CHEMICAL SENSORS BASED ON PYRIDYL IONOPHORES FOR SELECTIVE DETERMINATION OF SOME TRANSITION METAL IONS

A
Thesis Submitted

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By

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To

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Candidate's Declaration

I, hereby declare that the work presented in this thesis entitled **"Chemical Sensors Based on Pyridyl Ionophores For Selective Determination of Some Transition Metal Ions",** for fulfilment of the requirements for the degree of Doctor of Philosophy from School of Chemistry and Biochemistry, Thapar University, Patiala, is an authentic record of my own work carried out under the supervision of Dr. Susheel Mittal, Senior Professor, School of Chemistry & Biochemistry, Thapar University, Patiala, India. The matter presented in the thesis has not been submitted in part or full to any other university, institute for the award of any degree in India or abroad.

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Certified that the present work entitled **"Chemical Sensors Based on Pyridyl Ionophores For Selective Determination of Some Transition Metal Ions"**, submitted by Mr. Pawan Kumar, for fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry to Thapar University, Patiala, is an authentic and bonafide record of original research work carried out by him under my supervision at the School of Chemistry and Biochemistry. Further, the results embodied in this thesis, in full or in part, have not been submitted previously for the award of any other degree.

Susheel Mittal
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LIST OF ABBREVATIONS

ABBREVIATED FORM	FULL FORM
PIM	Polymer Inclusion Membrane
AFM	Atomic Force Microscopy
FTIR	Fourier Transform Infra Red Spectroscopy
o-NPOE	2-Nitrophenyloctylether
DOS	bis(n-octyl) sebacate
DBP	Dibutylphthalate
DOP	Dioctylphthalate
PVC	Polyvinylchloride
EDTA	Ethylenediamine tetra acetic acid
NaTPB	Sodium tetra phenyl borate
AAS	Atomic absorption spectroscopy
TEHP	Tris-(2-ethylhexyl) phosphate
CN	Chloronapthalin
DBBP	Dibutyl(butyl) phosphonate
KTpClPB	Potassium tetrakis (p-Chlorophenyl) borate
MPM	Matched potential method
FIM	Fixed interference method
CGE	Coated graphite electrode
EIS	Electrochemical impedance spectroscopy
TIMM	Transmission infrared spectroscopy
THF	Tetrahydrofuran
BA	Benzyl acetate
LOD	Limit of detection
CTA	Cellulose triacetate
BLM	Bulk liquid membrane
ISE	Ion selective electrode
ASS	All Solid State
CAChe	Computer added chemistry

dpaH	Dipyridylamine
bpy	2,2’-bipyridine
IUPAC	International Union of Pure & Applied Chemistry
E.M.F.	Electro motive force
ICP-AES	Inductive coupled plasma atomic emission spectroscopy
ICP-MS	Inductive coupled plasma atomic mass spectroscopy
TPOME	N',N",N"' tris(2-pyridyloxymethyl) ethane
WHO	World health organisation
EPA	Enviromental protection agency
SCE	Saturated calomel electrode
UV	Ultra violet
TPEN	N,N,N’,N’-tetrakis(2-pyridylmethyl) ethylenediamine
NR	Not reported
TBC	Tetrabutyl ammonium chloride
SDS	Sodium dodecyl sulphate
KSCN	Potassium thio cyanate
TETDS	Tetra ethyl thiuram disulphide
TOPO	tri-n-octylphosphine
BIS	2,6-Bis(benzimidazolyl) pyridine
‘tpydpa’	Di-2-pyridylaminoethylbenzene
‘mdpa’	1,3-Bis(di-2pyridylaminoethyl)benzene
‘pdpa’	1,4-Bis(di-2-pyridylaminoethyl) benzene
‘ditpy’	4’,4’’-(1,4-phenylene)bis(2,2’:6’,2’’-terpyridine)
BIP	2,6-Bis(benzimidazolyl)pyridine

Thesis Abstract

In the present study some pyridyl based ionophores were chosen for construction of ion selective electrodes and one pyridyl based ionophore was used for membrane transport studies. The linked 2,2'-dipyridylamine derivatives (mdpa, pdpa and tpydpa) and 4',4''-(1,4-phenylene)bis(2,2':6',2''-terpyridine) (ditpy) have been explored as neutral carrier ionophores for preparing poly (vinyl chloride) based electrodes selective to Ag(I) ions. Based on the stability constants determined by sandwich membrane method and the energy minimization studies using CAChe software (in case of 2, 2'-dipyridylamine derivatives), the ionophores were found selective for Ag (I) ions. Different compositions of the membrane were studied. The best performance in case of 'tpydpa' was found with the electrode composition (w/w): ionophore (3%); PVC (33%); o-NPOE (64%). This electrode exhibits Nernstian response with a slope of 59 mV/decade of activity in the concentration range $5.5x10^{-6}$M - $1.0x10^{-1}$M of Ag (I). The electrode shows satisfactory performance over a pH range of 3.0–9.0, with a fast response time of 14s**.** The best performance in case of 'ditpy' was found with the electrode composition (w/w): ionophore (5%); PVC (31%); NaTPB (3%); o-NPOE (61%). The electrode exhibits Nernstian response with a slope of 60 mV/decade of activity in the concentration range $5.5x10^{-5}$M - $1.0x10^{-1}$M of Ag (I). The electrode shows satisfactory performance over a pH range of 4.0–9.0, with a fast response time of 15s. In both cases response of the electrodes were highly selective to Ag^{+} ions over a number of uni-, di- and trivalent metal ions. Also, the electrodes have been used successfully as indicator electrodes in potentiometric titrations of Ag (I) ions and for determination of silver content in waste water.

Ionophore N',N'',N''' tris(2-pyridyloxymethyl) ethane (TPOME) has been used as an ionophore in a PVC based membrane for construction of lead ion selective electrode. The membrane electrode with a composition 33: 5: 62: 3 (PVC: TPOME: o-NPOE: NaTPB) exhibits Nernstian response towards Pb(II) ions with a slope 30mV/decade, over a concentration range of $1x10^{-5}$M to $1x10^{-1}$M. The potential response remains almost unchanged over pH range 3.7-6.4. The electrode shows fast response time of 15±2 seconds and a lifetime of four months. It shows good selectivity for Pb(II) ions over

other mono-, di- and trivalent cations. The electrode response is satisfactory in mixed solvent media up to 30% (v/v) non-aqueous contents. Selectivity of the ionophore for Pb(II) ions was determined by spectrophotometeric method. The electrode can also be used as an indicator electrode in the potentiometric titration of Pb(II) ions with standard chromate solution and its determination in real life samples. N,N,N′,N′-tetrakis(2-pyridylmethyl) ethylenediamine (I) as an ionophore has been used to develope as zinc ion-selective electrode. The best performance was observed with an electrode composition (w/w); PVC (30%), 2-nitro phenyloctylether (60%), ionophore (I) (5%) and sodium tetrakis(4-chlorophenyl) borate as lipophilic salt (NaTPB, 2%). The electrode shows a linear dynamic response in the concentration range $5.0x10^{-6}$ M to $1.0x10^{-1}$ M with a Nernstian slope of 30 mV/decade and a detection limit as $1x10^{-6}$ M. It has a response time of 20 seconds and can be used for at least 4 months without any significant divergence in potentials. The proposed sensor shows good selectivity with respect to alkali, alkaline earth and transition metal ions. It can be used in the pH range 3.0-8.0 and electrode has been used as an indicator electrode in potentiometric titrations of zinc(II) ions with Na_2S. The electrode also has been applied successfully for the determination of zinc ions in real life samples.

Transport experiments across polymer inclusion membrane (PIMs) containing BIP as a neutral carrier are presented. The physical immobilization of 2,6-Bis(benzimidazolylpyridine) (BIP) as an ion carrier and o-nitrophenyloctyl ether (o-NPOE) as plasticizer and cellulose triacetate(CTA) as the polymeric support was used to prepare polymer inclusion membranes. Transport experiments were carried out in a permeation cell in which membrane film was tightly clamped between two compartments. Different receiving phases were used for the study while the solutions of metal nitrates were used as source phases. The carrier concentration in the PIM was varied in the range 4 to 7 mg. The best results were obtained with membrane composition cotaining 5 mg carrier and HNO_3(0.001M) as the receiving phase. Samples of aqueous and source receiving phases were removed periodically via a sampling port with a syringe and analyzed to determine Zn^{2+} ion concentration by using atomic absorption spectroscopy method. The surface characterization of the membranes in all cases has been carried by scanning electron microscopy.

Chapter 1

INTRODUCTION

1.1 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 type of sensors. In the laboratory one of the best type of sensor is the litmus paper, which give a qualitative indication, by means of colour change. Sensors convert the chemical or electrical response (a voltage change) in observable display. The part of the device that carries out this conversion is called transducer.

We can divide sensors into three main types:

a) Physical sensors for measuring distance, mass, temperature, pressure etc.,
b) Chemical sensors which measures the chemical substances by chemical or physical responses.
c) Biosensors, which measures the chemical substances by using biological sensing element.

All these devices have to connect to a transducer of some sort, so that a visibly observable response occurs. Biosensors are really a subset of chemical sensors, but are treated as a topic in their own right. The key difference being that recognition element in biosensors is biological in nature.

1. 2 CHEMICAL SENSORS

1. 2. 1 Recognition Element

Recognition element, for example an ionophore is the key component of any sensor device. It imparts selectivity to a particular analyte or a group of analytes avoiding interferences from other species. For a suitable ionophore it is necessary to match the size and binding properties of the target species to make it or its derivatives selective towards the desired species. For example requirements for a potassium sensor will be very different from another alkali metal like sodium or any transition metal like cadmium

etc. Selection of a particular ionophore may be considered as an exercise in supramolecular chemistry. Adding to the functionality of ionophore can make it more specific towards a particular analyte. This can be used by tailoring the parent ionophore.

1. 3 CLASSIFICATION OF SENSORS

Based on the physical state of substances forming electrode membrane, potentiometric sensors are classified into

i. Ion selective electrode with solid membrane

The membrane can either be homogenous (a single crystal, a crystalline substance or a glass which is considered to be a solid with regard to the immobility of cationic groups) or heterogeneous when a crystalline substance is build into a matrix made from suitable polymer.

ii. Ion selective electrode with polymer based matrices

This type of electrodes incorporate different types of neutral carrier or ion exchange molecules. The binding sites are incorporated into semi rigid, but liquid state, plasticized polymer membrane. The most successful example is potassium electrode based on vanilomycin. This antibiotic molecule has an electron rich pocket in the centre into which potassium ions are selectively bound.

Based on the physical state of components of the membrane [1,2] ion selective electrodes are classified as follows.

1. 3.1 Glass membrane electrode

This type of electrodes makes use of glass membrane. The active sites on the surface or in the hydrated layer of glass are not free to move about during the time scale of measurement. The selectivity properties of the desired electrode can be produced by appropriate adjustment of glass composition.

1.3.2 Solid state sensors

The non-glass solid state sensors replace the glass membrane with ionically conducting membrane. The electrode body is composed of chemically resistant epoxy formulation. Sensing membrane is bonded to the electrode body which is composed of single, pure, nonporous material with a homogeneous mirror like surface of low micro porosity that

keeps sample retention to a minimum. The fluoride electrode is characteristic solid-state sensor

1.3.3 Gas Sensing electrodes

In this type of sensors gas permeable membrane is used to isolate the analyte from possible interferences in the sample. A thin buffer layer is used to trap the analyte gas and convert it to some ionic species that can be detected potentiometrically. For example ammonia gas can be monitored via the formation of ammonium ion (with an ammonium ion selective electrode) or via the shift in pH (with a glass pH-responsive electrode) within the buffer layer.

1.3.4 Biocatalytic membrane electrodes

In this type of electrodes generally, the membranes are multilayered composites containing one or more biocatalysts, often enzymes, immobilized in gel layer that coasts a conventional ion selective electrode. For the ammonium-ion-selective electrode, the enzyme urease is fixed in a layer of acrylamide gel held in place around the glass electrode bulb by a nylon mesh or cellophane film.

1.4 ELECTROCHEMICAL TRANSDUCERS

a. **Potentiometric:** These involve the measurement of the emf (potential) of the cell at nearly (10^{-12}A) zero current. The emf is proportional to the logarithm of concentration of the substance to be determined.
b. **Conductometric:** A number of reactions involve a change in composition of the solution which can be measured electrically.
c. **Voltammetric:** An increasing (or decreasing) potential is applied to the cell until oxidation (reduction) of the substance to be analyzed and there is sharp rise (fall) in the current to give a peak current. The height of the peak current is directly proportional to the concentration of 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 amperometry.
d. **FET-based sensors:** Miniaturization can 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 be used with voltametric or conductometric sensors also.

1.5 SUPRAMOLECULAR CHEMISTRY AND ION SELECTIVE ELECTRODE

Supramolecular chemistry can be defined as a field of chemistry, which studies the complex multimolecular species formed from molecular components that have relatively simpler structures. This field has been subjected to extensive research over the past four decades [2-6]. Scientists involved in supramolecular science design and study new chemical systems that are bound together reversibly by intermolecular forces, rather than by conventional covalent bonds (shared electrons). The field exploded when three of the pioneers of the field namely, Jean-Marie Lehn, Donald Cram and Charles Pedersen won the 1987 Nobel Prize in chemistry for synthesizing molecules and compounds with cavities and cages within which metal ions and other molecules could be bound. Research teams have also presented their pioneering works on the syntheses in the field. The syntheses majorly focus on specific groups of compounds, which, although a bit frightening for those out of the field, are invaluable to the experienced researcher. The host component is defined as an organic molecule or ion, whose binding sites converge in the complex and the guest component, is defined as any molecule or ion whose binding sites diverge in the complex.

Ion selective sensors, as their name implies, are based on the selective recognition of one specific ion (target ion), as compared to the other ions that may be present with it. This so-called selective recognition is then converted to a potential signal, which is a measure of the activity of the target ion. Many mechanisms have been suggested for the selective recognition of different ions in the electrodes [7], most of which focus on the selective complexation between the target ion and a specific species (the ion carrier or ionophore) that is incorporated in the liquid membrane of the electrodes, in order to create the desired selectivity. The selective complexation of target ions and ionophores, host guest chemistry, and in other words, the concept of supramolecular chemistry can be exploited in the design and construction of ion selective electrodes for different ionic species.

In general, the overall selectivity of host guest interaction depends on the following factors:

I. The number and type of donor atom available in the ligand molecule.
II. The relative position in terms of both their spacing and sequence within the ligand.
III. The electronic and structural nature of ligand backbone.
IV. Chelating and macrocyclic effect during complexation. Chelating groups increase the flexibility of the ligand but may reduce overall selectivity.
V. Branched group can be attached at proper position of host for high hydrophobicity avoiding crystallization of the membrane phase.
VI. Host-guest interaction must trigger an observable response.
VII. Changes in solvation of ligand and metal ion on complex formation.

1.6 ANALYTICAL TECHNIQUES

An analytical technique is a fundamental scientific phenomenon that has proved useful for providing information on the composition of substances. It consists of two methods

Classical techniques: Potentiometry is an example of analytical technique which is being used extensively in modern chemical analysis. Many analytical techniques available possess the varying degrees of selectivity, sensitivity, accuracy and precision, cost and rapidity. In volumetric analysis the analyte react 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 reaction. Gravimetric analysis usually involves the selective separation of the analyte by precipitation followed by the very non-selective measurement of mass. Voltammetric and gravimetric analyses can provide results accurate and precise to a few parts per thousands or better. But they require very large quantities of analyte and are well suited for major constituents.

Instrumental techniques: Instrumental techniques are used for many analyses and constitute the discipline of instrumental analysis. They are based on measurement of physical property of the sample, for example an electrical property or absorption of electromagnetic radiation. Examples are spectrophotometry (UV, visible,infrared), fluorimetry, atomic spectroscopy (absorption, emission), mass spectrometry, nuclear

magnetic resonance spectrometry(NMR), X-ray spectroscopy, electroanalytical chemistry (potentiometric, voltametric, electrolytic), chromatography (gas, liquid) and radiochemistry. Instrumental techniques are generally more sensitive and selective than classical techniques but are less precise, on the order of 1to 5% or so. These techniques are much more expensive. Chromatographic techniques are practically powerful for complex mixtures. They performs the measurement and separation steps simultaneously. Radiochemical methods make use of the specific properties that are characteristics of a particular nucleotide. These properties include the type and energy of the radiation, the half life and the decay scheme. Thermal analysis includes a group of techniques in which specific physical properties of the material.

Table 1.1: Comparison of Various Analytical Methods

Method	Approx. Range, (M)	Approx. Precision, %	Selectivity	Cost	Application
Kinetic Methods	10^{-2}-10^{-10}	2-10	Good-moderate	Moderate	Enzymes, Inorg.
Chromatography	10^{-3}-10^{-9}	2-5	Good	Moderate high	Multicomponent, Inorg.
Voltammetry	10^{-3}-10^{-10}	2-5	Good	Moderate	Org., Inorg.
Spectrophotometry	10^{-3}-10^{-6}	2	Good-moderate	Low Moderate	Org., Inorg.
Electrogravimetry	10^{-1}-10^{-4}	0.01-2	Moderate	Moderate	Org., Inorg.
Atomic Spectroscopy	10^{-3}-10^{-9}	2-10	Good	Moderate high	Multicomponent, Inorg.
Fluorometry	10^{-6}-10^{-9}	2-5	Moderate	Moderate	Org.,Inorg.
Gravimetry	10^{-1}-10^{-2}	0.1	Poor-Moderate	Low	Inorg.
Titrimetry	10^{-1}-10^{-4}	0.1-1	Poor-Moderate	Low	Org., Inorg.
Potentiometry	10^{-1}-10^{-6}	2	Good	Low	Inorg., Organic

1.7 ION SELECTIVE ELECTRODE WITH POLYMER BASED MATRICES

1.7.1 Ion selective electrodes

Ion selective electrode is a device which responds to one particular ion. This potentiometric device measures the potential against an appropriate electrode. The potential developed is proportional to the logarithm of activity of the ion of interest. The most successful ISE is still probably the glass pH electrode, generally used to adjust or control pH in aqueous and organic media. Compare to solid crystalline, ceramic and glass membrane ISEs, electrodes with polymeric membranes are widely used. Ionophore based sensors provide robust, portable, simple and relatively cheap method of analysis. The working concentration of most of the ISEs is 10^{-6}-10^{-1}M. It operates on the principle of concentration cell [8-13], in that it contains a selective membrane which develops potential due to concentration difference of ion across the membrane.

1.7.2 Polymer Matrix

Normally, the components of the membrane are supported by an inert lipophilic matrix where the mediator solvent behaves as a plasticizer conferring the required final features to the membrane [14]. Among the reported matrixes (polyurethanes, polysiloxanes,

silicon rubber etc.); PVC is the one which is most used [15-19]. This is the integral component of the ISEs and it provides mechanical strength to the membrane. Ideally, it is inert or has no chemical interaction with the target ion. Polymer ISE membranes are commonly prepared with poly(vinyl chloride). Also, the membranes have been constructed using a matrix of polysulfone, a porus polymer in sensor construction. Its stability makes it an attractive material for incorporation of biological material in the membrane [20].

1.7.3 Membrane Solvent

Membrane solvents also known as plasticizer are used to increase mechanical strength of the membrane which is required to give a homogenous organic phase. It is the dominating component of PVC membranes. The amount and nature of plasticizer greatly affect the selectivity behaviour of the membrane. It affects membrane selectivity through both extraction of ions into organic phase and influencing their complexation with ionophore [21-23]. The plasticizer which are commonly used in ISE-membrane are ortho-nitrophenyoctyl ether (o-NPOE, polar) or bis(2-ethylhexyl)sebacate (2BS, apolar), dibutyl phthalate (DBP, apolar). A plastizer change from polar to non-polar, is reported to reduce the M^{2+}-selectivity of the ISEs.

1.7.4 Ionic Additives

The prerequisite for a theoretical Nernstian response of the ISE is that no significant amount of primary ion may be co-extracted together with the ion of opposite charge sign; of measuring ion from the sample into the membrane phase. This means that the membrane is permeable only for ion with same charge sign of the measuring ion. This membrane characteristic is called permselectivity or Donnan Exclusion. Ionic additives also lower the electrical resistance of the membrane, which is of special importance in case of microelectrodes. They introduce selective response and hence, concentration of additives must be carefully controlled in the membrane phase. Cation-selective ISE membrane contains normally tetraphenyl borate derivatives as a lipophilic site, whereas anion selective membrane, a tetraalkylammonium salt for this purpose.

1.7.5 Lipophilic salt

The addition of lipophilic salt without ion exchanger properties reduces electrical resistance of membranes [24].

1.7.6 Ionophore

The ionophore or membrane-active recognition element can be ion exchanger or neutral macrocyclic compounds, having cavities or semi cavities to surround the target ion. An ideal ionophore forms relatively strong, selective and reversible complexes only with the target ion so that in the membrane no interference occurs. Additionally, the ionophore structure must contain sufficient number of lipophilic groups in order to keep its leaching rate from membrane phase to sample phase as low as possible.

1.8 RESPONSE MECHANISM

An electrochemical-measuring cell consists of two galvanic half cells: an ion selective electrode and reference electrode. The total potential difference (electromotive force, EMF) measured under zero current condition between two electrodes is the sum of local potential differences, arising at each electrochemical interface. A reference electrode is used to measure the working electrode potential of an electrochemical cell. It should have a stable electrochemical potential under zero current conditions. Membranes of ionophore based ISEs normally consists of a plasticized polymeric phase with poly vinyl chloride as polymer matrix, lipophilic ion exchanger sites and an ionophore. Such membranes are placed between two aqueous solutions, one being the sample and the other, so-called inner electrolyte. The response of ISEs has been described by using three models; kinetic model, the phase boundry potential model and membrane surface model [25-29]. According to 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 equalibria and electroneutrality condition within each phase and by assuming kinetic processes being fast between two phases. It directly relates the spontaneous equilibrium partitioning of ions across sample membrane interface to the phase boundry potential, emphasizing that the phase boundry potential across the sample-membrane interface is the result of ion-selective charge separation at that

interface. In most case of practical significance, the response of ISE can be described by the phase boundary potential, E_{PB}, because all other contributions of the emf of the potentiometric cell are sufficiently constant.

$$EPB = E + \frac{RT}{zF} \ lna1(aq)/a1(org)$$

Where R, T and F having usual meanings, z being the charge, and

$$E^{o}{}_{=} [\ \mu^{o}\ (aq)-\mu^{o}(org)]\ /zF$$

μ^{o} and a_1 being 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 membranes based on mass and charge balances and complex formulation equalibria. If $\mathbf{a_1}$(org) does not depend on $\mathbf{a_1}$(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 difference between a_1(aq) at the membrane surface and in the bulk of the sample. The influence of an interfering ion was first described with the still widely used empirical Nicolskii-Eisenman equation [30], which is an extension of Nernst equation.

1.9 SELECTIVITY AND INTERFERENCE

To determine the extent of interference by the ions other than primary ion is very important in ion selective electrode measurements. Several experimental methods for the determination of potentiometric selectivity coefficient are based on Nicolskii-Eisenman [30]. It is well established now that for $Z_i \neq Z_j$, the Nicolskii-Eisenman equation is not valid in the activity range when the primary ion and the interfering ion significantly contribute to the potential. 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.

1.10 POLYMER INCLUSION MEMBRANE

The polymer-based liquid membrane concept has been known for over 40 years [31,32] and has been proposed as a possible alternative to conventional solvent extraction. It has been used in preparing the sensing membranes in ion-selective electrodes. However, more recently such membranes have been termed as polymer inclusion membranes (PIMs) [33] and have been shown to exhibit excellent stability and versatility, particularly when compared to other liquid membrane types. Recent research on PIMs demonstrates increase in interest in these membranes [33,34]. PIMs are usually composed of an extractant (carrier), a base polymer (usually poly(vinyl chloride) (PVC) or cellulose triacetate (CTA) and a plasticizer or a modifier. The carrier is essentially a complexing agent or an ion-exchanger, responsible for binding with the species of interest and transporting it across PIM. This process relies upon the concentration gradient of the species/ carrier complex or ion pair formed within the membrane, which acts as the driving force enabling transport across the membrane. The base polymer provide the membrane with mechanical strength and the plasticizer provides elasticity and flexibility. The plasticizer decreases the glass transition temperature of the membranes and improves the compatibility of the membrane components. In some cases, carrier also acts as plasticizer and so additional plasticizer is not necessary. A modifier is occasionally added to the membrane composition to improve the solubility of the extracted species in the membrane liquid phase. Piera et al. [35] described several compatible combinations of frequently used base polymers and extractants and discussed the factor influencing the homogeneity, flexibility and mechanical strength of PIMs.

1.11 PYRIDYL BASED IONOPHORES

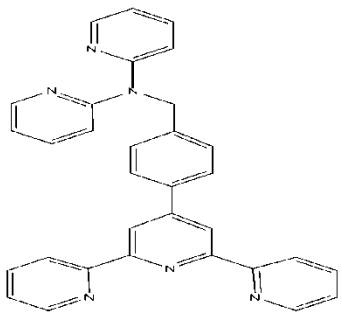
2,2'-Dipyridylamine (dpaH) is an aromatic amine, in some ways similar to 2,2'-bipyridine (bpy), but the central amine unit introduces several differences: (1) dpaH coordinates with six-membered chelate rings instead of five-membered rings for bpy; (2) the coordinated pyridine rings are not necessarily forced to near coplanarity as in bpy; (3) the ligand field strength of dpaH is greater than ethylenediamine, but closer to that of a single aromatic amine, e.g. that dpaH is less of a p-acceptor ligand than bpy [36]. The two-pyridine rings of dpaH are flexible in their coordination with metal centers, adopting either nearly coplanar or tilted pyridyl ring planes that vary from 2° to 42° of tilt. This

can be induced either electronically or stereochemically. Hence, the chemistry of 2,2'-dipyridylamine (dpa) and its derivatives has been the focus of a considerable number of investigations. For example, mono-, di- and tri-dpa derivatives have been reported in which the secondary nitrogen of each dpa is directly bound to an aryl core with such species being employed in studies that range from metal coordination and supramolecular chemistry to the synthesis of new luminescent materials. Pd(II) and Pt(II) complexes of such dpa derivatives have also been investigated as potential anticancer agents due to their structural similarity to cisplatin.

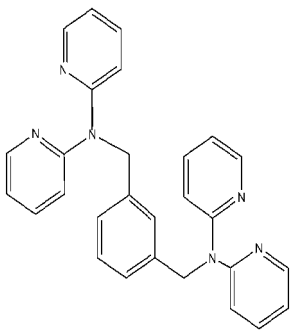
We have proposed some molecules that are available in the literature and related synthesized molecules. Some of these molecules have been used for ion-selective electrode preparation characterization and one for ion transport across the polymer inclusion membrane.

Pyridyl based ionophores are gaining increasing interest as tools for analysis and separation of metal ions as well as many biological and other applications. To monitor these carriers we have prepared PVC-membrane electrodes as analytical tools for monitoring a variety of metal ions.

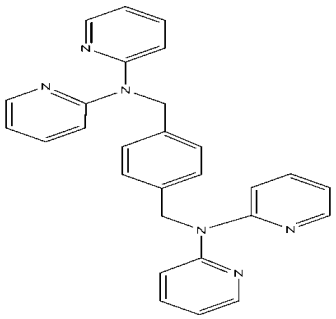
Some commercially available and synthesized pyridyl ionophores were used in fabrication and characterization as ion-selective electrodes for metal ions.



Di-2-pyridylaminoethyl-4-terpyridylbenzene (tpydpa)

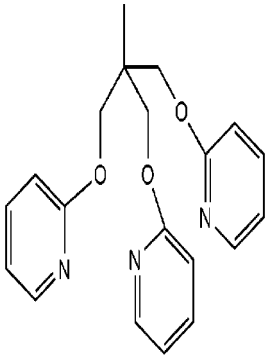


1,3-Bis(di-2-pyridylaminoethyl) benzene (mdpa)



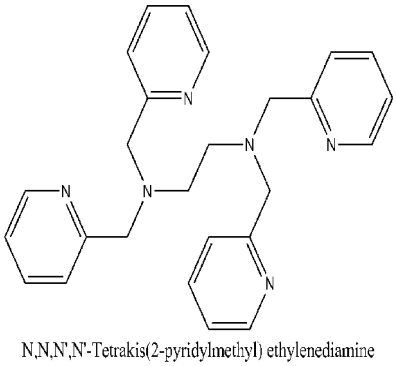
1,4-Bis(di-2-pyridylaminoethyl) benzene

(pdpa)



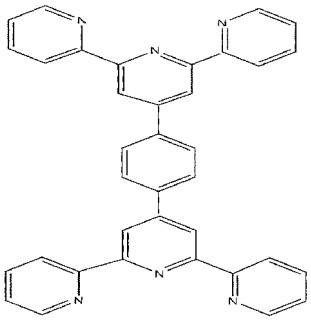
2,2'-(2-methyl-2-((pyridin-2-yloxy)methyl)propane-1,3-diyl)bis(oxy)dipyridine

(TPOME)



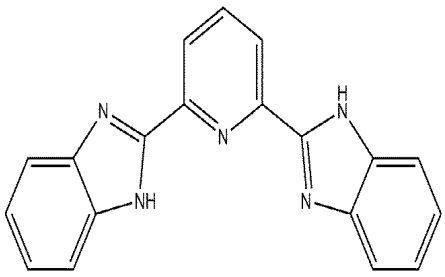
N,N,N',N'-Tetrakis(2-pyridylmethyl) ethylenediamine

(TPEN)



4',4'''-(1,4-phenylene) bis(2,2': 6',2''-terpyridine)

(ditpy)



2,6-Bis(2-benzimidazolyl) pyridine

(BIP)

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Chapter 2

Literature Review

Metal pollution in ambient environment assumes great importance in the present scenario. Unlike organic pollutants, natural processes of decomposition do not remove heavy metals. On the contrary, they may be enriched by organisms and can be converted to organic complexes that may be more toxic. Determination of metal ions in industrial wastes, soil, biological samples, aquatic ecosystem and other effluents has been of increasing concern because of their toxicity and non-biodegradability. Heavy metals accumulate in the environment from industrial sources thereby inhibiting the metabolism and break down of tissues of many organs, which results in the neurological poisoning if accumulated in human body. Above certain permissible limits, metal ions may be hazardous for human being **[1].** Potentiometric sensors and optical chemical sensors are devices of choice for such monitoring. In this context, soilid/liquid membranes containing ionophores are used to generate potential response due to difference in activity of the analyte solution on either side of the membrane and also optical properties of a material may be measured to collect quantitative information by the conventional methods of absorbance, fluorescence and reflectance spectroscopy **[2-8].**

One of the greatest applications of ionophores (macromolecules) in analytical chemistry is their use for separations, enrichment and analyses of ionic species. There has been an increase in the use of ionophores in optical chemical sensors. Ionophores are non-coloured ion-complexing organic molecules or lipophilic ion carriers, which are capable of reversibly binding to ions and transporting them across organic membranes by carrier translocation. Their most widespread application so far is in ion-selective membranes for detection of the target ions. 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.

Coordination chemistry, by its very nature, deals with metals and ligands. Metals are known to have preferences for certain ligands and for certain geometries on the basis of Pearsons concept **[9].** A rational approach toward ligand design for selective complexation of metal ions in solution, would be, for example, design of ligands as therapeutic reagents for the treatment of metal intoxication **[10],** design of functional groups for chelating ion-exchange materials. At the same time, an understanding of the principles of selectivity would be invaluable in understanding the metal ion selectivity displayed by biological cation transport systems such as in the cell wall **[11]** metal ion binding proteins or siderophores such as enterobactin and how metal ions are distributed in the environment. Ligands containing pyridyl residues normally show normal tendency for complex formation **[12-14]** as the homologues ligands in which these residues are substituted by aliphatic nitrogen groups, for example picolinic acid and 2-picolylamine, which can be compared with glycene and ethylenediamine. In spite of lower basicity of ligands containing pyridyl donors, the selectivity constants of homologus ligands with the same metal ions are often very similar and therefore the aromatic compounds bind more strongly in neutral and acidic media. This effect can be increased, if ligands are considered with enough donor groups to allow the formation of 1:1 compounds.

The neutral saturated nitrogen is widespread in ligands used in coordination chemistry. This is partly because it provides a synthetically convenient point of attachment for three other chelating groups **[14-15].** The unsaturated nitrogen donor pyridine is a stronger base than any of the saturated N donors. However, in aqueous solution, pyridine is a weaker base than the saturated nitrogen donors. This must arise partly because pyridine is a tertiary amine, unable to disperse the charge from Lewis acids to the solvent by hydrogen bonding.

The nitrogen is sp^2 (or sp) hybridized in pyridne, imidazole, azo, nitrile etc., ligands which leads to greater basic character in the orbitals used for bonding to the metal ion and hence more covalent bonding. These ligands can thus exert very high ligand field

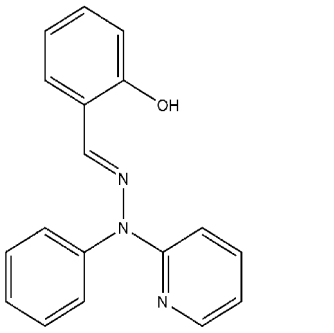
strengths, even though their proton basicity may be significantly less than that of the sp^3-hybridized saturated nitrogens. The low proton basicity of the unsaturated nitrogen donor can be of considerable help in designing ligands, since what *ultimately counts in many situations is not the formation constant of the metal ion with the ligand alone but also the relative difficulty of removing protons from the donor groups of the ligand so as to permit complex formation*. Another important aspect of the unsaturated nitrogen donors is the possibility of pi bonding between the ligand and the metal ion. Unsaturated donors such as the pyridyl or imidazole group have the ability to impart rigidity to the ligand system, due to the rigidity of aromatic ring systems. The ligand 1,10-phenanthroline (PHEN) forms complexes that are a fairly more stable than those formed by bpy (2,2'.bipyridyl) with the same metal ion. It seems reasonable to suggest that this effect is due to the fact that the PHEN is more effectively *preorganized* for coordination relative to the bpy. The bpy is highly strained in the conformer with 'the nitrogens cis to each other, as required for coordination to metal ions, because of the steric hindrance between the hydrogens in the 3- and 3'- positions, However, in PHEN this problem is overcome by fusing the two rings and forcing the ligand to remain in the correct conformation for coordination to a metal ion. This idea of *preorganisation"* is of considerable importance in ligand design**.** The promising results of Damu et al. [16] obtained for N-pyridylmethyl derivatives of macrocyclic ligands with heavy metal ions suggested that they might be useful as active compound in ion selective electrodes.

2.1 NATIONAL AND INTERNATIONAL STATUS OF ISEs ON PYRIDYL BASED IONOPHORES

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. 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, these compounds have attracted the attention of analytical scientists. Here, we present important contribution of research activities that concentrate on chemical sensors based on neutral carriers using pyridyl based acyclic and macrocyclic based ionophores. We

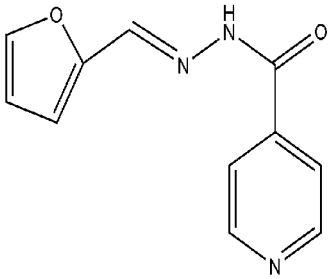
devoted the most attention on the sensing devices, sensing material and some important conclusions of the reported work.

Upadhyay et al. [17] have reported ionophore (2-((2-phenyl-2-(pyridin-2-yl)hydazono)methyl)pyridine) for europium selective electrode. The electrode exhibited a Nernstian slope and selectivity studies showed that this electrode have higher selectivity towards Eu^{3+} over a large number of cations. The electrode could be used to quantify europium in soil, binary mixtures and also used as an indicator electrode in the potentiometric titration of Eu^{3+} with EDTA. **Pourzavid et al. [18]** have reported sensor for neodymium ion using N-(furfuralidene)-N –isonicotinoylhydrazine as neutral ionophore and this sensor exhibits a Nernstian response over a wide concentration range $1.0x10^{-7}$ to $5.0x10^{-1}$M , working pH range 3.0 – 8.4, good selectivity and sensitivity to the neodymium ions. The sensor can be used over a period of 11 weeks without any considerable divergence in the potentials. **Mizani et al. [19]** have reported Zn (II) sensor based on N, N'-bis (2hydroxy -4-metoxybenzaldehyde)-2, 6-diamino pyridine. The sensor displays a linear dynamic range between 1.0×10^{-7} and 1.0×10^{-1} M, with a Nernstian slope with a workable pH range of 4.5-10.



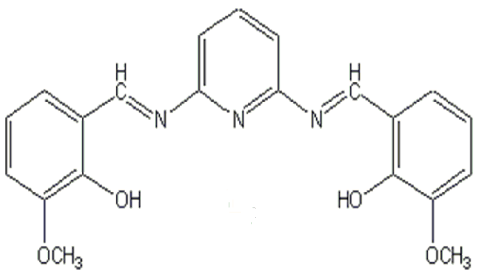
(2-((2-phenyl-2-(pyridin-2-yl)hydrazono)methyl)phenol)

(17)



(*E*)-*N*'-(furan-2-ylmethylene)isonicotinohydrazide

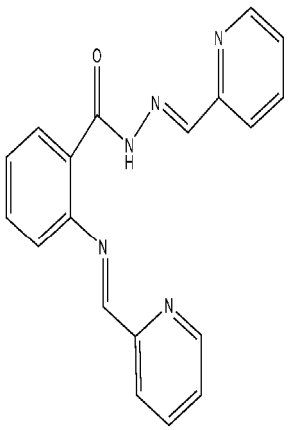
(18)



N, N'-bis (2hydroxy -4-metoxybenzaldehyde)-2, 6-diamino pyridine

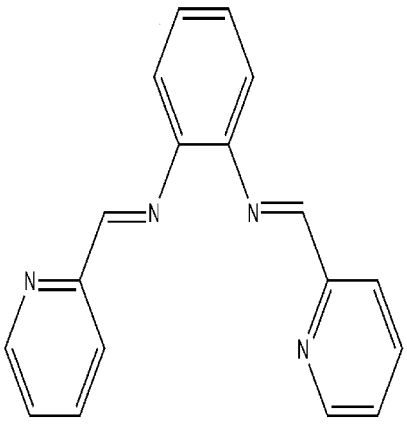
(19)

Fu et al. [20] reported a Zn^{2+}-selective electrode based on Schiff-base as ionophore. The effect of plasticizers on Zn^{2+} -selective electrodes has also been studied. The electrode revealed Nernstian behaviour over a wide concentration ranges of 1.0×10^{-6}-1.0×10^{-3} M and a workable pH range of 3.4–5.8. **Seo et al. [21** reported a Schiff base N,N'-bis(pyridin-2-ylmethylene)benzene-1,2-diamine as ionophore for preparing PVC-based membrane sensors selective to the silver ions. The sensor works well over a wide concentration range 1×10^{-7} to 1.0×10^{-3}M with a slope of 58.6 mV/decade and showed good selectivity to silver ion over a number of cations. **Ion et al. [22]** synthesised methyl pyridine derivatives of 14-membered tetraaza macrocycles, 3,11-Bis(2-pyridylmethyl-)3,7,11,17-tetraazabicyclo[11.3.1]-heptadeca-1(17)13,15-triene (22a) and 3,7,11-Tris(2-pyridylmethyl)-3,7,11,17-tetraazabicyclo-[11.3.1]heptadeca-1(17),13,15-triene (22b) and applied for electrodes in PVC membranes. Finally, 3,7,11-tris (2-pyridylmethyl)-3,7,11,17-tetraazabicyclo [11.3.1] heptadeca-1(17),13,15-triene which showed a remarkable selectivity for Cd^{2+} in the presence of Cu^{2+}, but not for Cd^{2+} in the presence of Pb^{2+} , was used as an ionophore in a Pb^{2+} ions selective sensor. The sensor exhibited the best performance, having a slope of 28.5±0.2 mVdecade^{-1} in the concentration range $1x10^{-6}$–$1x10^{-1}$M. The sensor showed good selectivity for Pb^{2+} ions over other monovalent, divalent and trivalent interfering cations. **Mollagh et al. [23]** developed PVC membrane and coated wire sensors based on 1-phenyl-3-pyridin-2-ylthiourea for Fe(III) ions with the best performance in the range 3.0×10^{-7}–1.0×10^{-2} M and a slope of 20.2 ± 0.8 mVdecade^{-1}.



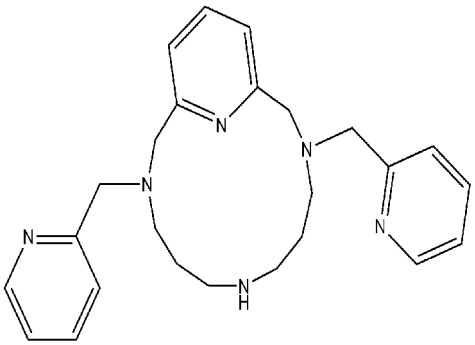
(*E*)-*N*'-(pyridin-2-ylmethylene)-2-((*E*)-pyridin-2-ylmethyleneamino)benzohydrazide

(20)



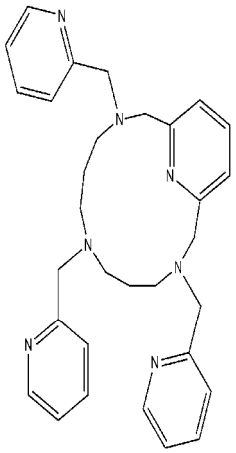
N,N'-bis(pyridine-2-ylmethylene) benzene-1,2-diamine

(21)



3,11-Bis(2-pyridylmethyl-)3,7,11,17-tetraazabicyclo[11.3.1]-heptadeca-1(17)13,15-triene

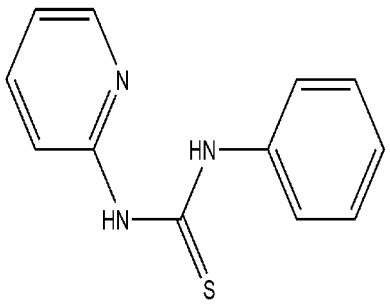
(22a)



3,7,11-tris(2-pyridylmethyl)-3,7,11,17-tetraazabicyclo [11.3.1] heptadeca-1(17),13,15-triene

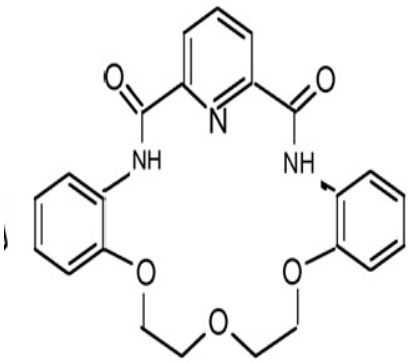
(22b)

Kazemi et al. [24] has reported benzo- and pyridine-substituted macrocyclic diamides as ion carriers for lead ions. The electrode based on 3,15,21-triaza-4,5;13,14-dibenzo-6,9,12-trioxabicycloheneicosa-1,17,19-triene-2,16-dione (24) exhibited a Nernstian response for Pb^{2+} ions over a wide concentration range of $3.6x10^{-6}$ to $1.3x10^{-2}$M. The electrode revealed good selectivities with respect to many cations including alkali earth, transition and heavy metal ions. The proposed sensor could be used in pH range of 3.7–6.5.



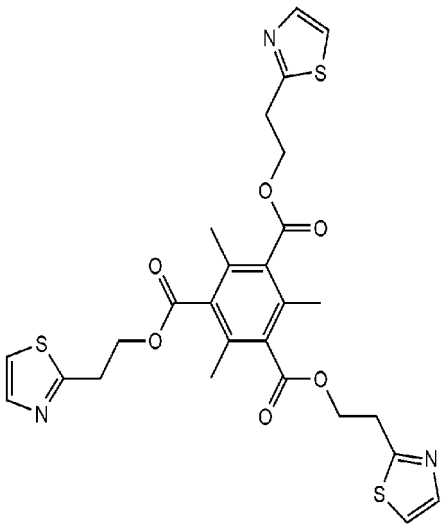
1-phenyl-3-pyridin-2-ylthiourea

(23)



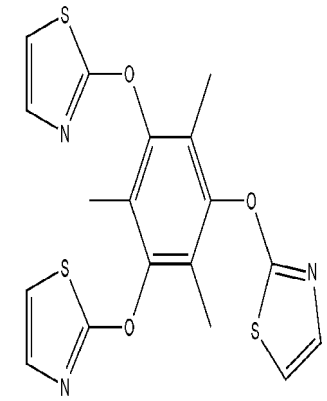
3,15,21-triaza-4,5;13,14-dibenzo-6,9,12-trioxabicycloheneicosa-1,17,19-triene-2,16-dione
(24)

Kim et al. [25] reported potentiometric evaluation of 1,3,5-tris(thiazolylcarbethoxy)-2,4,6-trimethylbenzene (25a), 1,3,5-tris(thiazolylhydroxy)- 2,4,6-trimethylbenzene (25b), 1,3,5-tris(thiazolylmethyl)-2,4,6-trimethylbenzene (25c), and 1,3,5-tris(thiazolylphenyl)-2,4,6-trimethylbenzene (25d), towards mono and divalent cations under various pH conditions are outlined. All electrodes showed substantial responses to silver ion under acidic condition, but there was almost nil response to many transition metal ions. The 25a- and 25c-based electrodes resulted in near Nernstian responses with low detection limits, while the 25a- and 25d-based sensor showed sub-Nernstian behavior below 40 mV/decade for Ag^{+} ions. **Evtugyn et al. [26]** reported potentiometric sensor based on glassy carbon electrode covered with polyaniline and neutral carrier, e.g., thiacalix[4]arene containing pyridine fragments in the substituents in the lower rim and applied for determination of Ag^{+} ions in the range from $5.0x10^{-7}$M to $1.0x10^{-2}$M.



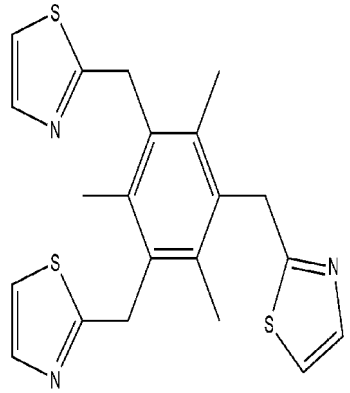
1,3,5-tris(thiazolylcarbethoxy)-2,4,6-trimethylbenzene

(25a)



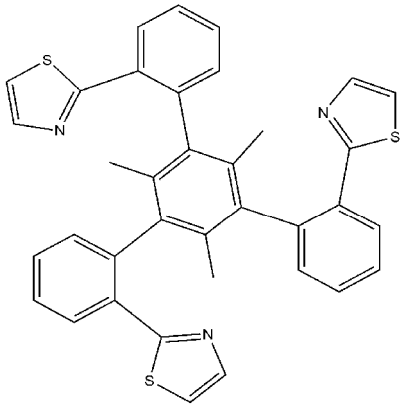
1,3,5-tris(thiazolylhydroxy) -2,4,6-trimethylbenzene

(25b)



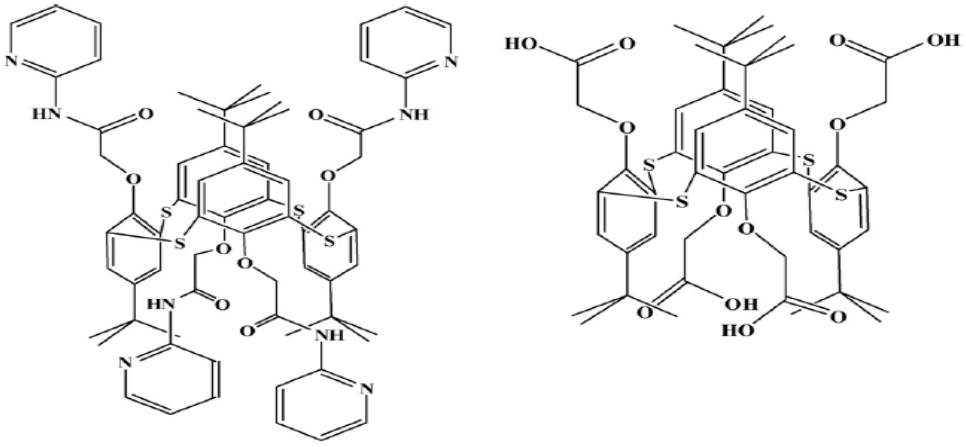
1,3,5-tris(thiazolylmethyl)-2,4,6-trimethylbenzene

(25c)



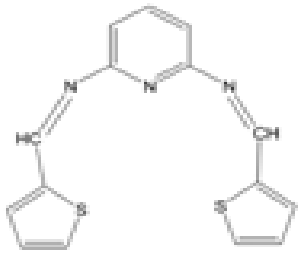
1,3,5-tris(thiazolylphenyl)-2,4,6-trimethylbenzene

(25d)



Thiacalix[4] arene derivatives

(26)

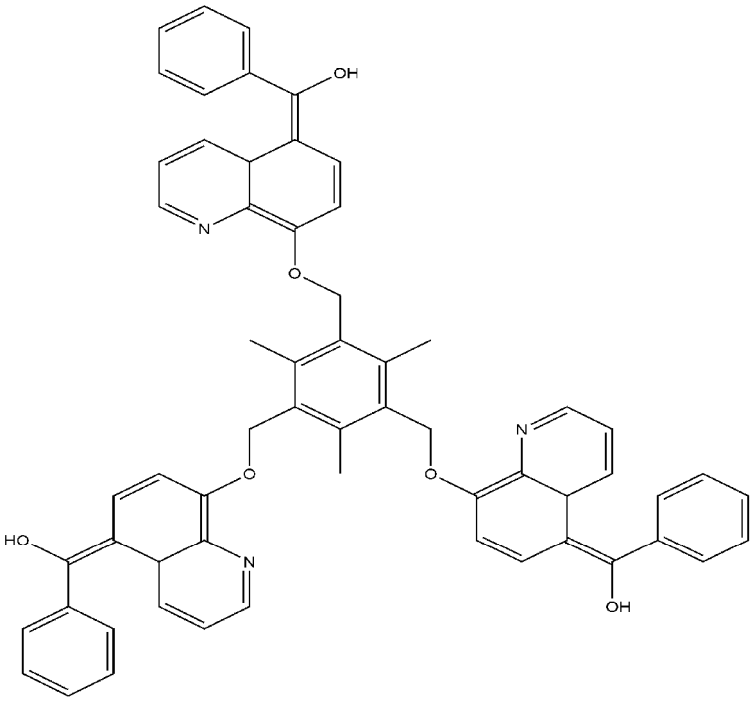


N,N'-bis-thiophen-2-ylmethylene-pyridine-2,6-diamine

(27)

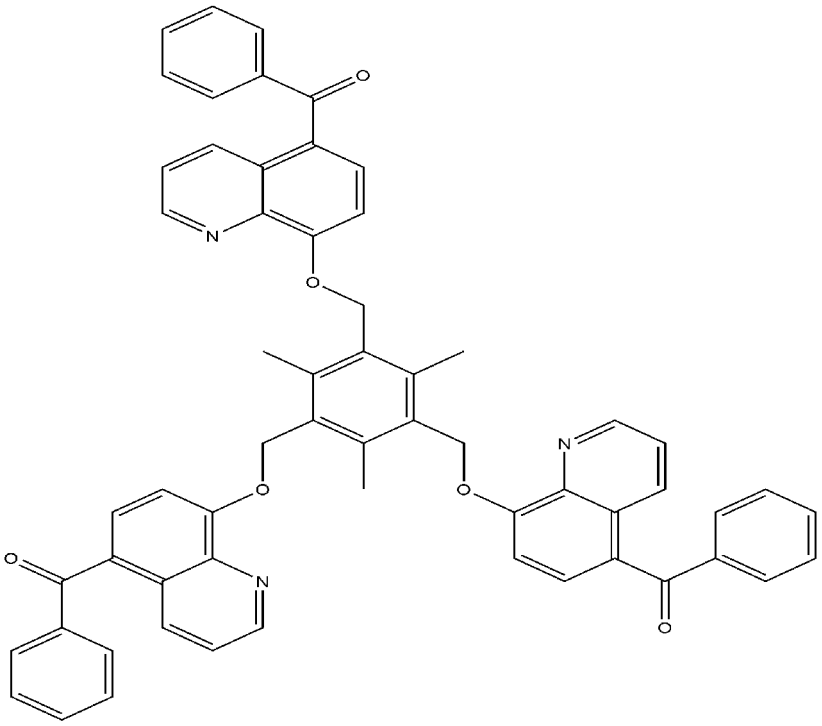
Kim et al. [27] reported polymeric electrodes for lead ion based on N,N'-bis-thiophen-2-ylmethylene-pyridine-2,6-diamine as an ion carrier. The membrane electrode gave an excellent Nernstian response and provided good sensitivity and selectivity for Pb^{2+} ions over a wide variety of other metal ions in pH 7.0 buffer solutions. The good sensitivity and selectivity towards lead ions are attributed to the strong complexation of lead ion to N,N'-bis-thiophen-2-ylmethylene-pyridine-2,6-diamine which has geometrically the proper cavity to coordinate to the ligand.

Mittal et al. [28] reported PVC membrane ion selective electrodes based on 1,3,5-Tris(8-quinolinoxymethyl)-2,4,6-trimethylbenzene (28a) for Cu(II) ions. Also their derivatives prepared by placing suitable substitutents at fifth position of 8-oxine moiety, i.e, 1,3,5-Tris(5-chloro-8-quinolinoxymethyl)-2,4,6-trimethylbenzene (28b), 1,3,5-Tris(5-benzoyl-8-quinolinoxymethyl)-2,4,6-trimethylbenzene (28c) and 1,3,5-Tris[(5-phenylhydroxymethylene)-8-quinolinoxymethyl]-2,4,6-trimethylbenzene (28d) ionophores have also been used to make copper-selective membrane electrodes. Among all the four electrodes, MO8HQ and HYD-8HQ ionophores based electrodes show excellent response towards Cu (II) ions. The electrodes having composition 33% PVC, 4% MO8HQ and 63% dibutyl phthalate (DBP) and 33% PVC, 6% HYD-8HQ, 63% dibutyl phthalate (DBP) exhibited a Nernstian response to Cu (II) ions in the range of 1.0×10^{-6} to 1×10^{-1} M. The electrode showed good selectivity for Cu (II) ions in comparison to heavy metal ions, transition metal ions and for alkali and alkaline earth metal ions. The electrode has been used as an indicator electrode in the potentiometric titration of Cu (II) ions with EDTA.



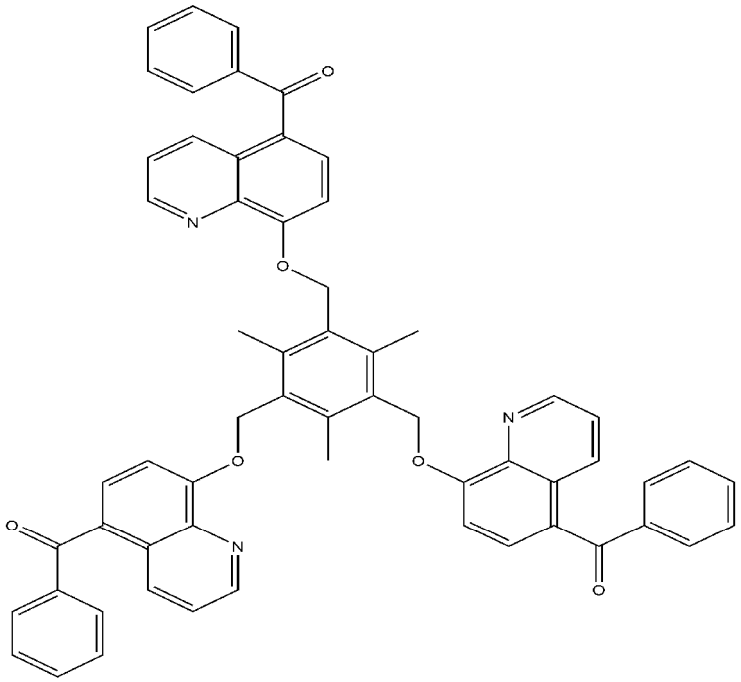
1,3,5-Tris[(5-phenylhydroxymethylene)-8-quinolinoxymethyl]-2,4,6-trimethylbenzene

(28a)



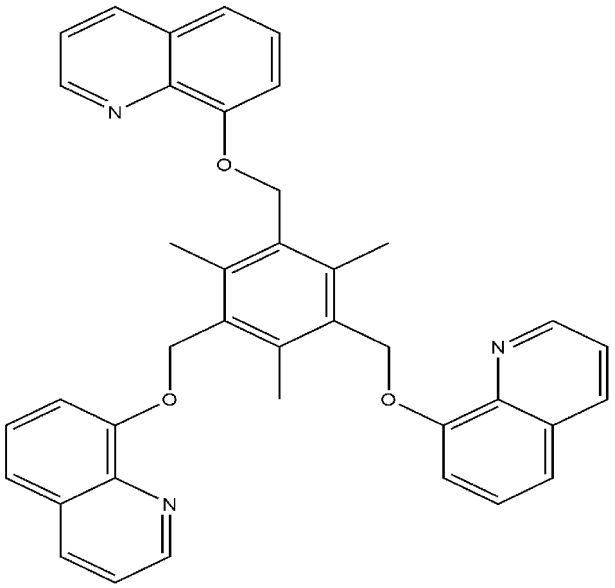
1,3,5-Tris(5-benzoyl-8-quinolinoxymethyl)-2,4,6-trimethylbenzene

(28b)



1,3,5-Tris(5-benzoyl-8-quinolinoxymethyl)-2,4,6-trimethylbenzene

(28c)



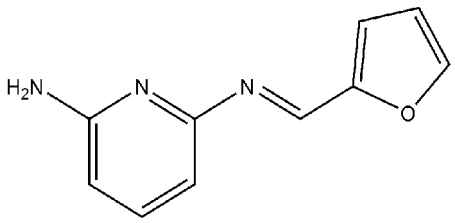
1,3,5-Tris(8-quinolinoxymethyl)-2,4,6-trimethylbenzene

(28d)

Norouzi et al. [29] reported that N-(2-furylmethylene) pyridine-2,6-diamine as an ionophore in the construction of a PVC-based membrane sensor selective for Nd^{3+} ions. The sensor response was Nernstian over a wide concentration range $1.0x10^{-5}$M to $1.0x10^{-2}$M and a life time of at least six weeks. **Oleksiak et al. [30]** reported synthetic

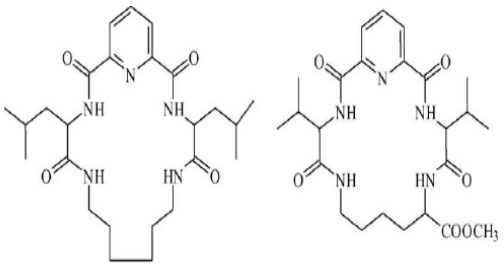
calix[4]arene-crown ionophores selective to Na^+ and Cs^+ ions recognition for ion-selective membrane electrodes. Electrodes of two different constructions: all-solid-state (ASS) (with conducting polymer layer on glassy carbon or platinum as ion-to-electron transducer) and conventional ion-selective electrode. Resistance of PVC membrane with ionophores were within the range 0.15–1.4 MΩ depending on the type of the outer electrolyte and its concentration.

Hassan et al. [31] reported cyclic tetrapeptide derivatives selective for Cu^{+2} ions. The sensors exhibited fast and stable near-Nernstian response over the concentration range $1.0x10^{-6}$ M to $1.0x10^{-2}$ M Cu^{+2} ions with a slope of 30.2–25.9 mV/decade in the pH 4.5–7.0. **Jeong et al. [32]** reported electrodes for Pb^{2+} based on N,N'-bis(salicylidene)-2,6-pyridinediamine as membrane carrier. Sensor exhibited Nernstian response and the limit of detection of −log a (M) = 6.04 to Pb^{2+} in $Pb(NO_3)_2$ solutions.



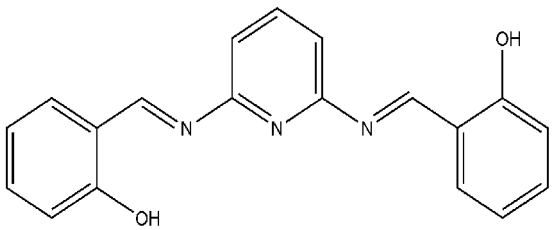
N-(2-furylmethylene)pyridine-2,6-diamine

(29)



Cyclic tetrapeptide derivatives

(31)

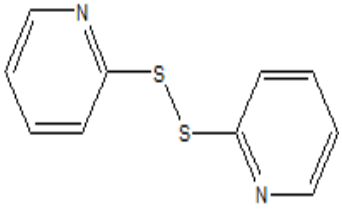


N,N'-bis(salicylidene)-2,6-pyridinediamine

(32)

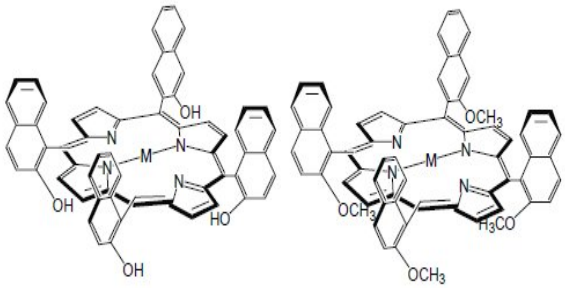
Akhond et al. [33] reported membrane sensor for La^{3+} ion based on 2,2′-dithiodipyridine as an ion carrier with good selectivity for La^{3+} ions over a wide variety of other metal ions. The electrode exhibited a slope of 20.0 ± 1.0 mV /decade of La^{3+} over a concentration range of 7.1 x 10^{-6} M to 2.2 x 10^{-2} M of La^{3+} with a workable pH range 3.3–8.0. **Lee et al. [34]** reported membrane electrodes for lead ion based on meso-tetrakis(2-hydroxy-1-naphthyl)porphyrin (I) and meso-tetrakis(2-methoxy-1-

naphthyl)porphyrin (II) displays a good Nernstian response (29.2±0.3 mV/decade) to Pb^{2+} in $Pb(NO_3)_2$ solutions over the linear range of $3.2x10^{-5}$ to $1x10^{-1}$M. **Ueda et al. [35]** reported 3-(2-pyridylethylimino)-2-butanoneoxime as an ionophore in PVC matrix for silver ions. The electrode exhibited good silver ion selectivity comparable to that of a quadridentate Schiff base N,N'-bis(2'-hydroxyimino-1'-phenylpropyleden)-1,3-propanediamine (35a) reported previously. The electrode developed gave pseudo Nernstian response (35.6 mV/decade) in the concentration range $5.0x10^{-7}$ M to $7.9x10^{-2}$M



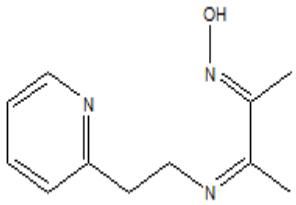
2,2'-dithiodipyridine

(33)



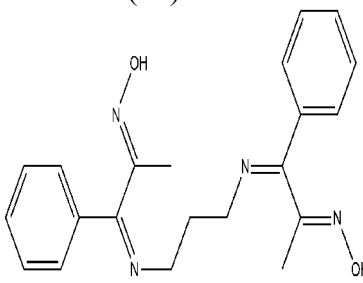
Porphyrin derivatives

(34)



3-(2-pyridylethylimino)-2-butanoneoxime

(35)

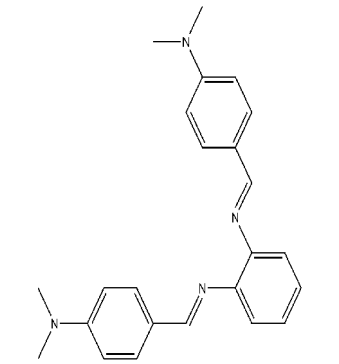


n,n'-bis(2'-hydroxyimino-1'-phenylpropyliden)-1,3-propanediamine

(35a)

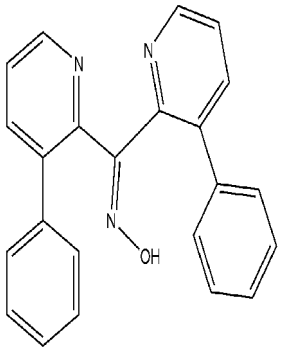
Mashhadizadeh et al. [36] reported N,N′-bis-(4-dimethylamino-benzylidene)-benzene-1,2-diamine as a suitable neutral carrier for Ni^{2+} ion. The sensor exhibits a Nernstian response for Ni^{2+} ions over a wide concentration range $2.0x10^{-7}$ M and $1.0x10^{-2}$ M with a slope of 30±1 mV/decade. **Saleh et al. [37]** reported a 5,6,7,8-Tetrahydro-8-thioxopyrido[4′,3′,4,5]thieno[2,3-d]pyrimidine-4(3H) one is used as a novel ionophore in plasticized poly(vinyl chloride) (PVC) matrix membrane sensor for uranyl ions. The sensor displays a rapid and linear response for uranyl ions over the concentration range $1.0x10^{-1}$M to $2.0x10^{-5}$M uranyl ion with a Nernstian slope of 30 mV/decade. The sensor exhibited good selectivity for uranyl ion over many inorganic cations and some

anions. **Amini et al. [38]** reported silver ion-selective electrodes based on methyl-2-pyridyl ketone oxime [38a], phenyl-2-pyridyl ketone oxime [38b] and bis[2-(o-carboxythiophenoxy)methyl]-4-bromo-1-methoxybenzene carriers. The electrodes exhibited linear responses with Nernstian slopes of 59.8–60.5 mV per decade within the range of $1x10^{-6}$ M to $1x10^{-1}$ M silver ion. The electrodes showed better selectivity for silver ions.



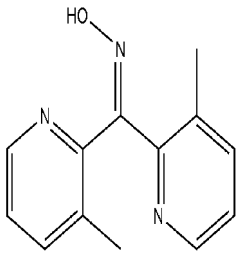
N,N'-bis-(4-dimethylamino-benzylidene)-benzene-1,2-diamine

(36)



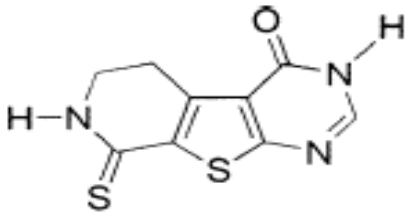
phenyl-2-pyridyl ketone oxime

(38a)



methyl-2-pyridyl ketone oxime

(38b)

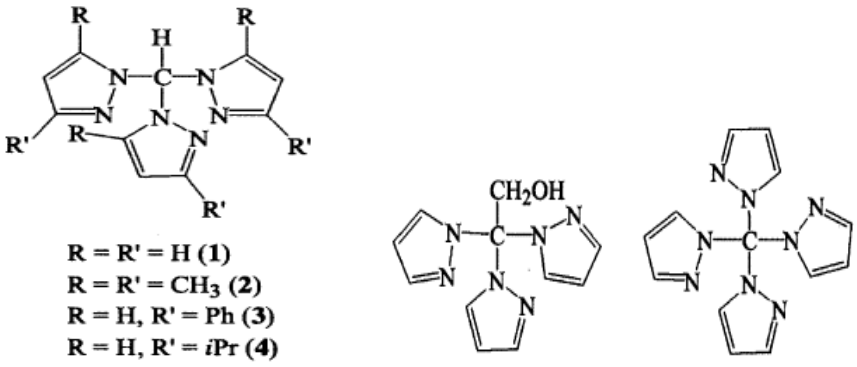


5,6,7,8-Tetrahydro-8-thioxopyrido[4′,3′,4,5]thieno[2,3-d]pyrimidine-4(3H) one

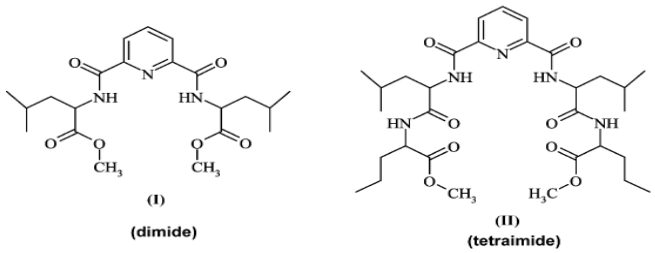
(37)

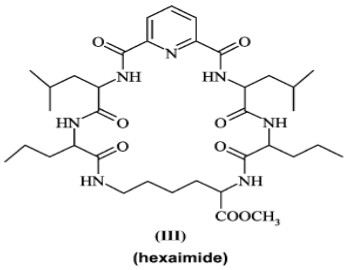
Yoshimoto et al. [39] reported polypyrazolylmethanes as neutral carrier for Cu^{2+} ions. HC(pz)3 (1), HC(3,5-Me2pz)3(2), HC(3-Phpz)3 (3), HC(3-iPrpz)3 (4), HOCH2C(pz)3 (5), and C(pz)4(6) were incorporated as an ionophore in PVC membrane. The selectivity of the electrodes changed with the substituents of polypyrazolylmethanes. The electrodes of 3, 4 and 6 were selective for Cu^{2+} at pH 5.5. The electrode of 5 was selective for Pb^{2+} and Cu^{2+} at pH 5.5. Since the selectivity coefficient log K of electrode 4 was less than −6.4 for the divalent cations, it was most selective for Cu^{2+} among Cu^{2+} selective electrodes ever reported. **Hassan et al. [40]** reported membrane sensors with cylindrical configuration for Pb^{2+} ions based on the use of three newly synthesized pyridine carboximide derivatives as neutral ionophores in plasticized PVC membranes. The sensors exhibit significantly enhanced response towards Pb^{2+} ions over the

concentration range $4x10^{-6}$ M – $1x10^{-2}$ M. The sensors displayed near-Nernstian slope of 26.0–33.1 mV/decade for Pb^{2+} ions. The sensors showed good selectivity for Pb^{2+} ions over a wide variety of other metal ions, long term stability, high reproducibility. **Lima et al. [41]** have reported the performance of calix[2]furano[2]pyrrole and related compounds used as neutral carriers for silver selective polymeric membrane electrode with a Nernstian response of 57.1 mV/decade for silver ions in the activity range $1x10^{-6}$ M to $1x10^{-2}$ M. The silver ion-selective electrode displayed very good selectivity for Ag^{+} ion against alkali and alkaline earth metal ions, NH_4^{+}, H^{+} and very low responses towards Hg^{2+} and Pb^{2+} ions. **Sadeghi et al. [42]** reported ion-selective electrode for lead ions based on piroxicam as an ionophore. The electrode responded to Pb^{2+} ions in a linear range from $1.0x10^{-5}$ M to $1.0x10^{-1}$ M with a slope of 30±0.2 mV/decade. Selectivity coefficients were determined with FIM and MPM.



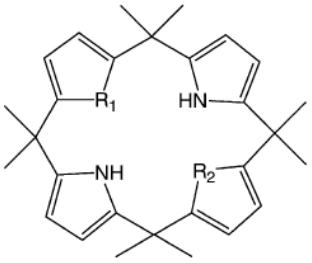
Polypyrazolylmethane derivarives
(39)



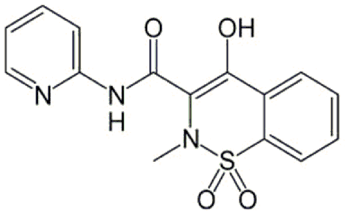


Pyridine carboxamide derivatives (40)

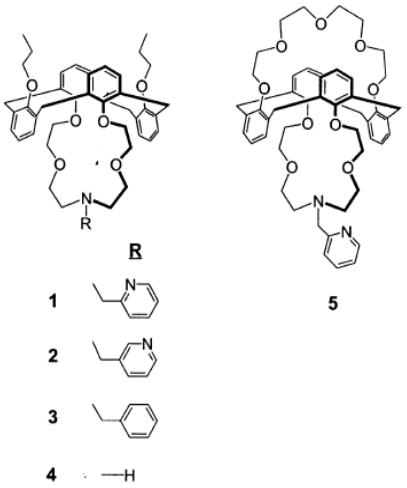
Park et al. [43] described five novel 1,3-alternate calix[4]azacrown ethers having 2-picolyl, 3-picolyl, and benzyl unit on the nitrogen atom are used as ionophores for transition metal-selective polymeric membrane electrodes. The electrode based on 2-picolyl armed 1,3-alternate calix [4] azacrown ether exhibited Nernstian response toward Cu^{2+} ion over a concentration range $1x10^{-4.5}$ M to $1x10^{-2.5}$ M. **Zeng et al.[44]** described that 25,27-Bis(6-hydroxymethyl-2-pyridylmethoxy)-26,28-dipropoxycalix[4]arene its derivative and 25,27-bis(6-diphenylphosphinomethylpyridylmethoxy)-26,28-dipropoxy 5,11,17,23-tetra-tert-butylcalix[4]arene have been characterized by Ion-selective electrodes (ISE) for Ag^{+} . **Hassan et al. [45]** reported tris(2-ethylhexyl)phosphate (TEHP) as both electroactive material and plasticizer and sodium tetraphenylborate (NaTPB) as an ion discriminator. The sensor displays a rapid and linear response for UO_2^{2+} ions over the concentration range $1x10^{-1}$–$2x10^{-5}$ M UO_2^{2+} with a cationic slope of 25.0±0.2 mV /decade. The second sensor contains O-(1,2-dihydro-2-oxo-1-pyridyl)-N,N,N′,N′-bis(tetra-methylene)uranium hexafluoro phosphate (TPTU) as a sensing material, sodium tetraphenylborate as an ion discriminator and dioctyl phenylphosphonate (DOPP) as a plasticizer. Linear and stable response for $1x10^{-1}$–$5x10^{-5}$ M UO_2^{2+} with near-Nernstian slope of 27.5±0.2 mV/decade are obtained. Interference from many inorganic cations is negligible for both sensors. **Mahmoud et al. [46]** reported 2,4,6-tri(2-pyridyl)-1,3,5-triazine for Fe^{2+} ions. The sensors displayed linear response from $5x10^{-7}$ M to 10^{-2} M. The pH does not affect the sensor performances within the pH range 3.2–7.1**. Saleh et al. [47]** reported a poly(vinyl chloride) matrix membrane sensor incorporating 7-ethylthio-4-oxa-3-phenyl-2-thioxa-1,2-dihydropyrimido[4,5] pyrimidine ionophore for Al^{3+} over a wide concentration range $1x10^{-5}$M to $1x10^{-1}$M with a slope of 19.5 mV /decade. Good selectivity for Al^{3+} in comparison with alkali, alkaline earth, transition and heavy metal ions and minimal interference are caused by Hg^{2+} and Pb^{2+} which are known to interfere with other aluminum membrane sensors.



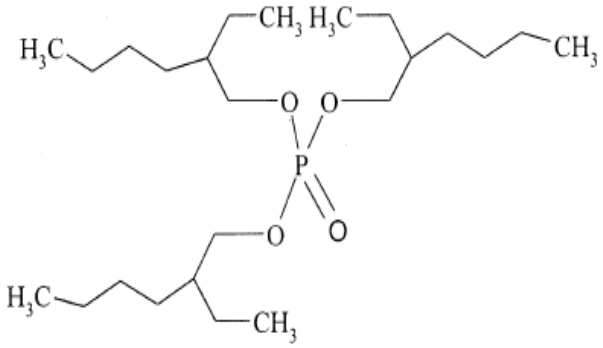
calix[2]furano[2]pyrrole
(41)



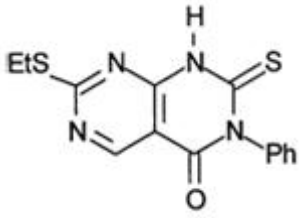
Piroxicam
(42)



Crown ether derivatives
(43)

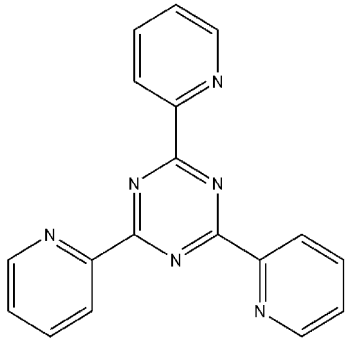


Tris(2-ethylhexyl) phosphate (45)



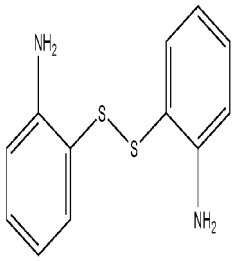
7-ethylthio-4-oxa-3-phenyl-2-thioxa-1,2-dihydropyrimido[4,5] pyrimidine (47)

Gholivand et al. [48] reported 2,2′-dithiodianiline as Cu^{2+} selective electrode. The electrode exhibited good potentiometric response for Cu^{2+} over a wide concentration range of $5.0x10^{-2}$M–$7.0x10^{-7}$M with Nernstian slope of 30±1 mV/ decade. The electrode exhibited 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+} ions.



2,4,6-Tri-(2-pyridyl)-1,3,5-triazine

(46)

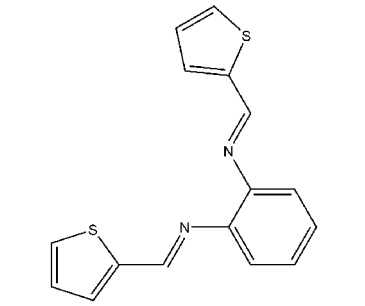


2,2'-dithiodianiline

(48)

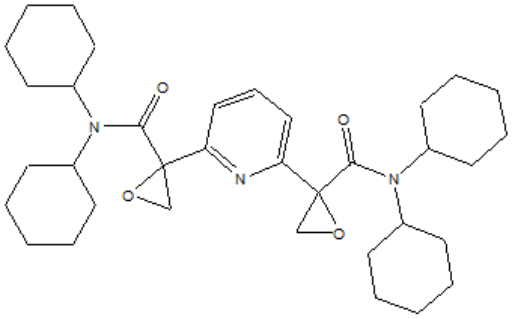
Zareh et al. [49] reported a coated platinum wire electrode based on N,N'-bis(2-thienylmethylene)-1,2 diaminobenzene for selective determination of Ag^{+} ions. The potentiometric responses are independent of pH in the pH range 5.0-9.0. The electrode showed a linear response for Ag^{+} ions over the concentration range of $1x10^{-6}$ to $1.0x10^{-1}$M. The proposed electrode displayed very good selectivity with respect to NH_4^{+}, alkali, alkaline earth and many transition metal ions. The electrode has been applied in potentiometric titrations of $AgNO_3$ and for determination of silver content in developed radiological films.

Qiana et al. [50] reported Sr^{+2} electrode based on N,N,N′,N′-tetracyclohexyl-2,6-pyridine-bis(methyleneoxy acetamide). It exhibits excellent properties with a Nernstian slope of 29 mV/decade $Sr^{2+}$and a linearity range of $2x10^{-5}$M to $1x10^{-2}$.



N,N'-bis(2-thienylmethylene)-1,2 diaminobenzene

(49)

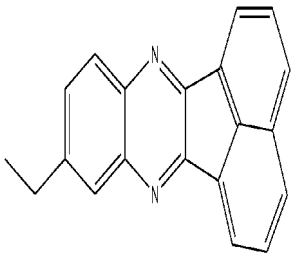


N,N,N',N-tetracyclohexyl-2,6-pyridine-bis(methyleneoxy acetamide)

(50)

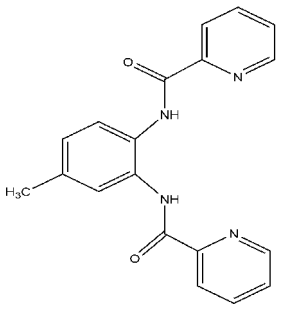
Reports on Pyridyl Based Ion Selective Electrodes by Ganjali *et al.*

Ionophore 9-ethylacenaphtho[1,2-b]quinoxaline [51] has been reported for sensing Fe^{3+} ions. The electrode displayed a Nernstian behaviour over concentration range 2.3×10^{-7}-5.0×10^{-2}M. Sensor have been reported for thulium ions using nanographene [52], a nano-material to modify the composition of carbon paste electrode and 4-methyl-1,2-bis(2-pyridinecarboxamido) benzene as an ionophore in presence of ionic liquid 1-n-butyl-3-methylimidazolium tetrafluoroborate. The sensor showed a Nernstian response with a slope of 19.9±0.3 mV $decade^{-1}$ in the concentration window of $1.0x10^{-6}$-$1.0x10^{-2}$ M. The nano-composite based Tm(III) sensors displayed very good selectivity with respect to a number of lanthanide and transition metal ions. Sensor has been reported for Gd^{3+} ions using N-(2-pyridyl)-N′-(4-nitrophenyl) thiourea [53] as an ionophore. The sensor exhibits a Nernstian slope of 19.95 ± 0.3 mV /decade over the concentration range of $3.0x10^{-7}$ to $1.0x10^{-1}$ M with a very good selectivity with respect to a number of lanthanide ions.



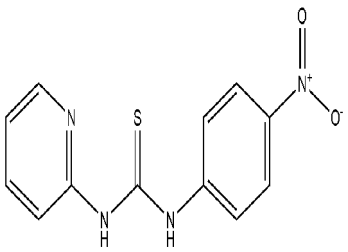
9-ethylacenaphtho[1,2-b]quinoxaline

(51)



N,N'-(4-methyl-1,2-phenylene)dipicolinamide

(52)

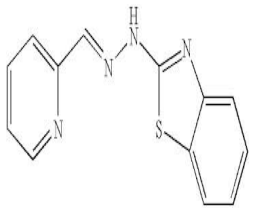


N-(2-Pyridyl)-N'-(4-nitrophenyl) thiourea

(53)

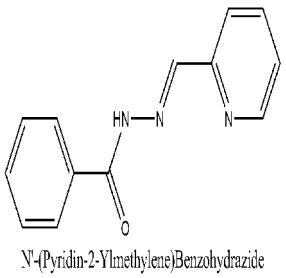
In another report pyridine-2-carbaldehyde-2-(4-methyl-1,3-benzothiazol-2-yl) hydrazone [54] has been used as an ionophore for preparing an Er^{3+} membrane sensor with high selectivity and with a Nernstian response of 21.8 ± 0.5 mV/decade of Er^{3+} activity, the linear range of the sensor was found to be $1.0x10^{-5}$ M to $1.0x10^{-2}$ M. Sensor for Pr^{3+} ions have been prepared based on N′-(pyridin-2-ylmethylene)benzohydrazide [55] as a carrier working over a wide concentration range $1.0x10^{-8}$ to $1.0x10^{-3}$ M. The proposed membrane sensor revealed very good selectivity toward Pr(III) ions over a wide variety of other metal ions including common alkali, alkaline earth and, specially, lanthanide

ions. The Pr(III) microelectrode was used as an indicator electrode for the titration of Pr(III) ions with a EDTA**.** N, N′-bis(2-quinolinecarboxamide)-1,2-benzene [56] has been used as a carrier in construction of Ho^{3+} selective sensor. The sensor showed a good Ho^{3+}selectivity and has a Nernstian slope of 19.5 ± 0.3 mV/decade of Ho^{3+} activity with a linear range from $2.0x10^{-5}$ to $1.0x10^{-2}$ M.



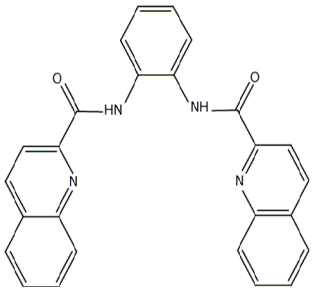
pyridine-2-carbaldehyde-2-(4-methyl-1,3-benzothiazol-2-yl) hydrazone

(54)



N'-(Pyridin-2-Ylmethylene)Benzohydrazide

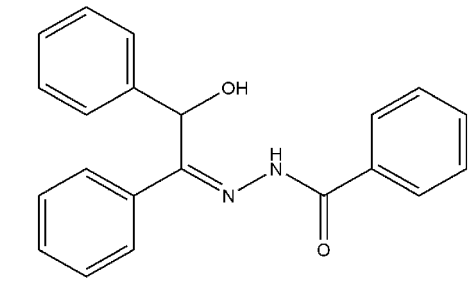
(55)



N, N′-bis(2-quinolinecarboxamide)-1,2-benzene

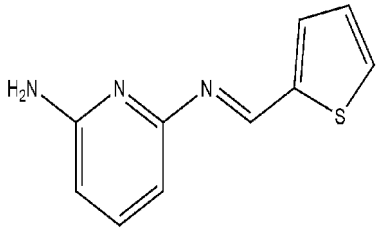
(56)

Application of N-(thien-2-ylmethylene)pyridine-2,6-diamine [58] in the construction of a novel Lu^{3+} PVC-based membrane sensor have been reported. The linear dynamic range of the sensor lies between $1.0x10^{-6}$ to $1.0x10^{-2}$ M with a Nernstian slope of 20.5±0.4 mV/decade. In another report, the ionophore N-(2-Pyridyl)-N-(4-methoxy phenyl)-thiourea [59] has been reported for the construction of a highly selective and sensitive La^{3+} membrane sensor. It works over the concentration range of $4.0x10^{-8}$ to $1.0x10^{-1}$M with a Nernstian slope of 19.6±0.2 mV/decade. The sensor displayed very good discrimination toward La^{3+} ions with regard to most common metal ions and lanthanide ions. The ionophore N,N'-bis(2- pyridinecarboxamide)-1,2-benzene [60] has been utilized for preparing Ho^{3+} ion selective sensor. The sensor showed a Nernstian response of 19.6 ± 0.2 mV/ decade of Ho^{3+} activity with a linear range from $1.0x10^{-5}$ M to $1.0x10^{-2}$ M.



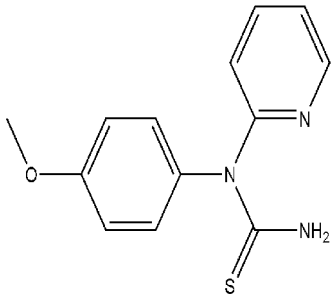
N'-(2-Hydroxy-1,2-diphenylethylidene) benzohydrazide

(57)



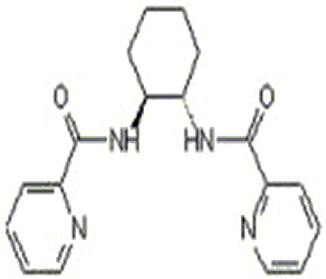
N-(thien-2-ylmethylene)pyridine-2,6-diamine

(58)



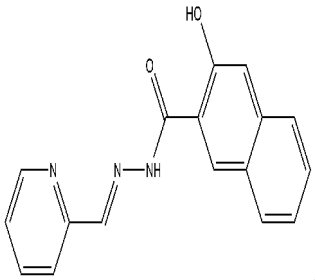
N-(2-Pyridyl)-N-(4-methoxy phenyl)-thiourea

(59)



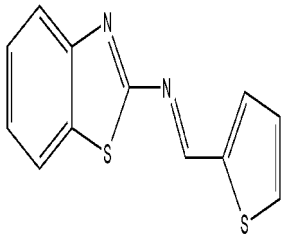
N,N'-bis(2- pyridinecarboxamide)-1,2-benzene(60)

A La^{3+} ion-selective membrane sensor containing 3-hydroxy-N'-(pyridin-2-ylmethylene)-2-naphthohydrazide [61] as a neutral carrier has been reported. It displayed a Nernstian behavior across the range of $1.0x10^{-2}$M - $1.0x10^{-7}$ M. A novel plasticized membrane sensor for Ho(III) ions based on N-(1-thien-2-ylmethylene)-1,3-benzothiazol-2-amine [62] as a neutral carrier has been prepared. The electrode exhibited a Nernstian response for Ho(III) ions over a particular concentration range $1.0x10^{-5}$ $-1.0x10^{-2}$M. The proposed sensor showed good selectivity for Ho(III) ions over the common alkali, alkaline earth and lanthanide ions. The sensor has been applied successfully as indicator electrode in potentiometric titrations of Ho(III) ion with EDTA and for determination of Ho(III) ion concentration in binary mixtures



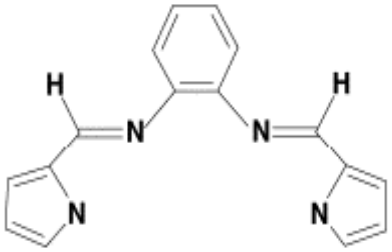
3-hydroxy-N′-(pyridin-2-ylmethylene)-2-naphthohydrazide

(61)



N-(1-thien-2-ylmethylene)-1,3-benzothiazol-2-amine

(62)

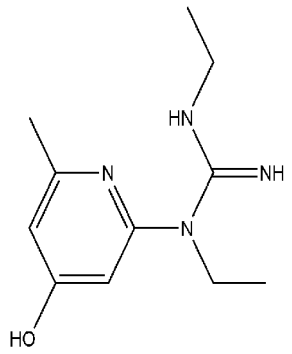


N,N,-bis(pyrrolidene) benzene-1,2-diamine

(63)

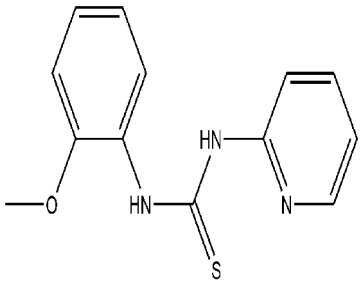
A terbium ion-selective solvent polymeric membrane sensor based on N,N,-bis(pyrrolidene) benzene-1,2-diamine [63] using bezylacetate as plasticizer has been reported. The sensor responded well over a wide linear range from $1.0x10^{-5}$M to $1.0x10^{-1}$M with a slope of 19.8 mV/decade. The sensor revealed good selectivity with respect to common alkali, alkaline earth, transition and heavy metal ions. The sensor has been used as an indicator electrode in potentiometric titration of fluoride ions, and in determination of F^- ion in some mouth wash preparations.

A europium ion selective PVC based membrane sensor using N,N-diethyl-N-(4-hydroxy-6-methylpyridin-2-yl) guanidine [64] as ionophore have been reported. The electrode displayed Nernstian behavior over a concentration range of $7.0x10^{-5}$M to $1.0x10^{-1}$M with a detection limit of $5.0x10^{-5}$M. The response of the electrode remained independent of pH in the range 3.0-7.0. The electrode exhibited selectivity towards Eu^{3+} with respect to alkali, alkaline earth, transition and heavy metal ions. Sensor developed has been applied as indicator electrode in potentiometric titration of Eu^{3+} and in determination of fluoride ion in mouth wash preparations. A ytterbium(III) sensor based on N-(2-pyridyl)-N′-(2-methoxyphenyl)-thiourea [65] as a carrier has been reported. The sensor exhibited a Nernstian response for Yb(III) ion over a concentration range of 1.0×10^{-6}–1.0×10^{-2} M. The sensor revealed very good selectivity for Yb(III) in the presence of several metal ions. It was successfully applied as indicator electrodes in the potentiometric titration of Yb(III) with EDTA and for the determination of fluoride ion in two mouth wash formulations. It was also used for determination of Yb(III) ion in Xenotime .



N,N-Diethyl-N-(4-hydroxy-6-methylpyridin-2-yl)-guanidine

(64)



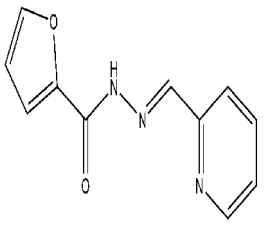
N-(2-pyridyl)-N'-(2-methoxyphenyl)-thiourea

(65)

Reports on Pyridyl Based Ion-Selective Electrode by Zamini *et al.*

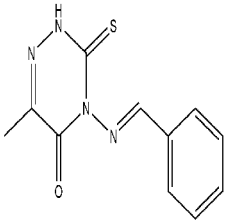
Sensor selective to Tb(III) ions has been prepared by using 4-amino-3-{2-[4-amino-6-methyl-5-oxo-4,5-dihydro-1,2,4-triazin-3(2H)-yliden]hydrazono}-6-methyl-3,4-dihydro-1,2,4-triazin-5(2H)-one [66] as a carrier. The sensor worked satisfactorily in the concentration range of 1.0×10^{-6} to 1.0×10^{-1} M with a Nernstian slope. The selectivity towards Tb^{3+} ions was greater in the presence of interfering mono-, di- and trivalent metal ions. The membrane sensor was used as an indicator electrode in the potentiometric titration of Tb(III) ions with EDTA. Analytically sensor has been applied to the determination of fluoride ions in mouth wash preparation sample and the Tb^{3+} recovery from various binary mixtures. La(III) ion-selective sensor based on N′-(1-pyridin-2-ylmethylene)-2-furohydrazide [67] as an excellent sensing material has been reported. The electrode showed a good selectivity for La(III) ion with respect to most common cations including alkali, alkaline earth, transition and heavy metal ions. The proposed sensor exhibited a wide linear response with slope of 19.2 ± 0.6 mV decade^{-1}. In another report Cu^{2+} ion selective a membrane sensor based on 6-methyl-4-(1-phenylmethylidene)amino-3-thioxo-1,2,4-triazin-5-one [68] as a sensing material has been reported. The electrode exhibited a Nernstian slope over a concentration range from $1.0x10^{-6}$ M to $1.0x10^{-1}$ M. Another copper ion selective membrane sensor have been prepared using 4-amino-6-methyl-1,2,4-triazin-3,5-dithione [69] as an ionophore. The sensor exhibited a Nernstian response for Cu^{2+} ions over a concentration range 1×10^{-6} M to 1×10^{-1} M. The electrode revealed a very good selectivity with respect to all common alkali, alkaline-earth, transition, and heavy-metal ions. The electrode has been applied as

an indicator electrode in the potentiometric titration of Cu(II) ions with EDTA. A sensor for gadolinium ion based on 6-methyl-4-{[1-(2-thienyl) methylidene]amino}3-thioxo-3,4-dihydro-1,2,4-triazin-5-(2H)-one [70] as a carrier has been reported. The sensor displayed a calibration response for Gd^{3+} ions over a wide concentration range of $1.0x10^{-6}$–$1.0x10^{-1}$M with Nernstian slopes of 19.8±0.2mV $decade^{-1}$. The selectivity coefficients for mono-, di-, and trivalent cations indicate good selectivity for Gd(III) ions over a large number of interfering cations.



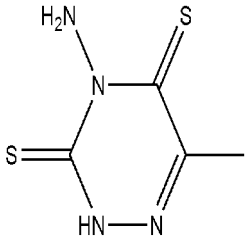
N'-(1-pyridin-2ylmethylene)-2-furohydrazide

(67)



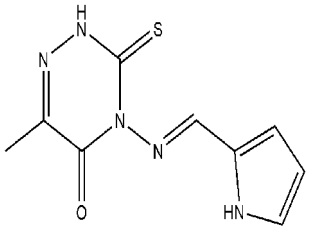
6-methyl-4-(1-phenylmethylidene)amino-3-thioxo-1,2,4-triazin-5-one

(68)



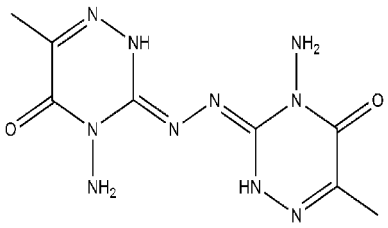
4-amino-6-methyl-1,2,4-triazin-3,5-dithione

(69)



6-methyl-4-{[1-(1h-pyrrol-2yl)methylidene]amino}-3-thioxo-3,4-dihydro-1,2,4-triazin-5(2h)-one.

(70)



4-amino-3-{2-[4-amino-6-methyl-5-oxo-4,5-dihydro-1,2,4-triazin-3(2H)-yliden] hydrazono}-6-methyl-3,4-dihydro-1,2,4-triazin-5(2H)-one

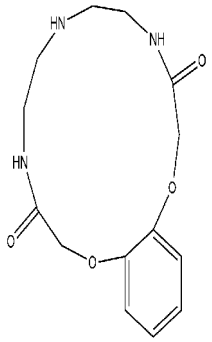
(71)

Reports on Pyridyl Based Ion-Selective Electrode by Shamshipur *et al.*

A cobalt (II)-selective graphite coated PVC based membrane electrode have been reported using a new dibenzopyridino-substituted macrocyclic diamide [71] as a neutral carrier. The electrode exhibits a Nernstian response for Co^{2+} ions over a very wide concentration range 7.0×10^{-7}–1.0×10^{-2} M. The sensor revealed good selectivities for Co^{2+} over a wide variety of alkali, alkaline earth, transition and heavy metal ions. It has been used as an indicator electrode in the potentiometric titration of Co^{2+} ions and in direct determination of cobalt ion in waste water samples.

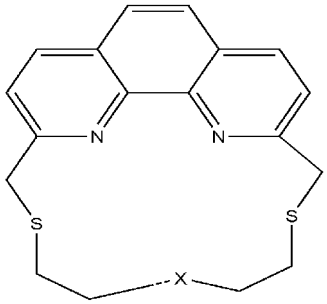
Sensors for Cu^{2+} ions have been reported based on three different mixed aza-thioether crowns containing a 1,10-phenanthroline sub-unit [72] to characterize their abilities as

copper(II) ion carriers in PVC-membrane electrodes. The electrode exhibited a Nernstian response for Cu^{2+} ions over a wide concentration range of $2x10^{-1}$M to $1x10^{-5}$ M. Another sensor has been reported for Cu^{2+} ions based on 5,6,7,8,9,10-hexahydro-2H-1,13,4,7,10-benzodioxatriaza cyclopentadecine3,11(4H,12H)-dione [73] The electrodes revealed a Nernstian behavior over wide Cu^{2+} ion concentration ranges of $1.0x10^{-7}$ M-$1.0x10^{-1}$ M for PME and $1.0x10^{-8}$- $1.0x10^{-1}$M for CGE. Sensor has been reported for neodymium ions based on 5-pyridino-2,8-dithia[9](2,9)-1,10-phenanthrolinephane [74]. The electrode exhibited a Nernstian response over a wide concentration range $1.0x10^{-6}$-$1.0x10^{-2}$M. The proposed electrode revealed a very good selectivity for Nd^{3+} over a wide variety of alkali, alkaline earth, transition, and heavy metal ions, including members of the lanthanide family other than Nd^{3+}. Polymeric membrane (PME) and coated graphite (CGE) silver-selective electrodes based on two synthesized mixed azathioether crowns containing a 1,10-phenanthroline sub-units [75] have been reported. The electrodes revealed a Nernstian behaviour over quite wide Ag^{+} ion concentration ranges. The electrodes were used, as indicator electrodes, in the potentiometric titration of silver ion and in the determination of Ag^{+} in waste water, photographic emulsion and radiographic and photographic films.



5,6,7,8,9,10-hexahydro-2H-1,13,4,7,10-benzodioxatriaza cyclopentadecine3,11(4H,12H)-dione

(73)



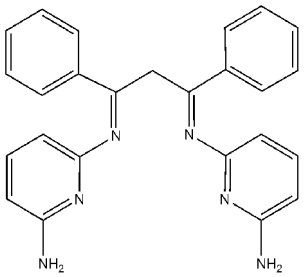
X= S: L1
X= O: L2
X=CH3 L3

Mixed azathioether

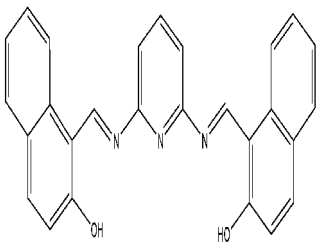
(75)

Reports on Pyridyl Based Ion-Selective Electrodes by Gupta *et al.*

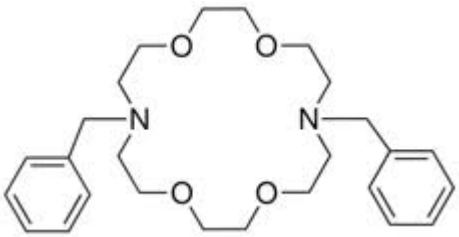
Schiff base 3-((6-aminopyridin-2-ylimino)-1, 3-diphenylpropylidene) pyridine-2, 6-diamine [76] have been used as carrier for Mn^{2+} ions. The sensor exhibits a working concentration range of 1.0×10^{-6} - 1.0×10^{-1} M. The selectivity coefficients determined by using match potential method (MPM) and fixed interference method (FIM) indicated high selectivity for Mn^{2+}. The application of prepared sensor has been demonstrated in determination of Mn (II) ions in spiked water samples and in some natural plant and edible species. One of the toxic metal lead has attracted attention of analytical chemists. The ionophore N,N'-Bis(2-hydroxy-1-napthalene)-2,6-pyridiamine [77] have been used as ionophore in PVC based membrane. The electrode exhibited a Nernstian response with concentration range $3.2x10^{-6}$M-$1.0x10^{-1}$M. The selectivity coefficient values were in the range of 1.0×10^{-2} to 1.0×10^{-4} for mono-, bi-, and trivalent cations and anions, which indicated good selectivity for Pb^{2+}. The sensor has a lifetime of six months and could be used as an indicator electrode in the potentiometric titration of Pb^{2+} vs. EDTA and also in the estimation of lead in waste water. The sensor showed a linear potential response for Pb^{2+} over wide concentration range 3.2×10^{-6} to 1.0×10^{-1} M. Sensor for Pb^{2+} ions has been reported based on N, N′-dibenzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane [78] as an ionophore. The sensor exhibited a Nernstian response for Pb^{2+} ions over a wide concentration range $8.2x10^{-6}$ M to $1.0x10^{-1}$ M.



3-((6-aminopyridin-2-ylimino)-1, 3-diphenylpropylidene) pyridine-2, 6-diamine (76)



N,N'-Bis(2-hydroxy-1-napthalene)-2,6-pyridiamine
(77)

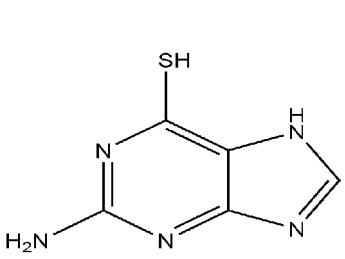


N, N′-dibenzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane
(78)

In another report Gupta et al. have tried 5-amino-1,3,4-thiadiazole-2-thiol and 2-amino-6-purinethiol for construction of ion selective electrodes. Out of these two, the ionophore 2-amino-6-purinethiol [79] has been reported as a carrier in mercury ion-selective membrane electrodes. The proposed electrode revealed a Nernstian response over Hg^{2+} ion in the concentration range of 7.0 x 10^{-8}-1.0 x 10^{-1} M. The electrode showed good discrimination toward Hg^{2+} ion with respect to most common cations. For evaluation of the analytical applicability, the electrode was used in the determination of Hg^{2+} ion in different environmental and biological samples. The practical utility of the membrane electrode has also been observed in the presence of surfactants.

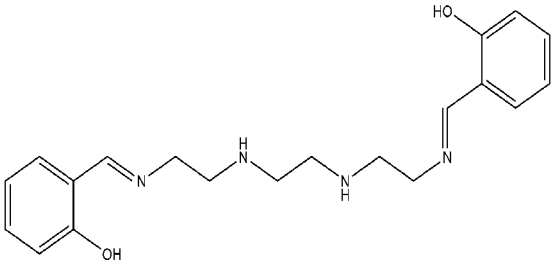
Sensor for Ce^{3+} ions has been prepared using N,N′-bis[2-(salicylideneamino)ethyl]ethane-1,2-diamine [80] as an ionophore. The plasticized membrane sensor exhibits a Nernstian response for Ce^{3+} ions over a wide concentration range $1.4x10^{-7}$ to $1.0x10^{-2}$ M. It was used as an indicator electrode in potentiometric titration of fluoride, carbonate and oxalate anions and determination of cerium in simulated mixtures. Cadmium(II) ion selective electrode based on cyanocopolymer matrices and 8-hydroxyquinoline [81] as ionophore have been reported. The electrodes showed a Nernstian slope of 29 mV per decade. Electrodes have shown an appreciable selectivity for Cd^{2+} ions in the presence of alkali and alkaline earth metal ions. The

cyano groups of the copolymers contributed significantly to enhance the selectivity of the electrode.



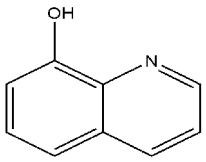
2-amino-6-purinethiol

(79)



N,N'-bis[2-(salicylideneamino)ethyl]ethane-1,2-diamine

(80)



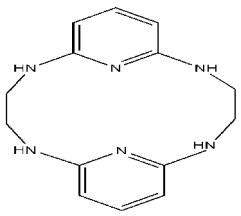
8-hydroxyquinoline

(81)

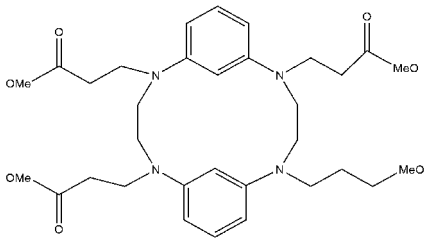
Reports on Pyridyl Based Ion-Selective Electrodes by Singh *et al.*

A PVC based membrane based on 2,3,4-pyridine-1,3,5,7,12-pentaazacyclopentadeca-3-ene [82] as an ion carrier for Ba^{2+}selective electrode have been reported. It worked well over a wide concentration range of the order of $1x10^{-6}$M –$1.0x10^{-1}$M with a Nernstian slope of 30.0mV/decade. Membrane sensors using macrocycles 2,3,4:9,10,11-dipyridine-1,3,5,8,10,12-hexaazacyclotetradeca-2,9-diene[83a] and 2,3,4:9,10,11-dipyridine-1,5,8,12-tetramethylacrylate-1,3,5,8,10,12-hexaazacyclotetradeca-2,9-diene[83b] for Co^{2+} ions[83] have been reported. The performance of the membrane based on 2,3,4:9,10,11-dipyridine-1,5,8,12-tetramethylacrylate-1,3,5,8,10,12-hexaazacyclotetradeca-2,9-diene was compared with polymeric membrane electrode (PME) and coated graphite electrode (CGE). The PME exhibited a Nernstian slope of 29.7mV $decade^{-1}$whereas CGE exhibited a Nernstian slope of 29.5mV $decade^{-1}$. The ionophore 3-(2-pyridinyl)-2H-pyrido[1,2,-a]-1,3,5-triazine-2,4(3H)-dithione [84] based PVC membranes has been prepared for Cu^{2+} selective sensors. The sensor worked in the concentration range $5.0\,x10^{-8}$M to $1.0\,x10^{-2}$ M with a Nernstian slope of 29.5 mV/ decade.

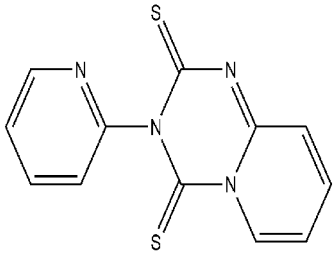
PVC membrane sensor for Sr^{2+} ions have been reported based on 5,7,12,14-dibenzo-2,3,9,10-tetraoxa-1,4,8,11-tetraazacyclotetradecane [85] as an ion carrier. The electrode exhibited a Nernstian response for Sr^{2+} ion over a wide concentration range $3.98x10^{-6}$M to $1.0x10^{-1}$ M with a slope of 29.0 ± 0.1 mV/decade.



2,3,4:9,10,11-dipyridine-1,3,5,8,10,12-hexaaza cyclotetradeca-2,10-diene (83a)

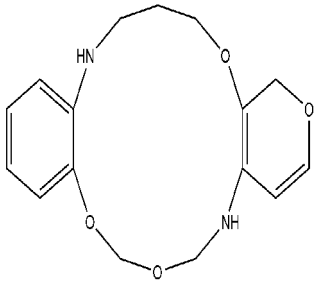


2,3,4:9,10,11-dipyridine-1,5,8,12-tetramethylacrylate-1,3,5,8,10,12-hexaazcyclotetradeca-2,10-diene (83b)



3-(2-pyridinyl)-2H-pyrido[1,2,-a]-1,3,5-triazine-2,4(3H)-dithione

(84)

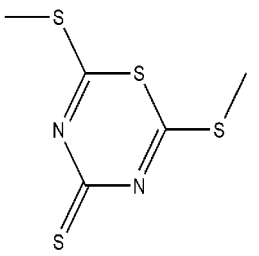


5,7,12,14-dibenzo-2,3,9,10-tetraoxa-1,4,8,11-tetraazacyclotetradecane

(85)

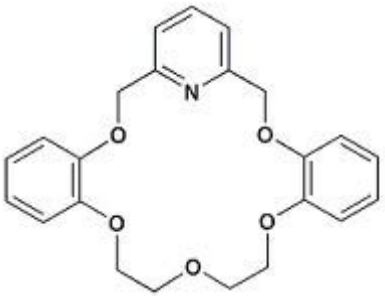
Reports on Pyridyl Based Ion-Selective Electrodes by Mahajan *et al.*

A membrane electrode based on bis-pyridine tetramide macrocycle [86] for silver ions have been reported. The electrode exhibited linear response over a wide concentration range $1.0x10^{-4}$- $4.0x10^{-5}$M. One more ion-selective electrodes for silver(I) ion, based on Schiff base p-tert-butyl calix[4]arene [87] derivatives containing N and O as binding sites have been reported. These electrodes works well over wide range of concentration $1.0x10^{-5}$ to $1.0x10^{-1}$ M with a Nernstian slope. These calix[4]arene derivatives, each showed excellent selectivities in ISE membranes against some of the alkali, alkaline and transition metals, even against the strongest interferent, Hg^{2+} ions. These silver(I) ion-selective electrodes were used as an indicator electrode for potentiometric titration of silver ions. 2,6-bis-methylsulfanyl-[1,3,5]thiadiazine-4-thione [88] is an ionophore which has been reported in construction of a silver ion-selective electrode. The electrode exhibited a near-Nernstian response of 52 mV/decade over a wide linear concentration range of $1.0x10^{-5}$ - $1.0x10^{-1}$M. The electrode exhibited excellent selectivity for silver ion over many of the alkali, alkaline-earth and transition metal ions.



2,6-Bis-methylsulfanyl-[1,3,5]thiadiazine-4-thione

(88)



dibenzopyridino-18-crown-6

(90)

Tavakkoli [89] reported a sodium ion- selective electrode based on dibenzopyridino-18-crown-6 as membrane carrier for preparing sodium ion selective electrode . The electrode exhibits a Nernstian response with a slope of 58.5 mV/decade within the concentration range of 1.0×10^{-4}-1.0×10^{-1} M. The sodium ion-selective electrode exhibited good selectivities with respect to alkali, alkaline earth and some transition metal ions.

2.2 MEMBRANE TRANSPORT LITERATURE REVIEW ON PYRIDYL BASED CARRIERS

Polymer inclusion membranes (PIM), classified earlier as solvent polymer membranes (SPM), were first developed by **Bloch et al. [90], Vofsi et al.[91]** in the early 1960s and applied for a selective removal of metal ions from technological waste waters. The overall preparation procedure of contemporary polymer inclusion membranes was proposed by **Sugiura et al. [92, 93]. Lamb et al. [94]** reported selective transport of Ag(I) across polymer inclusion membranes (PIMs) containing podands with pyridine and bipyridine donor groups offered excellent stability and high flux for separation of Ag(I) ion. Ag(I) ion could be specifically removed from a complex mixture containing high concentrations of Cd(II), Zn(II), Co(II), Ni(II), Pb(II) and Cu(II) ions. PIMs were stable for long periods and showed high flux and selectivity at practical levels. It was concluded that a stereochemically controlled substitution of the podand a remarkable effects of on Ag ion permeability. Thus, design of podand-type carriers based on guest-targeted ligand geometry and stereochemically controlled substitution provide a new, effective methodology in developing cation-specific membranes. The present type of PIMs was stable for long period experiments and showed high flux and selectivity for

Ag(I) ion at practical levels (j >2x10^{-5} mol/m^2 s). **Reddy et al. [95]** have reported facilitated transport of copper ions through chloroform bulk liquid membrane using 8-hydroxy quinoline. The effects of pH of the source phase, the nature of stripping agents in the receiving phase, presence of other cations, nature of synergistic reagents on the transport were investigated. A solution of 0.1 M nitric acid (HNO_3) served as receiving phase for maximum transport of the metal ion. Addition of 2-amino pyridine to the membrane phase had a synergistic effect and caused a pronounced enhancement in the transport, while citric acid or glycine did not change the transport significantly. Maximum transport efficiency was observed for Cu^{2+} ion when it was present in the concentration of 10^{-4} M. Transport of Cu^{2+} was found to be unaffected in the presence of 10-fold concentration of Pb^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+}, Fe^{2+} and Fe^{3+} ions. This system was applied for the recovery of copper in electroplating industrial waste water samples. **Kozlowskia et al. [96]** described the transport through polymer inclusion membranes (PIMs) for chromium(VI) anions removal from chloride acidic aqueous solutions. Transport of chromium(VI) through PIMs reduces the concentration of chromium(VI) in source aqueous phase from 1.0 to 0.0028 ppm. Competitive transport of chromium(VI), cadmium(II), zinc(II), and iron(III) from acidic aqueous solution across PIMs was found to be efficient for chromium(VI) (99%), and cadmium(II) (99%).

Castro et al. [97] studied the transport of Cu(II), Cd(II) and Ni(II) ions through a bulk liquid membrane (BLM) containing pyridine-2-acetaldehyde benzoylhydrazone (2-APBH) as carrier dissolved in toluene . Complete transport through the membrane took place according to the following order: Cd(II)>Cu(II)>Ni(II), with similar kinetic parameters obtained for Cu(II) and Cd(III). The proposed BLM was applied to the pre concentration and separation of metal ions in water samples with different saline matrices, and good agreement with the certified values was obtained. **Tasaki et al.[98]** reported a plasticized cellulose triacetate (CTA) membrane consisting of N-6-(t-dodecylamido)-2-pyridine carboxylic acid (t-DAPA) as a carrier for facilitated membrane transport of copper(II) from other divalent metal ions. The CTA−t-DAPA membrane exhibited uphill transport of copper(II) against the concentration gradient. The influences of the aqueous and membrane components on the permeability of

copper(II) were studied to elucidate its transport mechanism. In another report the same group reported two kinds of N-(6-alkylamido)-2-pyridine carboxylic acid **[99]** with a pyridine moiety and a carboxylic acid as chelating ligands for transport of copper(II) from aqueous solution. The selectivity for the metal ions with N-6-(2-ethylhexylamido)-2-pyridine carboxylic acid (EHPA) was in the following order: Cu(II) >> Zn(II) approximately Pb(II) approximately Ni(II) approximately Co(II) > Cd(II) > Mn(II). All metals tested in this study were selectively extracted at a lower pH by 2-3 units compared with commercial available alkyl carboxylic acids such as naphthenic acid and Versatic 10. It was demonstrated that t-DAPA was very stable to be incorporated into a polymer inclusion membrane (PIM) consisting of cellulose triacetate (CTA) as a base polymer and 2-nitrophenyl octylether (NPOE) as a plasticizer. This novel PIM containing t-DAPA as a carrier exhibited an excellent copper(II) transport characteristic and a high selectivity for copper(II) over cadmium(II) from aqueous solution. **Tsukube et al. [100]** discussed on a variety of double armed crown ethers were prepared in which amine, amide, ester, nitrile and pyridine moieties are attached as cation-ligating sidearms to diaza-12-crown-4 ring all these molecules characterized as Li^+ selective. **Tsukube et al. [101]** reported a designed series of acyclic podands so that three pyridine moieties cooperatively bind a guest Ag^+. Various experimental studies like liquid-liquid extraction, NMR binding, and computer calculation experiments revealed that podands with three pyridine donors in a proper geometry exhibit a perfect Ag^+ specificity. They selectively extracted Ag+ in the presence of equimolar Pb^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, and Zn^{2+}. Introduction of two chiral centers close to the pyridine binding sites surprisingly influences the Ag^+-binding ability of the podand. Fourteen new pyridine podands were evaluated as carriers in a liquid membrane transport system. A combination of ligand geometry and stereo controlled substitution provides excellent Ag^+-specific transport.

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Chapter 3

METHODOLOGY

Ion selective electrodes work on the basic principle of galvanic cell [1-3]. By measuring the electrode potential generated across a membrane by "targeted" ions, and comparing it to a reference electrode, a net change is determined. The magnitude of this change is directly proportional to the concentration of the selected ion. Potentiometric sensors have attracted great attention for their simple construction, low-cost, good selectivity, sensitivity and offer quantitative information using inexpensive and portable equipment [4]. Several analytical techniques, such as atomic absorption spectrometry (AAS) [5], inductive coupled plasma atomic emission spectrometry (ICP-AES), inductive coupled plasma mass spectrometry (ICP-MS)[6], anodic striping voltametry [7], chromatography [8], spectrophotometry [9] and low detection limit ion selective electrode (ISE) [10,11] etc. are available for quantification of the ions. Ion selective electrodes offer several advantages over several other available methods of analysis. Ion selective electrode determinations are not subjected to interferences such as colour in the sample. With few matrix modifications, the analysis for various ion can be conducted. The membrane in ISEs is attached to one end of the 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 two reference electrodes are constant, any change in cell potential is due to change in potential across the membrane.

3.1 REAGENTS AND CHEMICALS

High molecular weight polyvinylchloride (PVC), potassium tetrakis (4-chlorophenyl) borate (KTpClPB), sodium tetraphenylborate (NaTPB), metal nitrates were received from Sigma Aldrich (India), analytical reagent grade tetrahydrofuran (THF), nitric acid, sodium hydroxide were obtained from SD-fine (India). Solutions of metal nitrates were prepared in doubly distilled deionised water and standardized by the reported, method wherever necessary.

3.2 PREPARATION OF METAL SALT SOLUTION

The stock solution ($1.0x10^{-1}$ M) of the metal salt was prepared by dissolving appropriate amount of the metal salt in a volumetric flask and the solution was diluted using distilled water to the desired volume. All other solutions of different concentrations were made by serial dilution of the $1.0\ x10^{-1}$ M stock solutions.

3.3 INSTRUMENTS USED

All potentiometric experiments were carried out with a digital potentiometer (Euip-Tronics, EQ-602, accuracy, ±0.1mV, Mumbai India) and pH of the solution was monitored simultaneously using pH meter (Equip-Tronics, EQ-614, Mumbai India). Spectroscopic measurements were done with a spectrophotometer (Specord 205, Analytic Jena). For monitoring the metal ion concentration in transport experiments flame atomic absorption spectrophotometer (AAS 4129, Electronic Corporation of India) was used. Scanning electron microscope (SEM JEOL-6610 JAPAN) was used to study membrane surface morphology. SEM samples were coated with a very thin layer of gold by a sputter coater.

3.4 PREPARATION OF ELECTRODE

Membranes of ~ 0.2 cm thickness were obtained [12] by pouring a solution of the membrane components of PVC 29-33%, ligand 1-10% and orthonitrophenyloctylether 58-64% and appropriate amount of anionic additives dissolved in 2-3 mL of tetrahydrofuran(THF). The viscous solution of polymer thus obtained was poured in glass ring of 30mm diameter placed on a dust free pyrex glass plate. The solvent was allowed to evaporate slowly for about 24h at room temperature. To obtain membrane with similar characteristics, viscosity of the casting solution; rate of evaporation of solution was controlled so that thickness and morphology of the membrane remained almost unchanged. Membranes were then removed from the glass ring and circular pieces of 1.25cm diameter were cut and mounted on the ground end of pyrex glass tube with araldite and conditioned with metal ion solution for 24h.

3.5 E.M.F. MEASUREMENT

The potential measurements were carried out at 25 ± 0.1^{0}C with a digital Euip-Tronics potentiometer and pH of the solution was monitored simultaneously using pH meter.

Activities of the solutions were calculated according to Debye-Huckle equation [13]. All emf measurements were carried out with the following electrochemical cell assembly:

SCE ‖ test solution M^{n+} ∣ionophore membrane∣0.1 M M^{n+} ‖ SCE

3.6 CALIBRATION OF THE ELECTRODE

The electric potentials were determined for a series of standard solutions and a standard calibration curve was constructed. The concentration of the sample solution was determined by fitting the value in the standard curve. This is called direct calibration and is the most common and easiest way to calculate the concentration.

3.7 TEMPERATURE OF MEASUREMENT

Response of the chemical sensor is governed by Nernst equation which in turn is temperature dependent. The variation in temperature can lead to significant measurement errors. A single degree change in temperature can lead to errors greater than 4%. During experiments, the experimental set up was placed in thermostat temperature of which was maintained at 25± 0.1^0C.

3.8 STIRRING OF THE ANALYTE SOLUTION

While carrying out ion selective measurements, stirring was done continuously, which ensured a fresh supply of ions to the sensing portion of the ISE. Stirring of the solution was done using a teflon coated magnetic bead and a magnetic stirrer at a moderate speed.

3.9 RINSING OF THE ELECTRODE

ISE membranes were washed between measurements to ensure accurate observation of the readings. A steady stream of deionised or distilled water was used for this purpose. The excess water of electrode was wiped off by shaking it gently.

3.10 CONDITIONING OF THE ELECTRODE

One of the requirements of ISE is that it should remain moist at all times even when not in use. Hence the electrode was kept immersed in standard solution of primary ion when not in use.

3.11 SLOPE OF THE CALIBRATION CURVE

Slope of calibration curve was calculated from linear portion of the curve of the electrode. The theoretical value according to Nernst equation is 59.16 mV decade^{-1} for monovalent ion and 29.58 mV decade^{-1} for divalent ion.

3.12 RANGE OF LINEAR RESPONSE OF THE CALIBRATION CURVE

At very high and low target ion activities, there are deviations from linearity. Typically, the electrode calibration curve exhibits linear response in the range 1x10^{-6} M to 1x10^{-1}M.

3.13 DETECTION LIMIT OF THE CALIBRATION CURVE

According to the IUPAC recommendations [14,15], the detection limit is defined by the extrapolation of the two extrapolated linear parts of the ion selective calibration curve. Detection limit of the order of 10^{-5}-10^{-6}M has been measured for most of the ion-selective electrodes.

3.14 SELECTIVITY OF ISEs

Interfering species for an ISE may be any substance, other than the ion being measured, whose presence in the sample solution affects the measured emf of a cell. Interfering substances fall into two classes: "electrode/electrochemical" interferences and "chemical" interferences. Selectivity is one of the most important characteristics of an electrode, as it determines whether a reliable measurement in the sample is possible or not. The selectivity coefficient $K_{A,B}$ gives a measure of preference for the analyte of interest in comparison to the interfering ions. Negative value of $K_{A,B}$ indicate a preference of the electrode for the target ion relative to the interfering ion. The experimental selectivity coefficient depends on the activity and the method of their determination. Different methods of selectivity coefficient measurement are available in literature. The IUPAC suggests two methods [14-15]: separate solution method (SSM) and fixed interference method (FIM). Also, there is an alternative method of selectivity determination called matched potential method (MPM). Each of these methods has got advantages and disadvantages and there are no general rules pointing which method gives the true results. Selectivity coefficients were determined using FIM.

3.14.1 Separate solution method

In this method, the potential of a cell comprising an ion selective electrode and a reference electrode is measured with each of the two separate solutions, one containing the ion A at the activity a_A(but not B), the other containing the ion B at the same activity $a_B = a_A$ (but not A)[16]. If the measured values of E.M.F. are E_A and E_B, respectively, the value of $K^{Pot}_{A,B}$ may be calculated from the equation:

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

Z_A is the charge on primary ion A; Z_B is the charge on interfering ion B and R, T and F have their usual meanings.

3.14.2 Fixed interference method

In this method, emf of the cell comprising ion selective electrode and reference electrode is measured with solutions of constant activity of the interfering ions a_B and varing activity of the primary ion a_A. Intersection of the extrapolation of linear portion of this plot indicate the value of a_A which is to be used to calculate $K_{A,B}$ from Nikolski-Eisenmann equation.

$$K^{Pot}_{A,B} = a_A / (a_B)^{Z_A/Z_B}$$

Where Z_A and Z_B have the same sign positive or negative.

3.14.3 Matched potential method

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 is then given by the ratio of the resulting activities (concentration) of primary ions versus interfering ions. The selectivity coefficient, $K_{A,B}$, is determined [17] :

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

Where $\mathbf{a_A}$ is the initial activity of primary ions A and $\mathbf{a'_A}$ is the activity of A in presence of interfering ion at $\mathbf{a_B}$.

3.14.5 Limitation in interpretation of selectivity coefficient

Determination of selectivity coefficients can be carried out by different methods. There are several IUPAC recommended methods that are being used currently. Each method gives different selectivity coefficients. Due to empirical determination of selectivity coefficients, only the ratios of selectivity coefficients are used to evaluate the response of ionophores towards different metal ions. Every method of selectivity coefficient determination is associated with limitations like error due to multiple ion interaction, uncertainties of measurement, difficulty in applying the method. Most commonly the fixed interference method is employed for its good mix of realism and simplicity. The fixed interference concentration is commonly set to 0.1M or 0.01M, for system with good selectivity and lower concentration (0.001M or 0.0001M) for system having poorer selectivity.

3.15 DETERMINATION OF FORMATION CONSTANTS

The ionophore-complex formation constants were determined by a potentiometric method. Sandwich membrane was prepared by mechanically pressing together, the two individual membranes; the membrane with ionophore to the membrane without ionophore after blotting them individually and dried with filter paper. Experiments were carried out according to the sandwich membrane method [18,19]. In this method, the potential of sandwich membranes, $E_{m,}$ were determined by subtracting the cell potential for a membrane without ionophore from that of sandwich membrane for the same electrolyte system. The formation constant is then calculated from the following equation:

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

Where, L_T is the total concentration of the ionophore in the membrane segment, R_T is the concentration of the lipophilic ionic site additives, n is the ion-ionophore complexes stoichiometry, R, T and F are the gas constant, the absolute temperature and the Faraday

constant, respectively. The primary ion, I carry a charge z_i. The membrane potential E_m was determined by subtracting the cell potential for a membrane without ionophore, from that for the sandwich membrane. This method allows convenient determination of formation constant of ion-ionophore complexes within the membrane phase on the basis of transient membrane potential measurement on two layer sandwich membrane neglecting the ion pairs.

3.16 UV-VIS STUDY OF IONOPHORE METAL-ION INTERACTION

The ligand coordination with a metal ion can be investigated by spectroscopy. For example, from the UV-Vis spectra, it is possible to distinguish the interactions between the ligand and the ion. A substantial decrease in the absorbance at a certain wavelength of the ligand solution, after adding the ion solution stepwise, may give a new adsorption peak at another wavelength, which is related to complex formation. At the same time, the effects of the other ions on the spectrum of the carrier were investigated. The detectable changes in the UV-Vis spectra provided information on ionophore-metal ion interaction [20].

3.17 PREPARATION OF REAL LIFE SAMPLES

The applicability of the developed potentiometric sensors was tested for the determination of the metal ions in real life samples. A small volume (6-12mL) of effluent sample (sewage water) was taken in 100mL volumetric flask; pH was adjusted to 5.0 by adding buffer solution and then the solution was quantitatively diluted. The everyday battery waste sample was initially treated with a few drops of concentrated nitric acid and heated to dryness then dissolved in distilled water, filtered and then the solution was transferred into 100mL volumetric flask. The pH was adjusted to 6.0 by adding buffer solution and the solution was quantitatively diluted.

3.18 PREPARATION OF POLYMER INCLUSION MEMBRANE (PIM)

The PIM was prepared by following a reported procedure [21,22]. Cellulose triacetate (CTA) (100 mg) was dissolved in 20 mL of dichloromethane at room temperature. 100 mg of o-NPOE dissolved in 5 mL of dichloromethane was then added with the above solution. The mixture solution was then poured into glass ring placed on a glass plate.

After vigorous stirring, ionophore was added and the solution was stirred for 30 min to obtain a homogenous solution. Dichloromethane was allowed to evaporate overnight and the resulting membrane was separated from glass plate by immersion into cold water. Next, the membrane was soaked in distilled water for 2 h. The membrane was securely clamped between the two membrane holding compartments. The membrane assembly was then ready for use.

3.19 ION TRANSPORT EXPERIMENTS

Ion transport experiments were carried out in a permeation cell. Both, source and receiving aqueous phases (70cm^3 each) placed in two separate compartments were mechanically stirred at 600 rpm using teflon coated magnetic beads. Metal nitrates were used in the source phase, whereas solutions of HCl, HNO_3, EDTA or KSCN were used as the receiving phase. The PIM transport experiments were carried out at 25±0.2^{0}C by using water thermostat. Small samples of the aqueous receiving phase were taken periodically from the sampling port equipped with a syringe and analyzed by atomic absorption spectroscopy to determine zinc(II), cadmium(II), copper(II), nickel(II), and silver(I) concentrations. The kinetics of the transport across PIMs was described as first-order process in relation to the metal ion concentration [23,24], expressed by equation

$$\ln(C/C_i) = -kt$$

where, C is metal ions concentration in the source phase at a given time (M), C_i is the initial metal ions concentration in the source phase, k is the rate constant (s^{-1}), and t is the time of transport (s). The rate constant values for two independent transport experiments were averaged and standard deviation was calculated. The permeability coefficient (P) was calculated according to equation:

$$P = -\frac{V}{A}k$$

where, V is the volume of aqueous source phase (m^3), k is the rate constant (s^{-1}) and A is an effective area of membrane (m^2). The initial flux (J_i) is equal to

$$J_i = P \cdot C_i$$

The selectivity coefficient (S) was defined as the ratio of initial fluxes for M1 and M2 metal ions, respectively:

$$S = \frac{Ji,M1}{Ji,M2}$$

To describe the efficiency of metal removal from the source phase, the recovery factor (RF) was calculated:

$$RF(\%) = \frac{Ci - C}{Ci} x100$$

The reported values correspond to the average values of three replicates, with the standard deviation within 5%

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Chapter 4

RESULTS AND DISCUSSION

4a LINKED 2, 2'-DIPYRIDYLAMINE LIGAND SYSTEM AND TERPYRIDINE LIGAND SYSTEM AS ION SELECTIVE ELECTRODE FOR Ag(I) IONS

Abstract

The linked 2,2'-dipyridylamine derivatives (mdpa, pdpa and tpydpa) and 4',4''-(1,4-phenylene)bis(2,2':6',2''-terpyridine) (ditpy) have been explored as neutral carrier ionophores for preparing poly (vinyl chloride) based electrodes selective to Ag(I) ions. Based on the stability constants determined by sandwich membrane method and the energy minimization studies using CAChe software (in case of 2, 2'-dipyridylamine derivatives), the ionophores were found selective for Ag (I) ions. Different compositions of the membrane were studied. The best performance in case of 'tpydpa' was found with the electrode composition (w/w): ionophore (3%); PVC (33%); o-NPOE (64%). This electrode exhibits Nernstian response with a slope of 59 mV/decade of activity in the concentration range $5.5x10^{-6}$M - $1.0x10^{-1}$M of Ag (I). The electrode shows satisfactory performance over a pH range of 3.0–9.0, with a fast response time of 14s**.** The best performance in case of 'ditpy' was found with the electrode composition (w/w): ionophore (5%); PVC (31%); NaTPB (3%); o-NPOE (61%). The electrode exhibits Nernstian response with a slope of 60 mV/decade of activity in the concentration range $5.5x10^{-5}$M - $1.0x10^{-1}$M of Ag (I). The electrode shows satisfactory performance over a pH range of 4.0–9.0, with a fast response time of 15s. In both cases response of the electrodes were highly selective to Ag^{+} ions over a number of uni-, di- and trivalent metal ions. Also, the electrodes have been used successfully as indicator electrodes in potentiometric titrations of Ag (I) ions and for determination of silver content in waste water.

4a.1 INTRODUCTION

Silver is widely used in production of coins, jewellery, table-ware, alloys, in the manufacture of electrical apparatus, mirrors and chemicals for photographic process. Additionally it is used in the production of dental amalgams and burn creams as silver sulphadiazine cream (SSD) due to its antimicrobial properties [1-3]. Chronic absorption of silver may cause "Argyria" a blue/grey discoloration of various tissues, ocular injury, leukopenia and toxicity in kidney, liver and neurological tissues [4]. There are a good number of techniques for determination of silver metal ions such as atomic absorption spectroscopy(AAS) [5-6], inductively coupled plasma-atomic emission spectroscopy(ICP-AES) [7,8], inductively coupled mass spectroscopy(ICP-MS) [9,10], but all these methods are time consuming, involving sample manipulation, relatively expensive and required large infrastructure back up. Selective analytical methodologies, which are easily operated and involve harmless reagents, cost effective equipment, have therefore been proposed as alternative to standard methods. Potentiometric methods based on ion-selective electrodes are especially suited for such determination because they offer advantage such as selectivity, sensitivity, good precision, simplicity and low cost [11-14]. Silver selective potentiometric sensors based on ion carriers like podands, crown ethers and calixarenes derivatives have been reported [15-25]. In most of these approaches, sulfur was used as the coordinating site [26–37].

The silver ion recognition with most of these carriers relies on the hard–soft acid base (HSAB) concept [38]. According to this concept, carriers possessing sulfur atoms, soft base, have a good affinity to soft acids such as silver ions. Although these carriers showed a good discrimination from alkali, alkaline earth and some transition metals, mercury and lead ions strongly interfere. However, few attempts based on other binding sites; nitrogen and/or oxygen, have been reported [39–48], such as bis-pyridine tetramide [40], corrole [41], bis-oxime derivative diaza-crown ether [42], calixarenes [43–46] and pyridyl based podants [47-50]. The optimum conditions of best performance of the electrode, its selectivity to silver over other metals ions and application of the electrode have been examined. 2,2'-dipyridylamine (dpaH) is an aromatic amine, in some ways similar to 2,2'-bipyridine (bpy), but the central amine unit introduces several differences:

(i) dpaH coordinates with six-membered chelate rings instead of five-membered rings for bpy; (ii) the coordinated pyridine rings are not necessarily forced to near coplanarity as in bpy; (iii) the ligand field strength of dpaH is greater than ethylenediamine. The two-pyridine rings of dpaH are flexible in their coordination with metal centers. Hence, the coordination chemistry of 2, 2'-dipyridylamine (dpa) and its derivatives has been the focus of a considerable number of investigations [51]. For example, mono-, di- and tri-dpa derivatives have been reported [52,53,54] in which secondary nitrogen of each dpa is directly bound to an aryl core with such species being employed in studies that range from metal coordination and supramolecular chemistry to synthesis of new luminescent materials. Neutral dipyridylamine has been shown to form discrete complexes with silver.

4a.2 REAGENTS, INSTRUMENTS AND MEMBRANE PREPARATION

High molecular weight polyvinylchloride (PVC), *o*-nitrophenyloctylether (*o*-NPOE) and potassium tetrakis (p-chlorophenyl) borate (KTpCIPB), tetrahydrofuran (THF) were purchased from Aldrich (India) and used as received. Metal salt solutions of concentration 0.1M were prepared by dissolving AR grade metal nitrates in double distilled water and standardized wherever necessary. Working solutions of different concentrations were prepared by serial dilutions. Potentials were measured with an Equip-Tronics (EQ-602, accuracy, ± 0.1mV) potentiometer (Mumbai, India) and absorbances were measured by spectrophotometer (Specord 205, Analytic Jena, Germany) pH of the solution was monitored simultaneously with a conventional glass pH electrode.

Membranes were prepared by dissolving appropriate amounts of powdered PVC, plasticizer, ionophore ('tpydpa') according to Table 4a.1 and for ionophore 'ditpy' membranes were prepared according to Table 4a.2. The components were added in terms of weight percentages and dissolved in 5mL of THF. The homogenous mixture obtained after complete dissolution of all components was concentrated by evaporating THF slowly at 25° C so as to get an oily mixture. The concentrated mixture solution was poured in a glass ring of diameter 2 cm placed on smooth glass plate. The concentrated mixture solution was then allowed to evaporate for 24h at room temperature. Transparent

membranes so obtained were cut to the size and glued on one end of a pyrex glass tube with araldite adhesive. The membranes were equilibrated with 0.1M silver nitrate solution. The ratio of different membrane ingredients and the contact time were optimized to provide membranes which resulted in reproducible and stable potentials. Also, membranes having only PVC as the membrane ingredients (dummy membranes) were prepared to observe whether any background potentials were produced due to binding material or not. It was observed that potentials were not generated without the ionophore. The activities of metal ions were calculated by using modified form of the Debye-Huckel equation. All emf measurements were carried out with the following assembly:

Hg| Hg_2Cl_2,KCl(satd)| Int.Soln.($1x10^{-1}$M $AgNO_3$)| PVC Membrane| Test solution| Hg-Hg_2Cl_2,KCl(satd)

The concentrations of test solution were varied from $1x10^{-8}$M to $1x10^{-1}$M. Ionophores containing nitrogen atoms with electron donating tendency and insoluble in water, with high molecular weight were expected to act as a suitable ion carriers as reported in literature [55,56]. To investigate the suitability of the ionophore for comparison purposes, three ionophores; 'tpydpa', 'mdpa', 'pdpa' (Figure 4a.1) were used to prepare several PVC membranes based ion selective electrodes under identical conditions for a variety of metal ions, including alkali, alkaline earth and transition metal ions. Another ionophore 'ditpy' (Figure 4a.2) was used for preparing electrode selective to Ag(I) ion.

4a.3 IONOPHORE-METAL ION INTERACTION

4a.3.1 Energy minimization studies

Energy minimization studies of the metal-ionophore complexes were carried out with different metal ions carried with the help of CAChe software (for 'mdpa', 'pdpa', 'tpydpa') with MM3 calculations. The results are shown in Table 4a.3 using 1:1 and 1:2 Ag(I)-ligand complexation, assuming both coordinate as well as weak interactions between the ionophores and the metal ion shown in Table 4a.3. However, the experimental results are in agreement with weak-weak interactions between the metal

ion and the ionophore. Optimal conformations of ionophore 'tpydpa' before and after complexation are shown in Figure 4a.3.

4a.3.2 Spectrophotometeric method to study stoichiometry of metal ionophore

To study complexation between a metal ion and an ionophore ('tpydpa') spectrophotometeric method of continuous variation was used. A series of solutions were prepared containing a fixed amount of metal ion, with varying concentrations of the ionophore. The absorbances of these solutions were measured at a wavelength 281.1nm at which only the 2:1 metal:ionophore complex absorbs. A resulting plot of absorbance vs. ligand-to-metal mole ratio initially increases and then becomes constant, once the ligand to metal ratio has been achieved. The point at which the slope of the line changes corresponds to the ligand: metal ratio of the complex. This gave 2:1, metal ion: ionophore complexation as shown in Figure 4a.4.

4a.3.3 Determination of formation constants

In order to use the ionophore for a particular metal ion its interactions with different metal ions were studied by sandwich membrane method. In this method, fused segmented sandwich membrane yield information about the activity ratio on both sides of the membrane. It requires membrane potential measurement [57,58] on two layer sandwich membrane, where only one side contains the ionophore and other side of the membrane does not contain the ionophore. The membrane potential E_M is determined by subtracting the cell potential for a membrane without ionophore from that for the sandwich membrane. This method allows convenient determination of ion-ionophore complexes within the membrane phase on the basis of transient membrane potential measurement on two layer sandwich membrane neglecting the ion pairs. The values obtained of ion-ionophore complex are shown in Table 4a.4 for 'tpydpa' and 'ditpy'.

4a.4 POTENTIOMETRIC STUDIES

Optimization of membrane ingredients, energy minimization studies and stability constants (Table 4a.1, Table 4a.3 and Table 4a.4, respectively) of linked 2,2'-dipyridylamine derivatives indicated that only 'tpydpa' forms a strong interaction with

silver metal ions compared to other derivatives. Hence, only 'tpydpa' was subjected to further potentiometric studies**.** Based on potentiometric response of 'ditpy' toward different metal ions (Figure 4a.5) and stability constant determination it was used as an ionophore in construction of ion selective electrodes for Ag(I) ions.

4a.4.1 Effect of ionophore concentration

In preliminary experiments, membranes with and without carriers were prepared. The blank membrane did not show any response, whereas, in presence of proposed ionophore, 'tpydpa' the optimized membrane gave Nernstian response and remarkable selectivity for Ag^+ ion over several other metal cations. Preferential response towards Ag^+ ions is believed to be associated with selective coordination of ionophore to the Ag^+ ion. Ag^+ selective electrodes prepared with different amounts of ionophores have been evaluated and reported in the Table 4a.1. Since the sensitivity and selectivity of a given membrane electrode is significantly related to the composition of membrane, particularly, the amount of ionophore [59,60], the amount of ionophore, PVC and lipophilic additive salt were varied to study their effect on the potential response of the electrode. The results clearly indicate that composition of the electrode having ionophore less than or greater than 3% leads to non-Nernstian responses. This deviation in electrode response at higher and lower concentration of the ionophore is due to the loss of selectivity and enhanced interference of the lipophilic counter ions of the test solution as presumed in the phase boundary potential model of carrier based ISEs [61]. Comparison of electrodes have also been done using ionophore 'tpydpa', 'pdpa' and 'mdpa' at optimized composition (Table 4a.5) and corresponding plots are shown in Figure 4a.6. Based on their respective better performances, electrodes E_2 and E'_{10} containing ionophores 'tpydpa' and 'ditpy' were identified for further studies.

4a.4.2 Calibration curve, response time and lifetime of electrode

The polymeric membrane electrodes for Ag^+ ion based on the ionophore the 'tpydpa' were examined according to IUPAC recommendations [62] at various concentrations of inner filling solution of $AgNO_3$ solution in the range of $1.0x10^{-3}$M to $1.0x10^{-1}$M and the potential response of the electrode has been observed. It was observed that the best result in terms of slope and working concentration range has been obtained with inner

filling solution of concentration $1.0x10^{-1}$M. Thus, internal solution of concentration $1x10^{-1}$M of the primary ion solution was quite appropriate for smooth function of the proposed sensors. E.M.F. of the membrane electrode at varying Ag(I) concentration for 'tpydpa' ionophore based electrode showed a linear range from $1.0x10^{-5}$M to $1.0x10^{-1}$M with a Nernstian slope of 59 mV/decade. The detection limit was $5.0x10^{-6}$M as determined from the intersection of the two extrapolated segments of the calibration plots shown in Figure 4a.7. The 'ditpy' based electrode showed a linear range from $5.5x10^{-5}$M to $1.0x10^{-1}$M with a Nernstian slope of 60 mV/decade. The detection limit was $5.0x10^{-5}$M as determined from the intersection of the two extrapolated segments of the calibration plots shown in Figure 4a.8.

4a.4.3 Effect of pH on the response of Ag (I) selective electrodes

pH dependence of the electrode response was studied in the pH range of 3.0 – 11.0 in the solution. The pH was adjusted using NaOH (0.1M) and HNO_3 (0.1M) and the results are shown in the Figure 4a.9 and Figure 4a.10 for ionophore 'tpydpa' and 'ditpy', respectively. The potential response of the electrode remains constant in the pH range of 3.0–9.0 for 'tpydpa' based electrode. For 'ditpy' based electrode potential remains stable in the pH range 4.0-9.0 as shown in Figure 4a.10. At higher pH values, the potential decreases. The sudden decrease of potential at lower pH values may be attributed to the partial protonation of the ionophore while the decrease in potential at higher pH could be due to the formation of some soluble and insoluble complexes of Ag^+ which might have resulted in a loss of ability of the ionophore to sense Ag(I) ions.

4a.4.4 Effect of interfering ions on performance and selectivity of electrodes

Selectivity is the term which is used to describe utility of ion selective electrode. It gives the response of ion selective electrode for the primary ion in presence of secondary ion present in the solution, which is expressed in terms of potentiometric selectivity coefficients. Potentiometric selectivity coefficient ($K^{Pot}_{Ag,B}$) describes preference by the membranes for Ag^+ relative to an interfering ion B. In this work selectivity coefficients were determined by fixed interference method (FIM) as per IUPAC recommendations [63]. The concentration of interfering ion was fixed at $1x10^{-2}$M and concentration of silver ions was varied. The values of selectivity coefficient so determined are compiled

in Table 4a.6**.** Mercury is known to interfere in the determination of Ag^{+} ions but in case of proposed electrode the level of interference of Hg^{2+} is the same as that of other bivalent ions like Cd^{2+}, Zn^{2+} and Pb^{2+}. The selectivity coefficients values are of the order 10^{-2} for divalent and trivalent metal ions (except Na^{+} and K^{+}) which indicate that these ions will cause negligible interference on the functioning of proposed 'tpydpa' based silver electrode. Therefore, the proposed electrode can be used for the determination of Ag^{+} ions in the presence of certain interfering ions. A comparison of the proposed 'tpydpa' based electrode with reported electrodes is shown in Table 4a.7. The values of selectivity coefficient ($\log K^{Pot}_{Ag,B}$) determined for 'ditpy' based electrode for Co^{2+}, Cu^{2+}, Ni^{2+}, Ca^{2+}, Fe^{3+}, Tb^{3+}, K^{+}, Mg^{2+}, Al^{3+}, Cd^{2+}, Pb^{2+}, Hg^{2+} and La^{3+} were recorded as 0.079, 0.094, 0.082, 0.075, -2.340, -2.63, 0.021,0.063, 0.002, 0.156, -1.320 and -2.180, respectively. The selectivity coefficient data indicate that logK values are of the order 10^{-2} for divalent and trivalent metal ions Therefore, the electrodes can be used for the determination of Ag^{+} ions in the presence of certain interfering ions. A comparison of the reported 'ditpy' based silver selective electrodes with present electrode has been shown in Table 4a.8

4a.4.5 Effect of mixed solvents

In some cases, sample to be analyzed may be containing non-aqueous solvents and hence to study the effect of non-aqueous media, 'tpydpa' based sensor was subjected to performance in partially non aqueous media using methanol, ethanol, dimethylsulphoxide and dimethylformamide mixed with water in different proportions. The membrane does not undergo any appreciable change in working concentration range and in the slope up to 30% of the non-aqueous content in the mixed solvent media. The results are shown in Table 4a.9. The effect of partially non aqueous medium was also investigated for 'ditpy' based electrode in methanol-water, acetone-water, dimethylformamide-water mixtures using 10%, and 20% non-aqueous content as shown in Table 4a.10. However, beyond these ratios of non-aqueous contents the working concentration ranges for both ionophores decreased and the slopes increased beyond the Nernstian values.

4a.4.6 Microscopic study of membranes

To study the distribution of membrane ingredients in membrane phase, scanning electron microscopic study was carried out at different stages of membrane composition. Figure 4a.11.1 is the SEM image of the membrane containing PVC only. SEM images of the membrane containing PVC and o-NPOE; membrane containing PVC, o-NPOE and the ionophore 'tpydpa' and membrane containing PVC, o-NPOE and ionophore 'tpydpa' equilibrated with 0.1M $AgNO_3$ solution are shown in Figures 4a.11.2; 4a.11.3; and 4a.11.4, respectively. A remarkable change is noticed after addition of each membrane ingredient. PVC membrane surface without any other ingredient shows uniform homogeneity (Figure 4a.11.1 while Figure 4a.11.2 shows a uniform dense packing due to the presence of plasticizer on the PVC membrane. Further on addition of lipophilic salt, there is a huge change in morphology with non-preferential orientation no observable cracks and appeared to be composed of dense and loose aggregation of small particles as shown in Figure 4a.11.5. However, on addition of ionophore 'ditpy' 5%, a uniform distribution of ionophore can be seen in Figure 4a.11.6 taken after 24hours conditioning with Ag(I) salt solution. Figure 4a.11.7 shows membrane surface after its exhaustive use as ISE. Surface is clear as a non-uniform layer due to presence of Ag(I)- ionophore complexes randomly distributed.

4a.4.7 Potentiometric titrations and analytical application

The electrodes have been applied successfully for the end point determination of Ag (I) in the potentiometric titrations. The titration plot obtained for 'tpydpa' and 'ditpy' based electrodes are shown in Figures 4a.8 and Figure 4a.9, respectively. In both cases the plot corresponds to the 1:1 stoichiometry of Ag^+Cl^-. The sensors were also used for testing municipal waste water and the results obtained are in agreement with those obtained by AAS. Therefore, the proposed membrane electrodes can be used as an indicator electrode for potentiometric determination of Ag (I) ions both in potentiometric titrations and for quantification of silver ions in waste water.

4a.5 CONCLUSIONS

This work demonstrates that the electrode no. $\mathbf{E_2}$ is good for quantification of silver ion. The electrode exhibits excellent potentiometric performance. The best composition of the for 'tpydpa' electrode was found to be: Ionophore (3%); PVC (33%); o-NPOE

(64%). It responds to Ag^+ in Nernstian fashion, presents good selectivity over most of the cations of conventional Ag^+ electrodes proposed earlier and showed a low detection limit and good working range. This is characterized by long term potential stability and was successfully applied as indicator electrode in argentometric titrations. The electrode number **E_2** shown in Table 4a.1 is very good for quantification of silver ions as it exhibits excellent potentiometric performance. For 'ditpy' based electrode the best composition of the electrode was found to be electrode for **E'_{10}** with composition: Ionophore (5%); PVC (31%); o-NPOE (61%) and NaTPB (3%). It responds to Ag^+ in Nernstian trend, good selectivity over most of the cations of conventional Ag^+ electrodes proposed earlier and showed a low detection limit and good working range.

Table 4a.1: Optimization of membrane ingredients for 'tpydpa', 'pdpa' and 'mdpa' based electrodes for Ag(I) ions

Electrode No.	Ionophore (% w/w)	Lipophilic salt (KTClPB) (% w/w)	o-NPOE (%, w/w)	PVC (%, w/w)	Lower Detection Limit (M)	Slope (mV/decade)
E_1	1(tpydpa)	-	66.0	33.0	$1x10^{-5}$	41
E_2	**3**(tpydpa)	**-**	**64.0.**	**33.0**	**$1x10^{-5}$**	**59**
E_3	5(tpydpa)	-	62.0	33.0	$1x10^{-5}$	43
E_4	3(tpydpa)	1.1	62.9	33.0	$1x10^{-4}$	38
E_5	3(tpydpa)	2.2.	61.8	33.0	$1x10^{-3}$	62
E_6	3(tpydpa)	3.0	61.0	33.0	$1x10^{-5}$	58
E_7	2(pdpa)	-	65.0	33.0	$1x10^{-4}$	24
E_8	3(pdpa)	-	64.0.	33.0	$5x10^{-6}$	46
E_9	4(pdpa)	-	63.0	33.0	$1x10^{-3}$	39
E_{10}	3(pdpa)	2.2.	61.8	33.0	$1x10^{-3}$	62
E_{11}	3(pdpa)	3.0	61.0	33.0	$1x10^{-5}$	58
E_{12}	1(mdpa)		66.0	33.0	$5x10^{-5}$	29
E_{13}	3(mdpa)	-	64.0.	33.0	$1x10^{-4}$	52
E_{14}	5(mdpa)	-	62.0	33.0	$1x10^{-5}$	49
E_{15}	5(mdpa)	0.5	61.5	33.0	$1x10^{-5}$	28
E_{16}	7(mdpa)	-	60.0	33.0	$1x10^{-4}$	42
E_{17}	5(mdpa)	2.5	61.5	31.0	$1x10^{-4}$	47

Table 4a.2: Optimization of membrane ingredients for 'ditpy' based electrode for Ag(I) ions

Electrode No.	Ionophore (% w/w)	Lipophilic salt (NaTPB) (% w/w)	o-NPOE (%, w/w)	PVC (%, w/w)	Lower Detection Limit (M)	Slope (mV/decade)
E'_1	--	--	--	33	---	--
E'_2	--	--	67	33	---	--
E'_3	1	1	65	33	$1x10^{-4}$	34
E'_4	2	1	64	33	$6x10^{-5}$	36
E'_5	3	--	64	33	$1x10^{-3}$	42
E'_6	3	4	60	33	$1x10^{-4}$	41
E'_7	3	2	62	33	$1x10^{-5}$	40
E'_8	3	3	58	33	$1x10^{-5}$	37
E'_9	4	2	61	33	$5x10^{-4}$	45
E'_{10}	**5**	**3**	**61**	**31**	**$5x10^{-5}$**	**60**
E'_{11}	6	3	59	32	$1x10^{-4}$	53
E'_{12}	7	3	65	30	$1x10^{-4}$	49

Table 4a.3: Energy minimization studies of different ionophores ('tpydpa', 'mdpa','pdpa') with some metal ions for 1:1 and 1:2 complexes using CAChe 6.01 software

Metal Ion	Energy Values (kcal/ mol)					
	'tpydpa'		'mdpa'		'pdpa'	
	1:1	1:2	1:1	1:2	1:1	1:2
Without metal ion	88	88	52	52	52	52
Ag^+	441	236	165	601	675	597
Pb^{2+}	244	544	131	781	131	776
Hg^{2+}	291	538	187	709	187	689
Zn^{2+}	216	481	164	656	164	650

Table 4a.4: Formation constants for complexes of ionophores ' tpydpa', 'mdpa', 'pdpa' and 'ditpy' with some metal ions using sandwich membrane method

Metal ion	Log K_f ±SD*			
	'tpydpa'	'mdpa'	'pdpa'	'ditpy'
Ag^{+}	13.28±0.01	5.71±0.04	5.20±0.03	8.4±0.02
Hg^{2+}	6.49±0.03	5.76±0.04	5.38±0.03	1.9±0.03
Ca^{2+}	6.42±0.03	6.91±0.06	5.13±0.03	--
Cu^{2+}	5.68±0.01	5.90±0.03	5.60±0.01	3.2±0.05
Co^{2+}	5.85±0.05	6.16±0.01	5.47±0.05	3.3±0.01
Fe^{3+}	5.99±0.04	6.20±0.01	3.76±0.06	--
Ni^{2+}	5.58±0.08	6.03±0.01	5.81±0.04	2.8±0.03
Pb^{2+}	6.10±0.03	6.10±0.04	-	2.9±0.02
Sr^{2+}	6.12±0.03	-	5.23±0.04	--
Cd^{2+}	5.89±0.02	5.42±0.04	5.81±0.04	2.1±0.01
Pr^{3+}	---	---	---	2.4±0.01

*Mean Value±Standard deviation (three measurements)

Table 4a.5: Comparison of optimized composition of membranes for different ionophores ('tpydpa', 'pdpa', 'mdpa')

Ionophore (% w/w)	Lipophilic salt additive (KTClPB) (% w/w)	o-NPOE (% w/w)	PVC (% w/w)	Slope (mV/decade)	Lower Detection Limit (M)	Conc. Range (M)
3 (tpydpa)	-	64.0	33.0	59	$1x10^{-5}$	$5.5\ x10^{6}$-$1x10^{-1}$
3 (pdpa)	3.0	61.0	33.0	58	$1x10^{-5}$	$1.0\ x10^{-5}$-$1x10^{-1}$
3 (mdpa)	-	64.0.	33.0	52	$1x10^{-4}$	$1.0\ x10^{-4}$-$1x10^{-1}$

Table 4a.6: Potentiometric selectivity coefficients for Ag(I) ISE based on 'tpydpa' by fixed interference method

Metal Ion	log $K^{Pot}_{Ag,B}$	Metal Ion	log $K^{Pot}_{Ag,B}$
K^+	-0.6	Co^{2+}	-2.6
Sr^{2+}	-2.1	Pb^{2+}	-1.9
Hg^{2+}	-1.8	Ni^{2+}	-1.8
Mg^{2+}	-1.8	Fe^{3+}	-2.2
Cu^{2+}	-2.0	Ca^{2+}	-1.8
Cd^{2+}	-1.8	Zn^{2+}	-1.9

Table 4a.7: Comparison of proposed 'tpydpa' based silver selective electrode with the reported electrodes

Serial No	Ionophore [reference]	Working Conc. Range (M)	pH Range	Slope (mV/decade)
1	p-tertbutyl calix[4] arene [64]	$1.0x10^{-5}$-$1x10^{-1}$	1.0-6.0	58.0
2	3-(2-pyridylethylimino)-2-butanoneoxime [65]	$5.0x10^{-5}$-$7.9x10^{-1}$	---	59.0
3	2,2'-dithiobis(benzothiozole) [66]	$8.3x10^{-7}$-$9.4x10^{-2}$	2.0-7.5	59
4	Polystyrene based Me6(14) diene2$HClO_4$ [67]	$5.0x10^{-6}$-$1.0x10^{-1}$	2.5-9.5	53.0
5	Schiff base of [bis 5-(4-nitrophenyl azo)salisylaldimine] 1,8-diamino, 3,6-dioxooctan (BNSAO) [68]	$2.7x10^{-6}$-$1.9x10^{-2}$	2.5-70	56.0
6	Tweezer-type and non-tweezer-type ionophores [69]	$1.0x10^{-9}$-$1.0x10^{-3}$	---	60.0
7	tert-Butylcalix[4]arene tetra(allyl ether) [70]	$1.0x10^{-4}$-$1.0x10^{-1}$	---	58.0
8	Methyl-2-pyridyl ketone oxime (MPKO) [71]	$1.0x10^{-6}$-$1.0x10^{-1}$	2.5-8.5	59.8
9	Schiff base p-tert-butyl Calix[4]arene derivatives containing N and O as binding sites[72]	$1.0x10^{-5}$-$1.0x10^{-1}$	1.0-10.0	60.0
10	Calix[2]furano[2]pyrrole [73]	$1.0x10^{-6}$-$1.0x10^{-2}$	2.8-12.0	57.1
11	bis(dialkyldithiocarbamates) [74]	$1.0x10^{-6}$-$1.0x10^{-3}$	2.0-7.0	59.0
12	hexathia-18-crown-6 [75]	$6.0x10^{-6}$-$3.2x10^{-3}$	2.0-7.5	59.0
13	Benzothiazole Calix[4]arene [76]	$1.0x10^{-6}$-$1.0x10^{-2}$	2.0-8.0	57.0
14	Schiff base–p-tert-butylcalix[4]arene [77]	$1.0x10^{-5}$-$1.0x10^{-1}$	1.0-5.6	59.7
15	5,10,15-Tris(pentafluorophenyl)corrole[78]	$5.0x10^{-6}$-$1.0x10^{-1}$	4.0-8.0	54.8
16	2-aminothiophenol based dipodal [79]	$1.0x10^{-4}$-$1.0x10^{-1}$	3.3-8.0	60.0
17	5,6:17,18-dibenzo,11,12-(4-nitrobenzo)-2,3-bishydroxyimine)-7,16-dithia-10,13-dioxo-4,19-diazacyclooctadecane($N_2S_2O_6$)[80]	$2.5x10^{-5}$-$1.0x10^{-1}$	5.0-9.0	58.5

18	**This work**	**$5.5x10^{-6}$-$1.0x10^{-1}$**	**3.0-9.0**	**59.0**

Table 4a.8: Comparison of proposed 'ditpy' based silver selective electrode with the reported electrodes

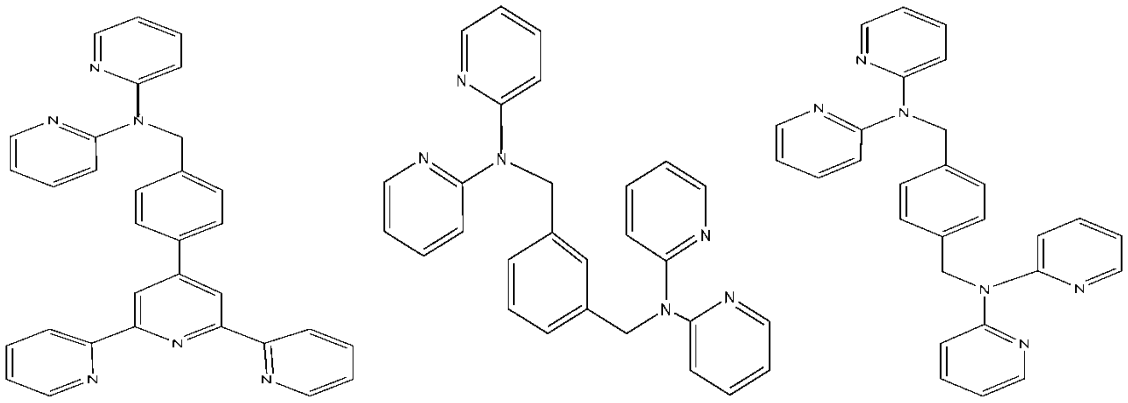
Serial No	Ionophore [reference]	Working Conc. Range (M)	pH Range	Slope (mV/decade)
1	Me_6(14) diene.2$HClO_4$ [81]	5.0×10^{-6}–1.0×10^{1}	53.0 ± 1.0	2.5-9.0
2	21-membered N3S4-azathiacrown ethers[82]	3.0×10^{-7} - 3.0×10^{-3}	----	3.0–8.9.
3	di-benzo-18-crown-6[83]	1.0 $x10^{-5}$-1.0 $x10^{-1}$.	59	4.0-9.0
4	calix[4]arene derivative[84]	1.0×10^{-1} to 1.0×10^{-5}	58.9	1.0-6.0
5	thiaazacrown ether derivative[85]	1.0×10^{-9} – 1.0×10^{-5}	60	
6	N,N'-Bis(2-thienylmethylene)-1,2-diamonobenezene[86]	1.0×10^{-1} to 1.0×10^{-5}	59.7	5.0-9.0
7	N,N_-Bis(3-methyl-1-phenyl-4-benzylidine-5-pyrazolone)propylenediamine[87]	1.0×10^{-1} to 1.0×10^{-6}	59.3	4.0-10.0
8	Calix[4]arene Substituted[88]	1.0×10^{-2} to 1.0×10^{-7}	58.4	4.0-6.7
9	$N_2S_2O_2$ macrocycle[89]	1.0x10-1 to 2.5x10-5	58.5	5.0-9.0
10	bis(dialkyldithiocarbamates) based[90]	1.0x10-3 to 1.0x10-6	60.0	2.0-9.0
11	N,N'-bis(pyridin-2-ylmethylene)benzene-1,2-diamine[91]	1.0×10^{-1} to 1.0×10^{-6}	58.6	3.0-8.0
12	(2-Pyridylmethoxy)-p-t-octylcali[4] arene[92]	1.0×10^{-2} to 5.0×10^{-5}	---	---
13	1,3-Benzocrown Macrocyclic Diamide[93]	$1.0\times10^{-3}$to 5.0×10^{-6}	57.8	3.0-9.0
14	Derivative of Porphyrin[94]	$1.0\times10^{-1}$to 1.0×10^{-7}	59.2	3.0-9.0
15	Schiff Base Derivatives[47]	$7.9\times10^{-2}$to 5.0×10^{-7}	35.6	
16	2,6-Bis-methylsulphanyl-[1,3,5] thiadiazine-4-thione [95]	$1.0\times10^{-1}$to 1.0×10^{-5}	52.0	1.8-7.1
17	**4',4'''-(1,4-phenylene) bis(2,2': 6',2''-terpyridine) (This work)**	**$1.0\times10^{-1}$to 1.0×10^{-5}**	**59.0**	**4.0-9.0**

Table 4a.9: Effect of mixed solvent media on slope and concentration range of the Ag(I) ISE based on 'tpydpa'

Solvent	Non Aqueous Content (% v/v)	Slope (mV/decade)
	0	59
Methanol	10	59
	20	59
	30	59
Acetone	10	62
	20	62
	30	63
DMF	10	61
	20	62
	30	60
DMSO	10	61
	20	61
	30	63

Table 4a.11: Effect of non-aqueous content on the response of Ag(I) ISE based on 'ditpy'

Solvent	Non Aqueous Content (% v/v)	Slope (mV/decade)
Water	0	60
Methanol	10	60
	20	60
Acetone	10	60
	20	60
DMF	10	60
	20	60



“tpydpa” **“pdpa”** **“mdpa”**

Figure 4a.1: Structures of ionophores, ‘tpydpa’, ‘mdpa’, ‘pdpa’

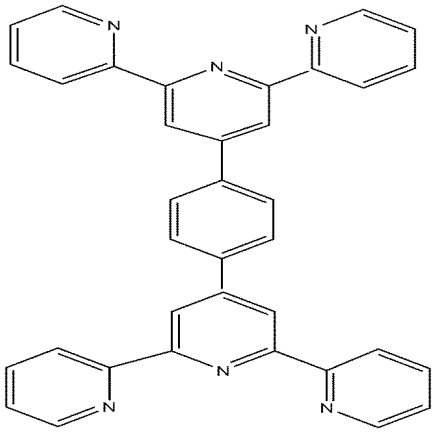


Figure 4a.2: Structure of ionophore ‘ditpy’

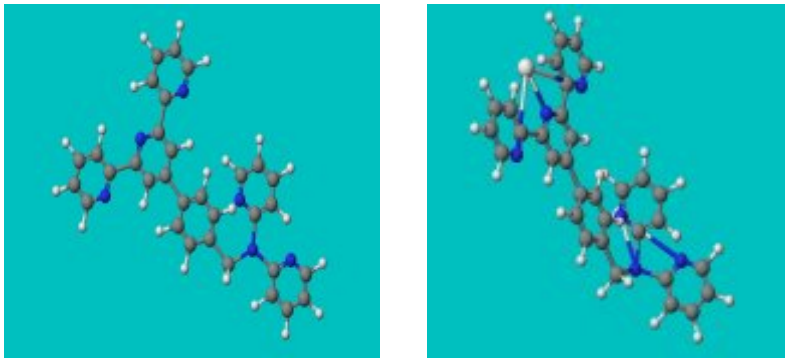


Figure 4a.3: Optimal conformation of the ionophore 'tpydpa' before complexation and after complexation

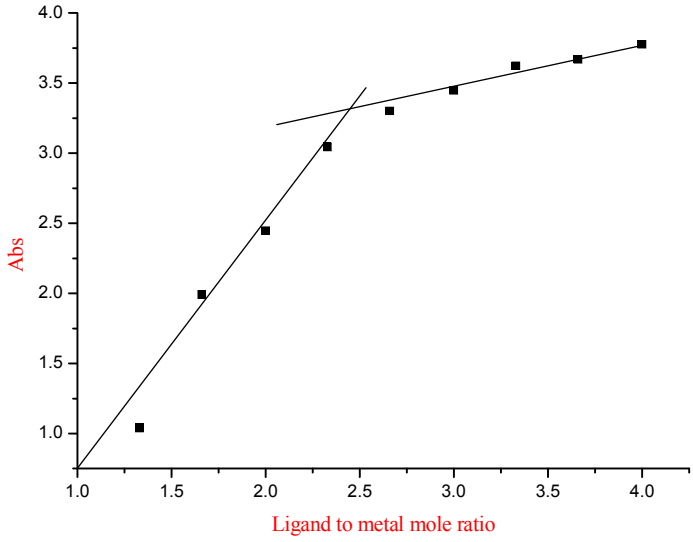


Figure 4a.4: Plots of absorbance versus mole ratio for silver 'tpydpa' complex (continuous variation method)

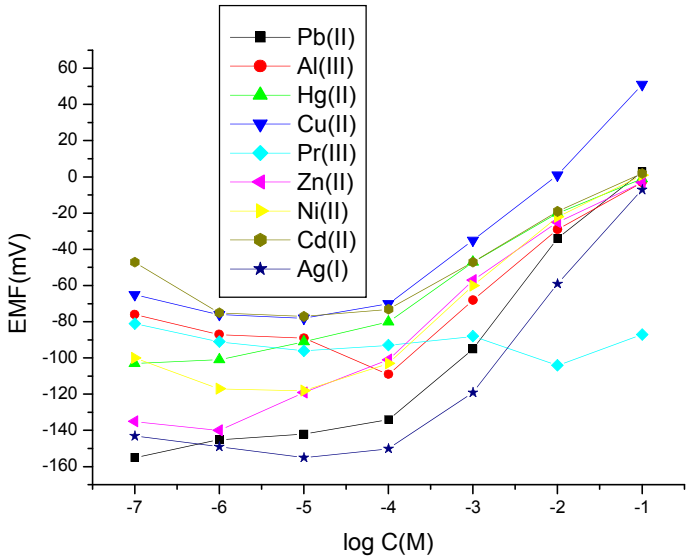


Figure 4a.5: Response of 'ditpy' with different metal ions

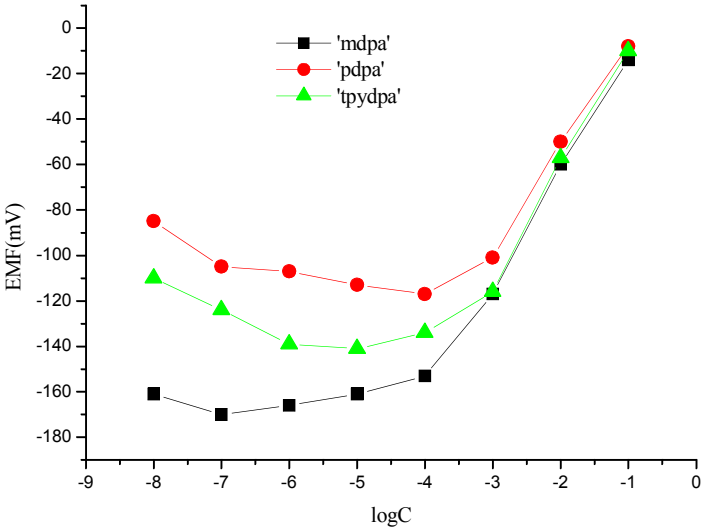


Figure 4a.6: Calibration curves for Ag (I) ISE with different Ionophores

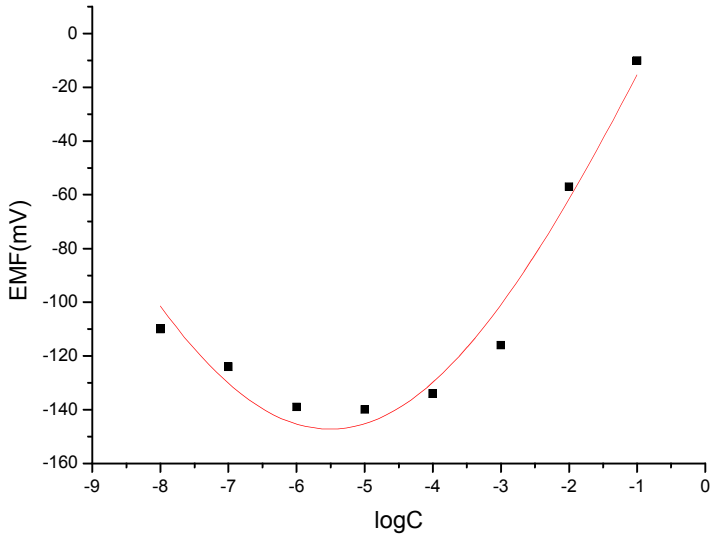


Figure 4a.7: Calibration curve for Ag (I) ISE with 'tpydpa' as ionophore

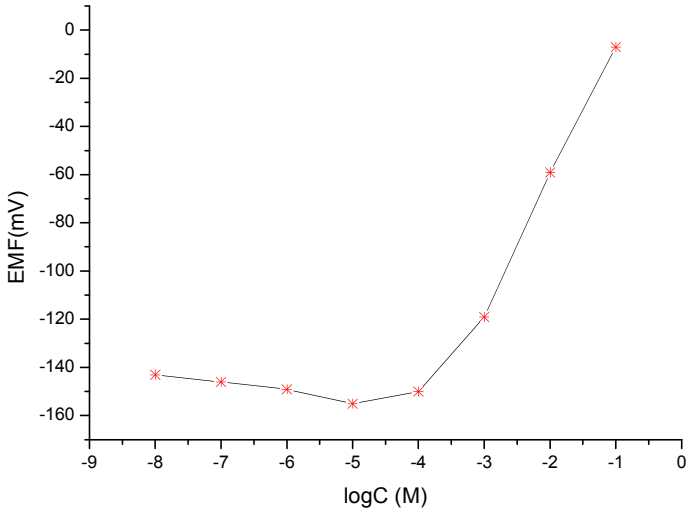


Figure 4a.8: Calibration curve for Ag(I) ISE with 'ditpy' as ionophore

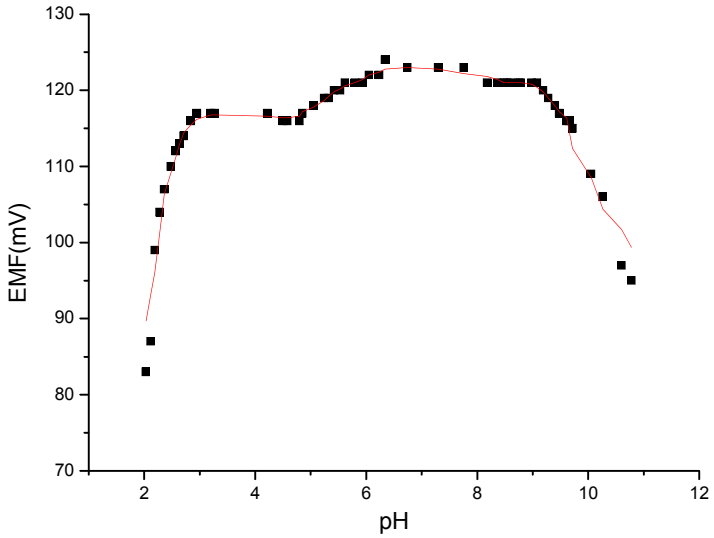


Figure 4a.9: Effect of pH on the response 'tpydpa' based Ag(I) ISE

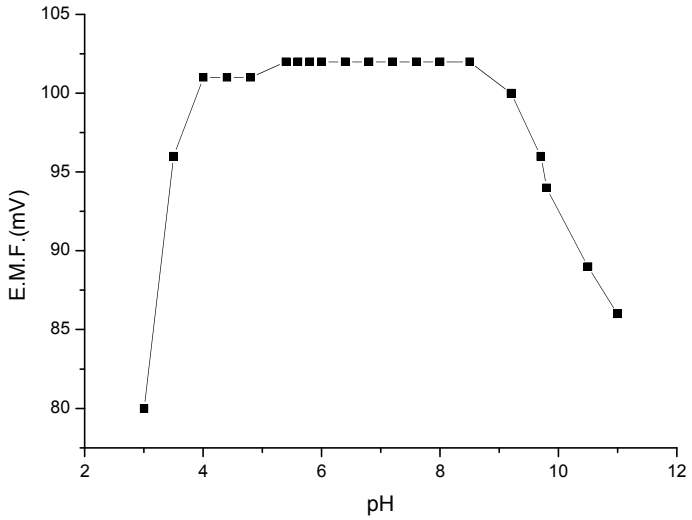


Figure 4a.10: Effect of pH on the response of 'ditpy' based Ag(I) ISE

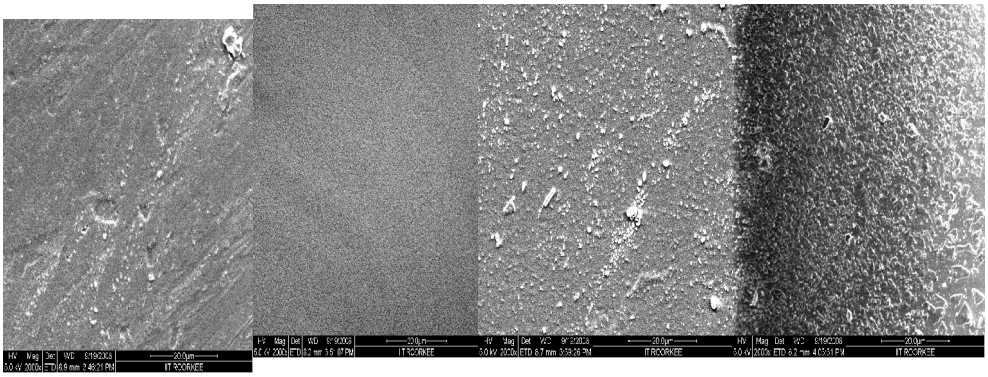
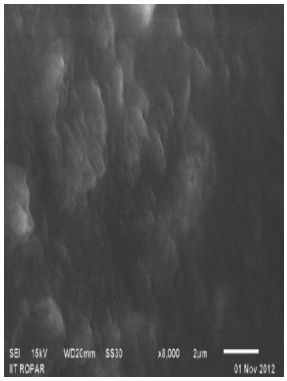
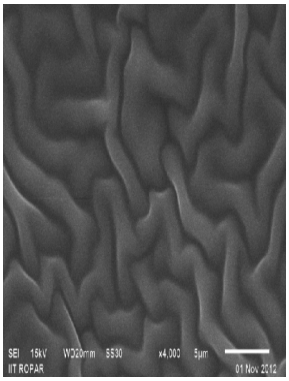


Figure 4a.11.1 **Figure 4a.11.2** **Figure 4a.11.3** **Figure 4a.11.4**





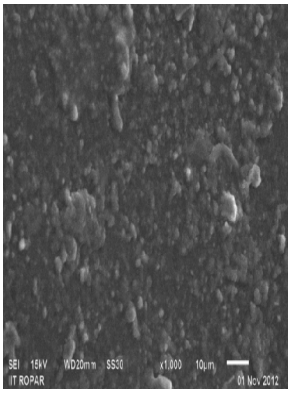


Figure 4a.11.5 **Figure 4a.11.6** **Figure 4a.11.7**

Figure 4a.11 SEM images of 'tpydpa' liquid membrane electrode for Ag(I) ISE at different stages of their development and use

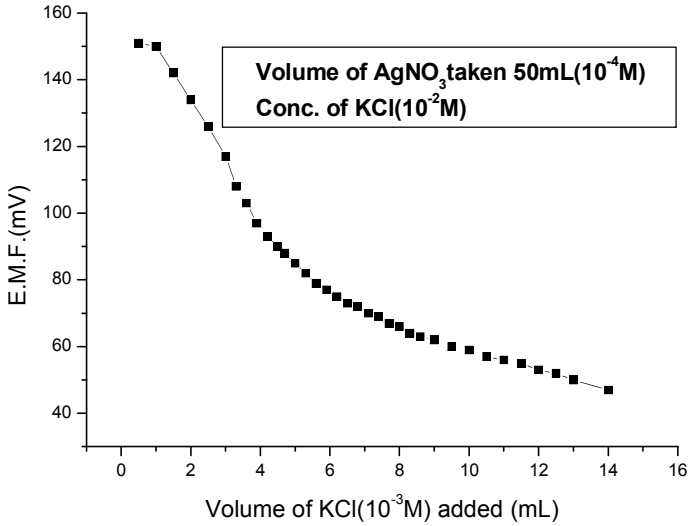


Figure 4a.12: Potentiometric Titration of 50mL of $1x10^{-4}MAgNO_3$ Vs $1x10^{-3}M$ KCl

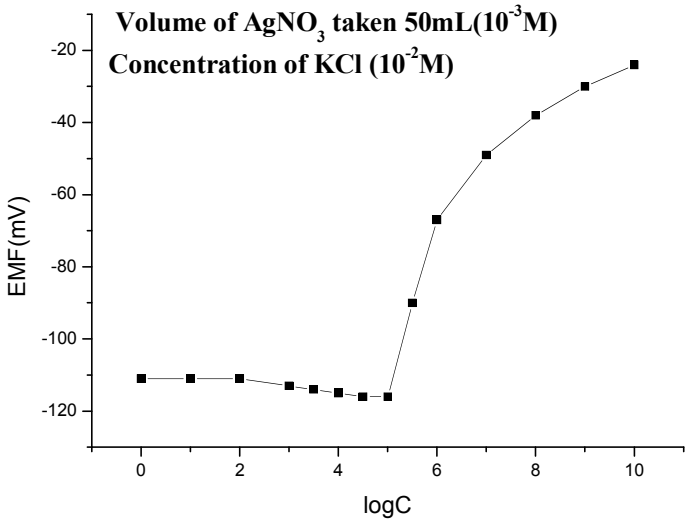


Figure 4a.13: Potentiometric titration of $AgNO_3$ Vs KCl

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4b N',N'',N''' TRIS(2-PYRIDYLOXYMETHYL) ETHANE AS ION SELECTIVE ELECTRODE FOR Pb(II) IONS.

Abstract

N',N'',N''' tris(2-pyridyloxymethyl) ethane (TPOME) has been used as an ionophore in a PVC based membrane. The membrane electrode with a composition 33: 5: 62: 3 (PVC: TPOME: o-NPOE: NaTPB) exhibits Nernstian response towards Pb(II) ions with a slope 30mV/decade, over a concentration range of $1x10^{-5}$M to $1x10^{-1}$M. The potential response remains almost unchanged over pH range 3.7-6.4. The electrode shows fast response time of 15±2 seconds and a lifetime of four months. It shows good selectivity for Pb(II) ions over other mono-, di- and trivalent cations. The electrode response is satisfactory in mixed solvent media up to 30% (v/v) non-aqueous contents. Selectivity of the ionophore for Pb(II) ions was determined by spectrophotometeric method. The electrode can also be used as an indicator electrode in the potentiometric titration of Pb(II) ions with standard chromate solution and its determination in real life samples. Surface morphology of membrane electrode at different stages of its development and use is also discussed.

4b.1 INTRODUCTION

The development of electroactive artificial ionophores for selective cation recognition has attained significant interest, as cations play a fundamental role in a wide range of chemical and biological processes[1,2]. Potnetiometric sensors have catched attention for their simple construction, low-cost, good selectivity, sensitivity and offer quantitative information using inexpensive and portable equipment[3]. Several analytical techniques, such as atomic absorption spectrometry (AAS) [4], inductive coupled plasma atomic emission spectrometry (ICP-AES), inductive coupled plasma mass spectrometry (ICP-MS)[5], Anodic stripping voltametry[6], chromatography[7], spectrophotometry[8] and low detection limit ion selective electrode (ISE) [9,10] etc. are available for quantification of lead. Lead is one of the most toxic and hazardous species because of its non-biodegradability. Common sources of lead exposure include industrial activities, production of pigments, anticorrosion coatings, car gases, soil, water, air and contaminated foods. For humans lead is a neurotoxic metallic element. Lead poisoning

occurs with repeated exposure to lead-containing environment, allowing lead to accumulate slowly in bones and teeth. Exposure to high concentration of lead can cause serious health problems, including nervous system dysfunction, hemotoxic effects, gastrointestinal tract alterations, interference in the metabolism of calcium and vitamin D and impaired hemoglobin formation, causing anemia [11]. The World Health organization (WHO) and U.S. Environmental Protection Agency (EPA) have established an action level of 15ppb for lead in drinking water [12].

Tripodal ionophores are gaining increasing interest as tools for analysis and separation of metal ions as well as for many biological and other applications. It is a unique class of complexing agents in which each of the three legs, containing at least one donor atom (X, Y and Z), connected to a bridgehead atom. The first new tripodal compound was reported in 2000 by Berrocal *et al.* with sulfate recognition properties for anion-selective electrodes [13]. Yan *et al.* synthesized 1,1,1-tris(N-ethyl-N-phenylamino-carboxylmethoxymethyl) propane and used it as an ionophore in PVC membrane electrode for the analysis of alkali and alkaline earth metal cations[14]. Kim *et al.* published a paper on new C-3 symmetric, tripodal trifluoroacetophenone derivatives as anion ionophores [15]. Mittal *et al* published a paper on 8-Hydroxyquinoline based neutral tripodal ionophore as a copper (II) selective electrode [16]. Several studies have shown that the tripodal ligands can be categorized by two main groups: flexible tripodal ligands and rigid tripodal ligands [17-23]. A number of lead-selective sensors have been developed, and many ligands have been investigated as lead-sensing agents as ionophores incorporated into the PVC membranes in ion selective electrodes [2].

Crown ether derivatives (18-crown-6 [24], monobenzo-15-crown-5[25], 4'-vinylbenzo-15-crown-5[26], 2'-methoxyethoxylsyn-dibenzo-16-crown-5 ether [27], dibenzopyridino-18-crown-6 [28], 1,10-dibenzyl-1,10-diaza-18-crown-6 [29], N,N'-dibenzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane [30], cryptand (222) [31], calixarene derivatives (4-t-butylcalix[4]arene) [32], 4-t-butylcaix[6]arene [33], 5,11,17,23-tetrakis[(p-carboxyphenyl)azo]-25,26,27,28-tetrahydroxycalix[4]arene [34], 5,11-dibromo-25,27-dipropoxycalix[4]arene [35], calixarene phosphine oxide derivatives [36-37], double-armed calix[4]arene amide derivatives [38], porphyrin ionophores

(5,10,15,20-tetrakis(3,4-dimethoxyphenyl) porphyrin [39], tetraphenylporpyrin [40], amide- linked diporphyrin xanthenes [41], and Schiff base derivatives (N,N'-bis(5-methyl salicylidine)-2,6-pyridinediamine [42], have been used as ionophores in lead selective sensors. Other ionophores employed for fabrication of lead ISEs are acyclic amides [43], macrocyclic oxamides [44], dithiomides [45], pyridine carboxamide derivatives [46], and 9,10-anthraquinone derivatives [47]. In this work, N',N'',N''' tris(2-pyridyloxymethyl) ethane (TPOME) ionophore is a flexible molecule containing the nitrogen donor groups. In this branch of tripodal ligands, N containing motifs are usually soft donor groups. The presence of donor groups in the tripodal ligand leads to complexation of the ligand with metal with a good formation constant. The chemical structure of TPOME used in this study as an ionophore is shown in Figure 4b.1

4b.2 EXPERIMENTAL

4b.2.1 Reagents, instruments and membrane preparation

High molecular weight polyvinylchloride (PVC), sodium tetraphenylborate (NaTPB), metal nitrates were received from Sigma Aldrich (India), Analytical reagent grade tetrahydrofuran (THF), nitric acid, sodium hydroxide were obtained from SD-fine (India). Solutions of metal nitrates were prepared in doubly distilled deionised water and standardized by the reported method wherever necessary. Working solution of different metal concentrations was prepared by diluting 0.1 M stock solution.

PVC based membranes [48] were prepared by dissolving different amounts of the ionophore, anion excluder NaTPB, and solvent mediator o-NPOE and PVC in THF. Different components were mixed in terms of weight percentages as per combination in Table 1. After complete dissolution of all the components, the homogenous mixture was concentrated by evaporating THF and then poured in glass rings placed on smooth glass plates. To obtain membrane with reproducible characteristics, the solvent evaporation was carefully controlled otherwise morphology and thickness of membranes shows significant variations which may ultimately affect sensor response. The transparent membranes so obtained were removed carefully from the glass plate. A 6mm diameter piece of the membrane was cut out and glued to one end of the "Pyrex" glass tube. The

membrane thus prepared was equilibrated for two days in Pb^{2+} (0.1M) solution. It is known that sensitivity, linearity and selectivity for a given ionophore depend significantly on the membrane composition and nature of plasticizers used [49]. Hence, several membranes of varying composition were prepared and investigated. The membrane which gave reproducible results and best performance characteristics was selected for detailed studies. The optimum composition of the membrane performing the best is given in the Table 4b.1.

The potential measurements were carried out at 25±0.1C with a digital Euip-Tronics potentiometer (EQ-602, accuracy, ±0.1mV, Mumbai India) and pH of the solution was monitored simultaneously using Equip-Tronics pH meter (EQ-614, Mumbai India) and conventional glass pH electrode.

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

Hg| Hg_2Cl_2,KCl(satd)| Int.Soln.($1x10^{-1}$M $Pb(NO_3)_2$| PVC Membrane| Test solution| Hg-Hg_2Cl_2,KCl(satd)

4b.3 RESULTS AND DISCUSSION

4b.3.1 Spectrophotometric study of TPOME- metal ion interaction

To explore the binding efficiency of TPOME towards various metal ions, UV-visible spectroscopic technique was applied [50]. The complexation ability of TPOME was examined in methanol medium taking equal volumes of the equimolar (1×10^{-5} M) ionophore and different metal solutions. Absorbances of complexes of TPOME observed with Pb^{2+}, Cu^{2+}, Co^{2+}, Ca^{2+} using spectrophotometry. A UV-visible spectrum of TPOME after the addition of metal ions shows a shift in position of absorption peaks and absorbance values as shown in Figure 4b.2. TPOME alone exhibits two absorption peaks at 280nm and at 227nm. Electronic spectra were recorded for 1:1 complex after the addition of required amounts of each ion. When Pb(II) interacts with TPOME, pronounced changes in the absorption spectra were observed. Absorption peak at 227nm shifted to 214nm (Blue shift) with an increase in intensity of the band, while the peak at 280nm shifted to 273nm (Blue shift) and intensity of the band decreased slightly. In case of all other metal ions, the peak at 280nm does not shift while the peak at 227nm shifted

to 214nm (Blue shift). This observation confirmed that the presence of Pb^{2+} resulted in remarkable change in position, intensity and shape of two absorption peaks. Hence, this study confirmed selectivity of the ionophore for Pb(II) ions.

4b.3.2 Determination of binding constants of TPOME using sandwich membrane method

The ionophore-complex formation constant was determined by a potentiometric method. Sandwich membrane was prepared by mechanically pressing together, the two individual membranes; the membrane with ionophore to the membrane without ionophore after blotting them individually and dried with filter paper. The experimental set up was same as described earlier. Experiments were carried out according to the sandwich membrane method [51-52]. In this method, the potential of sandwich membranes E_m were determined by subtracting the cell potential for a membrane without ionophore from that of sandwich membrane. The formation constant is then calculated from the following equation:

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

Where, L_T is the total concentration of the ionophore in the membrane segment, R_T is the concentration of the lipophilic ionic site additives, n is the ion-ionophore complexes stoichiometry, R, T and F are the gas constant, the absolute temperature and the Faraday constant. The tested ion, I carries a charge of z_i.

The membrane potential E_m was determined by subtracting the cell potential for a membrane without ionophore, from that for the sandwich membrane. The formation constant values obtained for ion-ionophore complexes are shown in following paras. This method allows convenient determination of the ion-ionophore complexes within the membrane phase on the basis of transient membrane potential measurement on two layer sandwich membrane neglecting the ion pairs. The calculated binding constants for Ag^{+}, $Sr,^{2+}$ Ca^{2+}, Cd^{2+}, Ni^{2+}, Cu^{2+}, Fe^{3+}, Co^{2+} and Pb^{2+} are 4.9, 5.5, 5.6, 5.1, 5.4, 6.0, 4.9, 5.4, and 6.1, respectively. The results show highest stability for lead ions as compared to other ions.

4b.3.3 Optimization of membrane ingredients and effect of ionophore concentration

In preliminary experiments, the membranes with and without carrier were prepared. The blank membrane showed insignificant selectivity towards Pb^{2+} ions and their responses were unreliable whereas, in presence of the proposed ionophore, the optimized membrane gave Nernstian response and remarkable selectivity for Pb^{2+} ions over several other metal cations. Preferential response towards Pb^{2+} ions is believed to be associated with selective coordination of the ionophore to the Pb^{2+} ions. Pb^{2+} selective electrodes prepared with different amounts of the ionophore have been shown in the Table 4.1(b). Since the sensitivity and selectivity of a given membrane electrode is significantly related to the composition of the membrane, particularly, the amount of the ionophore [53-54], PVC and additive were varied to study their effect on the potential response of the proposed electrode. The data clearly indicates the composition of the electrode having composition less than or greater than 5% leads to non-Nernstian responses. This deviation in the electrode response at high or lower concentration of the ionophore is due to the loss of the selectivity and enhanced interference of the lipophilic counter ions of the test solution as presumed in the phase boundry potential model of carrier based ISEs [55].

4b.3.4 Calibration curve, response time, life time of the electrode

The polymeric membrane electrode for Pb^{2+} ions based on ionophore TPOME have been examined according to IUPAC recommendations [56] at various concentration of inner filling solution of $Pb(NO_3)_2$ in the range of $1x10^{-3}$ to $1x10^{-1}$M and the potential response of the electrode have been observed. Best results in terms of slope and working concentration has been obtained with inner filling solution of concentration $1x10^{-1}$M. Emf of the membrane electrode at varying Pb(II) concentration shows a linear range from $1x10^{-5}$M to $1x10^{-1}$M with a Nernstian slope of 30mV/decade. The detection limit is $6x10^{-6}$M as determined from the intersection of the extrapolated segments of the calibration plots shown in Figure 4b.3.

4b.3.5 Effect of pH on the response of Pb(II) selective electrode

The influence of pH on the response of the electrode was studied for Pb(II) solution of concentration $1x10^{-3}$M (Figure 4b.4) in the pH range 3-9.7. The potentials were found to remain unaffected by the change in pH in the pH range 3.7-6.4. The sudden decrease of potential below pH 3.5 may be attributed to the partial protonation of the ionophore while the decrease in potential above pH 6.5 could be due to the formation of some soluble and insoluble complexes of Pb^{2+} such as $Pb(OH)^{+}$ and $Pb(OH)_2$ [57] which might have resulted in a loss of ability of the ionophore to sense Pb(II) ions.

4b.3.6 Effect of interfering ions on electrode performance and selectivity

Selectivity is the term which is used to describe the utility of the sensor. It gives the magnitude of selectivity of a sensor towards primary ion A in presence of secondary ions B present in the solution. It is expressed in terms of potentiometric selectivity coefficient ($K^{Pot}_{A,B}$). Potentiometric selectivity coefficients in the present case have been determined by fixed interference method (FIM) as per IUPAC recommendations [55,58]. The concentration of the interfering ion was kept fixed at $1x10^{-2}$M. The values of selectivity coefficient so determined for Na^{+}, Ca^{2+}, Mg^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}, Cd^{2+}, Hg^{2+}, Zn^{2+},La^{3+}, Fe^{3+}, and Ag^{+} are -0.33, -1.77, -2.02, -2.02 -1.80, -0.22, -0.80, -0.74, -2.04,-2.62, -2.76 and -0.33, respectively. The selectivity coefficient data indicate that logK values are in the order 10^{-2} for divalent and trivalent metal ions (except K^{+}, Cu^{2+}, Hg^{2+} and Ag^{+}). Therefore, the electrode can be used for the determination of Pb^{2+} ions in the presence of certain interfering ions. The electrodes already reported in literature generally suffer from strong interference by mercury ions, but the proposed electrode system shows good selectivity for copper ion even in presence of these ions. logK values for Pb^{2+} selective electrode are compared with those reported for other Pb(II) selective electrodes reported in literature in Table 4b.2.

4b.3.7 Surface characterization of the membrane electrode

The surface morphology of Pb^{2+} selective membrane is shown in Figure 4b.5. A remarkable change is noticed after addition of each membrane ingredient. PVC membrane surface without any other ingredient shows uniform homogeneity (Figure 4b.5.1) while Figure 4b.5.2 shows a uniform dense packing due to the presence of

plasticizer on the PVC membrane. Further, on addition of lipophilic salt, there is a huge change in morphology with non-preferential orientation, no observable cracks and the membrane appeared to be composed of dense and loose aggregation of small particles as shown in Figure 4b.5.3. However, on addition of TPOME ionophore 5%, a uniform distribution of TPOME can be seen in Figure 4b.5.4. Figure 4b.5.5 is the SEM image of membrane containing all components taken after 24h conditioning with Pb(II) salt solution. Figure 4b.5.6 shows membrane surface after its exhaustive use as ISE. Surface is clear as a non-uniform layer due to presence of Pb(II)- ionophore complexes randomly distributed. In Figure 4b.5.6 big change was observed in surface morphology with the appearance of a bare type PVC membrane, which might be due to leaching of membrane ingredients, after its lifetime of four months.

4b.4 APPLICATIONS

4b.4.1 Effect of electrode response in mixed solvent media

The effect of partially non aqueous medium was also investigated by using the sensor in methanol-water, acetone-water, dimethylsulfoxide-water mixtures using 10%, 20% and 30% non-aqueous content. However, beyond these non-aqueous contents, both working concentration range and slope of the calibration curve decreased drastically and results were slightly irreproducible.

4b.4.2 Potentiometric titration

To further determine analytical utility of the proposed potentiometric sensor, quantification of the Pb^{2+} ions was carried out by potentiometric titration using potassium chromate as a titrant. The titration curve (Figure 4b.6) obtained clearly shows change in slope corresponding to 1:1 stoichiometry of Pb(II) ion with chromate ion. It indicated that sensor is highly selective for Pb^{2+}. The sensor was also used for testing municipal waste water and the results obtained are in agreement with those obtained by AAS.

4b.5 CONCLUSIONS

The results obtained from this study revealed that the potentiometric PVC membrane based on N',N'',N''' tris(2-pyridyloxymethyl) ethane (TPOME) works as an excellent Pb^{2+} selective membrane electrode.

(I) The sensor developed using this ionophore exhibits wide operational concentration range, high selectivity, long term stability and fast response time with a long lifetime period of 4 months.

(II) The selectivity of the membcrane sensor towards Pb^{2+} ion for most of the cations is quite good and response characteristics of the proposed electrode are better in comparison to the earlier sensors in terms of selectivity for Pb(II) ions in presence of Hg(II) and other ions.

(III) The electrode can be used for practical determination of Pb^{2+} ion in real life samples.

***

Table 4b.1: Optimization of membrane ingredients and their response characteristics for Pb(II) selective electrode

Sr. No.	Ionophore (% w/w)	PVC (% w/w)	NaTPB (% w/w)	o-NPOE (% w/w)	Lower Detection Limit, M	Slope (mV/decade)
1	----	33	---	---	----	----
2	-----	33	----	67	---	-----
3	1.5	33	----	65.5	$5x10^{-5}$	33
4	2.0	33	----	65.0	$5x10^{-5}$	35
5	3.0	33	----	64.0	$6x10^{-5}$	37
6	5.0	33	----	62.0	$5x10^{-5}$	32
7	6.0	33	----	61.0	$1x10^{-5}$	30
8	8.0	33	----	59.0	$1x10^{-5}$	25
9	10.0	33	----	57.0	$6x10^{-5}$	25
10	3.0	32	1.5	63.5	$6x10^{-5}$	29
11	**5.0**	**30**	**3.0**	**62.0**	**$6x10^{-5}$**	**30**
12	6.0	29	6.0	59.0	$8x10^{-5}$	35
13	6.0	30	3.0	61.0	$1x10^{-4}$	29

Table 4b.2: Comparison of proposed Pb(II)-selective electrode with the reported Electrodes

Ionophore	Working Conc. Range (M)	pH Range	Slope (mV/decade)
Dibenzo 18-crown-6[59]	10^{-2} -10^{-6}	3.6-7.0	28
9,10-anthraquinone derivatives[60]	10^{-3}-10^{-6}	N.R.	29
Crown Ethers[61]	10^{-1} -10^{-5}	3.0-6.0	28
Bis(1'-hydroxy-2'-acetonaphthone)-2,2-diiminodiethylamine[62]	10^{-2} -10^{-6}	4.0-7.0	27.8
3,7,11-tris (2-pyridylmethyl)-3,7,11,17-tetraazabicyclo [11.3.1] heptadeca-1(17),13,15-triene[63]	10^{-1} -10^{-6}	5.0-8.0	28.5
N, N´-bis(2-hydroxy-1-napthalene)-2,6-pyridiamine (BHNPD)[64]	10^{-1} -10^{-6}	3.5-7.5	29
Piroxicam[65]	10^{-1}-10^{-5}	4.0-8.0	30
Polyaminoanthraquinone (PAAQ) microparticles[66]	10^{-1}-10^{-6}	1.0-6.0	29
calixarene carboxyphenyl azo derivate[67]	10^{-2} -10^{-6}	4.0-7.0	29
Benzo substituted diamides[68]	10^{-2}-10^{-6}	3.7-6.5	30
N,N'-Bis-thiophen-2-ylmethylene-pyridine-2,6-diamine[69]	10^{-1}-5x10^{-5}	N. R.	30
TPOME (this work)	**10^{-1} -10^{-5}**	**3.7-6.4**	**30**

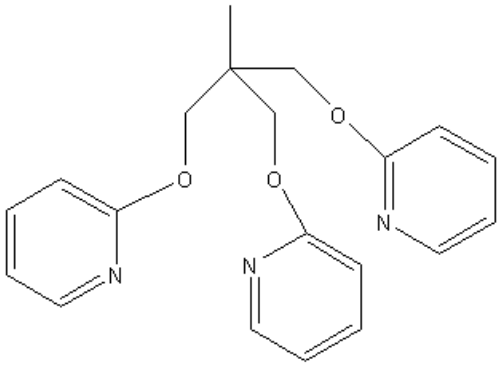

Figure 4b.1: Chemical structure of N',N'',N''' tris(2-pyridyloxymethyl) ethane (TPOME)

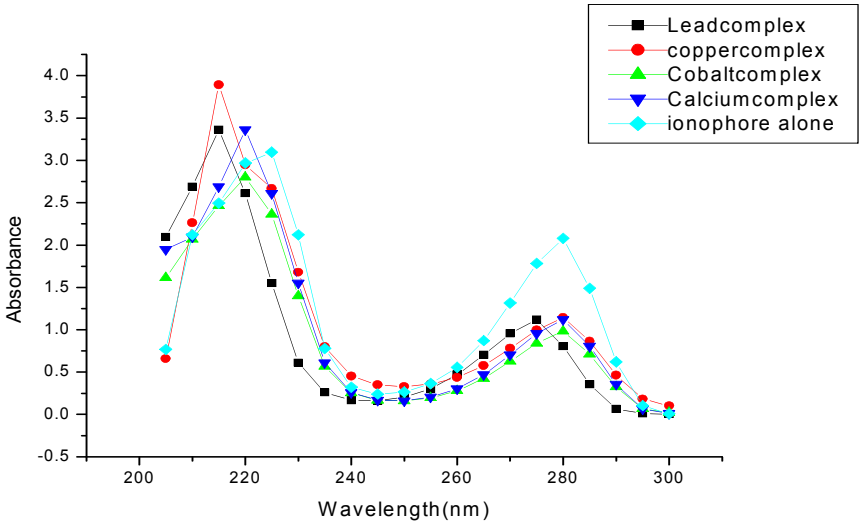

Figure 4b.2: Electronic spectra of TPOME ionophore with different metal ions

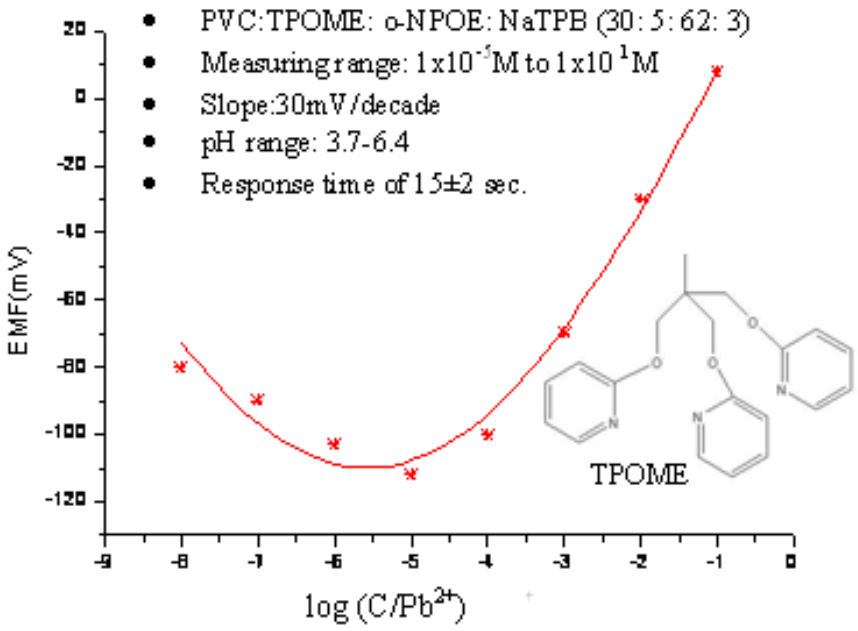

Figure 4b.3: Calibration curve for Pb(II)-selective electrode based on TPOME.

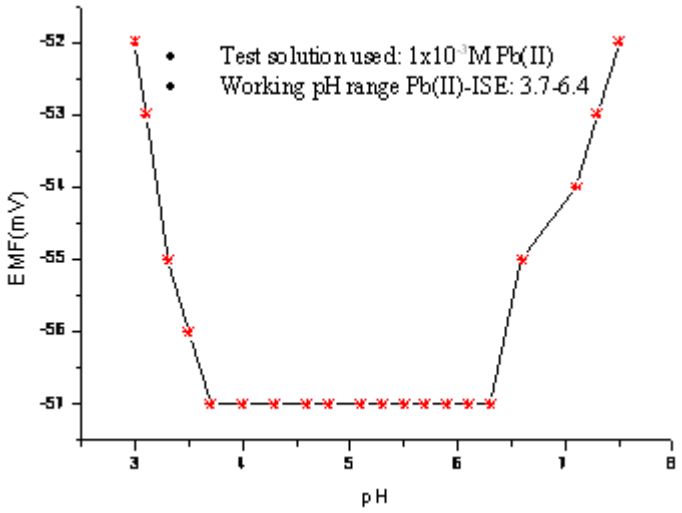

Figure 4b.4: Effect of pH on the response of TPOME based electrode

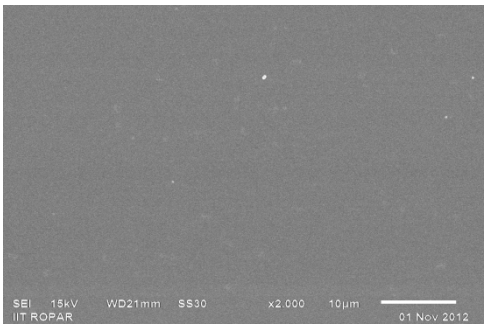

Figure 4b.5.1

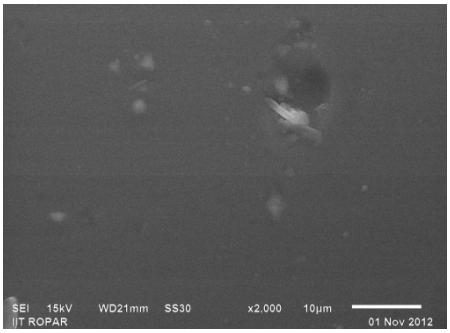

Figure 4b.5

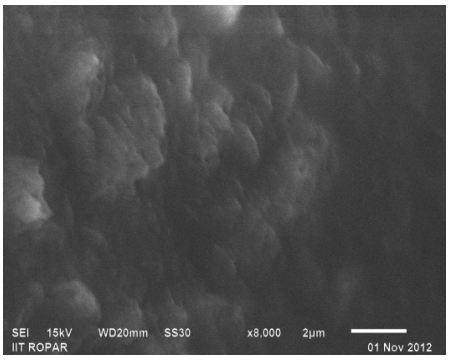

Figure 4b.5.3

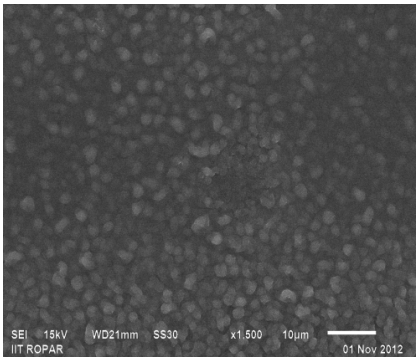

Figure 4b.5.4

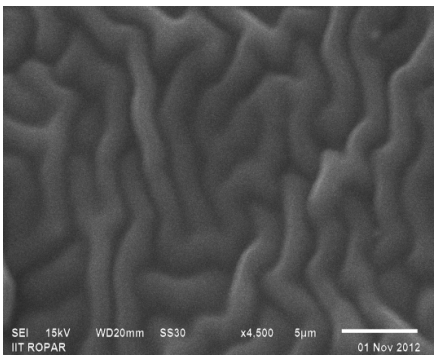

Figure 4b.5.5

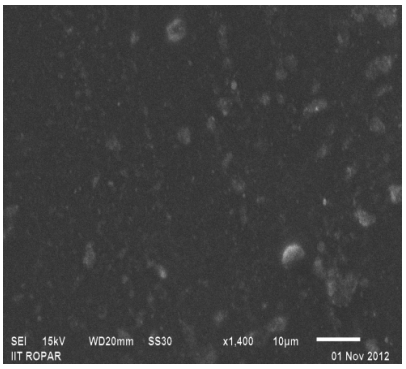

Figure 4b.5.6

Figure 4b.5.1: SEM image of membrane containing PVC only
Figure 4b.5.2: SEM image of membrane containing PVC and plasticizer o-NPOE
Figure 4b.5.3: SEM image of membrane containing PVC, o-NPOE and lipophilic salt only
Figure 4b.5.4: SEM image of membrane containinig PVC, o-NPOE, lipophilic salt and 5% TPOME
Figure 4b.5.5: SEM image of membrane containinig PVC, o-NPOE, lipophilic salt and 5% TPOME equalibrated with Pb(NO3)2 solution for 24h
Figure 4b.5.6: SEM image of membrane containinig PVC, o-NPOE, lipophilic salt and 5% TPOME after exhaustive use as Ag(I) ISE

Figure 4b.5: SEM images of liquid membrane based on TPOME at different stages of development and use

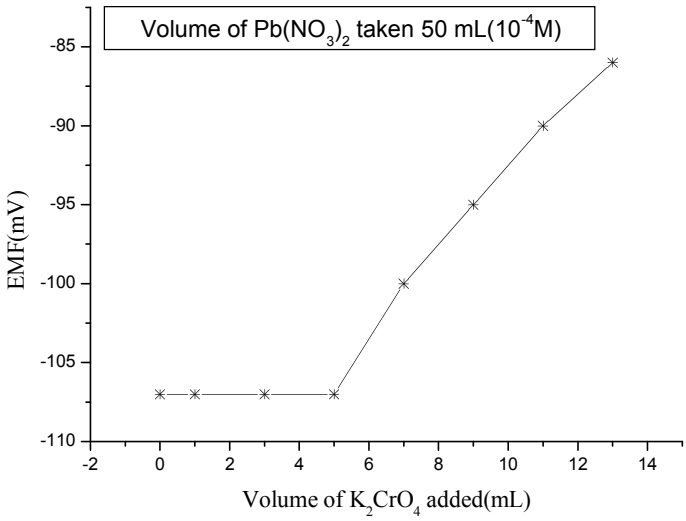

Figure 4b.6: Potentiometric titration of $Pb(NO_3)_2$ Vs K_2CrO_4

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4c N,N,N',N'-TETRAKIS(2-PYRIDYLMETHYL) ETHYLENEDIAMINE AS AN ION-SELECTIVE ELECTRODE FOR Zn(II) IONS

Abstract

A new PVC based liquid membrane containing N,N,N′,N′-tetrakis(2-pyridylmethyl) ethylenediamine (I) as an ionophore has been developed as zinc ion-selective electrode. The best performance was observed with an electrode composition (w/w); PVC (30%), 2-nitro phenyloctylether (60%), ionophore (I) (5%) and sodium tetrakis(4-chlorophenyl) borate as lipophilic salt (NaTPB, 2%). The electrode shows a linear dynamic response in the concentration range $5.0x10^{-6}$ M to $1.0x10^{-1}$ M with a Nernstian slope of 30 mV/decade and a detection limit as $1x10^{-6}$ M. It has a response time of 20 seconds and can be used for at least 4 months without any significant divergence in potentials. The proposed sensor shows good selectivity with respect to alkali, alkaline earth and transition metal ions. It can be used in the pH range 3.0-8.0 and electrode has been used as an indicator electrode in potentiometric titrations of zinc(II) ions with Na_2S. The electrode also has been applied successfully for the determination of zinc ions in real life samples.

4c.1 INTRODUCTION

Ion-selective electrodes find wide use in the fields of environment, medicine, agriculture and industry because they are of low cost effectiveness, portability, wide measuring range, sample non-destruction and offer many advantages over other methods of chemical analysis. Zinc is an essential trace element and second most abundant transition element after iron in the body[1-3]. The largest industrial use of zinc is as a protective coating for iron in a process called galvanizing with reference to the cathodic protection which zinc offers to the iron. Zinc is one of the transition metals which are used in paint, electroplating, pharmaceutical and chemical industry, die casting, soldering flux for soldering iron and thus occurs widely in the environment. In large quantity zinc is carcinogenic. It is also used in several lotions applied topically. Common zinc compounds found at hazardous waste sites include zinc chloride, zinc oxide, zinc

sulphate and zinc sulphide. Besides, it is also present in high protein foods and its large doses cause fever, chills, pulmonary manifestation, gastroenteritis, vomiting, nausea, anemia and renal failure. In view of its toxicity, the determination of zinc becomes important. Zinc ions are key structural components of a large number of proteins. Zinc is a toxic element and it's monitoring in biological, food and in environmental sample is very important.

During the last few decades, there has been a renewed resurgence in developing potentiometric membrane electrodes as devices for rapid, accurate, low cost and non destructive analysis of different samples with small volume samples. In recent years, a number of Zn^{2+} membrane sensors based on different ion carriers have been reported in the literature [4-10]. The main problem of these sensors is relatively low affinity for Zn^{2+} with respect to other metal ions such as Na^{+}, Mg^{2+}, Co^{2+}, etc. There are a few reports on Zn^{2+} selective electrodes in the literature [4-8]. Moreover, these potentiometric sensors lack stability, selectivity, long response time and are composed of considerable interference effect. Furthermore, the solid state electrodes were found to be of limited usefulness because of their instability and long response time. These difficulties prompted us to find an ionophore suitable to function as receptor for zinc selective electrode. Gagne et al. in 1982[11] synthesized this compound and since then it has not been used as potentiometric based ion sensing material for zinc(II) ions. Although it is not a new compound but extensive use in the field of cell biology made us to convert this molecule to a sensing material [12-15]. In the present work, we report the use of N,N,N′,N′-tetrakis(2-pyridylmethyl) ethylenediamine shown in Figure 4c.1 for preparing highly selective Zn^{2+} membrane electrode.

4c.2 EXPERIMENTAL SECTION

4c.2.1 Reagents, Apparatus and Membrane Preparation

High molecular weight polyvinylchloride (PVC), *o*-nitrophenyloctylether (*o*-NPOE) and tetrakis (p-chlorophenyl) borate (NaTPB), tetrahydrofuran (THF) were purchased from Aldrich (India) and used as received. Metal salt solutions of concentration 0.1M were prepared by dissolving AR grade metal nitrates in double distilled water and

standardized wherever necessary. The working solutions of different concentration were prepared by serial dilution.

Potentials were measured with an Equip-Tronics (EQ-602, accuracy, ± 0.1mV, India) potentiometer (Mumbai, India) and pH of the solution was monitored simultaneously with a conventional glass pH electrode.

Membrane were prepared by dissolving appropriate amounts of powdered PVC, plasticizer, ionophore (TPEN) according to Table 1 and were completely dissolved in 5 mL of THF. The components were added in terms of weight percentages. The homogenous mixture was obtained after complete dissolution of all components, concentrating by evaporating THF slowly at 25° C so as to get an oily concentrated mixture. The solution was poured in glass rings of diameter 2 cm placed on smooth glass plate. The solution was then allowed to evaporate for 24 h at room temperature. Transparent membranes so obtained were cut to the size and glued on one end of Pyrex glass tube with araldite adhesive. The tube so obtained with the membrane was filled with 0.1M zinc nitrate solution and was equilibrated with 0.1M zinc nitrate solution. The ratio of different membrane ingredients and the contact time were optimized to provide membranes which resulted in reproducible and stable potentials. Also the membranes having only PVC as the membrane ingredients (dummy membranes) were also prepared to observe whether any background potentials were produced due to binding material or not. It was observed that potentials were not generated without the ionophore. The activities of metal ions were calculated by using modified form of the Debye-Huckel equation. After equilibrating the membrane for two days in 0.1M $AgNO_3$ solution all emf measurements were carried out with the following assembly:

Hg| Hg_2Cl_2,KCl(satd)| Int.Soln.($1x10^{-1}$M $Zn(NO_3)_2$| PVC Membrane| Test solution| Hg-Hg_2Cl_2,KCl(satd)

The concentrations of test solution were varied from $1x10^{-8}$M to $1x10^{-1}$M.

4c.3 RESULTS AND DISCUSSION

Ligands to be used as ionophore in Zn^{2+} ion selective electrode should ideally fulfill certain conditions. They should be selective for zinc over several other metal ions, they should have rapid exchange kinetics and should be sufficiently lipophilic to

prevent leaching of the ligand into the solution surrounding the membrane electrode. The existence of six donating nitrogen in the ionophore used in the present study increases the stability of its zinc complex over other metal ions [15].

4c.3.1 Determination of the formation constant

In order to use the ionophore for a particular metal ion its interactions with different metal ions were studied by sandwich membrane method [16]. In this method, fused segmented sandwich membrane yield information about the activity ratio on both sides of the membrane. It requires membrane potential measurement on two layer sandwich membrane, where only one side contains the ionophore and other side of the membrane does not contain the ionophore. The membrane potential E_M is determined by subtracting the cell potential for a membrane without ionophore from that for the sandwich membrane. This method allows convenient determination of ion-ionophore complexes within the membrane phase on the basis of transient membrane potential measurement on two layer sandwich membrane neglecting the ion pairs. The values obtained of ion-ionophore complex are shown in Table 4c.1. The calculated formation constant for Zn^{2+}, Ni^{2+}, Cu^{2+}, Co^{2+}, Hg^{2+}, Cd^{2+}, Ca^{2+} and Mg^{2+} are 15.7, 6.0, 5.1, 5.1,4.9, 4.6, 4.1, and 4.0, respectively, which show highest stability for zinc ions as compared to other ions. Also the stability constants have been determined by E. Kawabata [15] using SC Database (IUPAC and Academic Software) show Zn^{2+}, Ca^{2+}, Mg^{2} are 15.1, 4.4 and 1.7, respectively, are in close agreement with our experimental results by sandwich membrane method (Table 4c.1). Moreover, reported works recommend the logarithmic complex formation constants ranging from 4.4 to 29.0 useful for fabricating ion selective electrodes [17-19].

4c.3.2 Effect of ionophore concentration

In preliminary experiments, membranes with and without carriers were constructed. The blank membrane did not show any measurable responses towards Zn^{2+} whereas, in presence of the proposed ionophore, 'TPEN' the optimized membrane gave Nernstian response and remarkable selectivity for Zn^{2+} ion over several other metal cations. Preferential response towards Zn^{2+} ions is believed to be associated with selective complexation of ionophore for Zn^{2+} ions. Zn^{2+} selective electrodes prepared

with different amounts of ionophores have been evaluated in the Table 4c.2. Since the sensitivity and selectivity of a given membrane electrode is significantly related to the composition of membrane, particularly, the amount of ionophore [20,21], the amount of ionophore, PVC and additive were varied to study their effect on the potential response of the proposed electrode. The results clearly indicate that composition of the electrode having ionophore less than or greater than 3% leads to non-Nernstian responses. This deviation in electrode response at higher and lower concentration of the ionophore is due to the loss of selectivity and enhanced interference of the lipophilic counter ions of the test solution as presumed in the phase boundary potential model of carrier based ISEs [22]. Comparison of the proposed electrode with reported zinc selective electrodes have been shown in Table 4c.3.

4c.3.3 Calibration curve, response time and lifetime of electrode

The polymeric membrane electrodes for Zn^{2+} ion based on ionophore TPEN have been examined for their potentiometric responses according to IUPAC recommendations [17] at various concentrations of inner filling solution of $Zn(NO_3)_2$ in the range of $1.0x10^{-3}$M to $1.0x10^{-1}$M. It was observed that the best result in terms of slope and working concentration range has been obtained with inner filling solution of concentration $1.0x10^{-1}$M. E.M.F. of the membrane electrode at varying Zn (II) concentration shows a linear range from $5.0x10^{-6}$M to $1.0x10^{-1}$M with a Nernstian slope of 30mV/decade. The detection limit was $5.0x10^{-6}$M as determined from the intersection of the two extrapolated segments of the calibration plot (Figure 4c.2)**.** The membrane having 5% ionophore (w/w) exhibited the best results. This composition gave reproducible Nernstian response (slope 30.0 mV/decade, ±5mV, standard deviation for 5 set of measurements) in the concentration range of $1x10^{-6}$M to $1x10^{-1}$M of Zn^{2+} (Figure 4c.2) and a response time of 20 seconds. The electrode $\mathbf{E_{10}}$ having optimized composition: PVC: plasticizer: Ionophore: lipophilic agent (33: 60: 5: 2) was chosen for further studies. Reversibility of the electrode signal, when changing and returning to the same concentration, is another property to be examined for ISE. This property also represents precision of the detection. Reversibility of the sensor was also

investigated alternatively by repeatedly measuring EMFs of two different concentrations, 10^{-4}M and 10^{-3}M of Zn^{2+} and obtained the same EMF for the corresponding solutions. Further, the response behavior did not change up to 4 months. It gave reproducible curve without observing any change in slope, detection limit and working concentration range. The electrode was kept dried and stored at room temperature when not in use.

4c.3.4 Effect of pH on the response of Zn (II) selective electrode

The pH dependence of the potential response of the electrode was studied in the pH range of 3.0-8.0 in the solution. pH of the solution was adjusted using NaOH (0.1M) and HNO_3 (0.1M) and the results are shown in the Figure 4c.3. As it is seen the potential response of the sensor remains constant in the pH range of 3.0-8.0 (Figure 4c.3). At higher pH values the potential decreases. This is due to the formation of some hydroxyl complexes of Zn(II) ions. At lower pH values, the potential increases due to the membrane responds to hydronium ion and Zn(II) ions. The sharp changes at higher pH may be due to the formation of some hydroxyl complexes of Zn(II) ions thereby causing interference. At lower pH values, the potential increase in values was due to the membrane response to hydronium ion and Zn(II) ions. Beyond these limits, however a relatively drastic drift in the potential versus pH was observed .The observed drift at higher pH values of this range could be due to the formation of $Zn(OH)_2$ in the solution. In acidic solution having low pH values, the ionophore could be protonated to some extent, which resulted in improper functioning of the membrane sensor to Zn(II) ion concentration**.**

4c.3.5 Effect of interfering ions on electrode performance and selectivity

Selectivity is the term which is used to describe utility of ion selective electrode. It gives the response of ion selective electrode for the primary ion in presence of secondary ion present in the solution, which is expressed in terms of potentiometric selectivity coefficients. Potentiometric selectivity coefficient ($K^{Pot}_{Zn,B}$) describes preference by the membranes for Zn^{2+} relative to an interfering ion B. In this work, selectivity coefficients were determined by fixed interference method (FIM) as per

IUPAC recommendations [24-25]. Selectivity coefficients were determined from the potential measurements on solutions containing fixed concentration of interfering ion ($1x10^{-2}M$) and varying concentrations of silver ions. The values of selectivity coefficient so determined are compiled in Table 4c.3**.** Mercury is known to interfere in the determination of Zn^{2+} ions but in case of proposed electrode the level of interference of Hg^{2+} is the same as that of other bivalent ions like Cd^{2+}, Cu^{2+} and Pb^{2+}. The selectivity coefficients values are of the order 10^{-2} for divalent and trivalent metal ions (except Na^{+} and K^{+}) which indicate that these ions will cause negligible interference on the functioning of proposed silver electrode. Therefore, the proposed electrode can be used for the determination of Zn^{2+} ions in the presence of certain interfering ions. A comparison of the proposed electrodes with the reported electrodes is shown in Table 4c.4 [26-41].

4c.3.6 Effect of mixed solvents

In some cases, sample to be analyzed may be containing non-aqueous media and hence to study the effect of non-aqueous media the proposed sensor was subjected to performance in partially non aqueous media using methanol, ethanol, dimethylsulphoxide and dimethylformamide mixed with water. The membrane does not undergo any appreciable change in working concentration range and in the slope up to 30 % of the non-aqueous content in the mixed solvent media. The results are shown in Table 4c.5.

4c.3.7 Effect of surfactants

Surfactants are widely used in households and various industries. Both cationic and anionic surfactants interact with the polymer membrane, thus extracting cations into the membrane phase [42] and results in increased background potential and lower the binding ability of the ionophore. This results in deteriorated detection limits, reduced response, slopes and lower selectivity for the primary ion [43]. The influence of the anionic surfactants (sodium dodecylsulphate, SDS) is comparatively large as it causes interference due to sodium ions from its dissociation and competition of SDS anion with ionophore anion in the primary ion complexation reaction. Cationic surfactant

(tetrabutyl ammonium chloride, TBC) is also potential interferant but less to anionic as its lipophilic cation competes effectively in the membrane and solution interface exchange with less lipophilic primary cation thus increasing the electrode detection limit and shortening its measurement range. Surfactants can also disturb the measurements because of their molecule adsorption on the membrane surface, which results in potential instability and prolonged time of electrode response. The performance of the electrode was evaluated by contaminating the sample solution with different concentration of the surfactants (SDS, TBC). The proposed electrode can tolerate cationic surfactant (TBC) concentration up to $1x10^{-5}$M and anionic surfactant (SDS) concentration up to $6.0x10^{-6}$M.

4c.3.8 Surface characterization of the membrane electrode

The surface morphology of Zn^{2+} selective membranes is shown in Figure 4c.4. A remarkable change is noticed after addition of each membrane ingredient. PVC membrane surface without any other ingredient shows uniform homogeneity (Figure 4c.4.1) while Figure 4c.4.2 shows a uniform dense packing due to the presence of plasticizer on the PVC membrane. Further, on addition of lipophilic salt, there is a huge change in morphology with non-preferential orientation no observable cracks and appeared to be composed of dense and loose aggregation of small particles as shown in Figure 4c.4.3. However on addition of TPEN ionophore 5%, a uniform distribution of TPEN can be seen in Figure 4c.4.4 taken after 24h conditioning with Zn(II) salt solution. Figure 4c.4.5 shows membrane surface after its exhaustive use as ISE. Surface is clear as a non-uniform layer due to presence of Zn(II)- ionophore complexes randomly distributed. In Figure 4c.4.6, big change was observed in surface morphology with appearance of a bare type PVC membrane, this may be due to leaching of membrane ingredients, after its lifetime of four months.

4c.4 APPLICATIONS

4c.4.1 Potentiometric titration

The electrode has been applied successfully for the end point determination on the potentiometric titration of Zn(II) ions against Na_2S solution. The titration plot is

shown in the Figure 4c.4, which corresponds to the stoichiometry of ZnS complex, therefore the proposed membrane electrode could be used as an indicator electrode for potentiometric determination of Zn (II) ions.

4c.4.2 Analysis of real life samples

The proposed electrode was used for the determination of Zn(II) ion concentration in the outer coating of dry cell. A definite amount of zinc sample was dissolved in nitric acid, heated to near dryness and the volume was made to 100mL. The results obtained from potentiometry using the proposed electrode (0.01±0.002ppm), were compared with results obtained by Atomic Absorption Spectrophotometer (0.033± 0.002ppm, from standard deviation of three measurements) which were in close agreement to each other.

4c.5 CONCLUSIONS

The results obtained from this study revealed that potentiometric PVC membrane based on N,N,N,N-Tetrakis(2-pyridylmethyl) ethylenediamine works as an excellent Zn(II) selective membrane electrode. The sensor developed using this ionophore exhibited wide operational range, high selectivity, long term stability and fast response time over a long period. The selectivity of membrane sensor towards Zn^{2+} ion is quite good for most of the cations and the response characteristics of the proposed electrode are good in comparison to the earlier sensors, which gave it added advantage. It also provides practical sensing possibility for determination of Zn^{2+} ion in real life samples.

Table 4c.1: Formation constants for complexes of ionophores TPEN some metal ions

Metal Ion	K_f	
	Sandwich method	**Kawabata et al. 2005**
Zn^{2+}	15.7	15.1
Cu^{2+}	5.1	N.R.
Co^{2+}	5.1	N.R.
Ni^{2+}	6.0	N.R.
Hg^{2+}	4.9	N.R.
Cd^{2+}	4.6	N.R.
Ca^{2+}	4.1	4.4
Mg^{2+}	4.0	1.7

N.R. Not reported

Table 4c.2: Optimization of membrane ingredients and their response characteristics

Electrode No.	**PVC (%, w/w)**	**o-NPOE (%, w/w)**	**Ionophore (% , w/w)**	**Anionic Site (NaTClPB) (% , w/w)**	**Slope (mV/decade)**	**Detection Limit(M)**
E_1	33.0	-	-	-	-	-
E_2	33.0	67.0.	-	-	-	-
E_3	33.0	66.0	1.0	-	43	$1x10^{-4}$
E_4	33.0	65.0	2.0	-	44	$1x10^{-4}$
E_5	33.0	64.0	3.0	-	38	$1x10^{-5}$
E_6	33.0	63.0	4.0	-	34	$1x10^{-5}$
E_7	33.0	62.0	5.0	-	30	$1x10^{-5}$
E_8	33.0	61.0	6.0	-	37	$1x10^{-5}$
E_9	33.0	61.0	5.0	1	30	$1x10^{-5}$
E_{10}	**33.0**	**60.0**	**5.0**	**2**	**30**	**$1x10^{-6}$**
E_{11}	33.0	59.0	5.0	3	32	$1x10^{-6}$

Table 4c.3: Potentiometric selectivity coefficients for Zn(II) ISE based on 'TPEN' by fixed interference method

Metal Ion	log $K^{Pot}_{Ag,B}$	Metal Ion	log $K^{Pot}_{Ag,B}$
Na^{+}	-1.1	Co^{2+}	-1.0
Sr^{2+}	-1.6	Pb^{2+}	-2.2
Hg^{2+}	-0.5	Ag^{+}	-1.0
Mg^{2+}	-1.5	Fe^{3+}	-2.5
Cu^{2+}	-2.1	Ca^{2+}	-1.4
Cd^{2+}	-1.6	Ni^{2+}	-1.5

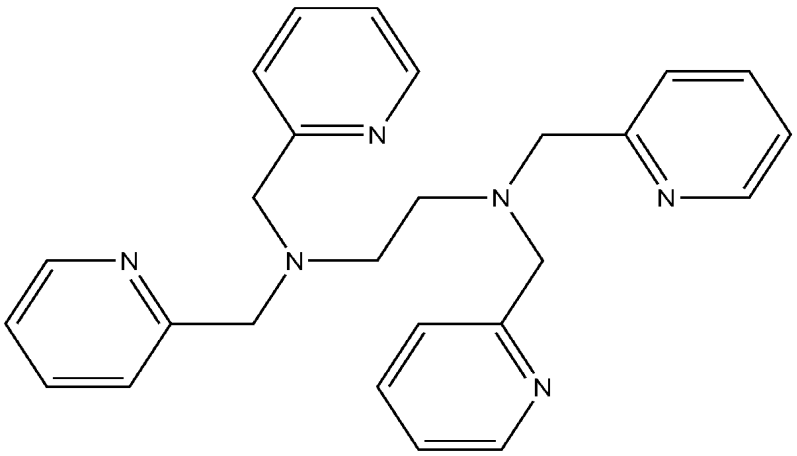
Table 4c.4: Comparison of the proposed electrode with the reported zinc selective electrodes

Sr. No	Name of the Ionophore[reference]	Measuring range (M)	pH Range	Slope (mV/decade)
1	Dibenzo-24-crown-8[26]	$1.0x10^{-5}$-$1x10^{-1}$	4.8-6.2	29.0
2	Tetra(2- aminophenyl) porphyrin[27]	$5.5x10^{-5}$-$1.0x10^{-1}$	3.0-6.0	26.5
3	Tetrabutyl thiuram disulphide[28]	$1.0x10^{-6}$-$1.0x10^{-1}$	3.5-6.5	28.0
4	Benzo substituted macrocyclic diamide[29]	$9.0x10^{-6}$-$1.0x10^{-1}$	3.0-70	30.0
5	5,6,14,15-Dibenzo-1,4-Dioxa-8,12-Diazacyclopentadecane-5,14-Diene[30]	$5.5x10^{-5}$-$1.0x10^{-1}$	1.5-7.0	22.0
6	Phorphyrin based ionophore[31]	$1.3x10^{-5}$-$1.0x10^{-1}$	3-7.4	30.0
7	3-[(2-Furylmethylene)amino]-2-thioxo-1,3-thiazolidine-4-one[32]	$1.0x10^{-6}$-$1.0x10^{-2}$	3.0-7.0	29.3
8	Tetraazamacrocycle[33]	$2.8x10^{-6}$-$1.0x10^{-1}$	2.5-8.5	28.5
9	4-tert-butylcalix[4] arene [34]	$9.8x10^{-6}$-$1.0x10^{-1}$	2.5-4.3	28.0
10	N,N-bis(acetylacetone)ethylenediimine [35]	$6.0x10^{-6}$-$3.2x10^{-3}$	3.2.-7.1	30.0
11	12-crown-4 [36]	$7.0x10^{-5}$-$1.0x10^{-1}$	2.8-5.5	29.0
12	bis(2,4,4-trimethylpentyl)dithiophosphinic acid [37]	$2.8x10^{-5}$-$1.0x10^{-1}$	2.1-6.9	30.1
13	N,N′-Bis(2-dimethylaminoethyl)-N,N′-dimethyl-9,10 anthracenedimethanamine [38]	$1.0x10^{-5}$-$1x10^{-1}$	3.0-7.5	30.0
14	5,6-benzo-4,7,13,16,21,24- hexaoxa-1,10-diazabicyclo[8,8,8]hexacos-5-ene [39]	$1.0x10^{-6}$-$1x10^{-1}$	2.8-7.3	29.1
15	Cryptand C2B22 [40]	$5.0x10^{-5}$-$5.0x10^{-2}$	4.0-7.0	24.0
16	benzo-substituted macrocyclic diamide[41]	$9.0x10^{-5}$-$1x10^{-1}$	3.0-7.0	29.0

17	**N,N,N,N-Tetrakis(2-pyridylmethyl) ethylenediamine (This work)**	**$1x10^{-6}$-$1x10^{-1}$**	**3.0-8.0**	**30.0**

Table 4c.5: Effect of mixed solvent media on slope and measuring range of the Zn(II)-ISE

Solvent	Non Aqueous Content (% v/v)	Slope(mV/ decade of activity)	Measuring Range (M)
Water	0	30	$1.0x10^{-6}$- $1.0x10^{-1}$
Methanol	10	30	$1.0x10^{-7}$- $1.0x10^{-1}$
	20	27	$5.5x10^{-6}$- $1.0x10^{-1}$
	30	30	$5.4x10^{-7}$- $1.0x10^{-1}$
Acetone	10	30	$5.4x10^{-7}$- $1.0x10^{-1}$
	20	40	$6.3x10^{-6}$- $1.0x10^{-1}$
	30	40	$1.0x10^{-4}$- $1.0x10^{-1}$
DMF	10	35	$1.9x10^{-5}$- $1.0x10^{-1}$
	20	32	$4.0x10^{-5}$- $1.0x10^{-1}$
	30	32	$5.0x10^{-5}$- $1.0x10^{-1}$



N,N,N,N-Tetrakis(2-pyridylmethyl) ethylenediamine

Figure 4c.1: Structure of ionophore TPEN

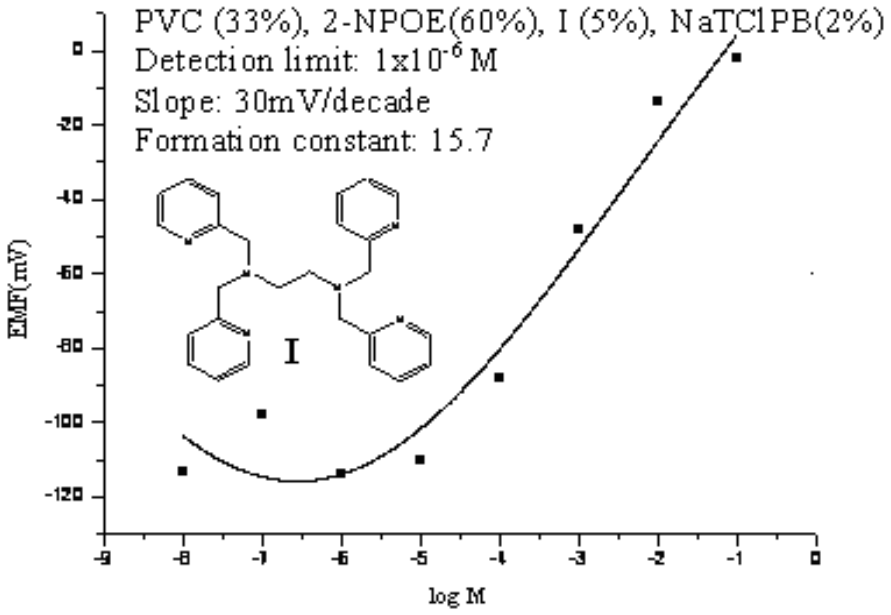


Figure 4c.2: Calibration curve for ionophore TPEN

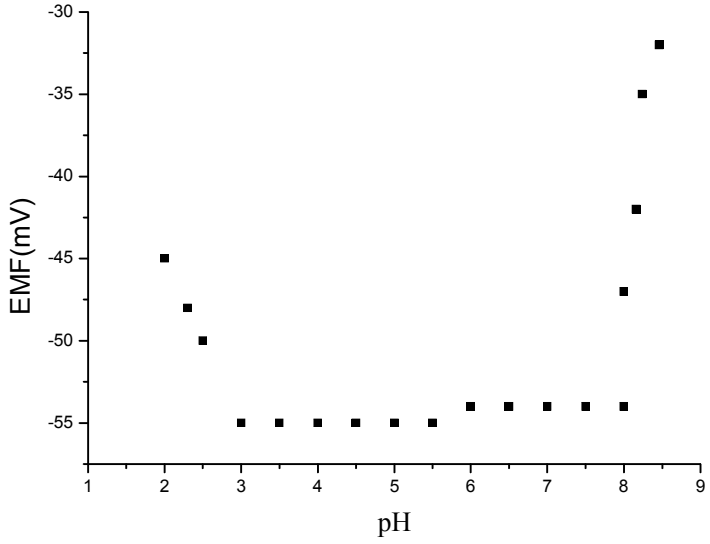


Figure: 4c.3: Effect of pH on TPEN based electrode

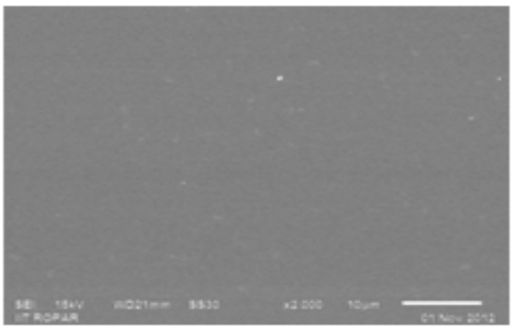


Figure 4c.4.1

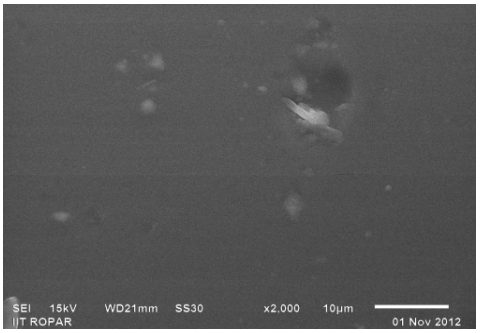
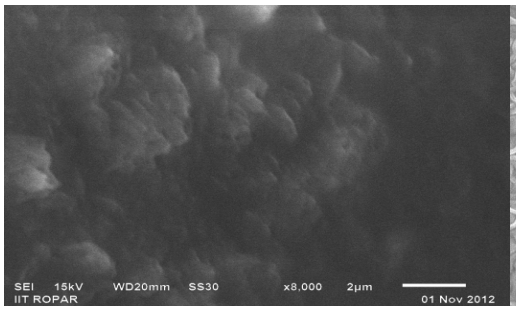


Figure 4c.4.2



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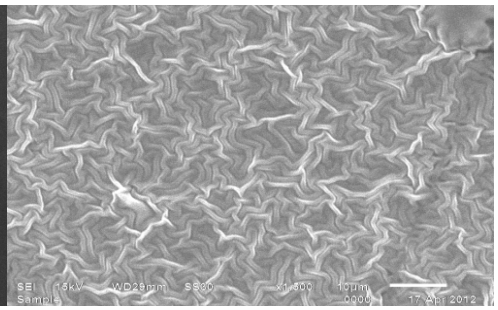
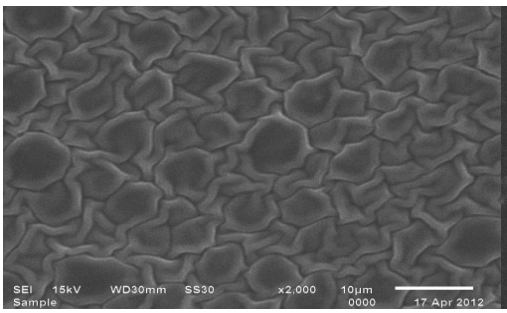


Figure 4c.4.4



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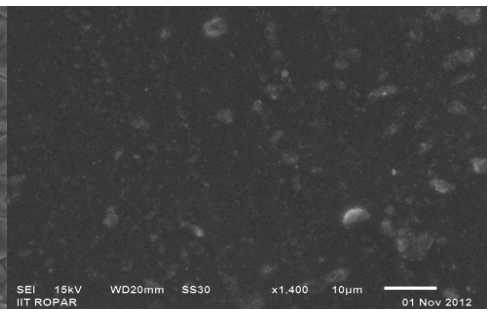

Figure 4c.4.6

Figure 4c.4: SEM images of liquid membrane based on TPEN at different stages of development and use

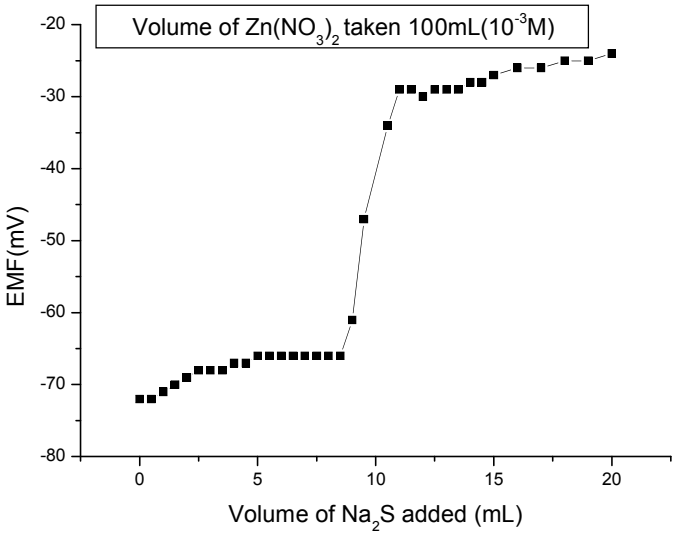

Figure 4c.5: Potentiometric Titration $Zn(NO_3)_2$ Vs Na_2S

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4d SELECTIVE TRANSPORT OF Zn(II) IONS ACROSS PLASTICIZED POLYMERIC MEMBRANE CONTAINING 2,6-BIS(BENZIMIDAZOLYL) PYRIDINE (BIP) AS A NEUTRAL CARRIER

Abstract

Transport experiments across polymer inclusion membrane (PIMs) containing BIP as a neutral carrier are presented. The physical immobilization of 2,6-Bis(benzimidazolylpyridine) (BIP) as an ion carrier and o-nitrophenyloctyl ether (o-NPOE) as plasticizer and cellulose triacetate(CTA) as the polymeric support was used to prepare polymer inclusion membranes. Transport experiments were carried out in a permeation cell in which membrane film (5.0 cm^2 effective surface) was tightly clamped between two compartments. Different receiving phases were used for the study while the solutions of metal nitrates were used as source phases. The carrier concentration in the PIM was varied in the range 4 to 7 mg. The best results were obtained with membrane composition cotaining 5 mg carrier and HNO_3(0.001M) as the receiving phase. Transport experiments were conducted at room temperature and both source and receiving phases were stirred at 600 rpm with synchronous motors. Samples of aqueous and source receiving phases were removed periodically via a sampling port with a syringe and analyzed to determine Zn^{2+} ion concentration by using atomic absorption spectroscopy method. Kinetics of the transport process through polymer inclusion membrane (PIM) is described by a first order reaction with respect to the metal ion concentration. The surface characterization of the membrane has been carried by scanning electron microscopy.

4d.1 INTRODUCTION

Polymer inclusion membranes classified earlier as solvent polymeric membranes (SPM) were first developed by Bloch *et al.* [1,2] in early 1960s and applied for selective removal of metal ions from technological waste waters. The overall preparation procedure of contemporary polymeric inclusion membranes was proposed by Sugira *et al.* [3,4] who optimized the composition of cellulose triacetate (CTA) based membranes. PIMs usually contain an extractant (carrier), a base polymer such as polyvinyl chloride or cellulose triacetate and a plasticizer or modifier. The carrier is essentially a

complexing agent or an ion exchanger, responsible for binding with the species of interest and transporting it across PIM. Concentration gradient is the driving force enabling transport across the membrane. The base polymer provides the mechanical strength to the membrane and plasticizer provides the elasticity and flexibility.

Kumar et al. [8] studied the transport of Ag(I) across PIM using tetra ethyl thiuram disulphide (TETDS) as a carrier. Nezhadali et al. [16] reported transport of Ag(I) through PIMs containing thioether donor macrocycles and Ag(I) could be separated from a solution containing equalimolar concentration of Zn(II), Ag(I), Cu(II), Cd(II) and Pb(II) ions.

PIMs are now regarded as alternatives to the typical liquid membrane system because of their improved property such as durability and log-term operation stability. Because of their high selectivity, PIM membranes were reported to be practical tool in an effective removal of the desired species [18]. Transport and separation of metal cations still remains the main purpose of PIM applications, however, the transport experiments with other chemical species e.g. organic and inorganic ions were also described [19]. The investigations are frequently focussed on the transport of transition and post transition metal ions, such as copper(II), zinc(II), cadmium(II), cobalt(II) or lead(II) with the use of a variety of ionophores. Some results presented by different authors are collected in Table 4d.1.

4d.2 EXPERIMENTAL

4d.2.1 Reagents, preparation of polymer inclusion membrane and instruments

The carrier 2,6-Bis(benzimidazolylpyridine) (BIP) (Figure 4d.1) (Aldrich INDIA) was used as received. Dichloromethane, cellulose triacetate (selectofore, Fluka) was used to prepare membrane. Analytical grade metal nitrate salts (Aldrich INDIA) were used as received for transport and selectivity studies. Zinc(II) standards for atomic absorption spectrophotometer were prepared from a spectroscopic standard(100mgL^{-1}). Triply deionised water was used in the experiments.

Plasticized polymeric membranes were prepared using a procedure similar to that reported by Sugiura et al. [3,4]. A dichloromethane solution of CTA (100 mg in 10 ml), plasticizer o-NPOE (100 mg) was prepared. After vigorous stirring, the required amount of carrier was added. The cocktail so obtained was poured into glass rings and allowed to evaporate overnight at room temperature and was poured into 6.0 cm^2 diameter flat bottom glass rings mounted on glass plate. The glass ring was set horizontally and covered loosely. The solution was allowed to evaporate over 24 h at room temperature.

4d.3 TRANSPORT STUDIES

Transport experiments were carried out in a permeation cell in which membrane film (5.0 cm^2 effective surface) was tightly clamped between two compartments. The aqueous source phase was $Zn(NO_3)_2$ (0.0001M) and the aqueous receiving phase was nitric acid (0.001- 0.02M) or EDTA(0.0001M) or KSCN(0.0001M). The carrier concentration in the PIM was changed in the range 4 to 7 mg. Transport experiments were conducted at room temperature (27^0C). Both source and receiving phases were stirred at 600rpm with synchronous motors. Samples of aqueous and source receiving phases were removed periodically via a sampling port with a syringe and analyzed to determine Zn^{2+} ion concentration by atomic absorption spectroscopy method. Kinetics of the transport process through polymer inclusion membrane (PIM) is described by a first order reaction with respect to the metal ion concentration

$$\mathbf{\ln(c/c_i) = -kt}$$

Where, c is the metal ion concentration (mol/dm^3) in the source phase at a given time, c_i is the initial concentration (M) in the source phase, k is the rate constant (s^{-1}) and t is the transport time (s).

To calculate the k value, a plot of $\ln(c/c_i)$ versus time was plotted. The rate constant values for triplicate transport experiments with the average and standard deviations were calculated.

The permeability coefficient (P) was calculated as follows:

$$\mathbf{P= - (V/A)k}$$

Where, V is volume of the aqueous source phase and A is area of the membrane. The initial flux (J_i) was determined as equal to:

$$J_i = Pc_i$$

To describe efficiency of the metal ion removal from the source phase the recovery factor (RF) was calculated as:

$$RF = (c_i\text{-}c)/c_i \times 100$$

The reported values correspond to the average of three replicates; the standard deviation observed was within 2%.

4d.4 RESULTS AND DISCUSSION

The neutral carrier BIP containing three nitrogen atoms in the molecule was involved in the complex formation with the metal ion. Also, carrier containing imino group in the system formed inclusion complexes with soft cations such as Zn^{2+}. To make use of this molecule for selective transport from one medium to another across PIM barrier, experiments were conducted with a number of receiving phases.

4d.4.1 Effect of receiving phase

During process, the metal ions were transported due to protonation and deprotonation reactions of the carrier, which occurred because of the difference between the source phase pH and the receiving phase pH. In case of macrocyclic carrier containing –NH groups, the host –guest complexation is connected with proton exchange process. On the basis of linear relations of ln (c/c_i) versus time (Figure 4d.3), the values of rate constant of transport through PIM with 2,6-bis(benimidazolylpyridine) were determined.

4d.4.2 Effect of carrier concentration

The transport of Zn^{2+} ions was examined through PIM including the carrier in the membrane at the range of concentration 4mg to 7mg (Table 4d.1). It was found that under optimal experimental conditions 80% of the total Zn^{2+} was transported after 5h across PIM containing 5mg of BIP as the carrier. The transport of the Zn^{2+} ions across the PIM was selective in presence of the metal ion such as Cu^{2+}, Ag^{+}, Cd^{2+}.

4d.4.3 SEM characterization of PIM

Scanning electron microscope (SEM JEOL-6610 JAPAN) was used to get the information about membrane surface morphology. SEM samples were coated with a very thin layer of gold by a sputter coater. The samples were placed inside the vacuum column through an air tight door. The scanning electron microscopy (SEM) observations of the membrane samples were made using a 5kV as light radiation source. The samples were mounted with conductive glue to the metal stubs and then coated with gold by sputtering. These samples were then viewed in the SEM at around 500x magnification. The SEM pictures of the surface of blank (CTA+o-NPOE) and membrane containing carrier are shown in Figure 4d.4. Figure 4d.4.1 shows the image of the membrane containing CTA only. Figure 4d.4.2 is the SEM image of the membrane having CTA and O-NPOE as its composition. Figure 4d.4.3 is the image of PIM containing 5% 2,6-Bis(benzimidazolyl) pyridine as carrier, CTA and O-NPOE. Figure 4d.4.4 is the SEM image of exhausted membrane containing all the components (CTA, carrier and O-NPOE).

4d.4.4 Selectivity studies

Transport of zinc ions across polymer inclusion membranes in presence of other metal ions was also studied. However, the recovery factor of zinc in presence of the metal ions such as Cd(II), Cu(II) and Ag(I) reduced to 47%, 42% and 33% , respectively

4d.5 CONCLUSIONS

In this study, the selectively facilitated transport of Zn(II) through a novel PIM containing 2,6-Bis(benzimdazolylpyridine) was investigated. The prepared PIM was characterized by using scanning electron microscopy.

The obtained results can be concluded as follows:

i. The transport of Zn(II) through the PIM was influenced by a number of variables, including Zn(II) concentration of the feed phase, ionophore concentration in the PIM and concentration of the stripping phase.

ii. The maximum transport of Zn(II) was obtained when the following experimental conditions were employed: PIM prepared with 5.0% 2,6-Bis(benzimidazolylpyridine) solution and stripping phase of 0.001M HNO_3. In addition, increasing the concentration of Zn(II) in the feed phase decreased the transport percentage.

iii. The Zn(II) was preferably transported against the other metal ions Cd(II), Cu(II), Ag(I) .

iv. The obtained results also showed that transport efficiency of the PIM was reproducible and it could be efficiently used in the long-term separation processes.

Table 4d.1: Some reported neutral carrier based PIMs

Name of carrier	Target Species	Base polymer/ Plasticizer	Reference
Pyridino and Bipyridino- podands	Ag(I)	CTA/2-NPOE	20
Calix[4] arene	Ag(I)	CTA/2-NPOE and TBEP	21
Acyclic polyether diamide and diamine	Ag(I)	CTA/2-NPOE and TBEP	22
N-Benzylated macrocycle	Ag(I)	CTA/2-NPOE	23
Dibenzo18-crown-6	Ag(I), Cu(II)	CTA/2-NPOE	24
Dibenzo18-crown-6	Cu(II)	CTA/2-NPOE	25
Dibenzo18-crown-6 derivative	Ag(I), Cu(II), Au(III)	CTA/2-NPOE	26
Diazadibenzocrown ethers	Pb(II)	CTA/2-NPOE	27
Diphosphaza-16-crown-6 derivatives	Cu(II), Co(II), Ni(II), Zn(II)	CTA/2-NPOE	28
Bathophenanthroline and Bathocuproine	Zn(II), Cu(II)	CTA/various plasticizer	29
4'-N-butylcarboxamidobenzo-15-crown-5	K(I), Li(I)	Sol-gel	30
Acyclic polyether di[N-(X) sulphonyl carboxamides	Ba(II)	CTA/2-NPOE	31
1,3-bis(dodecyloxy) calix[4] arene-crown-6 and 1,3-calix[4]-arene-biscrown-6	Cs(I)	CTA/2-NPOE	32
di-tert-butylcyclohexano-18-crown-6	Sr(II)	CTA/2-NPOE	33
PNP-16-crown-6 derivatives	Zn(II), Cd(II), Pb(II)	CTA/NPOE and NPPE	34
p- tert –Butylcalix[4]arene derivative	Pb(II)	CTA/NPOE	35
1-Alkylimdazole	Cu(II)	CTA/NPPE	36
1-Decylimidazole	Co(II), Ni(II), Zn(II), Cd(II)	CTA/NPOE	37
ω-Thiocaprolactum	Au(III)	CTA/NPOE	38
Crown ethers and cryptands	Ag(I), Cu(II)	NPOE	39
Undecyl-aza-18-crown-6	ReO_4^-	CTA/ NPOE	40
Calix[4] resorcinarenes	Pb(II)	CA/none	41
Calix[4] resorcinarenes	Zn(II), Cd(II), Pb(II)	CTA/NPOE	42
Crown ethers	Cs(I)	CTA/TBP	43
Lipophilic Acyclic Polyether	Ba(II)	CTA/NPOE	44
Calix[4]-crown-6	Zn(II), Cd(II), Pb(II)	CTA/NPOE	45, 46

Table 4d.2: Effect of stripping medium

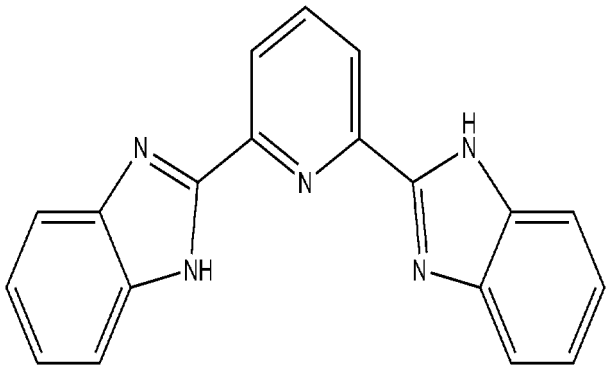
Stripping Medium	Transport Parameters			
	Rate constant (sec^{-1})	Permeability, P	Flux, Ji (mol cm^{-2} s^{-1})	Recovery Factor (%)
Distilled Water	No Transportation of metal ion			
KSCN	$2.3x\ 10^{-4}$	$39.2x\ 10^{-4}$	$45.47x10^{-4}$	57
EDTA	$3.5x10^{-5}$	$163.8x10^{-5}$	$38.61x10^{-5}$	18
HNO_3	$9.0\ x10^{-5}$	$89.6\ x10^{-7}$	$5.38x10^{-5}$	80

Experimental conditions 70 mL of M Zn^{2+} ($1x10^{-4}$) Receiving phase 70 ml of 0.02 M KSCN(0.02M), EDTA(0.001M) or HNO_3(0.001M) or H_2O.

Table 4d.3: Optimization of membrane components for PIM containing BIP as carrier

Sr. No.	Membrane composition (mg) (w/w)			Transport phenomenon parameters			
	CTA	Plasticizer	Ligand	Rate constant (s^{-1})	Permeability	Flux	Recovery Factor(%)
1	100	-------	--------	No Transport of the metal ion			
2	100	100	--------	No Transport of the metal ion			
3	100	100	4.0	$3.1x10^{-5}$	$86.8x10^{-5}$	$86.8x10^{-5}$	17
4	100	100	5.0	$9.0x10^{-5}$	$89.6x10^{-7}$	$5.38x10^{-5}$	80
5	100	100	6.0	$1.9x10^{-5}$	$93.5x10^{-5}$	$626x10^{-5}$	18
6	100	100	7.0	$1.4x10^{-5}$	$70x10^{-5}$	$64x10^{-5}$	32

Experimental conditions 70 ml of $1x10^{-4}$ M Zn^{2+} Receiving phase 70 ml of 0.001M HNO_3



2,6-Bis(benzimidazolyl)pyridine

Figure 4d.1: Structure of 2,6-Bis(benzimidazolyl) pyridine(BIP)

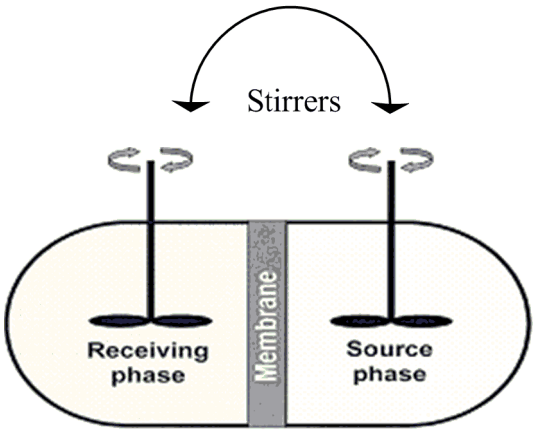


Figure 4d.2: Structure of transport assembly

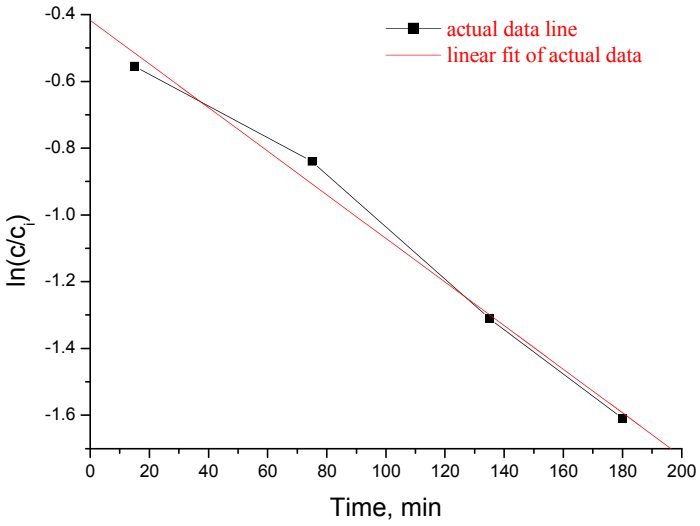


Figure 4d.3: Transport as first order kinetics through PIM

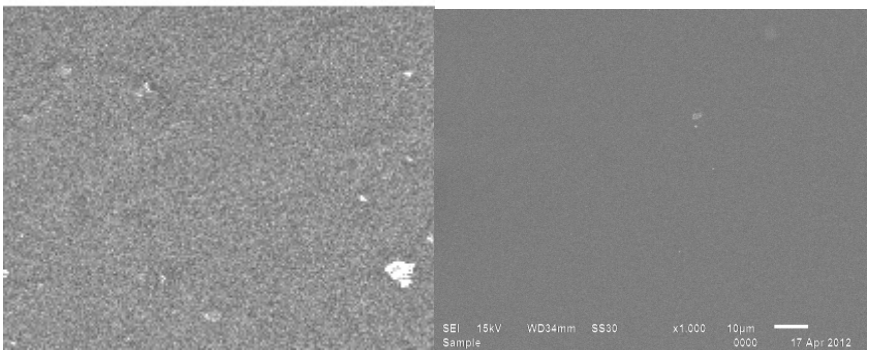


Figure 4d.4.1 **Figure 4d.4.2**

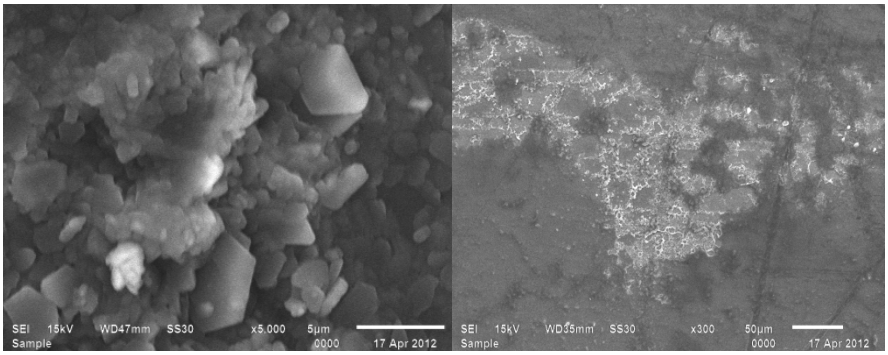


Figure 4d.4.3 **Figure 4d.4.4**

Figure 4d.4: SEM images of PIM at different stages of development and use

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46. M. Ulewicz, U. Lesinska, M. Bochenska, W. Walkowiak Physiochem. Prob. Miner. Process. 39 (2005) 107.

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List of Publication based on the present work in International Journals

1. Susheel K Mittal, **Pawan Kumar**, Ashok Kumar S K and Leonard F Lindoy. A Comparative Study of Linked 2, 2'-Dipyridylamine Ligand System as an Ion Selective Electrode for Ag (I) Ions. Int. J. Electrochem. Sci., 5 (2010) 1984 - 1995.
2. ***Pawan Kumar***, Susheel K Mittal, and Ashok Kumar S. K. Neutral Carrier-Based Zinc-Selective Electrode. Sensor Letters. Vo. 10, 1-6, 2012
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