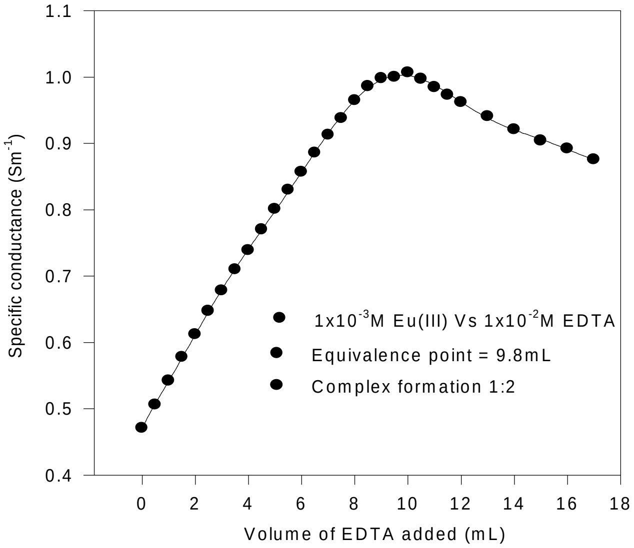

Figure 6.9: Titration curve for Eu(III) with EDTA

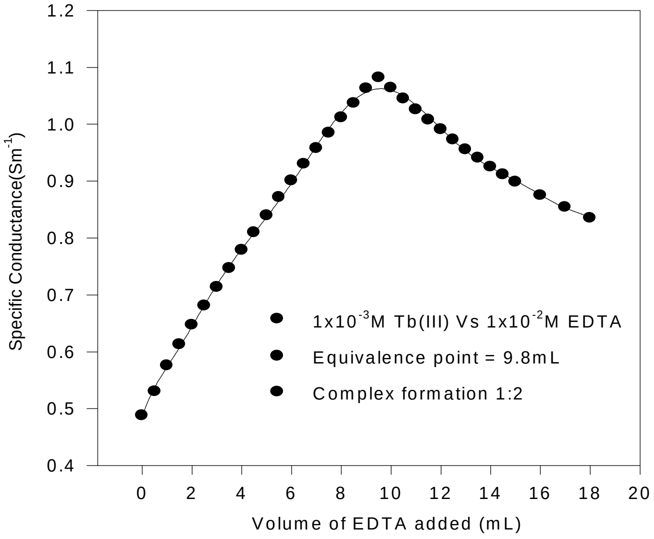

Figure 6.10: Titration curve for Tb(III) with EDTA

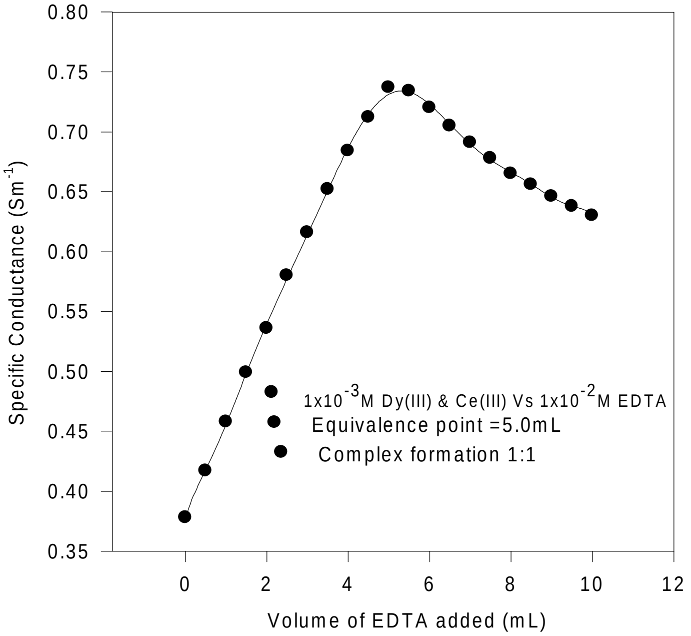

Figure 6.11: Titration curve for Dy(III) and Ce(III) with EDTA

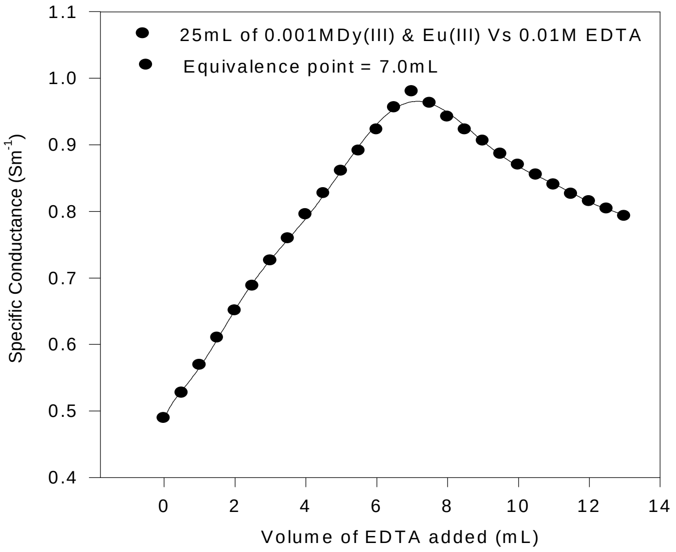

Figure 6.12: Titration curve for Dy(III) and Eu(III) with EDTA

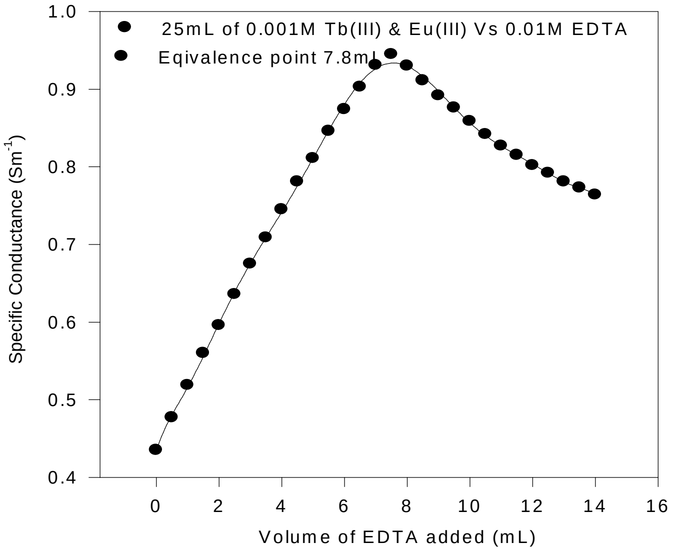

Figure 6.13: Titration curve for Tb(III) and Eu(III) with EDTA

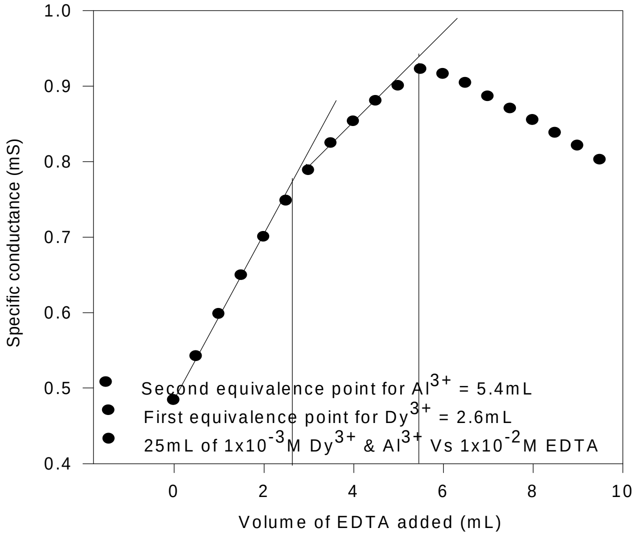

Figure 6.14: Titration curve for Dy(III) and Al(III) with EDTA

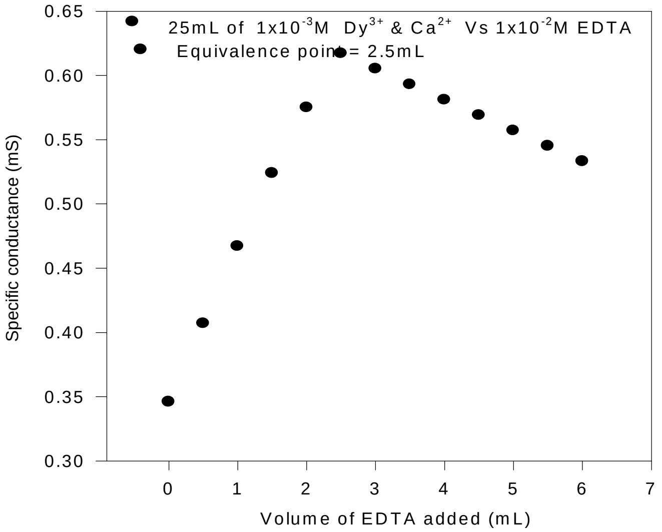

Figure 6.15: Titration curve for Dy(III) and Ca(II) with EDTA

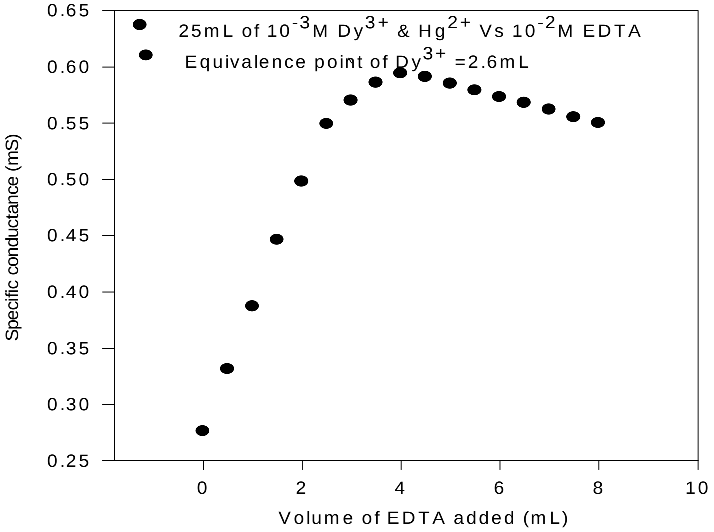

Figure 6.16: Titration curve for Dy(III) and Hg(II) with EDTA

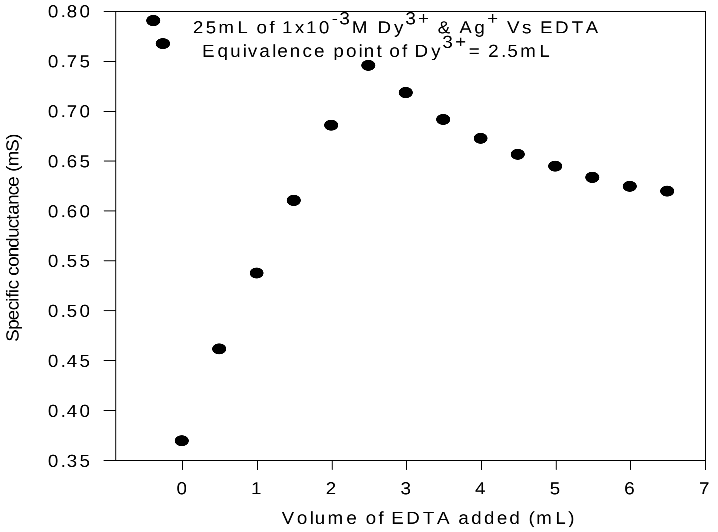

Figure 6.17: Titration curve for Dy(III) and Ag(I) with EDTA

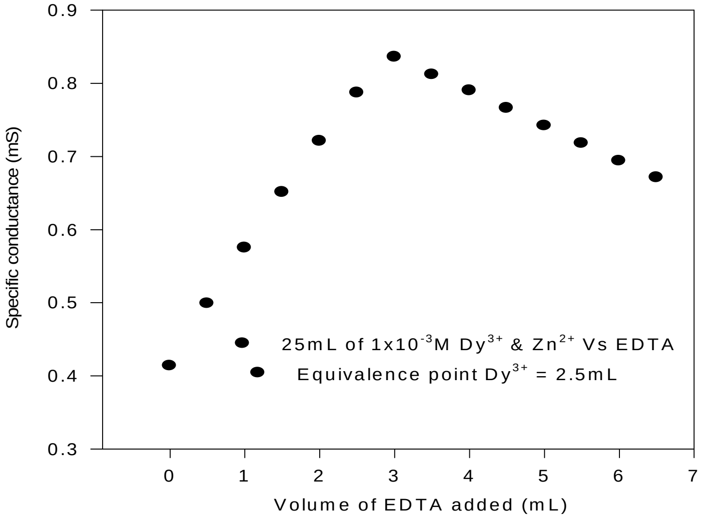

Figure 6.18: Titration curve for Dy(III) and Zn(II) with EDTA

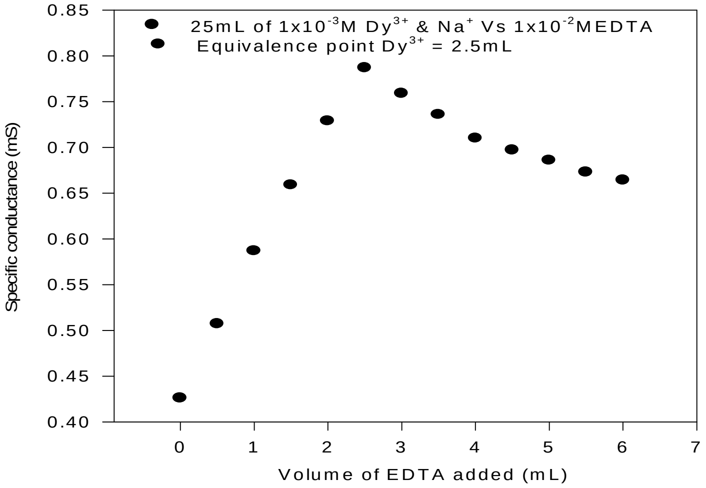

Figure 6.19: Titration curve for Dy(III) and Na(I) with EDTA

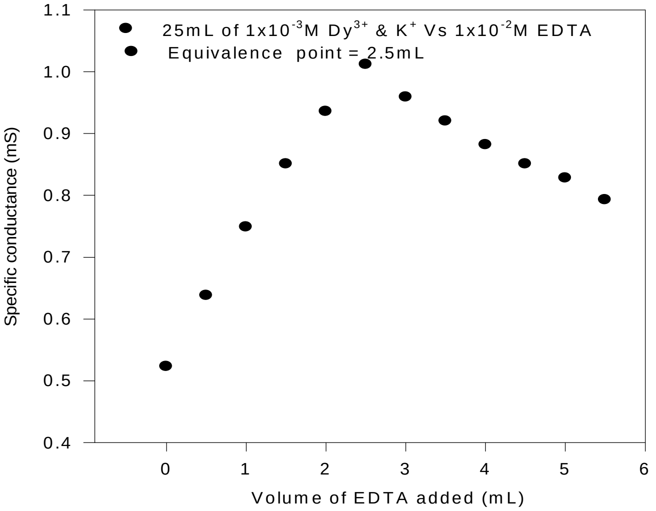

Figure 6.20: Titration curve for Dy(III) and K(I) with EDTA

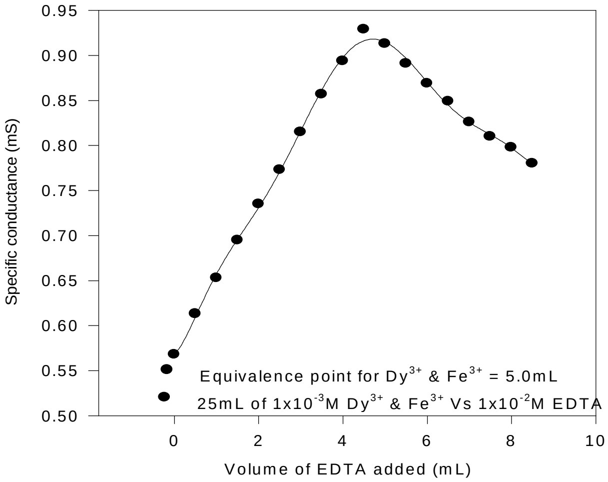

Figure 6.21: Titration curve for Dy(III) and Fe(III) with EDTA

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Conclusions and Summary

- Crown ethers and various acyclic compounds form stable complexes with various macrocyclic ligands similarly to alkali and alkaline earth metals because of the similarity of the radii between lanthanides and Na^+ or Ca^{2+} ions.

- Two rare earth potentiometric sensors for La(III) and Ce(III) were prepared using Dicyclohexano-18-crown-6 and Dibenzo-24-crown-8. Dibenzo-18-crown-6 was used as a calcium ion-selective electrode.

- Podal ionophores provide flexibility in selectivity towards metal ions and are gaining increasing interest as tools for their analysis and separation of metal ions.

- 9,10,Bis-(2-aminophenylthiomethyl)anthracene-based membrane electrodes exhibit Nernstian response for Cu (II) ions over a concentration range from $1x10^{-5}$ M to $1x10^{-1}$ M. The electrode shows a good selectivity for Cu (II) over a large number of other interfering ions. The working pH range is 4.0-8.0. The electrode works as an indicator electrode and can be used in mixed solvent media.

- 1,3,5-Tris(8-quinolinoxymethyl)-2,4,6-trimethylbenzene (MO8HQ) is used as a basic sensing material belonging to the group of tripodal ionophores. Also their derivatives prepared by placing suitable substitutents at 5th position of 8-oxine moiety;1,3,5-Tris(5-chloro-8-quinolinoxymethyl)-2,4,6-trimethylbenzene(5CHQ), 1,3,5-Tris(5-benzoyl-8-quinolinoxymethyl)-2,4,6-trimethylbenzene (5BHQ) and 1,3,5-Tris((5-phenylhydroxymethylene)-8-quinolinoxymethyl)-2,4,6-trimethyl benzene(HYD-8HQ) ionophores have been used to make copper-selective membrane electrodes. Amongst all the four electrodes, MO8HQ and HYD-8HQ ionophores-based electrodes show an excellent response towards Cu(II). The electrodes having composition [33% PVC, 4% MO8HQ and 63% dibutyl phthalate (DBP)] and [33% PVC, 6% HYD-8HQ and 61% dibutyl phthalate (DBP)] exhibit a good Nernstian response to Cu (II) ions in the range from $1.0x10^{-6}$ M to $1x10^{-1}$M with a slope of 29 mV per decade. The electrode shows a fast response time of 15 seconds and operates in a pH range 3.5-7.0. It shows a high selectivity for Cu (II) ions in comparison to heavy metal ions, transition metal ions and a good selectivity for alkali and alkaline earth metal ions. The electrode response and selectivity remains unchanged for at least 6 months. The electrode can be used, as an indicator electrode in the potentiometric titration of Cu (II) ions with EDTA. The main attention of this work was to know how to use 8-Hydroxyquinoline and its derivatives as sensing material as they are known to be the best chelators after EDTA.

- A 2-aminothiophenol based tripodal ionphore was investigated as silver-selective sensing material. Membranes with different amounts of ionophore show different response behaviour towards silver (I) ions. The ionophore, when taken as 4% in the membrane, exhibits a Nernstian behaviour (58 mV/decade) in the concetration range from $5\times10^{\bullet 5}$ M to $1\text{x}10^{-1}$ M while a membrane contaning 3% ionophore shows a semi-Nernstian (28 mV/dcade), and with 5% ionophore shows a sub-sub Nenstian (16 mV/decade) behaviour in the said concetration range. The membrane electrode can be used over a wide pH range of 4.0-8.0. The sensor has a response time of <20 seconds and can be used for at least 4-5 months without any considerable divergence in potential. The limit of detection was $1 \times 10^{\bullet 5}$ M. The ion selectivity of this electrode for Ag^+ was over 500 times higher that for alkali, alkaline earth and transition metal ions. The proposed sensor shows a fairly good discriminating ability towards Hg^{2+} ions in comparison to some hard and soft metals. The electrode was used in the direct determination of Hg^{2+} in aqueous solution and as an indicator electrode in potentiometric titration of Ag^+ ions.

- A 1,2,4,5-tetrakis(8-hydroxyquinolinoxymethyl)benzene ionophore was designed for molecular architecture at the electrode–solution interface and the utilization of supramolecular interactions in making chemical sensors using the zero current-based potentiometric technique. An 8-hydroxyquinoline based tetrapodal ionphore was investigated as silver-selective sensing material. The membrane sensor based on this ionophore shows a Nernstian response toward Ag^+ over the range from $1\text{x}10^{\bullet 5}$ M to $1\text{x}10^{-1}$ M. The sensing membrane can be used over a wide pH range of 4.0-8.0. The sensor has a response time of <15 seconds with good shelf life of 7 months. The limit of detection was $1\text{x } 10^{\bullet 5}$ M. The ion selectivity of this electrode for Ag^+ was over 500-1000 times high that for alkali, alkaline earth and transition metal ions. The electrode was used in the direct determination of Hg^{2+} in aqueous solutions and as an indicator electrode in potentiometric titration of Ag^+ ions. The electrode is extensively used as an indicator electrode for the determination of Ag^+ in various synthetic samples and also used for the determination of SCN^-, CN^-, S^{-2} and I^- contents present in the sample solution.

- 1,2,4,5-tetrakis(8-hydroxyquinolinoxymethyl)benzene has been used as an electro-active species incorporated in a thin polymeric support film coated directly on a metallic conductor electrode for silver determination. The electrode has been characterized by the electrode response, measuring range, detection limit and pH range. Selectivity coefficients of a number of metal ions have been determined. The electrode shows a good response to silver ions in presence of Hg^{2+} ions. The electrode is extensively used as an indicator electrode for the determination of Ag^+ in various synthetic samples and also used for the determination of SCN^-, CN^-, S^{-2} and I^- contents present in the sample solution. The lifetime of the electrode is 2 months. A new and precise method for finding the detection limit is proposed. This is a good sensor to discriminate between sliver and mercury separately, which could not identified by concentration cell technique.

- A new conductometric method has been developed for the determination of rare earth metal ions. Measurements were carried over a wide concentration range from $1x10^{-6}$ to $1x10^{-1}$ equivalents of Ln^{3+} ions. Conductometric titrations of La^{3+}, Ce^{3+}, Pr^{3+}, Sm^{3+} and Dy^{3+} against EDTA show sharp equivalence points at an 1:1 stoichiometry, while Nd^{3+}, Eu^{3+} and Tb^{3+} show an 1:2 ratio during complex formation. Detection limits of the conductometric determinations for the lanthanide ions were found to be $3x10^{-6}$ equivalents. Titrations of some binary solution mixtures of rare earth metal ions with alkali, alkaline earth and some transition metal ions against EDTA are also reported. This technique is useful for the determination of rare earth metal ion species and offers great advantages such as speed, easy procedures and low cost. This method is most suitable for the characterization of charged ionophores as a sensing material.

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List of Publications

A. Journals

1. Susheel K Mittal, **Ashok Kumar S.K.** and Harish Kumar Sharma, “PVC Based Dicyclohexano-18-crown-6 sensor for La(III) ions”, Talanta, 62(4), 2004, 801-805.
2. Susheel K Mittal and **Ashok Kumar S.K.**, “PVC Based Dibenzo-18-crown-6 sensor for Ca(II) ions”, Sensors and Actuators, B, **99** (2-3) 2004, 340-343.
3. Susheel K Mittal, **Ashok Kumar, S.K**. Sukdeep Kaur & Subodh Kumar, Potentiometric Performance of 2-Aminothiophenol Based Dipodal Ionophore as a Silver Sensing material, Sensors and Actuators, B (in press)

B. Papers Presented in Conferences

1. Neutral Tripodal Ionophores as Copper (II) Selective Electrodes, **Ashok Kumar S.K.,** Susheel K Mittal and Subodh Kumar, SLIET, Longowal, December, 2003.
2. Ionophores as Ion Sensors, Susheel K Mittal, **Ashok Kumar S.K.** and Subodh Kumar, International Conference on Electroanalytical Chemistry and Allied Topics (ELAC-2004), Goa, January 18-23, 2004.
3. 8-Hydroxy Quinoline Based Neutral Tripodal Ionophore for Cu(II) Selective Electrode, Susheel K Mittal, Subodh Kumar, **Ashok Kumar S.K.**, Harish K Sharma and Sukhdeep Kaur, 10th International Meeting on Chemical Sensors, Tsukuba Japan, July 11-14, 2004.
4. A Green Analytical Technique for sensing Low Concentrations of Lanthanide Ions, Susheel K Mittal, **Ashok Kumar S.K.,** Nidhi Rani Gupta, Harish K Sharma, Siloni Goel, National Conference on Sensors (NCS – 2005), TIET, Patiala, PP 90-91.
5. Coated Wire Ion Selective Electrode for Silver ions and its Applications, International Conference on Molecules to Materials, Susheel K Mittal**, Ashok Kumar. S.K.**, Nidhi Rani Gupta, Harish Kumar Sharma and Subodh Kumar, (ICMM-06), SLIET, Longowal.

C. Papers Communicated in Journals

1. PVC-based DB24C8 sensor for cerium (III) ions.
2. 8-Hydroxy quinoline based neutral tripodal ionophore as a copper (II) selective electrode and the effect of remote substitutents on electrode properties.
3. Copper(II) ion-selective electrode. A study of 9,10 Bis-(2-amino phenylthio methyl) anthracene as ionophore.
4. Spectrophotometric and potentiometric characterization of tetrapodal ionophore based on 8-hydroxy quinoline.
5. Coated wire ion-selective electrode for silver (I) and its applications.
7. A novel analytical technique for sensing low concentrations of lanthanides using EDTA as a sensing material.

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