TIN AND ZIRCONIUM BASED ION EXCHANGERS AS SENSORS FOR RARE EARTH METAL IONS

A
Thesis Submitted to
Thapar Institute of Engineering & Technology, Patiala
(Deemed University)
for the Degree of
DOCTOR OF PHILOSOPHY

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September - 2004

Dedicated to
the committed efforts
of my father
&
endless prayers
of my mother
for
my education....

CERTIFICATE

Certified that the work embodied in this thesis entitled, "*Tin and Zirconium Based Ion Exchangers as Sensors for Rare Earth Metal Ions*" which is being submitted by Mr. Harish Kumar Sharma in fulfillment of requirements for the award of the degree of Doctor of Philosophy in School of Chemistry & Biochemistry of Thapar Institute of Engineering and Technology (Deemed University), Patiala is a record of candidate's own work carried out by him under my supervision and guidance. The matter presented in this thesis has not been submitted in part or full for the award of any degree in any other University or Institute.

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ACKNOWLEDGEMENT

It is my proud privilege to express my most sincere and profound gratitude to my supervisor ***Dr. Susheel Mittal***, Professor and Head, School of Chemistry & Biochemistry, Thapar Institute of Engineering & Technology, Patiala (Deemed University), for his keen interest, constant encouragements, constructive comments and highly inspiring guidance during the course of the present work.

I am immensely grateful to Director, Thapar Institute of Engineering & Technology, Patiala (Deemed University) for providing the necessary laboratory facilities.

I also extend my sincerest and whole-hearted thanks to the other teachers and staff members of the SCBC for their direct or indirect help in course of the investigation.

I will be deceiving the purpose, if, I fail to acknowledge the love, help, care and endeavors rendered, in this pursuit, by Mr. Ashok Kumar S.K., my friend and co-worker.

I am thankful to Dr. S.M. Shivaprasad and Dr. Sushil Kumar, Research Scientists at NPL, New Delhi and the staff of TCIRD, Patiala for their help in characterization of the samples.

My tender sentiments are due to my fellow lab mates for providing me a congenial atmosphere in and outside the laboratory.

My heartiest felt gratitude is due to the management of M.M. Engineering College, Mullana (Ambala) especially ***Sh. Tarsem Kumar Garg***, Chairman for granting me necessary permission for achieving this goal and constant encouragement throughout the course of this work.

Financial support from All India Council for Technical Education, New Delhi and Indian National Science Academy, New Delhi for presenting a part of this work at 10th International Meeting on Chemical Sensors held at Tsukuba (Japan) in July, 2004 is thankfully acknowledged.

More sincerely felt is my debt to my parents and my brother who have always encouraged me for higher pursuits. Last but not the least; I am thankful to my wife whose confidence, unbounded love and care always helped me in finding strength. Finally, I owe something more to my sweet hearts ***Bhavya and Anchita*** from whom I borrowed several weekends and evenings for completion of this pursuit.

September, 2004 **(HARISH KUMAR SHARMA)**

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ABBREVIATED WORD	FULL FORM
DB18C6	Dibenzo-18-crown-6
EDTA	Ethylene Diammine Tetraacetic Acid
EMF	Electromotive Force
FIM	Fixed Interference Method
HPIC	High Performance Ion Chromatography
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectrometry
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
IR	Infrared spectra
ISE	Ion-selective electrode
MPM	Matched Potential Method
PIXE	Particle-induced X-ray Emission
PS	Polystyrene
PVC	Polyvinyl chloride
REE	Rare Earth Element
SEM	Scanning Electron Micrograph
SIMS	Secondary Ion Mass Spectrometry
SnBP	Tin (IV) boratophosphate
TGA	Thermo-gravimetric Analysis
THF	Tetra hydrofuran
XPS	X-ray Photoelectron Spectroscopy
ZrBP	Zirconium (IV) boratophosphate
ZrSbAs	Zirconium (IV) antimonoarsenate
ZrSbW	Zirconium (IV) antimonotungstate

CHAPTER - 1

INTRODUCTION

The growing area of sensors has permeated virtually all professional science and engineering branches. There are three types of sensors, i.e., physical, chemical and biosensors. Physical sensors are concerned with measuring physical quantities such as temperature and pressure where as, chemical sensors respond to a particular analyte in a selective way through a chemical reaction and can be used for the qualitative or quantitative determination of the analyte. Biosensors are really a subset of chemical sensors, but are often treated as a topic in their own right. A biosensor is a device incorporating a biological sensing element connected to a transducer.

All chemical sensors consist of a transducer, which transforms the response into a detectable signal on modern instrumentation, and a chemically-selective layer, which isolates the response of the analyte from its immediate environment. Chemical sensors have been widely used in such applications as critical care, safety, industrial hygiene, process control, product quality control, human comfort control, emission monitoring, automotive clinical diagnostics, home safety alarms and more recently, homeland security. In these applications, chemical sensors have resulted in both economic and social benefits. They can be classified according to the property to be determined as: electrical, optical, mass or thermal sensors and are designed to detect and respond to an analyte in the gaseous, liquid or solid state [1]. Compared to optical, mass and thermal sensors, electrochemical sensors are especially attractive, because of their remarkable detectability, experimental simplicity and low cost.

There are three main types of electrochemical sensors: potentiometric, amperometric and conductometric.

I) Potentiometric Sensors

They involve the measurement of emf (potential) of a cell at zero current. The emf is proportional to logarithm of the activity of substance being determined.

II) Amperometric or Voltammetric Sensors

An increasing (decreasing) potential is applied to the cell until oxidation (reduction) of the substance, to be analyzed, occurs and there is a sharp rise (fall) in the current to give a peak current. The height of the peak current is directly proportional to the concentration of the electro-active material.

III) Conductometric Sensors

They involve the measurement of conductivity at a series of frequencies. Most reactions involve a change in the composition of the solution, which normally results in a change in the electrical conductivity of the solution.

Potentiometric sensors have found the most widespread practical applicability since the early 1930's, due to their simplicity, familiarity and cost. There are three basic types of potentiometric devices: ion-selective electrodes (ISE), coated-wire electrode (CWE) and field-effect transistors (FET). In the classical CWE design, a conductor is directly coated with an appropriate ion-selective polymer membrane (usually polyvinyl chloride or polyvinyl benzyl chloride based) to form an electrode system which is sensitive to that of electrolyte concentrations. The great advantage is that the design eliminates the need for an internal reference electrode. This is particularly useful for the biomedical and clinical monitoring of different kind of analytes [2]. Ion-selective field-effect transistors (ISFET) work as an extension of CWE. An ISFET incorporates the ion-sensing membrane directly on the gate area of an FET. The FET is a solid-state device that exhibits high-input and low-output impedances and therefore, is capable of monitoring charge build up on the ion-sensing membrane. The advantage of ISFET is that it is possible to prepare small multisensor systems with multiple gates, for sensing several ions simultaneously, while their small size permits the *in vivo* determination of analytes [3].

An ion-selective electrode is an indicator electrode capable of selectively measuring the activity of particular ionic species. Such electrodes are mainly membrane based devices, consisting of permselective ion-conducting materials, which separate the sample from the inside of the electrode. Depending on the nature of the membrane, ISEs can be divided into three subgroups: glass, liquid or solid electrode. The most widely used electrode is the pH electrode, which is basically a glass membrane electrode. Applications of glass electrodes for monovalent cations, including sodium, lithium etc. are well known [4]. Liquid-membrane ISEs are based on water immiscible liquid ion exchangers [5] or neutral macrocyclic compounds [6] having molecule-sized cavities to surround the target ions.

There is a growing interest in the development of potentiometric sensors based on solid-state membranes. They can be made of single crystals, polycrystalline pellets or mixed crystals that are selective to anions or cations. Electrodes using synthetic inorganic ion exchangers form a very versatile group of ISEs. Synthetic ion exchangers are mixed with inert binders, like polystyrene, an epoxy resin or polyvinyl chloride etc., in an optimum proportion so as to provide working strength to the membrane. A large number of such electrodes have been prepared by Mittal et al. [7-10] and applied for the quantitative analysis of analyte samples.

Why Rare Earth Metal Ions?

The demand for the development of methods providing quantitative determination of trace metals in a variety of environmental matrices has increased as environmental protection has become a higher priority on the scientific agenda of the world's industrialized nations. Accurate determination of trace elements is often required to perform important environmental studies.

The selective determination of rare earth metal ions is complicated by similarities of their chemical properties and the fact that they all exist primarily as trivalent cations in solution [11]. Ion exchangers have the distinction of being the only successful technique for their separation and selective determination from mixtures.

Although, the knowledge of ion-exchange dates back to the middle of nineteenth century, little interest has been paid to this technique outside the fields of soil and water purification, until about three decades. The chief factor contributing to this indifference has been the lack of suitable ion exchangers that could be used readily for many problems of analytical chemistry. However, in recent years, the ion-exchange process has excelled in its applications in widely divergent fields such as chemistry, nuclear engineering, biology and medicine. Ion exchangers are accomplishing tasks that range from the recovery of metals from industrial wastes [12] to the separation of trace elements [13] and from catalysis of organic reactions [14] to the decontamination of water in cooling systems of nuclear reactors [15]. Uses of resins in ulcer therapy, edema therapy, as artificial kidneys, bacterial adsorbents, catalysts etc. testify to the widespread applications of these materials. In laboratories, ion exchangers are used as an aid in analytical and preparative chemistry.

Chemistry of Rare Earth Elements

Rare earth elements have been traditionally defined to include 4f block elements with atomic numbers 57-71, as well as, the elements yttrium and scandium which behave chemically similar to lanthanide elements. The chemical separation of these elements in matrices which contain mixed lanthanides is considered among the most difficult tasks in applied analytical chemistry [16]. This difficulty is largely due to the fact that lanthanides exhibit very similar chemical reactivity. Outermost electron shells of these elements are composed of 6s electrons. Their electronic configurations differ only in the low lying 4f orbital. The electronic configuration of free atoms of most of the lanthanide series is generally accepted to be [Xe] $4f^n5d^06s^2$ [17]. The difference in chemical reactivity of lanthanides, then, is likely to be influenced not by the configuration of the valence electrons but also by the trend in decreasing atomic radii with increasing atomic numbers. This "lanthanide contraction" is a consequence of the fact that for every additional proton in a nucleus, the corresponding electron is placed into the 4f shell, which is too diffused to efficiently screen the nucleus. Thus, the attraction of the nucleus for the outermost electron increases steadily with the atomic number of the lanthanide [18, 19].

Studies of the solution chemistry of rare earth elements are complicated by experimental uncertainties in the determination of coordination numbers and their stereo-chemistries. Many techniques have been applied to study the coordination chemistry of rare earth elements [20]. The predominant oxidation state for rare earth cations in solution is +3. However, divalent cations of samarium, europium and ytterbium also exist in solution. A study of the coordination of rare earth elements, with charge donating ligands, in solution has resulted in the discovery of many new complexes, exhibiting interesting geometries and coordination numbers for metal ions. Hydrated salts of cations have shown to frequently contain the $[Ln (H_20)_9]^{3+}$ ion. The nitrate ion NO_3^-, serves as a ligand in many aqueous complexes of rare earth elements, often yielding high coordination numbers for cations. For example, the complex, $[Ce (NO_3)_6]^{3-}$ has one of the largest coordination numbers known among lanthanides, with the cerium exhibiting a 12-coordinate geometry [21]. Organic acids such as oxalic, citric and tartaric acid have been shown to complex with the rare earth cations with high coordination numbers [22]. Other oxygen-containing ligands have also been found to complex these rare earth cations. For example, diketonates form 7 coordinate complexes with many of rare earth elements [21].

Inorganic Ion Exchangers

Early ion exchangers were largely inorganic in origin. Subsequently, the ion-exchange scene was dominated by synthetic organic resins because of reproducible preparations with excellent mechanical and chemical stability. In recent years, the interest in inorganic ion exchangers has been revived with the need for the high temperature separation of ionic components in radioactive wastes. In order to accomplish such separations, highly selective exchangers are required which are not only stable at high temperature but also have ion-exchange properties unaffected by the acidity and high radiation levels. Organic ion-exchange resins are not suitable for such applications, as changes in capacity and selectivity take place on exposure to radiation. Also, the degradation takes place at high temperatures.

Inorganic ion exchangers exhibit high selectivities for specific ions resulting in separation factors much larger than those exhibited by organic resins. They unlike organic ion exchangers have rigid structures and do not undergo appreciable dimensional change during ion-exchange reactions. The rigid structure leads to specific and unusual selectivities [23]. Earlier attention was focused on hydrous oxides, since it was known that they sorbed or co-precipitated many ions. It was soon discovered that hydrous oxides combined with anions such as phosphates, vanadates, molybdates and antimonates produced superior ion exchangers [24-27].

Classification of Inorganic Ion Exchangers

Inorganic ion exchangers were first classified by Vesely and Pekarek [28] in 1972. Since then, these materials have been reclassified periodically [29] with the development of new type of materials and with better understanding of their structures. In 1988, Clearfield [30] classified ion exchangers with significant ion-exchange capacity into 14 categories. Again in 1995, Clearfield [31] broadly classified ion exchangers into three categories based on their structures:

(I) Hydrous Oxides

Hydrous oxides have also been referred to as framework hydrates by England et al. [32]. This class largely contains hydrous oxides of zirconium and tin.

(II) Layered Ion Exchangers

These ion exchangers are either oxides / phosphates of group 4 and 14 or layered double hydroxides. Group 4 and 14 phosphates are the most extensively studied exchangers of this class.

(III) Exchangers with Tunnel Structures

Exchangers with tunnel structure were first reported by Clearfield [30] in 1988. Yin et al. [33] and Shen et al. [34] reported ion exchangers with octahedral tunnel of dimensions suitable for exchange of the hydrated Mg^{2+} ions. These compounds show remarkable selectivities and are readily converted to the H^+-form.

Crystalline Ion Exchangers

A new direction was given to the field of inorganic ion exchangers when Clearfield and Stynes [35] demonstrated that zirconium phosphate could be crystallized. The availability of crystals allowed the structure of this polymorph of zirconium phosphate to be determined and with this knowledge, the observed behavior could be explained in structural terms. It is generally understood that a very large number of inorganic compounds possess ion-exchange characteristics, like phosphates, tungstates, titanates, heteropoly acid salts and layered compounds including double hydroxides.

Heteropoly acid salts of polyvalent metals are of interest as they are superior to single insoluble salts of these metals since it is possible to vary their compositions and hence, to change their selectivity to a particular ion. Ammonium phosphotungstate and ammonium molybdophosphate were probably the first materials of this type which have been studied as ion exchangers [36].

Characterization of Inorganic Ion Exchangers

Inorganic ion exchangers are characterized by studying following properties:

Ion-exchange Capacity

Ion-exchange capacity of a material is determined for its characterization as an ion exchanger and for numerical calculations used in operations. An accepted way of defining the ion-exchange capacity is by giving the number of ionogenic groups contained per gram of the exchanger material, when the material is completely converted to H^+-form which is devoid of sorbed solutes and solvents. The characteristic constant obtained in this way is called scientific weight capacity and is expressed in units of milli-equivalents per gram. For a strong ion exchanger, the capacity can be readily calculated by direct titration, e.g. a strong cation exchanger can be titrated with a strong base, like sodium hydroxide. However, most of the synthetic inorganic ion exchangers behave as weak ion exchangers and therefore, their direct titration is not feasible. In weak ion exchangers, H^+ ions of the exchanger are replaced by cations of a neutral salt and the equilibrium ion-exchange capacity is then determined by pH titration.

Chemical Composition

Study of the chemical composition of an ion exchanger is helpful in understanding its structure and empirical formula.

Distribution Coefficients

On the basis of distribution coefficients, it is possible to predict the separation of one ion from the other. Distribution of an ion between exchanger phase and the solvent gives the measure of the selectivity of the exchanger for that particular ion. On the basis of selectivity, it is possible to separate different counter ions. The ion exchanger usually takes up certain ions in preference to other counter ions. The selectivity may depend upon following factors:

a) Donnan potential.
b) Sieve action.
c) Complex formation.

Spectroscopic Studies

Structural characterization of ion exchangers is done by conducting XRD, thermal analysis and spectroscopic studies. X-ray diffraction is used to determine the crystallinity of the ion-exchange materials. The wavelength of X-rays is of the same order of magnitude as the distance between atoms in crystalline materials and therefore, crystals act as diffraction gratings for X-rays. Thermo-analytical studies indicate the extent of hydration and thermal stability characteristics of the exchanger material. Infrared spectra are used to identify metal-oxygen bonds in the polymeric backbone of the ion exchanger.

Electrochemical Properties of Ion-exchange Membranes

Inorganic ion-exchange membranes have acquired particular significance due to their several distinct advantages over their organic counterparts such as the ability to withstand high temperature and ionizing radiations and the remarkably high selectivity [37]. The high electrical conductivity and better current efficiency of inorganic membranes have found their use in cells for electrolytic desalting of brackish water [38], fuel cells and electrical storage batteries [39]. The basic theory of permselective membranes and their electrochemical properties was first developed by Toerell [40] and by Meyer and Sievers [41]. According to this theory, the permselective properties of certain natural and artificial membranes can be explained by the existence, within the membrane, of the easily dissociated ions that are loosely bound to the fixed groups of the opposite charge.

An ideal permselective membrane, when subjected to a potential gradient, permits passage of cations to the exclusion of anions or vice versa. Thus, in an ideal membrane, the transport number of the mobile ion (counter ion) is unity and that of the ion of opposite charge (co-ion) is necessarily zero, regardless of the concentration of the outside solution. An ideal permselective membrane is difficult to produce, but can be closely approximated by a careful choice of such membrane variables as the composition and physicochemical properties. Choice of proper operating conditions of concentration and temperature is also important.

Analytical Applications of Inorganic Ion Exchangers

Synthetic inorganic ion exchangers have been useful, not only in the separation of radioactive materials and for use at elevated temperatures, but they have found several other analytical applications, too. Some of analytical applications of these ion-exchange materials include:

a) Use of ion-exchange membranes as ion-sensors in ion-selective electrodes.
b) Separation of one ion from the other on a column of the ion exchanger.
c) Use of ion exchanger beads to locate the end point in titrations.
d) Purification of substances on a large scale.
e) Solid-state separations.
f) Ion-exchange paper chromatographic separations.
g) Micro determination by ion-exchange colorimetry.
h) Specific spot tests.
i) Electrophoresis on ion-exchange papers.

Of these applications, the most important are separations of metal ions and the use of ion-exchange membranes as ion-selective electrodes. In the separations, the solution containing metal ions to be separated is passed through the column of the exchanger. Ions are exchanged by a stoichiometrically equivalent amount of counter ions present in the exchanger. Ions sorbed on the ion exchanger are eluted separately by a careful choice of the eluant. Numerous separations can be achieved on columns of synthetic inorganic ion exchangers.

Inorganic Ion Exchangers in Ion-Selective Electrodes

Synthetic inorganic ion exchangers can also be used as ion-sensors in ion-selective electrodes. All inorganic ion exchangers are not suitable for use as ion sensors, probably because of poor conducting characteristics of some of such materials. As inorganic ion exchangers are solid and insoluble, they are incorporated into some inert polymeric matrix so as to give heterogeneous membranes. An active sensor material should:

a) be physically compatible with the matrix.
b) be of the right grain size (1-15nm).
c) be mixed with the matrix support in right proportion (usually 50 mass percent).
d) undergo rapid ion-exchange at the membrane-solution interface.
e) have a low solubility product.

A suitable matrix support should:

a) be chemically inert and provide good adhesion for sensor particles.
b) be tough, flexible yet non-porous and crack resistant to prevent leakage of internal solutions.
c) not swell in sample solutions
d) be hydrophobic.

Membranes used as ion sensors can be classified as:

(i) Homogeneous Membranes
(ii) Heterogeneous Membranes

Homogeneous membranes can be made up of solid-state crystals or pressed pellets of organic/inorganic exchangers, while heterogeneous membranes contain some chemically inert binder to provide workable mechanical strength to the electro-active ion-exchange matrix. For the present work, heterogeneous membranes were used because of nature of the electro-active material (an inorganic ion exchanger) which is not strong enough to provide a homogeneous membrane.

Classification of Electrodes

Electrodes used currently can be divided into two groups:

1) electrodes suitable for measurement of ions
2) electrodes suitable for measurement of molecules.

The signal is provided by a so called 'basic electrode' and the measured component is produced by some chemical (e.g., enzyme reaction) or physical (diffusion, etc.) reaction of molecules.

How is the Electrode Potential Produced?

The establishment of an electrode potential is caused by charge separation at the surface of the electrode. Primary ions from the solution phase are chemisorbed onto the surface of the electrode and counter ions accumulate in the solution phase resulting in a charge separation. Chemical potential of the solute is responsible for the electrochemical signal. To express the thermodynamics, the Gibbs-Duham relation can be given as:

$$-\Delta G = nFE \qquad \text{.........} \ (i)$$

Where, 'ΔG' is change in the chemical potential of solute, 'n' the number of charges, 'F' the Faraday constant and 'E' the electrical potential.

Theory of Potentiometric Ion Sensors

Chemical sensing is a part of an information acquisition process in which some insight is obtained about the chemical composition of a system in real time. In this process, an amplified electric signal results from the presence of some chemical species. Generally, it consists of two distinct steps: Recognition and amplification, e.g. measurement of pH with a glass electrode. Interaction of an ion with the electrode is highly specific, but the power of the primary electric signal is very low. The source of signal (electrode) requires an amplifier (pH meter) in order to obtain the information in a useful and undistorted form. The recognition (selectivity) is provided by some chemical interaction, while a transducer converts an observed change into a measurable signal. The signal can subsequently be manipulated in different ways.

There can be two types of interactions: *a surface interaction*, in which the species of interest is adsorbed at the surface and a *bulk interaction* in which the species of interest partitions between the sample phase and the sensor. *The decrease of the energy is a driving force in all sensing processes*. Ion-selective electrodes are the oldest established chemical sensors and are comparatively well understood [42-45]. Their response characteristics including selectivities can be related to basic thermodynamic and kinetic processes [45].

An ion-selective membrane is the key component of all potentiometric ion sensors. It establishes the preference with which a sensor responds to the analyte in the presence of various interfering ions from the sample. If ions can penetrate the boundary between two phases, then an electrochemical equilibrium will be reached, in which different potentials in two phases are formed. If only one type of an ion can be exchanged between two phases, then the potential difference formed between the phases is governed only by activities of this target ion in these phases. When a membrane separates two solutions of different ionic activities (a_1 and a_2) and provided the membrane is only permeable to single type of ion, the potential difference (E) across the membrane is described by the Nernst equation:

$$\mathbf{E = const. + RT/zF \cdot \ln (a_2/a_1)} \qquad \text{.........(ii)}$$

If activity of the target ion in phase 1 (a_1) is kept constant, the unknown activity (a_x) in phase 2 is related to (E) by:

$$E = \text{const.} + RT/z_xF \cdot \ln (a_x/a_1) = \text{const} + S \cdot \log_{10} (a_x) \qquad \text{……… (iii)}$$

Where, $S = 59.16/z_x$ mV at 298 K and z_x - the charge of the analyte. The potential difference can be measured between two identical reference electrodes placed in two phases. In practice, the potential difference i.e., the electromotive force is measured between an ion-selective electrode and a reference electrode, placed in the sample solution. It is important to note that this is a *measurement at zero current* i.e., under equilibrium conditions. Equilibrium means that the transfer of ions from the membrane into solution is equal to the transfer of the same from the solution to the membrane. The measured signal is the sum of different potentials generated at all solid-solid, solid-liquid and liquid-liquid interfaces.

Using a series of calibrating solutions, a response curve or calibration curve of an ion-selective electrode can be measured and plotted as the signal (electromotive force) versus the activity of analyte. The linear range of the calibration curve is usually applied to determine the activity of the target ion in any unknown solution. However, it should be pointed out that only at constant ionic strength a linear relationship between the signal measured and the concentration of the analyte is maintained (because of the clear cut relationship between ion activity and concentration, occurring in such condition).

Ions present in the sample, for which the membrane is non-permeable (i.e., non-selective), will have no effect on the measured potential difference. However, a membrane truly selective for a single type of an ion and completely non-selective for other ions does not exist. For this reason, the potential of such a membrane is governed mainly by the activity of the primary (target) ion and also by the activity of other secondary (interfering) ions. The influence of the presence of interfering species in a sample solution on the measured potential difference is taken into consideration in the Nikolski-Eisenman formalism:

$$E = \text{const} + S. [\log (a_x) + (z_x/z_y). \log (K_{xy} \cdot a_y)] \qquad \text{……… (iv)}$$

where, ‘a_y’ is the activity of an interfering ion, ‘z_y’ its charge and ‘K_{xy}’ the selectivity coefficient (determined empirically).

Characterization of an Ion-selective Electrode

Properties of an ion-selective electrode are characterized by parameters, like:

Selectivity

Selectivity is one of the most important characteristics of an electrode, as it often determines whether a reliable measurement in the sample is possible or not. The selectivity coefficient (K_{xy}) has been introduced in the Nikolski-Eisenman equation. Most often it is expressed as the logarithm of (K_{xy}). Negative values indicate a preference for the target ion relative to the interfering ion. Positive values of log K_{xy} indicate the preference of an electrode for the interfering ion. The experimental selectivity coefficients depend on the activity and method of their determination. Different methods of the selectivity determination can be found in the literature. The IUPAC suggests two methods: Separate Solution Method (SSM) and Fixed Interference Method (FIM). There is also an alternative method of the selectivity determination called Matched Potential Method (MPM). Each of them has got advantages and drawbacks, and there are no general rules pointing which method gives the true result. Methods proposed by IUPAC with several precautions will give meaningful data.

Slope

Slope of the linear part of the calibration curve of the electrode: Theoretical value of the slope according to the Nernst equation is 59.16 mV per decade at 298 K for a single charged ion or

59.16/2 = 29.58 mV per decade for a double charged ion or 59.16/3= 19.72 mV per decade for a triple charged ion. However, in certain applications the value of the electrode slope is not very critical and a not-so-good value does not exclude its usefulness.

Range of Linear Response

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

Detection Limit

According to the IUPAC recommendation, the detection limit is defined by the cross-section of the two extrapolated linear parts of the ion-selective calibration curve. In practice, a detection limit of the order of 10^{-5}-10^{-6} M is measured for most of ion-selective electrodes. The observed detection limit is often governed by the presence of other interfering ions or impurities. If, for example, metal buffers are used to eliminate the effects which lead to the contamination of very dilute solutions, it is possible to enhance the detection limit down to 10^{-10} M.

Response Time

In earlier IUPAC recommendations, it was defined as the time between the instant at which the ion-selective electrode and a reference electrode are dipped in the sample solution (or the time at which the ion concentration in a solution is changed on contact with ISE and a reference electrode) and the first instant at which the potential of the cell becomes equal to its steady-state value within 1 mV or has reached 90% of the final value. This definition can be extended to consider the drift of the system. In this case, the second time instant is defined as the one at which the EMF/time slope becomes equal to a limiting value.

The present study deals with the preparation, characterization and analytical applications of ion-selective electrodes for some rare earth metal ions. These electrodes are based on ion-exchange materials which are already prepared, or are commercially available or have been prepared and characterized as novel ion exchangers during the course of this study.

Present Study - At a Glance

Main objectives of this research proposal were:

1. Development of ion-selective electrodes based on tin and zirconium based ion exchangers.
2. Characterization of the electrode system as ion-selective electrodes.
3. Determination of selectivity coefficients in presence of interfering ions.
4. Application of electrode systems as indicator electrodes in potentiometric titrations.

Accordingly, five membrane electrodes are being reported as sensors for the four rare earth metal ions viz., lanthanum (III), cerium (III), samarium (III) and praseodymium (III). Samarium (III) sensors have been based on zirconium (IV) boratophosphate and tin (IV) boratophosphate {Chapter 4}. A zirconium (IV) boratophosphate is a previously reported material where as tin (IV) boratophosphate is synthesized and characterized as novel ion-exchange material {Chapter 3.1}. A Cerium (III) sensor again is based on zirconium (IV) antimonoarsenate which has also been synthesized and characterized as a novel ion exchanger. Electrochemical studies were done on membranes based on this exchanger {Chapter 3.2}. The work on Ce (III) sensor based on this exchanger is given in Chapter 5.1. A Praseodymium (III) sensor based on zirconium (IV) antimonotungstate is given in Chapter 5.2. A Lanthanum (III) sensor has been prepared using dicyclohexano-18-crown-6 as an electro-active material {Chapter 6}.

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CHAPTER - 2

LITERATURE SURVEY

It is generally understood that a very large number of inorganic compounds, like phosphates, tungstates, titanates, heteropoly acid salts and layered compounds including double hydroxides, possess ion-exchange properties. Heteropoly acid salts of polyvalent metals are of interest as they are superior to single insoluble salts [1] of these metals since it is possible to vary their compositions and hence, to change their selectivity. Ammonium phosphotungstate and ammonium molybdophosphate were probably first materials of this type which were studied as ion exchangers.

During the last decade, only a few works [2-11] (Table 2.1) have been reported on ion exchangers containing heteropoly anions. Primarily, zirconium and tin (IV) based exchangers have been synthesized and most of the literature available is on studies related to their synthesis, ion-exchange behavior and analytical applications, like quantitative separation of metal ions. Preparation of stannic molybdophosphate has been reported by Marageh et al. [3]. They have studied the ion-exchange capacity, IR and thermo-gravimetry. Decontamination of cesium and strontium from aqueous nuclear waste solution has also been achieved. Mittal et al. [5] have reported the synthesis of crystalline and amorphous samples of tin (IV) antimonoarsenate at different pH values. The materials show high thermal and chemical stability. Distribution coefficients for 22 metal ions have been reported and structural studies based on Infrared (IR) spectra, X-ray diffractogram (XRD), Thermo-gravimetric analysis (TGA), Differential thermal analysis (DTA) are discussed. Some quantitative binary separations such as, Mg^{2+} - Mn^{2+}, Cd^{2+} - Mn^{2+}, Ba^{2+} - Mn^{2+}, etc. have also been reported.

Other tin based heteropolyacid salts reported in the last decade are tin (IV) sulfosalicylate [2] and tin (IV) molybdosilicate [4].

An even number of zirconium based ion exchangers containing heteropoly anions have been reported. Qureshi et al. [7] reported synthesis and ion-exchange behavior of zirconium (IV) arsenovanadate at pH 1. The material was fairly soluble in dilute mineral acids but insoluble in water, acetic acid, formic acid, ethanol, etc. Distribution coefficients of a large number of metal ions were reported in different solvent systems. Studies on zirconium (IV) selenomolybdate have been reported by Gupta et al. [10]. They have characterized the material using IR, X-ray, TGA, DTA etc. and its distribution coefficients are reported for 16 metal ions. It has been used for achieving binary separations, like Zn^{2+} - Cd^{2+}, Zn^{2+} - Co^{2+}, Ni^{2+} - Cd^{2+} and Ni^{2+} - Co^{2+}. Thind et al. [12] reported synthesis of zirconium boratophosphate and applied it for the quantitative separation of lanthanides. In addition to these compounds, zirconium (IV) molybdoarsenate [6], zirconium (IV) tungstophenolate [8] and zirconium (IV) tungstophosphate [9] have also been reported.

In addition to these tin and zirconium based ion exchangers, titanium (IV) tungstosilicate and titanium (IV) tungstophosphate have been reported by Siddiqui et al. [11]. Both the materials have shown monofunctional ion-exchange characteristics and are stable in HNO_3, HCl, H_2SO_4, acetone and benzene. Cr^{3+}, Fe^{3+} and Sn^{4+} are totally adsorbed on both the materials in demineralized water. Some binary and ternary separations are also reported.

Except for reviews of Clearfield [13, 14] and Sebesta [15] on synthesis, characterization and separation studies, no other literature dealing with mechanistic aspects of the ion-exchange process is available. Yao et al. [16] have used tin (IV) vanadopyrophosphate as a stationary phase for High Performance Liquid Chromatography for the amino acid analysis. Yoshimura [17] has applied synthetic ion exchangers as adsorbents in studies on solid phase spectrometry. Mittal [18] applied tin (IV) antimonophosphate as an analytical tool for the micro determination of copper by ion exchanger colorimetry. Gupta et al. [19] have reported the investigation of some kinetic parameters for M^{2+}-H^+ exchanges on zirconium (IV) tungstophosphate.

Table 2.1: Synthesis and ion-exchange properties of some heteropolyacid salts prepared in the last ten years

Ion –exchanger	Composition/ Empirical Formula	IEC (meq/g)	Selectivity	Ref. No.
Tin (IV) sulfosalicylate	--	--	--	2
Tin (IV) molybdophosphate	Sn:Mo:P = 43.5:23.6:1.0	0.87	Sr^{2+}, Cs^{+}, La^{3+}	3
Tin (IV) molybdosilicate	--	--	--	4
Tin (IV) antimonoarsenate	Sn:Sb:As = 3:1:1 $[(SnO_2)_3 (H_3SbO_4) H_3AsO_4)] 8H_2O$	1.00	Dy^{3+}, Er^{3+}, Gd^{3+}, Fe^{3+}, Pb^{2+}	5
Zirconium (IV) molybdoarsenate	--	--	--	6
Zirconium (IV) arsenovanadate	Zr:As:V = 3:2:1 $[(ZrO_2)_9 (H_3AsO_4)_6 (V_3O_9) (OH)_3]_p 10\ H_2O$	1.20	Cr^{3+}, Ba^{2+}, Al^{3+}, Mn^{2+}	7
Zirconium (IV) tungstophenolate	--	--	--	8
Zirconium (IV) tungstophosphate	--	--	--	9
Zirconium (IV) selenomolybdate	Zr:Se:Mo = 2.5:0.7:1.6	0.94	Cd^{2+}, Hg^{2+}, Pb^{2+}, Co^{2+}	10
Titanium (IV) tungstosilicate	--	0.44	Cr^{3+}, Fe^{3+}, Sn^{4+}	11
Titanium (IV) tungstophosphate	--	0.80	Cr^{3+}, Fe^{3+}, Sn^{4+}	11

Ion-exchange materials have also been used as ion-exchange membranes for various analytical applications, like purification of effluents from nuclear waste streams; decontamination of boiler feed water, treatment of industrial waste water, etc. Malik et al. [20-26] studied the effect of membrane potential and adsorption on permeability of ions without giving due consideration to the functional (porosity, swelling, electrical conductivity) and operational (ion-exchange capacity and permselectivity) behavior of the membrane material.

Studies on permeability, fixed charge density and selectivity of various inorganic ion-exchange membranes have provided reasonably clear picture of the functioning of these membranes in contact with simple electrolytes [27-32]. Beg et a1. [33, 34] applied the theory of absolute reaction rates to diffusion of ions through parchment supported cobalt phosphate, nickel phosphate and thallium dichromate membranes for calculation of various thermodynamic parameters, namely ΔH^*, ΔS^* and ΔF^*. However, there are very few reports on the use of inorganic ion exchangers as electro-active material in ion-selective electrodes.

According to a review of Eric Bakker [35], just a few years back, the area of ion-selective electrodes had become so saturated that leading scientists normally suggested their younger colleagues not to enter the area. Still, there has been a great development in this area in recent times, probably due to the possibility of lowering of detection limits and improving the selectivity. The first ion-selective electrode based on bulk membranes containing an ion carrier was introduced more than three decades ago. However, for many analytes, especially for anions and heavy metal ions, maximum ISEs have been reported in last ten years. Presently, ISEs form one of the most important groups of chemical sensors. Many reviews [35-41] on ISEs have been written covering all aspects of the ion exchanger based ISE. Recent reports [42-44] have demonstrated detection limits in picomolar range. Table 2.2 gives an exhaustive list of ion-selective electrodes based on heteropolyacid salts reported over last about twenty five years.

Most of the electrodes have been prepared using an epoxy resin (Araldite) as binder. Polystyrene has been used by Jain et al. [51] for a Cu^{2+}-selective electrode based on cerium

(IV) molybdophosphate. The electrode shows a linear measuring range of 10^{-4} M – 10^{-3} M. A polyvinyl chloride based dysprosium (III)-selective electrode using zirconium (IV) selenomolybdate was reported by Gupta et al. [56]. This electrode has a measuring range of $5x10^{-5}$ M to 10^{-1} M and a response time of 15 seconds. It can be used in the pH range of 2-9. A lanthanum (III)-selective electrode was reported by Mittal et al. [53]. It has tin (IV) antimonophosphate (70%) by weight as an electro-active material and araldite (30%) as a binder. Though this class of inorganic ion exchangers has been successfully used in making of ion sensors, the area remains almost unexplored as far as ion sensors for rare earth metal ions are concerned.

Selective determination of rare earth metal ions has always fascinated analytical chemists. Efforts have been on in this direction for last four decades. Hamaguchi et al. [57] studied the distribution coefficient (K_d values) of several rare earths- La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Er and Lu-on Diaion SK-1 cation-exchange resin and proposed the composition of the complex to be $M(SCN)_2Cl$. Agrawal et al. [58] used *N*-*m*-Tolyl-*m*-nitrobenzohydroxamic acid as a reagent for the separation and gravimetric determination of Ce^{3+}, La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+} and Gd^{3+}. The complexes were weighed as $(C_{14}H_{11}N_2O_4)_3M$ after drying. Daolio et al. [59] analyzed polynuclear complexes and mixed oxides containing 4f ions by secondary ion mass spectrometry (SIMS).

Inductively coupled plasma-mass spectrometry (ICP-MS) was used for determination of all rare earth elements, Y and Th using a Na_2O_2 sinter by Longerich et al. [60]. The application of ICP-MS to isotope ratios was also discussed with reference to the determination of $^{147}Sm/^{144}Nd$. Application of high-performance ion chromatography (HPIC) for analysis of rare earth elements (REE) in geological samples was described by Roex et al. [61].

Table 2.2: Ion-selective electrodes based on some heteropolyacid salts

Membrane composition	Selective for	Measuring Range (M)	Response Time (sec)	Working pH Range	Ref. No.

Caesium-12 tungstoarsenate/ Thallium-12 tungstoarsenate in Araldite	Cs^+/Tl^+	10^{-4}-10^{-1}	120	3-6	45
Thallium-12 molybdoarsenate in Araldite	Tl^+	10^{-3}-10^{-1}	40	4-6	46
Picolinium molybdoarsenate in Araldite	Tl^+	10^{-3}-10^{-1}	20	3.5-6.0	47
Ammonium 12 molybdophosphate in Araldite	NH_4^+	$3x10^{-4}$-$3x10^{-1}$	-	2-9	48
Strontium 12-tungstoarsenate in Araldite	Sr^{2+}	10^{-4}-10^{-1}	-	3-6	49
Rubidium 12- tungstoarsenate in Araldite	Ag^+	10^{-5}-10^{-1}	40	4-6	50
Cerium (IV) molybdophosphate (90%) in polystyrene (10%)	Cu^{2+}	10^{-4}-10^{-3}	-	-	51
Tin (IV) arsenoantimonate (50%) in Araldite (50%)	Pb^{2+}	10^{-4}-10^{-1}	10	2.5-5.5	52
Tin (IV) antimonophosphate (70%) in Araldite (30%)	La^{3+}	10^{-5}-10^{-1}	40	2.0-6.5	53
Zirconium (IV) boratophosphate (50%) in Araldite (50%)	Th^{4+}	10^{-4}-10^{-1}	10	3-5	54
Polyanniline Sn (IV) tungstoarsenate (50%) in Araldite (50%)	Cd^{2+}	10^{-4}-10^{-1}	25	3-8	55
Zirconium(IV) selenomolybdate in polyvinyl chloride	Dy^{3+}	$5x10^{-5}$ -10^{-1}	15	2-9	56

The technique was used for determining 12 REE in a wide variety of rock types. The eluted REE were reacted with a color complexing agent and detected photometrically using a UV/visible light detector at a wavelength of 520 nm. Kobayashi et al. [62] reported the chromatographic separation of REE using a column packed with 2-ethylhexyl hydrogen 2-

ethyl-hexylphosphonate (PC-88A)-loaded polymer resin prior to inductively coupled plasma atomic emission spectrometric (ICP-AES) measurements. A favorable separation of trace amounts of metals (La, Nd and Sm) from a large amount of terbium was achieved by elution with dilute hydrochloric acid. High performance liquid chromatography was used by Moraes et al. [63] for the rapid separation of rare earth metal ions followed by determination of the same by visible spectrophotometry at 535nm. Rare earth elements in a standard iron ore sample were determined as RE–EDTAs by bidirectional isotachophoresis–particle-induced X-ray emission (PIXE) by Hirokowa et al. [64]. Figueiredo et al. [65] reported the determination of lanthanides (La, Ce, Nd, Sm) in metallic gallium by instrumental neutron activation analysis (INAA).

Though different techniques have been used for determination of rare earth metal ions, the ion exchanger based ion-selective electrodes remain the best bet because of their easy fabrication and high selectivity [66]. Table 2.3 gives various ion-selective electrodes prepared so far, for rare earth metal ions.

Lanthanum (III)-selective electrodes have been reported by Harrel et al. [67], Shamsipur et al. [68], Gupta et al. [69] and Ganjali et al. [70-72]. Harrel et al. based their electrode on dinonyl naphthalene sulfonic acid in naptha solution diluted with nujol. The electrode has a slow response time of 5 minutes and measuring range 0.2 – 4×10^{-4} M. A comparison of the performance of two lanthanum-selective electrodes [PVC-based and coated graphite electrode based] using 1, 3, 5–trithiacyclohexane as an electro-active material was reported by Shamsipur et al. [68]. Ganjali et al. have based their La [III]-selective electrodes on bis (thiophenol) - phenylene 1, 3 – diamine [70], glicazide [71] and bis [2-mercaptoanil] diacetyl [72]. All these electrodes show Nernstian slope except for tin (IV) antimonophosphate [53] which gives a super-Nernstian slope. PVC has been used as a binder in almost all the reports.

Table 2.3: Ion-selective electrodes reported for rare earth metal ions

Membrane composition	Measuring Range (M)	Response Time (sec)	Slope of Calib. curve (mV/decade)	Working pH Range	Av. Life (Months)	Ref. No.
La (III)-selective electrodes						

Dinonylnaphthalenesulfonic acid in naptha solution diluted with Nujol		0.2 – 4x10^{-4}	5 Min.	20.0	4.0-5.5	-	67
1, 3, 5-trithiacyclohexane (2%) + PVC (30%) + AP (53%) + OA (15%)	PVC Memb.	8.0x10^{-6} - 5.0x10^{-2}	10	19.6	5.0-8.0	6	68
	Coated Graphite	4.0x10^{-8} - 1.0x10^{-2}	10	19.8	5.0-8.0	6	
Monoaza-12-crown-4 (7%) + PVC (48%) + NaTPB (8%) +DBBP (37%)		3.16x10^{-5} -1.0x10^{-1}	15	20.5	3.0-7.0	5	69
Bis (thiophenal) phenylen-1, 3-diamine (8%) + PVC (35%) + NaTPB (3%) + BA (54%)		1.0x10^{-7} - 1.0x10^{-1}	10	19.6	3.5-9.5	2	70
Tin(IV) antimonophosphate (70%) + Epoxy resin (araldite)		1.0x10^{-5} - 1.0x10^{-1}	30-40	41.0	2.0-6.5	-	53
Gliclazide (11%) + PVC (30%) + DBP (56%) +NaTPB (3%)		1.0x10^{-6} - 1.0x10^{-1}	15	20.1	4.0-8.0	-	71
Bis(2-mercaptoanil) diacetyl	PVC Memb.	1.0x10^{-5} - 1.0x10^{-1}	15	Nernst-ian	4.0-8.0	-	72
	Coated Graphite	1.0x10^{-6} - 1.0x10^{-1}	15	Nernst-ian	4.0-8.0	-	

Abbreviations:

PVC: Polyvinyl chloride; AP: Acetophenone; OA: Oleic Acid; BA: Benzyl acetate

NaTPB: Sodium tetraphenyl borate; DBBP: Dibutyl(butyl) phosphonate; DBP: Dibutyl phthalate

NPOE: Nitrophenyloctyl ether; KTCPB: Potassium tetrakis(4-chlorophenyl)borate

Ce (III)-selective electrodes						
1, 3, 5-trithiane (5%) + PVC (32%) + BA (45%) + OA (18%)	$5.0x10^{-5}$ - $1.0x10^{-1}$	15	19.4	5.0-8.0	5	73
1,3,5-trithiane in PVC (Coated graphite electrode)	$2.5x10^{-8}$ - $4.7x10^{-4}$	10	19.2	-	-	74
N-[(Z)-2-chloro-2-(1-hydroxy-1,1,1-triphenyl phosphoranyl)-1-ethenyl]-4-ethyl-1-benzene sulfonamide	$6.6x10^{-7}$ - $6.2x10^{-2}$	10	Nernst	4.5-8.5	4	75
2-aminobenzothiazole (3.3%) + PVC (24%) + OA (13%) + o-NPOE (59.7%)	$2.0x10^{-6}$ - $2.0x10^{-2}$	13	19.6	4.1-7.3	3	76
Sm (III)-selective electrodes						
1,4 -bis(3-thiapentylxanthato) Butane (10.2%) + PVC (28.7%) + NPOE (60.4%) + KTCPB (0.7%)	$2.0x10^{-6}$ - $5.0x10^{-3}$	5	19.7	4.5-6.7	-	77, 78
Glipizid (11%) + PVC (30%) + BA (53%) + NaTPB (6%)	$1.0x10^{-6}$ - $1.0x10^{-1}$	10	19.8	4.0-8.0	2	79
Yb (III)-selective electrode						
Cefixime (11%) + PVC (33%) + BA (50%) + NaTPB (6%)	$1.0x10^{-6}$ - $1.0x10^{-2}$	15	19.5	3.0-8.0	2	80
Gd (III)-selective electrode						
2-[{3-[(2-sulfanylphenyl)imino)-1-methylbutylidene}amino] Phenyl hydrosulfide (5%) + PVC (33%) + BA (61%) + NaTPB (2)	$1.0x10^{-5}$ - $1.0x10^{-1}$	-	19.8	4.0-8.0	9 weeks	81
Dy (III)-selective electrode						
Zirconium(IV) selenomolybdate in PVC	$5.0x10^{-5}$ - $1.0x10^{-1}$	15	18.3	2.0-9.0	-	56

A Cerium (III) sensor was reported by Shamsipur et al. [73] using a membrane composition as 1, 3, 5-trithiane (5%) + PVC (32%) + BA (45%) + OA (18%). It showed a linear response in the range $5.0\text{x}10^{-5}$ M -$1.0\text{x}10^{-1}$ M with a Nernstian slope of ~19.4 mV/decade. It was used as an indicator electrode in potentiometric titration of oxalate and fluoride ions and in the determination of F^- ion in some mouth-wash preparations. Another coated graphite electrode [74] for cerium (III) ions was reported by Shamsipur et al. using 1,3,5-trithiane as ionophore. It showed a detection limit of $2.0\text{x}10^{-8}$ M. Karami et al. [75] introduced a cerium-selective electrode on N-[(Z)-2-chloro-2-(1-hydroxy-1,1,1-triphenyl phosphoranyl)-1-ethenyl]-4-ethyl-1-benzene sulfonamide which has a detection limit of $2.3\text{x}10^{-7}$ M. This sensor was used for measurement of the cerium content in stainless steel samples. Recently, a new PVC membrane electrode based on 2-aminobenzothiazole {2-aminobenzothiazole (3.3%) + PVC (24%) + OA (13%) + o-NPOE (59.7%)} has been reported by Akhond et al. [76].

Ogata et al. [77, 78] reported samarium (III)-selective electrodes constructed on the basis of bis (alkylxanthato) alkanes and bis (thiaalkylxanthato) alkanes. Acceptable selectivity was obtained for Sm (III) determination against many of the transition, alkali, alkaline-earth and some lighter rare-earth metal ions. Ganjali et al. [79] prepared a samarium (III)-selective membrane sensor based on glipizid. The electrode has an average life time of only two months and is successfully used as an indicator electrode in potentiometric titration of Sm (III) ions with EDTA.

An ytterbium (III)-selective membrane electrode based on cefixime has been reported by Ganjali et al. [80]. It has a detection limit of $7.0\text{x}10^{-7}$ M. A new S-N Schiff's base, 2-[{3-[(2-sulfanylphenyl) imino)-1-methylbutylidene} amino] Phenyl hydrosulfide is reported as a gadolinium (III) sensor [81]. It has a detection limit of $3.0\text{x}10^{-6}$ M. It has been used for the determination of Gd (III) in a urine sample. Recently, a PVC membrane containing zirconium (IV) selenomolybdate inorganic ion exchanger as dysprosium (III) ion-selective electrode has been reported by Gupta et al. [56]. It has a detection limit of $3.8\text{x}10^{-5}$ M. The electrode can be used in partially non-aqueous medium and can be used for direct determination of Dy (III) in metaborate rock with an experimental error 2-4%.

Interestingly, most of sensors reported are based on organic ion exchangers and the area remains unexplored as far as use of inorganic ion exchangers is concerned. Liquid membrane electrodes suffer from the problem of leaching of the electro-active component into the analyte solution and a short life time. Synthetic ion exchangers have the characteristics of high selectivity and excellent thermal and chemical stabilities. These materials although polymeric in nature possess sufficient conductivity to provide suitable electro-active materials [66] in the preparation of ion-selective electrodes. Hence, there is sufficient scope for preparation of ion-selective electrodes for rare earth metal ions based on tin and zirconium ion exchangers.

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CHAPTER - 3

SYNTHESIS AND CHARACTERISATION OF ELECTROACTIVE MATERIALS

Inorganic ion exchangers have been synthesized under different conditions of synthesis and characterized for nearly four decades now, since the classical work of Amphlett [1]. Different types of inorganic ion exchangers and their applications in various fields are documented by Clearfield [2]. Inorganic ion exchangers, besides their other advantages, are important in being more stable at high temperature and radiation fields [1-4]. They are stable towards chemical degradation and possess sharp selectivity for metal ions over their organic analogs [5].

Hydrous oxides of group 4, 5, 6, 14 and 15 metals possess ion-exchange properties. They are characterized by having a bulk structure resembling to that of ceramic oxides, like sodium aluminosilicate. Their surface is largely covered with hydroxyl groups and both coordinated and hydrogen-bonded water molecules are present. Properties of these tunnel type structures of ZrO_2 and SnO_2 can be changed by the incorporation of framework hydrates, generally formed by metals in group 5 and 15, in their higher oxidation states. In such resulting structures, hydronium ions are distributed among crystallographic sites within the tunnels.

Amorphous and crystalline forms of tetravalent metal acid salts, generally called single salts, with the general formula M (IV) $(HXO_4)_2$. n H_2O { where, M represents Sn (IV), Zr (IV), Ti (IV), etc. and X represents P, W, Si, Mo, Se, As etc.} have been studied. Some single salts of tin (IV), like phosphates and antimonates, have shown some characteristics of ion exchangers [6]. However, studies have shown that mixed salts have better ion-exchange capacity, thermal and chemical stability as compared to single salts [7]. These mixed salts may have tetravalent metals such as Sn (IV), Zr (IV), Ti (IV), etc. in combination with any two anions from P, B, W, Si, Mo, Se, As, etc. These mixed salts are called double salts. Double salts of tin and zirconium [8, 9] have shown better ion-exchange characteristics than the corresponding single salts.

Zirconium boratophosphate was synthesized and its physico-chemical properties were studied by Thind et al. [10]. It was used for quantitative separation of a very important class of compounds, i.e., lanthanides. A search of the literature showed that no studies are reported on tin (IV) boratophosphate. We have, therefore, synthesized and characterized this exchanger and explored conditions under which it shows reproducible behavior. Tin (IV) antimonoarsenate prepared by Mittal et al. [11] also showed selectivity for some rare earth metal ions. So, a novel inorganic ion exchanger zirconium (IV) antimonoarsenate was also prepared and characterized by using analytical techniques, like IR, XRD, TGA, SEM and XPS.

The most important electrochemical property of membranes is the pronounced difference in permeability for counter ions, co-ions and neutral molecules and their high electrical conductivity. When in contact with electrolyte solutions of low or moderate concentrations, the membrane contains a large number of counter ions but relatively few co-ions due to Donnan exclusion. Counter ions are admitted to the membrane and thus, have little difficulty in passing through from one solution to the other. Co-ions on the other hand, are rather efficiently excluded from the membrane and thus, find it difficult to pass through. The membrane is permselective for counter ions. Permselectivity is reflected not only in differences in permeability, but also in electric potential difference which arises between two solutions (membrane potential). However, when concentrations of the solutions are increased, the Donnan exclusion becomes less efficient and the permselectivity gets reduced.

The degree of permselectivity of a membrane can be expressed in terms of the change in transport number of the mobile ion in a solution when the membrane is introduced into the solution.

Thus, the degree of permselectivity, P can be defined by:

$$P = \frac{t_{\text{mobile ion}} - t^{o}_{\text{mobile ion}}}{1 + t^{o}_{\text{mobile ion}}} \qquad \ldots\ldots\ldots\ldots (3.1)$$

Where, $t_{\text{mobile ion}}$ refers to the value of transport number in the membrane and $t^{o}_{\text{mobile ion}}$ is the value in free electrolyte solution.

Inorganic membranes were first prepared by Drawnieks and Bregman [12]. The effect of membrane potential and adsorption on the permeability of ions, electrical conductance, ion-exchange capacity and permselectivity were investigated by Malik et al. [13, 14]. The theory of absolute reaction rates was applied by Beg et al. [15, 16] to the diffusion of ions through cobalt and nickel phosphates and thallium dichromate membranes. Gnusin et a1 [17] investigated the dependence of a wide number of transport characteristics of inorganic ion-exchange membranes on the concentration. One such compound, i.e., zirconium (IV) antimonoarsenate has been used for electrochemical studies on a heterogeneous inorganic ion-exchange membrane.

3.1 SYNTHESIS AND CHARACTERIZATION OF TIN (IV) BORATOPHOSPHATE

ABSTRACT

A new inorganic ion exchanger, tin (IV) boratophosphate has been synthesized at different pH values. Amorphous sample prepared at pH 1 having an ion-exchange capacity of 0.80 meq/g was selected for further studies. The material is characterized by using various analytical techniques, like XRD, IR, TGA, SEM and XPS. In addition, ion-exchange capacity, chemical stability and distribution coefficient (K_d values) were also studied.

EXPERIMENTAL

Reagents

Tin (IV) chloride pentahydrate (Loba Chemie, India), boric acid and orthophosphoric acid (s.d. fine chem., India) were used for the synthesis. All other chemicals used were of analytical reagent (AR) grade. Standard solutions for the analytical work were prepared by either direct weighing of AR grade reagents or by indirect standardization. Demineralized water was prepared by passing distilled water through a cation exchanger (Amberlite IR-120) in the H^+-form packed in a column.

Instruments

An electric thermostated oven was used for drying the sample. An ISFET 701 pH meter (Delta TRAK, INC., USA Model 24003) was used for pH measurements. X-ray powder patterns were obtained with a Rigaku Dmax III C instrument and a Debye Scherrer camera. Infrared studies were made with a Bomem, MB-104 spectrophotometer using the KBr pellet technique. TGA studies were done on Mettler Toledo Star System. XPS studies were done on an aluminum anode (K_α radiation, $h\nu = 1486.6$ eV) at a pressure 2.66×10^{-5} Pa on a Mc Pherson ESCA-36 spectrometer. SEM images were obtained by using a JEOL JSM 840A electron microscope.

Preparation of Tin (IV) boratophosphate

Five samples of the exchanger were prepared by adding tin (IV) chloride (0.1 M, containing HF, 12 mL/L) solution to a continuously stirred mixture of boric acid (0.1 M) and orthophosphoric acid (0.1 M) at 60º C in a volume ratio 2:1:1 under the conditions given in Table 3.1.1. Gelatinous white precipitates were obtained and pH of the gel was adjusted by adding either HCl or NaOH solution. Precipitates were filtered, washed with DMW until free from halides and phosphates. The gel was air dried at 40º C. The dried product broke down into small granules when immersed in water. The material was converted into the H^+-form by treating it with HCl (0.1 M) for 24 hours with occasional shaking and intermittent changing the acid. Precipitates were washed with DMW in order to remove excess acid and were finally dried at 40º C.

Ion-exchange Capacity

Ion-exchange capacity of various samples was determined by column operation. Exchanger in the H^+-form was placed in a column containing a glass wool support. Sodium nitrate solution (1.0 M) was used as an eluent and about 400 mL of it was passed through the ion exchanger column containing 1 g of the exchanger at a rate of 5-10 drops per minute. Hydrogen ions eluted from the column were determined titrimetrically against standard solution of sodium hydroxide. Results are shown in Table 3.1.1.

Regeneration of Ion exchanger

Exhausted exchanger was regenerated by keeping it overnight in hydrochloric acid (0.1 N). It was then washed with demineralized water, till neutral. The exchange capacity was determined and this procedure was repeated five times. After five regenerations, ion exchanger loses 35% of its original capacity.

Sorption Studies

Distribution coefficients (K_d) were determined in DMW. 200 mg portions of the exchanger (in the H^+-form) were taken in 20 mL of different metal ion solutions and were kept for 24 hours with intermittent shaking to attain equilibrium.

Table 3.1.1: Conditions of synthesis and properties of tin (IV) boratophosphate

Sample No	Conditions of synthesis					Properties		
	Mixing volume ratio			Temperature (° C)	pH			
	SC (0.1 M)	BA (0.1 M)	PA (0.1 M)			Color in H^+ form	Morpho-logy	IEC meq/g
I	2	1	1	60	0	White	a	0.40
II	2	1	1	60	1	White	a	0.80
III	2	1	1	60	2	White	a	0.80
IV	2	1	1	30	0	White	a	0.40
V	2	1	1	40	1	White	a	0.70

a = amorphous; SC = stannic chloride; BA = boric acid; PA = phosphoric acid

K_d values were calculated by using the formula:

$$K_d = \frac{I - F}{F} \times \frac{20}{0.2} \qquad \text{………… (3.2)}$$

Where, *I* = Volume of EDTA (0.01 M) consumed by cations before equilibrium

F= Volume of EDTA (0.01 M) consumed by cations after equilibrium

All the metal ions used were determined by titrating against EDTA (0.01 M). Results are given in Table 3.1.2.

Table 3.1.2: Distribution coefficients (K_d) for metal ions on tin (IV) boratophosphate

Metal ion	**La^{3+}**	**Ce^{3+}**	**Nd^{3+}**	**Sm^{3+}**	**Eu^{3+}**	**Pr^{3+}**	**Tb^{3+}**	**Dy^{3+}**	**Y^{3+}**
K_d (ml/g)	20	11	29	**40**	13	25	36	28	11

Infrared Spectra

Infrared spectra for tin (IV) boratophosphate sample, dried at 40º C, were recorded in KBr pellet medium. Results are shown in Fig. 3.1.1.

X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectra (XPS) of the sample were obtained by using an aluminum anode (K_α radiation, hν =1486.6 eV) at a pressure 2.66×10^{-5} Pa on a Mc Pherson ESCA-36 spectrometer. Atomic ratios were estimated by integrating areas under peaks using the corresponding Scofield cross section for each atomic level involved [18]. Binding energies were calibrated against a C_{1s} of 284.6 eV [19]. Results are shown in Figs. 3.1.2 – 3.1.5.

Thermal Analysis

A thermo-gravimetric curve was obtained between 25º C and 700º C, with a heating rate of 10º C per minute, under nitrogen at a flow rate of 50.0 mL/minute. Results are shown in Fig. 3.1.6.

X-Ray Diffraction

X-ray diffraction studies of tin (IV) boratophosphate were done by powder method and Results are shown in Table 3.1.3 and Fig. 3.1.7.

Scanning Electron Microscopy

Scanning electron microscopy images of the sample were obtained by dispersing the powder on a double face conducting tape fixed on a brass support. Results are shown in Fig. 3.1.8.

RESULTS AND DISCUSSION

In this study, a weakly acidic cation exchanger, tin (IV) boratophosphate is being introduced as a new heteropolyacid salt of tin. Synthesis and properties of various samples, prepared under similar conditions (Table 3.1.1), clearly show that tin (IV) boratophosphate is a reproducible material. The exchanger can be regenerated and used over and over again for its cation-exchange capacity with a decrease of ≤35% of its original IEC after five regeneration cycles.

Table 3.1.3: d values of tin (IV) boratophosphate and c- tin (IV) phosphate in the H^+-form

d values (Å)	
SnBP	**c- SnP [20]**
4.60	7.90
3.71	4.23
3.41	3.47
2.71	3.17
2.57	2.65
1.49	2.48
1.39	2.42
1.29	2.36
1.27	2.14
1.25	2.09
1.22	2.01
1.16	1.95
1.13	1.91
1.08	1.80
	1.73
	1.62
	1.56
	1.53
	1.46
	1.43
	1.41

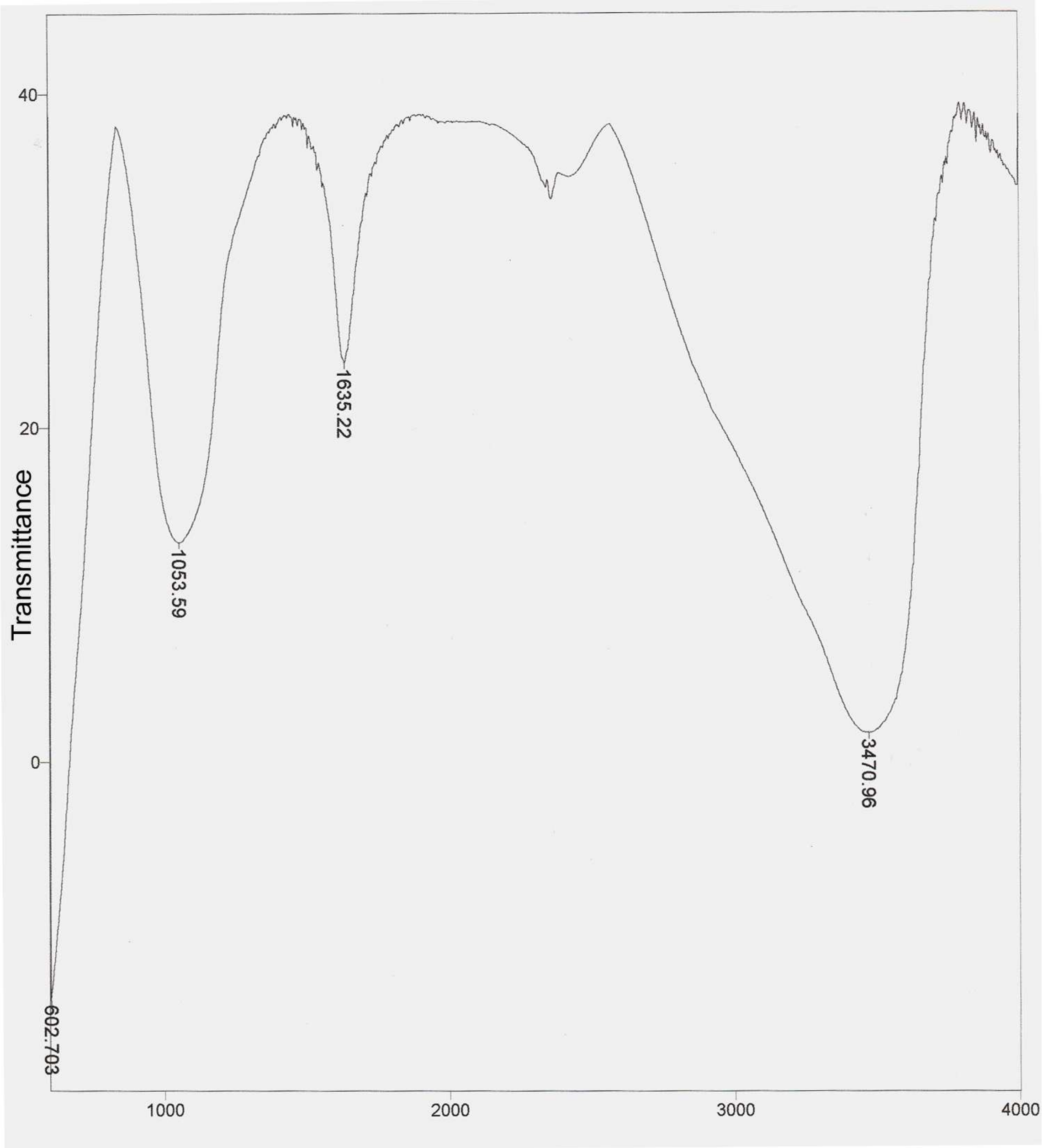
Synthesis of the material was carried out by introducing an aqueous solution of stannic chloride (0.1 M) maintained at 60º C to a homogeneous and continuously stirred dilute aqueous mixture solution of boric acid (0.1 M) and orthophosphoric acid (0.1 M) at 60º C. Stannic chloride is highly hygroscopic in nature and was added within 20 minutes of its preparation. Additions were done in lots at regular intervals. In order to introduce crystallinity in the structure, kinetics of chemical reaction between tin (IV), borate and phosphate ions were controlled. Stannic chloride gets hydrolyzed easily in aqueous medium and is available as hexachloro anion, which is not a suitable species to combine with borate and phosphate anions. Instead, an aqueous solution of SnF_4 is formed (by using HF), which is polymeric [21] and a suitable species to combine with borate and phosphate ions in a controlled way.

Precipitates, thus formed, are dried in air up to 40º C to remove excess water. The material is not dried to 100º C so as to retain the water of crystallization which is also responsible for its ion-exchange capacity.

IR spectra of the exchanger show sharp and strong bands at 1053, 1635, ~2300 and 3470 cm^{-1}. Based on the analysis of literature, the band at 1053 cm^{-1} may be assigned to stretching of P-O bonds in PO_4^{3-} group in the material [22]. Broad bands at 3470 cm^{-1} and 2300 cm^{-1} are due to –OH groups of interstitial water (or free water) and P-OH (acidic) stretches, respectively [23]. The sharp band at 1635 cm^{-1} is due to –OH deformation mode.

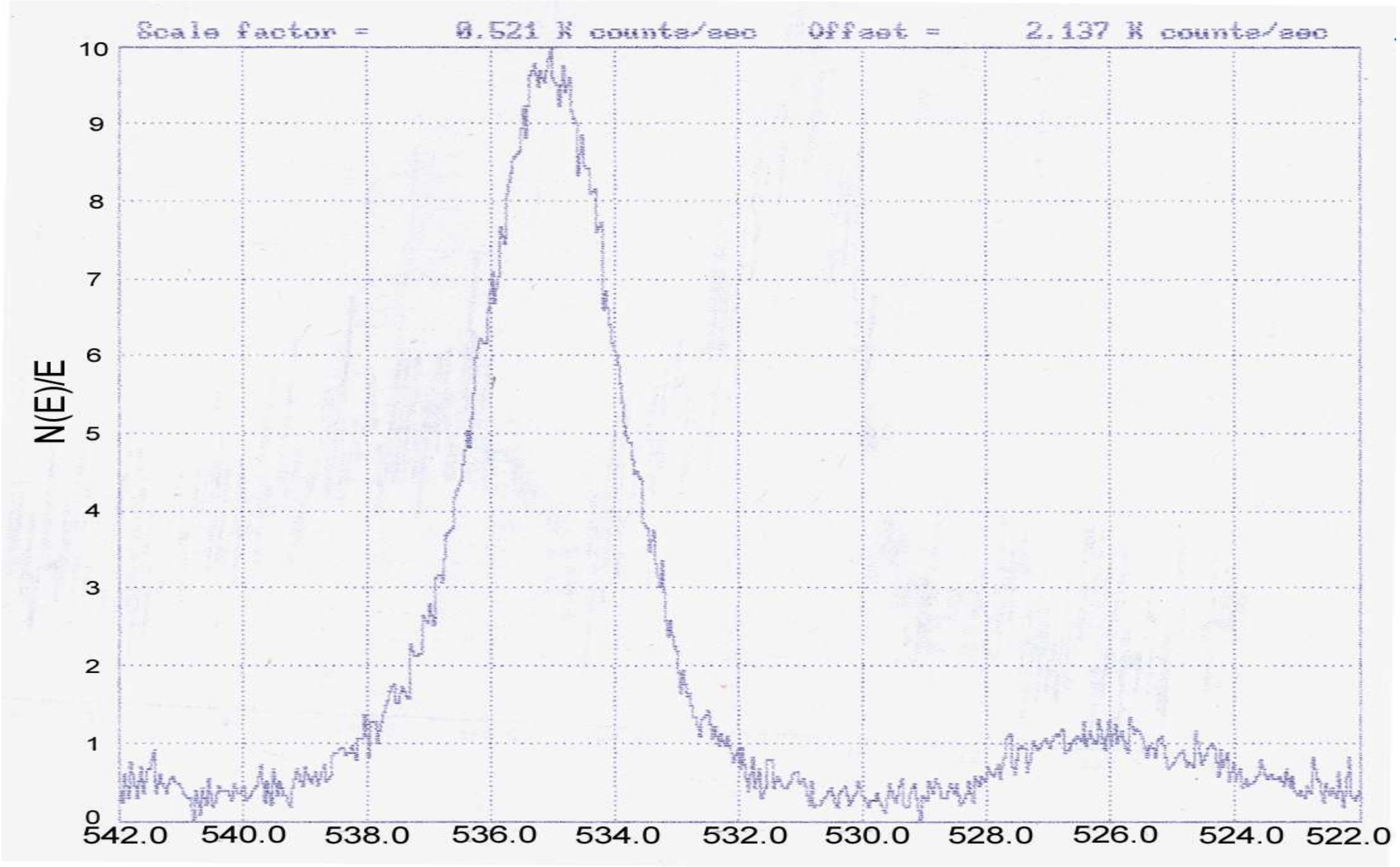
Elemental composition of the synthesized exchanger was done by XPS. As seen from the survey spectrum, the exchanger contains Sn, B, P and O which are characterized by peaks at doublet 490 eV, 499.2 eV [Sn 3d], 195 eV [B 1s], 137 eV [P 2p] and 535 eV [O 1s]. Atomic ratio of these elements is 19:27:7.5:46.5. Based on these data, an empirical formula of the synthesized exchanger can be represented as:

$$\mathbf{[(SnO_2)_{2.5}\,(H_3\,BO_3)_{3.6}\,(H_3PO_4)].nH_2O}$$



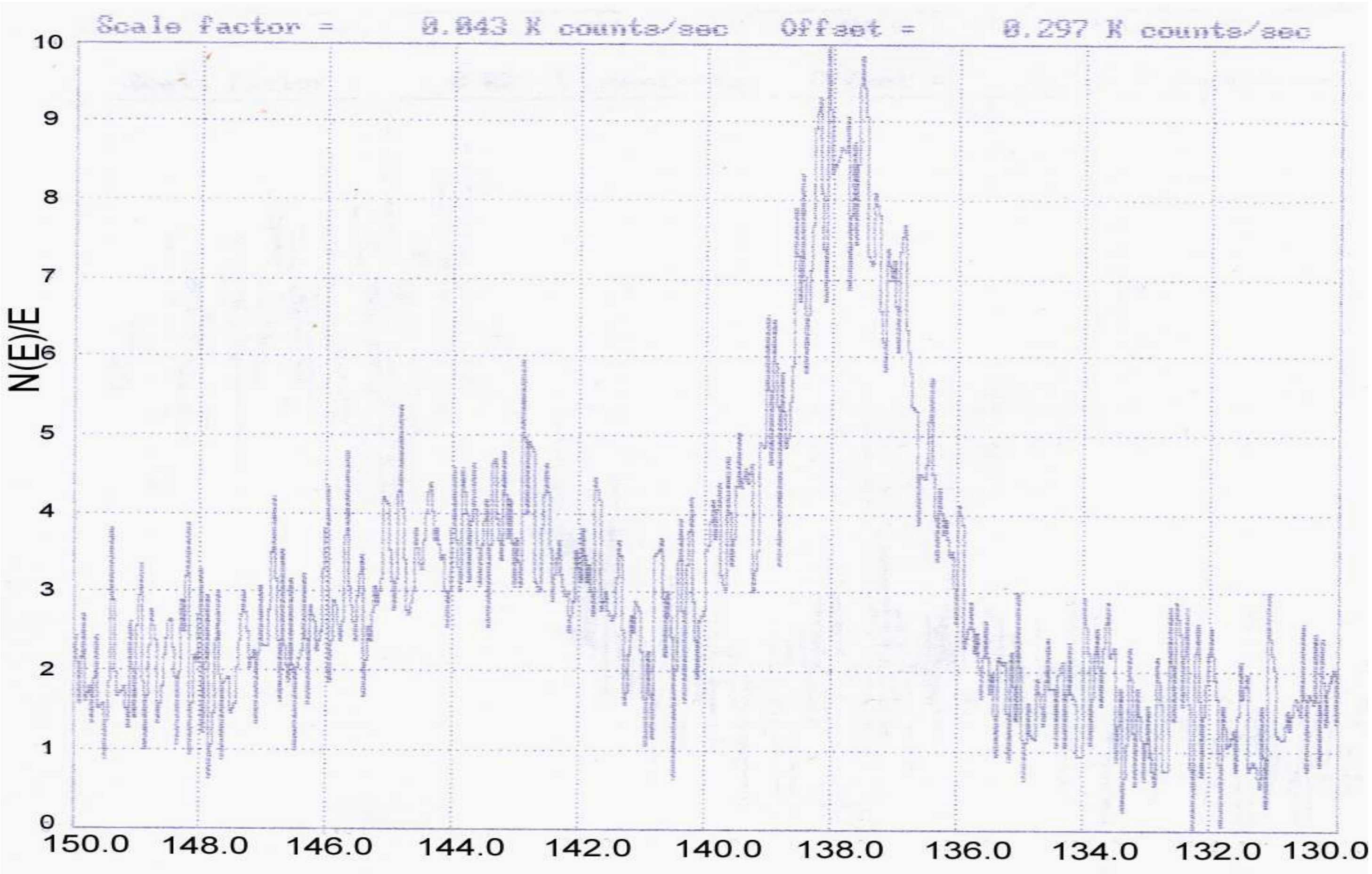
Wave number (cm^{-1})

Figure 3.1.1: IR spectrum of tin (IV) boratophosphate



Binding Energy (eV)

Figure 3.1.2: XPS spectrum of an SnBP layer; the O region



Binding Energy (eV)

Figure 3.1.3: XPS spectrum of an SnBP layer; the B region

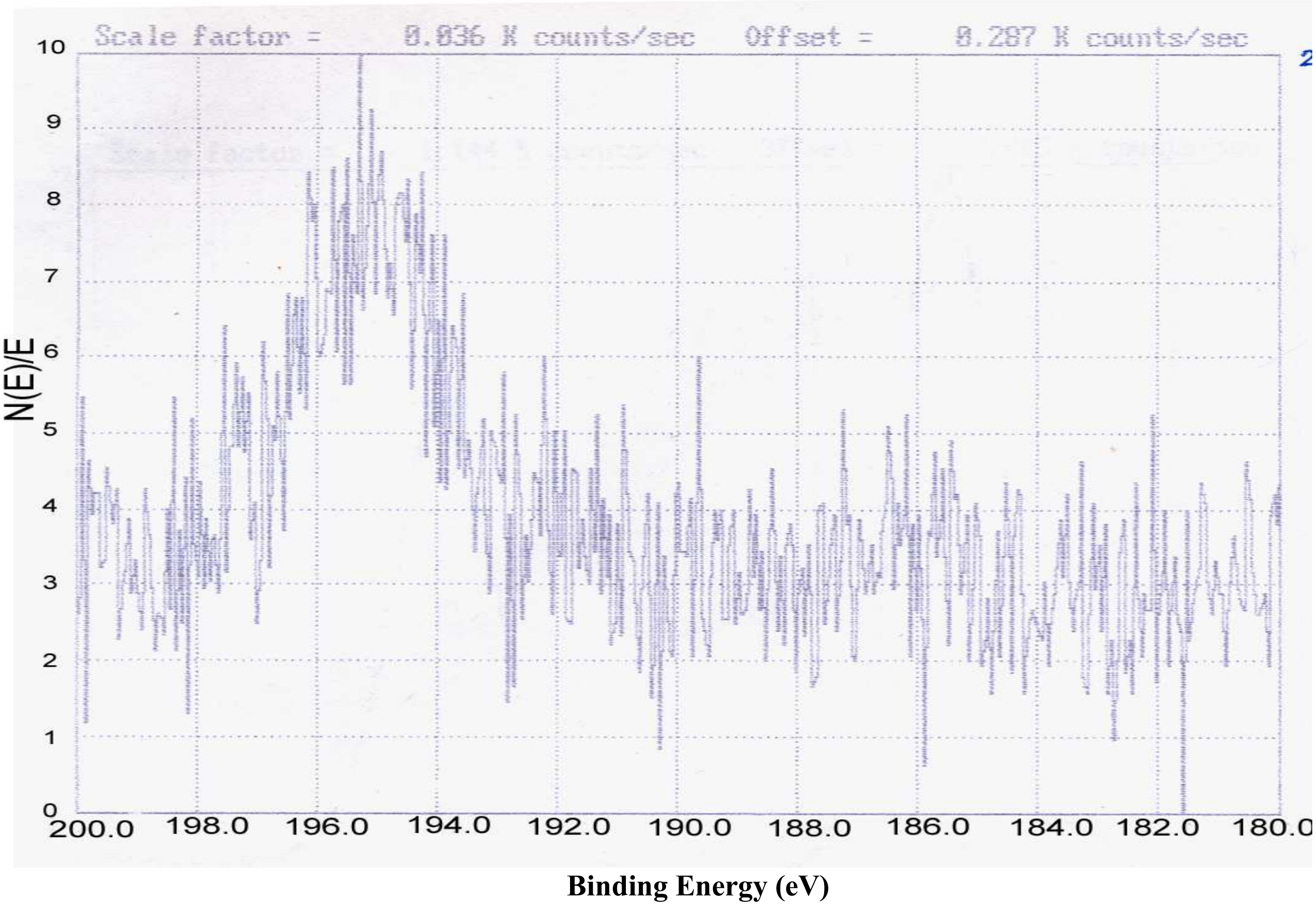
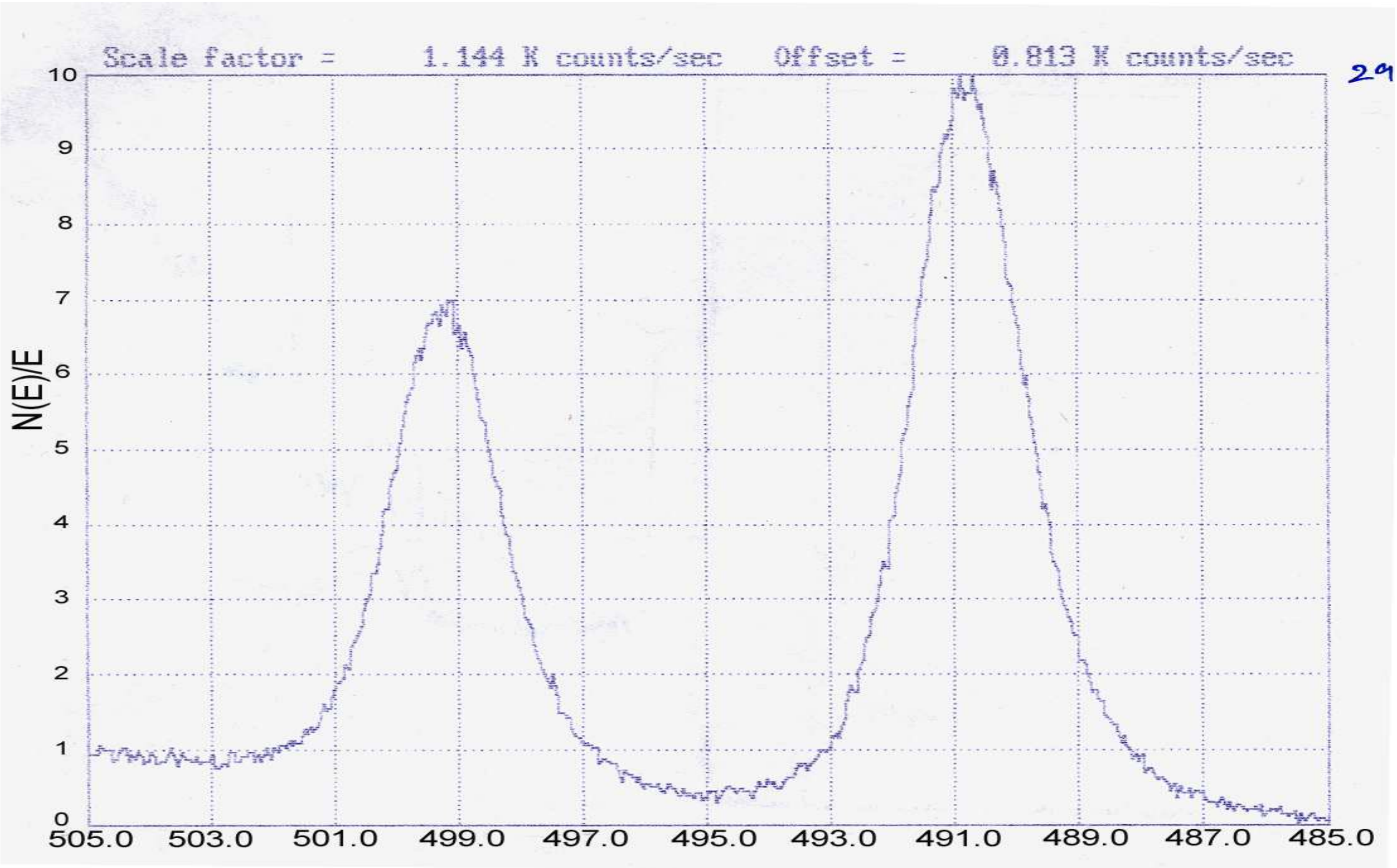


Figure 3.1.4: XPS spectrum of an SnBP layer; the P region



Binding Energy (eV)

Figure 3.1.5: XPS spectrum of an SnBP layer; the Sn region

This formula does not indicate relative fractions of different form of oxygen in the exchanger, which can be in the form of molecular water, hydroxyl group and oxide, as well.

The number of external water molecules (n) can be estimated from the thermo-gravimetric study. SnBP experiences a weight loss of 11% up to a temperature of 200º C. It is assumed that all the external water molecules are removed on heating the exchanger to this temperature. We can calculate the number of external water molecules 'n' by using Alberti formula [24], which is given as;

$$18\ n = X\ (M+18\ n)\ /\ 100 \qquad \ldots\ldots\ldots\ldots\ (3.3)$$

where, X is % weight loss at 200º C, (M+18 n) is molecular weight of the material and n, the number of external water molecules.

This gives the value of 'n' as 4.8≈ 5. So, the formula of the exchanger can be written as

$$\mathbf{[(SnO_2)_{2.5}\ (H_3BO_3)_{3.6}\ (H_3PO_4)].5H_2O}$$

with a molecular weight 792.

A further weight loss of nearly 6% up to 500º C may be attributed to the loss of coordinated water and hydroxyl groups besides the rearrangement of functional groups. These losses follow the regular trend of inorganic ion exchangers [25, 26].

X-ray powder diffraction studies (Fig. 3.1.7) show no diffraction lines for the exchanger. It indicates its amorphous nature. X-ray data for the prepared ion exchanger (SnBP) has been compared with that of crystalline tin (IV) phosphate [20] in H^+-form and values are reported in Table 3.1.3 which confirms the amorphous nature of the material.

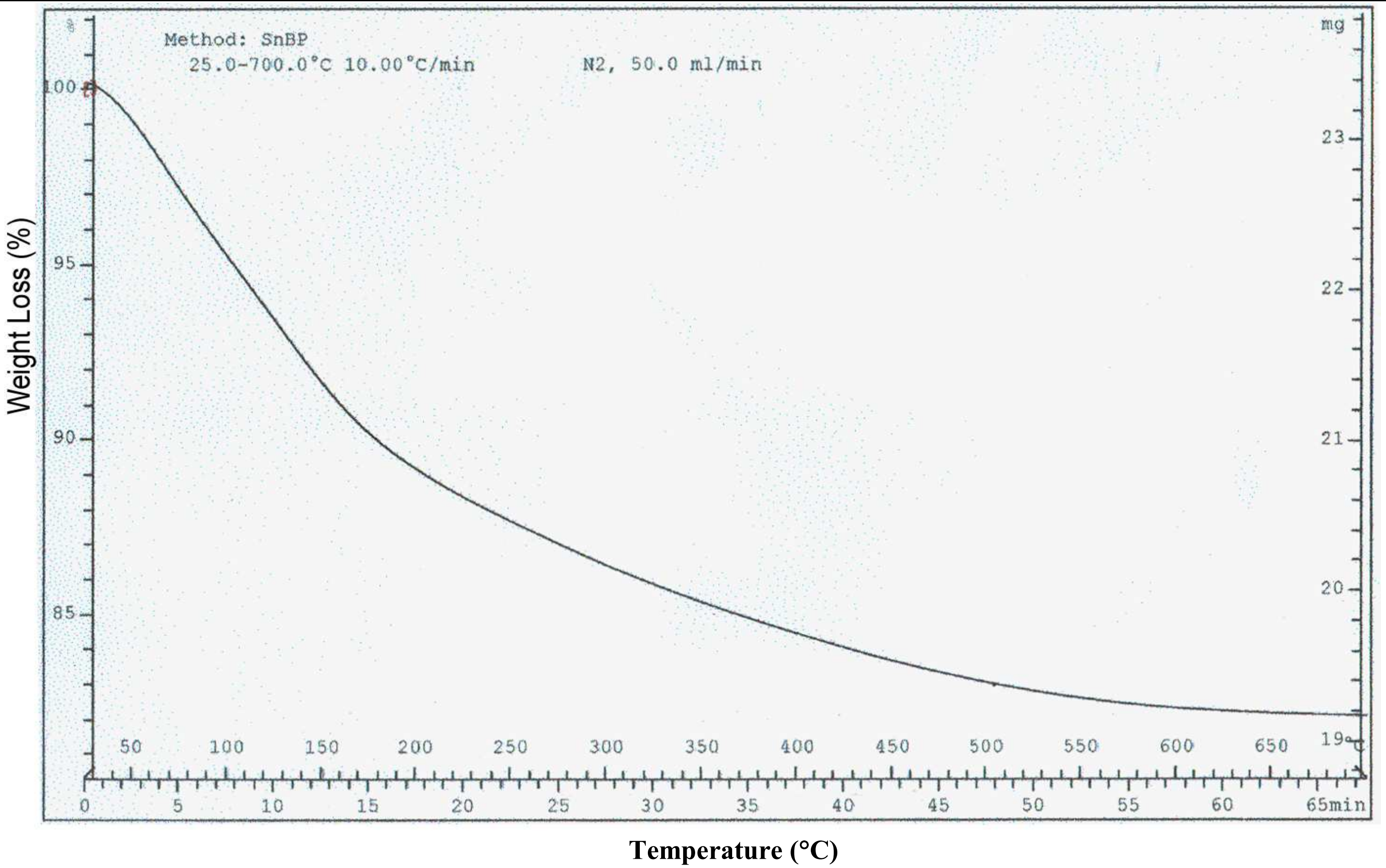


Figure 3.1.6: TGA curve of SnBP

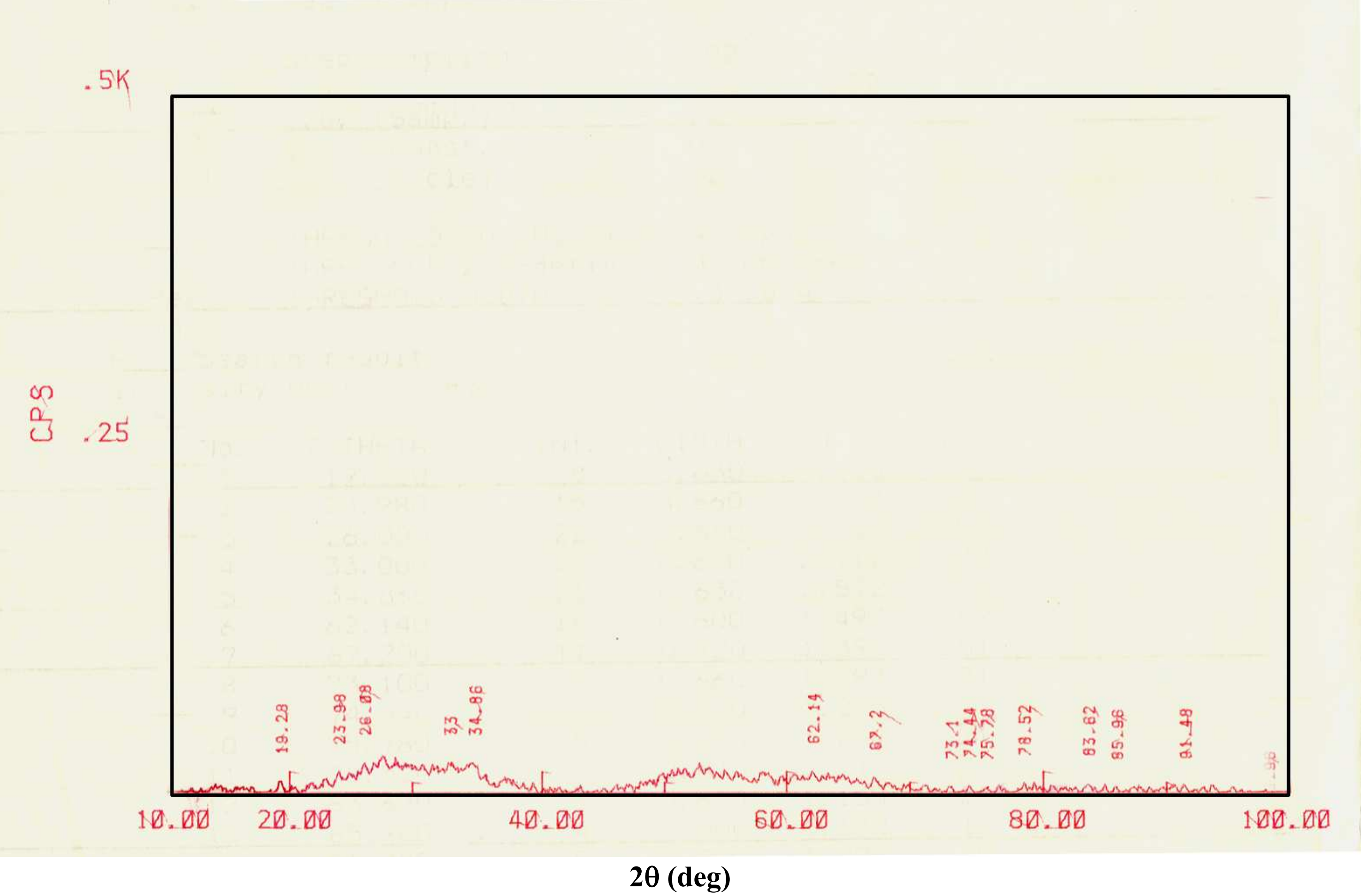


Figure 3.1.7: X–ray diffraction pattern of SnBP

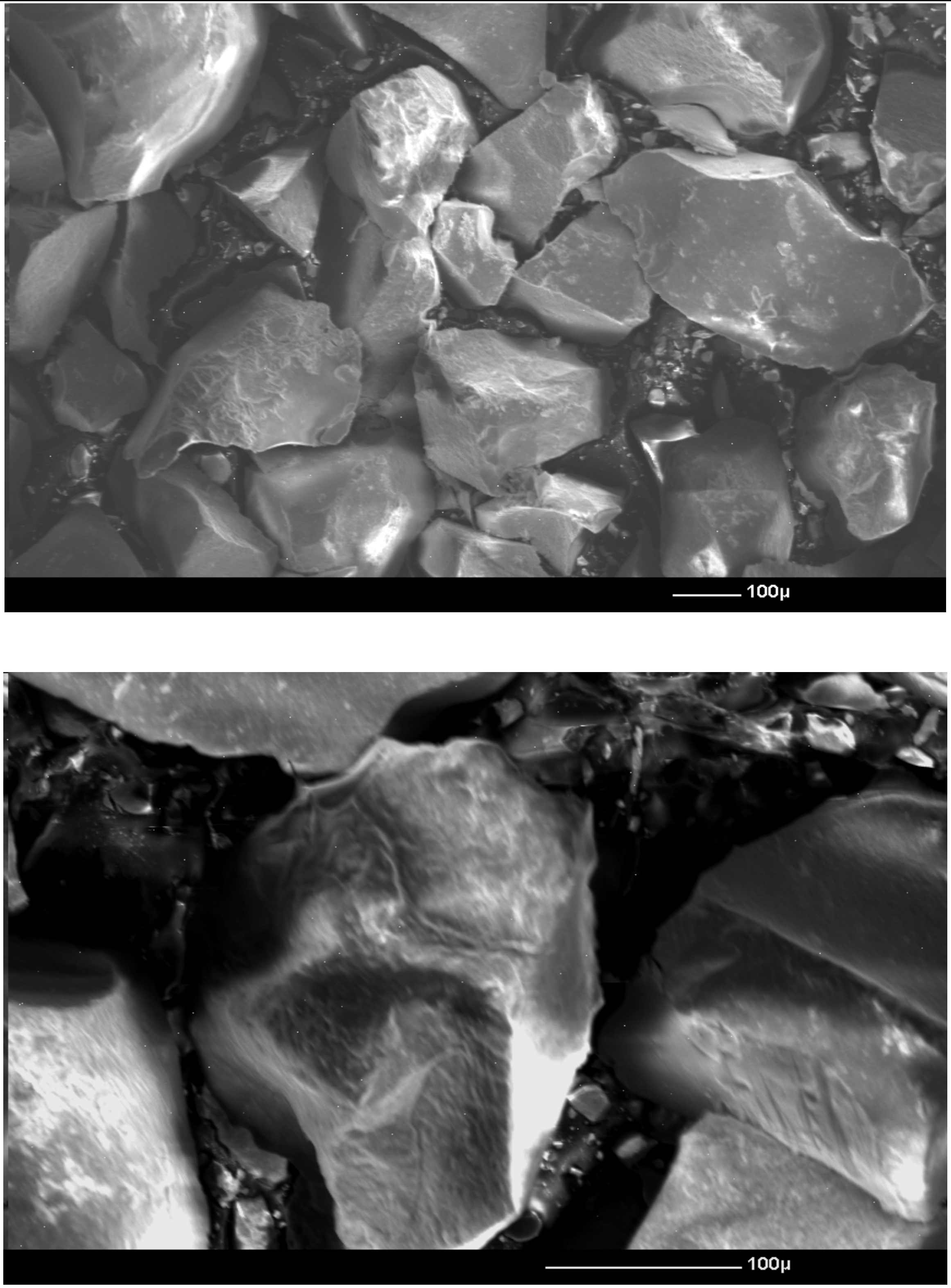


Figure 3.1.8: SEM images of a sample of SnBP

SEM images of tin (IV) boratophosphate show that its particles have a broad size range and an irregular shape. Lack of clearly defined morphology correlates with the low crystallinity of the compounds. There is seen a *tendency* to possess linearly layered structure of the material, as evidenced from the micrograph.

Application as Ion-selective Electrode

It was observed that tin (IV) boratophosphate shows different selectivities towards different metal ions. It shows maximum selectivity towards Sm^{3+} ions over other rare earth metal ions. Tin (IV) boratophosphate has been used as an electro-active component in the preparation of heterogeneous solid membrane electrodes sensitive for Sm^{3+} ions. Detailed studies on the electrode performance are reported in Chapter 4 [21]. The response of the electrode does not show much interference from alkali, alkaline earth, transition metal and other rare earth metal ions. It is workable in the partially non-aqueous medium, too.

***

3.2 SYNTHESIS, CHARACTERIZATION AND ELECTROCHEMICAL STUDIES OF ZIRCONIUM (IV) ANTIMONOARSENATE

ABSTRACT

A new inorganic ion exchanger, zirconium (IV) antimonoarsenate has been synthesized at different pH values. An amorphous sample prepared at pH 1 having an ion-exchange capacity of 0.40 meq/g was selected for further studies. The material is characterized using various analytical techniques, like XRD, IR, TGA and SEM, in addition to the ion-exchange capacity and distribution coefficient (K_d) studies. Electrochemical studies were carried out on ion-exchange membranes using polystyrene as a binder. Electrode potential measurements have been applied to determine electrical characteristics, like transport number, permselectivity and fixed charge density of the exchanger membrane. Halide salts of the alkali and alkaline earth metals were used as electrolytes. Effect of electrolyte concentration on transport numbers and permselectivity has also been studied.

EXPERIMENTAL

Reagents

Zirconyl oxychloride (LOBA Chemie, India), potassium pyroantimonate (BDH, England) and sodium arsenate (s.d. fine chem., India) were used for the synthesis. All other chemicals used were of analytical reagent (AR) grade. Standard solutions for the analytical work were prepared either by direct weighing of AR grade reagents or by indirect standardization. Demineralized water was prepared by passing distilled water through a cation exchanger in H^+-form (Amberlite IR-120) packed in a column.

Instruments

All the instruments used were same as described in Chapter 3.1.

Preparation of Zirconium (IV) antimonoarsenate

Five samples of the exchanger were prepared by adding zirconyl oxychloride (0.1 M) solution to a continuously stirred solution of potassium pyroantimonate (0.1 M) and sodium arsenate (0.1 M) at 60º C, in the volume ratio 2:1:1 under the conditions given in Table 3.2.1. Gelatinous white precipitates were obtained and pH of the gel was adjusted by adding either HCl or NaOH solution. Precipitates were filtered, washed with DMW until free from halides. The gel was air dried at 40º C. Dried product broke down into small granules when immersed in water. The material was converted into the H^+-form by treating it with HCl (0.1 M) for 24 hours with occasional shaking and intermittent changing the acid. The precipitates were washed with DMW in order to remove excess acid and were finally dried at 40º C.

Table 3.2.1: Conditions of synthesis and properties of ZrSbAs

Sample No	Conditions of synthesis					Properties		
	Mixing volume ratio			Temperature (° C)	pH			
	ZC (0.1 M)	PPA (0.1 M)	SA (0.1 M)			Color in H^+-form	Morpho-logy	IEC (meq/g)
I	2	1	1	90	0	White	a	0.35
II	2	1	1	90	1	White	a	0.40
III	2	1	1	60	2	White	a	0.30
IV	2	1	1	30	0	White	a	0.35
V	2	1	1	40	1	White	a	0.24

a = amorphous; ZC = zirconyl oxychloride; PPA = potassium pyroantimonate; SA = sodium arsenate

Ion-exchange Capacity

Ion-exchange capacity of various samples was determined by column operation as described in Chapter 3.1. Results are shown in Table 3.2.1.

Regeneration of Ion exchanger

Exhausted exchanger was regenerated by keeping it overnight in hydrochloric acid (0.1 N). It was then washed with demineralized water to remove the excess acid. Ion-exchange capacity was determined and this procedure was repeated five times.

Sorption Studies

Distribution coefficients (K_d values) were determined in DMW as described in Chapter 3.1. Results are given in Table 3.2.2

Table 3.2.2: Distribution coefficients (K_d) for metal ions on ZrSbAs

Metal ion	La^{3+}	Ce^{3+}	Nd^{3+}	Sm^{3+}	Eu^{3+}	Pr^{3+}	Tb^{3+}	Dy^{3+}	Y^{3+}
K_d(mL/g)	2	**32**	--	8	10	19	2	2	0

Infrared Spectra

Infrared spectra for Zirconium (IV) antimonoarsenate sample, dried at 40º C, were recorded in KBr pellet medium. Results are shown in Fig. 3.2.1.

Chemical Composition

A mass of 0.5 grams of the exchanger was dissolved in concentrated HCl. Zirconium [28] was determined spectrophotometrically. Antimony [29] was determined gravimetrically by pyragallol method and arsenic [30] was estimated iodometrically.

Thermal Analysis

The thermo-gravimetric curve was obtained between 25º C and 700º C with a heating rate of 10º C per minute under nitrogen at a flow rate of 50.0 mL/minute. Results are shown in Fig. 3.2.2.

X-ray Diffraction

X-ray diffraction studies were done by powder method and results are shown in Table 3.2.3 and Fig. 3.2.3.

Table 3.2.3: d values of zirconium (IV) antimonoarsenate in the H^+-form

d values(Å)	6.02	5.12	2.96	1.94	1.91	1.65	1.40	1.17	1.14	1.08

Scanning Electron Microscopy

Scanning electron microscope images of the sample were obtained by dispersing the powder on a double face conducting tape fixed on a brass support. Results are shown in Fig. 3.2.4.

Electrochemical Studies

Membranes were prepared, using polystyrene as a binder. Procedure for preparation of the membrane is given below:

Appropriate amount of a finely ground exchanger was thoroughly mixed with powdered polystyrene to give a 1:1 mixture. It was then heated at 99° C for 6 hours under a pressure of 2kg/cm^2 in the polymer film making equipment. After cooling to room temperature, the membrane was removed from the machine.

Membranes obtained were cut in the shape of discs of about 2.5 cm diameter using a sharp blade and those of good surface qualities were selected for further investigations.

Electrode Assembly

The selected membrane was pasted on one end of the electrode assembly using an epoxy resin as an adhesive. The membrane was fixed from backside to other part of the electrode assembly in the same way. Electrode chambers on either side of the membrane were filled with each electrolyte solution (1.0 M) such as lithium chloride, sodium chloride, potassium chloride, magnesium chloride and barium chloride for 16 hours to convert it into the appropriate cationic form. After equilibration, the electrode assembly was washed with demineralized water (DMW). The membrane was then kept immersed in DMW for 2 hours to remove excess electrolyte solution. When not in use, the electrode chambers were filled with demineralized water.

Electrode assembly was kept immersed in a water thermostat, maintained at 27±1° C, throughout the study. Membrane potential measurements were made using saturated calomel electrodes as reference electrodes. All emf measurements were carried out using the following cell assembly:

$$\mathbf{Hg\text{-}Hg_2Cl_2(s),\ KCl\ (Sat.)\ |\ soln.\ C_1\ ||\ membrane\ ||\ soln.\ C_2\ |\ KCl\ (Sat.),\ Hg_2Cl_2\text{-}Hg}$$

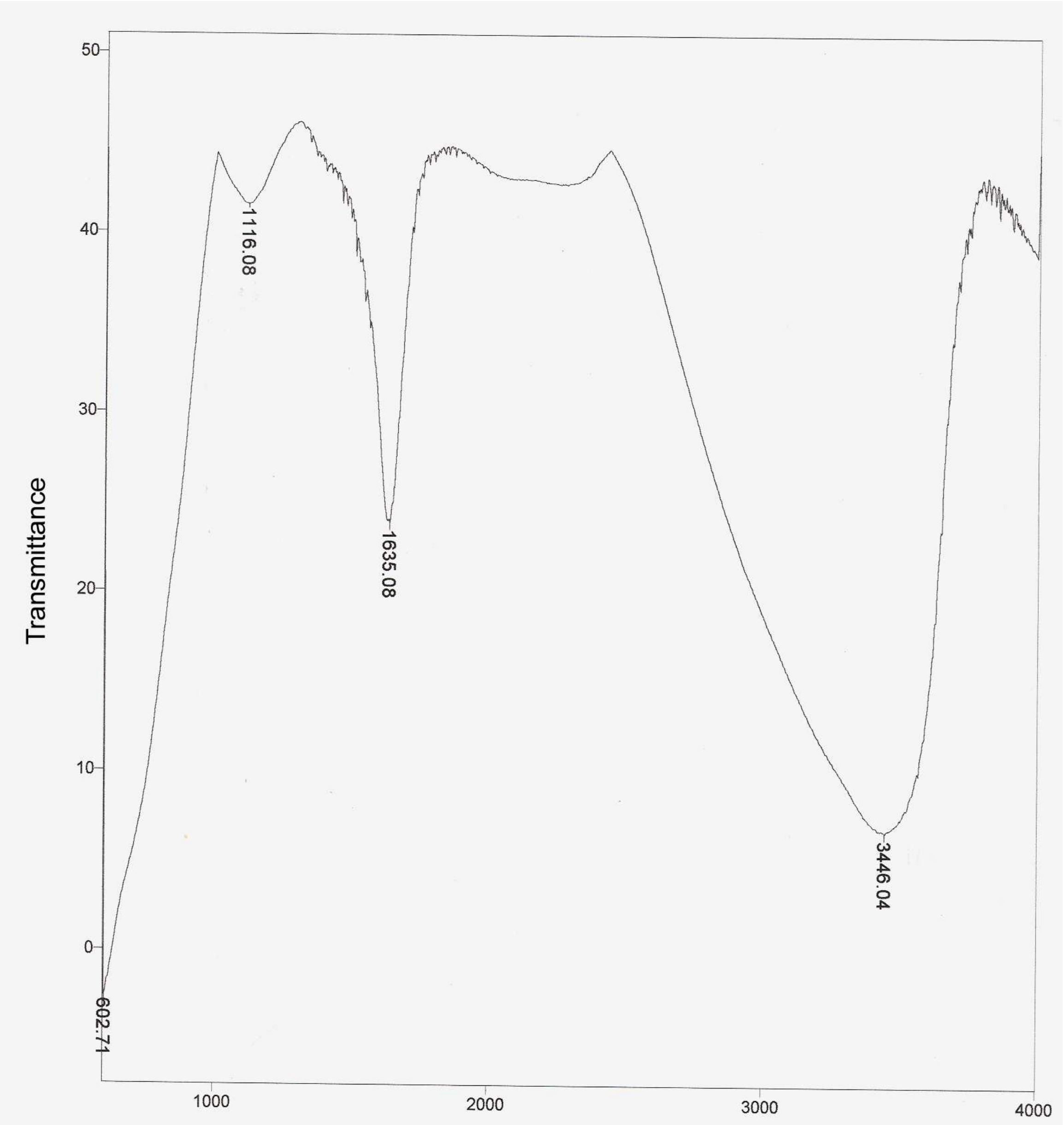
Potential measurements were made for different concentrations of the same electrolyte on two sides of the membrane in such a way that the concentration ratio δ (C_2/C_l) =10. The potential difference developed across the membrane was measured against reference electrodes on either side of the membrane using a digital potentiometer. The electrode chambers were rinsed with the electrolyte solution of next higher concentrations and then filled with the same solution. The membrane was allowed to equilibrate for 2 hours and a new potential difference was then noted.

Membrane potentials across the zirconium antimonoarsenate membrane were determined using 1:1 electrolytes such as lithium chloride, sodium chloride and potassium chloride and some 2:1 electrolytes such as magnesium chloride, calcium chloride, strontium chloride and barium chloride in an overall concentration range of 0.001 M to 0.5 M.

RESULT AND DISCUSSION

It is clear from Table 3.2.1 that five batches of zirconium (IV) antimonoarsenate (ZrSbAs) prepared under identical conditions show negligible variations in the ion-exchange capacity. Therefore, ZrSbAs is a reproducible material having an ion-exchange capacity of 0.40 meq/g for Na^+ ions. It can be regenerated and used over and over again. Even after five regenerations, the ion exchanger loses 35% of its original capacity.

IR spectrum of the exchanger in H^+-form indicates the presence of external water molecules in addition to the –OH groups and metal oxides, present internally in the material. In the spectrum, the broad band at around 3500 cm^{-1} can be attributed to O-H stretching frequency. A medium band at around 1600 cm^{-1} can be attributed to H-O-H bending band, being also representative of strongly bonded –OH groups in the matrix [31]. Weak band at around 1100 cm^{-1} represents the presence of $(AsO_4)^{3-}$ group in the material.



Wave number (cm^{-1})

Figure 3.2.1: IR spectrum of ZrSbAs

Results of the chemical analysis of the exchanger suggest the mole ratio of Zr:Sb:As as 16:11:1 . Based on this, following empirical formula can be suggested for the compound:

$$\mathbf{[(ZrO_2)_{16}\ (H_3SbO_4)_{11}\ (H_3\ AsO_4)]\cdot\ nH_2O}$$

The number of water molecules ‘n’ can be estimated from the percentage loss of the weight of the exchanger up to 200º C assuming that all the external water molecules are lost at this temperature. ZrSbAs experiences a weight loss of 12.5% up to a temperature of 200º C. Loss of weight beyond this temperature is not considered because that could be due to an irreversible condensation of the acidic groups. With this much information, the number of external water molecules can be found out by using the Alberti Formula [24], i.e.,

$$18n = X\ (M+ 18n)/100 \qquad \ldots\ldots\ldots\ldots(3.3)$$

Where, X is percentage weight loss of the exchanger at 200º C, M is molecular weight of the exchanger without water molecules and n is number of external water molecules.

Using this formula, the number of water molecules comes to be 33.25. So, a tentative molecular formula for the exchanger can be written as:

$$\mathbf{[(ZrO_2)_{16}\ (H_3SbO_4)_{11}\ (H_3AsO_4)]\cdot\ 33H_2O}$$

X-ray powder diffraction studies [Fig. 3.2.3] show no diffraction lines for the exchanger. It indicates an amorphous nature of the material.

SEM images of ZrSbAs show that its particles have a broad size range and an irregular form. Lack of clearly defined morphology speaks for its low crystallanity. Presence of linearly layered structure is also evidenced from the micrograph.

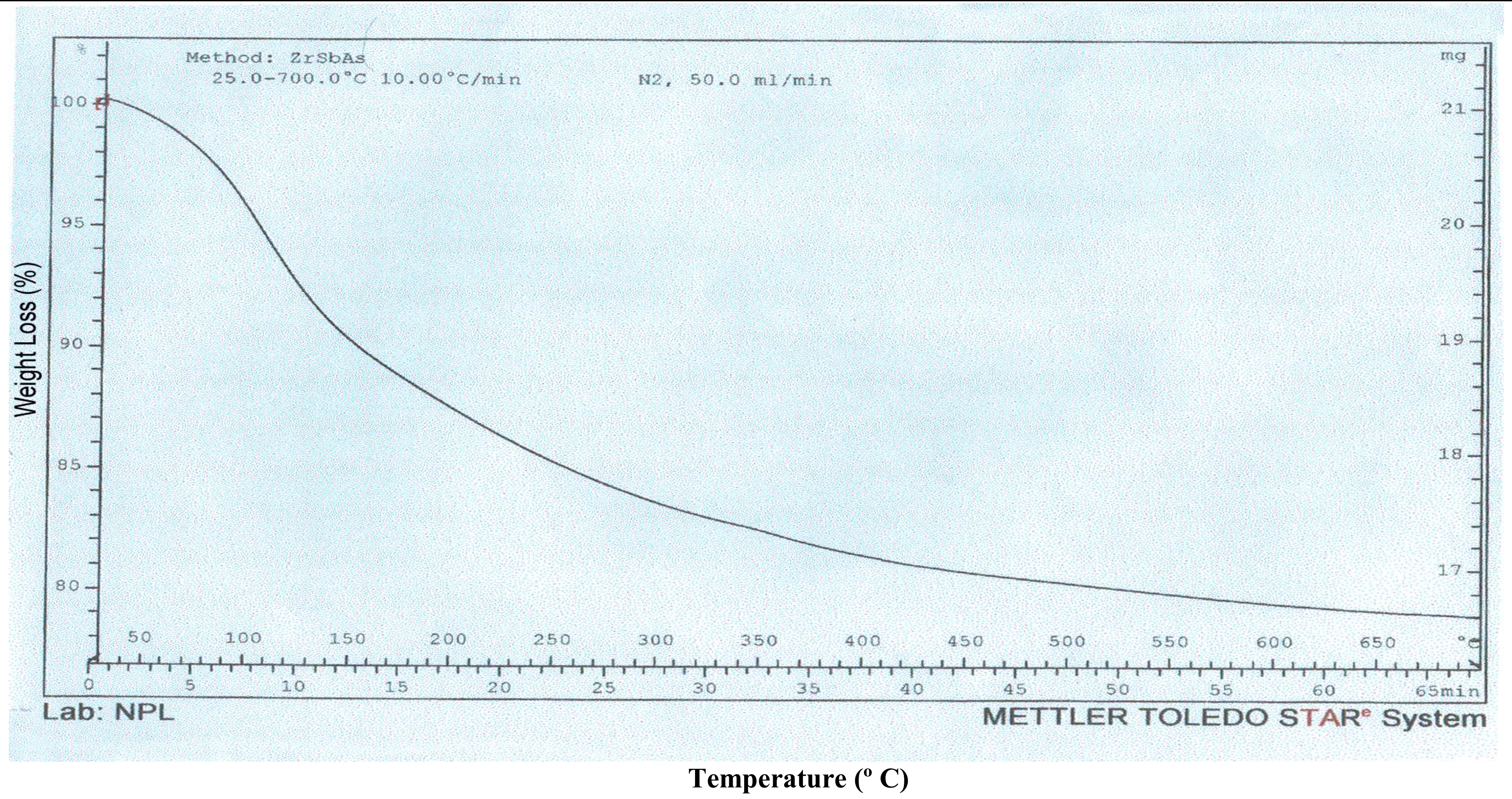


Figure 3.2.2: TGA curve of ZrSbAs

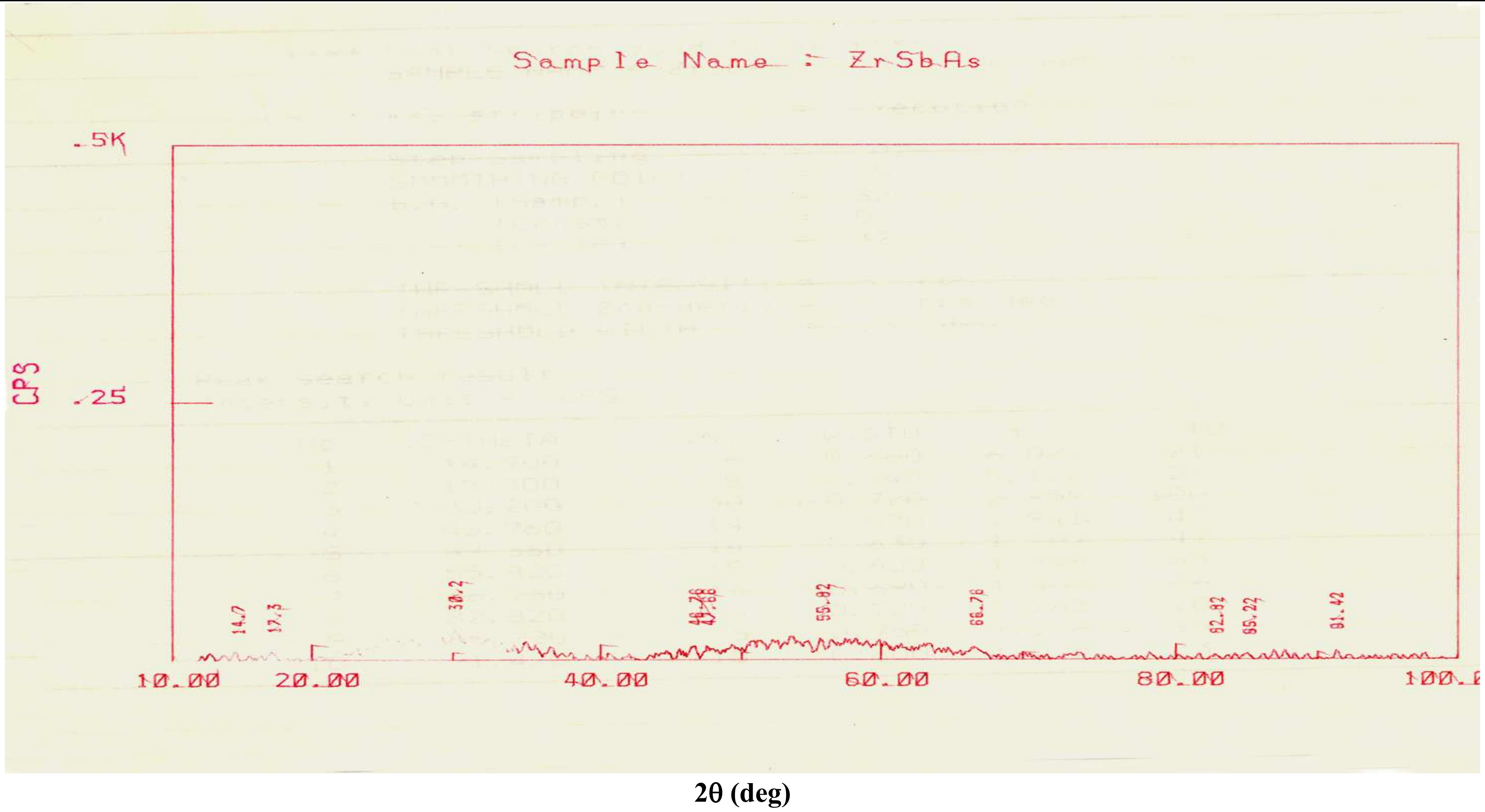


Figure 3.2.3: X–ray diffraction pattern of ZrSbAs

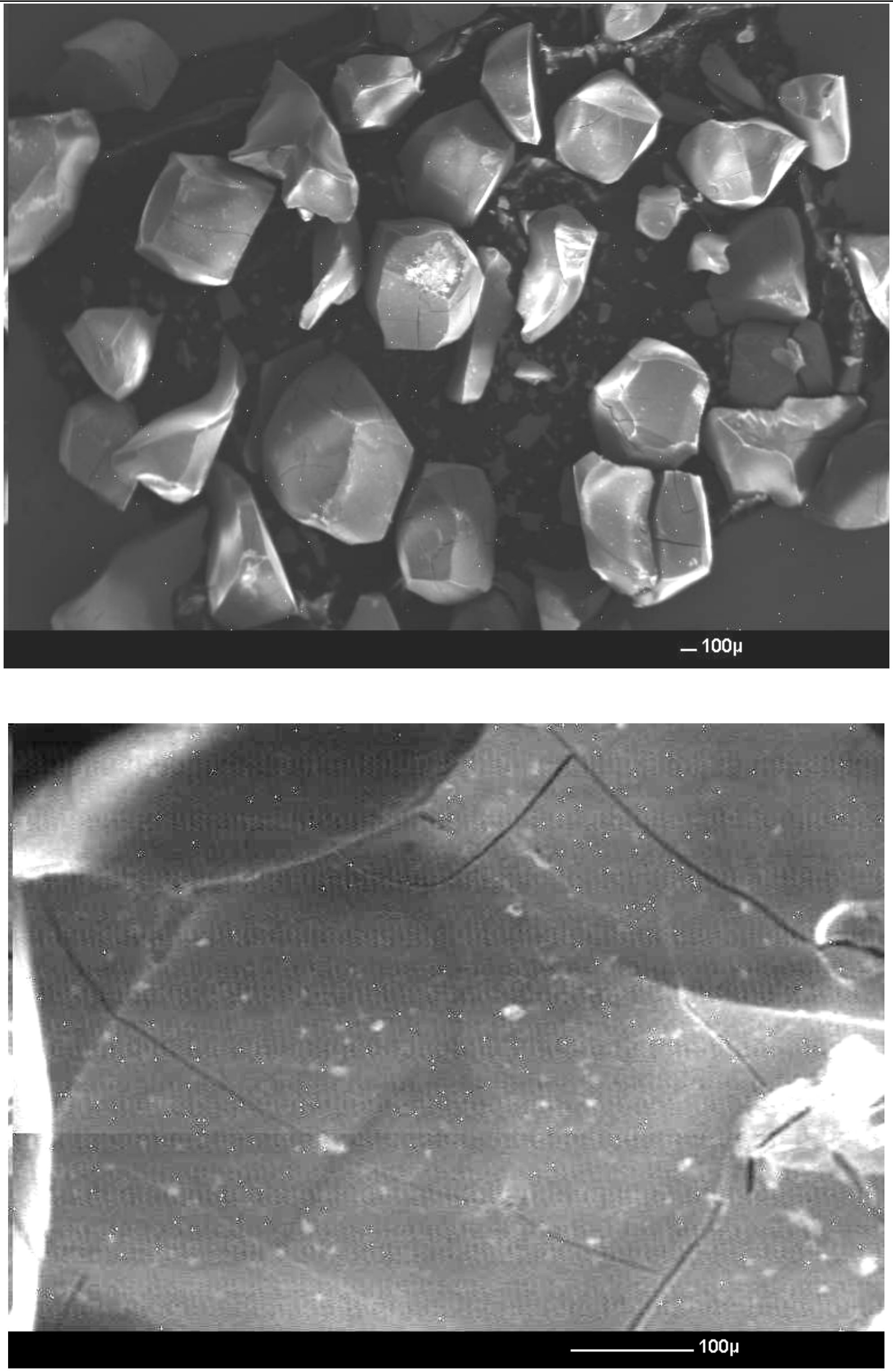


Figure 3.2.4: SEM images of a sample of ZrSbAs

Sorption studies show that ZrSbAs has a maximum selectivity for Ce^{3+} ions over other rare earth metal ions [Table 3.2.2]. Zirconium (IV) antimonoarsenate has been used as an electro-active component in preparation of the heterogeneous solid-state electrode sensitive to Ce^{3+} ions. Detailed studies on the electrode performance are reported in Chapter 5.1. The response of the electrode does not show much interference from alkali, alkaline earth, transition metal and other rare earth metal ions normally present along with cerium (III). It is workable in partially non-aqueous medium as well and has been used as an indicator electrode in titrations of Ce^{3+} ions against oxalic acid.

Electrochemical Studies

Membrane Potentials

A membrane separating electrolyte solutions of unequal concentrations exhibits a difference in electrical potential due to unequal ionic mobilities and is equal to the liquid junction potential in a non-selective membrane. In an ideally selective membrane, according to the TMS theory [33], membrane potential values are related to activities of the electrolyte on two sides of the membrane, a_1 and a_2:

$$\Delta\phi = 2.303\frac{RT}{F}(2\bar{t}_{+}-1)\log\frac{a_2}{a_1} \qquad \text{………… (3.4)}$$

Where, '$\Delta\phi$' is membrane potential across the membrane. The maximum electric potential is given by:

$$[(\Delta\phi)_{t=0}]_{\max} = \frac{RT}{nF}\ln\frac{a_2}{a_1} \qquad \text{………… (3.5)}$$

provided the solutions are dilute. $\Delta\phi$ varies with change in mean concentration of the electrolyte.

From Table 3.2.4, it is evident that higher membrane potentials are observed at lower concentrations of 1:1 and 2:1 electrolytes and the membrane potentials decrease with increase in concentration of the electrolyte. For 1:1 electrolytes, membrane potentials are in the order,

$$\mathbf{Li^+ > K^+ > Na^+}$$

This order of the membrane potentials prevails over the entire concentration range. Magnitude of the membrane potential depends on:

1. Diffusion potential across the membrane.
2. Size of the cation.
3. Exchangeability of the cation.

Transport Numbers

Transport numbers $\bar{t}_+$ in exchanger phase are calculated from the slope of the equation (3.4). Transport numbers and permselectivity values for 1:1 and 2:1 electrolytes are given in Table 3.2.5 and Table 3.2.6, respectively. It is observed that the transport numbers decrease with increase in concentration for all the electrolytes.

This is in accordance with the fact that with increase in concentration of the electrolyte, Donnan exclusion of the co-ions becomes less efficient resulting in a decrease in the transport number of the counter ion. This phenomenon supports the hypothesis that ion-exchange membranes behave in a selective manner and thus, the permselectivity [P_s] values decrease with increase in the mean electrolyte concentration [Table 3.2.6].

The electrical character of a membrane is expressed in terms of its fixed charge density. A fixed charge density of the zirconium (IV) antimonoarsenate membrane for 1:1 electrolytes has been evaluated by using Kobatake's equation [34] (Table 3.2.7).

Table 3.2.4: Membrane potential values of 1:1 and 2:1 electrolytes for zirconium (IV) antimonoarsenate membrane

Concentration of Electrolyte (M)	Membrane Potential (mV)						
	LiCl	NaCl	KCl	$MgCl_2$	$CaCl_2$	$SrCl_2$	$BaCl_2$
0.001-0.01	39	33	35	38	41	38	31
0.002-0.02	37	31	34	36	40	36	30
0.003-0.03	36	30	33	35	40	35	28
0.004-0.04	36	29	32	35	39	34	28
0.005-0.05	34	28	32	34	38	34	27
0.01-0.1	39	27	30	38	38	41	37
0.02-0.2	36	22	24	32	35	38	32
0.03-0.3	34	20	23	28	34	36	29
0.04-0.4	33	19	21	26	31	35	26
0.05-0.5	31	17	19	24	30	34	24

Table 3.2.5: Transport number ($\bar{t}_{+}$) at mean concentration for some 1:1 and 2:1 electrolytes for zirconium (IV) antimonoarsenate

Mean Concentration of Electrolyte	**1: 1 Electrolytes**			**2: 1 Electrolytes**			
(M)	**LiCl**	**NaCl**	**KCl**	**$MgCl_2$**	**$CaCl_2$**	**$SrCl_2$**	**$BaCl_2$**
0.0055	0.83	0.78	0.80	0.82	0.85	0.82	0.76
0.011	0.81	0.76	0.79	0.80	0.84	0.80	0.75
0.0165	0.80	0.75	0.78	0.80	0.84	0.80	0.74
0.022	0.80	0.75	0.77	0.80	0.83	0.79	0.74
0.0275	0.79	0.74	0.77	0.79	0.82	0.79	0.73
0.055	0.83	0.73	0.75	0.82	0.82	0.85	0.81
0.11	0.80	0.69	0.70	0.77	0.80	0.82	0.77
0.165	0.79	0.67	0.69	0.74	0.79	0.80	0.75
0.22	0.78	0.66	0.68	0.72	0.76	0.80	0.72
0.275	0.76	0.64	0.66	0.70	0.75	0.79	0.70

Table 3.2.6: Permselectivity values (P_s) at mean concentration for some 1:1 and 2:1 electrolytes for zirconium (IV) antimonoarsenate

Mean Concentration of Electrolyte	**1: 1 Electrolytes**			**2: 1 Electrolytes**	
(M)	**LiCl**	**NaCl**	**KCl**	**$MgCl_2$**	**$BaCl_2$**
0.0055	0.76	0.64	0.61	0.71	0.42
0.011	0.72	0.61	0.59	0.68	0.40
0.0165	0.71	0.59	0.57	0.68	0.38
0.022	0.71	0.59	0.51	0.68	0.38
0.0275	0.69	0.57	0.55	0.67	0.36
0.055	0.68	0.56	0.51	0.71	0.55
0.11	0.72	0.52	0.47	0.63	0.45
0.165	0.71	0.49	0.43	0.59	0.40
0.22	0.68	0.44	0.37	0.56	0.33
0.275	0.65	0.41	0.33	0.52	0.29

When a negatively charged membrane separates solutions of 1:1 electrolyte of different concentrations, the membrane potential is given by:

$$E_m = -\frac{RT}{F}\left[\frac{1}{\beta}\ln\frac{C_2}{C_1} - \left(1+\frac{1}{\beta}-2\alpha\right)\ln\frac{C_2+\alpha\beta\overline{X}}{C_1+\alpha\beta\overline{X}}\right] \qquad \text{………… (3.6)}$$

Where, $\alpha = \frac{u}{u+v}$ and $\beta = 1+\frac{KF\overline{X}}{u}$

E_m = membrane potential difference
u & v = molar mobilities of cation & anion respectively
K = constant depending on the solution viscosity
$\overline{X}$ = fixed charge density
F = Faraday constant

In order to evaluate α, β and $\overline{X}$, Kobatake has derived two useful limiting forms [a] and [b] of equation [3.6]

a) when $C_2 << \delta$ equation [3.6] may be written as:

$$\left|E_m^{\sigma}\right| = \frac{1}{\beta}\ln\delta - \left(\frac{\delta-1}{\alpha\beta\delta}\right)\left(1+\frac{1}{\beta}-2\alpha\right)\frac{C_2}{\overline{X}} \qquad \text{………… (3.6a)}$$

Where, $\left|E_m^{\sigma}\right|$ = absolute value of membrane potential given by $\left|E_m^{\sigma}\right| = FE_m/RT$ and $\delta = C_2/C_1$

from the plots of $\left|E_m^{\sigma}\right|$ vs. C_2 in low concentration region, a straight line with an intercept equal to *1/β in δ* is obtained [Fig. 3.2.5]. Thus, *β* can be evaluated.

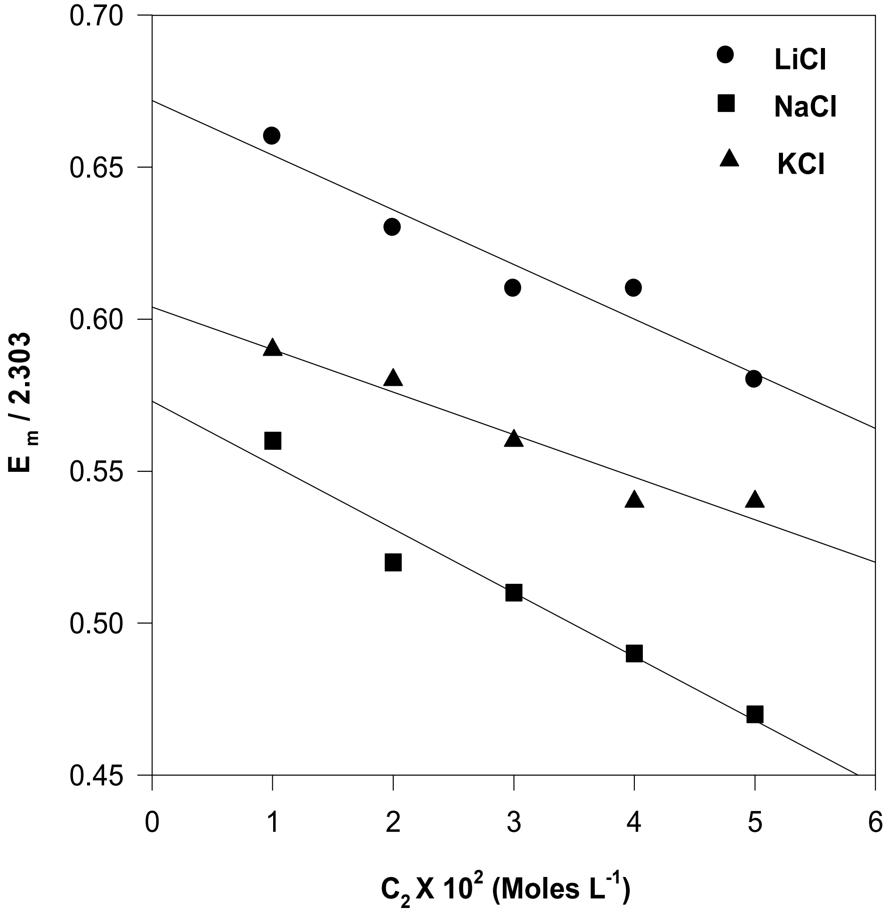


Figure 3.2.5: Plots of $\left|E_m^{\sigma}\right|$ / 2.303 vs. C_2 x 10^2

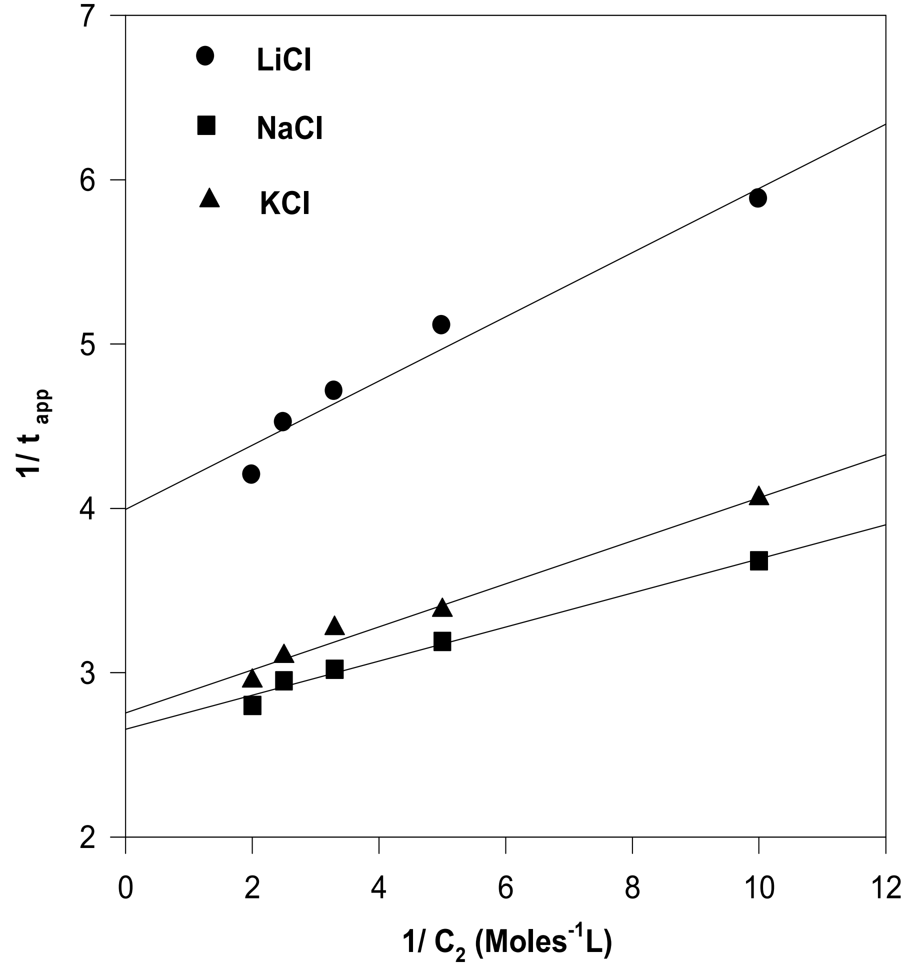


Figure 3.2.6: Plots of $1/\bar{t}_{-app}$ vs. $1/C_2$

b) At a fixed δ, inverse of the apparent transport number ($\bar{t}_{-app}$) for a co-ion species in a negatively charged membrane, varies linearly with inverse of the concentration C_2 at higher electrolyte concentrations, where $\bar{t}_{-app}$ is defined as:

$$\left|E_m^\sigma\right| = \left(1 - 2\bar{t}_{-app}\right)\ln\delta \qquad \text{………… (3.7)}$$

Substitution for $\left|E_m^\sigma\right|$ in equation [3.6] and expanding resultant expression for $1/\bar{t}_{-app}$ in powers of $1/C_2$ gives

$$\frac{1}{\bar{t}_{-app}} = \frac{1}{1-\alpha} + \frac{(1+\beta-2\alpha\beta)(\delta-1)\alpha}{2(1-\alpha)^2\ln\delta}\left(\frac{\bar{X}}{C_2}\right) \qquad \text{………… (3.6b)}$$

From equation [3.6b], it is clear that a plot of $1/\bar{t}_{-app}$ vs. $1/C_2$ [Fig. 3.2.6] at a fixed δ value should be a straight line with an intercept equal to *1/ (1-α)*, from where α can be evaluated.

For determining the fixed charge density $\bar{X}$ in dilute concentration range, the value of the slope determined from $\left|E_m^\sigma\right|$ vs. C_2 plots was equated with the slope of equation (3.6a), α and β being known earlier, $\bar{X}$ can be calculated.

$$slope = \frac{\delta-1}{\alpha\beta\delta}\left(1+\frac{1}{\beta}-2\alpha\right)\frac{1}{\bar{X}} \qquad \text{………… (3.8)}$$

Table 3.2.7: Values of parameters α, β, & $\bar{X}$ for zirconium (IV) antimonoarsenate membrane at δ = 10

Electrolyte	**α**	**β**	$\bar{X}$
LiCl	0.75	1.49	0.0332
NaCl	0.62	1.75	0.0568
KCl	0.64	1.66	0.0847

It is observed that $\bar{t}_{-app}$ decreases with an increase in mean concentration of the electrolyte. The dependence of $\bar{t}_{-app}$ on concentration of the electrolyte is just like that of the membrane potential dependence on concentration. These membrane-permeant interactions are an index of crystalline morphology [35], being more in amorphous and less in crystalline membranes. Low values indicate a lower degree of crystallinity of the exchanger material.

Observed values (Table 3.2.7) of the fixed charge density $\overline{X}$ are much lower than those expected from the fixed charge concentration of the exchanger. It indicates that a larger part of the internal fixed charges remains inactive. It may be due to the reason that the active fixed charges in these membranes are essentially those of the external surface of the grains. Due to the small grain size of the well ground exchanger powder [<250 mesh], free intergranular spaces are also very small, so that Donnan Salt Exclusion could take place. Thus, the electrical character of the membrane is established.

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CHAPTER – 4

SAMARIUM (III)-SELECTIVE ELECTRODES

ABSTRACT

Samarium (III)-selective electrodes have been prepared using zirconium (IV) boratophosphate (ZrBP) and tin (IV) boratophosphate (SnBP) as electro-active materials and epoxy resin, PVC, polystyrene as binding materials. In case of ZrBP, best performance is exhibited by a membrane having a composition: zirconium boratophosphate (10%) and poly vinylchloride (90%). This membrane works well over a wide concentration range of $1x10^{-5}$ M to $1x10^{-1}$ M of Sm (III) ions with a near-Nernstian slope of 20.2 mV/decade. Response time of the sensor is 15 seconds. In case of SnBP as an electro-active material, a membrane having a composition: exchanger (40%) and epoxy resin (60%), exhibits the best performance. This membrane works well over a wide concentration range of $1x10^{-5}$ M to $1x10^{-1}$ M of samarium ions with a super-Nernstian slope of 40.0 mV/decade. It has a fast response time of less than 10 seconds. For this membrane, the effect of internal solution has been studied and the electrode was successfully used in partially non-aqueous media, too. Selectivity coefficients have been determined by FIM, with respect to alkali, alkaline earth, some transition and rare earth metal ions that are normally present along with samarium in its ores. The electrodes can be used in the pH range 4.0-9.0. These sensors have been used as indicator electrodes in potentiometric titrations of Sm (III) ions against EDTA.

INTRODUCTION

Lanthanides are elements of rapidly growing importance. These are widely distributed in low concentrations throughout the earth's crust [1]. Samarium is an important member of this family. It is used as gasoline cracking catalyst, polishing compound and in the iron and steel industries to remove sulfur, carbon or other electronegative elements [2]. It is one of the rare chemicals, which can be found in houses in equipment such as color televisions, fluorescent lamps, energy-saving lamps and glasses. Samarium is mostly dangerous in the working environment due to the fact that its damps and gases can be inhaled with air. This can cause lung embolisms, especially during long-term exposure. Samarium can be a threat to the liver when it accumulates in human body. With water animals samarium causes damage to cell membranes, which has several negative influences on reproduction and on functions of the nervous system. Hence, it is very important to devise methods for its low level determination.

Available methods for low-level determination of rare earth ions in solutions include spectrophotometry [3], ICP-AES [4], isotope dilution mass spectrometry [5], neutron activation analysis [6], X-ray fluorescence spectrometry [7], etc. These methods are either time consuming, involve multiple sample manipulations or too expensive for most of the analytical laboratories.

Potentiometric sensors can offer an inexpensive and convenient method for analysis of rare earth metal ions in solutions. In spite of successful progress in design of highly selective membrane electrodes, there are only a few reports on selective electrodes for the rare earth metal ions. Ion-selective liquid membrane electrodes containing chelate ligand complexes, like crown ethers and their open chain analogs entrapped in polymer, suffer from the problem of leaching of the electro-active component and plasticizer from the polymer matrix into the sample solutions [8].

Inorganic ion-exchange membranes have several advantages over the organic ion exchangers, e.g. their ability to withstand ionizing radiations and high temperature without undergoing degradation and their remarkably high selectivity [9]. Ion-selective electrodes employing inorganic ion exchanger as ion sensors have been reviewed by Arnold and Solsky [10] and Buck [11]. It has been established that hydrous oxides combined with anions, such as phosphates, vanadates, molybdates and antimonates, produce superior ion exchangers [12-15]

Literature survey shows that there are only a few reports on samarium-selective electrodes. Samarium (III)-selective electrodes were prepared by Chowdhury et al. [16, 17] and Ganjali et al. [18] using neutral bis (thiaalkylxanthato) alkanes and glipizid as electro-active materials, respectively. But, all of these electrodes are based on organic ion exchangers. Therefore, it was interesting to use inorganic ion exchangers as electro-active materials for our studies.

Zirconium (IV) boratophosphate prepared by Thind et al. [19] was used for quantitative separation of some lanthanide elements, the exchanger showing greater selectivity for samarium. Encouraged by this, this exchanger was used as an electro-active material for preparation of a samarium (III)-selective electrode. Interestingly, tin (IV) analogue of this exchanger, prepared during this study, also showed selectivity for samarium (III) and was accordingly used for the preparation of another samarium (III)-selective electrode.

EXPERIMENTAL

Reagents

Zirconium (IV) oxychloride, tin (IV) chloride, boric acid, phosphoric acid needed for the preparation of zirconium (IV) boratophosphate [ZrBP] and tin (IV) boratophosphate [SnBP] were procured from s.d.fine chem. Ltd., India. Samarium (III) chloride (AR) and other rare earth chlorides needed for preparing the stock solutions were purchased from Indian Rare Earth Chemicals Ltd., India. All other chemicals were of analytical grade and hence, used as such. All rare earth metal ion solutions were standardized against EDTA solution using xylenol orange as an indicator. Double distilled deionised water was used throughout the experiments.

Instruments

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

Synthesis of Electro-Active Materials

Synthesis of Zirconium (IV) boratophosphate (ZrBP)

Zirconium (IV) boratophosphate was prepared by adding zirconyl oxychloride (0.1 M) (containing hydrofluoric acid, 12 mL/L) to a continuously stirred equimolar mixture of boric acid and phosphoric acid solutions at 60º C in a volume ratio of 2: 1: 1. Gelatinous white precipitates are obtained and pH of the gel is adjusted to 1.0 by adding either HCI or NaOH solution. Precipitates were filtered, washed (until free from halides and phosphates) and then dried at 40º C. Dried product broke down into small granules when immersed in water. The material was converted into H^+-form by keeping it in HCI (0.1 M) for 24 hours with intermittent changing the acid and finally dried at 40º C. The product was washed with DMW in order to remove excess acid.

Synthesis of Tin (IV) boratophosphate (SnBP)

Tin (IV) boratophosphate (SnBP) was prepared as described in Chapter 3.1.

Preparation of Membranes

A number of membranes were prepared using varying amounts of different binding materials such as an epoxy resin, PVC in THF solvent and polystyrene. ZrBP and SnBP in H^+-form are used as electro-active materials during preparation of the membranes.

Preparation of Epoxy Resin Based Membranes

Desired amount of finely powdered exchangers were mixed thoroughly with an epoxy resin in varying amounts (w/w) to make a near homogeneous paste, which was then spread between the folds of a butter paper. Glass plates were kept below and above the paper folds as supports. A pressure of 2.0 kg/cm^2 was applied over the glass plates for 24 hours and left to dry. The sheet of dried membrane thus obtained was then dipped in distilled water to remove paper from the membrane surface.

Preparation of PVC Membranes

PVC dissolved in THF solvent was mixed thoroughly with a desired weight of finely ground exchanger at room temperature. Mixture was stirred continuously till homogeneous slurry was obtained. The slurry was spread between folds of a filter paper and dried in air and membranes of 0.2 mm thickness were obtained. Dried membranes were dipped in distilled water to remove the paper and again dried at room temperature.

Preparation of Polystyrene Based Membranes

A desired amount of finely ground exchanger was mixed thoroughly with powdered polystyrene and the mixture was heated at ≈ 100° C for 6 hours under pressure (2000 lb/in^2) in the polymer film making equipment. The membrane was removed after cooling the equipment to room temperature.

Membranes obtained by various methods were cut in the shape of discs of about 2.0 cm diameters using a sharp blade and those of good surface qualities were selected for further investigations.

EMF Measurements

Membranes were fixed to one end of the glass tube of 1.8 cm (internal diameter) using an epoxy resin as adhesive. These electrodes were then equilibrated with Sm^{3+} ion solution (0.1 M) for 24 hours. The tube was filled 3/4th with Sm^{3+} solution (0.1 M) and immersed in a beaker containing test solutions of varying concentrations. All emf measurements were carried out using the following cell assembly:

$Hg\text{-}Hg_2Cl_2(s)$, KCl (Sat.) |0.1 M Sm^{3+} || membrane || test solution | KCl (Sat.), $Hg_2Cl_2\text{-}Hg$

A digital potentiometer (Equiptronics EQ-602, India) was used for the potential measurements at 25±0.1° C. Activities were calculated according to Debye-Huckel equation [20]. Test solutions were obtained by gradual dilution of Sm^{3+} solution (0.1M) and their potential measurements were made in unbuffered solutions.

RESULTS AND DISCUSSIONS

Optimization of Membrane Composition

The effect of membrane composition on the response of the electrodes was studied. For this purpose, performance parameters, like slope of the calibration curve, measurement range and response time, were compared for prepared electrodes. Results are given in Table 4.1 and Table 4.2.

Results show that the ZrBP electrode with ZrBP (10%) and PVC (90%) membrane composition exhibits the best performance with a slope of 20.2 mV/decade. It is seen that the nature and amount of the binding material hardly has any effect on the response of the SnBP electrode. All the electrodes showed super-Nernstian slope in the range of 40 – 42 mV per decade and the response is linear in the range $1x10^{-5}$ M to $1x10^{-1}$ M. Electrodes Sm-3(Z) and Sm-6(S) were selected for further studies for ZrBP and SnBP as electro-active materials, respectively, because of the fast response and wide concentration ranges.

Calibration Curve and Statistical Data

Potential measurements were made on the selected electrodes for different concentrations of Sm (III) ion solutions. EMFs were plotted against log of activities of samarium ions. Experiments were repeated five times to check the reproducibility of the electrode system. Standard deviations of ±1.0 mV (for ZrBP-based electrode) and ±0.9 mV (for SnBP-based electrode) were observed. Representative calibration curves are shown in Fig. 4.1 and Fig. 4.2, respectively. Amounts of the electro-active components (the ion exchangers) were varied as shown in Table 4.1 and Table 4.2.

Table 4.1: Optimization of membrane ingredients for ZrBP based membranes

Electrode No.	Amount of ZrBP (w/w %)	Binder	Slope (mV/decade)	Measuring Range (M)	Response Time (s)
Sm-1 (Z)	6	PVC	22.5	$1.0x10^{-4}-10^{-1}$	20
Sm-2 (Z)	8	PVC	9.9	$5.0x10^{-5}-10^{-1}$	15
Sm-3 (Z)	**10**	**PVC**	**20.2**	**$1.0x10^{-5}-10^{-1}$**	**15**
Sm-4 (Z)	12	PVC	17.1	$5.0x10^{-5}-10^{-1}$	20
Sm-5 (Z)	35	Epoxy resin	24.4	$1.0x10^{-4}-10^{-1}$	15
Sm-6 (Z)	50	Epoxy resin	19.1	$5.0x10^{-4}-10^{-1}$	12
Sm-7 (Z)	50	Polystyrene	14.4	$5.0x10^{-4}-10^{-1}$	20

Table 4.2: Optimization of membrane ingredients for SnBP based membranes

Electrode No.	Amount of SnBP (w/w %)	Binder	Slope (mV/decade)	Measuring Range (M)	Response Time (s)
Sm-1 (S)	30	PVC in THF	40	$2.0x10^{-5}-10^{-1}$	20
Sm-2 (S)	40	PVC in THF	42	$2.0x10^{-5}-10^{-1}$	20
Sm-3 (S)	10	Epoxy resin	40	$1.0x10^{-5}-10^{-1}$	15
Sm-4 (S)	20	Epoxy resin	40	$2.5x10^{-5}-10^{-1}$	15
Sm-5 (S)	30	Epoxy resin	42	$1.0x10^{-5}-10^{-1}$	15
Sm-6 (S)	**40**	**Epoxy resin**	**40**	**$1.0x10^{-5}-10^{-1}$**	**10**
Sm-7 (Z)	40	Polystyrene	42	$2.0x10^{-5}-10^{-1}$	15

Membrane compositions, ZrBP:PVC as 10%:90% and SnBP:epoxy resin as 40%:60%, show linearity in a concentration range of 1.0 x10^{-5} M to 1.0 x 10^{-1} M with slopes of 20.2 and 40.0 mV/decade, respectively. Limit of detection (1x10^{-5} M) was calculated according to IUPAC recommendations [11, 21] from intersection of the two extrapolated linear portions of the curves.

The ZrBP based electrode showed a near-Nernstian response, whereas, the SnBP based electrode shows an over-Nernstian behavior. Over-Nernstian response in the electrodes of this kind is common [22, 23]. The higher slope may be due to the poor permeability and incomplete permselectivity of the membrane matrix for the samarium ions. Membranes of this type sometimes show permeability for anions [24] as well. This preference for anions in lower concentration regions may also be responsible for the non-Nernstian behavior of the electrode.

Another reason for the non-Nernstian behavior of the electrode may also be the possible discrepancy between the ion activities in bulk and at the phase boundary, i.e. the uptake of the ions by the membranes results in a depletion zone of the analyte ions from the Nernst diffusion layer. This is supported by earlier reports of Jain et al. [22] and Malik et al. [23]. A super-Nernstian slope observed for Ag^+ and I^--selective electrodes have also been explained by Pungor et al. [25, 26]. A higher value of slope in no way hinders the determination of samarium (III) ions in the aqueous medium. The response time of the electrodes was less than 10-15 seconds. It is still lower for a relatively concentrated solution. The sensing behavior of the membranes remains unchanged when the potentials are measured either from low to high or high to low concentrations. These membranes could be used for at least six months without any measurable divergence. The electrodes were stored in Sm (III) ion solution (0.1 M) when not in use to avoid any change in the metal ion concentration in the membrane phase.

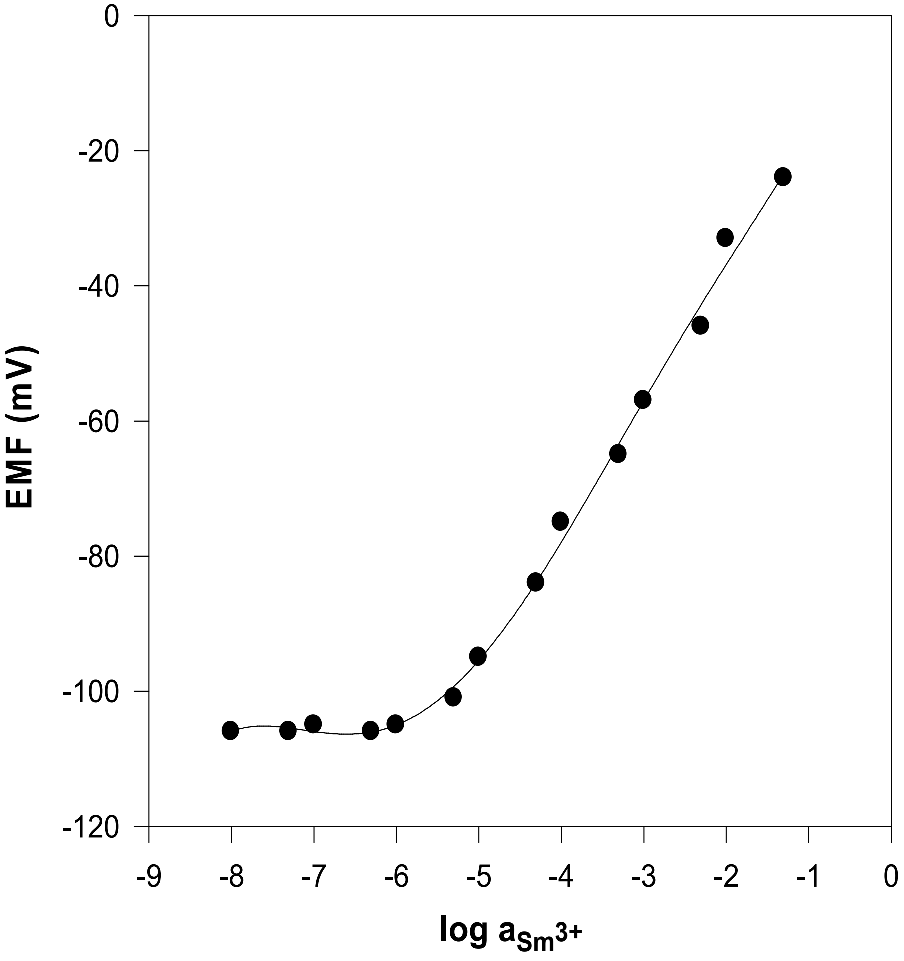

Figure 4.1: Calibration curve for Sm (III)-selective electrode based on ZrBP

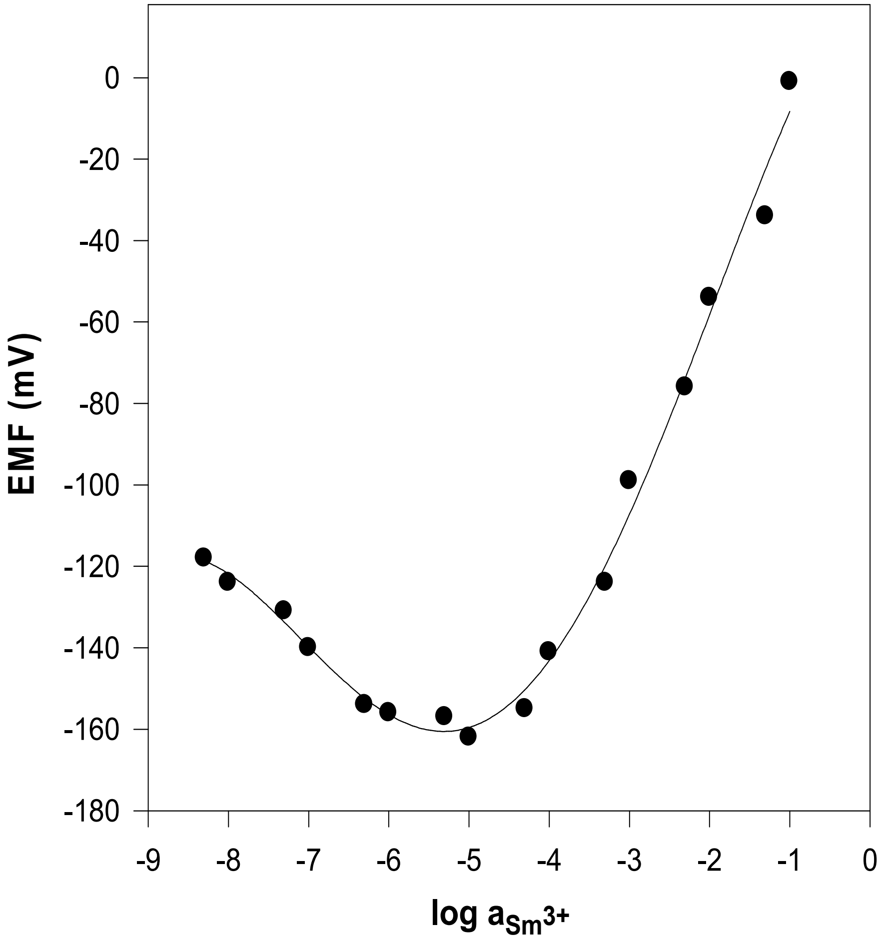

Figure 4.2: Calibration curve for Sm (III)-selective electrode based on SnBP

Effect of Internal Solution Concentration

The effect of internal solution on the response of the proposed sensor for Sm (III) ions was studied using 10^{-1} M to 10^{-3} M internal solution concentrations for SnBP based electrodes. Results are shown in Fig. 4.3. A variation in concentration of the internal solution does not have any significant effect on the response of the electrode except for an expected change in the intercept of the curves as observed by Ganjali et al. [18].

Effect of pH

The influence of pH on the potential response of the electrodes was studied using a Sm (III) concentration of 2×10^{-3} M for the ZrBP based electrode. The effect of pH of the primary ion solution on the SnBP based electrode response was studied for two concentrations (2×10^{-2} M and 2×10^{-3} M) of the Sm^{3+} ions. Experiments were conducted for a number of Sm^{3+} solutions, pH of which were adjusted between 2 to 12 by using suitable amounts of NaOH or HNO_3 solution.

Results are shown in Fig. 4.4 and Fig. 4.5. Emf is independent of pH in the range 6.0-10.0 and 6.0-9.0 for Sm (III) ions (2×10^{-3} M) for the ZrBP and SnBP based electrodes, respectively. For the SnBP based electrode, the workable pH range for 2×10^{-2} M Sm (III) ions concentration is 4.0 to 9.0. Thus, these ranges may be chosen as the working pH ranges for the electrode systems. Variation above and below this pH range may be due to the formation of $Sm(OH)_3$ and protonation of oxygen atoms of metal oxide or –P=O type groups in the exchangers, due to their tendency to hydrolyze at higher pH ranges.

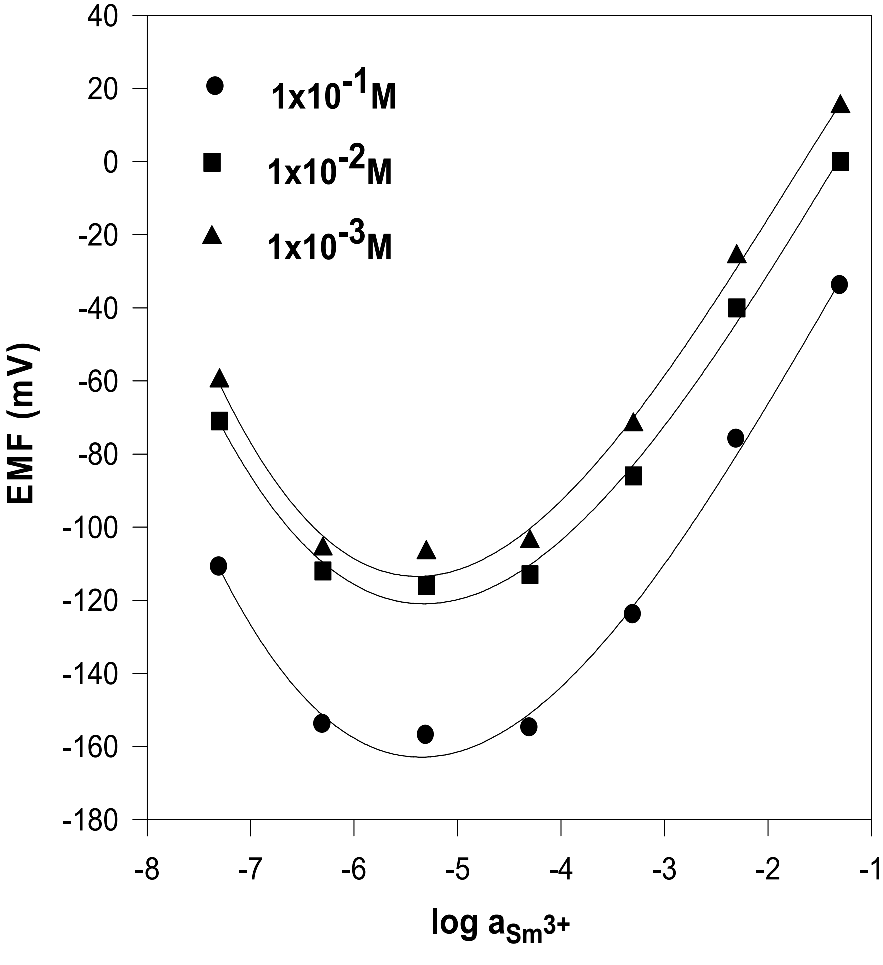

Figure 4.3: Effect of internal solution on response of the Sm (III)-selective electrode based on SnBP.

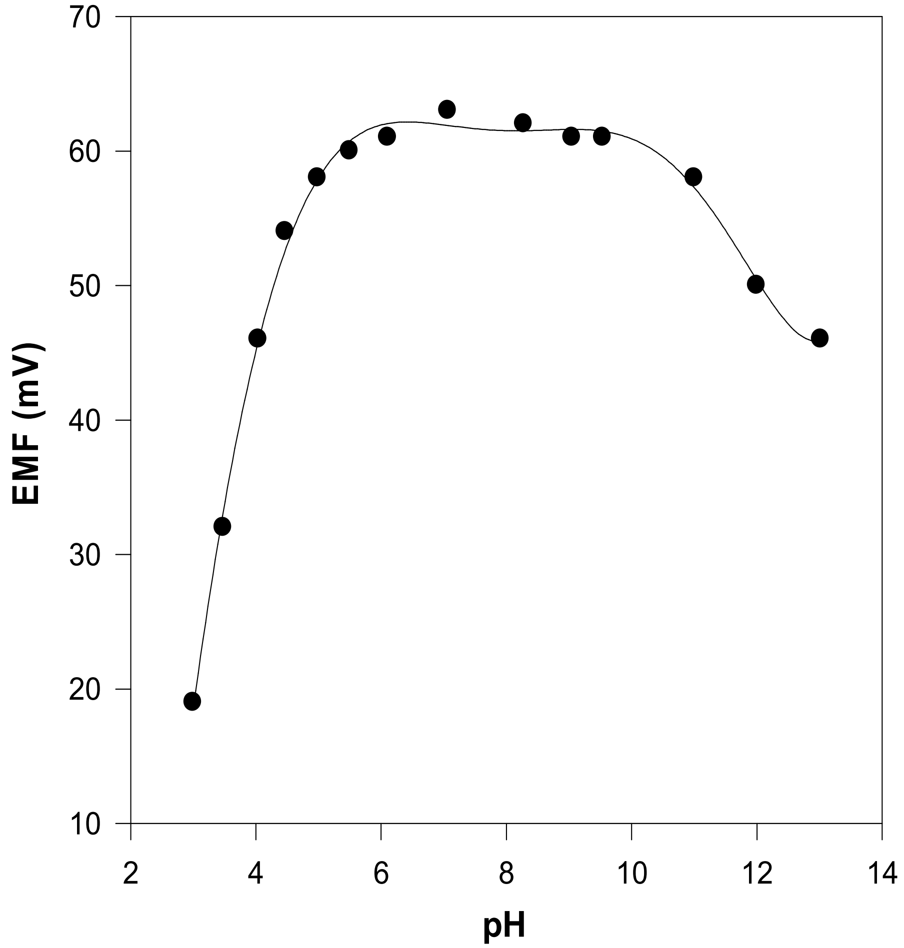

Figure 4.4: Effect of pH on the response of Sm (III)-selective electrode based on ZrBP

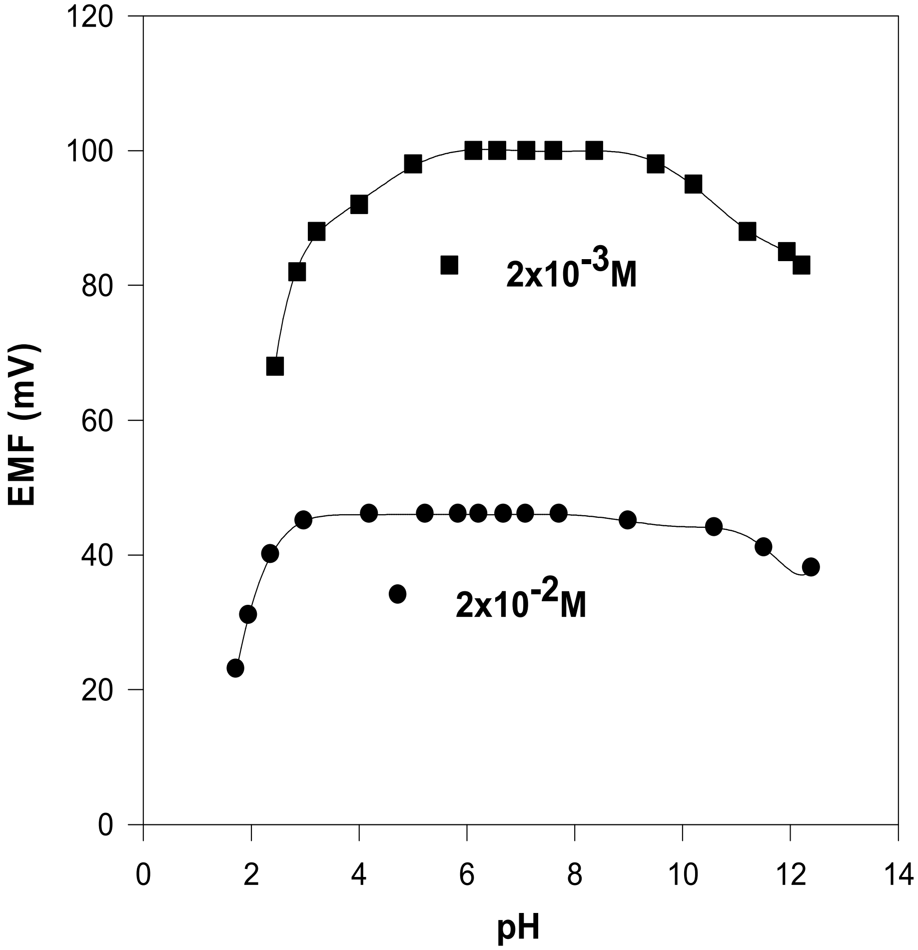

Figure 4.5: Effect of pH on the response of Sm (III)-selective electrode based on SnBP

Selectivity Coefficients and Analytical Properties of Sm (III)-selective Electrode

Selectivity is the single most important characteristic of any electrode which defines the nature of the device and extent to which it may be employed in the determination of a particular ion in presence of other interfering ions. Potentiometric selectivity coefficients of the samarium membrane electrode were evaluated by fixed interference method [FIM] [11, 21] at $1x10^{-3}$ M and $1x10^{-4}$ M interfering ion concentrations for the two electrodes. According to this method, a calibration curve is drawn for the varying primary ion concentration in a constant background of the interfering ion. The linear (i.e., Nernstian) response curve of the electrode is a function of the primary ion activity and is extrapolated until at the lower detection limit, it intersects with the observed potential for the background alone. The selectivity coefficient is calculated from these two extrapolated linear segments of the calibration curve,

$$K_{i,j}^{pot} = \frac{a_i}{a_j^{z_i/z_j}} \qquad \text{...........} \ (4.1)$$

Results are given in Table 4.3. It is obvious that the electrodes have a reasonably good selectivity with respect to other rare earth metal ions, considering the fact that all rare earths have identical sizes and properties. These electrodes also have a good selectivity over some common alkali, alkaline earth and transition metal ions. It is further obvious that, as the concentration of the interfering ion decreases, the selectivity of electrodes increases. Table 4.3 shows potentiometric selectivity coefficients of ZrBP and SnBP based sensors, respectively, in presence of interfering ions commonly present along with samarium in its common ores [27].

Table 4.3: Selectivity coefficient values for Sm (III)-selective electrodes based on ZrBP and SnBP as calculated by FIM method

Interfering ion (B)	**Selectivity Coefficient values** ($K_{A,B}^{Pot}$)			
	With ZrBP sensor		**With SnBP sensor**	
	At Interfering ion concentration		**At Interfering ion concentration**	
	10^{-3} M	**10^{-4} M**	**10^{-3} M**	**10^{-4} M**
La (III)	0.31	0.79	0.31	0.40
Ce (III)	0.25	0.31	0.25	0.31
Nd (III)	0.31	0.79	0.40	0.50
Eu (III)	0.40	0.50	0.40	0.50
Pr (III)	0.50	0.63	0.50	0.63
Tb (III)	0.25	0.31	0.32	0.40
Dy (III)	0.40	0.40	0.40	0.40
Y (III)	0.31	0.40	0.31	0.40
Fe (III)	0.25	0.31	0.25	0.25
Al (III)	0.31	0.79	0.10	0.31
Ca (II)	0.40	0.79	0.50	0.50
Na (I)	0.50	0.63	0.50	0.63

Effect of Partially Non-Aqueous Medium on the Working of Sm (III) Electrode

The proposed sensor based on SnBP was investigated in partially non-aqueous media using acetone, ethanol and acetonitrile mixtures with water. Table 4.4 indicates that the slope remains unaltered with the addition of non- aqueous solvents. Hence, the proposed sensor can be successfully used in partially non-aqueous medium. Plots of emf vs. activity of Sm (III) ions for partially non-aqueous media are shown in Fig. 4.6.

Potentiometric Titration

Potentiometric titrations were performed by using the proposed electrodes as indicator electrodes for titrations of Sm^{3+} (1.0 x 10^{-2} M) with EDTA solution (1.0x 10^{-1} M). Titration curves are shown in Fig. 4.7 and Fig. 4.8 for the ZrBP and SnBP based sensors, respectively. The curves show sharp inflexion points at the titrant volume corresponding to the formation of an 1:1 complex.

Life Time of Electrode

Life times of the electrodes are about six months, after which the electrodes become sluggish in response.

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Table 4.4: **Effect of partially non-aqueous media on the working of Sm (III)-selective electrode based on SnBP**

Solvent	Volume of solvent (v/v %)	Slope (mV/decade)	Measuring range(M)
Acetone	5	40.0	1.0x10^{-5} to 10^{-1}
	10	40.0	3.2x10^{-5} to 10^{-1}
	15	40.0	3.2x10^{-5} to 10^{-1}
	20	40.0	1.0x10^{-5} to 10^{-1}
Ethanol	5	40.2	1.0x10^{-5} to 10^{-1}
	10	40.1	2.0x10^{-5} to 10^{-1}
	15	40.0	1.0x10^{-5} to 10^{-1}
	20	40.2	4.3x10^{-5} to 10^{-1}
Acetonitrile	5	40.0	1.0x10^{-5} to 10^{-1}
	10	40.1	1.0x10^{-5} to 10^{-1}
	15	40.0	2.3x10^{-5} to 10^{-1}
	20	40.0	1.0x10^{-5} to 10^{-1}

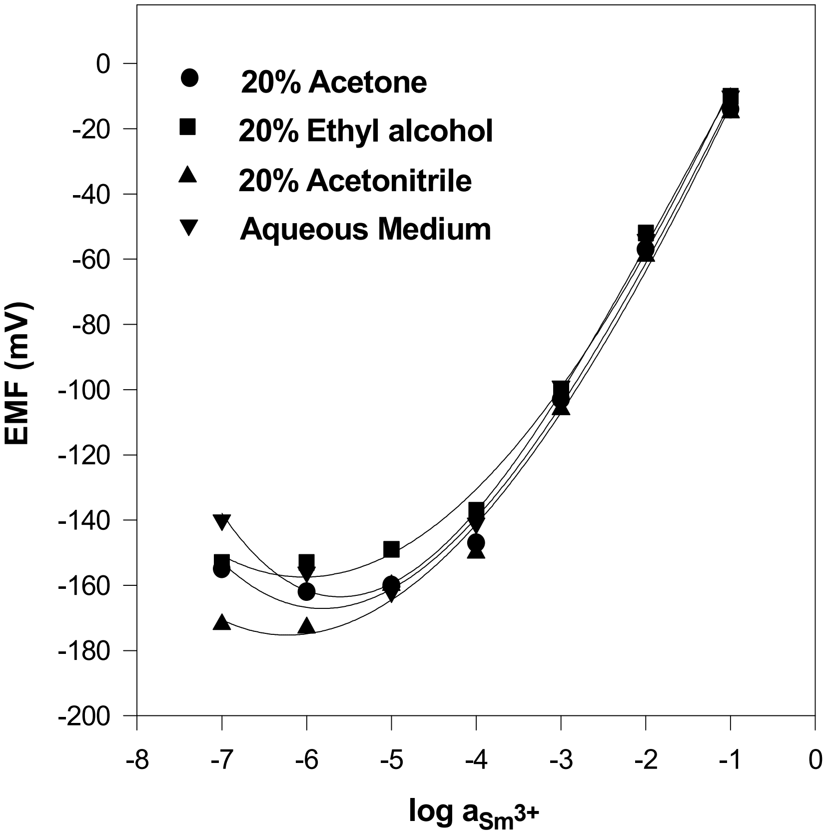

Figure 4.6: Effect of partially non-aqueous medium on Sm (III)-selective electrode based on SnBP.

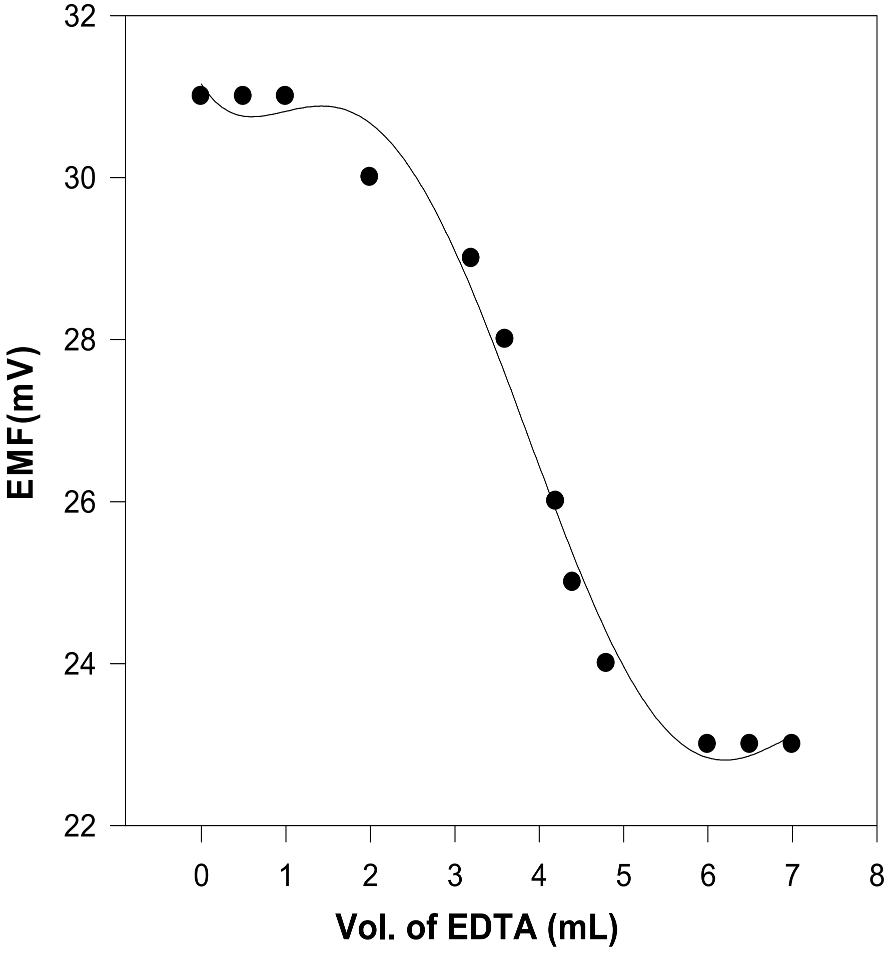

Figure 4.7: **Titration curve of Sm (III) ions with EDTA solution using ZrBP based electrode**

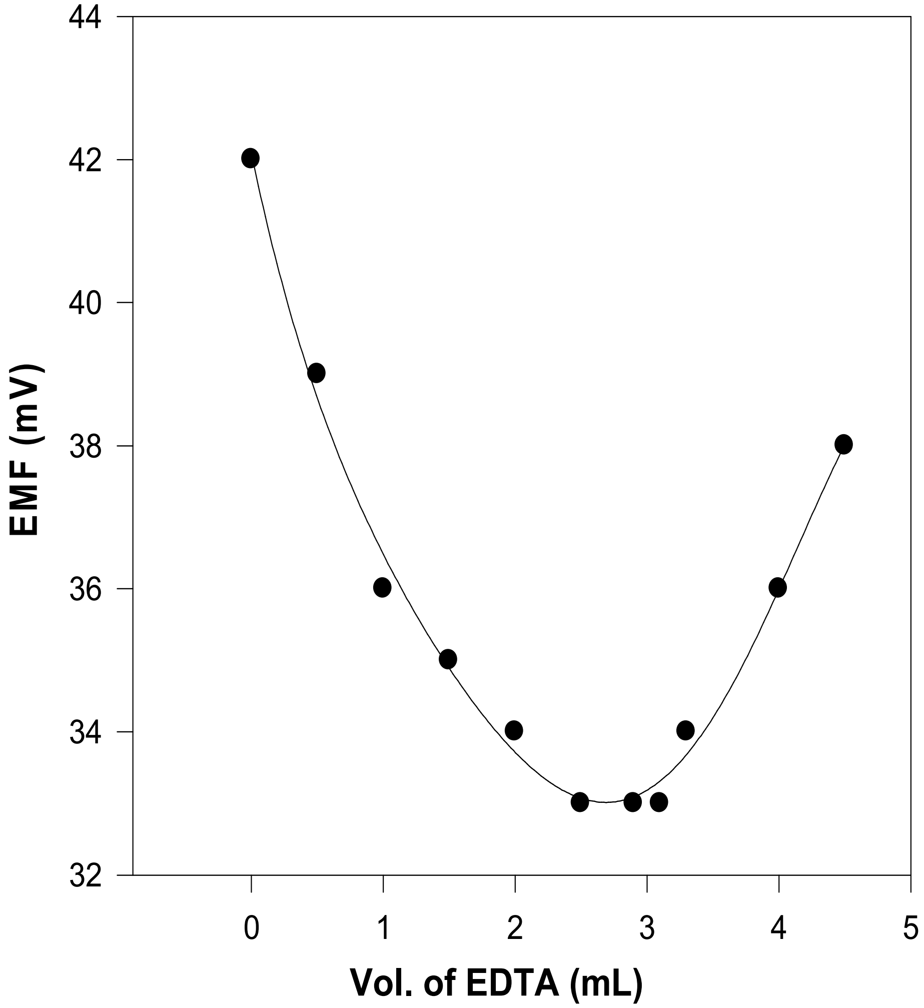

Figure 4.8: **Titration curve of Sm (III) ions with EDTA solution using SnBP based electrode**

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CHAPTER - 5

POTENTIOMETRIC SENSORS FOR CERIUM (III) AND PRASEODYMIUM (III) METAL IONS

The rare earth industry is growing steadily and an average increase over past several years has been 5-15%. Main applications involve the use of mixed rare earths as gasoline-cracking catalysts, as starting materials for making "Misch Metal" (Common commercial alloy of cerium containing around 45-65% Ce), the use of rare earth silicides for various metallurgical applications and as polishing compounds, and for carbon arcs used in movie projectors and search lights [1]. Practically, all petroleum-cracking units in the world use zeolite catalysts containing up to 5% weight of rare earth oxides. Misch metal is added to cast iron, to super alloys and stainless steel to improve castability and workability.

Rare earths are slightly toxic [2] in nature. These are dumped in the environment mainly by petrol producing industries. These metal ions gradually accumulate in soils and eventually lead to increasing concentration in human, animals and soil particles. In human beings, these can cause lung embolisms and can be a threat to liver, especially during long-term exposure. With water animals, these metal ions cause damage to cell membranes, which has several negative influences in reproduction and on functions of the nervous system [3].

Cerium and praseodymium are important members of the rare earth family. Cerium is most abundant of rare earth elements and is found in monazite, ceric bastnaesite and silicate rocks. It is widely used in production of ductile iron, cast iron and some stainless steels [4]. Praseodymium also, like other rare earth elements, is used as a catalyst in a wide variety of metallurgical operations, in lasers, masers, in industrial glass production, as polishing agent and in electronic components. Therefore, the determination of cerium and praseodymium in different samples is of special interest.

Available methods for low-level determination of rare earth ions in solutions include spectrophotometry, ICPMS, ICP-AES, isotope dilution mass spectrometry, neutron activation analysis, and X-ray fluorescence spectrophotometry [5-13]. All these methods are too expensive for most analytical laboratories. Potentiometric sensors can offer an inexpensive and convenient method for analysis of rare earth metal ions in solution, provided acceptable sensitivity and selectivity are achieved.

Inorganic ion-exchange membranes have several advantages over organic ion exchanger membranes, viz. their ability to withstand ionizing radiations and very high temperatures without undergoing degradation and their remarkably high selectivity [14]. Their high electrical conductivity and better current efficiency have found their use in cells for the electrolytic desalting of brackish water [15], fuel cells and electrical storage batteries [16]. Ion-selective electrodes employing inorganic ion exchangers as ion sensors have been reviewed by Arnold and Solsky [17] and Buck [18].

Cerium (III) ion sensors have been reported by Shamsipur et al. [19-21] using 1, 3, 5 trithiane as electro-active material. Recently, a cerium (III)-selective membrane electrode has been reported by Akhond et al. [22] using 2-amino benzothiazole. To the best of our knowledge, there is no previous report of a praseodymium (III) ion-selective electrode in literature. New inorganic ion exchangers, zirconium (IV) antimonoarsenate and zirconium (IV) antimonotungstate prepared in our laboratory showed selectivity towards cerium (III) and praseodymium (III) metal ions, respectively. Therefore, these exchangers have been used as electro-active materials for preparation of sensors for cerium and praseodymium metal ions.

5.1 ZIRONIUM (IV) ANTIMONOARSENATE BASED SENSOR FOR CERIUM (III) METAL IONS

ABSTRACT

Cerium (III)-selective membrane electrodes have been prepared using zirconium (IV) antimonoarsenate (ZrSbAs) as an electro-active material and epoxy resin, PVC and polystyrene as binding materials. A membrane having a composition: ZrSbAs (50%) and polystyrene (50%) gives the best performance. It works well over a wide Ce (III) ion-concentration range of 5×10^{-5} M to 1×10^{-1} M with a super-Nernstian slope of 52.0 mV/decade. It has a fast response time of 10 seconds and has an average lifetime of four months. The internal solution concentration does not have a significant effect on the response of the electrode except for a change in intercept of the calibration curves. The working pH ranges for Ce^{3+} solutions (1×10^{-2} M and 1×10^{-3} M) are 4.0-9.0 and 5.0-9.0, respectively. The proposed sensor shows a good selectivity for cerium (III) with respect to alkali, alkaline earth, some transition and rare earth metal ions that are normally present along with cerium in its ores. The effect of partially non-aqueous media on the response of the electrode has been studied. The electrode has also been used as an indicator electrode in potentiometric titrations of Ce (III) ions against oxalic acid.

EXPERIMENTAL

Reagents

Zirconyl oxychloride, potassium pyroantimonate and sodium arsenate required for the preparation of zirconium (IV) antimonoarsenate were procured from s.d. Fine Chem., India. Cerium chloride and other rare earth chlorides were purchased from Indian Rare Earth Chemicals Ltd., India. Since all the chemicals were of analytical grade, these were used as such.

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

Instruments Used

Various instruments used were the same as already described in Chapter 4. An Ion Analyzer (ORION, EA 940) was used for potentiometric measurements.

Synthesis of Zirconium (IV) antimonoarsenate (ZrSbAs)

Zirconium (IV) antimonoarsenate (ZrSbAs) was prepared as described in Chapter 3.2.

Preparation of Membranes

A number of membranes were prepared using varying amounts of different binding materials such as epoxy resin, PVC or polystyrene. ZrSbAs in H^+-form was used as an electro-active material. Various methods for the preparation of epoxy resin-based membranes, PVC-based membranes and polystyrene-based membranes were employed, as described in Chapter 4.

Membranes obtained by various methods were cut in the shapes of discs of about 2.0 cm diameter using a sharp blade and those of good surface qualities were selected for further investigations.

EMF Measurements

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

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

Potentiometric measurements were made using ORION (EA-940) Ion Analyzer, at 25 ±0.1° C. Activities were calculated according to Debye - Huckel equation [23]. Test solutions were obtained by gradual dilution of the stock solution. Potential measurements were made in unbuffered solutions to avoid interference from any foreign ion.

Storage of Electrodes

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

RESULTS AND DISCUSSION

Ion-selective electrodes work on the principle of measurements at zero current. The membranes are fixed in the electrode assembly and all measurements are made in a *concentration cell*. The concentration of the electrolyte on the inner side of the membrane is fixed at 0.1 M of Ce (III) ions while on the other side of the membrane it varies from 10^{-8} M to 10^{-1} M. Ions penetrate the boundary between the two phases and an electrochemical equilibrium is reached, in which different potentials in two phases are formed. If only one type of an ion can be exchanged between the two phases, then the potential difference formed between the phases is governed only by activities of this target ion in these phases. When the membrane separates two solutions of different ionic activities (a_1 and a_2) and provided the membrane is only permeable to this single type of ion, the potential difference (E) across the membrane is described by the Nernst equation:

$$\mathbf{E = const. + RT/zF \cdot \ln (a_2/a_1) \qquad .... (5.1)}$$

If the activity of the target ion in phase 1 (a_1) is kept constant, the unknown activity (a_x) in phase 2 is related to (E) by:

$$\mathbf{E = const. + RT/z_xF \cdot \ln (a_x/a_1) = const + S \cdot \log_{10} (a_x) \qquad .... (5.2)}$$

Where, S = $59.16/z_x$ mV at 298 K and z_x - the charge of the analyte. The potential difference can be measured between two identical reference electrodes placed in the two phases.

An experimental slope which agrees with the theoretical slope is referred to as the Nernstian slope, while the larger and smaller values are referred to as 'over-Nernstian' and 'sub-Nernstian, respectively.

No ionic strength adjustment buffer was used to avoid introduction of any unwanted foreign ions from the buffer. Moreover, the ionic strength does not change much during the study as experiments are done in dilute solutions only in the major part of the measuring range of the electrode (i.e., 10^{-6} M -10^{-1} M).

Optimization of Membrane Ingredients

The slope of the calibration curve, the measurement range and response time were noted for a number of electrodes having different compositions of binders and the exchanger. The results are shown in Table 5.1.1.

Table 5.1.1: Optimization of membrane ingredients for ZrSbAs based membranes

Electrode No.	ZrSbAs (wt. %)	Binder	Slope (mV/decade)	Measuring Range (M)	Response Time (s)
Ce-1	35	Araldite	50	$1.0\text{x}10^{-4}$-10^{-1}	15
Ce-2	40	Araldite	51	$6.3\text{x}10^{-5}$-10^{-1}	15
Ce-3	40	PVC in THF	52	$1.0\text{x}10^{-4}$-10^{-1}	20
Ce-4	40	Polystyrene	51	$3.9\text{x}10^{-5}$-10^{-1}	15
Ce-5	**50**	**Polystyrene**	**52**	**$5.0\text{x}10^{-5}$-10^{-1}**	**15**

The results show that the electrode Ce-5 with membrane composition ZrSbAs:polystyrene as 1:1, shows the best performance with a slope of 52.0 mV/decade, a measurement range $5\text{x}10^{-5}$ M to 10^{-1} M and a response time of less than 15 seconds. This electrode is used for the subsequent studies.

Calibration Curve

Experiments were conducted a number of times to check the reproducibility of the results. EMFs were plotted against log of activities of cerium ions and calibration curves were drawn for five sets of experiments. A standard deviation of ± 0.9 mV was observed.

A representative calibration curve using the electrode Ce-5 is shown in Fig. 5.1.1. The limit of detection [1.2×10^{-5}] was calculated according to IUPAC recommendations from the intersection of two extrapolated linear portions of the curve [18, 24]. The over-Nernstian response in electrode of this kind is common [25, 26]. Inorganic ion exchanger based membranes are not efficient in permeability of ions across their matrices as compared to organic ion exchanger membranes. The higher slope may be due to poor permeability and incomplete permselectivity of the membrane matrix for the cerium ion. Pungor et al. [27, 28] has also explained the super-Nernstian slope observed for Ag^+ and I^--selective electrodes. However, the non-Nernstian behavior of the electrode does not prevent it from being successfully applied to determine ions in question.

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

Influence of the Concentration of Internal Solution

Electrode responses were measured by changing the internal filling solution from 1×10^{-1} M to 1×10^{-4} M (Fig. 5.1.2). It was found that the variation in the concentration of the internal solution does not cause any significant difference in the potential response, except for an expected change in the intercept of the resulting curve. The concentration of the internal solution as 1×10^{-1} M is quite appropriate for the functioning of the electrode system.

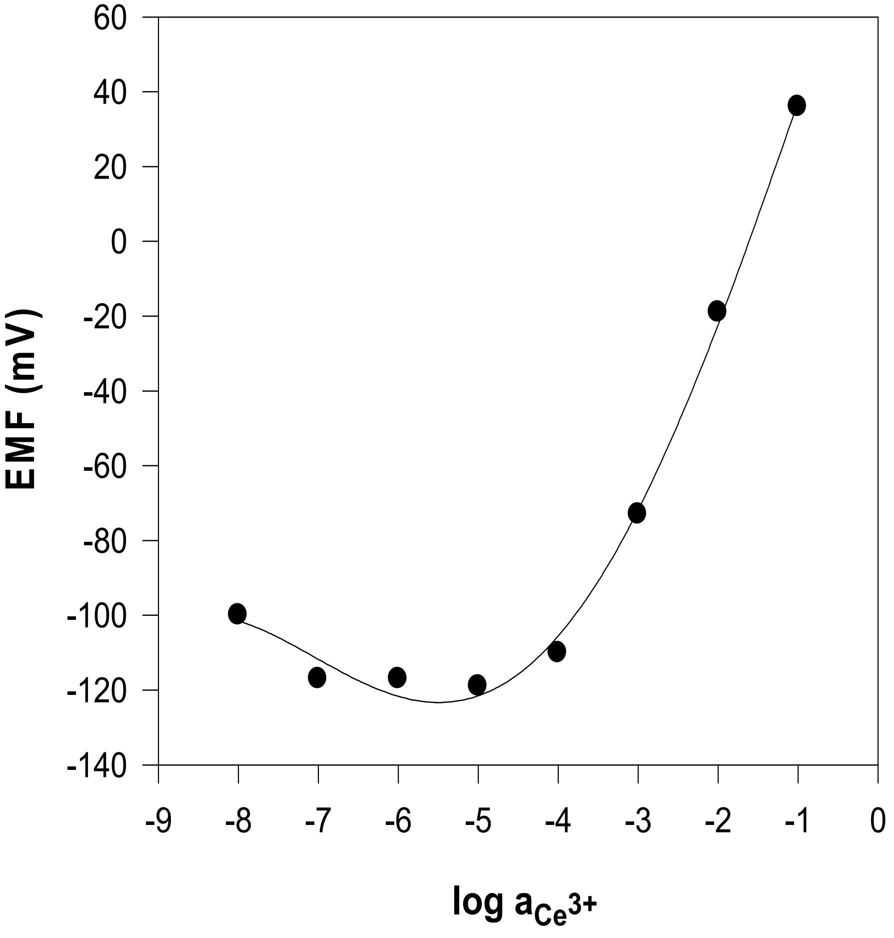

Figure 5.1.1: **Calibration curve for Ce (III)-selective electrode based on ZrSbAs**

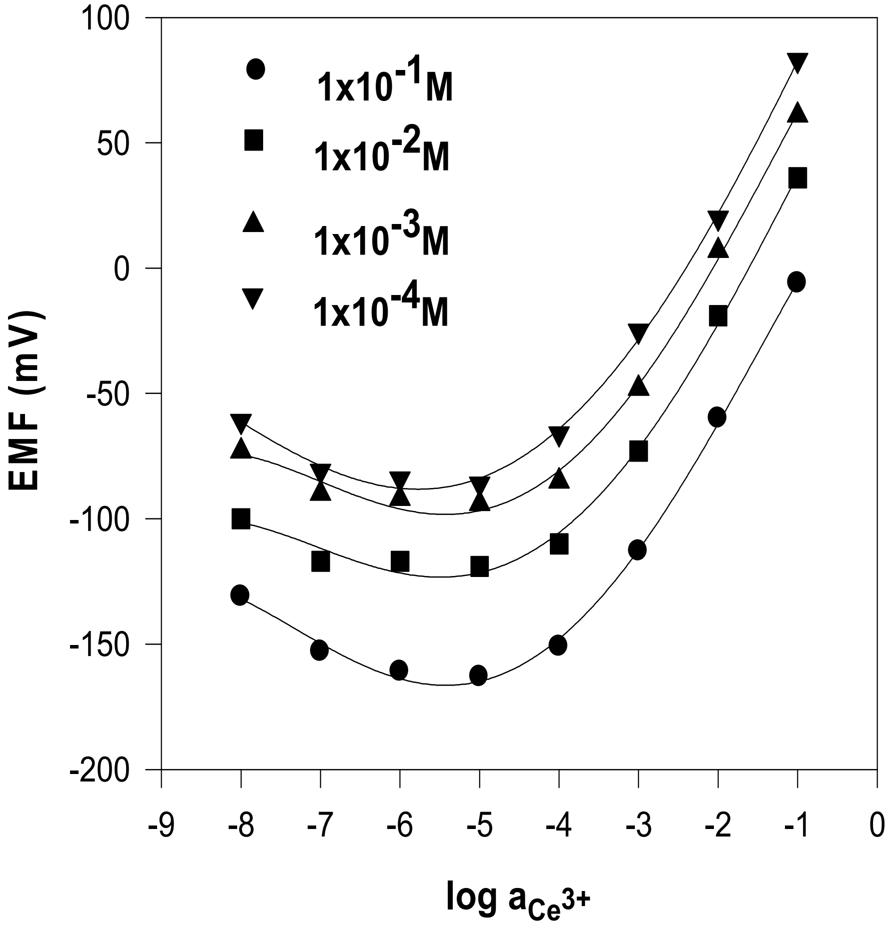

Figure 5.1.2: Effect of internal solution on potential response of the Ce (III)-selective electrode based on ZrSbAs

pH dependence of the Sensor

It is very important to find out the pH range where the electrode can work without interference from hydrogen ions present in aqueous solutions. The pH dependence of the sensor was tested by using 1.0 x 10^{-2} M and 1.0 x 10^{-3} M Ce^{3+} solutions over a pH range of 2.0 to 13.0 (Fig. 5.1.3). The pH was adjusted by the addition of small drops of hydrochloric acid (0.1 M) or sodium hydroxide (0.1 M), as required.

It is clear from Fig. 5.1.3 that the emf remains constant from pH 4.0 to 9.0 and 5.0 to 9.0 for $1x10^{-2}$ M and $1x10^{-3}$ M Ce^{3+} ion concentrations, respectively. Beyond this pH, a drift in emf is observed which may be due to the formation of hydroxy complexes of Ce^{3+} at higher pH and due to protonation of the exchanger in the membrane at lower pH.

Effect of Partially Non-Aqueous Media

The functioning of the sensor was also investigated in partially non-aqueous media using methanol-water, acetone-water and DMSO-water mixtures. It was found that the sensor assembly works well up to 20% non-aqueous content without showing any appreciable change in the working concentration range or slope (Fig. 5.1.4).

Potentiometric Selectivity

One of the most important characteristics of a membrane sensor is its response for the primary ion in presence of other ions, which is measured in terms of the potentiometric selectivity coefficient $(K_{A,B}^{Pot})$. The fixed interference method (FIM) at the interfering ion concentration $1x10^{-3}$ M and $1x10^{-4}$ M is adopted in the present case to determine the selectivity coefficient data (Table 5.1.2).

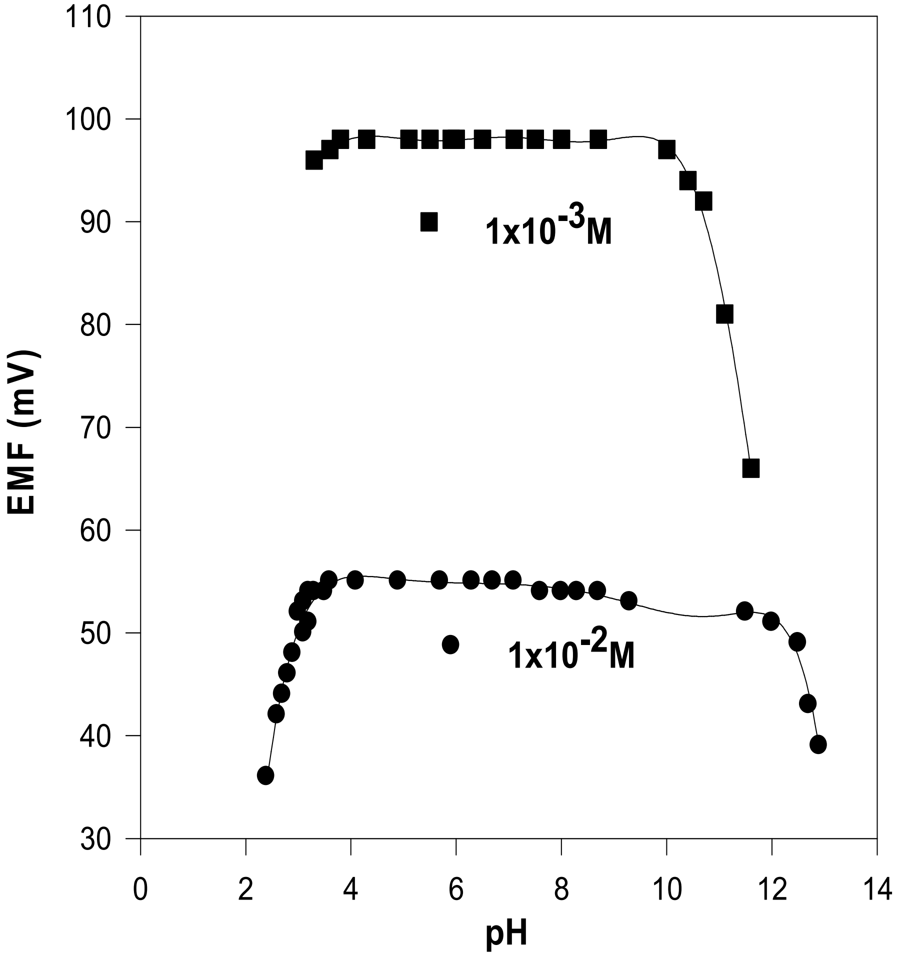

Figure 5.1.3: **Effect of pH on the response of Ce (III)-selective electrode based on ZrSbAs**

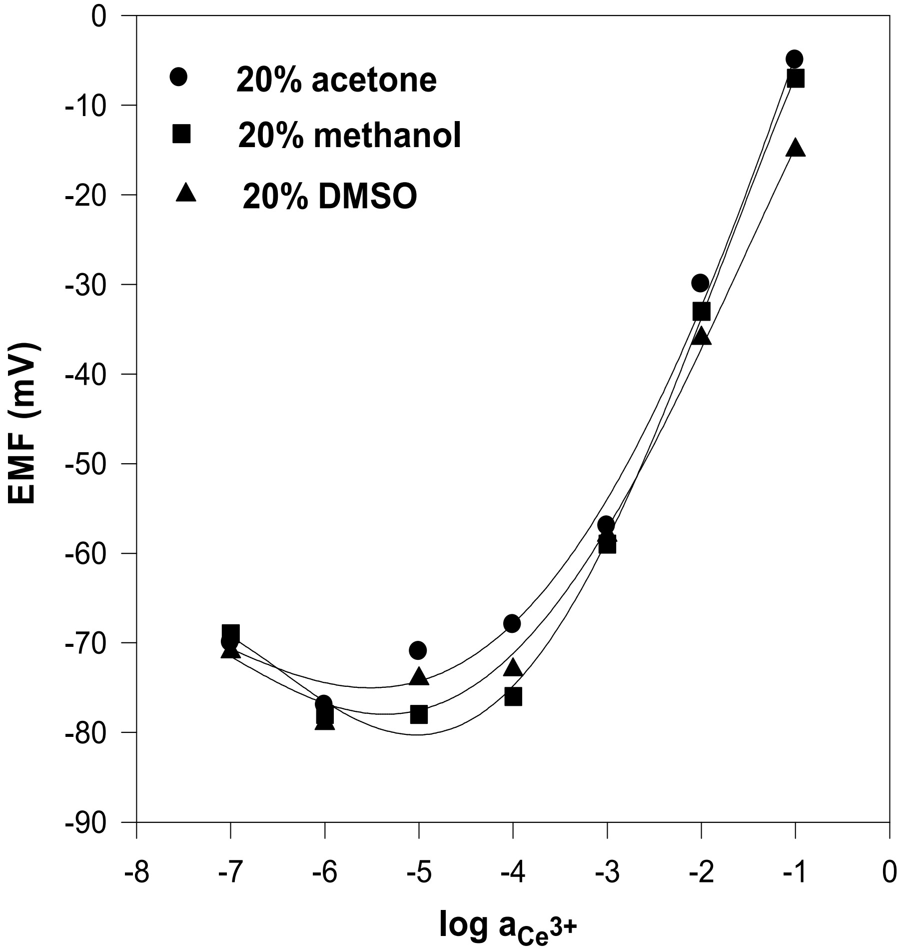

Figure 5.1.4: Effect of partially non-aqueous media on the response of Ce (III)-selective electrode based on ZrSbAs

Following expression is used for this purpose:

$$K_{A,B}^{Pot} = \frac{a_A}{(a_B)^{z_A/z_B}} \qquad \text{………… (5.3)}$$

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

It can be seen from Table 5.1.2 that the electrode has a reasonably good selectivity for Ce^{3+} ions in the presence of other rare earth metal ions, some alkali, alkaline earth and transition metal ions. The selectivity is good in the sense that all the rare earth metal ions have identical sizes and properties.

Analytical Application

The analytical applicability of the sensor was tested by using it as an indicator electrode in the potentiometric titration of Ce^{3+} ion solution. 50.0 mL of Ce^{3+} solution ($1x10^{-2}$ M) was titrated against oxalic acid solution ($1x10^{-1}$ M). The curve is not a standard sigmoid shaped [Fig. 5.1.5]. However, a very good inflection point corresponding to Ce-oxalate stoichiometry is observed which shows that this sensor can be used for determination of Ce^{3+} ions potentiometrically.

Lifetime of Electrode

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

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Table 5.1.2: Selectivity coefficient values for Ce (III)-selective electrode based on ZrSbAs as calculated by FIM method

Interfering ion (B)	**Selectivity Coefficient values $(K_{A,B}^{Pot})$**	
	Interfering ion concentration	
	10^{-3} M	**10^{-4} M**
La (III)	0.31	0.40
Sm (III)	0.25	0.31
Nd (III)	0.40	0.50
Eu (III)	0.40	0.50
Pr (III)	0.50	0.63
Tb (III)	0.32	0.40
Dy (III)	0.40	0.40
Y (III)	0.31	0.40
Fe(III)	0.25	0.25
Al (III)	0.10	0.31
Ca (II)	0.50	0.50
Na (I)	0.50	0.63

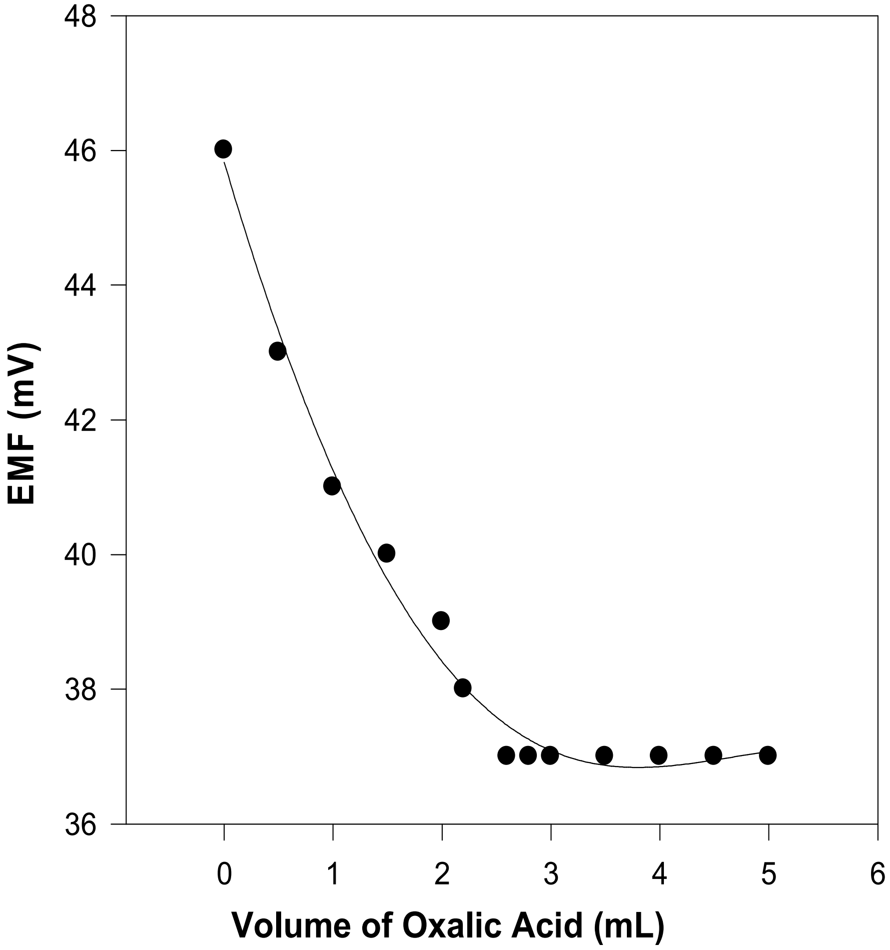


Figure 5.1.5: Titration curve of Ce (III) ions with oxalic acid solution using Ce (III)-selective electrode based on ZrSbAs

5.2 ZIRCONIUM (IV) ANTIMONOTUNGSTATE BASED SENSOR FOR PRASEODYMIUM (III) IONS

ABSTRACT

Praseodymium-selective electrodes have been prepared using PVC and polystyrene as binders with zirconium (IV) antimonotungstate as an electro-active material. The electrode assembly was interfaced to an Orion Analyzer (Model EA-940) using Labview software from National Instruments, USA. All experimental results were recorded on a computer interfaced further to an ion analyzer. Both membranes have been used for further studies. These membranes work well over a concentration range of $5x10^{-5}$ M to $1x10^{-1}$ M of Pr^{3+} ions with a near-Nernstian slope of 25.0 mV/decade. The polystyrene based membrane has a fast response time of 10 seconds as compared to a PVC based membrane that gives a response time of 15 seconds. The effect of internal solution has been studied for both membranes. The working pH range for both membranes is the same i.e., 4.5-9.0. Selectivity coefficients are determined using the matched potential method (MPM) for a number of metal ions, normally present along with praseodymium in its ores. Finally, these electrodes are used as indicator electrodes for potentiometric titrations of Pr^{3+} ions against EDTA solution.

EXPERIMENTAL

Reagents

Zirconyl oxychloride, potassium pyroantimonate and sodium tungstate required for the preparation of ZrSbW were procured from s.d. fine chem., India. Hydrofluoric acid was purchased from Ranbaxy, India. Praseodymium chloride and other rare earth chlorides were purchased from Indian Rare Earth Chemicals Ltd., India. Since all chemicals were of analytical grade, these were used as such.

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

Instruments Used

All instruments used were the same as described in Chapter 4. An Ion Analyzer (ORION EA 940) interfaced to Pentium IV PC with Data Acquisition Card from National Instruments, USA was used for potentiometric measurements.

Synthesis of Zirconium (IV) antimonotungstate

Zirconium (IV) antimonotungstate was prepared by adding zirconyl oxychloride (0.1 M, containing 12 mL/L hydrofluoric acid) to a continuously stirred equimolar mixture of potassium pyroantimonate and sodium tungstate at 60° C in a volume ratio of 2:1:1. Gelatinous white precipitates were obtained and the pH of the gel was adjusted to 1.0 by adding either HCl or NaOH solution. Precipitates were filtered, washed until free from halides and dried at 40° C. The dried product broke down into small granules when immersed in water. The material was converted into the H^+-form by keeping it in HCl

(0.1 M) for 24 hours with intermittent changing the acid and finally dried at 40° C. The product was washed with DMW to remove excess acid.

Preparation of Membranes

The membranes were prepared using varying amounts of different binding materials such as an epoxy resin, polyvinylchloride or polystyrene and ZrSbW in H^+-form as the electro-active material. Various methods for preparation of these membranes were used as described in Chapter 4.

The prepared membranes were cut in the shape of circular discs (2.0 cm diameter) and those of good surface qualities were selected for further studies.

EMF Measurements

The membranes were fixed to one end of glass tubes of 1.8 cm internal diameter using an adhesive and were equilibrated with Pr^{3+} solution (0.1 M) for 3 days. The tube was filled with Pr^{3+} solution (0.1 M) as an internal solution and immersed in a beaker containing test solutions of varying concentration. All emf measurements were made using assembly as:

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

The measurements were made with an Ion Analyzer (Orion, Model EA-940) using the software from National Instruments, USA. The experiments were conducted in an air thermostat maintained at 25±0.1° C. All the experimental results were recorded on a computer interfaced further to an ion analyzer. Activities were calculated using the Debye Huckel equation [23]. The performance of the sensor was investigated by measuring its EMF in praseodymium chloride solutions prepared in a concentration range from 10^{-8} M to 10^{-1} M by serial dilutions. All readings were taken in unbuffered solutions.

RESULTS AND DISCUSSIONS

The performance parameters of the electrodes, like the slope of the calibration curve, the measurement range and response time are given in Table 5.2.1. It is evident that all the three electrodes exhibit a super-Nernstian response (expected Nernstian slope is 19.7 mV/decade.)

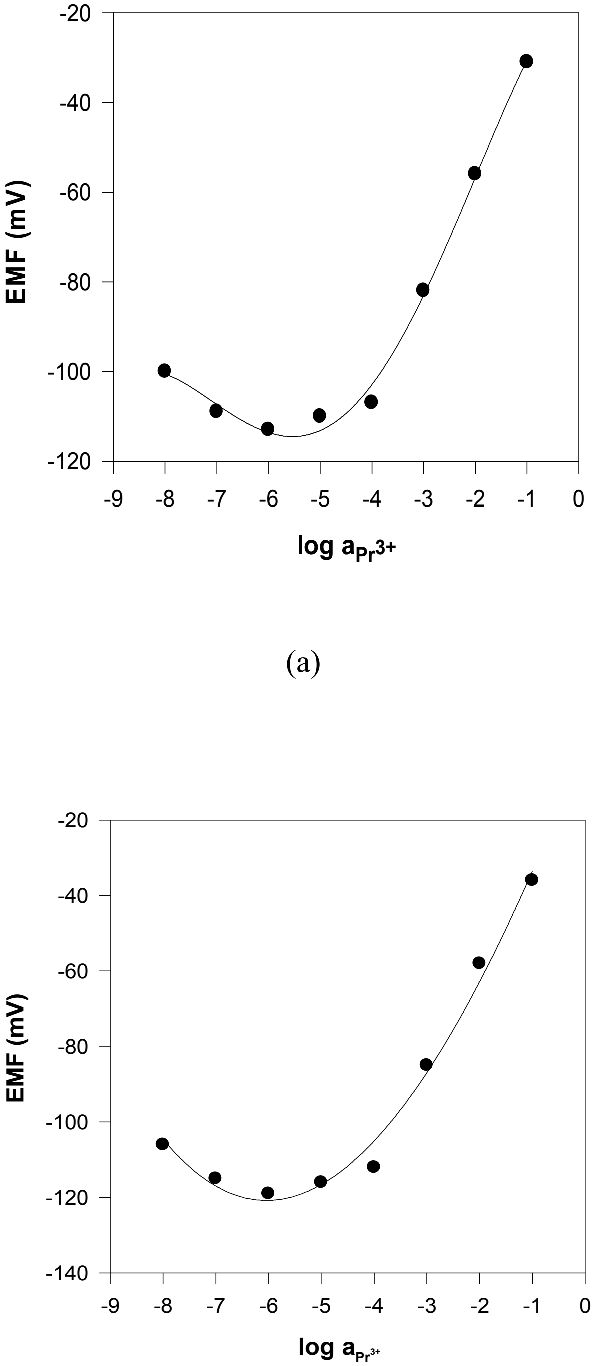
However, the electrodes Pr-2 and Pr-3 based on polystyrene and PVC showed almost equal slopes of the calibration curves and measurement ranges. It was interesting to carry out further studies with both of these electrodes.

Table 5.2.1: Optimization of membrane ingredients for ZrSbW based membranes

Electrode No.	ZrSbW (Wt. %)	Binder	Slope (mV/decade)	Measuring Range (M)	Response Time (s)
Pr-1	50	Araldite	40	$2.0\text{x}10^{-5}$-10^{-1}	20
Pr-2	**50**	**Polystyrene**	**25**	**$2.0\text{x}10^{-5}$-10^{-1}**	**10**
Pr-3	**50**	**PVC**	**25**	**$1.0\text{x}10^{-5}$-10^{-1}**	**15**

Calibration Curves

The optimum equilibration time for the membrane electrodes (using 10^{-1} M Pr $^{3+}$ solution) was about 12 hours which is sufficient to generate stable potentials for Pr $^{3+}$ solutions in the range of 1.0 x 10^{-4} M to 1.0 x 10^{-1} M [Figs. 5.2.1 (a) and (b)]. The limit of detection [18, 24], as determined from the intersection of the two extrapolated segments of the calibration curves, was $2.0\text{x}10^{-5}$ M and $5.0\text{x}10^{-5}$ M, respectively.



(a)

(b)

Figure 5.2.1: Calibration curves for Pr (III)-selective electrode based on (a) ZrSbW in polystyrene (b) ZrSbW in PVC

Effect of the Internal Solution Concentration

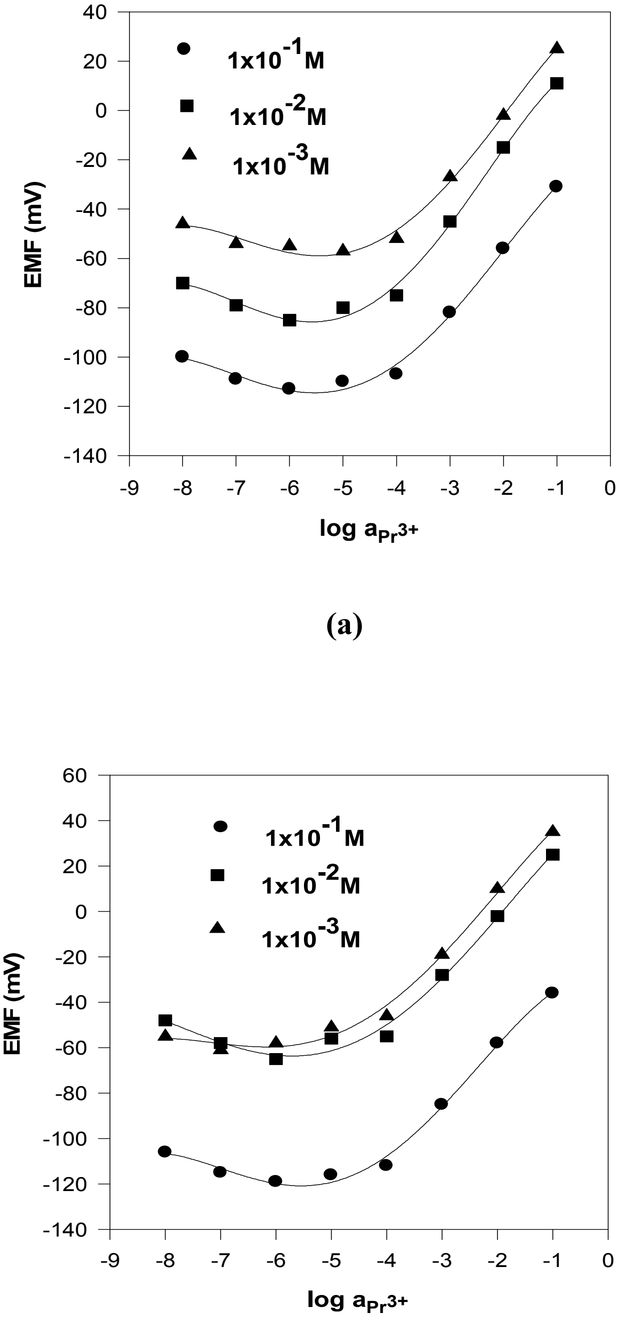
Emf measurements were made for different concentrations of Pr^{3+} ions as internal solutions. The concentrations were changed from 1.0 x 10^{-3} M to 1.0 x 10^{-1} M and the potential responses of the two Pr^{3+} ion-selective electrodes were recorded. It was found that the variation in concentration of the internal solution does not have any significant effect on the potential response, except for the change in intercepts of resulting curves. The results are shown in Fig. 5.2.2. A Pr^{3+} solution concentration of 1.0 x 10^{-1} M is quite appropriate for the functioning of both electrodes Pr-2 and Pr -3.

Effect of pH

The effect of pH on both electrodes was studied with Pr^{3+} ion solution (1.0 x 10^{-3} M). The pH was adjusted using appropriate amounts of HCl and NaOH. As it is evident from Fig. 5.2.3, the electrode responses are stable in the pH range 4.5 to 9.0. Above pH 9.0, the Pr (III) signal diminishes with a further increase in pH of the solution. This is probably due to the formation of $Pr(OH)_3$ in the system. On the other hand, as the pH decreases below 4.5, the emf decreases due to the protonation of the exchanger in the membrane.

Selectivity of the Electrode

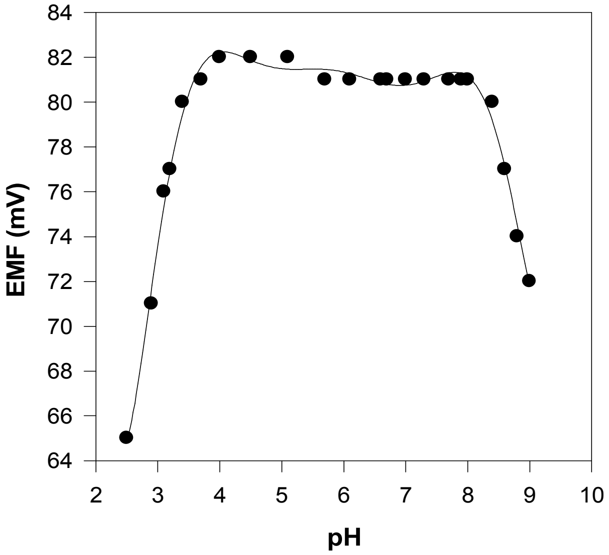
The potentiometric selectivity coefficients for praseodymium ions over other interfering ions were determined by the matched potential method (MPM) [24, 29]. This method is recommended by IUPAC to overcome the difficulties associated with the methods based on the Nicolsky-Eisenman equation [30]. According to this method, the specified activity (concentration) of the primary ion (A) is added to a reference solution and the potential is measured.



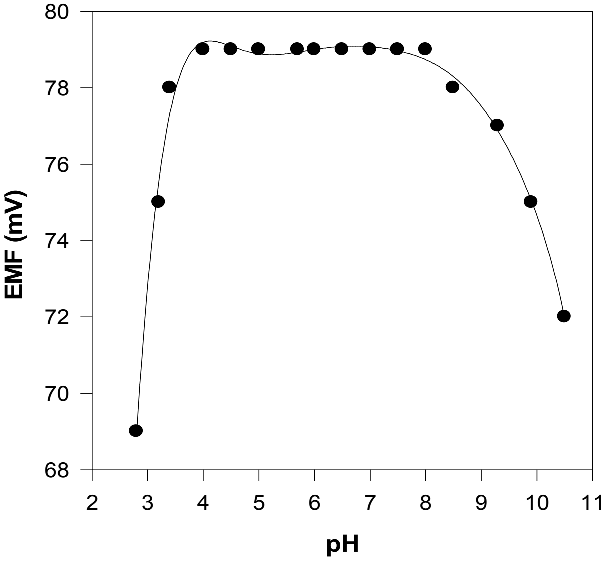
(a)

(b)

Figure 5.2.2: Effect of internal solution on Pr (III)-selective electrode based on (a) ZrSbW in polystyrene (b) ZrSbW in PVC



(a)



(b)

Figure 5.2.3: Effect of pH on response of Pr (III)-selective electrode based on (a) ZrSbW in polystyrene (b) ZrSbW in PVC

In a separate experiment, the interfering ion (B) is successively added to an identical reference solution until the measured potential matches that, obtained before by adding primary ions. The matched potential selectivity coefficient is then given by the resulting primary ion to the interfering ion activity (concentration) ratio. The resulting $(K_{A,B}^{Pot})$ values for the proposed Pr (III) sensor are summarized in Table 5.2.2. As seen in the table, the alkali, alkaline earth, transition metal ions and other rare earth metal ions used as interfering ions will not disturb the functioning of the Pr (III) ion-selective membrane electrode significantly.

Table 5.2.2: Selectivity coefficient values for Pr (III)-selective electrodes based on PS membrane made from ZrSbW as calculated by MPM method

Interfering ion (B)	**Selectivity Coefficient values $(K_{A,B}^{Pot})$ at a matching potential of**	
	10 mV	**20 mV**
La (III)	0.43	0.36
Ce (III)	0.25	0.31
Nd (III)	0.40	0.50
Eu (III)	0.83	0.80
Sm (III)	0.50	0.63
Tb (III)	0.75	0.73
Dy (III)	0.53	0.74
Y (III)	0.31	0.40
Fe (III)	0.35	0.37
Al (III)	0.30	0.29
Ca (II)	0.60	0.54
Na (I)	0.09	0.10

Analytical Applications

The proposed Pr (III) sensor electrodes were found to work well under laboratory conditions. These were used as indicator electrodes in the potentiometric titration of Pr (III) solution versus EDTA solution.

Electrode Pr-2 was used as an indicator electrode for the titration of 20 mL Pr (III) solution (10^{-2} M) against EDTA solution (10^{-1} M), while electrode Pr-3 was used for the titration of 10 mL Pr (III) solution (10^{-2} M) against EDTA solution (10^{-1} M). The resulting titration curves are shown in Fig. 5.2.4. The curves are not standard sigmoid shaped which may be due to the Na^+ ion interference as disodium salt of EDTA was used for the titration. However, a good inflection point corresponding to Pr-EDTA stoichiometry is observed which shows that these electrodes can be used for the determination of Pr^{3+} ion potentiometrically.

Lifetime of Electrode

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

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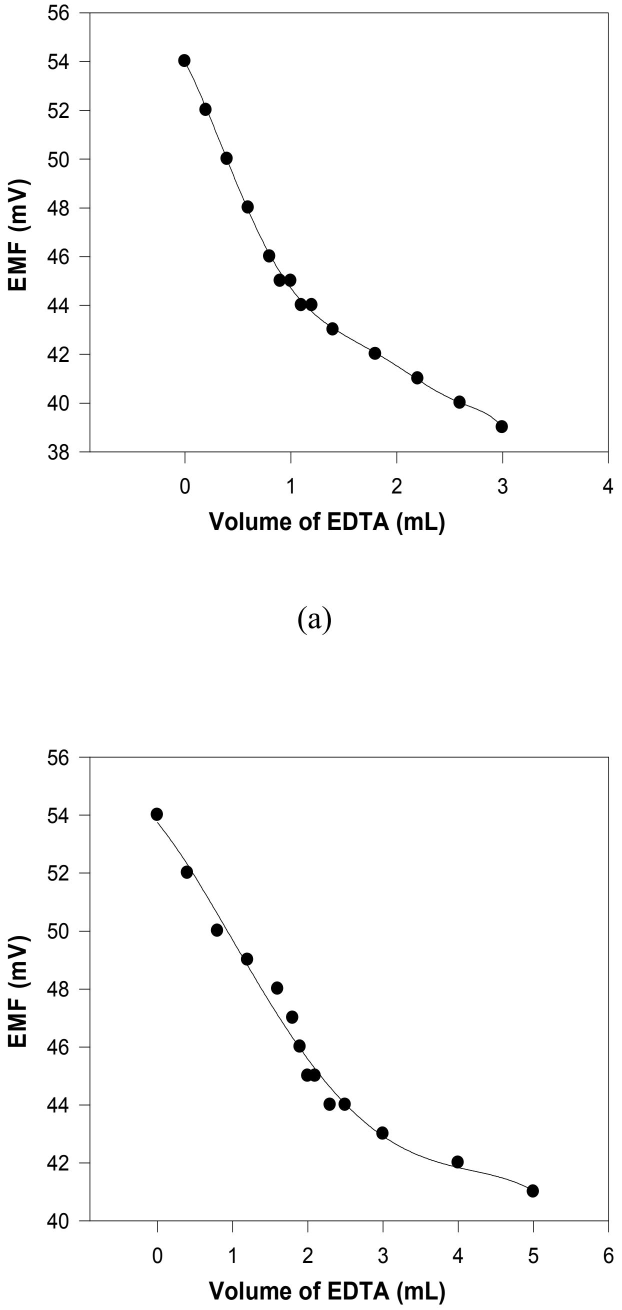

(a)

(b)

Figure 5.2.4: Titration curves of Pr (III) ions with EDTA solution using Pr (III)-selective electrode based on (a) ZrSbW in polystyrene (b) ZrSbW in PVC

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CHAPTER – 6

PVC-BASED POTENTIOMETRIC SENSOR FOR La (III) IONS

ABSTRACT

A new PVC-based ion-selective electrode (ISE) using dicyclohexano-18-crown-6 as a neutral carrier is developed for lanthanum (III) ions. The electrode comprises of dicyclohexano-18-crown-6 (6%), PVC (33%) and ortho-nitrophenyl octyl ether (o-NPOE) (61%). The electrode shows a linear dynamic response in a concentration range of $1x10^{-6}$ M to $1x10^{-1}$ M with a Nernstian slope of 19.0 mV/decade and a detection limit of $5x10^{-7}$ M. It has a response time of <30 seconds and can be used for at least five months without any significant divergence in potentials. The selectivity coefficients for mono-, di- and trivalent cations indicate a good selectivity for La (III) ions over a large number of interfering cations. The sensor has been used as an indicator electrode in potentiometric titrations of La (III) with EDTA. The membrane is successfully applied in partially non-aqueous medium. It can be used in the pH range 4-9.

INTRODUCTION

Lanthanum is found in rare-earth minerals such as cerite, monazite, allanite, and bastnasite. Pure lanthanum has very few applications being almost limited to the scientific research. In spite of this, the metallurgical industry is the only commercial domain where the metal finds application [1]. Some rare-earth chlorides such as lanthanum chloride ($LaCl_3$), are known for their anticoagulant properties although they should be used with great care. Lanthanum salts are generally considered to have low or moderate toxicity [2]. Lanthanum nitrate treatment promotes the germination of neutral rice seeds [3]. Because of the increasing industrial use of lanthanum compounds as well as their enhanced discharge and its useful and harmful biological activity, the determination of lanthanum has been of a recent increasing concern [4].

Available methods for low-level determination of rare-earth ions in solution [5-9] are either time-consuming, involving multiple analysis or too expensive for most analytical laboratories. Potentiometric sensors offer an inexpensive and convenient method for the analysis of rare-earth metal ions in solution, provided acceptable sensitivity and selectivity are achieved. In spite of the successful progress in the design of highly selective ionophores for various metal ions, there are only a limited number of reports on the development of selective ionophores for lanthanum [10-17].

Lanthanides are expected to form stable complexes with various macrocyclic ligands, similar to alkali and alkaline earth metals, because of the similarity of radii between lanthanides and Na^+ or Ca^{2+} ions. In fact, it was mentioned in the first report on crown ethers by Pedersen (1967) [1] that some crown ethers formed complexes with La (III) and Ce (III) in solution. However, attention has been focused, mainly on complexes of alkali and alkaline earth metal ions.

Since their introduction about 30 years ago, liquid membrane ion-selective electrodes (using plasticized PVC membranes) have become well established and highly relevant analytical tools. Although various polymer matrices such as polyurethane, silicone rubber and polyacrylates have been tested, plasticized PVC membranes are still considered to be the best choice. Several problems may arise in case of improper choice of binder. These include the leaching of electro-active components from the membrane, the deposition of the membrane and interface processes between the membrane and the transducer. Regarding the membrane deposition, it is often mentioned that membrane materials should be cross-linkable. Through the intimate contact of the cured membrane with the organic solvent, any compound that is not covalently bound may be leached out, leading to a deterioration of the final sensor properties. Leaching of membrane components is a serious problem resulting in an increase of noise levels.

The main objective of this work is to introduce a selective and sensitive electrode for lanthanum ions for the potentiometric monitoring of trace amounts of La (III) by using DC18C6 as an electro-active component in PVC based membrane.

EXPERIMENTAL

Reagents

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

Electrode Preparation

A homogenized mixture of about 1 gram with components: PVC, 33%; DC18C6, 6%; o-nitro phenyl octyl ether, 61% was dissolved in 2-3 mL of THF at room temperature. The viscous solution thus obtained was poured in a glass ring of 30 mm diameter placed on a dust free Pyrex glass plate [18]. The solvent was allowed to evaporate slowly for about 24 hours at room temperature. To obtain membranes with similar characteristics, viscosity of the casting solution and the rate of solvent evaporation were controlled so that thickness and morphology of membranes remain almost unchanged. The prepared membranes were removed from the glass plate and circular pieces of 1.25 cm diameter were cut and mounted on the ground end of the Pyrex glass tube using an epoxy resin as an adhesive. The membranes were conditioned with La $(NO_3)_3$ (0.1 M) solution for 24 hours.

EMF Measurements

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

Hg-Hg_2Cl_2(s), KCl (sat.) | 0.1 MLa^{3+} || membrane || test solution La^{3+} | KCl (sat.), Hg_2Cl_2-Hg

A digital potentiometer (Equiptronics EQ-602, India) was used for potential measurements at 25±0.1° C. Activities were calculated according to the Debye-Huckel equation [11]. Standard La $(NO_3)_3$ solutions were obtained by gradual dilution of La $(NO_3)_3$ (0.1 M) solution and their potential measurements were done in unbuffered solutions.

RESULTS AND DISCUSSION

Trivalent lanthanide ions have the outer shell electronic configuration as [Xe] $4f^{(1-14)}$ $5d^1 6s^2$. Bonds between the lanthanum ion and the macrocycle DC18C6 are mainly ion-dipole and non-directional, and are similar to those between alkali metal ions and crown ethers, since the 4f electrons are effectively shielded. DC18C6 forms a stable complex with lanthanum [La (III)] ions, as supported by high stability constants. This means that the stability of complexes might be unusually sensitive to the size of the lanthanide ion primarily because of the electrostatic and steric effects. So, a unique selectivity for La (III) ions is expected with DC18C6 ligand. The formation of La (III) complexes with DC18C6 was reported in the original paper of Pedersen (1967) but details are not available. However, some detailed studies are available in some other references [19-21].

Optimization of the Membrane Composition

The membrane composition and the nature of plasticizer influence the sensitivity and selectivity of an electrode [22-24]. The effect of composition on the response of the electrode was investigated. For this purpose, performance characteristics, like slope of the calibration curve, measurement range and detection limit, were studied (Table 6.1). Results show that the electrode with the ratio PVC:o-NPOE:DC18C6; 33%:61%:6%, exhibit the best response with a slope of 19.0 mV per decade. As it is obvious from Table 6.1, o-NPOE is a more effective solvent medium than DBP in preparing the La (III) ion-selective electrode. The quantity of ion carrier DC18C6 was also found to affect the sensitivity of the membrane electrode. The sensitivity of the electrode response increases with increasing ionophore content until a value of 6 % (w/w) is reached. A further addition of ionophore results in a decreased slope of the electrode.

Detection Limit, Response Time, Reproducibility and Life Time

The working concentration range and slopes for all membrane electrodes are given in Table 6.1. The electrode composition; PVC:DC18C6:o-NPOE as 33:6:61 (wt %), shows a linearity in a concentration range from 1×10^{-6} M to 1×10^{-1} M with a slope of 19.0 mV/decade(see Fig 6.1). However, the addition of KTpClB did not significantly improve the working concentration range. Hence, this membrane was studied in detail as a La (III)-selective electrode and all further studies were carried out on this membrane. Repeated monitoring of potentials (five identical measurements) on whole of the concentration range gave a standard deviation of ±1.0 mV.

To obtain better electrode properties, solvent mediators such as o-NPOE, DBP and 2BES were also tested. The membrane based on o-NPOE exhibits a Nernstian slope of 19.0 mV/decade over a wide concentration range of 1×10^{-6} M to 1×10^{-1} M, while plasticizers DBP and 2BES show slopes as 17.0 mV/decade and 14.0 mV/decade, respectively. Further, the electrode based on 2-NPOE has a better response than the other two mediators. The limit of detection (1×10^{-6} M) was calculated according to IUPAC recommendation [25, 26] from the intersection of two extrapolated linear portions of the curve. The response time of the electrode is least for the electrode La-6, i.e., 25 seconds and for all other electrodes it is greater than 30 seconds. The sensing behavior of the membrane remains unchanged when potentials are recorded either from low to high or high to low concentrations. This membrane electrode could be used for at least five months without any measurable divergence. The electrodes were stored in La $(NO_3)_3$ (0.1 M) when not in use to avoid any change in lanthanum-ion concentration in the membrane phase.

Table 6.1: Optimization of membrane ingredients

No.	PVC (Wt%)	Plasticizer, NPOE (Wt %)	DC18C6 (Wt %)	KTpClB (Wt %)	Slope (mV/decade)	Linear range (M)	Detection limit (M)
La-1	33	67	--	--	5.0	$1x10^{-4}$-$1x10^{-1}$	$5x10^{-3}$
La-2	33	65	2	--	10.0	$1x10^{-4}$-$1x10^{-1}$	$1x10^{-3}$
La-3	33	64	3	--	12.0	$1x10^{-4}$-$1x10^{-1}$	$1x10^{-3}$
La-4	33	63	4	--	15.0	$1x10^{-4}$-$1x10^{-1}$	$1x10^{-4}$
La-5	33	62	5	--	17.0	$1x10^{-5}$-$1x10^{-1}$	$3x10^{-5}$
La-6	**33**	**61**	**6**	**--**	**19.0**	**$1x10^{-6}$-$1x10^{-1}$**	**$1x10^{-6}$**
La-7	33	60	7	--	18.5	$1x10^{-6}$-$1x10^{-1}$	$1x10^{-5}$
La-8	33	59	8	--	14.0	$1x10^{-6}$-$1x10^{-1}$	$1x10^{-5}$
La-9	33	61(DBP)	6	--	17.0	$1x10^{-6}$-$1x10^{-1}$	$1x10^{-5}$
La-10	33	61(2-BES)	6	--	14.0	$1x10^{-4}$-$1x10^{-1}$	$1x10^{-3}$
La-11	33	65	--	2	8.0	$1x10^{-4}$-$1x10^{-1}$	$5x10^{-3}$
La-12	33	58	6	2	18.0	$1x10^{-6}$-$1x10^{-1}$	$1x10^{-6}$
La-13	33	57	6	3	18.0	$1x10^{-6}$-$1x10^{-1}$	$1x10^{-6}$

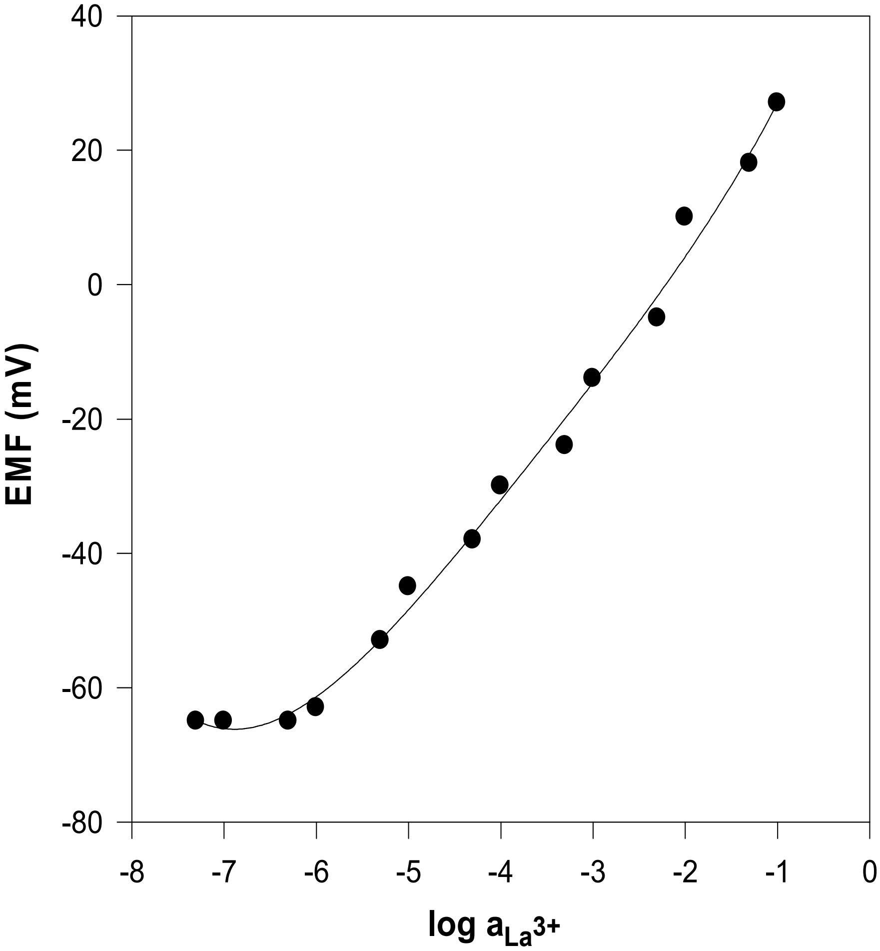

Figure 6.1: Calibration curve for the La (III) ion-selective electrode

Effect of Internal Solution Concentration

The influence of the concentration of the internal solution on the potential response of the La^{3+} ion-selective electrode was studied [27]. The results show that the variation in the concentration ($1x10^{-1}$ M - $1x10^{-4}$ M) of the internal solution changes the slope. A $1x10^{-4}$ M concentration of internal solution is quite appropriate for a smooth functioning of the electrode system. The results are shown in Table 6.2 and in Fig. 6.2

Table 6.2: Effect of internal solution concentration on the membrane electrode

Electrode Composition	Internal solution concentration, M	Slope, mV/decade	Measuring range, M	Detection limit, M
Electrode La- 6	$1x10^{-1}$	16.0	$1x10^{-1}$-$1x10^{-6}$	$6.3x10^{-6}$
	$1x10^{-2}$	17.0	$1x10^{-1}$ $1x10^{-6}$	$1.0x10^{-6}$
	$1x10^{-3}$	19.0	$1x10^{-1}$-$1x10^{-6}$	$1.0x10^{-6}$
	$1x10^{-4}$	19.0	$1x10^{-1}$-$1x10^{-6}$	$1.0x10^{-6}$

Effect of pH

The influence of pH on the response of the electrode was studied for different concentrations of the primary ion ($1x10^{-2}$ M, $1x10^{-3}$ M and $1x10^{-4}$ M) over the pH range 2-12 as shown in Fig. 6.3. The pH was adjusted by introducing small drops of HNO_3 (0.1 M) or NaOH (0.1 M) as per requirement. The buffer solutions were not used to adjust the required pH as it would unnecessarily introduce cations and anions from the buffer and might affect the results. EMF is independent of the pH in the range of 4-9. Therefore, this range can be chosen as the working pH range for the electrode assembly. However, variations in emf above and below this pH range may be due to the formation of La $(OH)_3$ and protonation of oxygen atoms of the DC18C6, respectively.

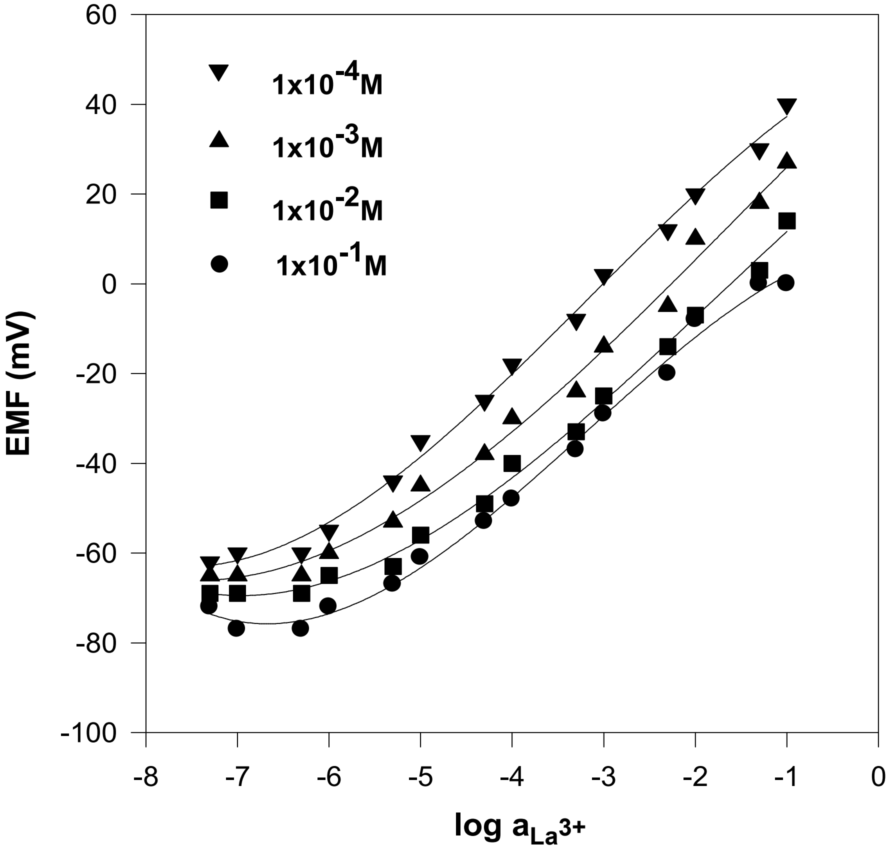

Figure 6.2: **Effect of internal solution concentration on potential responses of La (III) ion-selective electrode**

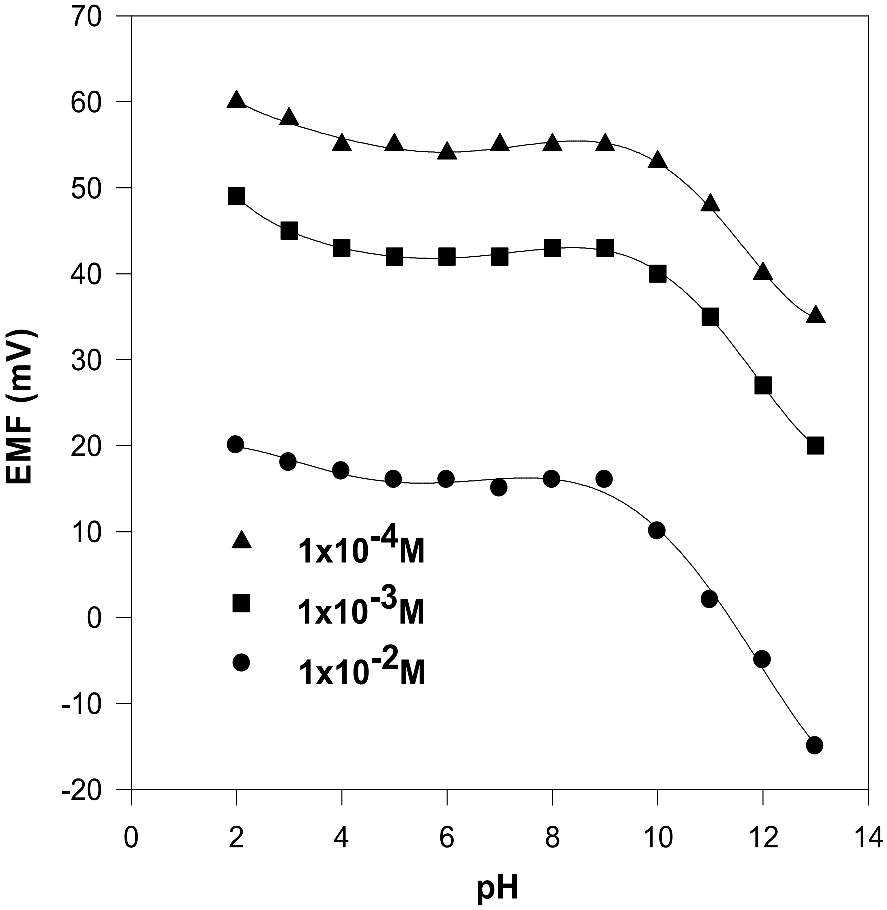

Figure 6.3: Effect of pH on the response of La (III) ion-selective electrode at different La (III) ion concentrations.

Selectivity Coefficients and Analytical Properties of Lanthanum-Selective Electrode

The selectivity is perhaps the most important characteristic of any electrode, which defines the nature of the device and the extent to which it may be employed in the determination of a particular ion in presence of other interfering ions. Potentiometric selectivity coefficients of lanthanum membrane electrodes were evaluated by the Fixed Interference Method (FIM) [25, 26] at 1x10^{-3} M concentration of interfering ions and the Matched Potential Method (MPM) [25, 26]. The MPM is recommended by IUPAC to overcome difficulties associated with methods based on the Nicolsky-Eisenman equation. According to this method, the specified activity of the primary ion (A) is added to a reference solution, and the potential is measured. In a separate experiment, the interfering ion (B) is successively added to an identical reference (containing primary ion) solution until the measured potential matches to that obtained only with primary ions. Table 6.3 shows potentiometric selectivity coefficients of a DC18C6 based lanthanum-selective electrode. The selectivity data indicate that the $K_{La,M}^{Pot}$ values are of the order 10^{-2} for trivalent metal ions. Therefore, the electrode can be used for the determination of La^{3+} ions in the presence of certain interfering ions.

Effect of Partially Non-Aqueous Medium on the Working of La (III) Electrode

The proposed sensor was investigated in partially non-aqueous media using methanol, ethanol and acetone mixtures with water. Fig 6.4 and Table 6.4 indicate that the slope is decreased from 19.0 mV/decade to 17.0 mV/decade with the addition of non-aqueous solvents. An increase in the non-aqueous content beyond 30% causes a significant decrease in the slope. In acetone medium, a significant change in emf, slope, measuring range and detection limit is observed. This may be due to the dynamic complex formation and decomplexation between DC18C6 and La (III) in the water-acetone mixture.

Table 6.3: The selectivity coefficient values of La (III)-selective electrode as calculated by fixed interference method and matched potential method

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

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

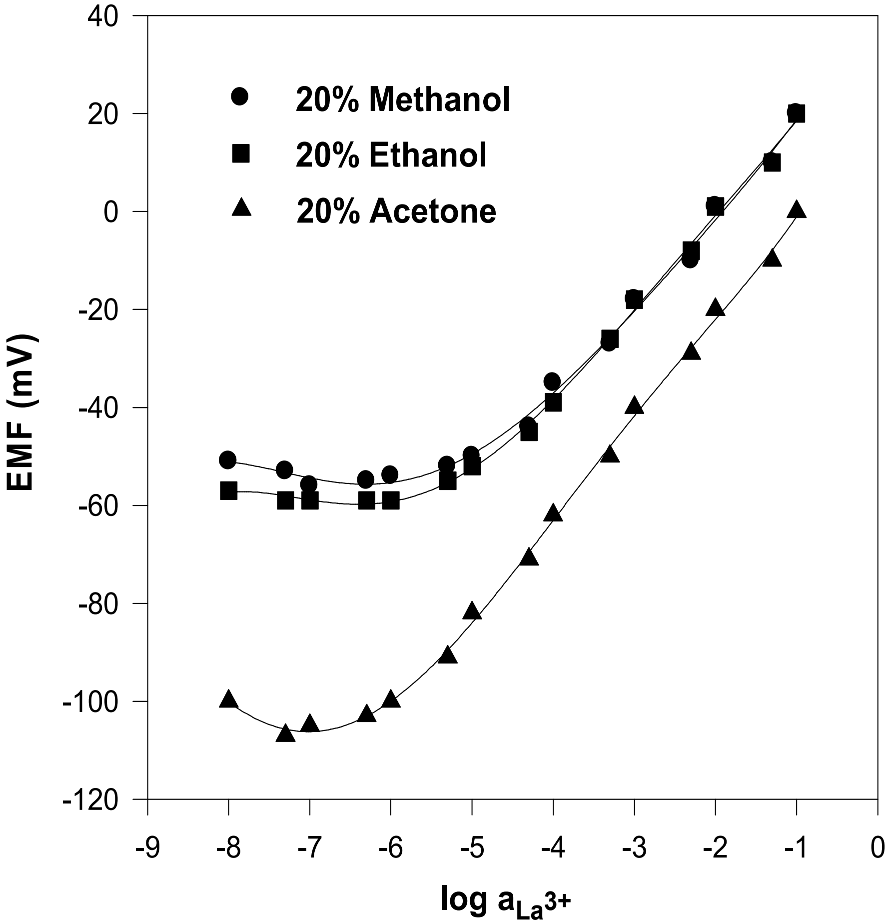

Figure 6.4: Effect of partially non-aqueous medium on potential response

Table 6.4: Effect of partially non-aqueous medium on the working of La (III) electrode

Non-aqueous solvent	Solvent content (% v/v)	Slope (mV/decade)	Working Conc. range (M)
Methanol	0	19	1.0×10^{-6} to 1×10^{-1}
	10	18	3.2×10^{-6} to 1×10^{-1}
	20	18	3.2×10^{-6} to 1×10^{-1}
	30	17	5.0×10^{-6} to 1×10^{-1}
Ethanol	0	19	1.0×10^{-6} to 1×10^{-1}
	10	18	2.0×10^{-6} to 1×10^{-1}
	20	18	2.0×10^{-6} to 1×10^{-1}
	30	17	4.3×10^{-6} to 1×10^{-1}
Acetone	0	19	1.0×10^{-6} to 1×10^{-1}
	10	19	1.0×10^{-6} to 1×10^{-1}
	20	19	5.0×10^{-7} to 1×10^{-1}
	30	19	2.3×10^{-6} to 1×10^{-1}

Potentiometric Titration

Potentiometric titrations were performed by using the proposed electrode as an indicator electrode for the titration of 25 mL of La^{3+} ions ($1x10^{-4}$ M) against EDTA ($1x10^{-3}$ M). The pH of the solution was adjusted to 7-8 using dilute ammonia solution. The titration curve is shown in Fig. 6.5. The curve shows a sharp inflexion point at the titrant volume corresponding to the formation of 1:1 complex of lanthanum ions with EDTA.

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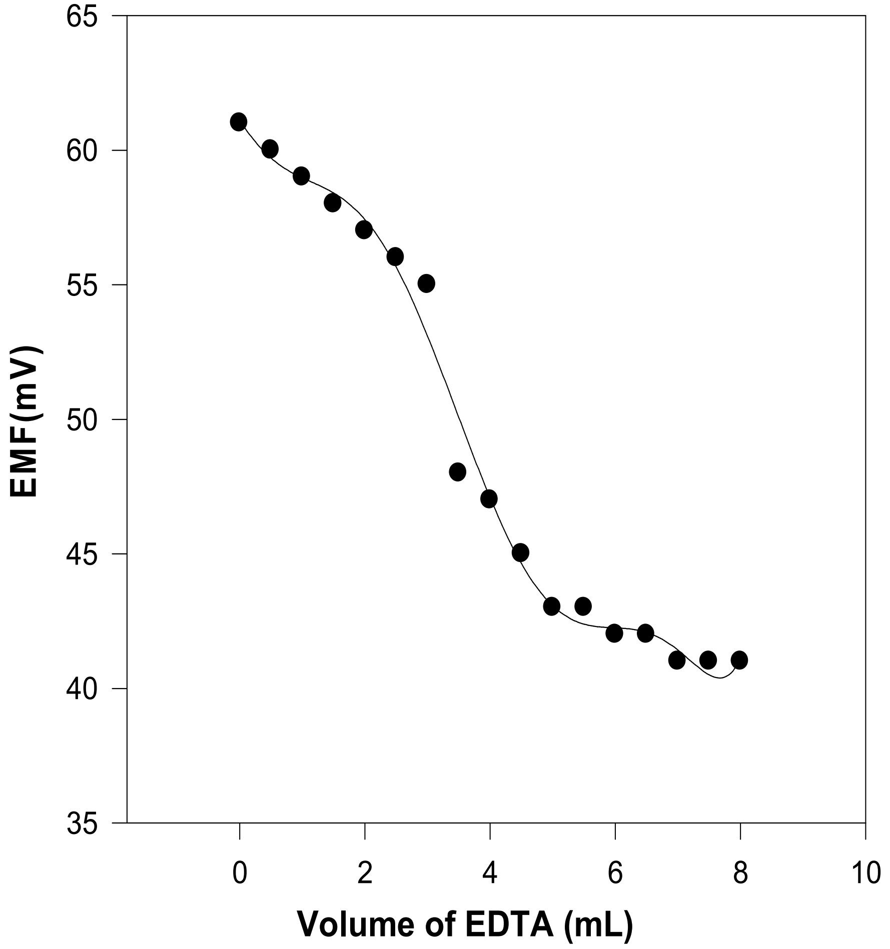

Figure 6.5: **Titration curve of La (III) ($1x10^{-4}$ M) with EDTA solution ($1x10^{-3}$ M) using La (III)-selective electrode**

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SUMMARY

The selective trace level determination of rare earth metal ions has always been a challenge for analytical chemists since all rare earth metal ions have identical sizes and properties. Ion exchangers have the distinction of being the only successful technique for separation and determination of them. Some tin and zirconium based ion exchangers have been used as electro-active materials for preparing membrane electrodes for some rare earth metal ions.

Synthetic procedures have been optimized to prepare a good quality of ion exchangers possessing workable particle geometry, chemical and thermal stabilities. Studies, like ion-exchange capacity, distribution coefficients for a number of rare earth metal ions, chemical composition and thermal stabilities, are reported for SnBP and ZrSbAs. The study of distribution coefficients for various metal ions suggests that SnBP is selective for Sm (III) ions while ZrSbAs is selective for Ce (III) ions.

Structural studies of SnBP and ZrSbAs have been carried out with the help of X-ray powder diffractogram, infrared analysis, XPS analysis, TGA analysis and SEM micrographs. X-ray diffractograms of both SnBP and ZrSbAs show their amorphous character. On basis of the chemical analysis and thermal studies, tentative molecular formulae have been proposed for both prepared ion exchangers. SEM photographs of SnBP and ZrSbAs show that their particles have a broad size range and an irregular form. The lack of clearly defined morphology correlates with the low crystallanity of compounds. The presence of linear layered structures is also evidenced from micrographs.

Electrochemical studies have been done on zirconium (IV) antimonoarsenate (ZrSbAs) by preparing ion-exchange membranes using polystyrene as a support material. Potential differences were measured across the membranes; keeping the electrode assembly

immersed in a thermostat maintained at 27±0.1° C. Experimental results indicate that the ion exchanger possesses selectivity.

Ion-selective electrodes are reported for samarium (III), cerium (III), praseodymium (III), and lanthanum (III) metal ions. Samarium (III)-selective electrodes have been prepared using zirconium (IV) boratophosphate (ZrBP) and tin (IV) boratophosphate (SnBP) as electro-active materials. A cerium (III) sensor is based on zirconium (IV) antimonoarsenate (ZrSbAs), while zirconium (IV) antimonotungstate (ZrSbW) has been used as an electro-active material for praseodymium (III) sensor. A lanthanum (III) sensor is based on dicyclohexano-18-crown-6.

A number of membranes having varying amounts of electro-active materials were prepared using an epoxy resin, PVC or polystyrene as binding materials. In case of ZrBP, the best performance is exhibited by a membrane having a composition: zirconium boratophosphate (10%) and poly vinylchloride (90%). This membrane works well over a wide concentration range of $1x10^{-5}$ M to $1x10^{-1}$ M of Sm (III) ions with a near-Nernstian slope of 20.2 mV/decade. The response time of the sensor is 15 seconds. In case of SnBP as an electro-active material, the best performance is exhibited by a membrane having a composition of 40% exchanger and 60% epoxy resin. This membrane works well over a wide concentration range of $1x10^{-5}$ M to $1x10^{-1}$ M of samarium ions with a super-Nernstian slope of 40.0 mV/decade. It has a fast response time of less than 10 seconds. The working pH range for both electrodes is 4.0-9.0.

In case of cerium, the best performance is given by a membrane having a composition: ZrSbAs (50%) and polystyrene (50%). It works well over a concentration range of $5x10^{-5}$ M to $1x10^{-1}$ M of cerium ions with a super-Nernstian slope of 52.0 mV/decade. It has a fast response time of 10 seconds. The working pH ranges for 10^{-2} M and 10^{-3} M Ce^{3+} solutions are 4.0-9.0 and 5.0-9.0, respectively.

A new ion-selective electrode (ISE) based on dicyclohexano-18-crown-6 as a neutral carrier has been developed for lanthanum (III) ions. The electrode comprises of dicyclohexano-18-crown-6 (6%), PVC (33%) and ortho-nitrophenyl octyl ether (o-NPOE) (61%). The electrode shows a linear response in a concentration range of 1×10^{-6} M to 1×10^{-1} M with a near-Nernstian slope of 19.0 mV/decade and a detection limit of 5×10^{-7} M. It has a response time of <30 seconds and the working pH range is 4.0 – 9.0.

Praseodymium-selective electrodes have been prepared, which are based on PVC and polystyrene as binders, using zirconium (IV) antimonotungstate as an electro-active material. Both membranes have been used for further studies. These membranes work well over a concentration range of 5×10^{-5} M to 1×10^{-1} M of Pr^{3+} ions with a near-Nernstian slope of 25.0 mV/decade. The polystyrene based membrane has a fast response time of 10 seconds as compared to a PVC based membrane that gives a response time of 15 seconds. The working pH range for both membranes is same i.e., 4.5-9.0.

Selectivity coefficients have been determined by FIM for Sm (III), Ce (III) and La (III) sensors. For the Pr (III) sensor and La (III) sensor, same has been done using the matched potential method (MPM). All proposed sensors reveal good selectivities with respect to alkali, alkaline earth, some transition and rare earth metal ions that are normally present along with respective metal ions in their ores. The sensors have also been used as indicator electrodes in potentiometric titrations of metal ions against EDTA solution in case of Sm (III), Pr (III) and La (III) sensors, while for the Ce (III) sensor the same has been done using oxalic acid. The effect of internal solution has been studied and electrodes were successfully used in partially non-aqueous media, too. All electrodes have an average lifetime of about five months.

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LIST OF PUBLICATIONS

1. PVC based dicyclohexano-18-crown-6 sensor for La (III) ions
   S.K.Mittal, Ashok Kumar S.K. and Harish Kumar Sharma
   Talanta, 62 (2004) 801-805.
2. Samarium (III)-selective membrane sensor based on tin (IV) boratophosphate
   S.K.Mittal, Harish Kumar Sharma and Ashok Kumar S.K.
   Sensors, 4 (2004) 125-135.
3. Synthesis of new zirconium based ion exchangers and their characterization
   S.K. Mittal, P.P. Singh and Harish Kumar Sharma
   Journal of Ion-exchange (Japan), (In press).
4. Synthesis and Characterization of tin (IV) boratophosphate: a new inorganic ion exchanger
   S.K. Mittal and Harish Kumar Sharma
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5. Samarium (III)-selective electrode based on zirconium (IV) boratophosphate
   S.K. Mittal and Harish Kumar Sharma
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6. Electrochemical studies on polystyrene based membrane of zirconium (IV) antimonoarsenate
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   (Under revision)
7. Zirconium (IV) antimonoarsenate based sensor for cerium (III) metal ions
   S.K. Mittal and Harish Kumar Sharma
   (Under preparation)
8. Zirconium (IV) antimonotungstate based sensor for praseodymium (III) ions
   S.K. Mittal and Harish Kumar Sharma
   (Under preparation)
9. Synthesis and characterization of zirconium (IV) antimonoarsenate
   S.K. Mittal and Harish Kumar Sharma
   (Under preparation)

Conference Papers

1. Samarium (III)-selective membrane sensor based on Tin (IV) boratophosphate
   S.K.Mittal, Harish Kumar Sharma and Ashok Kumar S.K.
   Presented at 10th International Meeting on Chemical Sensors held at Tsukuba (Japan) from July 11-14, 2004 (Technical Digest 3P 045)
2. Samarium (III)-selective electrodes
   S.K. Mittal and Harish Kumar Sharma
   Presented at 6th CRSI National Symposium held at IIT, Kanpur from Feb. 6-8, 2004 (Abstract 272)
3. Synthesis and characterization of some inorganic ion exchangers
   S.K. Mittal, P.P. Singh, Harish Kumar Sharma and Ashok Kumar S.K.
   Presented at NCMRT-2003 held at TIET, Patiala, (Proc. pp 33-42)