ANALYTICAL SELECTIVITY AND FUNCTIONAL PROPERTIES OF SOME ION EXCHANGE MEMBRANES

A THESIS

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CHEMISTRY

By

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Dedicated to My Late Grand Father

Shri Kishan Lal Tomar

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled, **"ANALYTICAL SELECTIVITY AND FUNCTIONAL PROPERTIES OF SOME ION EXCHANGE MEMBRANES"** in fulfilment of the requirement for the award of the degree of Doctor of Philosophy, submitted in the Department of Chemistry of this University, is an authentic record of my own work carried out during the period from July, 1989 to December, 1993 under the supervision of Prof. S.K. Srivastava.

The matter embodied in this thesis has not been submitted by me for the award of any other degree.

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ABSTRACT

The development of high performance chemical sensors is a fast growing area in the field of analytical science and technology. Chemical sensors are analytical systems for measuring ions and molecules in solution. The most widely studied chemical sensors are the potentiometric based electrochemical devices i.e., ion-selective electrodes. Potentiometric ion-selective electrodes detect changes in electrode potential or membrane potential arising from the specific adsorption or other interactions of ionic species onto the surface of the sensitive layer. In order to be analytically useful the process must be selective with respect to the species of interest.

Ion-selective electrodes find many applications in the analysis of raw materials and for quality control of the products due to the speed, sensitivity, cost, reliability and non consumption of the sample in the process. These are specially useful tool for monitoring environment or waste water and also in biological studies particularly in the field of clinical chemistry where a large number of samples and the need for a rapid method of analysis, rule out many slower, more involved methods. Besides this the device can be used irrespective of the colour, viscosity etc. of the test solution and almost no sample preparation is necessary.

A survey of literature as well as market reveals the availability of electrodes for mono and bivalent cations. Sensors for polyvalent cations and anions are still not commercially available. Besides this there is a big question mark on the selectivity of sensors commercially available and also the one being reported in literature. As such investigations, to obtain tailor made material to provide electroactive phase having specific selectivity for a particular ion, are called for.

The work included in this thesis deals with the development of sensors with the help of some ionic polymers and inorganic gels exhibiting ion exchange characteristics. The details are presented in the following sequence :

An inorganic gel polytungstoantimonate, is reported to possess high selectivity for bivalent viz., Cd^{2+}, Zn^{2+}, Cu^{2+}, etc. ions. In view of this, it was thought desirable to observe the electroanalytical selectivity of this gel material and explore the utility of the membranes of this substance for the estimation of bivalent cations. Efforts made in this direction are given below:

Heterogeneous membranes using araldite as binder were prepared and relevant functional properties like water content, porosity, swelling, electrolyte absorption and conductance were determined. The values of water content, porosity and swelling were found to be negligibly small, thus magnifying the importance of exchange sites in the gel membrane. The conductance of the membrane is found to decrease with ionic radii.

The electrode exhibits a near Nernstian response for cadmium ions in the range 6.31×10^{-5}-1.00×10^{-1}M at pH 5-7 with a slope of 26 mV/decade of concentration. The response time is less than one minute and the potentials stay constant for more than three minutes. The electrode assembly has very limited validity in partially non-aqueous medium. Monovalent ions cause some interference in the working of this assembly, but bivalent and polyvalent ions cause negligible interferences. This electrode has significant effect of surfactants. Titrations involving cadmium nitrate have also been monitored by using this membrane sensor.

Same inorganic ion exchanger has also been used for the preparation of Zn^{2+} selective sensor. It responds to Zn^{2+} ions in the range of 5.00×10^{-5}-1.00×10^{-1}M at pH 3.5-6.0. Variation of membrane potentials in partially non-aqueous medium has been studied and it is observed that upto 20% non-aqueous content the sensor shows nominal increase in slope with simultaneous slight decrease in working concentration range. Monovalent ions cause a little interference while bivalent and polyvalent cations like Pb^{2+}, Cd^{2+}, Al^{3+} etc. do not interfere. Small additions of surfactant upto 5.0×10^{-5}M concentration does not cause any interference but higher concentrations of surfactants are likely to interfere. The sensor has also been used as an end point indicator in potentiometric titrations involving Zn^{2+} ions. A comparative assessment indicates a better performance of the membrane sensor for the evaluation of zinc in comparison to cadmium ions.

Tin oxide has been reported to possess promising selectivity for some anions like PO_4^{3-}, CrO_4^{2-}, VO_3^- etc. Preliminary investigations suggested the utility of the membrane sensor for the estimation of VO_3^- or CrO_4^{2-} ions. Functional properties of this membrane sensor are also quite low and comparable to the membranes of the same class. The tin oxide membrane in polystyrene binder gives excellent response for vanadate ions. It can be used to estimate vanadium in the range 2.51×10^{-4}-1.00×10^{-1}M and exhibits very good selectivity towards these ions with reasonably fast response time over a wide pH range 4 to 10, though the behaviour in partially non-aqueous medium is not so good. In the presence of anionic surfactant (upto a concn. of 1.00×10^{-4}M) sodium dodecyl sulphate, no adverse effect, on the working of the sensor is observed. The electrode assembly could also be used as an indicator electrode in the titrimetric estimation of vanadium. Efforts were also made to see the selectivity of this membrane for chromate ions. Although the working concentration range (1.78×10^{-4}-1.00×10^{-1}M) for chromate ions is somewhat better in comparison to vanadate ions, the other factors like selectivity, effect of non-aqueous medium and the presence of surfactant etc. suggest that the membrane will form a better sensor for the estimation of vanadium.

The use of organic resins specially chelating polymeric resins are finding importance as scavenger of metal ions. Resins of this type exhibit a very selective behaviour towards some heavy metal ions. In view of the importance of such compounds 2-hydroxy naphthaldoxime formaldehyde resin has been tried as an electroactive phase in the membrane sensors for Pb^{2+} ions. Membranes were prepared using PVC as well as polystyrene as binders. Functional properties like water content porosity, swelling and electrolyte absorption could be determined only in the case of polystyrene based membranes and the same are found to be quite low in comparison to the values recorded for inorganic gel membranes comparison.

Polystyrene based membrane electrode of the said resin shows linear response in the range 1.58×10^{-4}-1.00×10^{-1}M concentration of lead ions with a slope of 35 mV/decade of concentration while the PVC based membrane sensor have comparatively lower working concentration range i.e., 3.16×10^{-4}-1.00×10^{-1}M for the same (Pb^{2+} ions) with a still higher slope of 40 mV/decade of concentration. Both the electrodes are operational in a pH range 4 to 7. Both the electrodes have a very limited validity in partially non-aqueous medium. Selectivity coefficient values suggest the interference of monovalent ions while bivalent and polyvalent cations are found to have very low values of this parameter. Mixed run plots clearly indicate the utility of the electrode even in the presence of lower concentrations (upto 1.00×10^{-4}M) of monovalent ions. Higher concentration of surfactants cause significant interference. Both the membranes can be used as an indicator electrode in potentiometric titrations of Pb^{2+} ions with EDTA. A comparative assessment reveals a better performances of polystyrene based membrane as a sensor for lead ions in comparison to the PVC based one.

The electroanalytical selectivity of one more such resin (2-salicylaldene aminothiopehnol formaldehyde) for cadmium and zinc ions both has been investigated. Membranes were fabricated with the above resin using both polystyrene and PVC as the binder material.

Polystyrene based membranes were characterized in terms of water content, porosity, swelling, electrolyte, absorption and conductance. These membranes show response for cadmium ions in a wide concentration range 1.00×10^{-4}-1.00×10^{-1}M with a slope of 15mV/decade of concentration. In this case also the performance is better than those of PVC based membranes where the range is 1.79×10^{-4}-1.00×10^{-1}M and the slope of the plot is 12mV/decade of concentration. Potentials stay constant over a pH range of 4-6. Similarly for zinc ions the working concentration range (1.26×10^{-4}-1.00×10^{-1}M) for polystyrene based membrane is better than the PVC based one where the range is from 2.51×10^{-4} to 1.00×10^{-1}M. Even the slope of the plot is better for polystyrene based membrane.

The response of polystyrene based membranes are generally faster in comparison to PVC based membranes in both the cases.

Cadmium can be estimated in solution having 15% non-aqueous content with a polystyrene based membrane sensor while the PVC membrane does not function in non-aqueous medium. Estimation of zinc, in partially non-aqueous medium, is not possible at all. Selectivity coefficient pattern in the case of cadmium ions suggests the superiority of polystyrene supported membranes over the PVC based ones. Even in the case of zinc ions, polystyrene based membrane electrodes are superior. Polystyrene supported membranes, during the estimation of Cd^{2+} ions, have higher tolerance limit of monovalent cations and surfactants ions.

Polystyrene as well as PVC based membranes act as good end point indicators in potentiometric titrations of Cd^{2+} and Zn^{2+} with EDTA.

Thus it can be concluded that the membrane sensor incorporating 2-salicylaldene amino thiophenol formaldehyde as an electroactive phase in polystyrene, is a better sensor for cadmium in comparison to zinc and it is quite obvious that the choice of the binder influences the response, slope and selectivity of the membrane. Use of polystyrene as binder exhibits an improved response and selectivity.

In the end (last chapter) the applications of polytungstoantimonate and 2-salicylaldene amino thiophenol membranes, for the estimation of Zn^{2+} and Cd^{2+} in three waste water samples, are described. The results achieved with the electrodes fabricated in this lab. compare well with the values obtained by the help of more sophisticated techniques.

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A paper entitled "A membrane sensor for the estimation of vanadium as vanadate"was accepted for the presentation in the "Seventh international conference on sensors and actuators" held in Yokohama, Japan in August 1993.

CONTENTS

CHAPTER - I

GENERAL INTRODUCTION

I.1. Introduction

Ion-selective electrodes or sensors in general has been a subject of rapidly increasing interest over the last three decades and their development has opened up a large new field of potentiometry. The speed at which this field has developed is a measure of the degree to which the electrodes and probes meet the requirements of the average analyst for rapid, accurate and low cost analysis. In situations where analysis is performed frequently, these probes are replacing existing techniques; in other case such as "On Line" monitoring, the use of a potentiometric sensor has made feasible, the measurements which are otherwise almost impossible. The growth of these applications has been fast in relation to the growth of other techniques partly because the sensors themselves became widely available commercially soon after their development and are in some cases also quite easy to make in laboratory. The scope of work in this particular area of research has further widened with the advent of Gas and Bio sensors. Despite these developments, very few sensors are commercially available for polyvalent anions and cations and the one available for monovalent ions also suffer with the problems of sensitivity, slope and effect of aging etc. Naturally more and more investigations in this direction are called for.

The best known ion-selective electrode, so for recognized, is the hydrogen electrode which has now become an essential equipment of every analytical lab. It traces it's discovery to Cremer (1906) and Haber and Klemen Siewicz (1909) who found that certain glasses respond to hydrogen ion activity. The response of the glass electrode was commonly believed to be a result of migration of hydrogen ions through the thin glass membrane. Studies carried out by Karreman and Eisenman (1962) and the work of Stephanova et al. (1963) provided the insight necessary for the development of new ion-selective electrodes. At present sensors are available for Na^+, K^+, Ag^+, Mg^{2+}, Ca^{2+}, Cd^{2+}, Cu^{2+}, NH_4^+, S^{2-}, I^-, Cl^-, CN^-, SO_4^{2-} etc. ions. The electrodes are available from many manufacturers and as newer methods of preparation of ISEs are developed, several kits for the preparation of different electrodes using a common body or housing have been introduced.

Potentiometric sensors can be divided into three subgroups :

(a) Ion sensors

(b) Gas sensors

(c) Bio sensors

I.a. Ion sensors

Although some research activity in this field started quite early, systematic investigations started in 1940 when Pungor and co-workers (1,2) studied the behaviour of silver iodide precipitate as a model substance. Their paper dealt with the development of the first heterogeneous precipitate based electrode. Recently the number of precipitate based ion sensors has increased significantly and these involve electrodes of both homogeneous and heterogeneous structures.

Since the discovery of the first precipitate based ion selective electrode, a large number of papers have appeared in literature dealing with various theoretical as well as practical aspects and this unambiguously reflects the interest generated in this area of research. Special importance is given to this field in view of the fact that it allows a simple and selective determination of various anions and cations for which the classical methods are cumbersome and the available more sophisticated techniques involve costly equipments viz., ICP etc.

The research activity on ISEs was very much boosted with the development of the lanthanum (III) fluoride membrane electrode for the estimation of F^- by Frant and Ross (3), followed a year later by a liquid membrane electrode for calcium by the same workers (4).

Another significant development at this time was the work of Stefanac and Simon (5) on neutral carrier antibiotics which showed valinomycin to be very selective for potassium.

Initial investigations and subsequent work done in this field is summarized in numerous review articles published from time to time (6-8). Some specialized reviews by Fricke (9), Freiser (10) and Moody (11,12) provide an exhaustive and detailed information on the subject.

Periodic reviews in "Analytical Chemistry" (13-24) cover all the recent publications in this field, including theory, methodology and applications of ion-selective electrodes. Membranes prepared from gels/precipitates etc. can vary from homogeneous single crystal (3), pressed pellets (25, 26), to heterogeneous dispersions (27) of the active material in an inert matrix, e.g., silicon rubber, polystyrene and PVC.

Since all the precipitates and polymeric materials can not be fused or mechanically pressed into stable membranes, heterogeneous solid-state membrane electrodes (1) were fabricated by incorporating silver halide powders into flexible, hydrophobic inert binders of silicon rubber. Electrodes of this type are also known as `Pungor' electrodes. Many binding materials have been used including PVC, polyethylene etc. (28).

Voluminous literature in this area of research has piled up in the last three decades. It is not possible to present here the bibliography of all significant land marks, however, the work done in the last two decades is being mentioned in brief, in subsequent pages.

Among the various cations numerous efforts have been made to develop sensors for Na^+, K^+, Rb^+, Cs^+, Cu^{2+}, Cd^{2+}, Pb^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} etc. Coetzee and co-workers (29-31) first started work on the epoxy resin based membranes of tungsto and molybdo phosphates and found these selective to Cs^+ and Tl^+ ions. In this laboratory, Malik, Srivastava and co-workers (32) developed electrodes selective to Tl^+ and Cs^+ ions using membranes of tungstoarsenates while Jain and co-workers utilized heteropolyacid salts to prepare sensors for Tl^+. (33,34) and Rb^+ (35) ions. Solid-state electrodes for molybdate ions (36,37) have also been reported from this laboratory. Besides this Srivastava and co-workers have made exhaustive investigation on inorganic ion exchange gels as electroactive phase and have fabricated sensors for Hg(II), Pb(II) and Cr(VI) (38-40).

Investigations on fluoride ions estimation are still continuing. Maurizio Bettinelli (41) has reported an ion sensor for the determination of fluorine in environmental reference materials. Some Russian workers have examined the selectivity of fluoride electrode for chloride, bromide and iodide as interferents in non-aqueous medium (42). The performance of six chelating reagents has been studied for masking zirconium (IV) in the determination of fluoride with an ISE. Fluoride was successfully determined at a concentration of 10^{-5}M dm^{-3} in presence of 10^{-6} mol dm^{-3} zirconium (43) and Smid (44) has measured fluoride in non-linear region by blank adjustment method using his own electrode. Determination of fluoride in presence of water soluble organic substances is also possible using a fluoride sensor (45). Xie and co-workers (46) have worked on the growth of lanthanum fluoride crystals for fluoride ISEs.

Potentiometric titrations of fluoride as such (47) and in acidic medium could be done using a fluoride ISE (48).

The electrochemical properties and preparation of lead(II) ion selective membrane electrodes have been studied by using precipitates of sulphides, oxides, selanides and other salts of lead together with silver sulphide (49-53). A solid membrane sensor made with titanium arsenate as membrane material and araldite as binder has been reported by Srivastava and co-workers (39) for the measurement of lead ion activity in the concentration range from 5.00×10^{-5} to 1.00×10^{-1}M. The electrode can work in the pH range 2-5 and is tolerant of ethanol up to a content of 30% V/V. Tyagi and co-workers (54) have also reported a bismuthtungstate based solid membrane sensor for lead (II).

Apart from inorganic ion exchangers, some sensors based on neutral carriers have also been successfully used for the estimation of lead (55-57). Very recently Borraccino and co-workers (58) have reported a polymer based membrane sensor for Pb^{2+} with a detection range of 1 μm to 8.4 mM.

Solid state sensors for cadmium has also been a subject of interest. These have incorporated inorganic gels and polymers as electroactive phase (58-61). Rakhman'ko and co-workers (62) have reported a PVC based membrane sensor for cadmium having dibutyldidecyl ammonium sulphate as electroactive phase. Some good sensors (63, 64) have also been proposed for Zn^{2+} ions by various workers. Very recently Lindner and co-workers (65) have used zinc selective ionophores for potentiometric and optical sensors. All the ionophores exhibit proton interference and to compensate it, the pH of the buffer solution must be > 6.

Crown ethers have played an important role in the development of ion-selective electrodes due to their specific selectivity extraction efficiency for metal ions. A number of potassium-selective electrodes based on crown ethers have been reported and their performance investigated. These electrodes incorporate bibenzo-24-Crown-8 (66), 4,4'-di-t-butyl dibenzo-30-Crown-10 (67), dibenzo-30-Crown-10 (68), naphtho-15-Crown-5 (69), bis (benzo-15-crown-5) derivatives (70) dialkyl (dibenzo-18-Crown-6) (71), mono (nitro-benzene-15-crown-5) and bis(benzo-15-crown-5) derivatives (72), 15,15'-octamethylene bis(benzo-15-crown-5) (73), benzo-15-Crown-5 and benzo-18-crown-6 linked by an o- or m-phenylene bis(oxymethylene) group or two benzene-15-crown-5 molecules correspondingly linked (74). Valinomycin neutral carrier-based electrodes have also been prepared (75-76). Two molecules of benzo-15-crown-5 linked at 15-position by m-phenylene bis(methyl amino) group or their derivatives have been used in the preparation of K^+-selective PVC-based electrodes (77). The electrode has high selectivity for potassium over other alkali and alkaline earth metal ions. Rani et al. have also reported an electrode by incorporating crown ether-heteropolyacid precipitate in PVC matrix (78). The electrode tolerated non-aqueous content up to 20%.

Recently Brzozka and co-workers (79) developed a PVC based electrode by incorporating NN'-substituted 4,13-diaza-18-crown ethers.

Membrane electrodes with 2-methyl quinolyl or 2-methyl quinolyl-1-oxide groups showed high selectivity for Hg^{2+} ions. A rectilinear response was obtained from 0.01 μm to 1.0 mM Hg^{2+}. Sakamoto (80) has reviewed the development of Li^+selective 14-crown-4-derivatives and their application to Li^+ ion sensing. Very recently Sheen and Shih (81) have reported a lead ion-selective electrode based on crown ethers. Near Nernstian response were obtained for 0.1 M to 10 μM Pb^{2+} with a slope of 30 mV decade^{-1}. Some more sensors based on crown ethers and their derivatives have been reported for the estimation of Na^+, K^+, Li^+, Cs^+ and Rb^+ (82-86).

The use of calixarenes and cryptands are finding importance as active agents for chemical sensors because of a very selective behaviour towards some ions over the other. Foster and co-workers (87) incorporated calixarenes into plasticized PVC membranes to produce ion-selective electrodes. Functional group modifications to the calixarenes, and changes in the cavity size and molecular conformation, allowed the selectivity of the corresponding electrodes to be controlled. Sensors for Na^+, K^+ and Cs^+ were constructed from neutral carrier electrode membranes comprising of 0.7% ionophore 0.2% K tetrakis-(p-chloro phenyl) borate, 66.1%

2-nitro phenyl octyl ether and 33% PVC. Tetrameric calixarenes substituted with CO groups gave electrodes highly selective to Na$^+$, whereas hexameric calixarenes give good Cs$^+$ selectivity. Another sensor (88) based on p-t-butyl calix[4]arene tetra ethyl ester in PVC matrix has shown Nernstian response with a detection limit of 10-30 μM for Na$^+$ ions. Based on calixarene O'Connor and co-workers (89) have developed a potentiometric ion-selective electrode for silver, the electrode displays a linear response for Ag$^+$ in the concentration range of 0.1 to 100 μM with a slope of 50 mV/decade. It has also been used in potentiometric titration of silver. Very recently, Domansky and co-workers (90) have developed a sodium-selective membrane electrode based on p-tert-butyl calix[4]arene methoxy ethyl ester. Rb$^+$ selectivity of PVC membranes based on cryptands with thiourea fragment has been discussed by Lukayanenko (91). The sensor is found to be selective to Rb$^+$ ions over the range 0.1mM to 0.1M with response time of 2-5 seconds.

I.1.b. Gas Sensors

A potentiometric membrane sensor that responds to gases does so by physically separating an inner electrolyte solution from the external sample solution. The physical separation is constructed so as to allow for gaseous diffusion to occur between the outside and inside fluids. The diffusion of specific gases alters an equilibrium within the inner electrolyte that is sensed by a fundamental type ion-selective electrode (i.e. pH electrode). This separation can be as simple as an air gap across which gases diffuse as dictated by their partial pressures in the external sample solution and the inner electrolyte solution. This approach was demonstrated in the construction of both ammonia and carbon dioxide sensors using a pH electrode to sense the hydrogen ion shift during the electrode operation (92). Other indicator electrodes can be used as well.

Solid state potentiometric sensors are some of the most robust chemical sensors. These are designed as structures in which both ionic and electronic conductors are combined. The cell emf may depend on the mixed potential of the working electrode and may be affected by suitable additives. This is a possible way of achieving selectivity of these sensors. In most cases these do not contain water, can be operated at high temperatures, and for that reason do not suffer from the common interference from ambient humidity. The largest group of this type sensor is based on the ZrO_2 solid electrolyte which makes it particularly suitable for detection of oxygen (93, 94) and CO_2 (95, 96). Some oxygen sensors (97, 98) that are operational from room temperatures to high temperatures are based on LaF_3. Ammonia (99, 100) gas sensing electrodes have been used for a wide variety of analytical applications.

I.1.c. Bio sensors

Potentiometric bio sensors are devices that derive their selectivity from some biochemical process with some common and distinguishing characteristics. Invariably, the bioselective moiety is immobilized on some kind of support. These can be implemented either in a microscopic or in a macroscopic version.

Models that describe the relationship between the out put signal and concentration are usually complex, and the range of substrates tends to be wide. Use of enzymes, particularly glucose oxidase, leads the field of bio sensors because of great potential as analytical tools for biologically important compounds (101, 102,23). Electropolymerization of pyrrole has been an useful way to immobilize enzymes on electrode surfaces (103, 104). Recently Matsue and co-workers (105) reported an enzyme-based switching device responsive to NADH, taking advantage of the conductivity change in the polypyrrole induced by an enzyme catalyzed reaction. Various reviews (106-108) dealing with development and recent trends in bio sensor field have appeared in literature.

Inspite of voluminous literature available on this subject, mostly the publications deal with the development of sensors showing response to mono/bivalent ions. Even the commercially available ones are sensing either monovalent or bivalent ions. Efforts to fabricate electrodes for multivalent ions have not met with success and exhaustive investigations in this direction are called for . Besides this the applications of ion-selective electrodes are expected to increase substantially, in coming years, with the availability of tailor made electrode materials. This provides a lot of scope for improvement and automated instrumentation, there by simplifying its use.

I.2. The problem

In this laboratory inorganic gels have been exploited for the development of sensors for some heavy metal ions. Some of the products possess promising selectivity and are used for monitoring toxic ions in waste water besides estimating metals in analytical chemistry labs.

In the course of these investigations, a new inorganic ion exchanger, polytungstoantimonate has been developed and is found to possess good selectivity for some bivalent ions (109). The product has been tried as a membrane sensor for Cd^{2+} and Zn^{2+} ions and detailed investigations carried out on the proposed electrodes formulate a part of the subject matter of this dissertation.

The ion exchange and membrane behaviour of hydrous oxides has also been a subject of study (110-111) for quite some time. Most of the work reported in this direction deals with Zr & Fe oxides. Sorption behaviour of tin oxide (112, 113) has also been observed under different physical conditions. Consequently investigations were also planned to study the membranes of this compound and the sensor was found to exhibit very good response to vanadium and chromium (as anions). These findings are also described in this thesis.

Chelating ion exchange resins are found to possess specific selectivity for some metal ions and play an important role in separation processes. Keeping in view the behaviour of such organic polymeric products, two compounds namely 2-salicylaldene amino thiophenol formaldehyde and 2-hydroxy naphthaldoxime formaldehyde (114) have been tried for the estimation of Cd^{2+}, Zn^{2+} and Pb^{2+}.

The investigations reported in this thesis are in the following sequence :

The significant contributions and achievements made in this subject, in the last few years are reported in the introductory chapter while the basic principles, methodology and experimental details are described in chapter II. Preparation and characterization of the two inorganic gels polytungstoantimonate and tin oxide and the polymer resins 2-salicylaldene amino thiophenol formaldehyde and 2-hydroxy naphthaldoxime formaldehyde are also mentioned in the same chapter. These products have subsequently been used as electroactive phase in the fabrication of membrane sensors.

The functional properties and electrochemical selectivity of polytungstoantimonate and tin oxide membranes are recorded in chapter III, while similar investigations made with the two organic resins are mentioned in chapter IV of this thesis.

Chapter V includes some practical application of the sensors - the subject of study of these investigations.

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CHAPTER - II

METHODOLOGY AND MATERIALS

II.1. Synthesis and characterization of inorganic gels (Polytungstoantimonate and tin oxide)

During the last three decades inorganic ion exchangers have attracted much attention as these exhibit better selectivity and stability towards temperature and ionizing radiations. Among the different class of compounds of this type, the insoluble salts of polybasic metal ions, heteropolyacid salts and hydrous oxide of some metals like Zr, Sn, Fe, Al etc. have been studied intensively and these show important ion exchange characteristics. Some of the compounds, having good ion exchange properties have been prepared in this laboratory also (1-4).

Investigations are also in progress to have tailor made materials for the fabrication of "Ion-Selective Electrodes" possessing ideal selectivity. In the process, inorganic ion exchangers have also been tried and some good sensors have been proposed from this laboratory for the estimation of some cations and anion (5-8). Investigations reported by the group have been summarized in a review article written by Coetzee (9) in Ion-Selective Electrodes Reviews.

A new synthetic inorganic ion exchanger polytungstoantimonate has recently been reported to possess promising selectivity for multivalent metal ions (10). As such it was considered worthwhile to utilize this product and explore the possibility of using it's membrane for the estimation of some metal ions. Besides this another product tin oxide (11-12) is also known to possess good ion exchange characteristics which are highly pH dependent. The same can also be tried for the fabrication of membrane sensors and the methodology adopted for the investigations, is given in subsequent pages.

II.1.a. Synthesis of polytungstoantimonate gel

Chemicals and reagents

Antimony pentachloride (Fluka A.G.) was used as such. All the other reagents were AR grade chemicals (BDH/E. Merck/S. Merck).

Synthesis

Five samples of polytungstoantimonate having different compositions were prepared by mixing 0.1M solution of antimony pentachloride taken in 4.0M HCl/0.05M aqueous solution of potassium pyroantimonate with 1.2M/0.6M sodium tungstate solution in water. The mixture in each case except B_1(Table-1) was acidified with 35 ml of conc. HCl and was digested at steam temperature or refluxed as shown in Table-1. The product was then allowed to settle. It was filtered and washed with deionized water several times until free from soluble antimony and tungsten. pH of the washings was found to be 3.1. The product was dried in air, broken down into small particles and sieved into 50-100 mesh size. The material was converted into H^+ form by shaking with 2.0M HNO_3 intermittently for one day and the excess acid was washed with deionized water. It was first air-dried and then dried in vacuo over $CaCl_2$. The conditions of preparation are summarized in Table-1.

Table-1

Synthesis and properties of polytungstoantimonate

Batch No.	conc. (mole)		Mixing volume ratio Sb(V) W(VI)	Digestion temperature & time (h)	Colour (state)	W/Sb ratios	H^+ ion liberation capacity meq/g for Na^+
	Sb	W					
B_1.	0.1(AP)	1.2	1:1	Steam temp. (2)	Yellow (glassy)	15.14	0.81
B_2.	0.05(PP)	0.6	1:1	Steam temp. (2)	Yellow (glassy)	35.10	0.83
B_3.	0.05(PP)	0.6	2:1	Steam temp. (2)	Light Yellow (glassy)	18.87	0.78
B_4.	0.05(PP)	0.6	1:1	Refluxed (8.5)	White (amorphous)	-	0.47
B_5.	0.05(PP)	0.6	1:1	Steam temp. (8.5)	Light Yellow (amorphous)	-	0.61
B_6.	0.10(AP)	1.2	1:1	Steam temp. (4)	Yellow (glassy)	13.56	0.73

AP = antimony pentachloride, PP = potassium pyroantimonate

Complete analysis of the exchanger material was done by standard chemical and instrumental methods. Tungsten was determined gravimetrically as $WO_2(C_9H_6ON)_2$ and antimony was determined iodimetrically using standard iodine solution after reduction of Sb(V) to Sb(III) with red phosphorus and iodine. To test the accuracy, tungsten was again determined spectrophotometrically by the standard thiocynate method and antimony was estimated spectrophotometrically by the iodide method.

Chemical stability of the samples was tested by treating 1.0 g. of the exchanger material (50-100 mesh H^+ form) with 100 ml of required acid/alkali/salt solution for four hours. Tungsten and antimony were determined in the solution spectrophotometrically by thiocynate and iodide methods respectively. The exchangers have a little tendency to leach in alkali solutions, but it is inhibited in presence of salt solutions. Due to it's higher stability in acids, the exchanger B_1 was selected for further investigations.

Characterization of the product

The mole ratio of Sb, W and H_2O in polytungstoantimonate (sample B_1) is $Sb:W:H_2O = 2:30:12.98$. Hence, the probable composition of the material may be written as $Sb_2O_5.30WO_3.13H_2O$.

IR Spectra

IR spectra of polytungstoantimonate (sample B_1) were recorded without heating (a) and after heating (b) at 800 ^oC. A broad absorption band between 3600 and 3200 cm^{-1} with the maximum at 3400 cm^{-1}(a)/3450 cm^{-1}(b) is characteristic of interstitial water molecule and OH groups associated with hydrogen bonding between them and a band between 1700 and 1500 cm^{-1} with the maximum at 1610 cm^{-1}(a) is due to the deformation mode of interstitial water molecule. A well defined peak occurring at 350 cm^{-1}(a) and a broad band between 900 and 600 cm^{-1}(a) are due to νW-O and νSb-O modes respectively. It also indicates the presence of metal-oxygen polymeric species in the sample. Absorption bands due to OH group decrease in intensity on heating. Shifting of the broad band of 900-600 cm^{-1}(a) to a sharp peak at 800 cm^{-1}(b) on heating at 800 ^{o}C indicates the breaking down of polymeric species and the formation of metal oxide. Apart from this the absence of sharp peak at 1610 cm^{-1} in the heated sample (b) indicates the loss of interstitial water molecule.

Ion exchange behaviour of the product (Polytungstoantimonate)

The product is non crystalline in nature. Although the exchange capacity of the sample B_2 (Table-1) is maximum, sample B_1, in view of it's better stability was chosen for subsequent investigations. The selectivity sequence of some cations on this material is as follows :

$$Cu^{2+} > Zn^{2+} > Cd^{2+} > Co^{2+} > Bi^{3+} > Ca^{2+}$$

The uptake of monovalent ions is reported to be much less in comparison to bivalent ions. Preliminary investigations with the membrane of this compound exhibited some promising response for Cd^{+} and Zn^{2+} ions. As such detailed investigations were taken up for the estimation of these two ions with the help of the membrane sensor incorporating polytungstoantimonate as electroactive phase.

II.I.b. Synthesis of tin oxide

Chemicals and reagents

Granulated tin (PFIZER) and sodium stannate were reagent grade chemicals while other reagents were of analaR grade.

Synthesis procedure

The compound has been prepared from both metallic tin as well as sodium stannate. Besides this the preparation has been done under four different conditions as summarized in Table-2. The products were filtered off and washed with distilled water till the pH of the filtrate was 3.0-3.5 (in case of batch 1) and 7.5 to 8.0 (in case of batch 2,3 and 4). The exchanger were dried at (60±5) °C.

Table-2

Synthesis and chemical composition of exchangers

Batch No.	Reagents used	Mixing ratio	Temp. and time	Drying temp. (°C)	Appearance in OH form	pH of mother liquor after synthesis	Chemical composition SnO_2/H_2O
1.	Metallic tin + conc.HNO_3	3:10 Wt/ Vol.	Room temp. over night	60±5	White crystalline	HNO_3 medium	1:1.64
2.	$Na_2SnO_3,3H_2O$,(1M) +$(NH_4)_2SO_4$,(1M)	1:1 Vol./ Vol.	Room temp. over night	60±5	White crystalline	8.0	1:2.12
3.	$Na_2SnO_3,3H_2O$, (0.5M)+HCl,(2M)	1:1 Vol./ Vol.	Room Temp. over night	60±5	White crystalline	9.0	1:1.49
4.	$Na_2SnO_3,3H_2O$, 0.5(M)+HCl,(2M)	1:1 Vol./ Vol.	Reflux 4 hrs.	60±5	White crystalline	8.9	1:1.57

Characterization

Tin was determined iodimetrically as well as gravimetrically as SnO_2. About 1.0 g of the exchanger was weighed accurately in silica crucible. It was ignited at 800 °C in a muffle furnace and weighed. The difference in weight was the amount of water lost and the weight of residue was the amount of anhydrous tin oxide. From these results the water of crystallization was calculated by the method of Alberti et al. and the compositions of hydrated tin (IV) dioxide are given in Table-2.

IR Spectra

In each case a broad peak was obtained for all the samples at 3100-3500 cm^{-1} and another less broad peak at 1630 cm^{-1} for weakly adsorbed water, peak at 3400 cm^{-1} is due to OH-stretching and peak at 1630 cm^{-1} is due to H-O-H bending. Two peaks at 990 cm^{-1} and 1250 cm^{-1} which may be due to coordinated water molecules were observed in batch 2 and 3 only. These two peaks are not prominent in batch 4 and are absent in batch 1. The broad peak at 600 cm^{-1} is due to Sn-O polymerization.

Ion exchanger behaviour

The total ion exchange capacity of the samples was determined for chloride ion and the same was found to be maximum for the sample obtained by batch 2 (1.008 meq/g). Cation exchange capacity of the sample was also determined and the same was found to be much less in comparison to anion exchange capacity. Interestingly the chemical stability of the compound became better after heating it to 300 °C. As such the product obtained by batch 2, was chosen for further investigations. The selectivity sequence of various anions on this exchange material follows the order

$$PO_4^{3-} > AsO_4^{3-} > CrO_4^{2-} > VO_3^- > SCN^- > MnO_4^-$$

Preliminary investigations with tin oxide membrane exhibit good response for CrO_4^{2-} and VO_3^- ions. As such detailed studies were taken up for the estimation of these two anions.

II.2. Synthesis and characterization of organic resins

Organic resins have also been explored for the development of membrane sensors. Later work in this direction involves the use of 2-salicylaldene amino thiophenol formaldehyde and 2-hydroxy naphthaldoxime formaldehyde resins for the estimation of metal ions. These may exhibit better selectivity in comparison to inorganic exchangers. As such it was considered worthwhile to try these two organic chelates as electroactive phase in the preparation of ion-selective membranes.

II.2.a. Synthesis of 2-salicylaldene amino thiophenol formaldehyde (STF)

Chemicals and regents

Salicylaldehyde, O-amino thiophenol formaldehyde and sodium hydroxide. All chemicals were of A.R. grade.

Synthesis procedure

2-salicylaldene amino thiophenol was prepared by keeping salicylaldehyde and O-amino thiophenol in the ratio 1:1.1 in toluene solutions. The compound separates out in three hours. It was filtered under suction and finally recrystallized. Formaldehyde and 2-salicylaldene amino thiophenol were mixed in 2.2:1 molar ratio and to this 10% (w/w) of 40% aqueous sodium hydroxide solution was added. The mixture was refluxed in an oil bath at 120±1 °C for two hours. The resinous mass was poured into a clear container and dried at 100±1 °C for fifteen hours. It was then powdered and sieved through a 100 mesh sieve.

II.2.b. Synthesis of 2-hydroxy naphthaldoxime formaldehyde resin (HDF)

Chemicals and reagents

2-hydroxy naphthaldehyde, hydroxy ammonium chloride, ethanol etc. All chemicals were of analytical reagent grade.

Synthesis procedure

2-hydroxy naphthaldehyde (0.05M) was converted to the corresponding oxime using hydroxy ammonium chloride and double distilled ethanol. 2-hydroxy naphthaldoxime was then mixed with formaldehyde in the molar ratio 1:4.2 . To the mixture, 3% (w/w) of 40% aqueous sodium hydroxide was added. The solution was refluxed at 115±1 °C in an oil bath for seven hours and the resinous mass so obtained, was poured into a clean container and dried at 100±1 °C for ten hours. The resin was finely powdered and sieved through a 100 BSS (British standard size) sieve.

Structural characterization of STF & HDF

Elemental analysis

The results of carbon hydrogen and nitrogen analysis of the resins are given in Table-3

Table-3

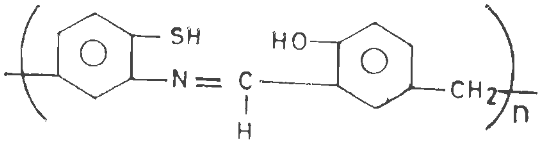
Elemental analysis of STF and HDF resins

Resin designation	% C	% H	% N	Number average mol. wt $\overline{Mn}$
STF	69.82(70.00)	4.49(4.58)	5.71(5.83)	2700
HDF	72.19(72.00)	4.94(5.00)	4.96(7.00)	2625

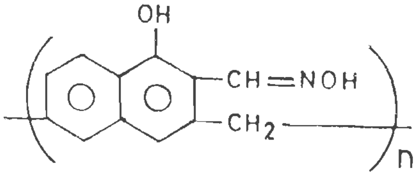
(Figures in parenthesis indicate theoretical values)

Theoretical values have been calculated by assuming the proposed structures of the repeating units as shown below.

STF



HDF



Number average molecular weight $\overline{Mn}$ was determined by vapour phase osmometry in THF at 30 °C. Excellent agreement in experimental and theoretical values points to the validity of proposed structures. This is further substantiated by IR studies.

IR Studies of the resins

The importance of infrared spectroscopy in structural elucidations and analysis of polymers and resins is well recognized. A comparison of the IR spectrum of monomer and the resin showed the presence of vibrational frequencies of methylene groups in resin spectrum there by indicating the reaction of monomer with formaldehyde.

The infrared spectrum of 2-salicylaldene amino thiophenol formaldehyde resin exhibited a broad band at 3400 cm^{-1} due to the hydroxyl group. Bands at 1615 cm^{-1}, 1415 cm^{-1} and 1260 cm^{-1} were attributed to C=N, phenolic OH, and C-O stretching respectively. Methylene bridges appeared at 1465 cm^{-1} and 900 cm^{-1} with a small peak at 770 cm^{-1} representing the rocking mode.

In case of 2-hydroxy naphthaldoxime formaldehyde resin the bands at 1450, 1410, 1370, 1355 cm^{-1} represented the methylene bending modes. Bands appearing at 875 and 840 cm^{-1} were assigned to C-H out of plane deformation and a small peak at 710 cm^{-1} was due to rocking mode of methylene group in the resin. The presence of hydroxyl group was indicated by the appearance of a broad peak at 3400 cm^{-1}. Thus the IR spectra support the presence of methylene linkages in the resins.

Sorption behaviour of the two orangnic resins

Both the resins exhibit very good uptake for a number of metal ions. The order of adsorption of some metal ions on 2-salicylaldene amino thiophenol formaldehyde (STF) is

$$Pd^{2+} \approx Fe^{2+} > Cu^{2+} > Cd^{2+} > Ni^{2+} > Zn^{2+} > La^{3+} > Eu^{3+} > UO_2^{2+}$$

while the selective uptake of the metal ions on 2 hydroxy naphthal doxime formaldehyde (HDF) is in the following sequence

$$Fe^{2+} \approx Co^{2+} > Pb^{2+} > Zn^{2+} > Cu^{2+} > Ni^{2+} > Pd^{2+}$$

II.3. Requirements of the precipitate based ion-selective electrodes.

There are certain stringent requirements which any material must satisfy before it can act as a successful membrane in a solid state electrode device. Moody and Thomas (13) have summarized the properties of the solids to be incorporated in solid membrane sensors.

The active sensor material must preferably be non-porous, that is, imporous, solicit the minimum photoelectric response, must have good mechanical strength and not be readily scratched or abrazed. Besides this, it is ideal if the substance is available as a large crystal or else it should have sufficient tenacity to be mouldable as a membrane. During the pressure process, stress may cause the decomposition of metal. This metal can be a serious drawback, since the electrode could then be subjected to interference from redox systems. Further it is also important that the membrane material should be water insoluble. In addition to this, it must also exhibit a good selectivity as well as good time response characteristics. For practical maneuvering it should be capable of easy tight sealing to the electrode body, otherwise leak paths would arise between the internal reference solution and the sample solution. For ideal conditions it should be capable of producing a Nernstian response.

For the construction of heterogeneous membranes a suitable matrix support is required. In addition to the above requirements, the active material should be physically compatible with the matrix. Further it should be of the right grain size (1-15 nm) which is a function of precipitation technique. It is of utmost importance that the sensor material must be mixed with the matrix support in the right proportion. This is essential in order to maintain physical contact between sensor particles, and provide electrical conduction through the membrane, otherwise the resistance may be too high. The material should undergo rapid ion exchange at the membrane sample interface.

Virtually all commonly available ion-exchanging solids, used as single crystals or pressed pellets, have been successfully tried in heterogeneous form and translated into practical and commercial reality. Commonly used binders are PVC, polystyrene, silicon rubber and araldite. The presence of binder does not affect the mode of operation.

II.3.a. Preparation of polystyrene supported membranes

The solid state electrodes fall conveniently into two classes, homogeneous and heterogeneous. Pungor has emphasized that the terms homogeneous and heterogeneous relate to the composition, and not function, of an electrode. Any theoretical discrimination between the two classes is undesirable owing to their similar mechanisms. The membrane of a typical solid state electrode is an "all-in one" sensor-cum-support matrix, whereas a heterogeneous membrane comprises of at least two components, one the active sensor such as a simple insoluble salt, a chelate or ion exchange resin, and the other an inactive matrix support.

It was in 1950, with the advent of ion exchange resins, that heterogeneous membranes incorporating the commercially available ion exchangers into thermoplastic polymers were prepared by Wyllie and Patnode (14) by hot pressing a mixture of ion exchange granules and polystyrene. Since then heterogeneous membranes have been prepared by using a number of methods.

Heterogeneous electrodes include those where the active materials are dispersed in the widely used inactive support e.g.,polystyrene (8,15,16) and poly vinyl chloride (17-19).

The suitable matrix support must be chemically inert, provide good adhesion for the sensor particles, be hydrophobic, tough, flexible, yet non-porous and crack resistant to prevent leakage of internal solution. The matrix should not swell in sample solutions. Any extensive swelling disrupts the active chain of sensor particles.

Heterogeneous membranes, obtained by embedding polystyrene in respective gels, were found to be quite satisfactory and better than the araldite based membranes. Various physico-chemical properties could easily be studied with these membranes. The following method based on U.S. Patent NO .2, 614, 976(20) was employed to prepare the membranes.

Preparation

Polystyrene granules were heated in a glass tube in sulphuric acid bath at 200 °C. The molten mass was allowed to cool down to room temperature and the polystyrene rod was taken out after breaking the glass tube. The polystyrene rod was ground to fine particles by putting it against a lathe. It was then finally ground to get a 50 mesh sieve product.

Membranes were prepared by mixing an appropriate amount of polystyrene and inorganic/organic resin and heating the homogeneous mass in a die kept in a metallurgical specimen mount press at a particular temperature and pressure. The optimum quantity of polystyrene needed to prepare a stable membrane was determined by trial.

The optimum temperature, pressure and other conditions like rate of cooling etc, were fixed up after a great deal of preliminary investigations. Membranes prepared in this way were quite stable and did not show any dispersion in water or in different electrolyte solutions. It took almost two months to ascertain the best conditions which provide stable membranes capable of generating reproducible potentials. These membranes were also examined under an electron microscope for cracks and homogeneity of the surface.

II.3.b. Preparation of poly vinyl chloride based membranes

A vast majority of polymer-matrix based ion-selective electrodes are reported to have been prepared by using poly vinyl chloride as support. These electrodes also come under the category of heterogeneous electrodes and poly vinyl chloride is being used as a matrix support for a very long time (21-23).

PVC satisfies all the requirements of a successful binder. Ion-selective electrodes that are constructed from PVC contain specific ingredients that imparts the desired response characteristics. With the advent of polymer-matrix membranes, specially PVC, the electrode life increases tremendously. The PVC matrix membrane electrode offer good mechanical resistance and pressure effects and although several other materials have been assessed, PVC is still by far the most commonly used support matrix.

Thomas (24,25) has also recommended PVC as the most significant polymer support. Moody, Saad and Thomas provide a detailed comparison of various PVCs, with other polymeric materials in their response characteristics (26). Investigations made in this direction show the response mechanism of PVC based membrane electrodes and reveal the existence of dissociated fixed exchange sites within the PVC matrix that contribute to the electrode's response and selectivity. If there were any disadvantages of using PVC as a support matrix it would be in its poor adhesion to certain materials that are desired for commercial applications.

There has been a continued growth in the number of PVC membrane electrodes that have been prepared for a variety of substances. These electrodes can be prepared by incorporating any of the many ion exchange agents within a plasticized PVC matrix. Thomas and Moody are the pioneers in developing PVC based sensors and have constructed an epoxy-based all solid-state poly vinyl chloride matrix membrane selective for calcium ions (18).

Preparation

After studying the added advantage of PVC based membranes, we have also tried the fabrication of membrane sensors using the organic resins on PVC matrix.

Organic resin was found to be completely soluble in tetrahydrofuran (which is a prerequisite condition for constructing a PVC membrane). A known amount of resin was first dissolved into a known amount of of THF. PVC powder was then, sprinkled on this solution. After thoroughly stirring the mixture, it was poured into the glass casting ring resting on a glass plate. After stirring, the solution should not be poured immediately as there are quite a few bubbles formed as a result of constant stirring. The solution should be poured very gently and care should be taken that no bubbles are formed in the membrane sheet. This was left for a sufficient time to allow the solvent to evaporate. Glass ring with adhering membrane was carefully removed from the glass plate. If solvent remains on the under surface, place the ring with adhering membrane in a plastic container and store it for a day to allow complete solvent evaporation.

The membrane was cut away from the inner edge of the ring and it looked like a fine plastic sheet. The membrane was stored in a plastic container.

The amount of exchanger PVC and THF used was also ascertained by trial. To obtain an absolutely bubble free membrane number of membranes were tried until a uniform and smooth bubble free membrane was cast. Bubbles in the membrane can cause serious interferences in membrane potentials. This method of preparation of the membrane was used by Gragg and Moody in 1974 (27). Another method for the construction of PVC membrane electrode has recently been developed by Lima (17). These procedures have been suitably modified suiting to our requirements.

II.3.c. Preparation of araldite based membranes

Some times the heterogeneous membranes prepared by embedding the exchanger in polystyrene or PAC matrix are not of adequate strength and get broken during the use or do not show adequate electrochemical performance. In such cases araldite can be used as a binder. Some araldite based membrane electrodes (6,8) have already been reported from this laboratory.

Preparation

The powdered samples of the electroactive material and araldite were mixed up thoroughly, in the required ratio, on a watch glass and the paste was made homogeneous. This was then spread out thinly over a piece of filter paper and gently pressed and left as such in the air for 24 hours. When the membranes get dried up, circular pieces of ≈ 2.0 cm diameter were cut manually with the help of razor and adhering filter paper was also removed. A number of membranes were thus prepared and only those having smooth surface showing no cracks and undulations (checked under optical microscope) and a regular thickness (≈ 0.5 mm) were selected for further studies. The minimum amount of araldite required to give adequate stability to membranes was determined by trial and it was found that membranes, of polytungstoantimonate gel as electroactive phase prepared with 20% araldite by weight were sufficiently stable and could be used for longer periods.

II.4. Determination of functional properties of membranes

The first pre-requisite for understanding the performance of an ion exchange membrane, particularly the perm-selective one, is it's complete physico-chemical characterization. A survey of the existing literature reveals that this particular aspect of membrane phenomenon has received lesser attention. Comprehensive and critical studies on the characterization of the ion exchange membranes, is therefore, duely justified. Normally the process involves the determination of those parameters which affect the electrochemical properties of the membrane e.g., porosity, electrolyte absorption, electrical conductance etc.

The first major attempt to establish standard methods for membrane characterization was reported on the dried collodion membranes (28). Hale and co-workers (29) examined the effect of resin content and the degree of crosslinking of the resin on the physical and electrochemical properties of membrane while Wyllie and Kannan (30) reported that if a rigid plastic, such as polystyrene is used, the properties of the ion exchange membranes gel modified. Gregor (31,32) and Kawabe(33) studied the characterization of ion exchange membranes in a number of different exchange states and correlated this information with it's structure. From this laboratory Jain and co-workers (34) have reported functional properties of pyridinium molybdoarsenate and rubidium and copper(II)tungstoarsenate membranes while Srivastava and co-workers investigated the functional properties and permeability of chromium ferricynide and cerium(IV)molybdate membranes (35).

The electrical conductance of membrane systems are also quite important (36). The ohmic resistance of a membrane of high ionic selectivity measured under standard conditions provides an accurate and quantitative measure of relative ionic permeabilities. Generally, larger the conductivity, greater is the ionic permeability and vice versa. A number of techniques have been used by various workers (37) for the measurement of membrane conductance. Barrer (38) measured the resistance with and without a membrane in 0.01M solution of chloride or nitrate of the ion under study. The difference between the two was taken as the membrane resistance. Lakshminarayanaiah (37) has given a direct method of measuring the membrane resistance which gives better results as compared to the methods followed by earlier workers. Surface studies also play an important role in the functioning of a membrane electrode. Recently a detailed methodology of surface studies and it's effect on the membrane was reported by Marco(39).

Standard methods used for the determination of functional properties (water content, porosity, swelling, electrolyte absorption and electrical conductance) are given below :

II.4.a. Water content

The membrane was soaked for 24 hours in a solution of 1.00M concentration of electrolyte. It was then washed several times with distilled water, wiping out the adhering liquid with a blotting paper. The soaked membrane was weighed and later dried to a constant weight in a vacuum desiccator at 60 ^{o}C. The difference in the two weighings, divided by the weight of the wet membrane was taken as the water content.

II.4.b. Porosity

It was determined by the method followed by Mizutani and Nishimura (40) and was calculated using the formula

$$\Sigma = \frac{\text{Water content}}{A.L.\ \rho_w}$$

where, A is the area of the membrane, L the thickness and ρ_w is the density of water.

II.4.c. Swelling

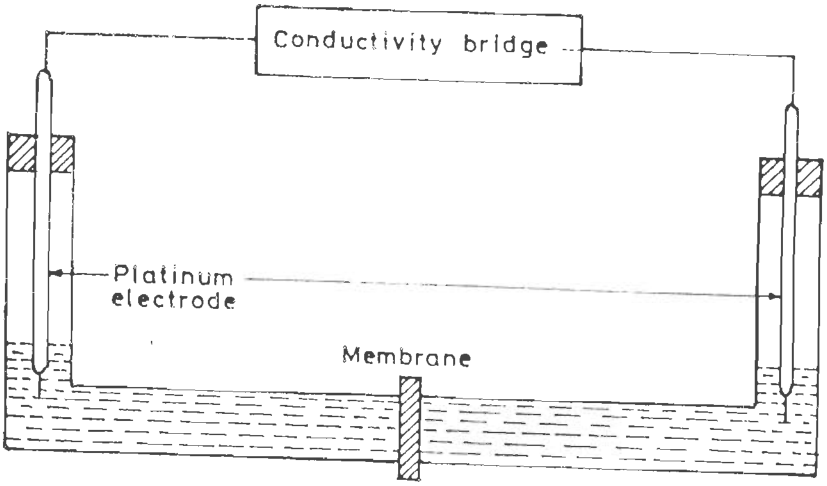
After measuring thickness of the dry membrane it was immersed in a solution of electrolyte for one day and the thickness was measured again after wiping it out with blotting paper. Difference between the thickness of dry and swollen membrane was taken as a measure of swelling.

II.4.d. Electrolyte absorption

The membrane after attaining equilibrium in electrolyte solution was wiped free of adhering electrolyte and dipped in 20 ml of distilled water. It was intermittently shaken and left as such for a few hours. The solution was transferred to a 100 ml measuring flask. The whole process was repeated three to four times and the entire solution was collected in a measuring flask. It was finally made upto the mark by distilled water and the strength was measured conductometrically.

II.4.e. Conductance

The modified method adopted by Lakshminarayanaiah and Subrahmanayam (37), which makes use of mercury pool on both sides of the membrane to minimize polarization at the membrane interface, was employed for conductance measurement. The experimental set up is shown below :



The membrane was cemented in between the two half cells with the help of araldite and kept in contact with electrolyte solution of 0.1M concentration. The solution was then replaced by mercury previously equilibrated with the electrolyte solution of the same concentration and the conductance was measured by connecting the platinum electrodes to a conductivity bridge.

II.5. Theory and measurement of membrane potentials

The use of ion-selective electrodes depends on the determination of membrane potentials. These potentials can not be determined directly, but can be easily derived from the e.m.f. values for the complete electro-chemical cells, which comprise the membrane separating solutions 1 and 2 as well as the two reference electrodes (41).

When the ion exchange membrane separates two solutions 1 and 2 both containing the same counter ion A, a membrane potential (E_m) is developed across the membrane due to the diffusion of counter ions from higher to lower concentration. The membrane potential (E_m), which is the sum of the diffusion and Donnan potentials, is given by the expression (i) :

$$E_m = \frac{RT}{ZF} \left[\ln \frac{\left(a_A\right)_2}{\left(a_A\right)_1} - \left(Z_Y - Z_A\right) \int_1^2 \bar{t}_Y \, d \ln a_{\pm} \right] \qquad \text{(i)}$$

where A = counter ion, Y = co-ion, Z = charge on ions and $\bar{t}_Y$ = transference number of the co-ions in the membrane phase; $\left(a_A\right)_1$ and $\left(a_A\right)_2$ represents activities of the counter ions in solutions 1 and 2 and $a_{\pm}$ is the mean ionic activity of the electrolyte.

In the above expression, the right hand side consists of two terms. The first term gives the thermodynamic limiting values of the concentration potential and the second term denotes the diffusion potentials due to co-ion flux in membrane.

If the membrane is considered to be an ideally perm-selective membrane ($\bar{t}_Y = 0$), then the equation (i) takes the form of the Nernst Equation.

$$E_m = \pm \frac{RT}{Z_A F} \ln \frac{\left(a_A\right)_2}{\left(a_A\right)_1} \qquad \text{(ii)}$$

This equation simply represents Donnan potential for an ideally perm-selective membrane or it can be said that it gives the thermodynamic limiting values of concentration potential. Equation (ii) takes (+)ive sign for cation and (-)ive sign for anion.

The membrane potential measurement is carried out using a cell setup of the following type :

External saturated calomel electrode (SCE)	Test solution (2)	Membrane	Internal solution (1)	Internal saturated calomel electrode (SCE)

$E_L(2)$ $E_L(1)$

As a general practice, the concentration of one of the solution (say 1) is maintained constant (usually 0.1M) and this solution is referred as internal or reference solution and a saturated calomel electrode dipped in this internal solution as internal reference electrode. The membrane together with internal solution and internal reference electrode is one compact unit which, as a whole, is called as membrane electrode. This membrane electrode is then immersed in solution 2, usually referred as external solution or test solution, having SCE as an external reference electrode. Some other electrodes like silver/silver chloride electrode may also be used as reference electrodes. The e.m.f. of this potentiometric cell is given by the following expression :

$$E_{cell} = E_{cal} + E_L\,(2) + E_m + E_L\,(1) - E_{cal} \qquad \ldots\ldots \text{(iii)}$$

where E_{cal}, E_L and E_m refer to calomel electrodes, junction and membrane potentials, respectively. Combining equation (ii) and (iii), the equation (iii) takes the form

$$E_{cell} = E_{cal} - E_{cal} + E_L(2) + E_L(1) \pm \frac{RT}{Z_A F} \ln \frac{(a_A)_2}{(a_A)_1} \quad \ldots\ldots \text{(iv)}$$

For cation exchange membrane,

$$E_{cell} = \left[E_L(1) + E_L(2) - \frac{RT}{Z_A F} \ln (a_A)_1\right] + \frac{RT}{Z_A F} \ln (a_A)_2 \quad \ldots\ldots\ldots \text{(v)}$$

As activities of internal solution are kept constant and the values of $E_L(1)$ and $E_L(2)$ are also almost constant, the term in parenthesis may be taken equal to a constant, E^o. Further, the values of $E_L(1)$ and $E_L(2)$ are negligibly small (due to salt bridge being used), the cell potential in the above equation may approximately be taken as membrane potential.

The equation (v) reduces to

$$E_{cell} = E^o + \frac{RT}{Z_A F} \ln (a_A)_2 \quad \ldots\ldots\ldots\ldots \text{(vi)}$$

It is obvious from this equation that the cell potential would change with the change in concentration (or activity) of the cation in external or test solution 2. At 25 ^oC, value of RT/Z_AF comes out to be equal to $0.059/Z_A$ volt. If the plot between cell potential and log activity has a slope of $0.059/Z$ volt, the membrane is said to give Nernstian response. These plots are called Nernst plots and the slope as Nernstian slope. It has been generally observed that only few membranes of ion exchanging materials show Nernstian response (42,43) and that too within a limited concentration range (say 10^{-4} to 10^{-1}M). Outside this range, potential vs log activity plots deviate from linear Nernstian behaviour. At lower concentrations, deviation originates due to H^+ ion (available by the dissociation of water) competing with electrolyte counter ion and at higher concentrations due to co-ion transference (43).

II.6. Ion-selective electrodes

If the ion exchange membrane exhibits a linear variation in potential with changing concentration of external solution (in contact with it) it can be used to determine the ionic activity in test solution, if the activity in the other one is known. If the membrane electrode responds selectively to a particular ion, it is usually referred to as an ion-selective electrode (ISE).

II.6. Selectivity of electrodes

No ion-selective electrode responds exclusively to the ion for which it has been designed, although it is often more responsive to this primary ion in comparison to others. If another interfering ion is present at a concentration which is large with respect to the primary ion, the electrode response will have contributions from both the primary and interfering ions. The degree of selectivity of the electrode for the primary ion, A, with respect to an interfering ion B, is expressed by the potentiometric selectivity coefficient, $K^{Pot}_{A,B}$. The selectivity coefficient is defined by the general Nikolskii equation for the electrode potential :

$$E = E_o \pm \frac{RT}{Z_A F} \ln \left[a_A + \sum_B K^{Pot}_{A,B} \, a_B^{Z_A/Z_B} \right] \quad \ldots\ldots\ldots\ldots \text{(vii)}$$

where Z_A and Z_B are the charges on ions A and B and F^o is the standard potential of the electrode. This equation is applicable to nearly all the electrodes (44).

When an electrode is ideally selective to A in comparison to B, the value of $K^{Pot}_{A,B}$ should be much less than unity. Conversely, if, as occasionally happens, the electrode responds preferentially to B rather than A, $K^{Pot}_{A,B}$ will be greater than unity. Further, for ions A and B of same charge and activity, a value of $K^{Pot}_{A,B} = 1$ shows that the membrane responds equally to both the primary and interfering ions. For different values of Z_A and Z_B, the $K^{Pot}_{A,B}$ values showing equal membrane response, both to ion A and B would be different and these have been worked out using equation (vii) for same activity of primary and interfering ions and are shown in Table-4. When the $K^{Pot}_{A,B}$ values are smaller than those limiting values listed in Table-4, the interfering ion is said to cause less interference. Ideally a zero value of $K^{Pot}_{A,B}$ indicates no interference. However, in practice, $K^{Pot}_{A,B}$ values about 1000 times smaller than the limiting values of Table-4 are taken to indicate that the interfering ions do not cause significant interference and the electrode is said to be sufficiently selective.

Thus, in order to assess the selectivity of a membrane, it is necessary to determine selectivity coefficient values. Several methods (44) have been described for the experimental determination of selectivity coefficients. These methods fall in two categories :

(i) Separate solution method, and

(ii) Mixed solution method.

(i) Separate Solution Method

In this method, the potential of the electrode under investigation is measured first in solutions containing the primary ion A with no B present (E_A) and then in solutions containing the interfering ion B with no A present (E_B). $K^{Pot}_{A,B}$ is calculated from the activities of A and B in different solutions and the electrode potentials (44).

$$E_A = E^o + \frac{RT}{ZF} \ln a_A \quad \ldots\ldots\ldots (viii)$$

$$E_B = E^o + \frac{RT}{ZF} \ln K^{Pot}_{A,B} (a_A)^{Z_A/Z_B}$$

From these equations

$$\log K^{Pot}_{A,B} = \frac{E_B - E_A}{2.303\ RT/ZF} + \log \frac{a_A}{a_B^{Z_A/Z_B}} \quad \ldots\ldots (ix)$$

The term 2.303 RT/ZF is the slope of the Nernst plot. As most of the solid membranes exhibit deviation from Nernstian behaviour, the experimental slope `S' differs from theoretical slope, i.e., 2.303 RT/ZF. Thus, it is desirable to use `S' instead of Nernstian slope for the calculation of $K^{Pot}_{A,B}$ (45) and so equation (ix) becomes

$$\log K^{Pot}_{A,B} = \frac{E_B - E_A}{S} + \log \frac{a_A}{a_B^{Z_A/Z_B}} \quad \ldots\ldots\ldots (x)$$

The separate solution method of measuring $K^{Pot}_{A,B}$, although simple to perform, can not be recommended as this reflects selectivity in separate solutions and the selectivities in mixed solution (containing both A and B) are likely to be slightly different.

(ii) Mixed Solution Method

Mixed solution method are always preferred to separate solution method. These entail the measurement of the electrode potential in a range of solutions containing different activities of A and B both. For simplicity in interpreting the results, it is usual to prepare solutions either with a constant a_B and varying a_A or with a constant a_A and varying a_B. Conventionally, the first method is preferred as it usually corresponds more closely to the situation in samples. The second method has been used particularly when H^+ is the interfering ion. In this case curves are produced showing the electrode potential in solution of constant a_A but varying pH (44).

If a range of solutions with constant a_B and varying a_A are prepared and the electrode potentials measured in these solutions are plotted against pa_A, a curve of the type shown in Fig.1 is usually obtained.

In the region PQ the electrode is responding in a Nernstian manner to the primary ion, A. As a_A decreases, the electrode potential is increasingly affected by the constant activity of B and in the region QR the electrode shows a mixed response to both A and B. From R to S the potential is constant as the electrode is responding entirely to the constant a_B and the effect of the decreasing a_A is not detectable. There are several methods for calculating $K^{Pot}_{A,B}$ from the data presented in Fig.1. Some of these are described here :

Method 1

The first method depends on finding graphically the point T. The potential corresponding to point T can be produced either by a_B or by a_A. Thus, $E_A = E_B$ at point T. Therefore, from equation (ix) :

$$\log K_{A,B}^{Pot} = \log \frac{a_A}{a_B^{Z_A/Z_B}}$$

Thus, knowing the value of a_A and a_B from the figure corresponding to point T, $K_{A,B}^{Pot}$ can be calculated form equation (xi). This method is known as Fixed Interference Method and is most widely used as per IUPAC recommendation. However, this method is only suitable if RS is a straight line (44, 46).

Method 2

In this method, potential E_A and E_{AB} are measured using solutions of primary ions only and a mixture of primary and interfering ions, respectively. From equation (vii) and (viii), we get

$$K_{A,B}^{Pot} = \frac{a_A}{a_B^{Z_A/Z_B}} \left[10^{\frac{E_{AB} - E_A}{2.303\ RT/Z_F}} - 1 \right]$$

or

$$K_{A,B}^{Pot} = \frac{a_A}{a_B^{Z_A/Z_B}} \left[10^{\frac{E_{AB} - E_A}{S}} - 1 \right]$$

where S is the slope of the plot.

II.6.b. Activity coefficient

Ion-selective electrodes sense the activity, rather than the concentration of ions in solutions. Therefore, concentrations, are required to be converted into activities. In order to calculate activities from concentrations, the activity coefficients (f) are required and various equations have been proposed from time to time for the calculation of activity coefficient values but the

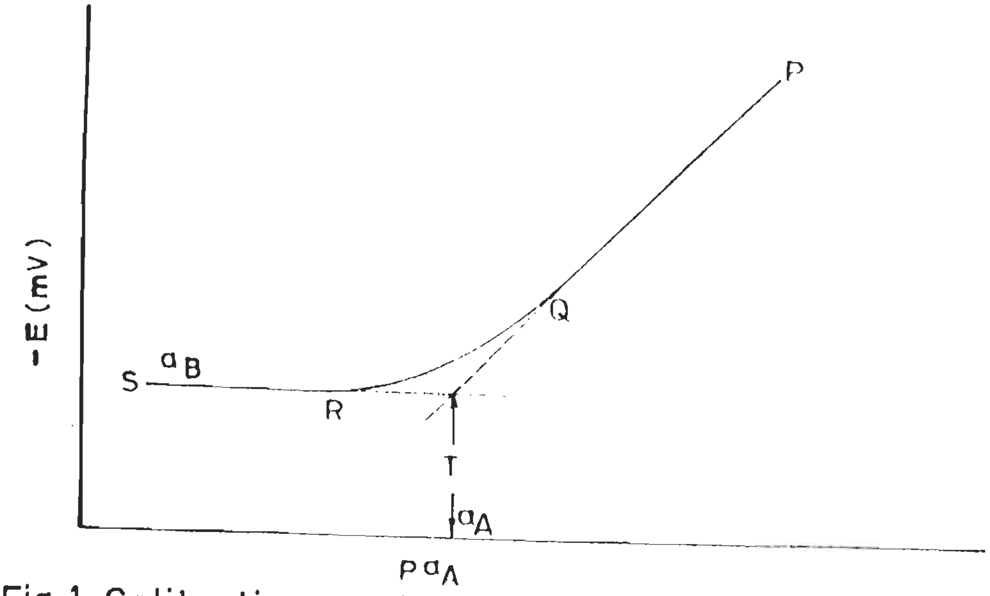


Fig. 1 Calibration graph illustrating Method 1 for determination of selectivity coefficients

equation most widely used is the following which is known as extended form of Debye-Huckel equation (42) :

$$\log f = -\frac{AZ^2 \sqrt{\mu}}{1 + \sqrt{\mu}}$$

where, f is the activity coefficient, Z is the charge of the ionic species, μ is the ionic strength and A is a constant equal to 0.511 at 25 °C. This equation has been used for the calculation of single ion activity throughout work.

Table-4

$K^{Pot}_{A,B}$ values for interfering ions indicating equal response to the membrane as that of primary ion.

Charge on primary (A) Z_A	Charge on interfering ion (B) Z_B	$K^{Pot}_{A,B}$ value for equal response of A and B
1	1	1.00
1	2	0.10
1	3	0.05
2	1	100.00
2	2	1.00
2	3	0.20

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CHAPTER - III

INORGANIC GEL MEMBRANES

III.1. Introduction

In an ever increasing search for suitable materials which can be used for the preparation of ion-selective electrodes, the use of inorganic ion exchangers has been looked into by various workers. A review by C.J. Coetzee (1) deals with various aspects of ion-selective electrodes based on inorganic ion exchangers. He has pointed out that these electrodes may not be highly selective but nevertheless are useful for many analytical applications.

Ion-selective electrodes based on the membranes of inorganic ion exchangers have been extensively studied in this laboratory and the use of cesium and thallium (I) tungstoarsenate membranes have been reported by Malik and co-workers (2) for the estimation of cesium and thallium ions. Besides this strontium tungstoarsenate membrane (3) was fabricated for the estimation of strontium ions and the same electrode was used by them for the measurement of the activity and critical micelle concentration of cationic surfactants (4). The use of pyridinium molybdoarsenate membrane (5) as pyridinium selective electrode has also been proposed. Srivastava and co-workers (6) prepared araldite based chromium hexacyanoferrate(II) membranes and found these sensitive to hexacyanoferrate(II) anion. Recently an inorganic gel membrane sensor for mercury (7) has also been reported by Srivastava and co-workers. An electrode made of a mixture of lead molybdotungstate and perrhenate has been used for the determination of molybdate, phosphate, chromate and hydroxides (8). Purdy (9) used zinc orthophosphate and zinc mercuric thiocynate as an inorganic exchanger for making a zinc selective electrode.

Various workers (10-14) have tried to develop sensors for the estimation of phosphate using inorganic gels like nickel phosphate, silver phosphate, $Ag_2S:PbS:PbHPO_4$, $LaPO_4$ etc. Estimation of chromium as chromate has also been reported using various ion exchange membranes (15-17).

Investigations reported on ion sensors are periodically reviewed by Janata (18-20) in the journal "Analytical Chemistry".

Recently a new polytungstoantimonate gel possessing good ion exchange characteristics and chemical stability has been prepared and reported (21). This product is non crystalline in nature and exhibits the following selectivity sequence :

$$Cu^{2+} > Zn^{2+} > Cd^{2+} > Co^{2+} > Bi^{3+} > Ca^{2+}.$$

It was considered worthwhile to study the electrochemical performance of the membranes of this compound. The compound has maximum selectivity for copper, but the membrane does not respond to copper ions. In heterogeneous membranes the binder material present along with the compound does affect its selectivity pattern and the sensor is found to possess better selectivity for Cd^{2+} and Zn^{2+} ions. A detailed discussion regarding the estimation of these two ions is given in the following paragraphs and a comparative evaluation of the utility of the membrane sensor for determining Cd^{2+} and Zn^{2+} ions concentration has also been made.

Tin oxide has been reported by various workers (22,23) for its exchange characteristics under different physical conditions and it shows promising selectivity for some polyvalent anions in the sequence $PO_4^{3-} > CrO_4^{2-} > AsO_4^{3-} > VO_3^{-} > SCN^{-} > MnO_4^{-}$. Consequently investigations were planned to explore the utility of tin oxide membranes as sensors to some anions of analytical interest. As per selectivity sequence tin oxide has maximum affinity for PO_4^{3-}, but as usual the heterogeneous membrane is not sensitive towards this ion. Preliminary investigations reveal the utility of the membrane sensor for the estimation of chromate and vanadate ions and systematic investigations on this subject are given below.

The proposed inorganic ion exchangers meet all the stiff requirements demanded by solid membranes as such. As homogeneous membranes could not be prepared with these compounds the heterogeneous membranes were fabricated using the methods discussed in Chapter II.

III.2.a Functional properties of polytungstoantimonate membranes

Membranes incorporating polytungstoantimonate, as electroactive phase, have been prepared using 20% araldite as the binder material and characterized by the methods given in Chapter II. The functional properties of the membranes such as swelling, electrolytic absorption, porosity and conductance affect its electrochemical performance. In case of homogeneous solid membranes, these properties depend only on the nature of electroactive phase and the mode of the preparation of the membrane while in heterogeneous membranes, these also depend on the amount and the nature of binder used. For example if the amount of binder used is large, it may render the membrane impermeable to all ions. Binder material would cause insulation of membrane particles and make it non-conducting. On the other hand, if too little amount of binder is used, heterogeneous membranes may be too fragile and may breakdown during the course of investigations, similarly too much swelling and electrolyte absorption would also cause a detrimental effect on the electrochemical performance of membrane sensors.

III.2.b. Water content, porosity, swelling and electrolyte absorption

Membranes normally imbibe water when kept in contact with it for some time. This property, called water content, is expressed as the weight ratio of water to wet membrane. It is observed that the amount of water incorporated is moderately low (Table-1) in comparison to the membranes of the same class (3). Porosity is the volume of water incorporated in the cavities per unit membrane volume and is calculated from water content data. Porosity value is of the same order as the water content of membrane.

When a dry membrane is immersed in water or electrolyte solution, swelling takes place. The solution penetrates into the membrane structure, occupying interstices which are already present or which develop as a result of the different swelling properties of membrane material and the binder. The interstices act as a film and the diffusion of different electrolytes become possible by film diffusion, besides the normal diffusion, through the membrane material. In some cases swelling results in the permeation of otherwise impermeable species.

The magnitude of swelling depends on the gel structure and also on the amount of binder present in membrane. Swelling should be small for membrane to exhibit a good electrochemical performance. The small values of porosity and swelling, for the membrane under investigation, suggest that interstices are negligible and diffusion across the membrane should occur mainly

Table-1

Water content, porosity, swelling and electrolyte absorption values for polytungstoantimonate membrane.

Membrane	Water content per gram of wet membrane (g)	Porosity	Swelling (mm)	Amount of electrolyte absorbed per gram of wet membrane (M)
Polytungstoantimonate	0.5578	0.1335	0.280	7.0×10^{-2}
Strontium tungsto arsenate	0.0630	0.1390	0.100	5.7×10^{-5}

Table-2

Specific conductance of membrane in different cationic forms.

Cations	Specific conductance (milli mhos cm^{-1})
Na^{+}	5.2×10^{-1}
K^{+}	6.1×10^{-1}
Tl^{+}	6.2×10^{-1}
Li^{+}	6.2×10^{-1}
Cd^{2+}	7.2×10^{-2}
Pb^{2+}	7.4×10^{-2}
Zn^{2+}	7.0×10^{-2}
Cu^{2+}	5.1×10^{-2}
Ba^{2+}	8.2×10^{-2}
Ni^{2+}	4.4×10^{-2}
Fe^{3+}	3.3×10^{-2}
Al^{3+}	3.2×10^{-2}
Cr^{3+}	3.1×10^{-2}

through exchange sites. The magnitude of electrolyte absorption is also quite low and the value is compatible to water content and swelling data of the membrane (Table-1).

III.2.c. Specific conductance

The conductance of membrane in different cationic forms were measured using the method recommended by Lakshminarayanaiah et al. All measurements have been made with membranes previously equilibrated with electrolyte solution and so well identified counter ions were the only conducting species in the membrane matrix.

Constant values of membrane conductance, obtained in 2~3 minutes time, indicate a negligible polarization on the mercury membrane interface.

The results of specific conductivity data (Table-2) for polytungstoantimonate membrane exhibits the following sequence for various ions.

$[Tl^{+} = Li^{+} > K^{+} > Na^{+}] > [Ba^{2+} > Pb^{2+} > Cd^{2+} > Zn^{2+} > Cu^{2+} > Ni^{2+}] > [Fe^{3+} > Al^{3+} > Cr^{3+}]$.

Trivalent cations have low and monovalent ones have high values of conductance where as the bivalent cations fall in between.

III.3. Electrochemical performance of the membrane using polytungstoantimonate gel as electroactive phase

As mentioned above the homogeneous membranes of the compound could not be prepared. As such heterogeneous membranes of polytungstoantimonate gel containing 20% araldite, were prepared by the procedure described in Chapter II.

III.3.a. Estimation of Cd^{2+} ions

For the estimation of cadmium ions the membranes were equilibrated with 1.00M cadmium nitrate solution for 3-4 days. Only those membranes which were stable and generated reproducible potentials were selected for subsequent studies. The potentials obtained after equilibration period were stable and reproducible. Repeated monitoring of potentials at a fixed concentration gave a standard deviation of 0.2 mV in the higher concentration range and 0.4 mV in low concentration range.

Membrane potentials were measured at 30±1 °C against saturated calomel electrodes. 0.1 M cadmium nitrate solution was taken as the reference and potentials were measured proceeding from low to high concentrations. If the measurements were made from high to low concentrations, erratic results were obtained owing to `memory' effect and the difficulty of removing adsorbed ions from the surface of the membrane sensor.

Membrane potentials, observed in contact with cadmium ions solutions (10^{-6}-10^{-1}M), maintaining a reference solution of 0.1M concentration, are shown in Figure-1. The plots are liner in the range 6.31×10^{-5} to 1.00×10^{-1}M concentration and the slope of the plot is 26 mV per decade of concentration. Thus the assembly exhibits a behaviour which is quite close to Nernstian value.

In order to observe the effect of concentration, plots have also been made with 5.0×10^{-2} and 1.0×10^{-2}M reference solutions (Figure-2 & Table-3) and the same are found to be linear in the region 7.91×10^{-5}-1.00×10^{-1}M and 1.00×10^{-4}-1.00×10^{-1}M concentration of Cd^{2+} ions thereby indicating that the working concentration range of membrane electrode decreases with a decrease in

Table-3

Working concentration range of the membrane sensor for Cd^{2+} ions with reference solution of varying concentration.

Reference solution concentration (M)	Slope mV/decade of concentration	Working concentration range (M)
1.00×10^{-1}	26	$6.31 \times 10^{-5} - 1.00 \times 10^{-1}$
5.00×10^{-2}	23	$7.91 \times 10^{-5} - 1.00 \times 10^{-1}$
1.00×10^{-2}	23	$1.00 \times 10^{-4} - 1.00 \times 10^{-1}$

Table-4

Performance of electrode system in 20, 30 and 50% (volume by volume) non-aqueous medium.

percentage	Slope mV/decade of concentration	Working concentration range (M)
x	26	$6.31 \times 10^{-5} - 1.00 \times 10^{-1}$
Ethanol		
20	26	$3.10 \times 10^{-4} - 1.00 \times 10^{-1}$
30	28	$3.10 \times 10^{-4} - 1.00 \times 10^{-1}$
50	35	$3.10 \times 10^{-4} - 1.00 \times 10^{-1}$
Methanol		
20	31	$3.10 \times 10^{-4} - 1.00 \times 10^{-1}$
30	33	$3.10 \times 10^{-4} - 1.00 \times 10^{-1}$
50	40	$3.10 \times 10^{-4} - 1.00 \times 10^{-1}$

Table-5

Selectivity of the electrode system for cadmium ions in the presence of 1.00×10^{-2}M concentration of interfering ions (as calculated by Fixed Interference and Mixed Solution methods).

Interfering ion	Selectivity coefficient [$K^{Pot}_{A,B}$]	
	Fixed Interference Method	Mixed Solution Method
Na^+	31.62	23.52
K^+	28.28	19.95
Tl^+	19.95	11.52
Li^+	17.21	7.31
Ag^+	19.95	11.11
NH_4^+	28.18	8.54
Mn^{2+}	3.16×10^{-1}	1.76×10^{-1}
Pb^{2+}	3.55×10^{-1}	1.50×10^{-1}
Zn^{2+}	5.42×10^{-1}	1.64×10^{-1}
Ba^{2+}	3.98×10^{-1}	1.22×10^{-1}
Sr^{2+}	3.55×10^{-1}	2.49×10^{-1}
Co^{2+}	2.39×10^{-1}	1.67×10^{-1}
Ni^{2+}	3.16×10^{-1}	2.21×10^{-1}
Cu^{2+}	3.16×10^{-1}	1.76×10^{-1}
Mg^{2+}	3.16×10^{-1}	1.76×10^{-1}
Al^{3+}	4.82×10^{-2}	2.68×10^{-2}
La^{3+}	4.82×10^{-2}	2.68×10^{-2}

Table-6(a)

Performance of the electrode system in presence of the detergent cetyl pyridinium chloride (CPC).

Untreated membrane

Concentration of CPC (M)	Slope mV/decade of concentration	Working concentration range (M)
x	26	6.31×10^{-5} - 1.00×10^{-1}
5.00×10^{-5}	26	6.31×10^{-5} - 1.00×10^{-1}
1.00×10^{-4}	25	3.98×10^{-4} - 1.00×10^{-1}
1.00×10^{-3}	23	1.00×10^{-3} - 1.00×10^{-1}
1.00×10^{-2}	19	4.46×10^{-3} - 1.00×10^{-1}

Table-6(b)

Performance of the membrane conditioned with 1.00×10^{-3}M cetyl pyridinium chloride (CPC).

Concentration of CPC (M)	Slope mV/decade of concentration	Working concentration range (M)
x	27	5.01×10^{-5} - 1.00×10^{-1}
5.00×10^{-5}	27	7.07×10^{-5} - 1.00×10^{-1}
1.00×10^{-4}	25	1.78×10^{-4} - 1.00×10^{-1}
1.00×10^{-3}	23	1.00×10^{-3} - 1.00×10^{-1}
1.00×10^{-2}	18	1.99×10^{-3} - 1.00×10^{-1}

concentration of reference solution. The value of slope also goes down to 23 mV/decade of concentration. Besides this, the magnitude of membrane potentials generated with 5.00×10^{-2} and 1.00×10^{-2}M concentration of cadmium ions, are also quite small. Thus the necessary optimum concentration of the reference solution, for smooth functioning of the proposed membrane sensor, is 1.00×10^{-1}M.

III.3.b. Response and life time

The response time of the said membrane is almost 50 seconds i.e., in this time stable potentials are obtained. The same response time is obtained whether the measurements are made from low to high concentration or vice versa. The potentials stay constant for more than three minutes and are quite reproducible. This membrane can be used for a period of 2-3 months without showing any drift in potentials. If necessary, it can be equilibrated again with 1.00M $Cd(NO_3)_2$ solution for 4-5 days continuously. If this treatment fails the membrane is to be discarded and the fabrication of a new one becomes necessary.

III.3.c. pH effect

Potential vs pH plot is shown in Figure-3. Potentials do not change in the range 5 to 7 and this may be taken as the working pH of this electrode assembly. A sharp change in potentials in acidic as well as in basic media may be due to the interference of hydrogen and hydroxyl ions.

III.3.d. Solvent effect

The utility of the electrode assembly has also been investigated in partially non-aqueous medium. Potential vs concentration plots in 20, 30 and 50% (v/v) ethanolic and methanolic solutions are shown in Fig. 4 & 5. Although the response is linear in partially non-aqueous solutions, the working concentration range of the sensor goes down with simultaneous change in slope of the plot (Table-4). Along with it, the membrane drifts away from Nernstian behaviour and the response time of the sensor also increases with non-aqueous content. As such the electrode assembly has very limited validity even in partially non-aqueous media.

III.3.e. Selectivity

The selectivity of the proposed assembly for Cd^{2+} ions, in presence of other cations, has been examined by Fixed Interference and Mixed Solution methods and reported in terms of selectivity coefficients. Potentials are observed at a fixed concentration of interfering ions (1.00×10^{-2}M). The values of the selectivity coefficient for a number of interfering ions, as computed from the potential data are given in Table-5. The selectivity coefficient pattern (as calculated by Fixed Interference method) indicates significant interference of monovalent ions where as bivalent and multivalent ions do not seem to disturb the working of this electrode assembly. Selectivity coefficients as obtained by Mixed Solution method, are in general lower in comparison to the one obtained by Fixed Interference method. There is a marked difference in the values obtained by the two methods for

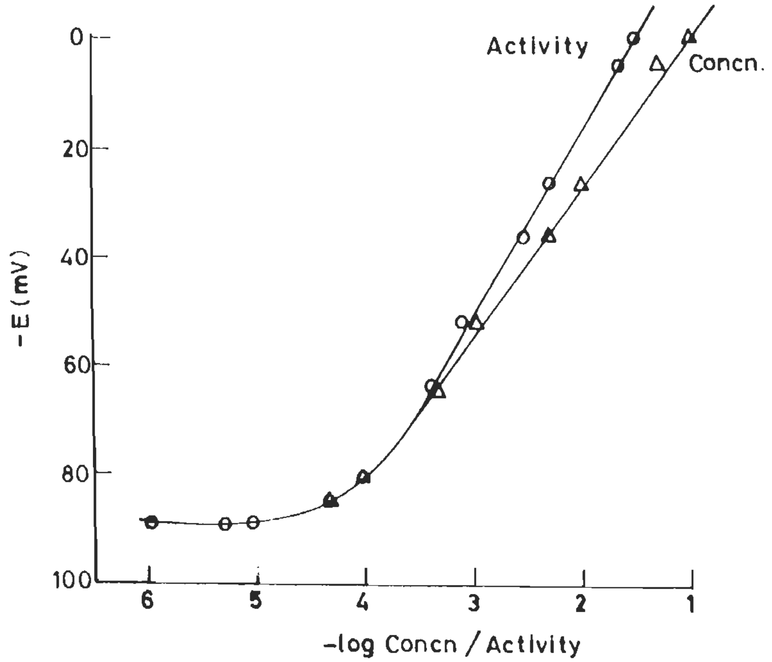

Fig. 1 Potential vs log $[Cd^{2+}]$ plots

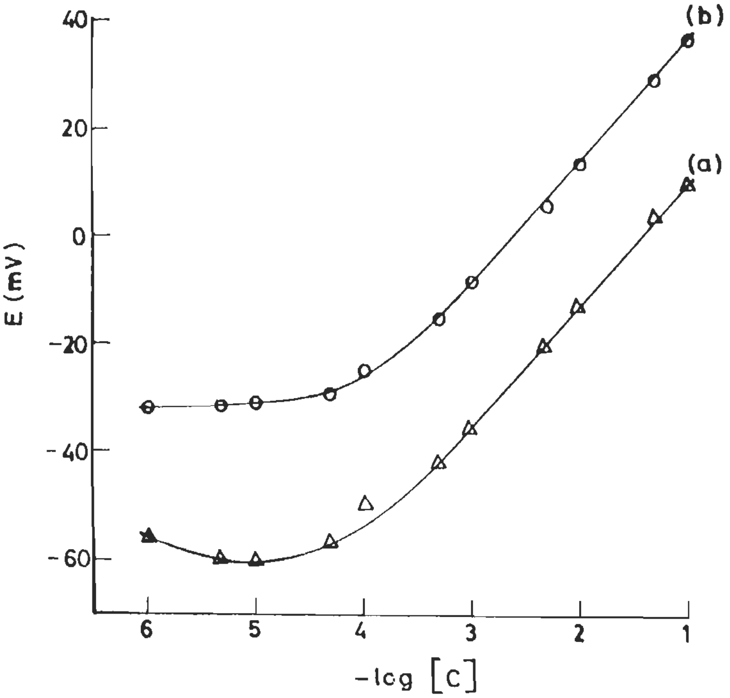

Fig. 2 Potential vs log $[Cd^{2+}]$ plots with reference solution concn. (a) 5×10^{-2} M (b) 1×10^{-2} M

Polytungstoantimonate membrane

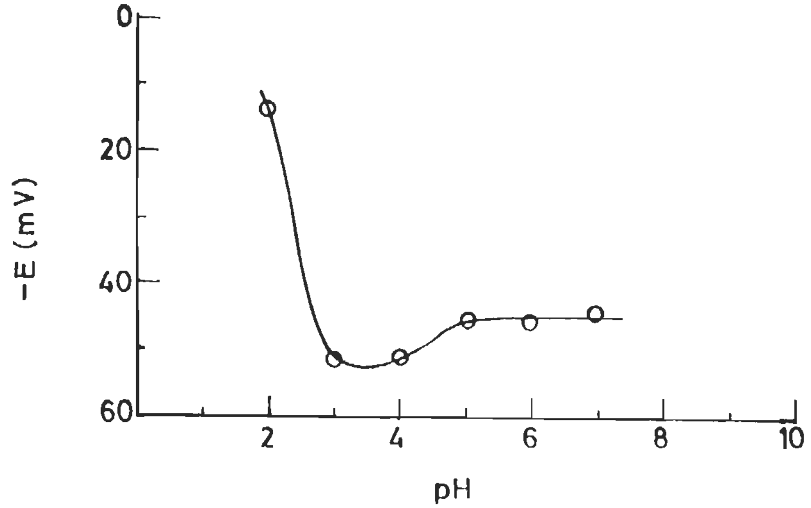

Fig. 3 Potential vs pH plot $\left[Cd^{2+} \text{ concn} = 1.0 \times 10^{-3} M\right]$

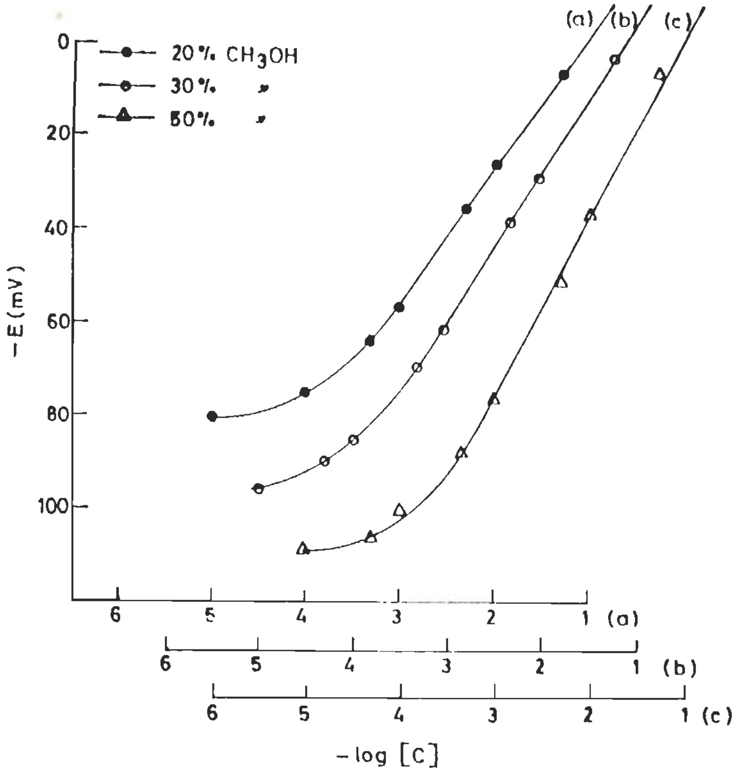

Fig. 4 Potential vs $[Cd^{2+}]$ plots in partially non-aqueous medium

Polytungstoantimonate membrane

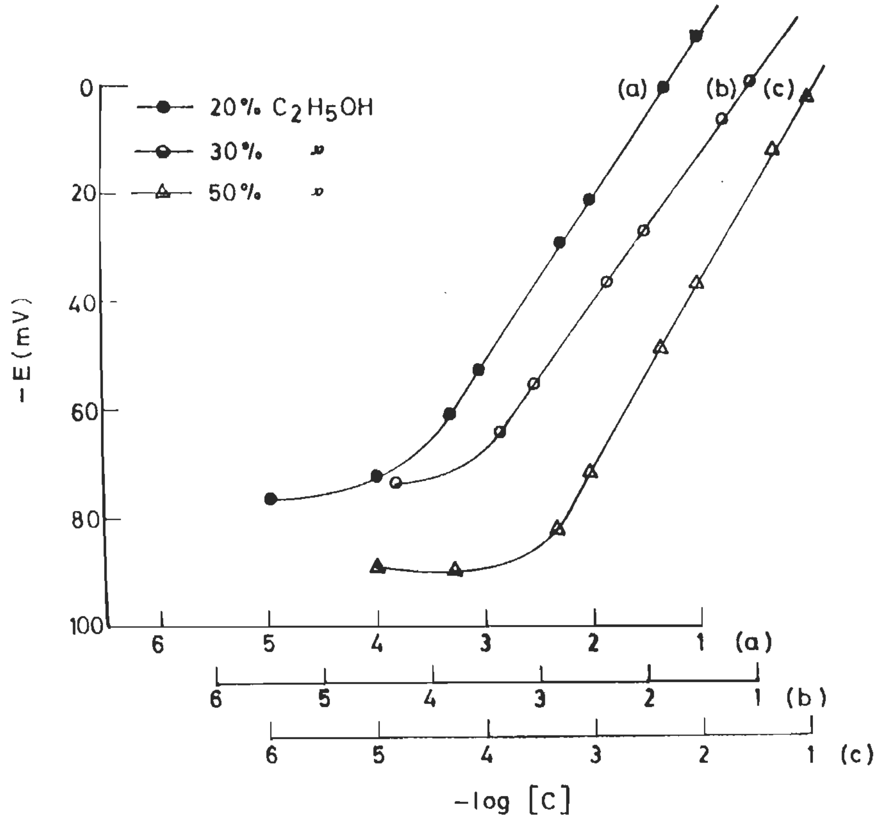

Fig. 5 Potential vs $[Cd^{2+}]$ plots in partially non-aqueous medium

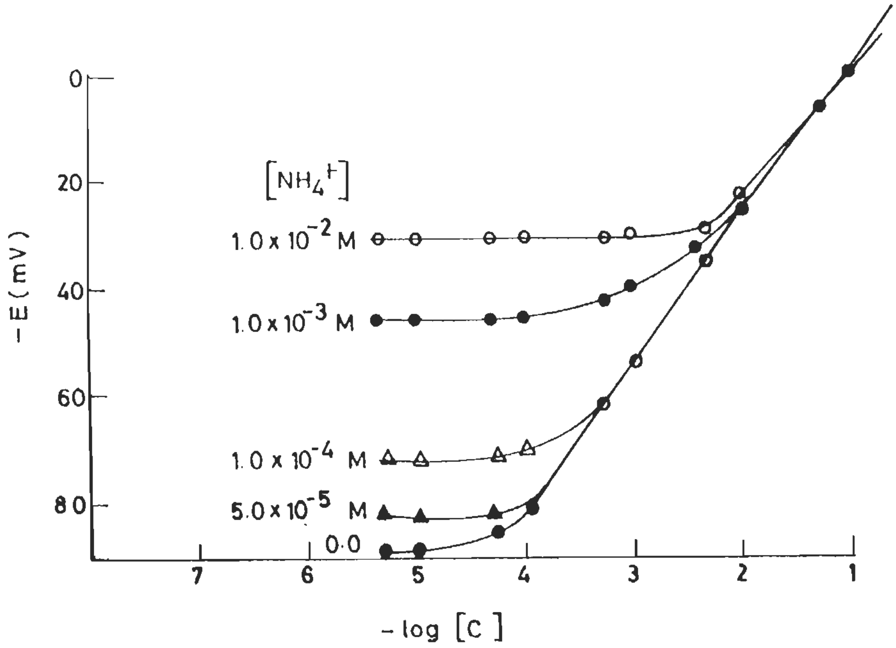

Fig. 6(a) Potential vs log $[Cd^{2+}]$ plots in the presence of NH_4^+ of varying concn.

Polytungstoantimonate membrane

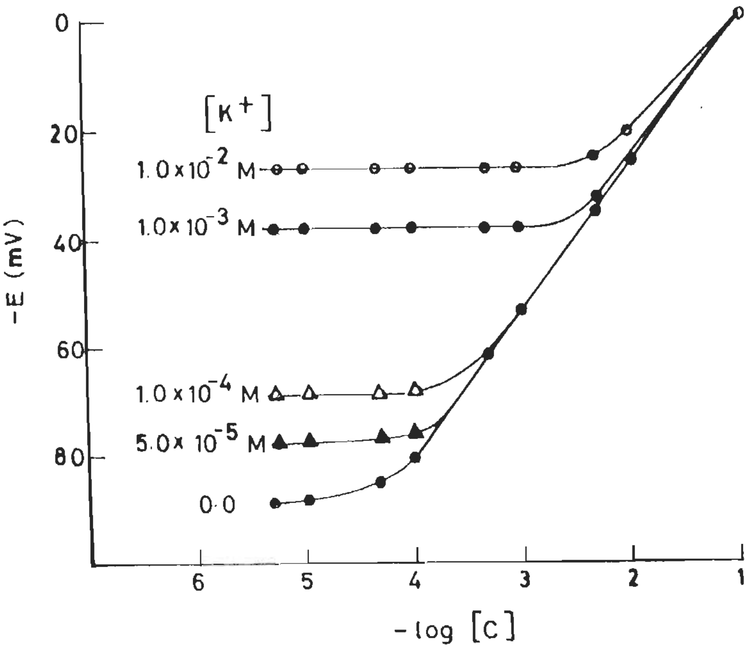

Fig. 6 (b) Potential vs log $[Cd^{2+}]$ plots in the presence of K^+ of varying concn.

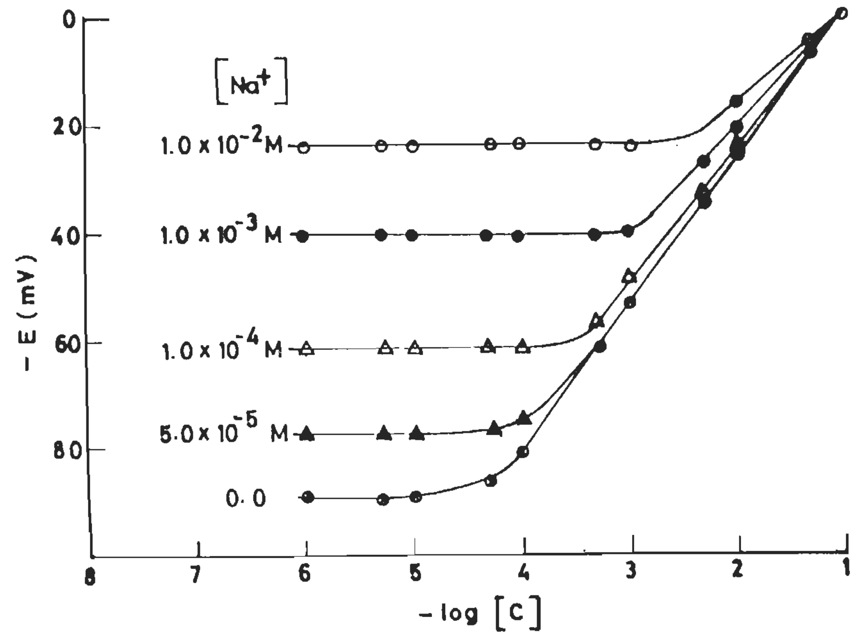

Fig. 6 (c) Potential vs log $[Cd^{2+}]$ plots in the presence of Na^+ of varying concn.

Polytungstoantimonate membrane

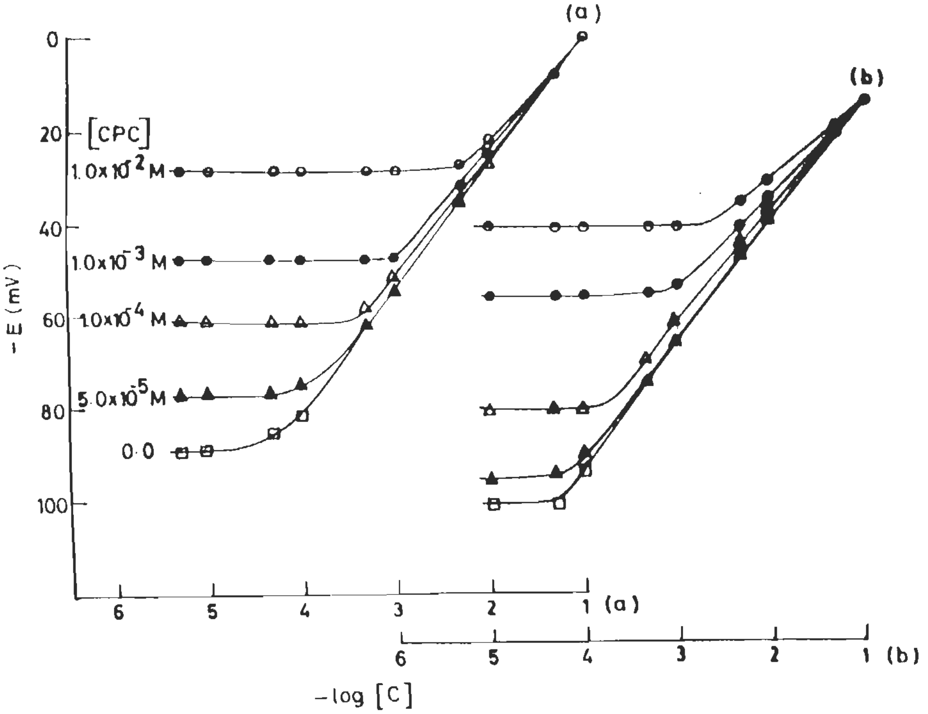

Fig. 7 Potential vs log $[Cd^{2+}]$ plots in the presence of CPC of varying concn. with untreated membranes (a) and treated membranes (b)

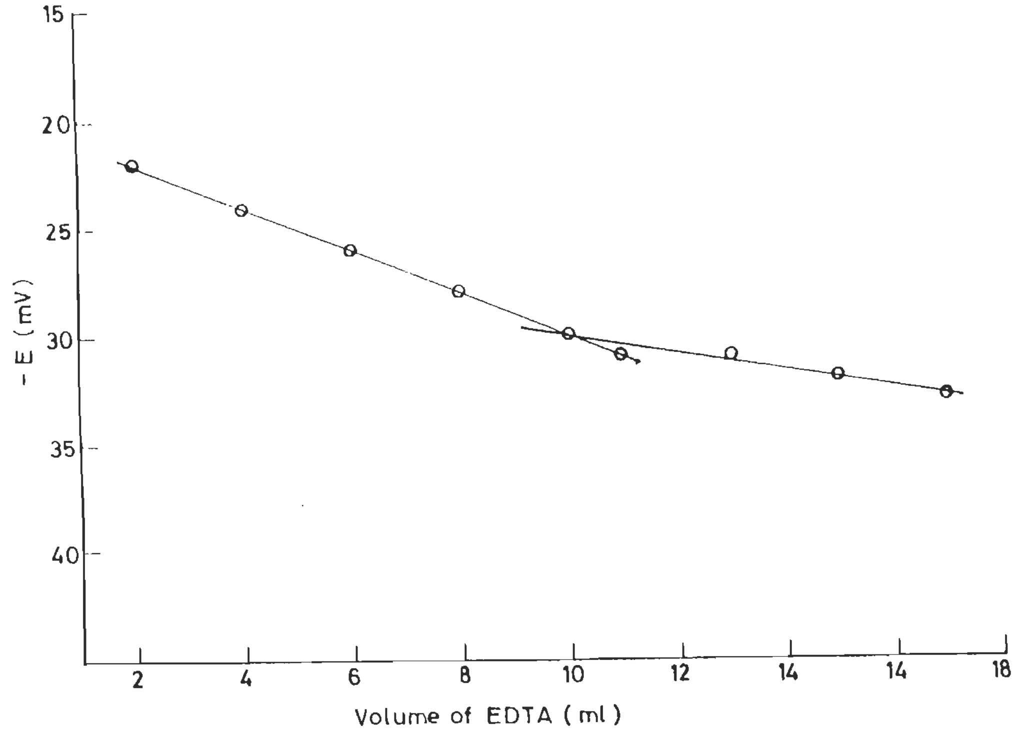

Fig. 8 Titration plot of 10ml of 1.0×10^{-2} M Cd^{2+} ions with 1.0×10^{-2} M EDTA solution

Polytungstoantimonate membrane

monovalent ions. The monovalent ions seem to record lesser interference if the values obtained by Mixed Solution method are taken into consideration. Some research publications (24-26) have also expressed doubts on the validity of the data obtained by Fixed Interference method.

In order to assess the working feasibility of the membrane sensor, in presence of monovalent cations, some mixed runs were made having different concentrations of interfering monovalent and Cd^{2+} ions. Potential vs concentration plots made at various interfering levels of NH_4^+, Na^+, K^+ are shown in Fig.6(a) to 6(c). It is evident that these ions do not cause any disturbance upto a concentration of 5.0×10^{-5}M or less. Beyond this concentration the sensor can not be used in the presence of monovalent cations viz NH_4^+, Na^+, K^+ etc. Other multivalent ions would normally not interfere unless present in very large concentration, a situation which would hardly arise.

III.3.f. Effect of surfactant

Quite often the proposed assembly may be applied to estimate the metal ion in presence of detergents and other similar substances. As such the working of the membrane sensor has also been checked in presence of surfactant ions. Potential with Cd^{2+} ions were observed in presence of varying concentrations of a cationic detergent cetyl pyridinium chloride and the results are shown in Table 6(a) & Fig-7. Smaller concentrations of surfactant (upto 5.0×10^{-5}M) do not disturb the working of this electrode where as higher concentrations do cause interference. The working concentration range of the sensor and it's slope, both undergo a change. Since the surfactants are likely to be present in traces only, there would not be any difficulty in using the sensor under these conditions.

Efforts were also made to condition the membrane by treating it with the surfactant solutions of 1.00×10^{-3}M concentration to make it immune to the disturbance caused by the presence of higher concentrations of the same. Data given in Table 6(b) shows the performance of the treated membrane. Although the sensor does not develop immunity to the effect of detergent at higher concentrations, one interesting feature is the enhancement of the working concentration range of the treated membrane sensor [Table-6(b)]. The level of interference, at larger concentrations of detergent, also goes down.

III.3.g. Titration

The practical utility of the sensor has been observed by using it as an indicator electrode for the titration of Cd^{2+} ions with EDTA. Figure-8 exhibits the change in potential when 1.00×10^{-2}M EDTA solution is added to 1.00×10^{-2}M Cd^{2+} solution. Although the changes observed in potentials are not large, the end point is quite sharp and the perfect stoichiometry is also observed in this case. The shapes of titration curves are not the same as are normally observed in potentiometric titrations. The removal of Cd^{2+} ions result in a decrease in membrane potential and beyond the end point the potential almost stays constant and the change is also nominal.

III.4.a. Estimation of Zn^{2+} ions

For the estimation of zinc ions, the membrane having polytungstoantimonate as electroactive phase was immersed in a solution of $ZnSO_4$ of 1.00M concentration. Equilibration of the membrane with Zn^{2+} ions continued for almost four days. The time of equilibration was fixed up after some preliminary studies and the membranes so equilibrated, generated stable and reproducible potentials when interposed between the test solution and internal reference solution of 0.10M $ZnSO_4$. Potentials were monitored periodically, at a fixed concentration and the standard deviation was found to be 0.2 mV. Membrane potentials were measured in the range 10^{-6} to 10^{-1}M proceeding from low to higher concentration at 30±1 °C against saturated calomel electrodes.

The electrode demonstrates a linear response for Zn^{2+} ions in 5.00×10^{-5}-1.00×10^{-1}M concentration range (Fig.9). The slope of the plot being exceptionally low viz. 18 mV/decade of concentration. Inspite of this drawback (Non Nernstian behaviour of the membrane), the sensor can be used in the above mentioned concentration range for determining the concentration of Zn^{2+} ions.

Reference solutions of different concentrations have also been tried but this did not improve the working of the electrode assembly. Calibration plots (Fig.10) with reference solution of 5.00×10^{-2} and 1.00×10^{-2}M Zn^{2+} ion concentrations show that the magnitude of potentials as well as the working concentration range (Table-7) decreases, as the concentration of reference solution is reduced. As such 1.00×10^{-1}M reference solution gives the best performance and the same has been used in the entire

Table-7

Working concentration range of the membrane sensor for Zn^{2+} ions with reference solution of varying concentration.

Reference solution concentration (M)	Slope mV/decade of concentration	Working concentration range (M)
1.00×10^{-1}	18	5.00×10^{-5} - 1.00×10^{-1}
5.00×10^{-2}	18	5.00×10^{-5} - 1.00×10^{-1}
1.00×10^{-2}	18	7.90×10^{-5} - 1.00×10^{-1}

Table-8

Performance of electrode system in 20, 30 and 50% (volume by volume) non-aqueous medium.

percentage	Slope mV/decade of concentration	Working concentration range (M)
x	18	5.00×10^{-5} - 1.00×10^{-1}
Ethanol		
20	20	1.00×10^{-4} - 1.00×10^{-1}
30	26	1.00×10^{-4} - 1.00×10^{-1}
50	26	1.00×10^{-4} - 1.00×10^{-1}
Methanol		
20	20	1.00×10^{-4} - 1.00×10^{-1}
30	22	1.58×10^{-4} - 1.00×10^{-1}
50	36	1.77×10^{-4} - 1.00×10^{-1}

Table-9

Selectivity of the electrode system for zinc ions in the presence of 1.00×10^{-2} M concentration of interfering ions (as calculated by Fixed Interference and Mixed Solution methods).

Interfering ion	Selectivity coefficient $[K^{Pot}_{A,B}]$	
	Fixed Interference Method	Mixed Solution Method
Na^+	17.20	11.49
K^+	19.95	5.81
Tl^+	12.85	0.00
Li^+	9.50	0.00
Ag^+	13.45	3.90
NH_4^+	17.18	4.98
Mn^{2+}	2.39×10^{-1}	6.90×10^{-2}
Pb^{2+}	2.39×10^{-1}	6.90×10^{-2}
Cd^{2+}	3.55×10^{-1}	1.02×10^{-1}
Ba^{2+}	3.55×10^{-1}	1.02×10^{-1}
Sr^{2+}	2.65×10^{-1}	7.68×10^{-2}
Co^{2+}	2.15×10^{-1}	6.23×10^{-2}
Ni^{2+}	2.39×10^{-1}	6.90×10^{-2}
Cu^{2+}	2.39×10^{-1}	6.90×10^{-2}
Mg^{2+}	2.39×10^{-1}	6.90×10^{-2}
Al^{3+}	3.82×10^{-2}	1.78×10^{-2}
La^{3+}	3.75×10^{-2}	1.72×10^{-2}

Table-10(a)

Performance of the electrode system in presence of the detergent cetyl pyridinium chloride (CPC).

Untreated membrane

Concentration of CPC (M)	Slope mV/decade of concentration	Working concentration range (M)
x	18	5.00×10^{-5} - 1.00×10^{-1}
5.00×10^{-5}	18	5.00×10^{-5} - 1.00×10^{-1}
1.00×10^{-4}	18	1.58×10^{-4} - 1.00×10^{-1}
1.00×10^{-3}	16	5.01×10^{-4} - 1.00×10^{-1}
1.00×10^{-2}	10	1.58×10^{-3} - 1.00×10^{-1}

Table-10(b)

Performance of the membrane conditioned with 1.00×10^{-3}M cetyl pyridinium chloride (CPC).

Concentration of CPC (M)	Slope mV/decade of concentration	Working concentration range (M)
x	20	3.98×10^{-5} - 1.00×10^{-1}
5.00×10^{-5}	20	3.98×10^{-5} - 1.00×10^{-1}
1.00×10^{-4}	20	1.41×10^{-4} - 1.00×10^{-1}
1.00×10^{-3}	18	3.54×10^{-4} - 1.00×10^{-1}
1.00×10^{-2}	14	1.25×10^{-4} - 1.00×10^{-1}

investigations with this electrode assembly.

III.4.b. Response and life time

The response time of this membrane sensor has been measured at various concentrations of test solution. It is reasonably fast, stable potentials are obtained within a minute and no changes are normally observed upto 5 minutes. The electrode assembly has been used for four to five months time without observing any drift in potentials but it is likely to get contaminated after a long continuous use.

III.4.c. pH effect

The pH dependence of the electrode potential has been tested over the range 1 to 6.5 for $1.00\text{x}10^{-3}$M Zn^{2+} ions (Fig.11). The potentials are constant within the range 3.5 to 6.0 which may be taken as the working pH range of this electrode system. A sharp change at low pH values probably accounts for the competition due to (H^{+}) ions under these circumstances.

III.4.d. Solvent effect

Variation of membrane potentials in a partially non-aqueous medium has also been studied. The plots, having 20, 30 and 50% (v/v) non-aqueous content are shown in Fig. 12 & 13. The data computed in Table-8, shows that working concentration range of the membrane sensor for Zn^{2+} ions goes down from $5.00\text{x}10^{-5}$-$1.00\text{x}10^{-1}$M to $1.00\text{x}10^{-4}$-$1.00\text{x}10^{-1}$M in 20% ethanolic and methanolic medium with a nominal increase in slope. Any further decrease in the working concentration range is not observed even upto a 50% non-aqueous content (ethanolic) although a little increase in slope (26 mV/decade concentration) is observed. While with an increase in methanol content (upto 50%), the working concentration range goes down to 1.77×10^{-4}- 1.00×10^{-1}M with a two fold increase in slope (36 mV/decade concentration).

III.4.e. Selectivity

In order to investigate the selectivity of this membrane, the response of the electrode was examined in the presence of various foreign ions. Potentiometric selectivity coefficients (Table-9) are obtained by both the Fixed Interference and Mixed Solution methods. The value of this parameter is generally quite low for polyvalent cations. As such these ions do not interfere. High selectivity coefficient values (as calculated by Fixed Interference method) suggest that monovalent cations do interfere in the working of the sensor but at the same time even in the case of monovalent cations comparatively low values of this parameter are obtained by Mixed Solution method. In order to assess the actual disturbance caused by the monovalent cations, at various concentrations, some mixed runs were made at four different concentrations of interfering monovalent ions. Plots in the case of Na^+, K^+ and NH_4^+ ions are shown in Fig.14(a)- 14(c). Potential verses log $[Zn^{2+}]$ plots at a level of interference of 5.00×10^{-5}M almost completely overlap the plot obtained in solutions having no interfering ions. As the concentration of monovalent ions increases, a divergence from the original plot is quite apparent. Thus the electrode system can be safely operated in the presence of 5.00×10^{-5}M concentration of monovalent cations. Although the selectivity parameter has zero values in the case of Tl^+ and Li^+

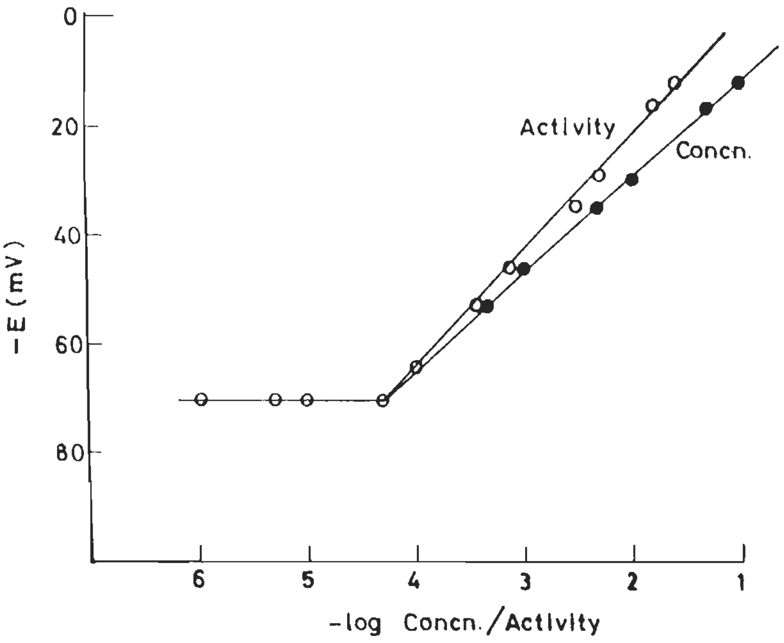

Fig. 9 Potential vs log $[Zn^{2+}]$ plots

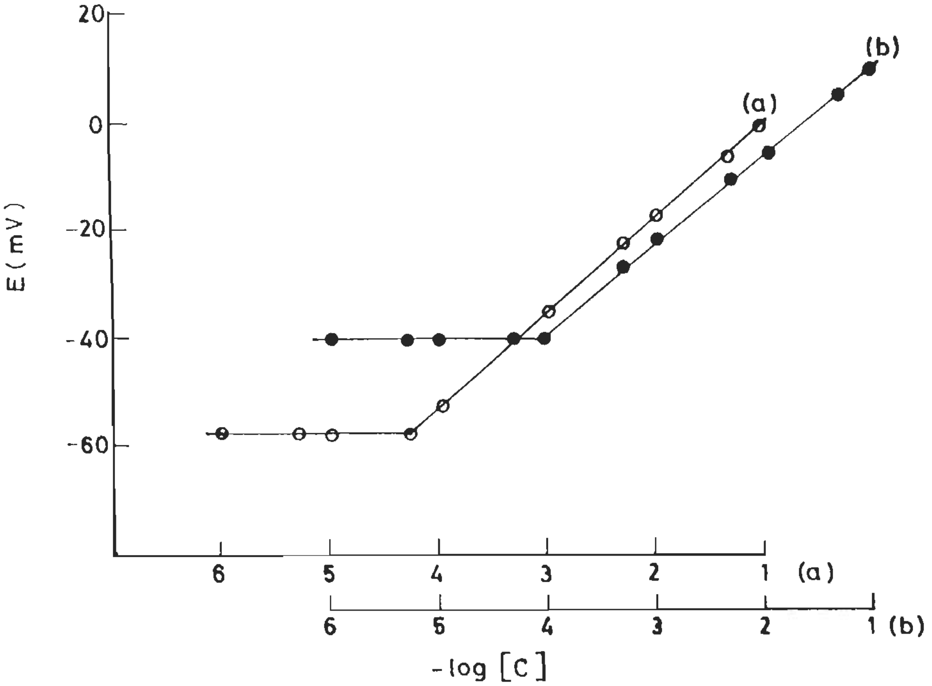

Fig. 10 Potential vs log $[Zn^{2+}]$ plots with reference solution concn. (a) 5.0×10^{-2} M (b) 1.0×10^{-2} M

Polytungstoantimonate membrane

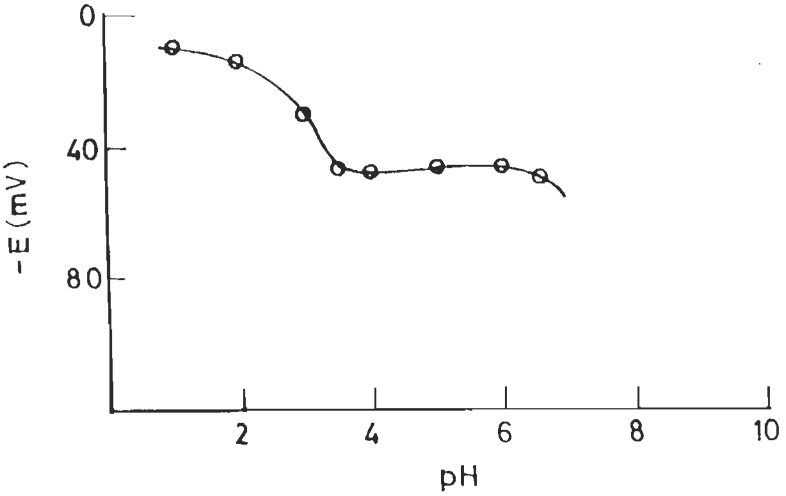

Fig. 11 Potential vs pH plot [Zn^{2+} concn. = 1.0×10^{-3}M]

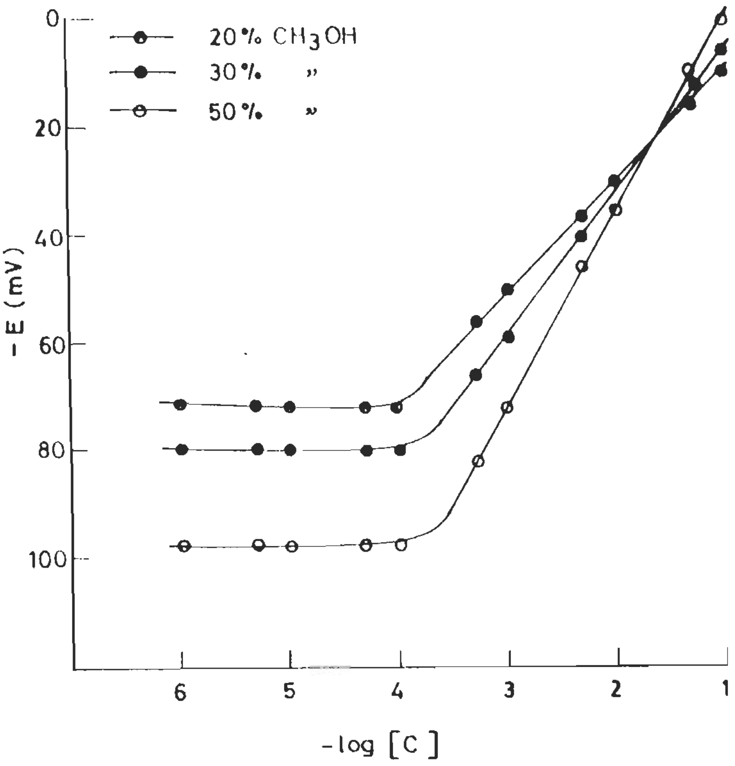

Fig. 12 Potential vs [Zn^{2+}] plots in partially non-aqueous medium

Polytungstoantimonate membrane

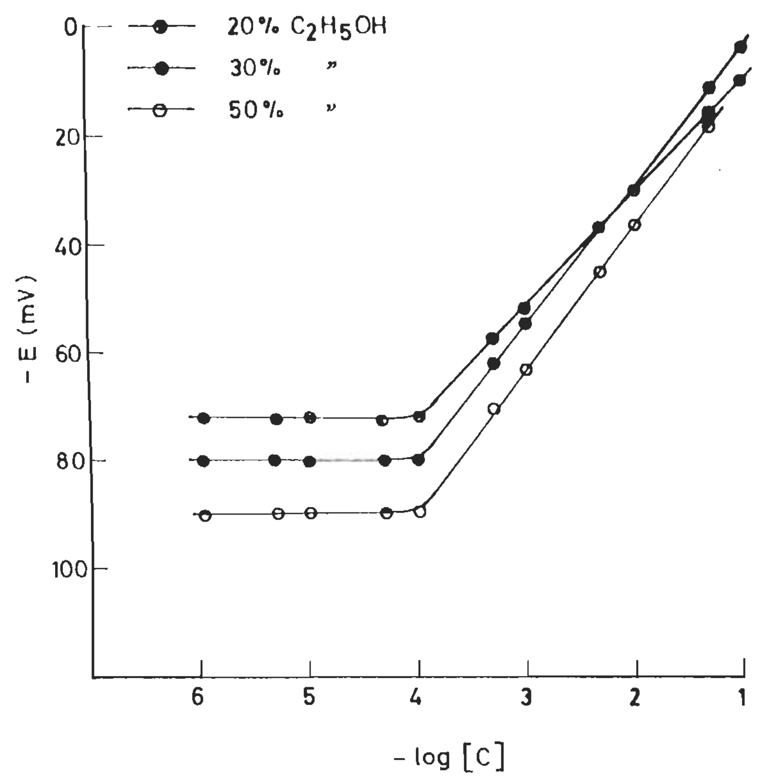

Fig. 13 Potential vs $[Zn^{2+}]$ plots in partially non-aqueous medium

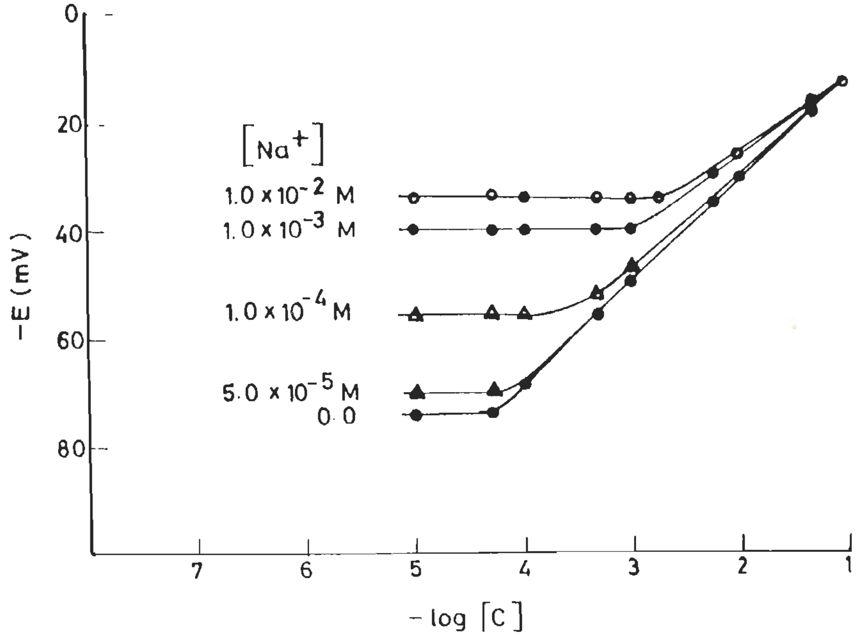

Fig. 14 (a) Potential vs log $[Zn^{2+}]$ plots in the presence of Na^+ of varying concn.

Polytungstoantimonate membrane

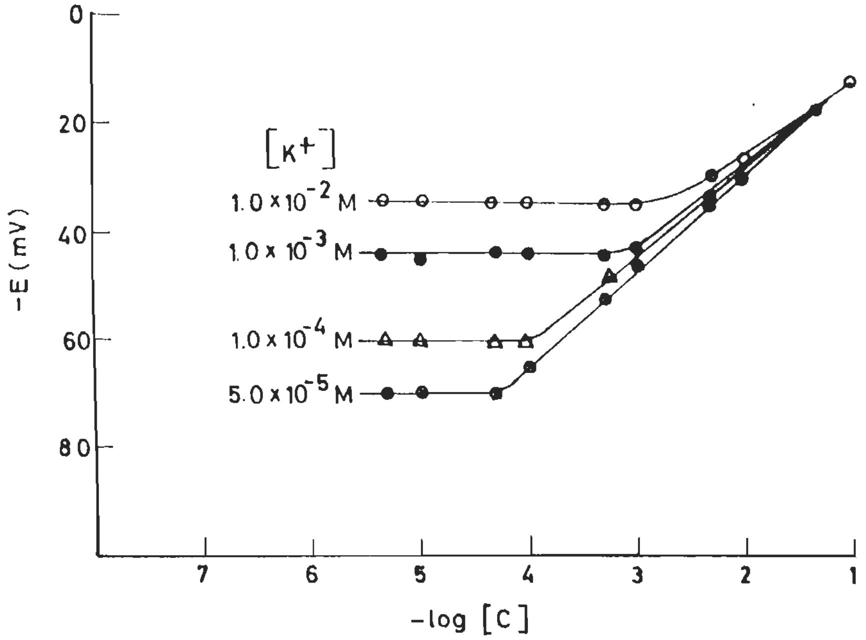

Fig. 14(b) Potential vs log $[Zn^{2+}]$ plots in the presence of K^+ of varying concn.

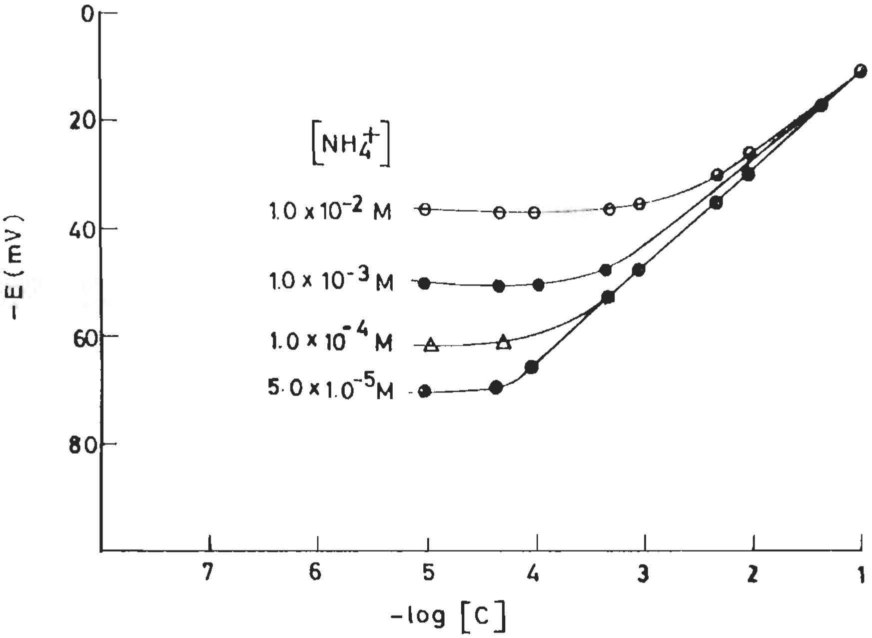

Fig. 14(c) Potential vs log $[Zn^{2+}]$ plots in the presence of NH_4^+ of varying concn.

Polytungstoantimonate membrane

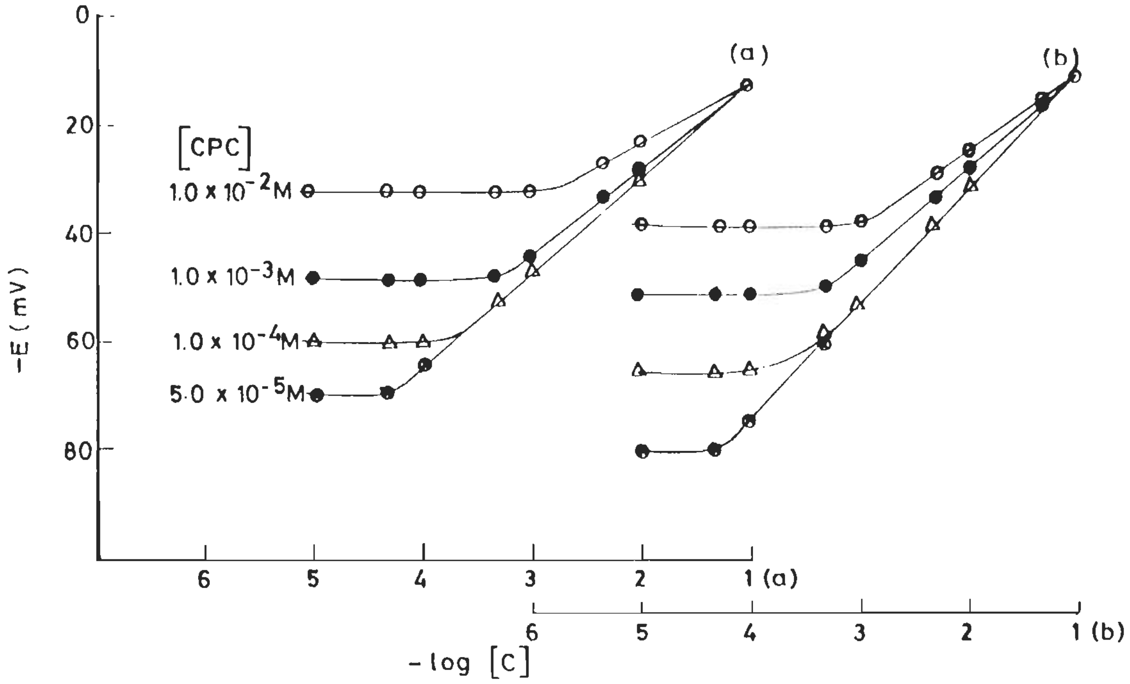

Fig.14(d) Potential vs log $[Zn^{2+}]$ plots in the presence of CPC of varying concn. with untreated membranes (a) and treated membranes (b)

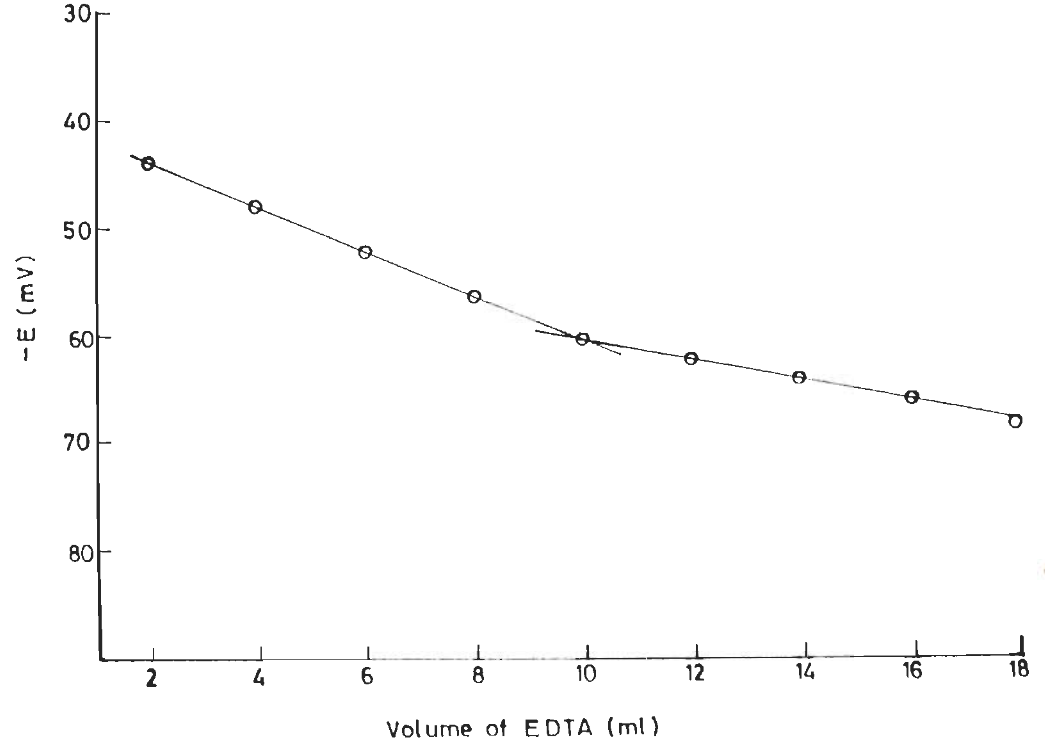

Fig. 15 Titration plot of 10 ml of 1.0×10^{-2} M Zn^{2+} ions with 1.0×10^{-2} M EDTA solution

Polytungstoantimonate membrane

even these two ions do interfere if present at concentrations > 5.00×10^{-5}M .

III.4.f. Effect of surfactant

In actual practice the estimation of Zn^{2+} is quite often required in presence of surfactant and other similar impurities. As such the working of membrane sensor has also been checked in presence of a cationic surfactant cetyl pyridinium chloride. The plots of potential versus log $[Zn^{2+}]$ in presence of varying concentration of cetyl pyridinium chloride is shown in Figure-14(d) and the results are depicted in Table-10(a). The original curve is repeated upto a 5.00×10^{-5}M concentration of surfactant ions. Beyond this concentration the detergent cation causes a significant interference.

Earlier workers have made the sensor immune to the disturbing effect by treating and conditioning it with surfactant solution at higher concentrations. As such this electrode was also treated with 10^{-3}M cetyl pyridinium chloride solution for 2 days and the potentials observed with the conditioned membrane are shown in Fig-14(d) and the corresponding data is mentioned in Table-10(b). Although the working concentration range of the treated membrane is more than the original one the sensor can only be used in the presence of 5.00×10^{-5}M surfactant concentration. Beyond this concentration even the treated membrane can not be used in presence of surfactant cations.

III.4.g. Titration

The membrane sensor is a good end point indicator in the potentiometric titrations for Zn^{2+} ions. The titration of 10 ml of $1.00x10^{-2}M\ Zn^{2+}$ ions with $1.00x10^{-2}M$ EDTA solution is shown in Figure-15. The inflexion point in the curve corresponds to the stoichiometric ratio of EDTA required to neutralize the zinc sulphate solution. This method is much more convenient in comparison to the standard titration methods and the estimation of dilute solutions can also be performed successfully.

III.5. A comparison of the performance of polytungstoantimonate membrane sensor for the estimation of Cd^{2+} and Zn^{2+} ions.

A comparative utility of the polytungstoantimonate membrane for the estimation of Cd^{2+} and Zn^{2+} ions shows better performance for zinc. It can be estimated in a wider range of concentration ($5.00x10^{-5}$ to $1.00x10^{-1}M$) as compared to Cd^{2+} ions ($6.31x10^{-5}-1.00x10^{-1}M$) although it exhibits Nernstian behaviour for Cd^{2+} ions in comparison to zinc for which a quite low value of slope is recorded.

The response time is also much better in the case of Zn^{2+} ions and the sensor is tolerant of changes in pH, over wider range (3.5-6) in the case of zinc in comparison to Cd^{2+} ions for which the working pH range is 5-7.

The performance of the electrode assembly is better in partially non-aqueous medium of Zn^{2+} ions.

The selectivity coefficient pattern clearly establishes the superiority of the membrane electrode for Zn^{2+} ions. The values are comparatively lower for interfering ions vis a vis zinc ions.

The membrane sensor is found to be a good end point indicator in the potentiometric titration of both Cd^{2+} and Zn^{2+} ions.

Thus it seems that the membrane, under investigation is a better sensor for Zn^{2+} ions although it can also be used for the estimation of Cd^{2+} with some restrictions. It is quite apparent that the sensor would fail to respond if both the ions are simultaneously present in the same solution.

III.6. Functional properties of tin oxide membranes

Homogeneous membranes of tin oxide could not be prepared as cracks developed at the early stage itself and the membrane was found to be very much fragile. So heterogeneous membranes embedded with polystyrene in a fixed ratio (binder content 15%) at temperature 95 ^{o}C under pressure of 6500-7000 psi were prepared. This gives a stable membrane which does not dissipate in water or salt solutions. The amount of polystyrene required for the preparation of membrane was arrived at after a good deal of experimentation. The detailed method of preparation for such membranes is described in Chapter II.

The functional properties of the membranes such as water content, swelling, porosity, electrolyte absorption and conductance affect its electrochemical performance. For example lower values of porosity and swelling suggest that the interstices available are less and so there is a good probability that diffusing ion travels across the membranes via exchange sites. Naturally the membrane should exhibit a better electrochemical performance.

III.6.a. Water content, porosity, swelling and electrolyte absorption

When a dry membrane is immersed in water or electrolyte solution, swelling takes place and the solution penetrates into the membrane structure and occupies the interstices. These interstices are either already present on the membrane matrix or develop on immersion due to different swelling properties of membrane material and binder. The interstices act as a film and the diffusion of different electrolytes also becomes possible by film diffusion besides the normal diffusion through the membrane material. The magnitude of swelling thus depends on the gel structure as well as the amount of binder present in the membrane.

A lesser amount of water is incorporated into this membrane and the value is fairly comparable to the membranes of the same class (27).

Porosity, as calculated from the water content data, is the volume of water incorporated in the cavities per unit membrane volume. Tin oxide membranes (Table 11) have moderately low values of porosity and swelling, thereby suggesting that diffusion through these membranes would depend on the exchange sites rather than porosity. Thus in a membrane having low values of porosity, water content and swelling, the number of interstices available are lesser in comparison to one having relatively larger values of these parameters. The membrane under investigation should, therefore, respond selectively to a particular ion.

Lesser electrolyte absorption in tin oxide membranes is compatible to values observed for other parameters (Table-11).

Table-11

Water content, porosity, swelling and electrolyte absorption values for tin oxide membrane.

Membrane with binder polystyrene	Water content per gram of wet membrane (g)	Porosity	Swelling (mm)	Amount of electrolyte absorbed per gram of wet membrane (M)
Tin oxide	0.1700	0.3894	0.020	5.2×10^{-2}
Fe-Zr oxide	0.2014	0.2053	0.008	4.8×10^{-4}
Cr-Zr oxide	0.1908	0.1944	0.008	3.8×10^{-4}

Table-12

Conductance of tin oxide membrane in different ionic forms.

Ions	Conductance (micro mhos x 10^{-4})
VO_3^-	0.20
CH_3COO^-	0.75
Br^-	2.30
NO_3^-	1.70
Cl^-	2.20
I^-	2.35
BrO_3^-	2.70
SO_4^{2-}	0.31
CrO_4^{2-}	0.34
$C_2O_4^{2-}$	1.50
$[Fe(CN)_6]^{4-}$	3.64

III.6.b. Specific conductance

The conductance of tin oxide membrane in different anionic forms at 10^{-1}M concentrations were measured. A constant value of membrane conductance is observed in all the measurements. These results point to negligible polarization on the mercury membrane interface.

Specific conductivity data (Table-12) show the following sequence for the various anions.

$[Fe(CN)_6]^{4-} > BrO_3^- > I^- > Br^- > Cl^- > NO_3^- > C_2O_4^{--} > CH_3COO^- > CrO_4^{--} > SO_4^{--} > VO_3^-$

It is observed that the conductance decreases with decreasing ionic radii in case of halide ions while no such correlation, either on the basis of ionic size or hydration, is observed in the case of other anions.

III.7. Electrochemical performance of the membrane using tin oxide as electroactive phase.

Being guided by the selectivity sequence of the electroactive phase i.e., tin oxide, the membrane was tried for the estimation of PO_4^{3-} ion which shows maximum uptake on the exchanger material. The sensor did not show any selectivity for this anion and all efforts made in this direction failed. Investigations revealed some promising results in the case of two anions, CrO_4^{2-} and VO_3^-.

III.7.a. Estimation of CrO_4^{2-} ions

For the estimation of CrO_4^{2-} ions, the membranes having tin oxide as an electroactive phase were equilibrated with 1.00M potassium chromate solution for five days, the solution being intermittently replaced. The membrane equilibrated for shorter durations did not develop stable potentials while the potentials obtained after this equilibrium period were stable and reproducible. Potentials were repeatedly monitored at a fixed concentration and a standard deviation of 0.4 mV was observed in the functional concentration range of the sensor for chromate ions. Potentials were measured with chromate ions in the concentration range of 10^{-6} to 10^{-1}M proceeding from low to higher values at 30±1 ^{o}C and the same are recorded in Fig. 17.

The plot (Fig.16) is linear in the concentration range 1.78×10^{-4} to 1.00×10^{-1}M and is Nernstian in nature (slope of the plot being 30 mV/decade of concentration). For a membrane showing Nernstian behaviour, the value of slope of the plot for bivalent ions should be 29 mV/decade of concentration. In very dilute solutions the response of electrode deviates from linear behaviour.

Normally in the cell, devised for measuring potentials, a reference solution of 1.00×10^{-1}M concentration is used. Reference solutions of different concentrations have also been tried but this did not improve the working of the electrode assembly. Calibration plots have also been made with 5.00×10^{-2} and 1.00×10^{-2}M potassium chromate as reference solutions. It is observed (Fig.17 & Table 13) that the magnitude of potential falls as we reduce the concentration of reference solution. Naturally it can be inferred that a reference solution of 1.00×10^{-1}M concentration gives the best performance and the same has been used in the entire investigations with this electrode assembly.

Table-13

Working concentration range of the membrane sensor for chromate ions with reference solution of varying concentration.

Reference solution concentration (M)	Slope mV/decade of concentration	Working concentration range (M)
$1.00\text{x}10^{-1}$	30	$1.78\text{x}10^{-4}$- $1.00\text{x}10^{-1}$
$5.00\text{x}10^{-2}$	26	$2.51\text{x}10^{-4}$- $1.00\text{x}10^{-1}$
$1.00\text{x}10^{-2}$	25	$2.51\text{x}10^{-4}$- $1.00\text{x}10^{-1}$

Table-14

Performance of electrode system in 15, 30 and 50% (volume by volume) non-aqueous medium.

percentage	Slope mV/decade of concentration	Working concentration range (M)
x	30	$1.78\text{x}10^{-4}$- $1.00\text{x}10^{-1}$
Ethanol		
15	19	$5.00\text{x}10^{-5}$- $1.00\text{x}10^{-1}$
30	24	$7.94\text{x}10^{-5}$- $1.00\text{x}10^{-1}$
50	26	$7.94\text{x}10^{-5}$- $1.00\text{x}10^{-1}$
Methanol		
15	21	$1.00\text{x}10^{-4}$- $1.00\text{x}10^{-1}$
30	17	$2.25\text{x}10^{-4}$- $1.00\text{x}10^{-1}$
50	24	$5.00\text{x}10^{-4}$- $1.00\text{x}10^{-1}$

Table-15

Selectivity of the electrode system for chromate ions in the presence of 1.00×10^{-2}M concentration of interfering ions (as calculated by Fixed Interference and Mixed Solution methods).

Interfering ion	Selectivity coefficient $[K^{Pot}_{A,B}]$	
	Fixed Interference Method	Mixed Solution Method
Cl^-	28.12	7.28
Br^-	25.11	21.28
I^-	28.10	23.82
NO_3^-	19.90	16.91
CH_3COO^-	19.90	19.80
BrO_3^-	17.81	12.67
ClO_3^-	19.90	9.31
IO_3^-	17.80	10.41
SCN^-	17.80	10.41
$C_2O_4^{2-}$	1.25×10^{-1}	8.89×10^{-2}
SO_4^{2-}	2.24×10^{-1}	1.04×10^{-1}
$S_2O_3^{2-}$	1.99×10^{-1}	7.15×10^{-2}
PO_4^{3-}	3.83×10^{-2}	1.79×10^{-2}
$Fe(CN)_6^{3-}$	4.29×10^{-2}	2.51×10^{-2}

Table-16(a)

Performance of the electrode system in presence of the detergent sodium dodecyl sulphate (SDS).

Untreated membrane

Concentration of SDS (M)	Slope mV/decade of concentration	Working concentration range (M)
x	30	1.78×10^{-4} - 1.00×10^{-1}
1.00×10^{-4}	28	5.01×10^{-4} - 1.00×10^{-1}
1.00×10^{-3}	23	7.94×10^{-4} - 1.00×10^{-1}
1.00×10^{-2}	20	3.16×10^{-3} - 1.00×10^{-1}

Table-16(b)

Performance of the membrane conditioned with 1.00×10^{-3}M sodium dodecyl sulphate (SDS).

Concentration of SDS (M)	Slope mV/decade of concentration	Working concentration range (M)
x	30	1.00×10^{-4} - 1.00×10^{-1}
1.00×10^{-4}	28	3.16×10^{-4} - 1.00×10^{-1}
1.00×10^{-3}	27	5.01×10^{-4} - 1.00×10^{-1}
1.00×10^{-2}	23	1.25×10^{-3} - 1.00×10^{-1}

III.7.b. Response and life time

The response time of the electrode has been measured at various concentrations of potassium chromate solutions and the same is found to be one minute at all dilutions. Besides this potentials stay constant for more than five minutes, after which a slow drift is observed. The electrode assembly has been used for a period of 4-5 months without observing any disturbance. After prolonged used it can be regenerated for better results.

III.7.c. pH effect

The working pH range of the electrode assembly has also been ascertained at a concentration of 1.00×10^{-3}M K_2CrO_4 solution. Potentials stay constant in a wide pH range 7-10 (Fig.18), which may be taken as the working pH range of the electrode assembly. It is also quite well known that below pH 7 dichromate ions and above pH 7 chromate ions do exist in solution.

III.7.d. Solvent effect

The working of this electrode assembly has also been observed in partially non-aqueous medium. Figure 19 & 20 depict the plots obtained for potentials with this membrane sensor in partially non-aqueous solution of Cr(VI). The change observed in the effective concentration range of the sensor and also in the slope of the plots with increasing concentration of non-aqueous content are mentioned in Table-14 and present some interesting results. In 15% ethanolic medium the working concentration range of the sensor gets enhanced from 1.78×10^{-4}-1.00×10^{-1}M to 5.00×10^{-5}-1.00×10^{-1}M with a significant decrease in slope from 30 to 19 mV/decade of concentration. Similarly in 15% methanolic medium also the working concentration range of the proposed sensor increases to 1.00×10^{-4}-1.00×10^{-1}M but the decrease observed in the slope of the plot is smaller (21 mV) in comparison to ethanolic solution. On further increasing the ethanol content (30 & 50%) the working concentration range of the sensor, however, goes down a little i.e., 7.94×10^{-5}-1.00×10^{-1}M with a better slope (24 & 26 mV/decade of concentration respectively). At the same time, a further increase in the methanolic content (30%) reduces the working concentration range of the sensor and the slope of the plot also goes down. In 50% methanolic solution the working concentration range further goes down to 5.00×10^{-4}-1.00×10^{-1}M and an increase in the slope (24 mV/decade of concentration) of plot is observed in this case also. Thus the electrode assembly can be safely used with advantage, in fifteen percent alcoholic solutions and it is not advisable to use the sensor in solutions having higher non-aqueous content.

III.7.e. Selectivity

The interference of other ions, if present, along with the determinand ion should also be known before using the electrode assembly. As such the disturbing effects of other ions have also been measured in terms of selectivity coefficients by routine methods. The values obtained by Fixed Interference method are mentioned in Table-15. It is observed that the bivalent and polyvalent anions have low $K_{A,B}^{Pot}$ values and normally these should not cause any disturbance in the working of the membrane electrode. High selectivity coefficient values in the case of

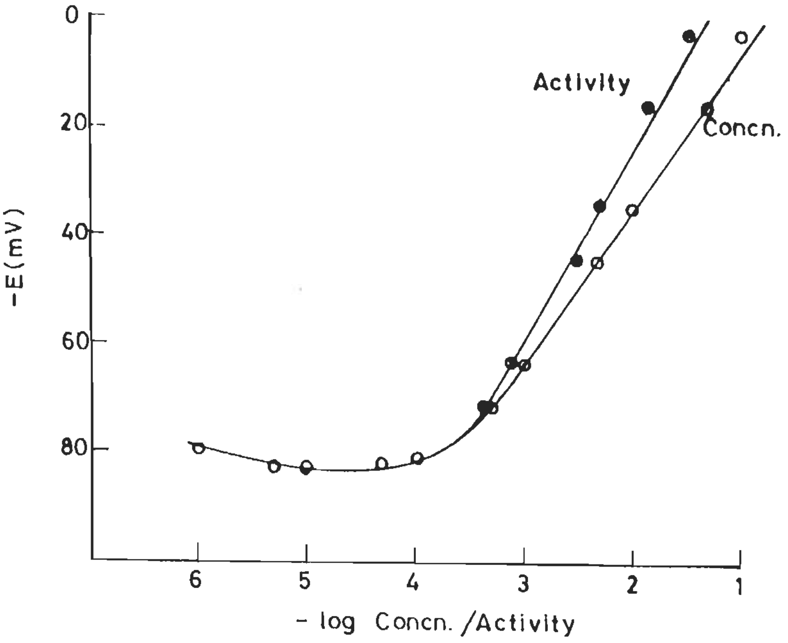

Fig. 16 Potential vs log $[CrO_4{}^{2-}]$ plots

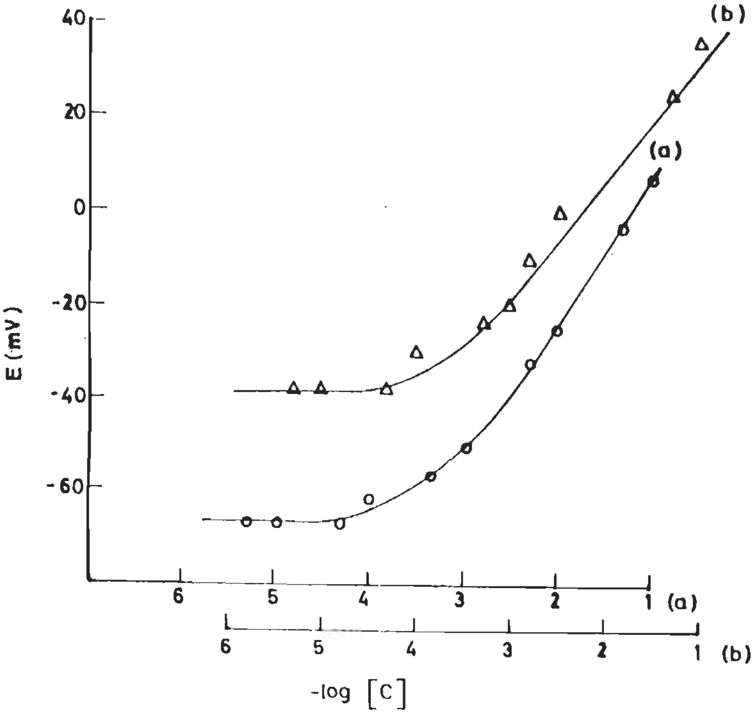

Fig. 17 Potential vs log $[CrO_4{}^{2-}]$ plots with reference solution concn. (a) 5.0×10^{-2} M (b) 1.0×10^{-2} M

Tin Oxide membrane

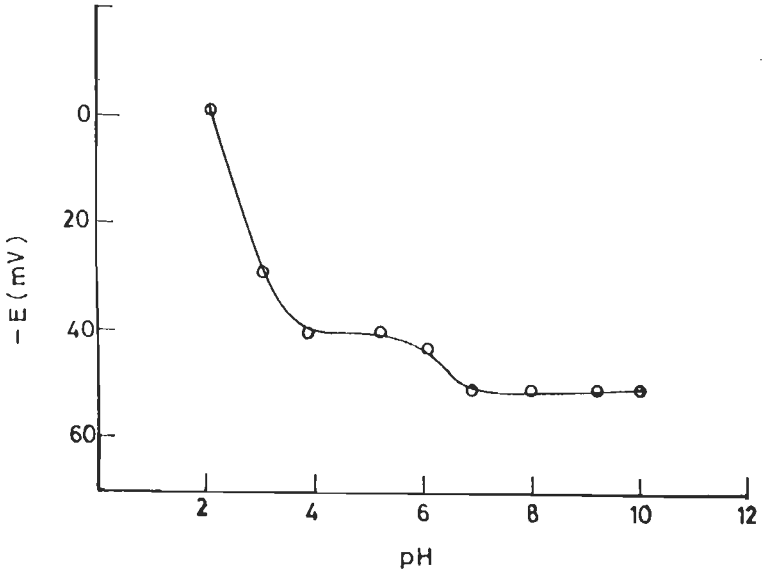

Fig.18 Potential vs pH plot $[CrO_4^{2-}$ concn $= 1.0 \times 10^{-3}$ M$]$

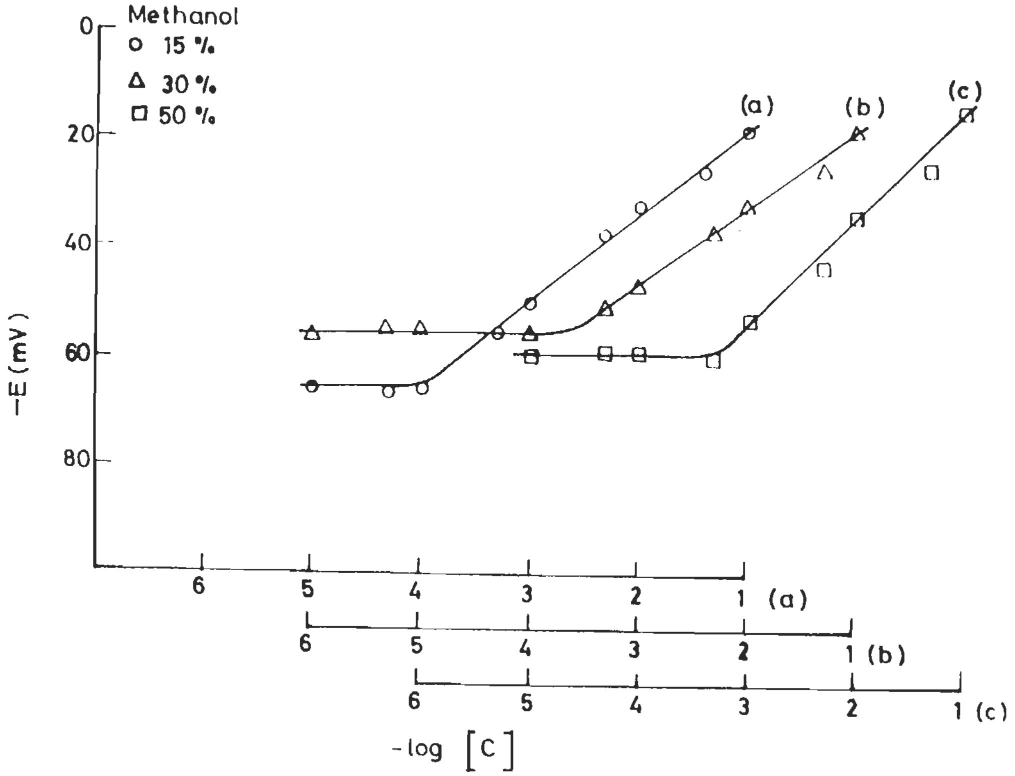

Fig.19 Potential vs log $[CrO_4^{2-}]$ plots in partially non-aqueous medium

Tin Oxide membrane

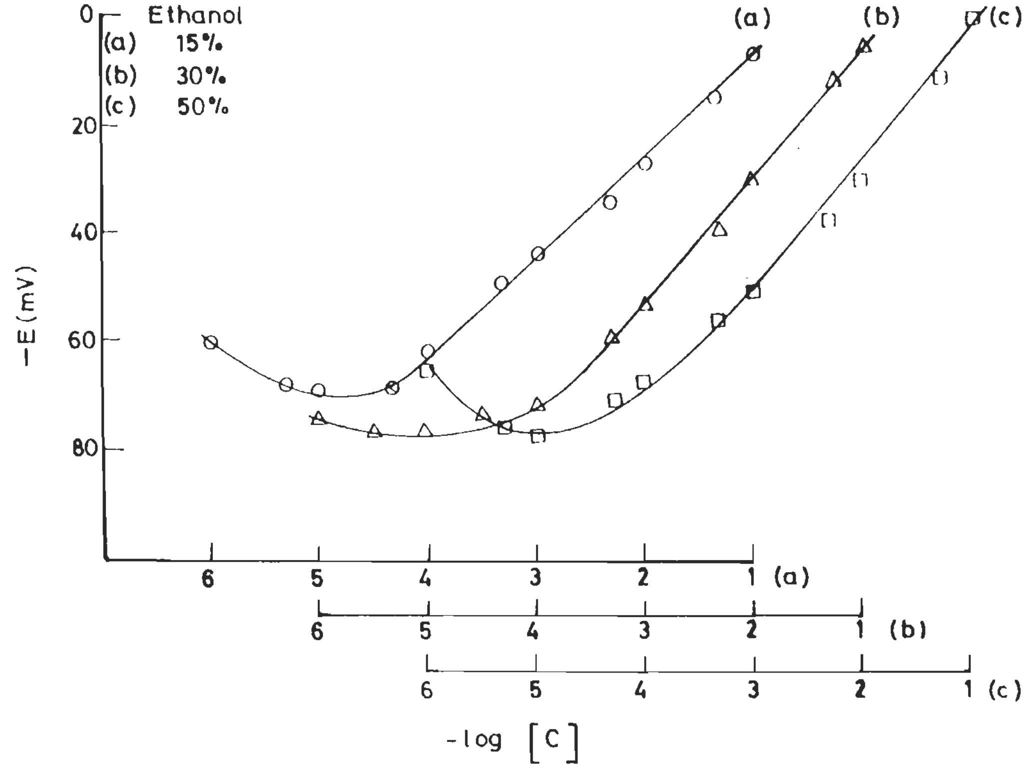

Fig. 20 Potential vs log $[CrO_4^{2-}]$ plots in partially non-aqueous medium

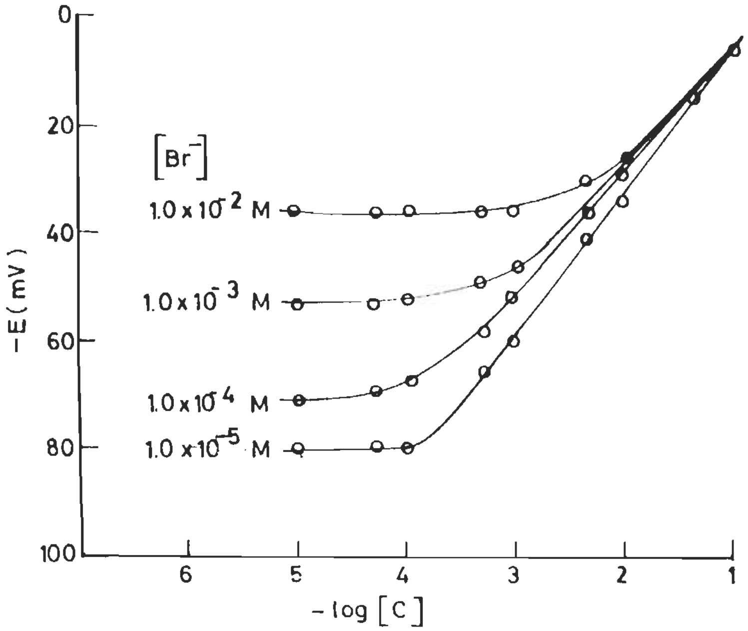

Fig. 21(a) Potential vs log $[CrO_4^{2-}]$ plots in the presence of Br^- of varying concn.

Tin Oxide membrane

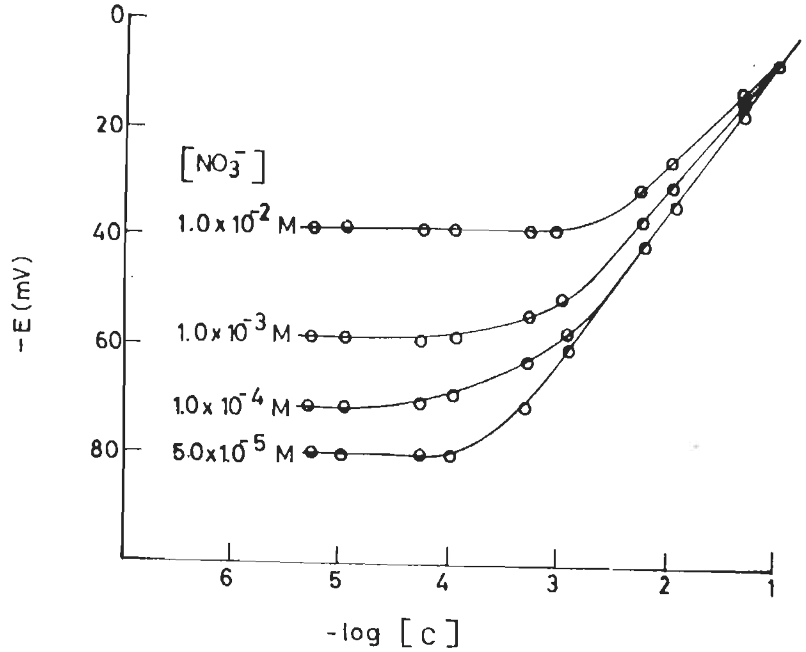

Fig. 21(b) Potential vs log $[CrO_4^{2-}]$ plots in the presence of NO_3^- of varying concn.

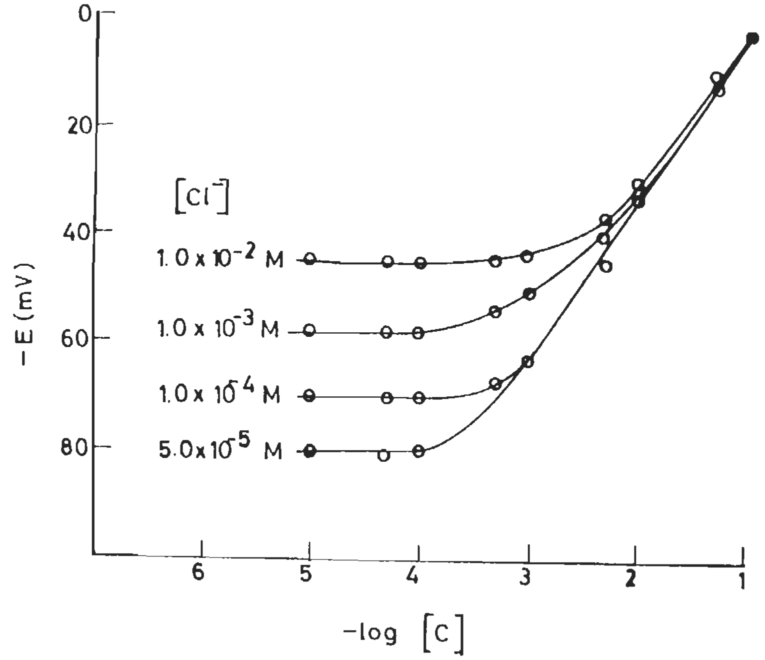

Fig. 21(c) Potential vs log $[CrO_4^{2-}]$ plots in the presence of Cl^- of varying concn.

Tin Oxide membrane

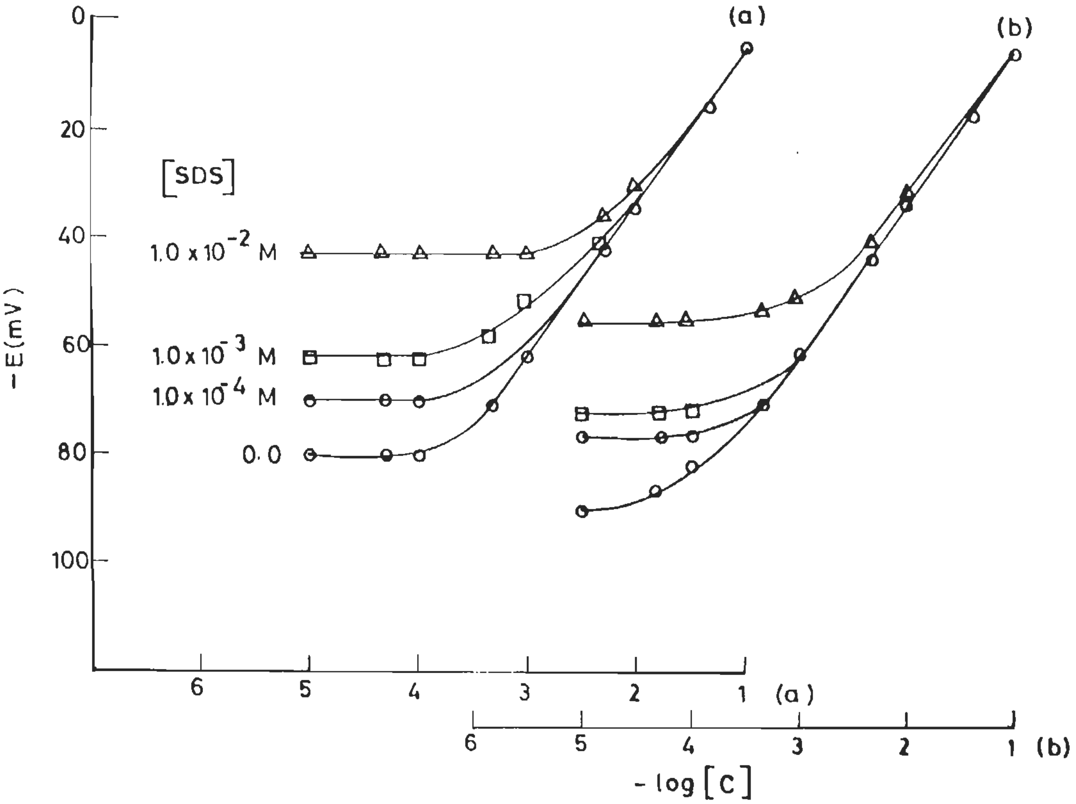

Fig. 22 Potential vs log [CrO_4^{2-}] plots in the presence of SDS of varying concn. with untreated membranes (a) and treated membranes (b)

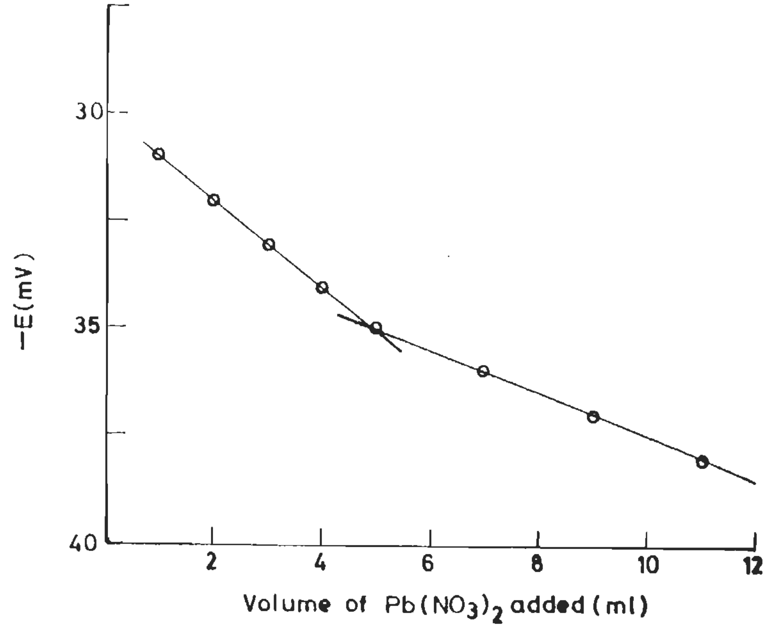

Fig.23 Titration plot of 10ml of 1.0×10^{-2} M CrO_4^{2-} ions with 1.0×10^{-2} M $Pb(NO_3)_2$

Tin Oxide membrane

monovalent anions reflect significant interference in the working of the proposed sensor, when such ions are present. Mixed Solution method has also been used to obtain the selectivity coefficient values and the data recorded in Table-15 shows much lower level of interference by almost all the anions. Even the values (Table-15) are lower for monovalent ions, in comparison to what has been obtained by Fixed Interference method. In order to see the actual interference level of the monovalent ions, (in view high $K^{pot}_{A,B}$ values) some mixed runs were also observed. Potentials were monitored at different chromate ion concentration and various levels of concentration of interfering ions. The plots for the same at various concentrations of interfering ions given in Fig.21(a)-21(c), reveal a complete tolerance of the interfering ion upto a level for $5.00\text{x}10^{-5}$M concentration. Beyond this concentration the monovalent ions do interfere and it would not be possible to use the electrode assembly for measuring Cr(VI) concentration in their presence.

III.7.f. Effect of surfactant

The working of the electrode in presence of varying concentration of an anionic surfactant, sodium dodecyl sulphate, has also been assessed (Figure-22) and the results depicted in Table-16(a) reveal the disturbing influence of the surfactant anion. In presence of $1.00\text{x}10^{-4}$M sodium dodecyl sulphate, the working concentration range goes down from $1.78\text{x}10^{-4}$-$1.00\text{x}10^{-1}$M to $5.01\text{x}10^{-4}$-$1.00\text{x}10^{-1}$M with a small change in slope of the plot from 30 to 28mV/decade of concentration. The interference increases with increasing detergent concentration, thereby causing a significant reduction in the working concentration range of the sensor and the slope of the plot also goes down.

In some cases the disturbing effect of the surfactants can be over come by conditioning it with the detergent solution. As such the membrane sensor was treated with 1.00×10^{-3}M sodium dodecyl sulphate solution for 2 days. Potential vs concentration plots obtained with the treated membrane (Fig.22) show an enhancement in the working concentration range of the assembly but the treated electrode also records a good amount of interference (Table-16) even when smaller amounts (1.00×10^{-4}M) of surfactant anion is present in solution. As such the proposed electrode assembly can not be used for the estimation of chromate ions in the presence of anionic surfactants. Efforts made to make the assembly immune to the effect of surfactant did not meet with any success.

III.7.g. Titration

It has also been possible to use the sensor as an indicator electrode for the titration of chromate ions (Fig.23). The titration curve of 10 ml of 1.00×10^{-2}M K_2CrO_4 with 1.00×10^{-2}M $Pb(NO_3)_2$ is depicted in this diagram. The end point is quit sharp and the striking feature is the perfect stoichiometry observed in this case.

III.8.a. Estimation of vanadium as vanadate ions

Membrane sensors incorporating tin oxide as the electroactive phase, were tried for the estimation of CrO_4^{2-} ions according to the preferential uptake but the results are not very encouraging . The electrode does not show good selectivity for chromate ions as the interference of other anions is quite significant. The results obtained have already been discussed in preceding pages. Consequently efforts were made to use the electrode assembly for the estimation of vanadate which falls next in the selectivity series of tin oxide. The results were found to be quite encouraging and the characteristic features of the assembly are given below.

Membranes were equilibrated with 1.00M sodium vanadate solution for five days. Equilibration time was fixed up after some preliminary investigations and only those membranes which were stable and generated reproducible potentials were selected for subsequent studies. Repeated monitoring of potentials at a fixed concentration gave standard deviation of 0.2 mV in higher concentration range and 0.4 mV in lower concentration range.

Potentials across the membrane were measured in presence of a wide concentration range of VO_3^- ions against saturated calomel electrodes at 30±1 ^oC. 0.1M sodium vanadate solution was taken as reference and observations were made proceeding from low to higher vanadate ion solution concentration. Erratic results were obtained when the measurements were made from high to low concentrations owing to `memory' effect and the difficulty of removing adsorbed ions from the surface of the membrane sensor.

Membrane potentials observed when interposed between reference solution (0.1M) and test solutions of sodium vanadate (10^{-6}-10^{-1}M), are plotted against log concentration in Fig.24. The membrane potentials exhibit linearity in the range 2.51×10^{-4}-1.00×10^{-1}M and the slope of the plot is 19 mV/decade of concentration. Thus the sensor can be used to estimate vanadium as vanadate in the concentration range 2.51×10^{-4} to 1.00×10^{-1}M although the behaviour is non Nernstian in nature.

To see the effect of varying concentrations of reference solutions, calibration plots have also been made by taking reference solutions of 5.00×10^{-2}M and 1.00×10^{-2}M concentration. It is observed (Table-17 and Fig.25) that the magnitude of potential drops as we reduce the concentration of reference solution. Consequently it is quite justified to use a reference solution of 0.1M sodium vanadate in the entire investigations with the assembly.

III.8.b. Response and life time

The response time i.e., the time required for the generation of stable potentials, is 50 seconds, potentials stay constant for five minutes and thereafter a slow divergence is observed. This membrane can be used for a period of about 5 months without showing any drift in potentials. If necessary, it can be equilibrated again with 1.00M sodium vanadate solution for 2-3 days. If the treatment fails the membrane should be discarded and a new one be fabricated again.

III.8.c. pH effect

The pH range, in which this sensor can be used, has also been determined (Fig.26). Potentials do not change in the wide pH range 4 to 10 which may be taken as the working pH of this electrode system. A sharp change in potentials in acidic media may be due the interference of hydrogen ions.

Table-17

Working concentration range of the membrane sensor for vanadate ions with reference solution of varying concentration.

Reference solution concentration (M)	Slope mV/decade of concentration	Working concentration range (M)
1.00×10^{-1}	19	2.51×10^{-4}- 1.00×10^{-1}
5.00×10^{-2}	17	3.60×10^{-4}- 1.00×10^{-1}
1.00×10^{-2}	16	5.01×10^{-4}- 1.00×10^{-1}

Table-18

Performance of electrode system in 15, 30 and 50% (volume by volume) non-aqueous medium.

percentage	Slope mV/decade of concentration	Working concentration range (M)
x	19	2.51×10^{-4}- 1.00×10^{-1}
Ethanol		
15	16	3.16×10^{-4}- 1.00×10^{-1}
30	15	5.62×10^{-4}- 1.00×10^{-1}
50	15	8.91×10^{-4}- 1.00×10^{-1}
Methanol		
15	17	5.00×10^{-4}- 1.00×10^{-1}
30	16	6.31×10^{-4}- 1.00×10^{-1}
50	15	7.08×10^{-4}- 1.00×10^{-1}

Table-19

Selectivity of the electrode system for vanadate ions in the presence of 1.00×10^{-2}M concentration of interfering ions (as calculated by Fixed Interference method).

Interfering ion	Selectivity coefficient $[K^{Pot}_{A,B}]$
Cl^-	5.01×10^{-2}
Br^-	19.9×10^{-2}
I^-	3.16×10^{-2}
NO_3^-	3.55×10^{-2}
CH_3COO^-	4.25×10^{-2}
BrO_3^-	3.55×10^{-2}
ClO_3^-	3.55×10^{-2}
IO_3^-	3.16×10^{-2}
SCN^-	4.25×10^{-2}
$C_2O_4^{2-}$	6.70×10^{-3}
SO_4^{2-}	1.58×10^{-3}
$S_2O_3^{2-}$	3.16×10^{-3}
CrO_4^{2-}	1.58×10^{-3}

Table-20(a)

Performance of the electrode system in presence of the detergent sodium dodecyl sulphate (SDS).

Untreated membrane

Concentration of SDS (M)	Slope mV/decade of concentration	Working concentration range (M)
x	19	2.51×10^{-4} - 1.00×10^{-1}
1.00×10^{-4}	18	2.51×10^{-4} - 1.00×10^{-1}
1.00×10^{-3}	15	2.51×10^{-4} - 1.00×10^{-1}
1.00×10^{-2}	9	2.51×10^{-4} - 1.00×10^{-1}

Table-20(b)

Performance of the membrane conditioned with 1.00×10^{-3}M sodium dodecyl sulphate (SDS).

Concentration of SDS (M)	Slope mV/decade of concentration	Working concentration range (M)
x	18	1.77×10^{-4} - 1.00×10^{-1}
1.00×10^{-4}	18	1.77×10^{-4} - 1.00×10^{-1}
1.00×10^{-3}	15	1.77×10^{-4} - 1.00×10^{-1}
1.00×10^{-2}	11	1.77×10^{-4} - 1.00×10^{-1}

III.8.d. Solvent effect

The applicability of the electrode assembly has also been observed in partially non-aqueous medium. Potential vs concentration plots in 15, 30 and 50% (v/v) ethanolic and methanolic solutions are shown in Fig. 27 & 28. Although response is linear in partially non-aqueous medium, the working concentration range and slope of the sensor goes down with gradual increase in non-aqueous content. In 50% ethanol content the working concentration range of the sensor goes down from 2.51×10^{-4}M-1.00×10^{-1}M to 8.91×10^{-4}M-1.00×10^{-1}M and in 50% methanolic medium working concentration range reduces to 7.08×10^{-4}-1.00×10^{-1}M with small decrease in slope of the plot from 19 to 15 mV/decade of concentration. Along with this, the response time of the sensor also increases in partially non-aqueous medium.

III.8.e. Selectivity

The interferences of other ions, if present, along with the primary ion, are estimated by Fixed Interference method. Potentials were observed at a fixed concentration of interfering ion (1.00×10^{-2}M) and varying concentrations of primary ion. The selectivity coefficient for different anions are given in Table-19. The values reflect a very good selectivity of the membrane sensor for vanadate ions. It is observed that a large number of anions would not interfere at all in the working of this membrane electrode and the sensor displays ideal selectivity for the determinand ion.

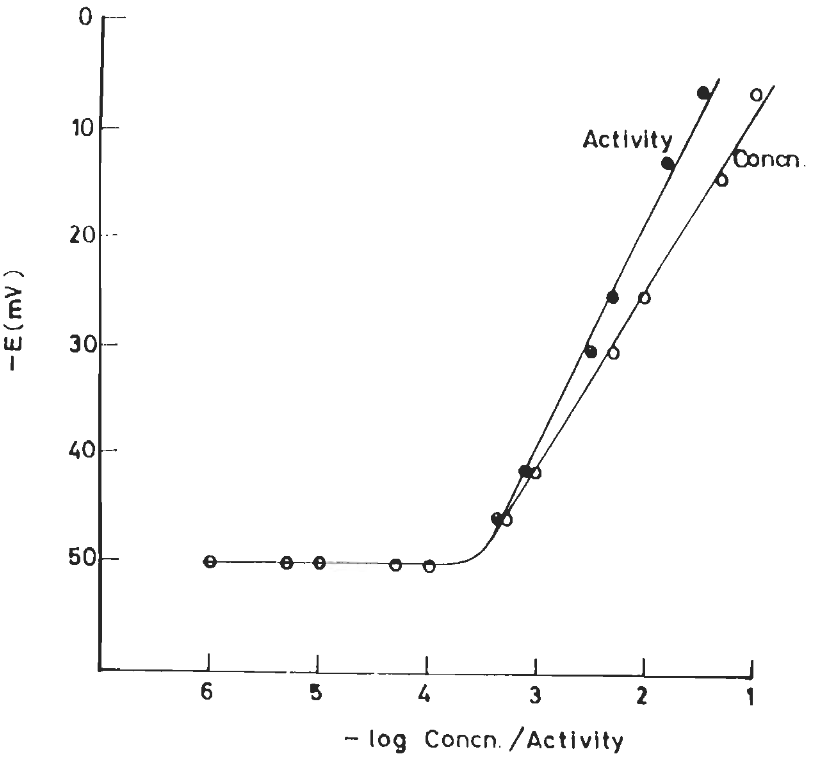

Fig. 24 Potential vs log$[VO_3^-]$ plots

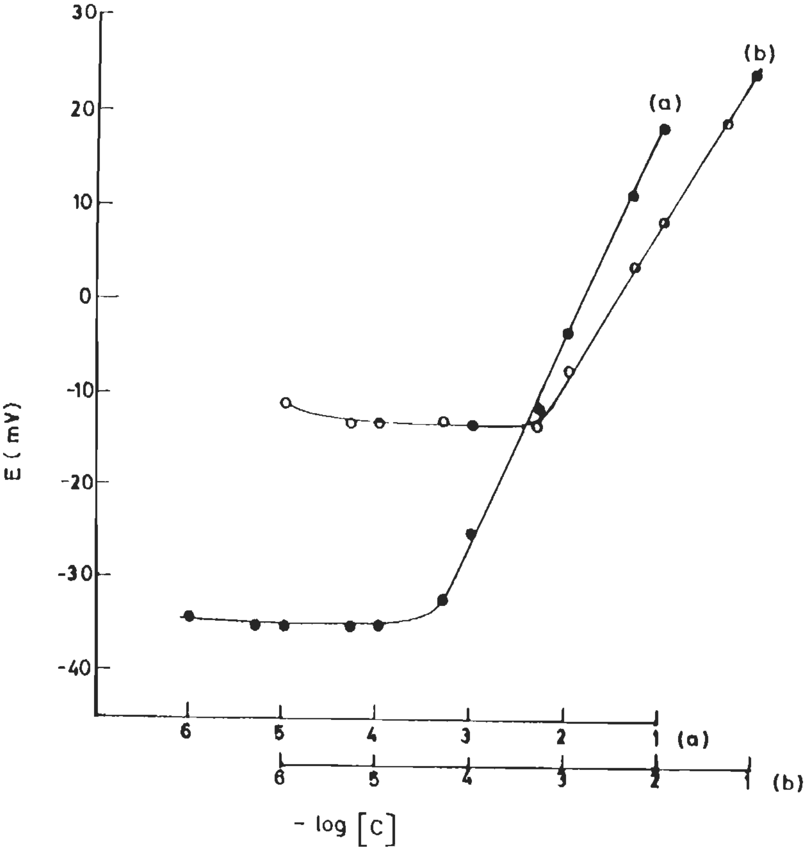

Fig. 25 Potential vs log$[VO_3^-]$ plots with reference concn (a) 5.0×10^{-2} M (b) 1.0×10^{-2} M

Tin Oxide membrane

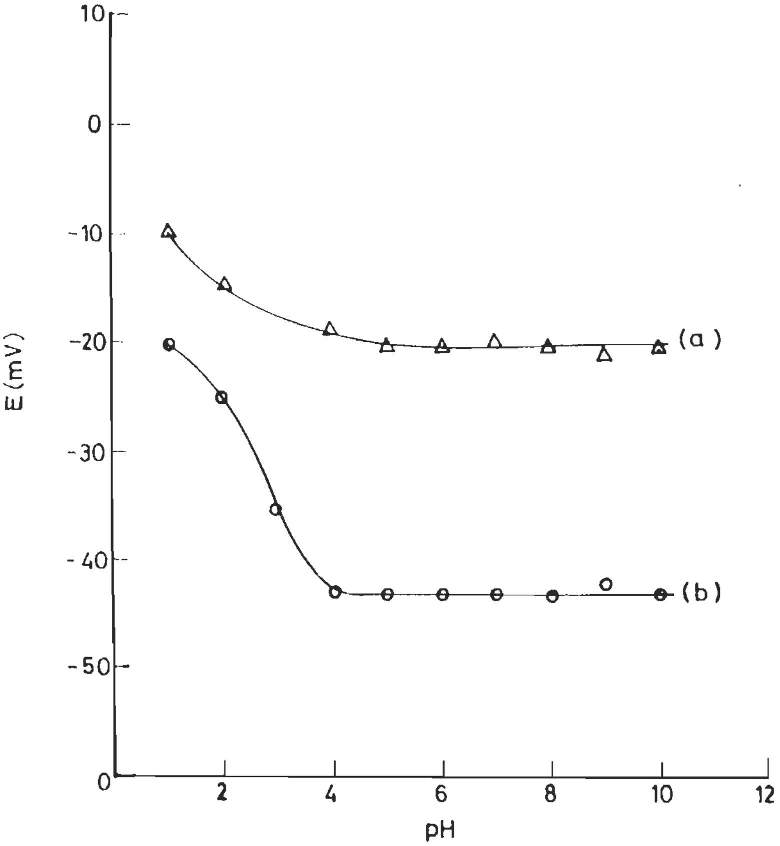

Fig. 26 Potential vs pH plots [VO_3^- concn. = (a) 1.0×10^{-2} M (b) 1.0×10^{-3} M]

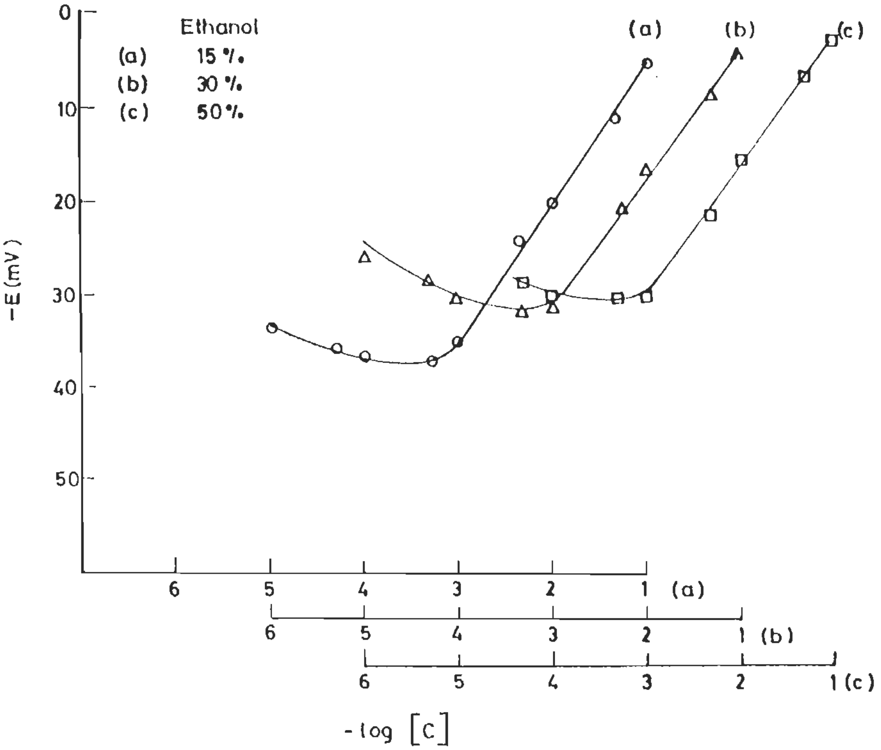

Fig. 27 Potential vs log [VO_3^-] plots in partially non-aqueous medium

Tin Oxide membrane

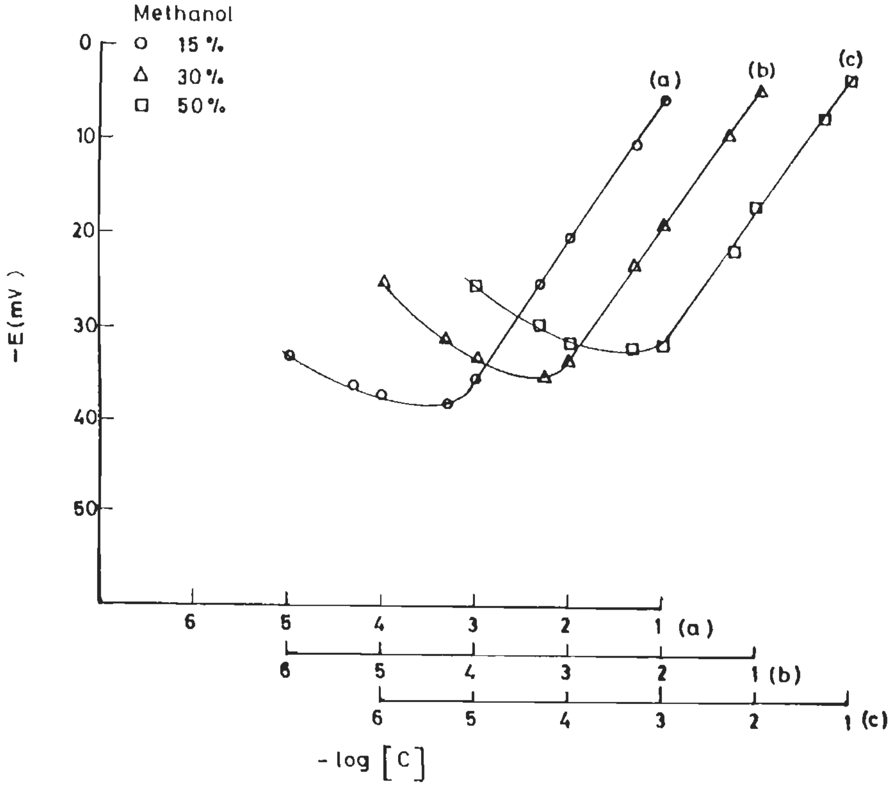

Fig. 28 Potential vs log $[VO_3^-]$ plots in partially non-aqueous medium

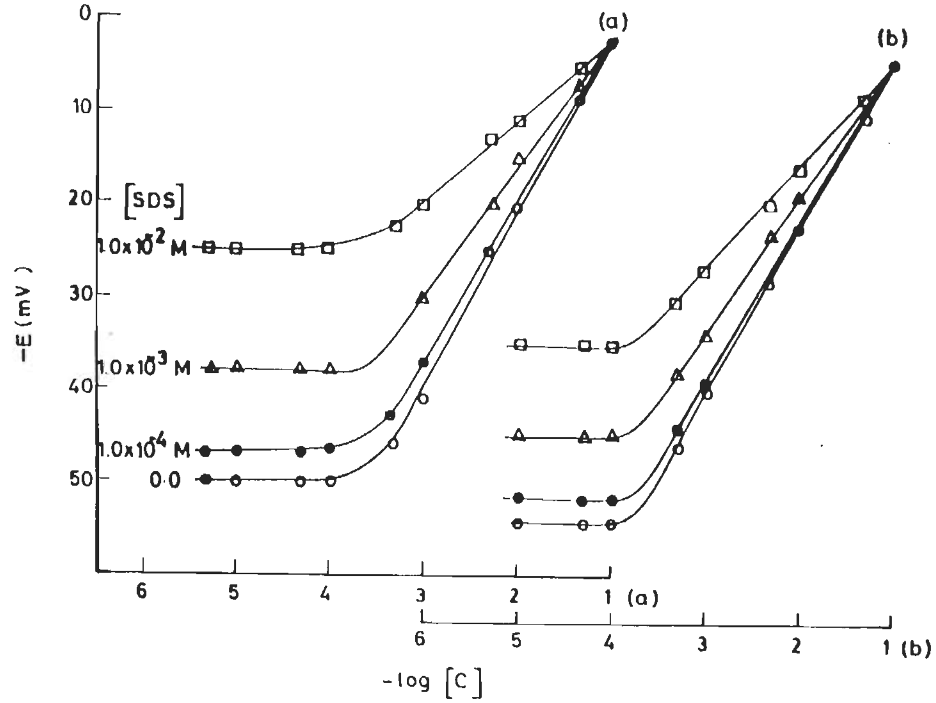

Fig. 29 Potential vs log $[VO_3^-]$ plots in the presence of SDS of varying concn. with untreated membranes (a) and treated membranes (b)

Tin Oxide membrane

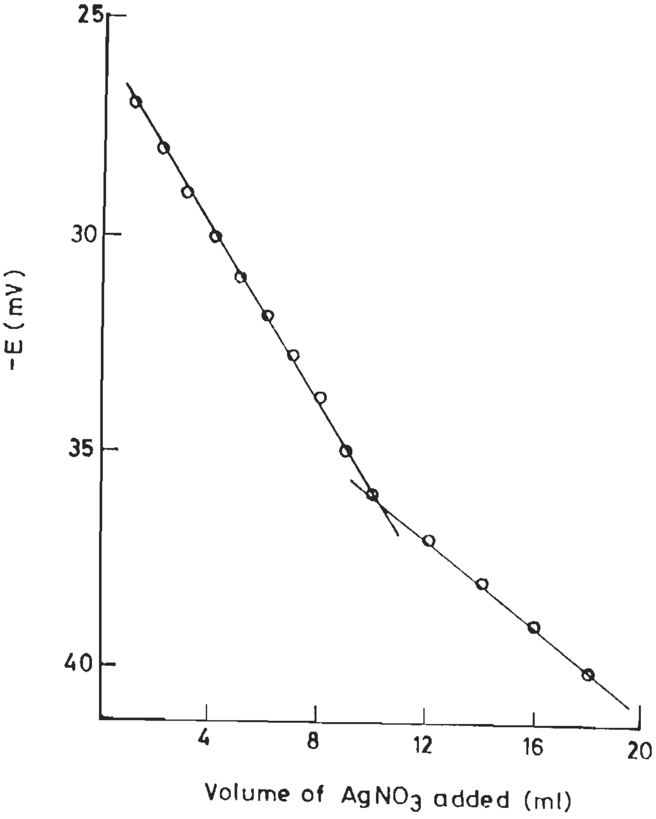

Fig. 30 Titration plot of 10ml of 1.0×10^{-2} M VO_3^- ions with 1.0×10^{-2} M $AgNO_3$

Tin Oxide membrane

III.8.f. Effect of surfactant

The effect of the presence of surfactant ions, on the estimation of vanadate, has also been studied. Fig.29 and Table 20(a) reveal very interesting results. No change in working concentration range (2.51×10^{-4}M-1.00×10^{-1}M) is observed with an increase in concentration of surfactant, sodium dodecyl sulphate, though slope of the plot goes down. There is absolutely no interference of the surfactant upto a concentration of 1.00×10^{-4}M and the increasing concentration of the same does not affect the functional concentration range although the slope of the plot undergoes a significant decrease.

III.8.g. Titration

The membrane sensor can also be applied as an end point indicator in a potentiometric titration involving VO_3^- ions. The titration plot of 10 ml of 1.00×10^{-2}M vanadate ions with 1.00×10^{-2}M Ag NO_3 is shown in Fig.30. The inflexion point in the curve corresponds to the stoichiometric ratio of $AgNO_3$ required to remove the vanadate ions.

III.9. A comparative evaluation of tin oxide membrane as a sensor for Cr(vi) as CrO_4^{2-} and V(v) as VO_3^-

A comparative evaluation of the proposed sensor exhibits a better performance of the same for the estimation of vanadate ions. It is possible to quantitatively estimate vanadium as vanadate in the range of 25 to 9894 ppm and 20 to 11601 ppm of chromium can be determined with the help of this electrode assembly.

Vanadate ions can be sensed over a wider pH range viz., 4-10 as compared to the working pH range of 7 to 9 for chromate ions.

The response time of the membrane sensor is much less in the case of VO_3^- ions. Besides this the performance of the electrode in partially non-aqueous medium is superior for VO_3^- in comparison to CrO_4^{2-} ions. A slight enhancement in the working concentration range of the assembly for chromate is observed in 15 percent non-aqueous solutions but this is also accompanied with a sharp fall in the slope of the plot. The trend increases with increasing non-aqueous content of the solution. Almost the same behaviour is observed when the assembly is used for the estimation of VO_3^- ions. Here also the increasing non-aqueous content (15 percent onwards) reduces the concentration range of the electrode assembly with simultaneous reduction in slope as well.

The selectivity coefficient pattern of the interfering ions for chromate and vanadate (Table 15 and 19) also clearly establishes the superiority of the sensor as an electrode for the estimation of V(v). The membranes acts as a good end point indicator in the potentiometric titrations for both the ions i.e., CrO_4^{2-} & VO_3^- . In both the cases the end points are equally sharp and equivalence point corresponds to exact stoichiometry.

The performance of the sensor in presence of surfactants is also better for vanadate ions as the working concentration range of the assembly does not change with increase in surfactant concentration though the fall in slope is observed in both the cases.

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CHAPTER - IV

ORGANIC RESIN MEMBRANES

IV.1. Introduction

In an ever increasing search for suitable materials which could be used for the preparation of ion-selective electrodes, the use of polymeric organic gels and neutral carriers like crown ethers and cryptands have also been looked by various workers. These compounds specially ionic polymers and crown ethers show high selectivity (high Kd values) for one or more in comparison to other ions and therefore have been tried for the fabrication of membrane sensors. Ionic products are considered to possess better selectivity and exchange characteristics.

Various types of polymers have been tried for casting the membrane sensors and much of the work done in this respect has been presented by Moody, Saad and Thomas (1). Several electrodes involving polymers and neutral carriers embedded in an inert matrix, viz., silicon-rubber, poly vinyl chloride, polystyrene and polyethene are reported in literature (2). A number of ion-selective electrodes of this class are commercially available and some significant work done in this field is mentioned in the following paragraphs.

A vast majority of polymer-matrix ion-selective electrodes have been prepared by using poly vinyl chloride as the membrane support (3,4). Some important PVC based electrodes exhibiting good selectivity for Li^+, Na^+, K^+, Cs^+, Cd^{2+}, Zn^{2+}, Pb^{2+} etc. ions are described below.

The first most important Li^+ electrode was developed using lipophilic diamide (5) and lithium complex of 12-crown (6) as neutral carriers. The electrode exhibited near Nernstian and sub Nernstian response at low and high concentrations, respectively.

Christian and Xia, later developed a PVC-based electrode by incorporating tri octyl-phosphine oxide (TOPO) as neutral Li^+ carrier (7). Besides this several other PVC based electrodes have been reported for Li^+ ions (8-10).

PVC based Na^+ selective electrodes (11) described by Wu et al. were based on tri glycollic bis diamides. These possess good selectivity and are suitable for the determination of sodium in water with a high magnesium content. Other sodium-selective electrode (12) reported by Zhuang has been found to be useful for the determination of sodium concentration in blood. Thomas and co-workers also developed sodium and potassium selective electrodes in which crown ethers were immobilized in PVC matrix (13). These electrodes were found to be suitable for determining sodium and potassium concentration in serum. Sodium selective electrodes based on lipophilic calixarene derivatives (14) have also been used for sodium assay of human sera.

Bis (crown ether) esters and 15-crown-5-phosphotungstic acid precipitate have been embedded in PVC matrix for the construction of Cs^+-selective electrode (15,16). This electrode shows good selectivity for cesium in comparison to alkali and transition metal ions. Chen and Feng made use of Cs-tetraphenyl borate complex in nitro benzene incorporated in PVC, but the electrode suffered with serious interference from potassium (17).

The use of calixarenes and cryptands are finding importance as active agents for chemical sensors because of a very selective behaviour towards some ions over the other. Foster and co-workers (18) incorporated calixarenes into plasticized PVC membranes to produce ion-selective electrodes. Functional group modifications to the calixarenes, and changes in the cavity size and molecular confirmation, allowed the selectivity of the corresponding electrodes to be controlled. Sensors for Na^+, K^+ and Cs^+ were constructed from neutral carrier electrode membranes comprising of 0.7% ionophores 0.2% K tetrakis-(p-chloro phenyl) borate, 66.1% 2-nitro phenyl octyl ether and 33% PVC. Tetrameric calixarenes substituted with CO groups gave electrodes highly selective to Na^+, whereas hexameric calixarenes give good Cs^+ selectivity. Another sensor (19) based on p-t-butyl calix[4]arene tetra ethyl ester in PVC matrix has shown Nernstian response with a detection limit 10-30 μm for Na^+ ions. Based on calixarene, O'Connor and co-workers (20) have developed a potentiometric ion-selective electrode for silver. The electrode displays a linear response for Ag^+ in the concentration range of 0.1 to 100 μm with a slope of 50 mV/decade. It has also been used in potentiometric titration of silver. Very recently, Domansky and co-workers (21) have developed a sodium-selective membrane electrode based on p-tert-butyl calix[4]arene methoxy ethyl ester. Rb^+ selectivity of PVC membranes based on cryptands with thiourea fragment has been discussed by Lukayanenko (22). The sensor is found to be selective to Rb^+ ions over the range 0.1 mM to 0.1 M with a response time of 2-5 seconds.

Several lead-selective electrodes have been constructed and their performance investigated. The most important ones are PVC based (23, 24), where synthetic macrocyclic compounds are used as active membrane components. Hirata and Date reported Pb^{2+} selective electrodes (25) consisting of a mixture of lead sulfide and silicon rubber coated on to a Pt wire. Recently a group of amides and oxamides (neutral carriers) have also been used as potential ionophores for lead ions in polymeric membrane electrodes (26).

Solid state sensors for cadmium has also been a subject of interest. These have incorporated polymers as electroactive phase (27-29). Rakhman'kO and co-workers (30) have reported a PVC based membrane sensor for cadmium having di butyl di decyl ammonium sulphate as electroactive phase. Some good sensors (31, 32) have also been proposed for Zn^{2+} ions by various workers. Very recently Lindner and co-workers (33) have used zinc-selective ionophores for potentiometric and optical sensors. All the ionophores exhibit proton interference and to compensate it, the pH of the buffer solution must be >6.

Two chelating ion exchange resins, 2-salicylaldene aminothiophenol formaldehyde and 2-hydroxy naphthaldoxime formaldehyde have been prepared, characterized and found to be highly selective for Cd^{2+}, Zn^{2+} and Pb^{2+}, which is reflected by their high k_d values (Chapter II). More over these can be easily dissolved in tetrahydrofuran, thus enbling the fabrication of PVC based membranes. As such it was thought desirable to explore the possibility of using the membranes of these compounds as ion sensors.

Consequently heterogeneous membranes of these ion exchangers were prepared using both polystyrene and PVC as inert binders and their electrochemical performance was observed. A comparison has also been drawn between the two kinds of binder based membranes.

IV.2. 2-hydroxy naphthaldoxime formaldehyde resin - a membrane sensor for lead ions

Binders play an important role in the casting and functioning of membrane electrodes. These, however, do not affect the mode of operation. Besides polystyrene, epoxy resins and poly vinyl chloride are widely used as matrix support in the preparation of heterogeneous membranes. Although several materials have been tried, PVC is found to be the most suitable and commonly used binder. PVC matrix membranes are easy to fabricate and offer good mechanical resistance and pressure effects. Polystyrene membranes need specialized equipment for preparation but these are easy to handle and sometimes exhibit better performance as compared to PVC membranes. Both polystyrene as well as PVC based membranes have been prepared incorporating 2-hydroxy naphthaldoxime formaldehyde as electroactive phase and the functional properties and their utility in the estimation of lead are described below.

IV.2.a. Functional Properties

Some parameters necessary to characterize the membranes are given in Table 1.

Water content, porosity, swelling etc. could only be estimated in the case of polystyrene based membrane while conductance measurements were possible in case of both polystyrene as well as PVC based membrane.

The polystyrene based membrane of 2-hydroxy naphthaldoxime formaldehyde has a low order of swelling, porosity, water and electrolyte uptake.

Table-1

Water content, porosity, swelling and electrolyte absorption values for 2-hydroxy naphthaldoxime formaldehyde resin membrane.

Membrane	Water content per gram of wet membrane (g)	Porosity	Swelling (mm)	Amount of electrolyte absorbed per gram of wet membrane (M)
Organic resin	0.0284	0.0389	0.253	6.2×10^{-2}
Inorganic gel*	0.5578	0.1335	0.280	7.0×10^{-2}

*Inorganic gel polytungstoantimonate membrane (Table-1, Chapter II)

Table-2

Specific conductance of membrane in different cationic forms.

Cations	Specific conductance (milli mhos cm^{-1})	
	PVC based membrane	Polystyrene based membrane
Na^+	1.9×10^2	6.0×10^2
K^+	2.4×10^2	2.8×10^2
Pb^{2+}	4.3×10^2	4.5×10^2
Cu^{2+}	3.5×10^2	3.7×10^2
Ca^{2+}	3.8×10^2	3.8×10^2
Mg^{2+}	4.1×10^2	4.3×10^2

This indicates that the amount of water incorporated in membrane matrix is very less and the porosity value also reflects a low value of volume of water per unit membrane volume.

The magnitude of swelling, however, depends on the gel structure and the nature and amount of binder present in membrane. PVC based membranes do not swell at all while polystyrene supported membrane exhibits little swelling. Electrolyte uptake of the polystyrene based membrane (Table-1) is also compatible with the values of other parameters. The values recorded for this sensor (Table-1) are comparable and of the same order as observed for 2-salicylaldene aminothiophenol formaldehyde membrane (IV.4.a) and these are much lower than the one obtained in the case of the inorganic gel membranes (Table-1, Chapter III).

The conductance values of PVC as well as polystyrene based membranes in different cationic forms are given in Table-2. There is no apparent gradation either with size, swelling or charge on the ion. The higher values obtained in the case of polystyrene based membranes are indicative of a better performance by these as ion sensors in comparison to the other one.

IV.3. Estimation of lead

IV.3.a. Polystyrene based membranes

Membrane sensors incorporating 2-hydroxy naphthaldoxime formaldehyde resin as the electroactive phase and polystyrene (10%) as binder (prepared at 55 ^{o}C by the method discussed in chapter II), were also tried for the estimation of Pb^{2+} ions. The results were found to be quite encouraging and the characteristic features of the assembly are given below.

Membranes equilibrated with 1.00 M lead nitrate solution for five days, generate stable and reproducible potentials. Repeated monitoring of potentials at a fixed concentration of 1.00×10^{-3}M lead ions solution have standard deviation of ±0.2mV. Potentials measured with Pb^{2+} ions in the concentration range of 10^{-6} to 10^{-1} M, proceeding from low to higher values at 30±1 °C, are recorded in Fig.1. The plot is linear in the concentration range 1.58×10^{-4} to 1.00×10^{-1} M and is non Nernstian in nature (slope of the plot being 35 mV/decade of concentration).

Normally in the cell, devised for measuring potentials, a reference solution of 1.00×10^{-1} M concentration is used. Reference solutions of different concentrations have also been tried but this did not improve the working of the electrode assembly. Calibration plots have also been made with 5.00×10^{-2}M and 1.00×10^{-2}M lead nitrate as reference solutions. It is observed (Fig.2 & Table-3) that the magnitude of potential falls as we reduce the concentration of reference solution. Naturally it can be inferred that a reference solution of 1.00×10^{-1} M concentration gives the best performance and the same has been used in the entire investigations with this electrode assembly.

The response time of the electrode has been measured at various concentrations of lead nitrate solutions and the same is found to be 50-55 seconds at all dilutions. Besides this potentials stay constant for more than five minutes, after which a slow drift is observed. The electrode assembly has been quite frequently tried for a period of three months without observing any disturbance. When not in use it is stored in water and cross contamination is avoided.

Table-3

Working concentration range of the polystyrene based membrane sensor for lead ions with reference solution of varying concentration.

Reference solution concentration (M)	Slope mV/decade of concentration	Working concentration range (M)
$1.00x10^{-1}$	35	$1.58x10^{-4}$- $1.00x10^{-1}$
$5.00x10^{-2}$	33	$3.55x10^{-4}$- $1.00x10^{-1}$
$1.00x10^{-2}$	23	$1.12x10^{-3}$- $1.00x10^{-1}$

Table-4

Performance of electrode system in 15, 30 and 50% (volume by volume) non-aqueous medium.

percentage	Slope mV/decade of concentration	Working concentration range (M)
x	35	$1.58x10^{-4}$- $1.00x10^{-1}$
Ethanol		
15	40	$1.78x10^{-4}$- $1.00x10^{-1}$
30	46	$3.16x10^{-4}$- $1.00x10^{-1}$
50	50	$3.98x10^{-4}$- $1.00x10^{-1}$
Methanol		
15	40	$1.99x10^{-4}$- $1.00x10^{-1}$
30	41	$2.82x10^{-4}$- $1.00x10^{-1}$
50	50	$3.55x10^{-4}$- $1.00x10^{-1}$

Table-5

Selectivity of the electrode system for lead ions in the presence of 1.00×10^{-2}M concentration of interfering ions (as calculated by Fixed Interference and Mixed Solution methods).

Interfering ion	Selectivity coefficient $[K^{Pot}_{A,B}]$	
	Fixed Interference Method	Mixed Solution Method
Na^+	19.95	2.49
K^+	3.16	1.89
Tl^+	10.15	6.09
Li^+	14.33	8.60
Ag^+	14.33	8.60
NH_4^+	10.00	2.60
Mn^{2+}	1.14×10^{-1}	6.88×10^{-2}
Zn^{2+}	2.02×10^{-1}	1.21×10^{-1}
Cd^{2+}	1.80×10^{-1}	1.08×10^{-1}
Ba^{2+}	1.61×10^{-1}	9.66×10^{-2}
Sr^{2+}	1.43×10^{-1}	8.58×10^{-2}
Co^{2+}	1.80×10^{-1}	1.08×10^{-1}
Ca^{2+}	1.43×10^{-1}	8.58×10^{-2}
Cu^{2+}	1.28×10^{-1}	7.68×10^{-2}
Mg^{2+}	1.01×10^{-1}	6.06×10^{-2}
Al^{3+}	3.21×10^{-2}	1.93×10^{-2}
La^{3+}	2.27×10^{-2}	1.36×10^{-2}
Fe^{3+}	3.52×10^{-2}	2.11×10^{-2}

Table-6(a)

Performance of the electrode system in presence of the detergent cetyl pyridinium chloride (CPC).

Untreated membrane

Concentration of CPC (M)	Slope mV/decade of concentration	Working concentration range (M)
x	35	1.58×10^{-4} - 1.00×10^{-1}
1.00×10^{-4}	35	1.58×10^{-4} - 1.00×10^{-1}
1.00×10^{-3}	34	3.16×10^{-4} - 1.00×10^{-1}
5.00×10^{-3}	31	5.00×10^{-4} - 1.00×10^{-1}
1.00×10^{-2}	29	1.00×10^{-3} - 1.00×10^{-1}

Table-6(b)

Performance of the membrane conditioned with 1.00×10^{-3}M cetyl pyridinium chloride (CPC).

Concentration of CPC (M)	Slope mV/decade of concentration	Working concentration range (M)
x	40	1.00×10^{-4} - 1.00×10^{-1}
1.00×10^{-4}	40	1.00×10^{-4} - 1.00×10^{-1}
1.00×10^{-3}	39	1.99×10^{-4} - 1.00×10^{-1}
5.00×10^{-3}	35	3.16×10^{-4} - 1.00×10^{-1}
1.00×10^{-2}	34	7.94×10^{-4} - 1.00×10^{-1}

The pH range, in which this sensor can be used, is determined by observing potentials at different levels of hydrogen ion concentration. No change in potentials is observed in the range 4 to 7 (Fig.3) which may be taken as the working pH range of this electrode system. A sharp change in potentials in acidic medium may be assigned to the interference of hydrogen ions.

The membrane electrode can not be used in non-aqueous or partially non-aqueous solvents. Potentials recorded in 15, 30 and 50% ethanolic and methanolic solvents are depicted in Fig.4 & 5 and Table-4. Although the response is linear in partially non-aqueous medium as well, the working concentration range goes down with an increase in the slope of the plot with increasing non-aqueous content.

The disturbing effects of other ions on the working of the electrode assembly for lead ions have also been assessed in terms of selectivity coefficients. The selectivity coefficient pattern (as calculated by Fixed Interference method and mentioned in Table-5) shows that bivalent and polyvalent cations have low K^{Pot}_{AB} values and normally these should not cause any interference. High values in the case of monovalent cations reflect significant interference in the working of the proposed sensor, when such ions are present. Mixed Solution method has also been used to determine the selectivity coefficient values and the data recorded in Table-5 shows much lower level of interference by almost all the cations. Even the values are lower for monovalent ions, in comparison to what has been obtained by Fixed Interference method. In order to see the actual interference level of the monovalent cations, some mixed runs have also been recorded where the

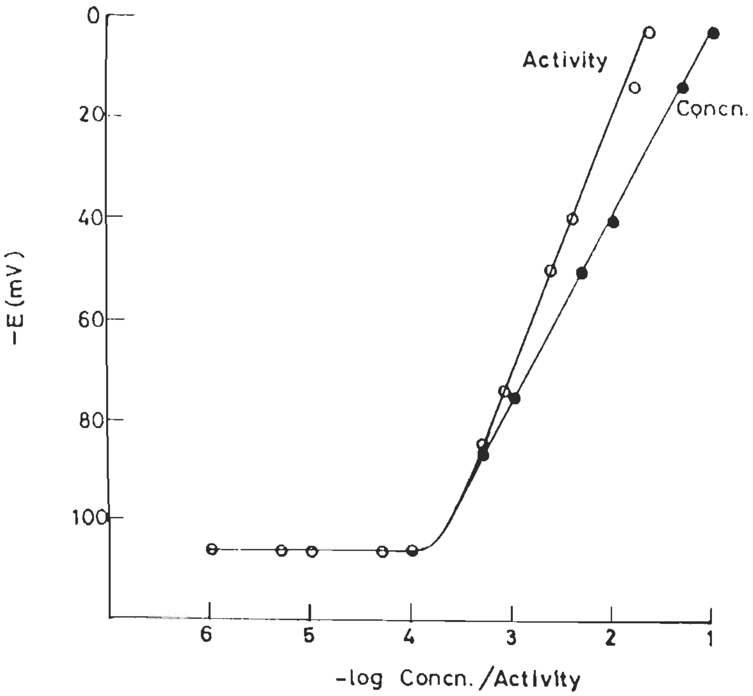

Fig. 1 Potential vs log $[Pb^{2+}]$ plots

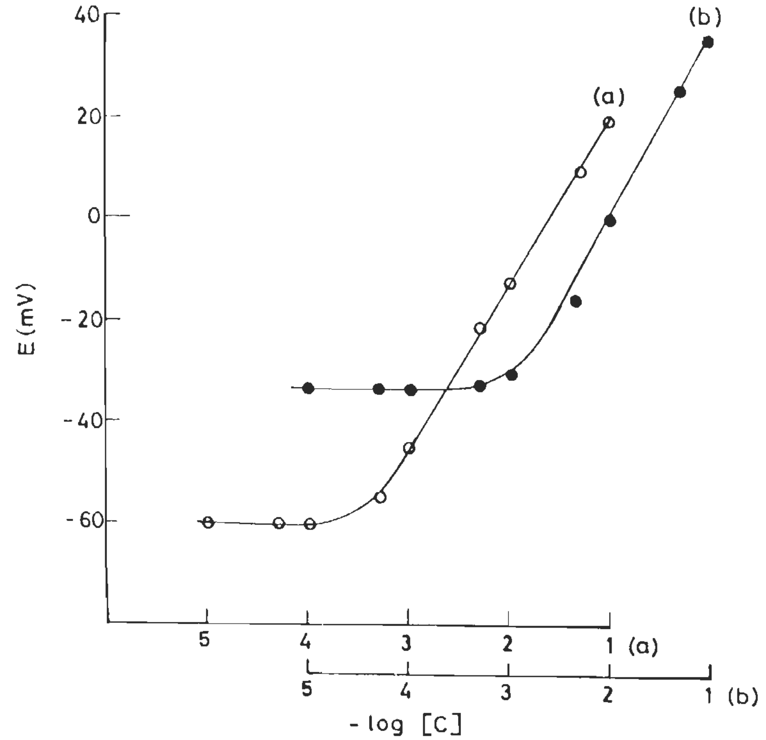

Fig. 2 Potential vs log $[Pb^{2+}]$ plots with reference concn.
(a) 5.0×10^{-2} M (b) 1.0×10^{-2} M

Polystyrene based membrane of 2-hydroxy naphthaldoxime formaldehyde

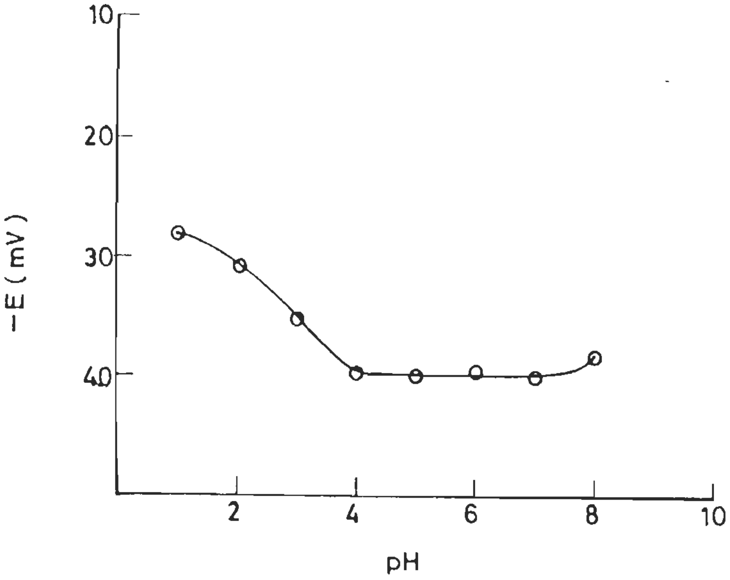

Fig. 3 Potential vs pH plot $[Pb^{2+}$ concn. $= 1.0 \times 10^{-2}$ M$]$

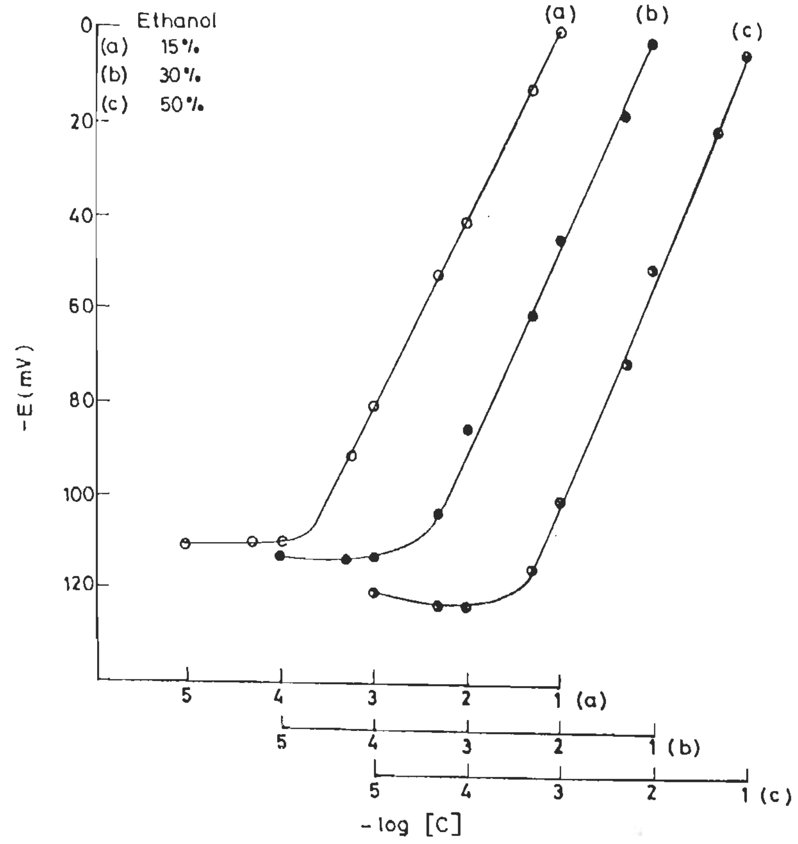

Fig. 4 Potential vs log $[Pb^{2+}]$ plots in partially non-aqueous medium

Polystyrene based membrane of 2-hydroxy naphthaldoxime formaldehyde

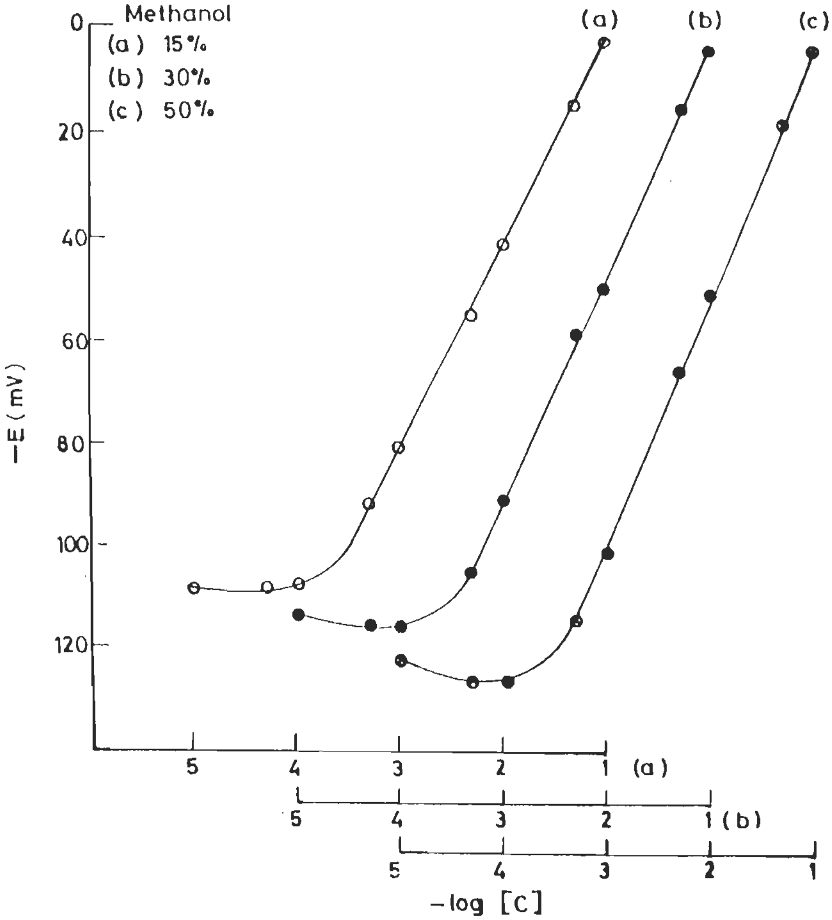

Fig. 5 Potential vs log $[Pb^{2+}]$ plots in partially non-aqueous medium

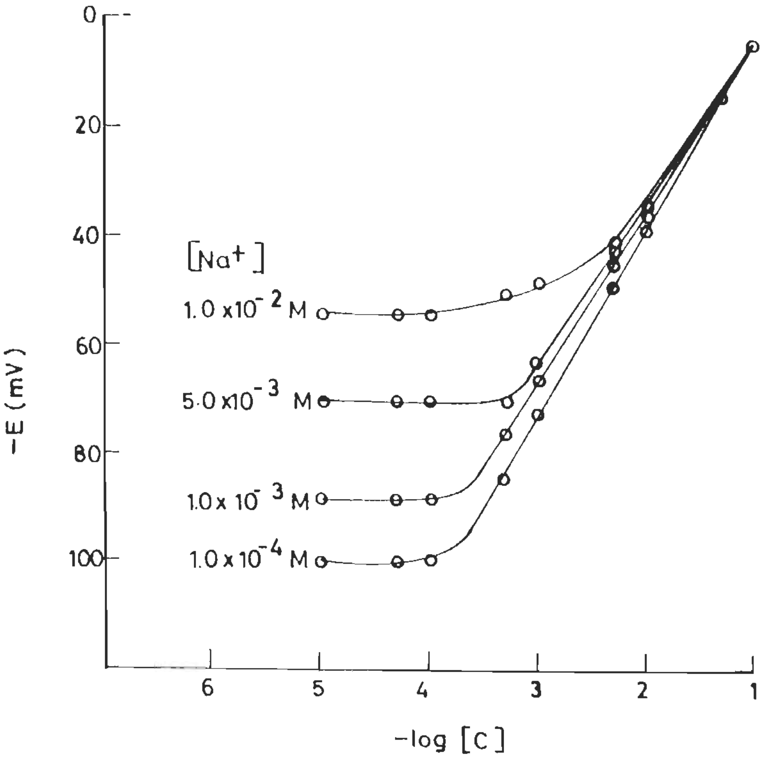

Fig. 6(a) Potential vs log $[Pb^{2+}]$ plots in the presence of Na^+ of varying concn.

Polystyrene based membrane of 2-hydroxy naphthaldoxime formaldehyde

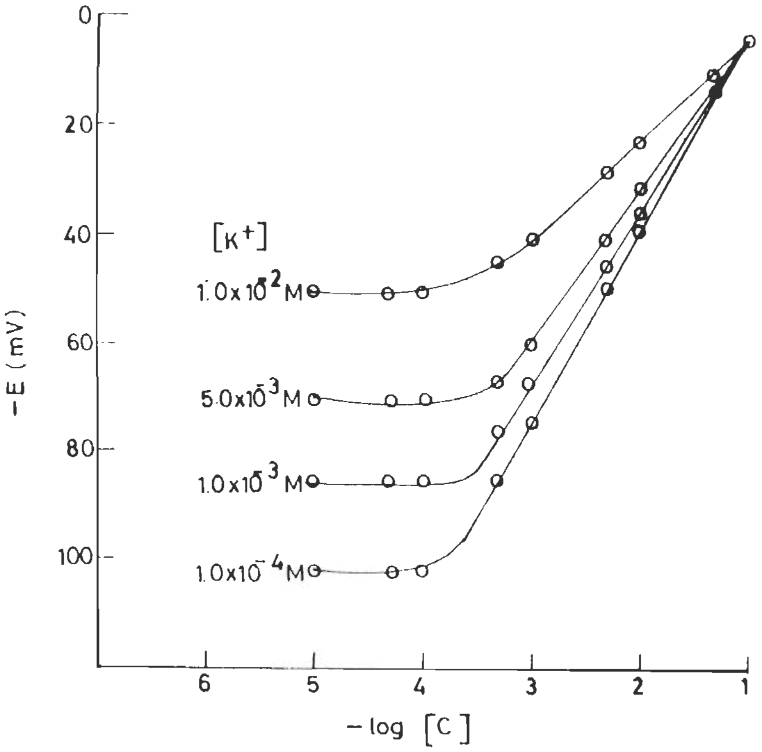

Fig. 6 (b) Potential vs log $[Pb^{2+}]$ plots in the presence of K^+ of varying concn.

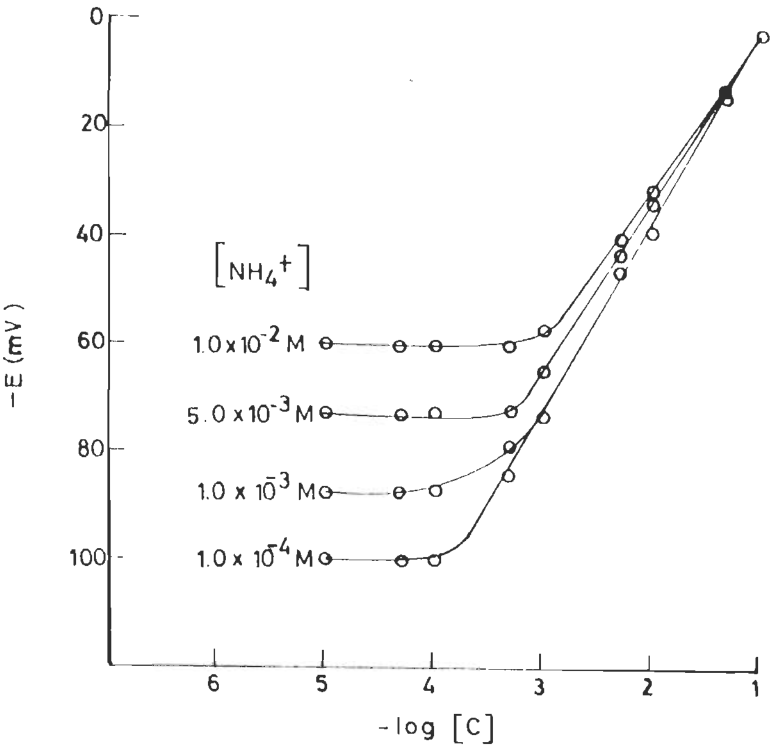

Fig. 6 (c) Potential vs log $[Pb^{2+}]$ plots in the presence of NH_4^+ of varying concn.

Polystyrene based membrane of 2-hydroxy naphthaldoxime formaldehyde

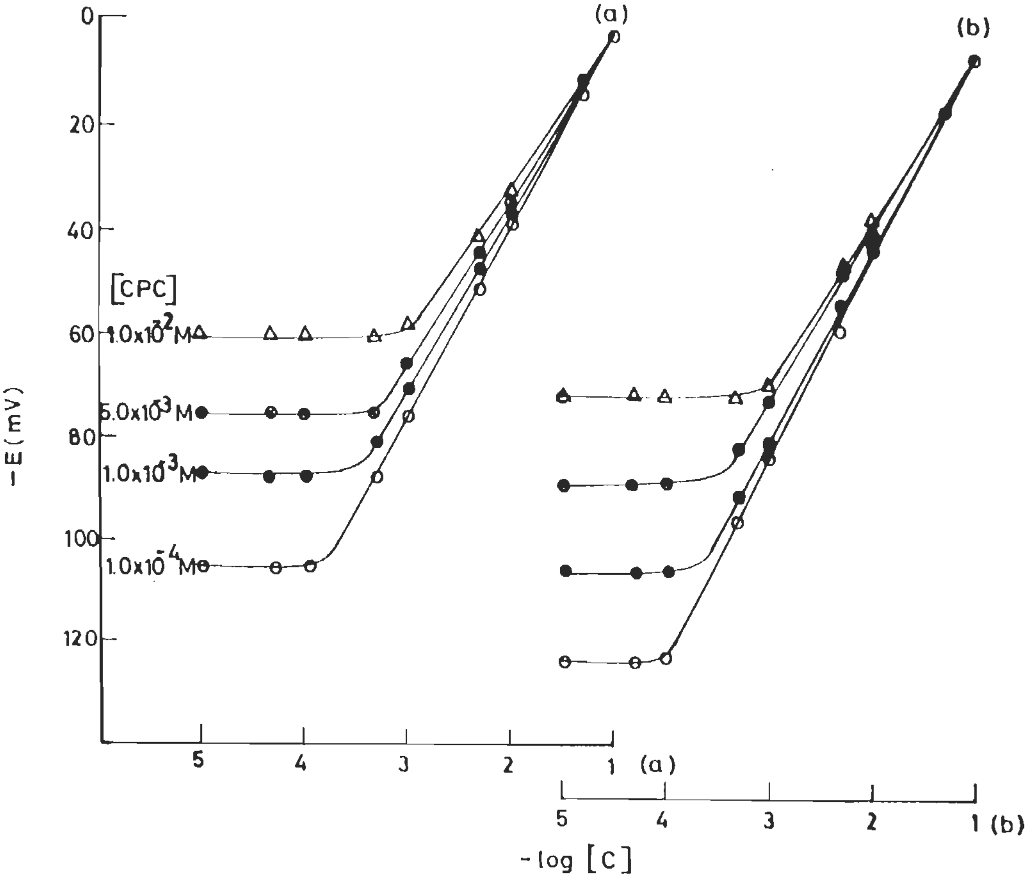

Fig. 7 Potential vs log $[Pb^{2+}]$ plots in the presence of CPC of varying concn. with untreated membranes (a) and treated membranes (b)

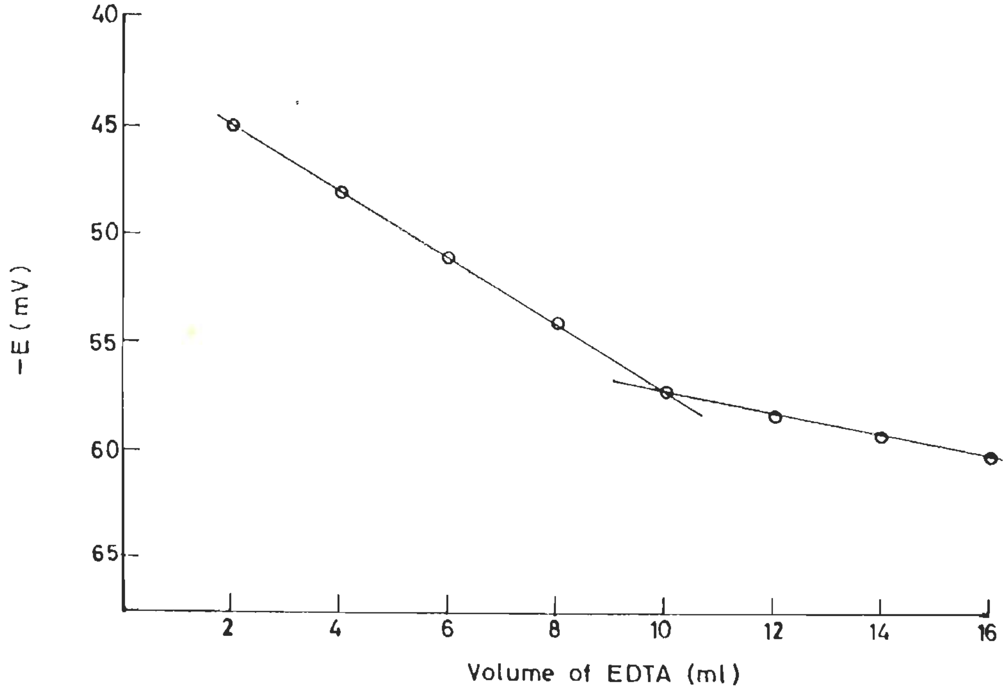

Fig. 8 Titration plot of 10ml of 1.0×10^{-2}M Pb^{2+} ions with 1.0×10^{-2}M EDTA solution

Polystyrene based membrane of 2-hydroxy naphthaldoxime formaldehyde

potentials are monitored at different lead ion concentration and various levels of concentration of interfering ions. The plots at varying concentrations of Na^+, K^+ and NH_4^+ ions are given in Fig.6(a) to 6(c). These reveal a complete tolerance of the interfering ion upto a level of $1.00x10^{-4}M$ concentration. Beyond this concentration the monovalent ions do interfere and it would not be possible to use the sensor for measuring Pb^{2+} ion concentration in their presence at concentrations $>1x10^{-4}M$.

Interference of cationic surfactant ions have also been investigated on the functioning of the membrane sensor. The plots of potential vs log $[Pb^{2+}]$ in presence of varying concentration of cetyl pyridinium chloride are shown in Fig. 7(a) and the results are depicted in Table-6(a). This indicates a tolerance of detergent ion at and lower concentrations than $1.00x10^{-4}M$. Beyond this amount the detergent ion starts causing interference. In presence of $1.00x10^{-3}M$ cetyl pyridinium chloride, the working concentration range reduces from $1.58x10^{-4}$-$1.00x10^{-1}M$ to $3.16x10^{-4}$-$1.00x10^{-1}M$ with small change in slope of the plot from 35 to 34 mV/decade of concentration. The interference increases with increasing detergent concentration, there by causing a significant reduction in the working concentration of the sensor and the slope of the plot also goes down.

In some cases, the disturbing effects of the surfactants can be overcome by conditioning the membrane sensor with the surfactant solution. As such the membrane was treated with $1.00x10^{-3}M$ cetyl pyridinium chloride solution for 3 days. Potential vs concentration plots obtained with the treated membrane (Fig-7b and Table-6b) show an enhancement in the working concentration range of the assembly but the treated electrode also suffers with a good amount of interference. As such the proposed sensor can only be used in the presence of 1.00×10^{-4}M surfactant concentration. Beyond this concentration even the treated membrane can not be used in presence of surfactant cations.

The proposed membrane sensor is a good end point indicator in the potentiometric titration for lead ions. The titration of 10ml of 10^{-2}M lead nitrate with 10^{-2}M EDTA solution is shown in Fig.8. Though the fall in potentials, observed, is less but the end point is quite sharp and represents perfect stoichiometry.

IV.3.b. PVC based membranes

The organic resin, under investigation, dissolves well in tetrahydrofuran, a precondition to use PVC. Membranes using this binder material and resin in 1:1 ratio were prepared as described in Chapter II.

For the estimation of Pb^{2+} ions the PVC based membranes were equilibrated with 1.00M lead nitrate solution for five days. Equilibration time was fixed up after preliminary investigations and only those membranes which were stable and generated reproducible potentials, were used for further investigations.

Membrane potentials were measured at 30±1 °C, against saturated calomel electrodes, proceeding from lower to higher concentration of lead ions.

Potentials recorded with 1.00×10^{-6} to 1.00×10^{-1}M concentration of lead nitrate against 1.00×10^{-1}M concentration of reference solution are shown in Fig.9. The electrode demonstrates a linear response for Pb^{2+} ions in 3.16×10^{-4}-1.00×10^{-1}M concentration range. The slope of the plot (Fig.9) being high viz., 40mV/decade of concentration reflects the non Nernstian behaviour of the membrane sensor. Inspite of this drawback it can be used for the estimation of lead in the specified concentration range.

The electrode assembly is found to function best with 1.00×10^{-1}M reference solution. It is evident by observing the potentials with reference solution of varying concentration. Potential vs concentration plots (Fig.10) with 5.00×10^{-2} and 1.00×10^{-2}M reference solutions of Pb^{2+} ions generate potentials of low magnitude and the working concentration range is also small (Table-7). Thus the necessary optimum concentration of the reference solution, for smooth functioning of the proposed membrane electrode is 1.00×10^{-1}M.

The response time of this sensor has been measured at various determinand ion concentrations. Stable potentials are obtained in a minutes time and no changes are normally observed upto four/five minutes. It has also been possible to use the electrode assembly for three to four months with out recording any drift in potentials etc. In case of cross contamination it is to be regenerated or prepared afresh.

Reliability of the electrode is determined by periodically monitoring the potentials at 1.0×10^{-2}M concentration of lead ions and the standard deviation of almost 20 measurements is ±0.4mV.

Potential vs pH plots at 1.0×10^{-2}M lead ion concentration are shown in Fig-11. Potentials stay constant in the range 4 to 7 and this may be taken as the working pH range for the estimation of lead ions. A sharp change in acidic medium may be due to the

Table-7

Working concentration range of the PVC based membrane sensor for lead ions with reference solution of varying concentration.

Reference solution concentration (M)	Slope mV/decade of concentration	Working concentration range (M)
1.00×10^{-1}	40	3.16×10^{-4} - 1.00×10^{-1}
5.00×10^{-2}	40	5.01×10^{-4} - 1.00×10^{-1}
1.00×10^{-2}	38	7.94×10^{-4} - 1.00×10^{-1}

Table-8

Performance of electrode system in 15, 30 and 50% (volume by volume) non-aqueous medium.

percentage	Slope mV/decade of concentration	Working concentration range (M)
x	40	3.16×10^{-4} - 1.00×10^{-1}
Ethanol		
15	42	3.55×10^{-4} - 1.00×10^{-1}
30	48	5.62×10^{-4} - 1.00×10^{-1}
50	51	6.31×10^{-4} - 1.00×10^{-1}
Methanol		
15	42	3.55×10^{-4} - 1.00×10^{-1}
30	45	5.01×10^{-4} - 1.00×10^{-1}
50	50	5.62×10^{-4} - 1.00×10^{-1}

Table-9

Selectivity of the electrode system for lead ions in the presence of 1.00×10^{-2} M concentration of interfering ions (as calculated by Fixed Interference and Mixed Solution methods).

Interfering ion	Selectivity coefficient $[K^{Pot}_{A,B}]$	
	Fixed Interference Method	Mixed Solution Method
Na^+	31.62	12.17
K^+	7.94	5.15
Tl^+	28.18	16.91
Li^+	25.17	15.10
Ag^+	19.95	11.95
NH_4^+	14.13	4.78
Mn^{2+}	3.16×10^{-1}	1.89×10^{-1}
Zn^{2+}	4.47×10^{-1}	2.69×10^{-1}
Cd^{2+}	2.82×10^{-1}	1.69×10^{-1}
Ba^{2+}	3.51×10^{-1}	2.11×10^{-1}
Sr^{2+}	1.80×10^{-1}	1.08×10^{-1}
Co^{2+}	2.02×10^{-1}	1.21×10^{-1}
Ca^{2+}	1.80×10^{-1}	1.08×10^{-1}
Cu^{2+}	1.61×10^{-1}	9.66×10^{-2}
Mg^{2+}	1.28×10^{-1}	7.68×10^{-2}
Al^{3+}	3.52×10^{-2}	2.11×10^{-2}
La^{3+}	3.21×10^{-2}	1.93×10^{-2}
Fe^{3+}	3.52×10^{-2}	2.11×10^{-2}

Table-10(a)

Performance of the electrode system in presence of the detergent cetyl pyridinium chloride (CPC).

Untreated membrane

Concentration of CPC (M)	Slope mV/decade of concentration	Working concentration range (M)
x	40	3.16×10^{-4} - 1.00×10^{-1}
1.00×10^{-4}	40	3.16×10^{-4} - 1.00×10^{-1}
1.00×10^{-3}	34	4.46×10^{-4} - 1.00×10^{-1}
5.00×10^{-3}	31	7.94×10^{-4} - 1.00×10^{-1}
1.00×10^{-2}	20	1.41×10^{-3} - 1.00×10^{-1}

Table-10(b)

Performance of the membrane conditioned with 1.00×10^{-3}M cetyl pyridinium chloride (CPC).

Concentration of CPC (M)	Slope mV/decade of concentration	Working concentration range (M)
x	36	1.58×10^{-4} - 1.00×10^{-1}
1.00×10^{-4}	36	1.58×10^{-4} - 1.00×10^{-1}
1.00×10^{-3}	31	1.77×10^{-4} - 1.00×10^{-1}
5.00×10^{-3}	31	5.62×10^{-4} - 1.00×10^{-1}
1.00×10^{-2}	27	1.00×10^{-3} - 1.00×10^{-1}

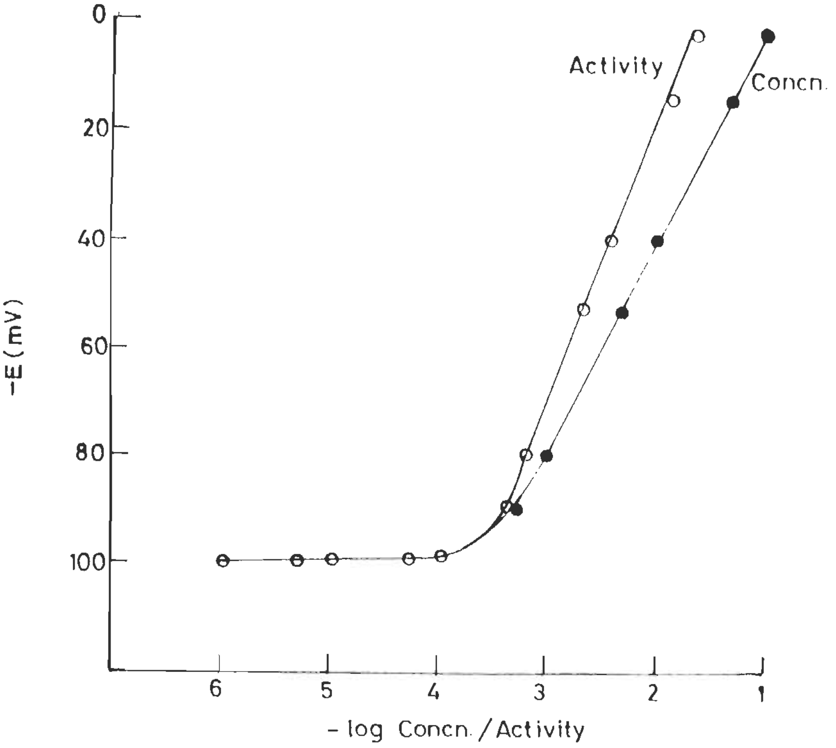

Fig. 9 Potential vs log $[Pb^{2+}]$ plots

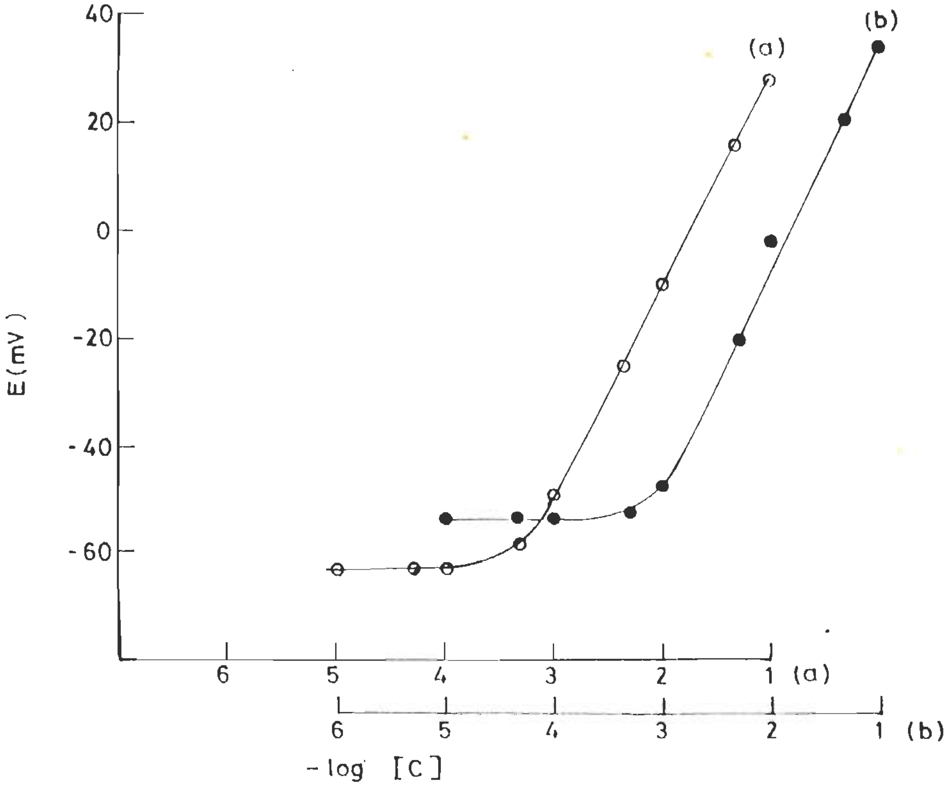

Fig.10 Potential vs log $[Pb^{2+}]$ plots with reference solution concn. (a) 5.0×10^{-2} M (b) 1.0×10^{-2} M

PVC based membrane of 2-hydroxy naphthaldoxime formaldehyde

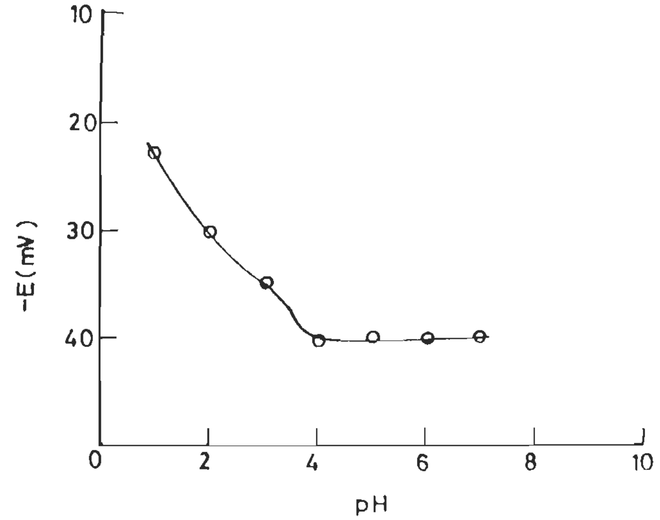

Fig. 11 Potential vs pH plot [Pb^{2+} concn. = 1.0×10^{-3} M]

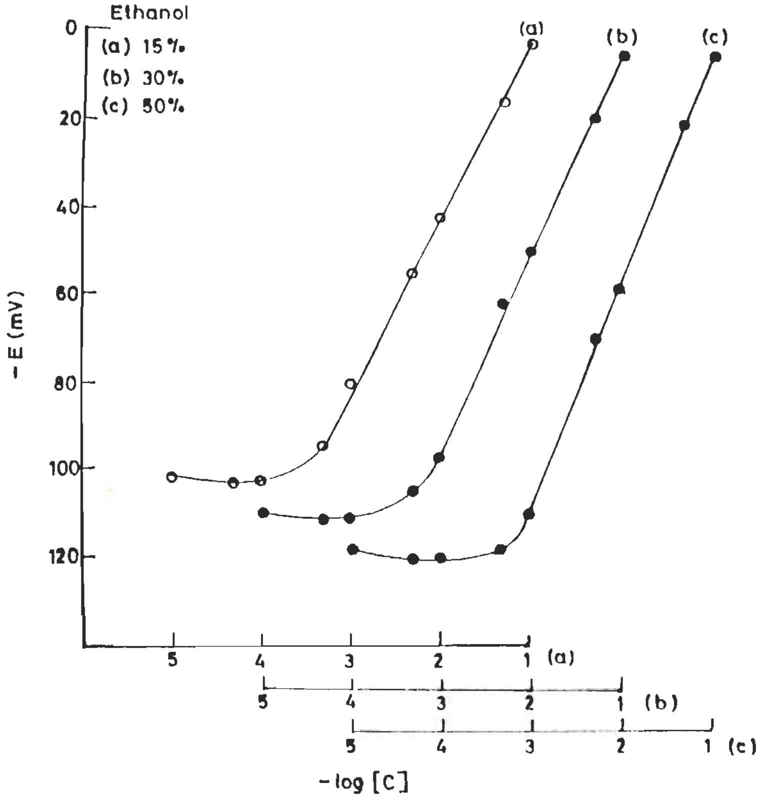

Fig. 12 Potential vs log [Pb^{2+}] plots in partially non-aqueous medium

PVC based membrane of 2-hydroxy naphthaldoxime formaldehyde

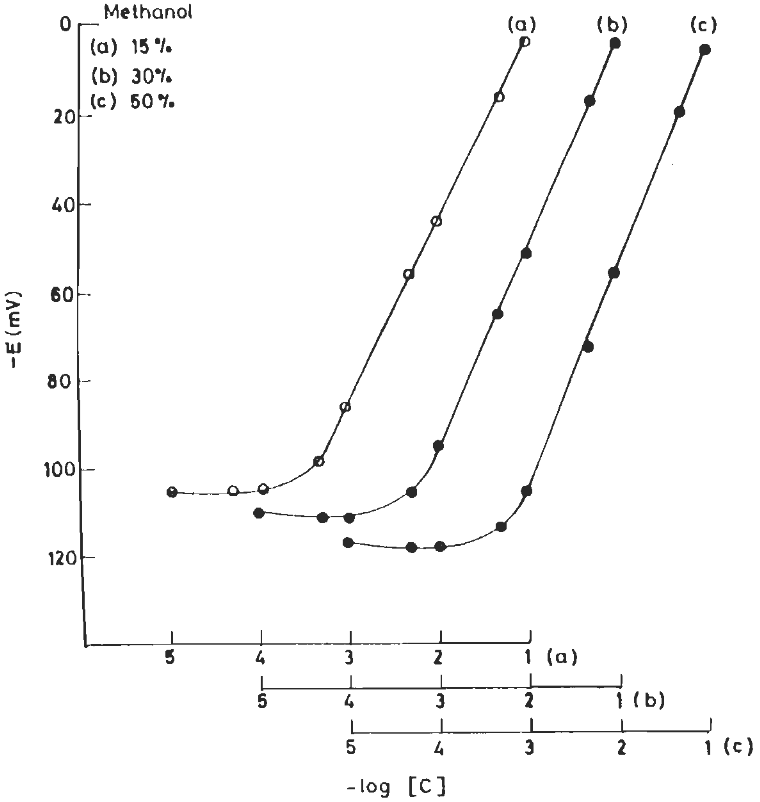

Fig. 13 Potential vs log $[Pb^{2+}]$ plots in partially non-aqueous medium

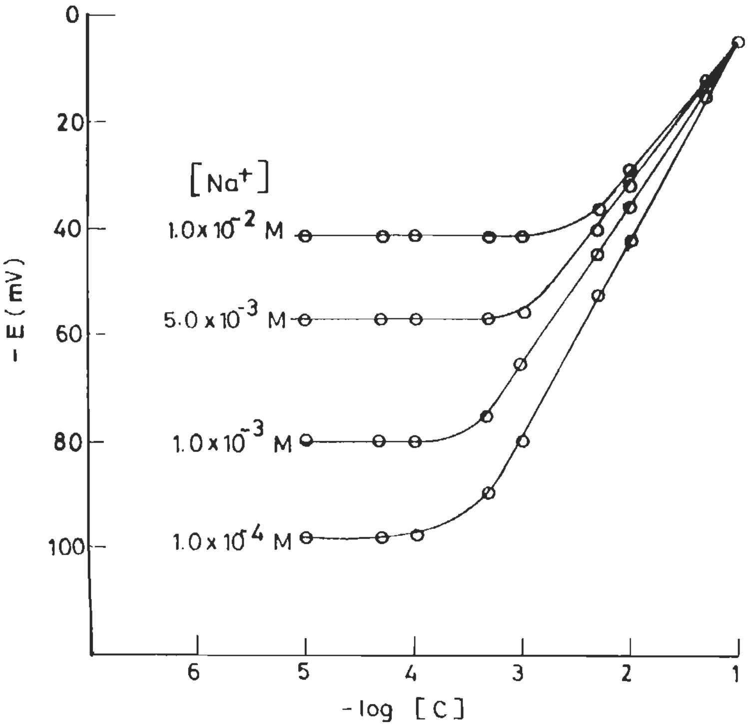

Fig. 14 (a) Potential vs log $[Pb^{2+}]$ plots in the presence of Na^+ of varying concn.

PVC based membrane of 2-hydroxy naphthaldoxime formaldehyde

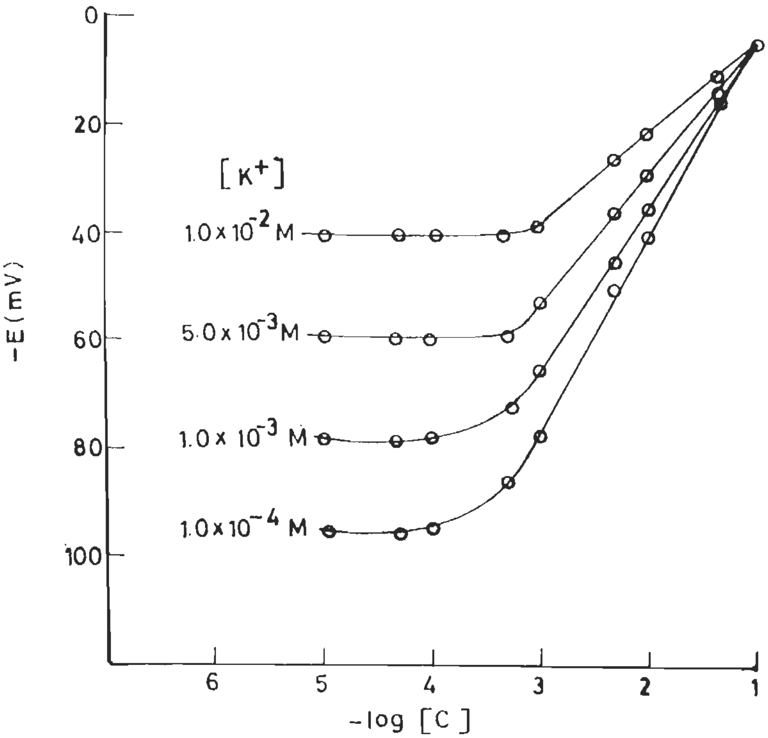

Fig. 14(b) Potential vs log [Pb^{2+}] plots in the presence of K^+ of varying concn.

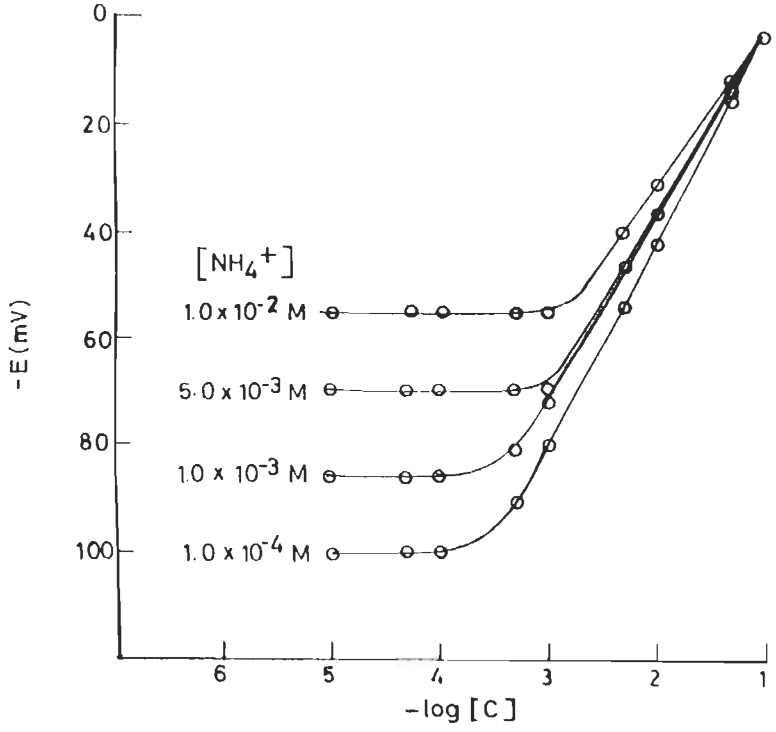

Fig. 14(c) Potential vs log [Pb^{2+}] plots in the presence of NH_4^+ of varying concn.

PVC based membrane of 2-hydroxy naphthaldoxime formaldehyde

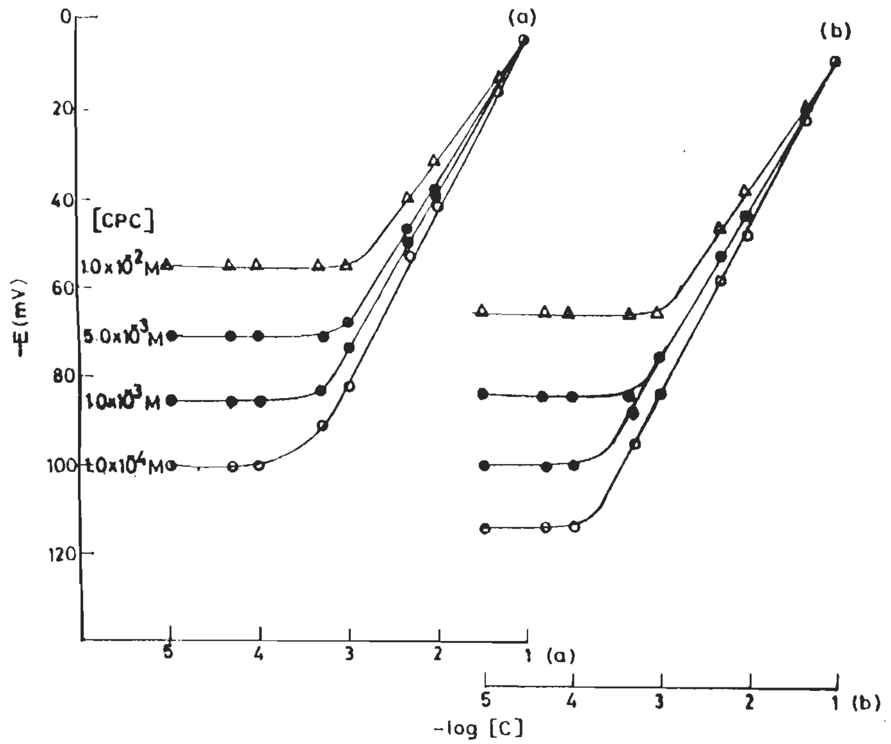

Fig. 15 Potential vs log $[Pb^{2+}]$ plots in the presence of CPC of varying concn. with untreated membranes (a) and treated membranes (b)

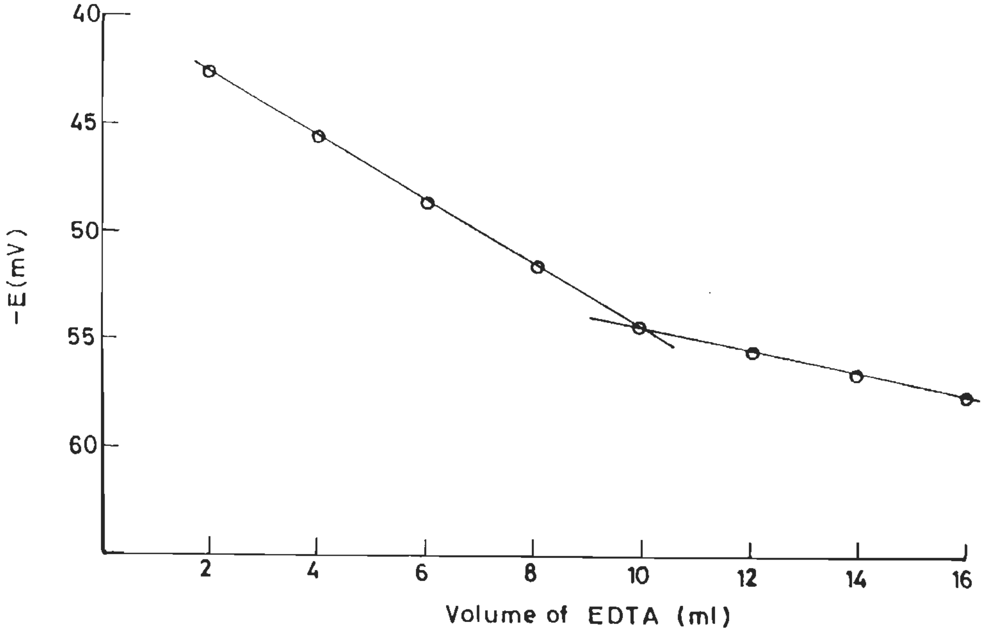

Fig. 16 Titration plot of 10ml of 1.0×10^{-2} M Pb^{2+} ions with 1.0×10^{-2} M EDTA solution

PVC based membrane of 2-hydroxy naphthaldoxime formaldehyde

interference of hydrogen ions.

The applicability of the proposed sensor in partially non-aqueous medium has also been observed. Potential vs concentration plots in 15, 30 and 50% (v/v) non-aqueous content are shown in Fig. 12 & 13. The data computed in Table-8, indicates reduction in the linear portion of potential vs concentration plot in non-aqueous medium. The decrease is however nominal when the non-aqueous content is 15%. A further increase in non-aqueous content causes serious interference. Thus the electrode assembly can only be used in aqueous medium or partially non-aqueous solvent when its content is not more than 15%.

The performance of an electrode is judged by its selectivity for the determinand ion in presence of other ions. This is assessed by obtaining the selectivity coefficients of other ions in comparison to lead and the same has been estimated by two methods the Fixed Interference and Mixed Solution methods.

The selectivity coefficient ($K_{A,B}^{Pot}$) values as obtained by both the method at 1.00×10^{-2}M concentration of interfering ions are given in Table-9. The value of this parameter is generally low for polyvalent cations and so these ions would not interfere. All monovalent ions register high selectivity coefficient values and would cause a serious interference in the working of this membrane assembly. The values obtained by Mixed Solution method are in general, of lower magnitude as compared to one obtained by Fixed Interference method. Even the values (Table-9) obtained in the case of monovalent ions by Mixed Solutions method are lower than what has been obtained by Fixed Interference method.

In order to assess the actual level of interference by the monovalent ions, some mixed runs were also observed i.e., potential vs concentration plots in contact with lead ions, containing different concentration of other monovalent ions (Fig.14a to 14c). A perusal of the plots (Fig. 14a to 14c) reveal that these ions too do not cause any interference upto a level of concentration 1.00×10^{-4}M or less. Beyond this concentration, the sensor can not be used in presence of monovalent viz. Na^+, K^+, NH_4^+ etc. ions. Other multivalent ions would normally not interfere unless present in very large concentrations - a situation which is hardly met with.

Effect of the presence of surfactant ions during the estimation of lead has also been studied. Potentials with Pb^{2+} ions were observed in presence of varying concentration of a cationic detergent, cetyl pyridinium chloride and the results are shown in Table-10(a). Smaller concentrations of surfactant (upto 1.00×10^{-4}M) do not disturb the working of this membrane electrode whereas higher concentrations do cause interference. Working concentration range of the membrane sensor and it's slope, both undergo a change in the presence of surfactant ions. Since the surfactant is likely to be present in traces only, there would not be any difficulty in using the electrode assembly under these conditions.

Efforts were also made to condition the membrane by treating it with the surfactant solution of 1.00×10^{-3}M concentration so that it becomes immune to the disturbances caused by the presence of higher concentration of the same. Although the electrode does not develop immunity to the presence of cationic surfactant ions at higher concentrations, the working concentration range of the conditioned membrane is enhanced from 3.16×10^{-4}-1.00×10^{-1}M to 1.58×10^{-4}-1.00×10^{-1}M with a simultaneous decrease in slope from 40 to 36 mV/decade concentration (Table-10b and Fig.15).

The practical utility of the sensor has also been observed by using it for the titration of Pb^{2+} ions with EDTA. Figure-16 exhibits the change in potential when 10^{-2}M EDTA solution is added to 10^{-2}M Pb^{2+} solution. Although the changes observed in potentials are not large, the end point is quit sharp and stoichiometric.

IV.3.c. Comparative evaluation.

A comparative assessment of the two i.e., PVC and polystyrene based membranes shows a much better performance of the polystyrene supported sensor.

The range of concentration in which lead ion can be measured is quite large in the case of polystyrene supported membrane. Response time is also less for this particular membrane and above all the polystyrene based membrane exhibits much better selectivity for lead ions over other cations. Selectivity coefficient values for monovalent cations in this case are much smaller than the one obtained in the case of PVC based electrode assembly.

IV.4. 2-Salicylaldene aminothiophenol formaldehyde resin - a membrane sensor for cadmium and zinc ions.

Homogeneous membranes of this resin could not be prepared. Membranes obtained by pressing the material even at very high pressure were unstable and got dispersed when kept in contact with electrolyte solutions. As such heterogeneous membranes embedded with polystyrene and PVC were prepared. 10% polystyrene based membranes were prepared at 55 °C under pressure of 6500-7000 psi and PVC based membranes having organic resin and PVC in 1:1 ratio were prepared by dissolving in THF and then spreading the homogeneous mixture on a smooth glass plate in a ring. The amount of binder required was arrived at after a good deal of experimentation. The methodology for the preparation of both the membranes is given in chapter II.

IV.4.a. Functional properties

The first prerequisite for understanding the performance of an ion exchange membrane is its complete physico-chemical characterization. The process involves the determination of those parameters which affect the electrochemical properties of the membrane i.e., porosity, electrolyte absorption, water content, swelling and electrical conductance.

As observed with 2-hydroxy naphthaldoxime formaldehyde (IV.2.a) the functional properties in the case of 2-salicylaldene aminothiophenol formaldehyde resin could only be determined with polystyrene based membranes while conductance measurements were possible with PVC based membranes as well.

These membranes also exhibit a very low order of swelling porosity, water content and electrolyte absorption in comparison to inorganic gel membranes (Table-11).

Only a small amount of water is incorporated within the membrane matrix. Porosity values also indicate that the volume of water incorporated per unit membrane volume is quite low.

Table-11

Water content, porosity, swelling and electrolyte absorption values for 2-salicylaldene amino thiophenol formaldehyde membrane.

Membrane	Water content per gram of wet membrane (g)	Porosity	Swelling (mm)	Amount of electrolyte absorbed per gram of wet membrane (M)
Organic resin	0.0294	0.0395	0.221	5.8×10^{-2}
Inorganic gel*	0.5578	0.1335	0.280	7.0×10^{-2}

*Inorganic gel polytungstoantimonate membrane (Table-1, Chapter II)

Table-12

Specific conductance of membrane in different cationic forms.

Cations	Specific conductance (milli mhos cm^{-1})	
	PVC based membrane	Polystyrene based membrane
Na^+	5.7×10^{-1}	5.4×10^{-1}
K^+	3.8×10^{-1}	2.0×10^{-1}
Tl^+	5.2×10^{-1}	5.1×10^{-1}
Li^+	8.1×10^{-1}	8.0×10^{-1}
Cd^{2+}	4.6×10^{-2}	4.2×10^{-2}
Pb^{2+}	5.2×10^{-2}	5.1×10^{-2}
Zn^{2+}	8.5×10^{-2}	8.4×10^{-2}
Cu^{2+}	6.3×10^{-2}	6.3×10^{-2}
Ba^{2+}	4.5×10^{-2}	4.2×10^{-2}
Al^{3+}	4.2×10^{-3}	3.8×10^{-3}
Cr^{3+}	7.8×10^{-3}	7.4×10^{-3}

The magnitude of swelling depends on the gel structure and also on the amount and nature of the binder material present in membrane. Organic resin membranes normally swell to a small extent.

Low values of porosity and swelling suggest more orderly diffusion through these membranes i.e., via the exchange sites and thus a better electroanalytical performance is expected out of these. But, in actual practice this does not happen and the membranes deviate from ideal behaviour. The magnitude of electrolyte absorption is also consistent to the observed values of water content and swelling.

The conductance of polystyrene as well as PVC based membranes in different cationic forms were measured by the method proposed by Lakshminarayanaiah et al. (Ref. 37 Chapter II).

Specific conductivity data (Table-12) of both the membranes shows the following sequence for various cations :

$[Li^{+} > Na^{+} > Tl^{+} > K^{+}] > [Zn^{2+} > Cu^{2+} > Pb^{2+} > Ba^{2+} \approx Cd^{2+}] > [Cr^{3+} > Al^{3+}]$

Membranes in various cationic forms (monovalent) record higher while the one labelled with multivalent cations register low values of conductance. It is not possible to correlate the conductance data with the ionic size etc. Overall the conductance values are higher for PVC based membranes.

IV.5. Electroanalytical performance of 2-Salicylaldene amino thiophenol formaldehyde membranes

Based on the selectivity sequence of 2-salicylaldene aminothiophenol formaldehyde resin, its membranes were prepared and tried for the estimation of a number of metal ions. On the basis of its performance, this particular sensor has been investigated for the quantitative determination of Cd^{2+} and Zn^{2+} ions. Membranes were prepared using both polystyrene and PVC as inert binding material. The binding material, when incorporated with the sensing compound is known to alter its selectivity pattern and the organic resin membrane is found to exhibit very good response for Cd^{2+} and Zn^{2+} ions. Detailed investigations in this regard were initiated and the utility of polystyrene and PVC based membranes of the compound 2-salicylaldene aminothiophenol formaldehyde resin in the estimation of Cd^{2+} and Zn^{2+} are described in this section. A comparative assessment of the proposed electrode assembly for the estimation of both the ions, Cd^{2+} and Zn^{2+} has also been made in the end.

IV.5. Estimation of cadmium ions

IV.5.a. Polystyrene based membrane

For the estimation of cadmium ions, the membrane having 2-salicylaldene aminothiophenol formaldehyde as electroactive phase was immersed in a solution of Cd^{2+} ions of concentration 1.0M. Equilibration time was fixed up by some preliminary studies and the membranes so equilibrated, generated stable and reproducible potentials when interposed between the test solution and internal reference solution (0.10M Cd^{2+}).

Potentials were monitored periodically, at a fixed concentration and the standard deviation was found to be 0.2 mV. Membrane potentials were measured in the range 10^{-6} to 10^{-1}M proceeding from low to higher concentration at 30±1 ^{o}C against saturated calomel electrodes.

The electrode demonstrates a linear response for Cd^{2+} ions in $1.00x10^{-4}$-$1.00x10^{-1}$M concentration range (Fig.17), the slope of the plot being low viz., 15mV/decade of concentration. Inspite of this non Nernstian behaviour of the membrane, the sensor can be used for measuring Cd^{+2} ions in the above mentioned concentration range.

To see the effect of changing the concentration of the reference solution plots have also been made with $5.00x10^{-2}$ and $1.00x10^{-2}$M reference solutions (Fig.18 & Table-13) and the same are found to be linear in the region $1.41x10^{-4}$-$1.00x10^{-1}$M and $1.58x10^{-4}$-$1.00x10^{-1}$M concentration of Cd^{2+} ions respectively. Thus the working concentration range of membrane electrode decreases with a decrease in concentration of reference solution. The value of slope also goes down to 12 mV/decade of concentration. Besides this, the magnitude of membrane potentials generated with $5.00x10^{-2}$ and $1.00x10^{-2}$M concentration of Cd^{2+} ions, are also quite small. Consequently the necessary optimum concentration of the reference solution, for smooth functioning of the proposed membrane sensor, is $1.00x10^{-1}$M.

The response time of the proposed membrane is almost 45 seconds i.e., in this time stable potentials are obtained. The potentials stay constant for more than two minutes and are quite reproducible. This membrane can be used for a period of 3-4 months without showing any drift in potentials. If necessary, it can be equilibrated again.

The pH dependence of the electrode potential has been tested over the range 1 to 7.00 for 10^{-2}M Cd^{2+} ions (Fig.19). The potentials are constant within the range 4 to 6 which may be taken

Table-13

Working concentration range of the polystyrene based membrane sensor for cadmium ions with reference solution of varying concentration.

Reference solution concentration (M)	Slope mV/decade of concentration	Working concentration range (M)
$1.00\text{x}10^{-1}$	15	$1.00\text{x}10^{-4}$- $1.00\text{x}10^{-1}$
$5.00\text{x}10^{-2}$	13	$1.41\text{x}10^{-4}$- $1.00\text{x}10^{-1}$
$1.00\text{x}10^{-2}$	12	$1.58\text{x}10^{-4}$- $1.00\text{x}10^{-1}$

Table-14

Performance of electrode system in 15, 30 and 50% (volume by volume) non-aqueous medium.

percentage	Slope mV/decade of concentration	Working concentration range (M)
x	15	$1.00\text{x}10^{-4}$- $1.00\text{x}10^{-1}$
Ethanol		
15	15	$1.00\text{x}10^{-4}$- $1.00\text{x}10^{-1}$
30	20	$1.99\text{x}10^{-4}$- $1.00\text{x}10^{-1}$
50	22	$2.23\text{x}10^{-4}$- $1.00\text{x}10^{-1}$
Methanol		
15	15	$1.00\text{x}10^{-4}$- $1.00\text{x}10^{-1}$
30	18	$1.58\text{x}10^{-4}$- $1.00\text{x}10^{-1}$
50	20	$1.58\text{x}10^{-4}$- $1.00\text{x}10^{-1}$

Table-15

Selectivity of the electrode system for cadmium ions in the presence of 1.00×10^{-2} M concentration of interfering ions (as calculated by Fixed Interference and Mixed Solution methods).

Interfering ion	Selectivity coefficient $[K^{Pot}_{A,B}]$	
	Fixed Interference Method	Mixed Solution Method
Na^+	19.45	7.02
K^+	19.95	7.18
Tl^+	19.95	7.18
Li^+	10.00	3.60
Ag^+	17.78	6.40
NH_4^+	19.95	7.18
Mn^{2+}	1.99×10^{-1}	7.18×10^{-2}
Pb^{2+}	3.16×10^{-1}	1.14×10^{-1}
Zn^{2+}	3.16×10^{-1}	1.14×10^{-1}
Ba^{2+}	3.16×10^{-1}	1.14×10^{-1}
Sr^{2+}	2.82×10^{-1}	1.01×10^{-1}
Co^{2+}	2.51×10^{-1}	9.04×10^{-2}
Ca^{2+}	3.16×10^{-1}	1.14×10^{-1}
Cu^{2+}	2.82×10^{-1}	1.01×10^{-1}
Mg^{2+}	3.16×10^{-1}	1.14×10^{-1}
Al^{3+}	5.49×10^{-2}	1.98×10^{-2}
La^{3+}	7.94×10^{-2}	2.85×10^{-2}
Fe^{3+}	6.76×10^{-2}	2.43×10^{-2}

Table-16(a)

Performance of the electrode system in presence of the detergent cetyl pyridinium chloride (CPC).

Untreated membrane

Concentration of CPC (M)	Slope mV/decade of concentration	Working concentration range (M)
x	15	1.00×10^{-4} - 1.00×10^{-1}
6.00×10^{-4}	15	1.00×10^{-4} - 1.00×10^{-1}
1.00×10^{-3}	15	3.16×10^{-4} - 1.00×10^{-1}
5.00×10^{-3}	12	5.01×10^{-3} - 1.00×10^{-1}
1.00×10^{-2}	11	1.99×10^{-3} - 1.00×10^{-1}

Table-16(b)

Performance of the membrane conditioned with 1.00×10^{-3}M cetyl pyridinium chloride (CPC).

Concentration of CPC (M)	Slope mV/decade of concentration	Working concentration range (M)
x	15	7.08×10^{-5} - 1.00×10^{-1}
6.00×10^{-4}	15	7.08×10^{-5} - 1.00×10^{-1}
1.00×10^{-3}	14	1.78×10^{-4} - 1.00×10^{-1}
5.00×10^{-3}	12	3.16×10^{-4} - 1.00×10^{-1}
1.00×10^{-2}	11	1.00×10^{-3} - 1.00×10^{-1}

as the working pH range of this electrode assembly. A sharp change at low pH values probably reflects the competition of hydrogen ions under these circumstances.

Variation of membrane potentials in a partially non-aqueous medium has also been studied. Potential vs concentration plots in 15, 30 and 50% (V/V) ethanolic and methanolic solutions are shown in Fig.20 & 21. Cd^{2+} ions can be estimated with the proposed sensor in partially non-aqueous solvent having non-aqueous content (ethanol & methanol) up to 15%. But with further increase in non-aqueous content the working concentration range of the sensor goes down with a simultaneous increase in slope of plot (Table-14).

Selectivity of the proposed sensor for Cd^{2+} ions over other cations has been obtained by both the Fixed Interference and Mixed Solution methods (Table-15). The value of this parameter is generally quite low for multivalent cations. High selectivity coefficient values (as calculated by Fixed Interference method) suggest that monovalent cations do interfere in the working of the sensor.

Selectivity coefficient values as obtained by the Mixed Solution method are generally smaller in comparison to those obtained by Fixed Interference method. Even in the case of monovalent ions, the values obtained by Mixed Solution method are much smaller and in order to assess the working feasibility of the membrane sensor, in presence of monovalent cations, some mixed runs have also been made having different concentration of interfering (monovalent) and Cd^{2+} ions. Potential vs concentration plots made at various interfering levels of Na^{+}, K^{+} and NH_4^{+} are

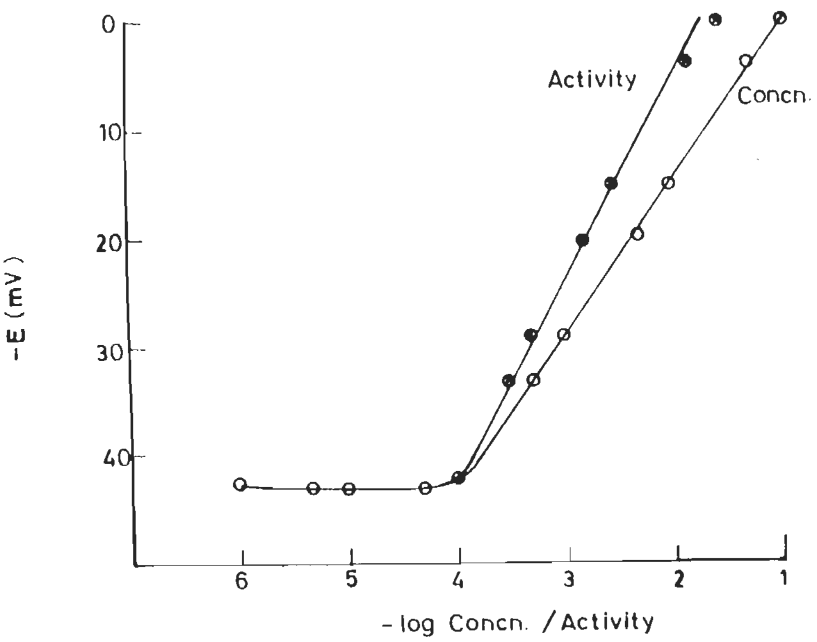

Fig.17 Potential vs log $[Cd^{2+}]$ plots

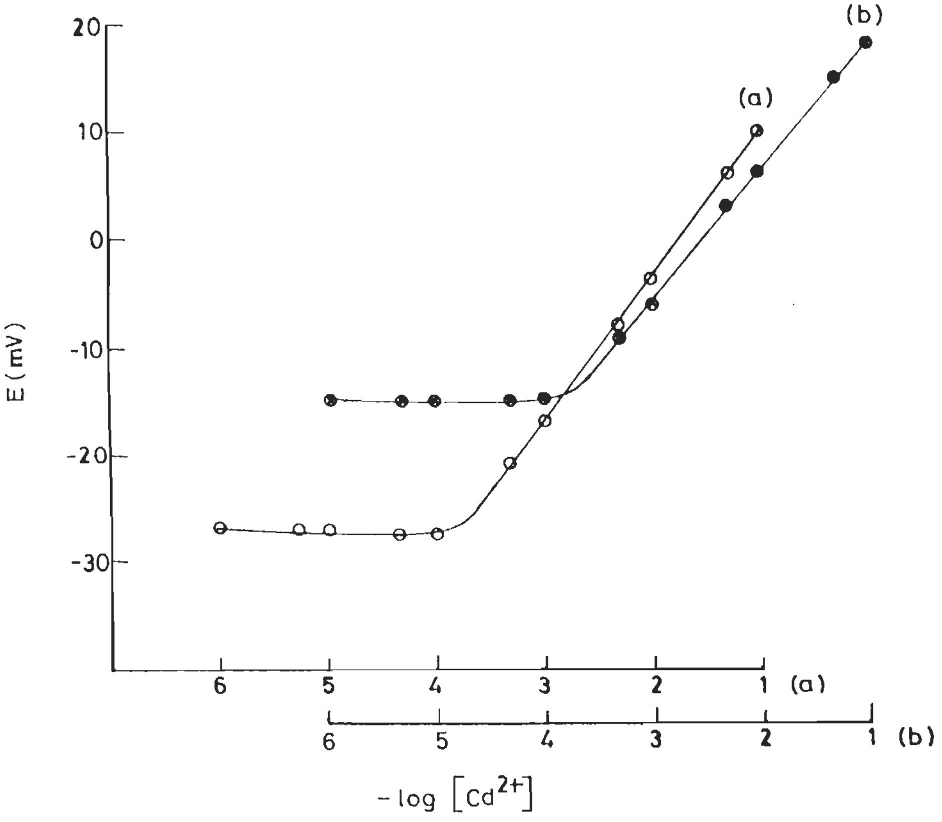

Fig. 18 Potential vs log $[Cd^{2+}]$ plots with reference concn. (a) 5.0×10^{-2} M (b) 1.0×10^{-2} M

Polystyrene based membrane of 2-Salicylaldene aminothio phenol formaldehyde

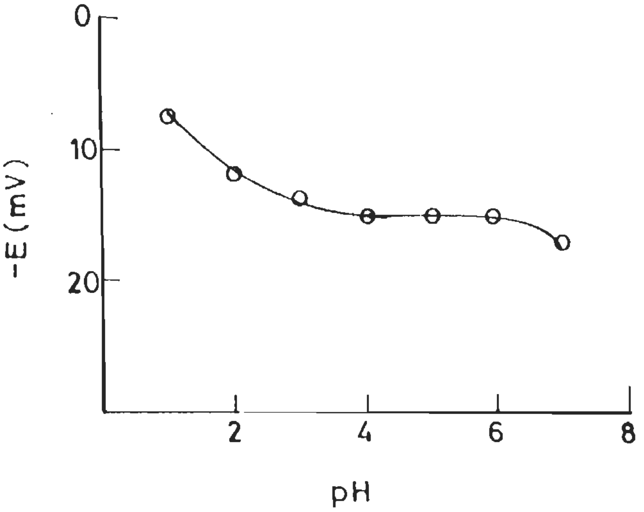

Fig. 19 Potential vs pH plot [Cd^{2+} concn. = 1.0×10^{-2} M]

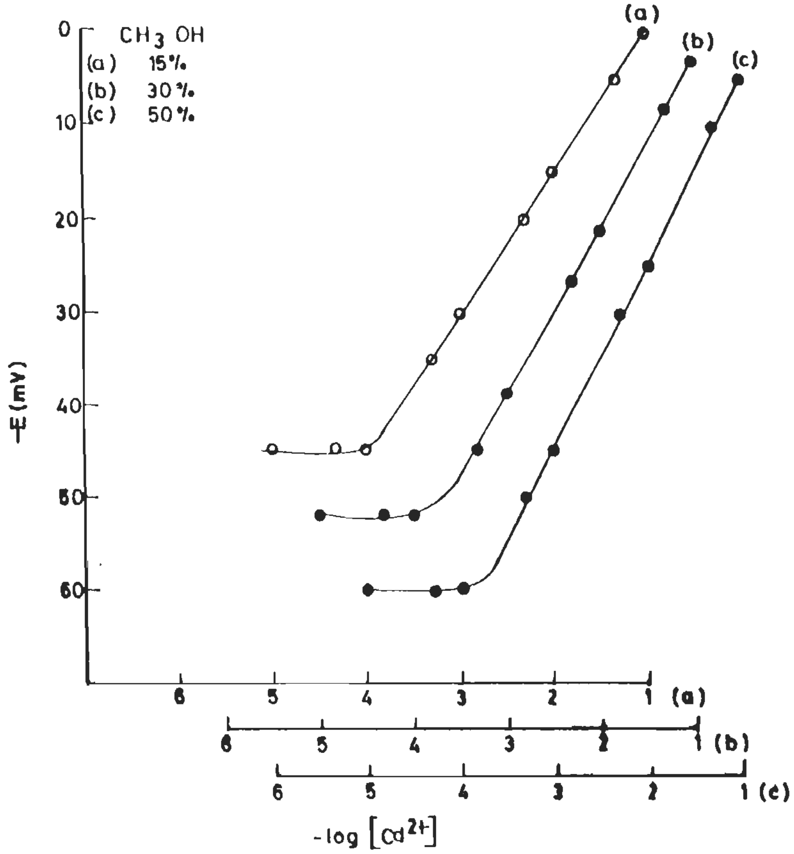

Fig. 20 Potential vs log [Cd^{2+}] plots in partially non-aqueous medium

Polystyrene based membrane of 2-Salicylaldene aminothio phenol formaldehyde

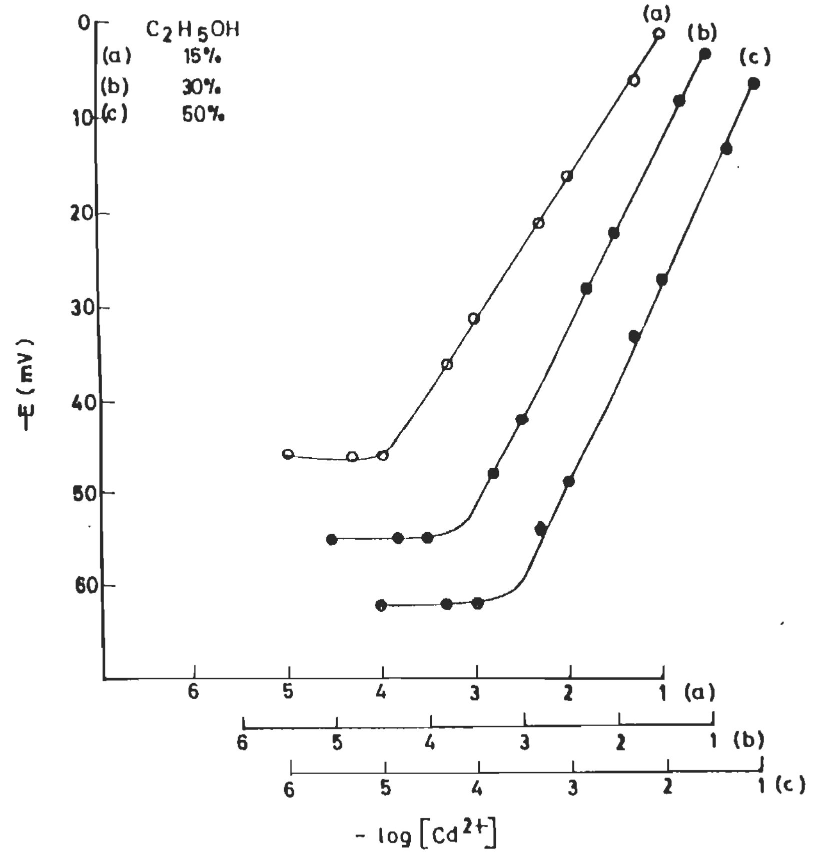

Fig. 21 Potential vs log $[Cd^{2+}]$ plots in partially non-aqueous medium

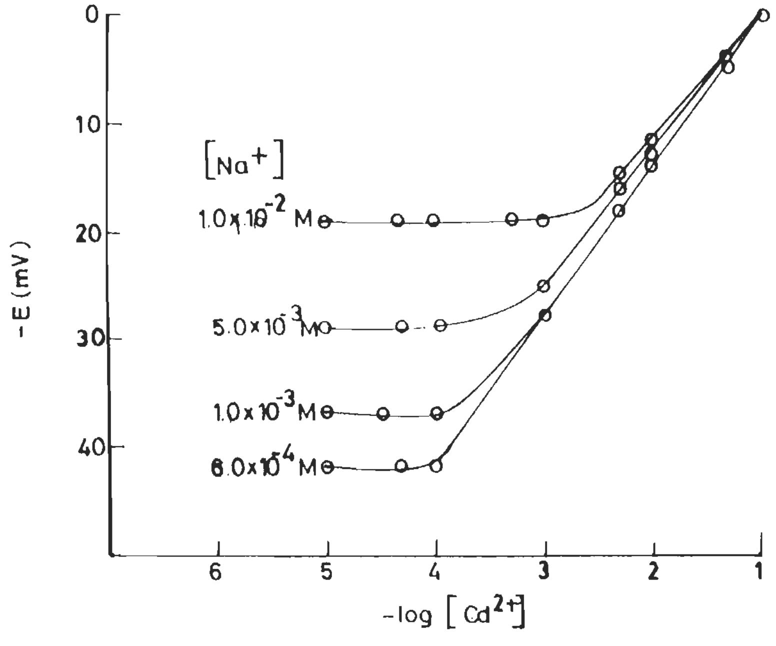

Fig. 22(a) Potential vs log $[Cd^{2+}]$ plots in the presence of Na^+ of varying concn.

Polystyrene based membrane of 2-Salicylaldene aminothio phenol formaldehyde

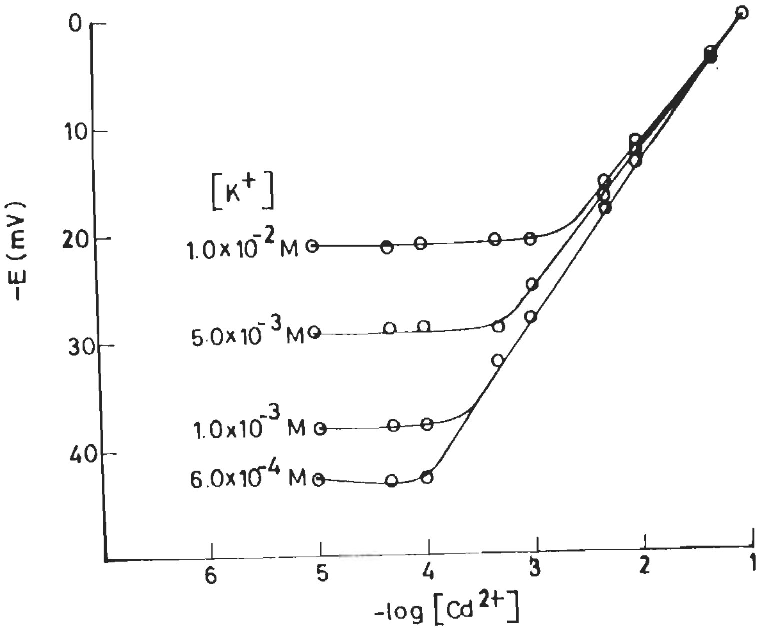

Fig. 22(b) Potential vs log $[Cd^{2+}]$ plots in the presence of K^+ of varying concn.

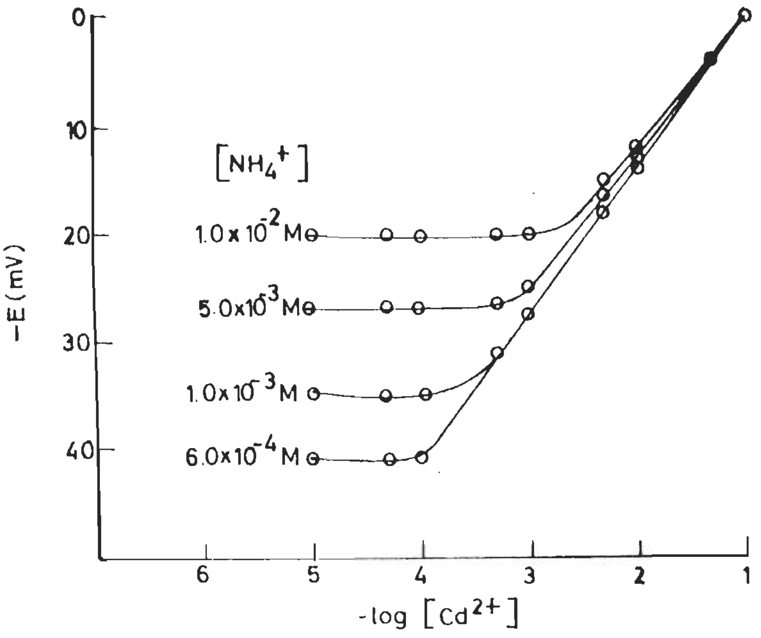

Fig. 22(c) Potential vs log$[Cd^{2+}]$ plots in the presence of NH_4^+ of varying concn.

Polystyrene based membrane of 2-Salicylaldene aminothio phenol formaldehyde

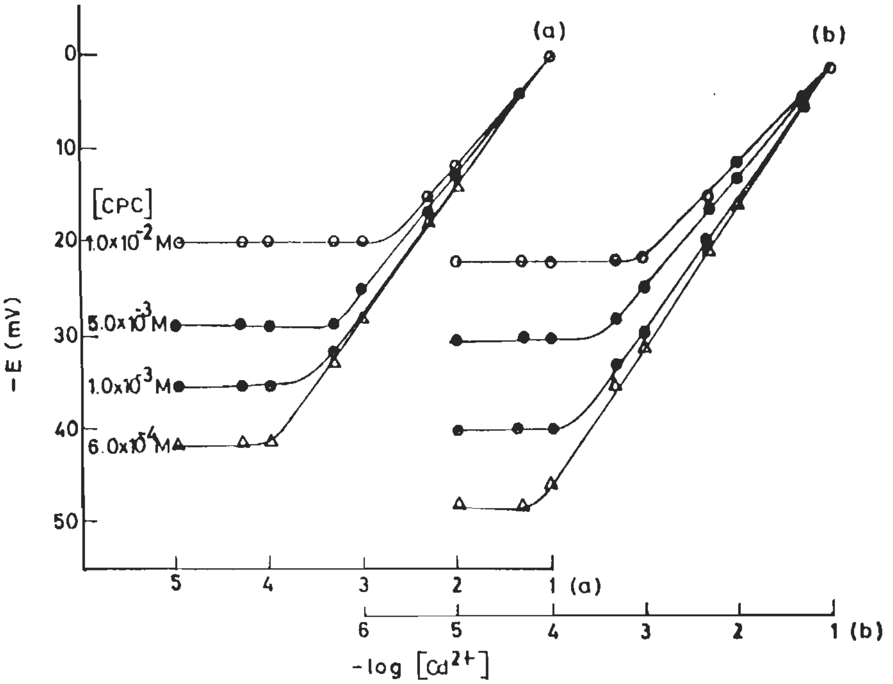

Fig. 23 Potential vs log $[Cd^{2+}]$ plots in the presence of CPC of varying concn. with untreated membranes (a) and treated membranes (b)

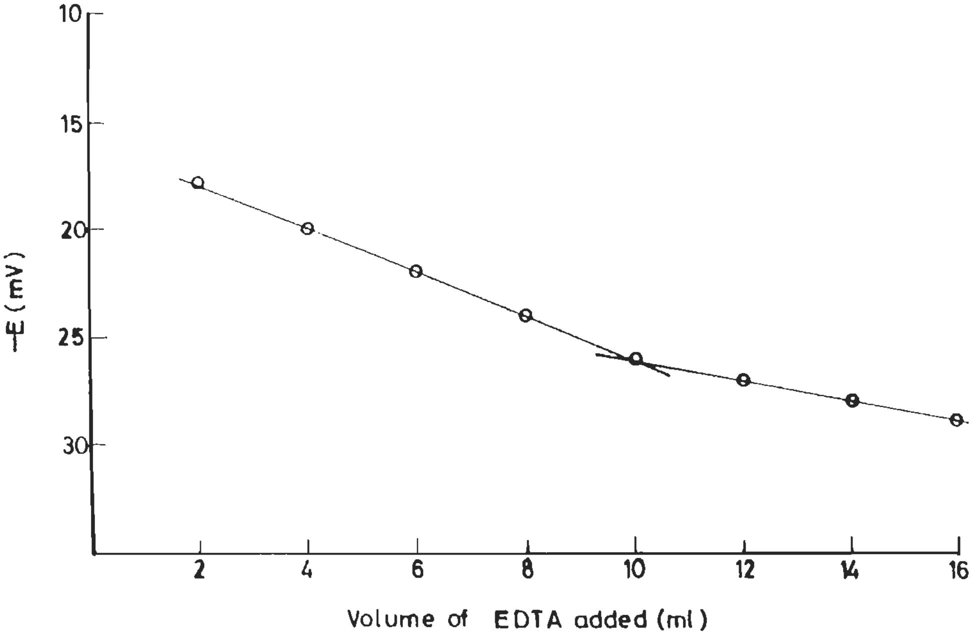

Fig. 24 Titration plot of 10ml of 1.0×10^{-2} M Cd^{2+} ions with 1.0×10^{-2} M EDTA solution

Polystyrene based membrane of 2-Salicylaldene aminothio phenol formaldehyde

shown in Fig.22(a) to 22(c). It is evident that these ions do not cause any disturbance upto a concentration of 6.00×10^{-4}M or less. Beyond this concentration the sensor can not be used in the presence of monovalent cations. Other multivalent ions would normally not interfere unless present in very large concentration, a situation which would hardly arise.

Effect of anions on the working of membrane electrode has also been observed and anions like chloride do not interfere with the estimation of cadmium.

In actual practice the estimation of Cd^{2+} is quite often required in presence of surfactant and other similar impurities. As such the working of the membrane sensor has also been checked in presence of a cationic surfactant, cetyl pyridinium chloride. The plots of potential vs log $[Cd^{2+}]$ in presence of varying concentration of cetyl pyridinium chloride is shown in Figure 23 and the results are depicted in Table-16(a). Smaller concentrations of surfactant (upto 6.00×10^{-4}M) do not disturb the working of this electrode where as higher concentrations do cause interference and the working concentration range and slope of the sensor undergoes a change. Since the surfactants are likely to be present in traces only, there would not be any difficulty in using the sensor under these conditions.

Efforts were also made to condition the membrane by treating it with the surfactant solution of 1.00×10^{-3}M concentration to make it immune to the disturbances caused by the presence of higher concentrations of the same. Data given in Table-16(b) shows the performance of the treated membrane. Although the sensor does not develop immunity to the effect of detergent at higher concentrations, one interesting feature is the enhancement of working concentration range of the treated membrane sensor from 1.00×10^{-4}-1.00×10^{-1}M to 7.08×10^{-5}-1.00×10^{-1}M [Table-16(b)]. The level of interference, at larger concentrations of detergent, also goes down.

The practical utility of the sensor has been observed by using it as an indicator electrode for the titration of Cd^{2+} ions with EDTA. Figure 24 exhibits the change in potential when 10^{-2}M EDTA is added to 10^{-2}M Cd^{2+} solution. The end point is quite sharp and a perfect stoichiometry is also observed for this titration. The shape of the curve are not the same as is normally observed in potentiometric titrations. The removal of Cd^{2+} ions results in a decrease in membrane potential and beyond the end point the change in potentials is nominal.

IV.6.b. PVC based membranes

The PVC based membranes of 2-salicylaldene aminothiophenol formaldehyde resin were equilibrated with 1.0M $Cd(NO_3)_2$ solution for 2-3 days. The potentials obtained after this period were quit stable and reproducible.

The sensor exhibits response with Cd^{2+} ions with non Nernstian slope of 12mV/decade of concentration in a wide range of concentration, 1.79×10^{-4}-1.00×10^{-1}M, which is taken to be the effective working range of this electrode assembly. The plots are shown in Fig.25.

Reference solutions of different concentrations have also been tried but this did not improve the working of the electrode assembly. The magnitude of potentials generated as well as the

Table-17

Working concentration range of the PVC based membrane sensor for cadmium ions with reference solution of varying concentration.

Reference solution concentration (M)	Slope mV/decade of concentration	Working concentration range (M)
1.00×10^{-1}	12	1.79×10^{-4}- 1.00×10^{-1}
5.00×10^{-2}	12	2.51×10^{-4}- 1.00×10^{-1}
1.00×10^{-2}	10	2.51×10^{-4}- 1.00×10^{-1}

Table-18

Performance of electrode system in 15, 30 and 50% (volume by volume) non-aqueous medium.

percentage	Slope mV/decade of concentration	Working concentration range (M)
x	12	1.79×10^{-4}- 1.00×10^{-1}
Ethanol		
15	13	1.99×10^{-4}- 1.00×10^{-1}
30	17	3.16×10^{-4}- 1.00×10^{-1}
50	18	3.16×10^{-4}- 1.00×10^{-1}
Methanol		
15	13	1.79×10^{-4}- 1.00×10^{-1}
30	17	3.16×10^{-4}- 1.00×10^{-1}
50	20	3.16×10^{-4}- 1.00×10^{-1}

Table-19

Selectivity of the electrode system for cadmium ions in the presence of 1.00×10^{-2} M concentration of interfering ions (as calculated by Fixed Interference and Mixed Solution methods).

Interfering ion	Selectivity coefficient $[K^{Pot}_{A,B}]$	
	Fixed Interference Method	Mixed Solution Method
Na^+	25.19	9.04
K^+	28.18	10.15
Tl^+	17.78	6.40
Li^+	19.95	7.18
Ag^+	25.19	9.04
NH_4^+	22.39	8.58
Mn^{2+}	2.24×10^{-1}	8.06×10^{-2}
Pb^{2+}	4.47×10^{-1}	1.61×10^{-1}
Zn^{2+}	3.55×10^{-1}	1.28×10^{-1}
Ba^{2+}	3.98×10^{-1}	1.43×10^{-1}
Sr^{2+}	3.16×10^{-1}	1.14×10^{-1}
Co^{2+}	2.82×10^{-1}	1.01×10^{-1}
Ca^{2+}	2.82×10^{-1}	1.01×10^{-1}
Cu^{2+}	2.82×10^{-1}	1.01×10^{-1}
Mg^{2+}	2.24×10^{-1}	8.06×10^{-2}
Al^{3+}	5.49×10^{-2}	1.98×10^{-2}
La^{3+}	5.01×10^{-2}	1.80×10^{-2}
Fe^{3+}	6.76×10^{-2}	2.43×10^{-2}

Table-20(a)

Performance of the electrode system in presence of the detergent cetyl pyridinium chloride (CPC).

Untreated membrane

Concentration of CPC (M)	Slope mV/decade of concentration	Working concentration range (M)
x	12	1.79×10^{-4} - 1.00×10^{-1}
5.00×10^{-4}	12	1.79×10^{-4} - 1.00×10^{-1}
1.00×10^{-3}	12	7.08×10^{-4} - 1.00×10^{-1}
5.00×10^{-3}	10	1.00×10^{-3} - 1.00×10^{-1}
1.00×10^{-2}	9	2.51×10^{-3} - 1.00×10^{-1}

Table-20(b)

Performance of the membrane conditioned with 1.00×10^{-3}M cetyl pyridinium chloride (CPC).

Concentration of CPC (M)	Slope mV/decade of concentration	Working concentration range (M)
x	13	1.00×10^{-4} - 1.00×10^{-1}
5.00×10^{-4}	13	1.00×10^{-4} - 1.00×10^{-1}
1.00×10^{-3}	13	3.98×10^{-4} - 1.00×10^{-1}
5.00×10^{-3}	10	5.62×10^{-4} - 1.00×10^{-1}
1.00×10^{-2}	9	1.26×10^{-3} - 1.00×10^{-1}

working concentration range of the sensor goes down with a decrease in concentration of the reference solution (Fig.26 & Table-17). As such it is inferred that a reference solution of 1.00×10^{-1}M concentration gives the best performance and the same has been used in the entire investigations with this electrode assembly.

Response time of the proposed sensor at various test solution concentrations is reasonably fast and stable potentials are generated within a minute. Repeated monitoring of potentials at a fixed concentration has a standard deviation of 0.2mV. The PVC incorporated membranes have longer life times and better stability. This membrane also does not leach easily and is normally used for four to five months. Minor contaminations can be removed by regular equilibration of the membrane and avoiding cross contamination.

The effect of pH has also been observed to ascertain the working pH range of this membrane sensor. Potentials remains constant in the pH range 4 to 6 (Fig.27), which is thus taken to be the working range of this electrode assembly.

The PVC based membrane sensor is also functional in partially non-aqueous medium. Potential vs concentration plots in 15, 30 and 50% ethanolic and methanolic solutions are shown in Figs.28 and 29. Upto 15% non-aqueous content (Table-18), normally no interference is observed, showing the utility of the sensor even in partially non-aqueous medium. On increasing the non-aqueous content the slope of the plot increases with a decrease in working concentration range of the sensor. Response time also increases with an increase in the non-aqueous content.

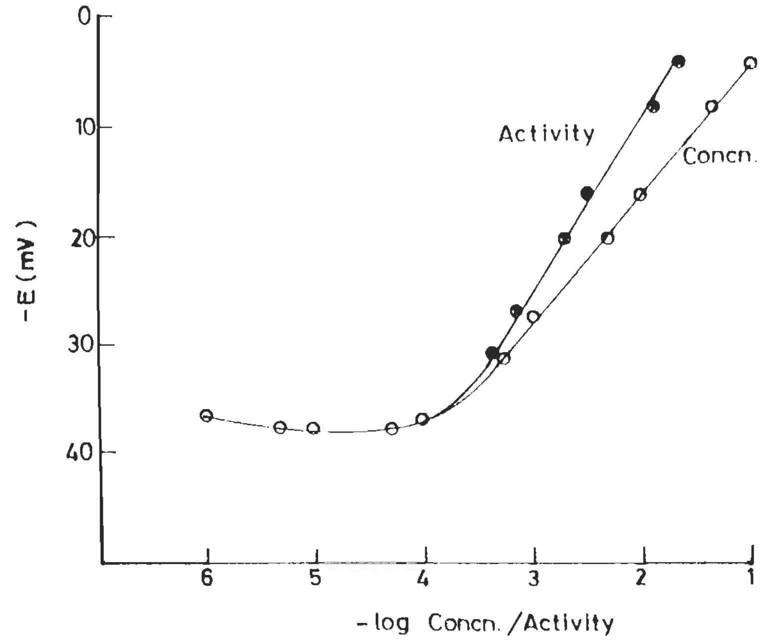

Fig. 25 Potential vs log $[Cd^{2+}]$ plots

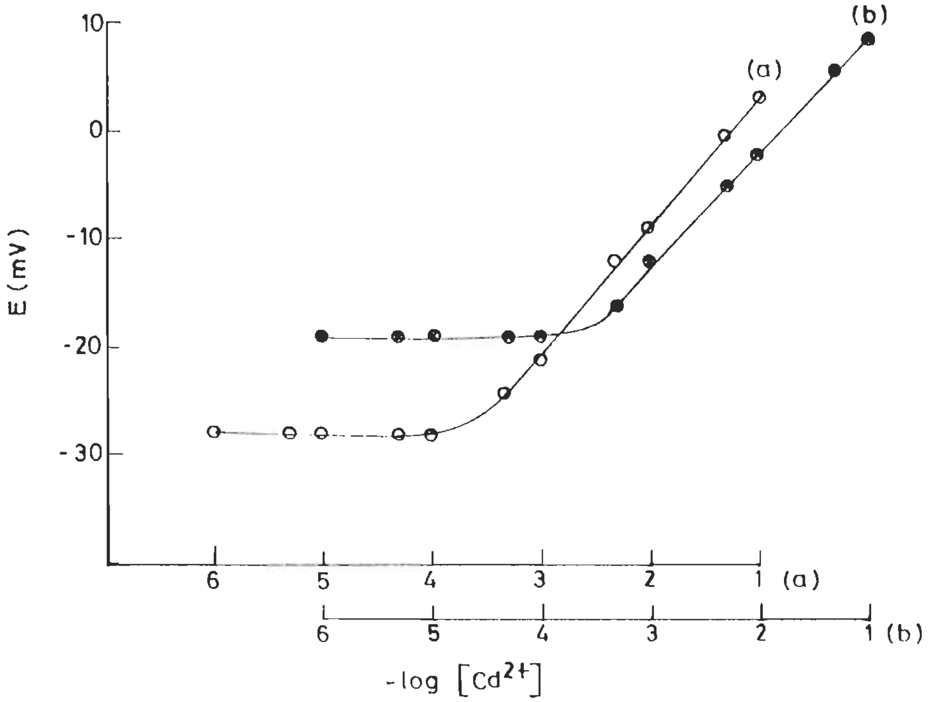

Fig. 26 Potential vs log $[Cd^{2+}]$ plots with reference concn.
(a) 5.0×10^{-2} M (b) 1.0×10^{-2} M

PVC based membrane of 2-Salicylaldene aminothio phenol formaldehyde

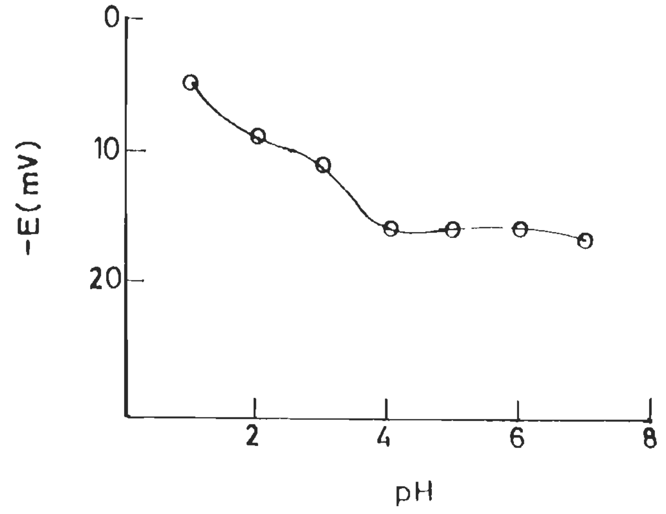

Fig. 27 Potential vs pH plot [Cd^{2+} concn. = 1.0×10^{-2} M]

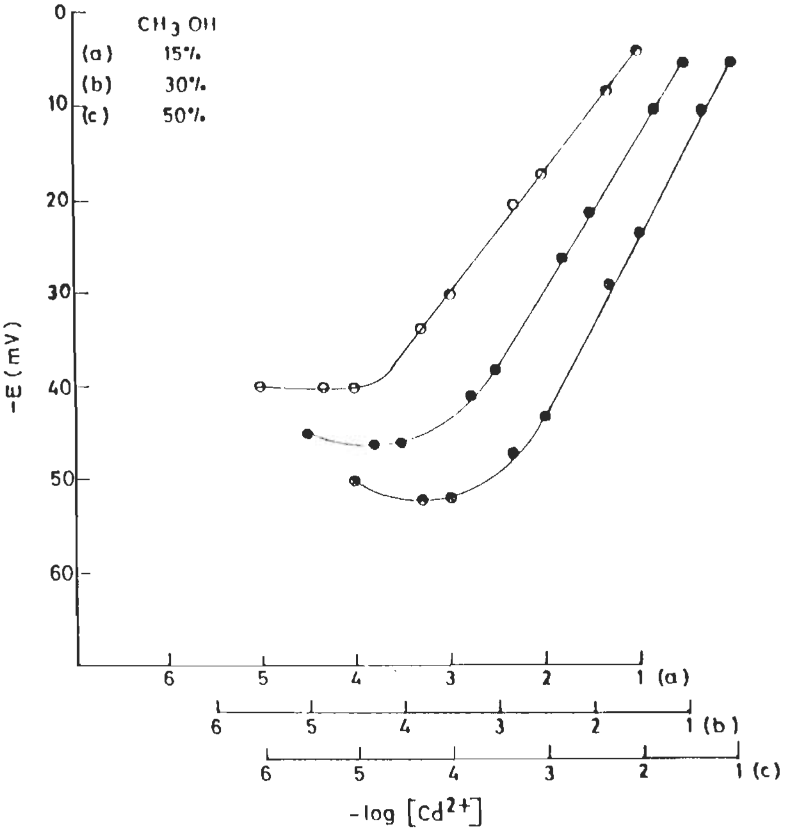

Fig. 28 Potential vs log [Cd^{2+}] plots in partially non-aqueous medium

PVC based membrane of 2-Salicylaldene aminothio phenol formaldehyde

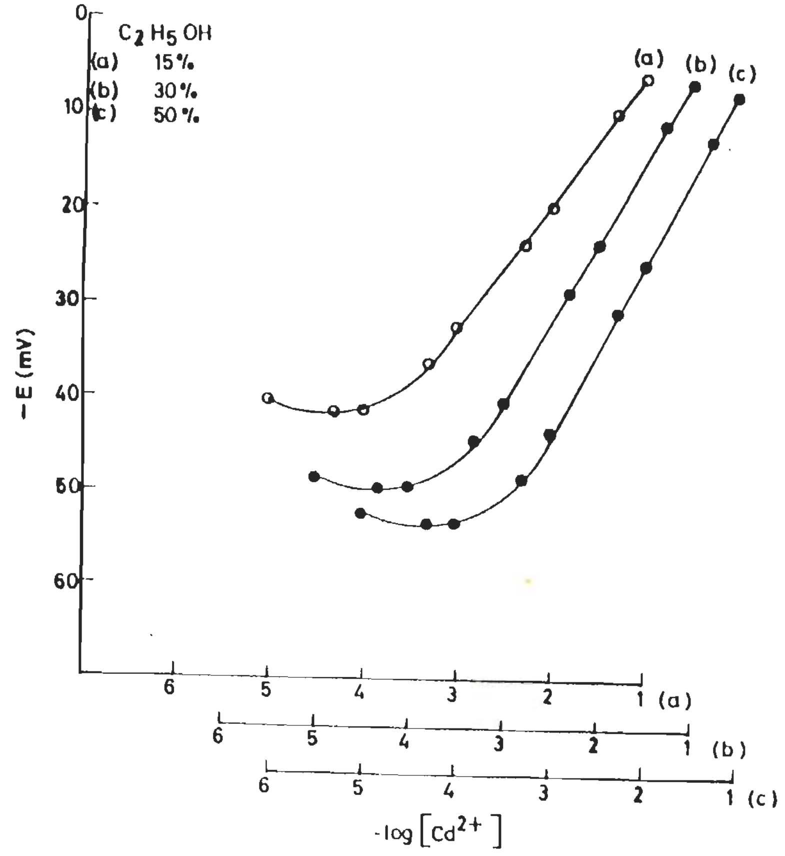

Fig. 29 Potential vs log $[Cd^{2+}]$ plots in partially non-aqueous medium

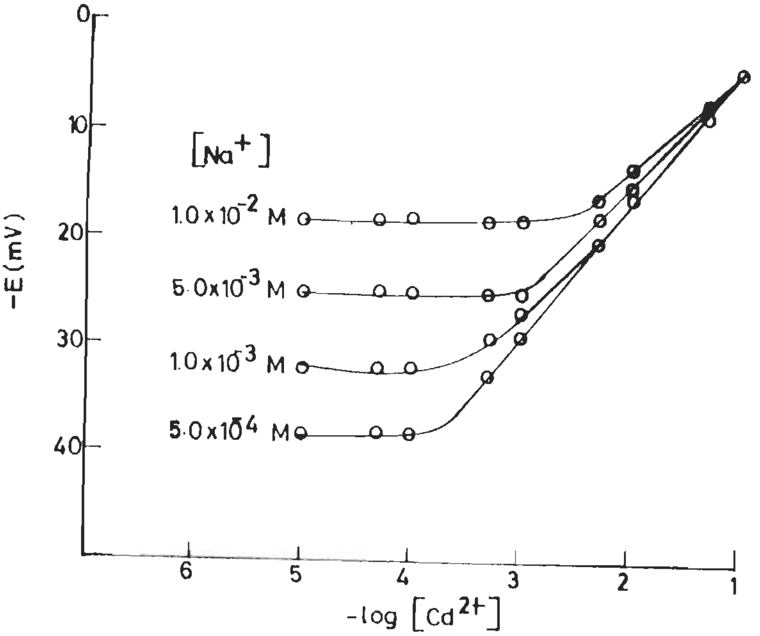

Fig. 30(a) Potential vs log $[Cd^{2+}]$ plots in the presence of Na^+ of varying concn.

PVC based membrane of 2-Salicylaldene aminothio phenol formaldehyde

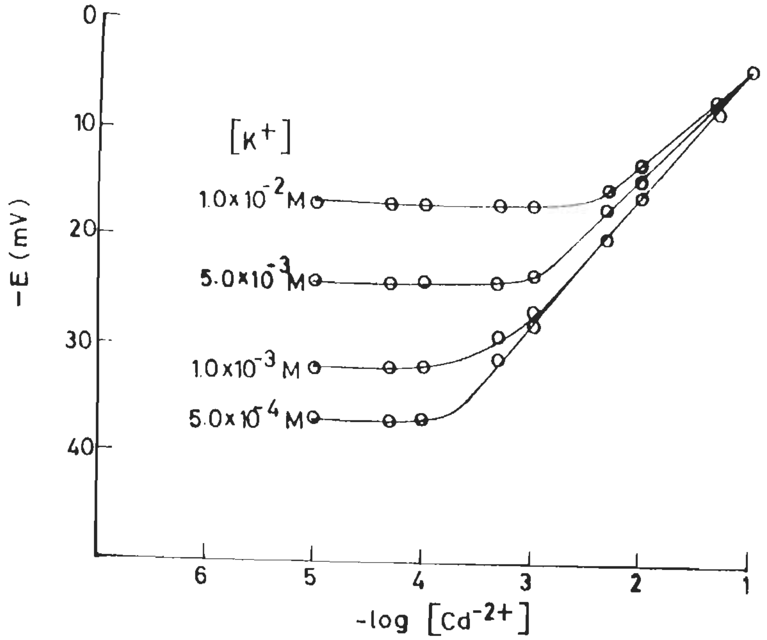

Fig. 30(b) Potential vs log $[Cd^{2+}]$ plots in the presence of K^+ of varying concn.

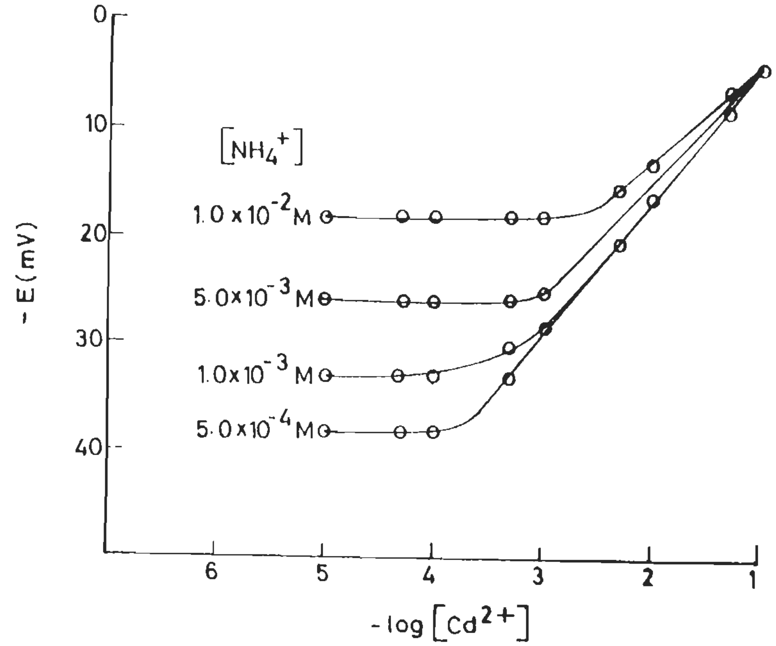

Fig. 30(c) Potential vs log $[Cd^{2+}]$ plots in the presence of NH_4^+ of varying concn.

PVC based membrane of 2-Salicylaldene aminothio phenol formaldehyde

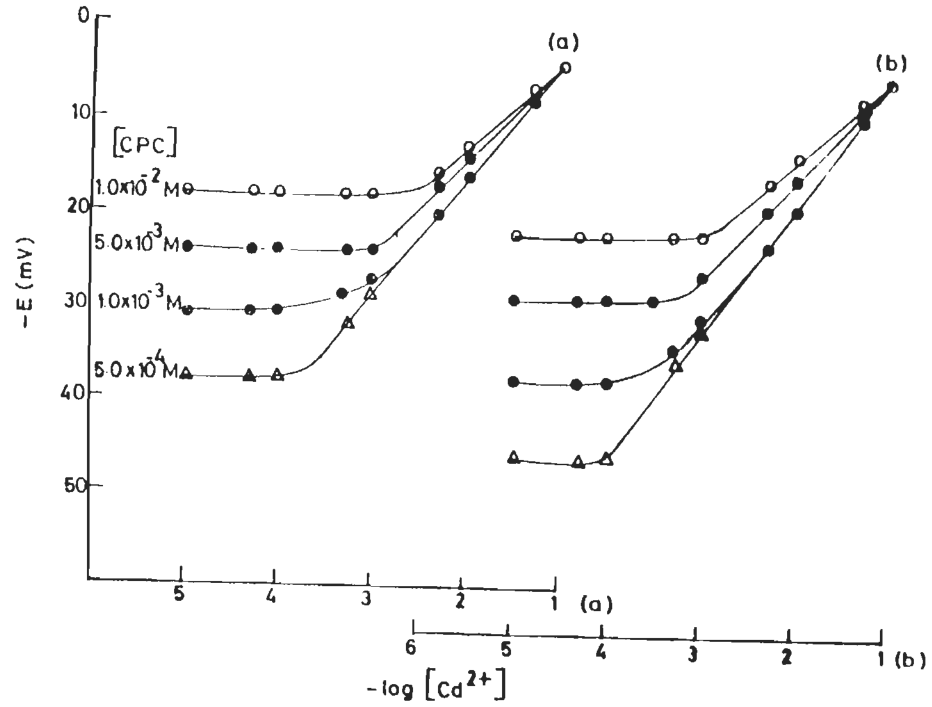

Fig. 31 Potential vs log$[Cd^{2+}]$ plots in the presence of CPC of varying concn. with untreated membranes (a) and treated membranes (b)

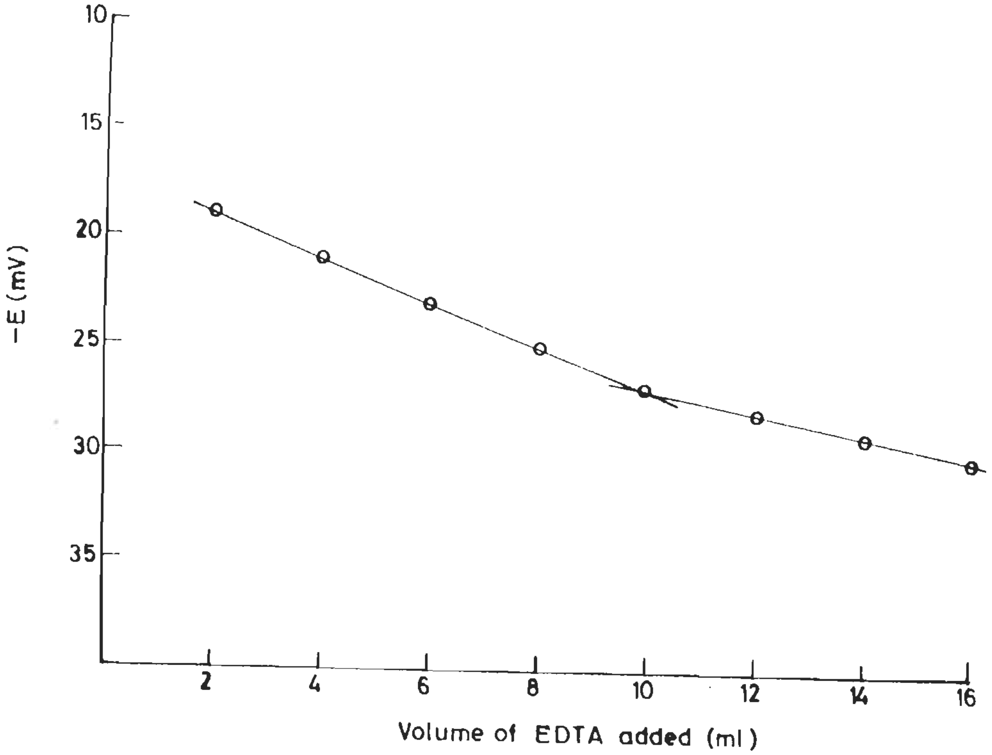

Fig. 32 Titration plot of 10ml of 1.0×10^{-2} M Cd^{2+} ions with 1.0×10^{-2} M EDTA solution

PVC based membrane of 2-Salicylaldene aminothio phenol formaldehyde

The membrane sensor exhibits fairly good selectivity for Cd^{2+} ions over other cations. Selectivity coefficient as estimated by Fixed Interference (Fixed interference=$1.00x10^{-2}M$) and Mixed Solution methods are given in Table-19.

Monovalent cations have high selectivity coefficient values in comparison to other bivalent and trivalent ions. In general the Mixed Solution method depicts a lesser level of interference even in the case of monovalent cations. Polyvalent cations have low values (of the order of 10^{-2}) and would cause no interference.

Some mixed runs in presence of monovalent cations like Na^+, K^+ and NH_4^+ (Fig.30a to 30c) suggest that the electrode can safely be operated upto a level of $5.00x10^{-4}M$ concentration of these ions.

In this case also the replacement of nitrate by chloride does not change the behaviour or working of the electrode assembly.

The effect of cationic surfactant cetyl pyridinium chloride, has also been investigated. The presence of surfactant causes a reduction in the potentials generated by the sensor in comparison to those obtained in the absence of surfactant. There is no change in potential vs $[Cd^{2+}]$ plot obtained in the presence of $5.00x10^{-4}M$ cetyl pyridinium chloride. On further increasing the surfactant concentration the working concentration range of the electrode and the slope of the plot goes down.

Efforts to generate immunity in the membrane sensor by treating it with $1.00x10^{-3}M$ cetyl pyridinium chloride failed though a slight increase in working concentration range in the treated membrane from $1.79x10^{-4}$-$1.00x10^{-4}$ to $1.00x10^{-4}$-$1.00x10^{-1}M$ is quite apparent from Fig.31 and Table- 20.

The sensor has also been successfully used for potentiometric titrations of Cd^{2+} ions. The titration plot of 10 ml of 1.00×10^{-2}M $Cd(NO_3)_2$ with 1.00×10^{-2}M EDTA is shown in Fig 32. The inflection point may be taken as the equivalence point.

IV.6.c. A comparative evaluation of the selectivity of PVC/Polystyrene based membranes

A comparative assessment of the performance of two membranes (based on PVC and polystyrene) reveals that the polystyrene based membrane is a better sensor for cadmium ions.

Though the working pH range and the behaviour in partially non-aqueous medium is almost similar for both the membranes, the working concentration range and the selectivity coefficient values obtained in the case of polystyrene supported one establishes its superiority over PVC based membrane. Response time is also less in the case of polystyrene supported membrane.

IV.7. Estimation of zinc

IV.7.a. Polystyrene based membranes

Membranes, incorporating 2-salicylaldene amino thiophenol formaldehyde as electroactive phase, were equilibrated with 1.00M zinc sulphate solution for five days. Equilibration time was fixed up after some preliminary investigations and only those membranes which were stable and generated reproducible potentials were selected for subsequent studies.

Potentials observed when the membrane is interposed between reference and test solutions of zinc sulphate, are plotted against log concentration of Zn^{2+} ions in Fig.33. The membrane potentials exhibit linearity in the range 1.26×10^{-4}-1.00×10^{-1}M and the slope of the plot is 15 mV/decade of concentration. Thus the sensor can be used to estimate zinc in the concentration range 1.26×10^{-4} to 1.00×10^{-1}M although the electrode is non Nernstian in nature.

To see the effect of varying concentrations of reference solutions calibration plots have also been made by taking reference solutions of 5.00×10^{-2} and 1.00×10^{-2}M concentrations. The magnitude of potential drops (Table-21 & Fig.34) as we reduce the concentration of reference solution. As such it is justified to use a reference solution of 1.00×10^{-1}M zinc sulphate in subsequent investigations.

Membrane potentials stay constant in the pH range of 4 to 6.5, which is the working pH of this electrode assembly Fig.35.

The response time of the electrode is measured at various concentrations of salt solutions and the same is found to be of the order of 70 seconds at all dilutions.

The standard deviation observed, at a fixed concentration of 1.00×10^{-3}M zinc sulphate, is ±0.2 mV for several measurements. Potentials stay constant for about 2 minutes after which a very slow drift is observed. A single membrane has been used to estimate Zn^{2+} ions for a period of 3-4 months without observing any significant change in its performance. Periodic equilibration with primary solution keeps the membrane working for a longer time.

The performance of the membrane electrode has also been assessed in partially non-aqueous medium. Potential vs $[Zn^{2+}]$ in solutions containing 15, 30 and 50% of ethanol and methanol are shown in Figs.36 and 37.

Table-21

Working concentration range of the polystyrene based membrane sensor for zinc ions with reference solution of varying concentration.

Reference solution concentration (M)	Slope mV/decade of concentration	Working concentration range (M)
1.00×10^{-1}	15	1.26×10^{-4} - 1.00×10^{-1}
5.00×10^{-2}	14	1.58×10^{-4} - 1.00×10^{-1}
1.00×10^{-2}	13	1.77×10^{-4} - 1.00×10^{-1}

Table-22

Performance of electrode system in 15, 30 and 50% (volume by volume) non-aqueous medium.

percentage	Slope mV/decade of concentration	Working concentration range (M)
x	15	1.26×10^{-4} - 1.00×10^{-1}
Ethanol		
15	16	1.76×10^{-4} - 1.00×10^{-1}
30	19	3.16×10^{-4} - 1.00×10^{-1}
50	20	3.16×10^{-4} - 1.00×10^{-1}
Methanol		
15	16	1.58×10^{-4} - 1.00×10^{-1}
30	18	1.99×10^{-4} - 1.00×10^{-1}
50	21	3.16×10^{-4} - 1.00×10^{-1}

Table-23

Selectivity of the electrode system for zinc ions in the presence of $1.00\text{x}10^{-2}$M concentration of interfering ions (as calculated by Fixed Interference and Mixed Solution methods).

Interfering ion	Selectivity coefficient [$K^{Pot}_{A,B}$]	
	Fixed Interference Method	Mixed Solution Method
Na^+	25.17	9.04
K^+	25.17	9.04
Tl^+	19.95	7.18
Li^+	35.48	12.77
Ag^+	32.36	11.65
NH_4^+	28.18	10.15
Mn^{2+}	$2.82\text{x}10^{-1}$	$1.01\text{x}10^{-1}$
Pb^{2+}	$5.01\text{x}10^{-1}$	$1.80\text{x}10^{-1}$
Cd^{2+}	$5.01\text{x}10^{-1}$	$1.80\text{x}10^{-1}$
Ba^{2+}	$3.98\text{x}10^{-1}$	$1.43\text{x}10^{-1}$
Sr^{2+}	$3.16\text{x}10^{-1}$	$1.14\text{x}10^{-1}$
Co^{2+}	$3.51\text{x}10^{-1}$	$1.28\text{x}10^{-1}$
Ca^{2+}	$3.51\text{x}10^{-1}$	$1.28\text{x}10^{-1}$
Cu^{2+}	$3.51\text{x}10^{-1}$	$1.28\text{x}10^{-1}$
Mg^{2+}	$3.51\text{x}10^{-1}$	$1.28\text{x}10^{-1}$
Al^{3+}	$6.31\text{x}10^{-2}$	$2.27\text{x}10^{-2}$
La^{3+}	$5.37\text{x}10^{-2}$	$1.93\text{x}10^{-2}$
Fe^{3+}	$8.71\text{x}10^{-2}$	$3.14\text{x}10^{-2}$

Table-24(a)

Performance of the electrode system in presence of the detergent cetyl pyridinium chloride (CPC).

Untreated membrane

Concentration of CPC (M)	Slope mV/decade of concentration	Working concentration range (M)
x	14	$1.26\text{x}10^{-4}$ - $1.00\text{x}10^{-1}$
$7.00\text{x}10^{-5}$	14	$1.26\text{x}10^{-4}$ - $1.00\text{x}10^{-1}$
$1.00\text{x}10^{-3}$	14	$3.55\text{x}10^{-4}$ - $1.00\text{x}10^{-1}$
$5.00\text{x}10^{-3}$	13	$1.00\text{x}10^{-3}$ - $1.00\text{x}10^{-1}$
$1.00\text{x}10^{-2}$	12	$2.51\text{x}10^{-3}$ - $1.00\text{x}10^{-1}$

Table-24(b)

Performance of the membrane conditioned with $1.00\text{x}10^{-3}$M cetyl pyridinium chloride (CPC).

Concentration of CPC (M)	Slope mV/decade of concentration	Working concentration range (M)
x	15	$1.00\text{x}10^{-4}$ - $1.00\text{x}10^{-1}$
$7.00\text{x}10^{-5}$	15	$1.00\text{x}10^{-4}$ - $1.00\text{x}10^{-1}$
$1.00\text{x}10^{-3}$	15	$3.16\text{x}10^{-4}$ - $1.00\text{x}10^{-1}$
$5.00\text{x}10^{-3}$	14	$7.08\text{x}10^{-4}$ - $1.00\text{x}10^{-1}$
$1.00\text{x}10^{-2}$	13	$1.58\text{x}10^{-3}$ - $1.00\text{x}10^{-1}$

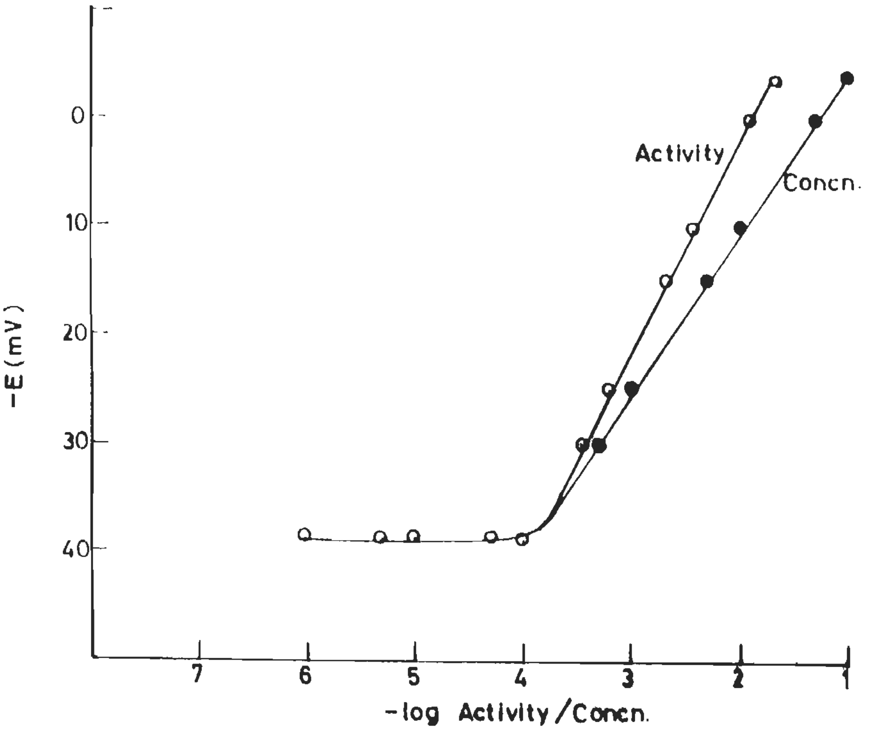

Fig. 33 Potential vs log$[Zn^{2+}]$ plots

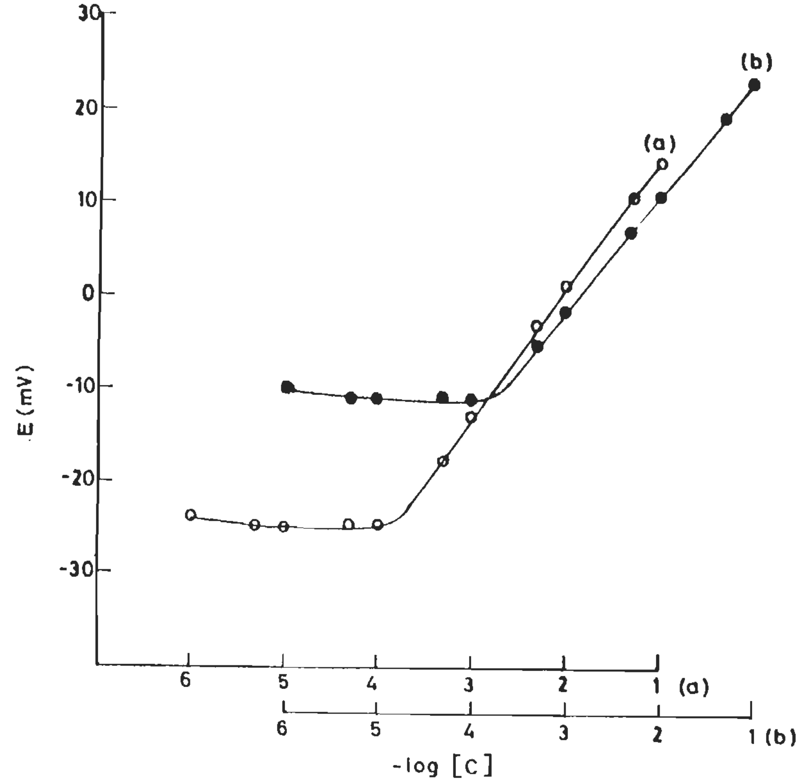

Fig.34 Potential vs log$[Zn^{2+}]$ plots with reference solution concn.
(a) 5.0×10^{-2}M (b) 1.0×10^{-2}M

Polystyrene based membrane of 2-Salicylaldene aminothio phenol formaldehyde

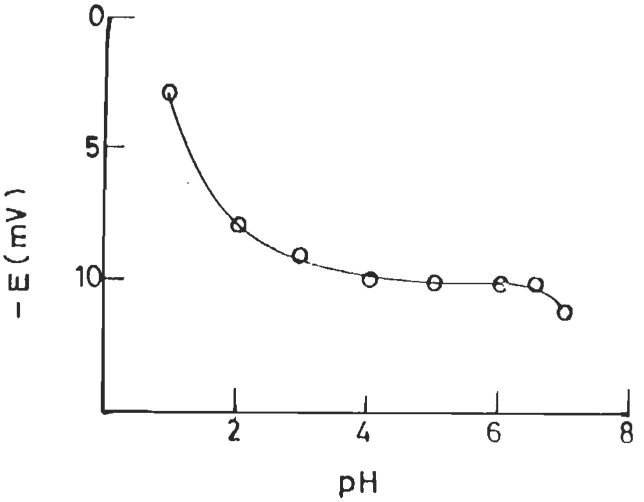

Fig. 35 Potential vs pH plot $[Zn^{2+}$ concn. = 1.0×10^{-2} M]

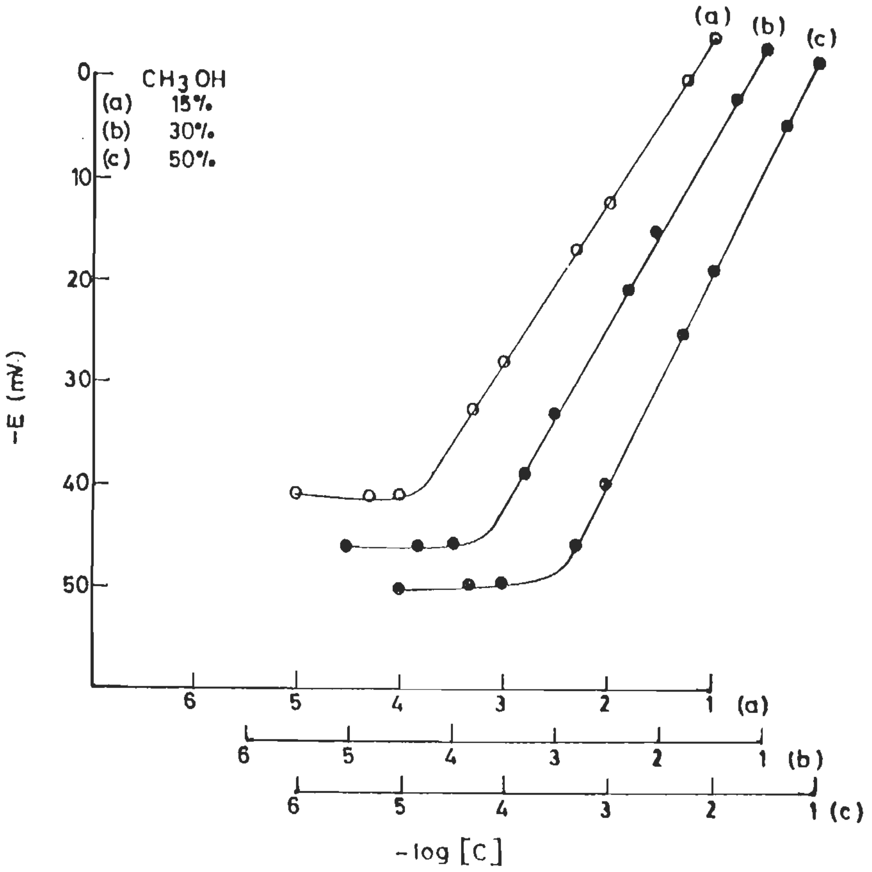

Fig. 36 Potential vs log$[Zn^{2+}]$ plots in partially non-aqueous medium

Polystyrene based membrane of 2-Salicylaldene aminothio phenol formaldehyde

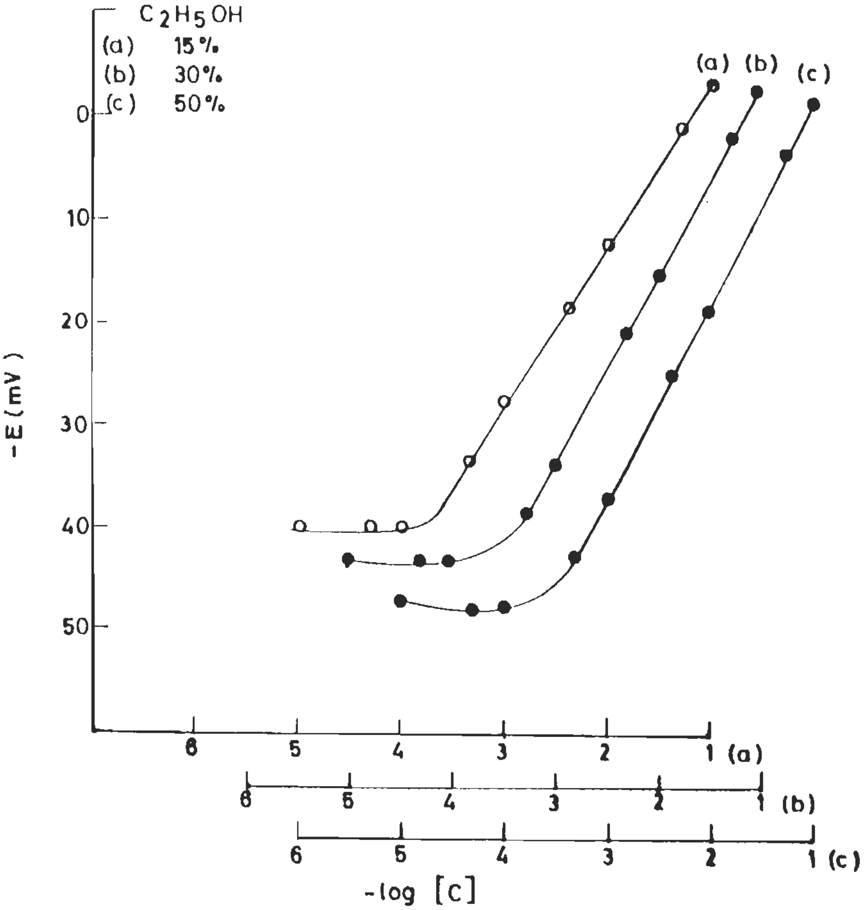

Fig. 37 Potential vs log$[Zn^{2+}]$ plots in partially non-aqueous medium

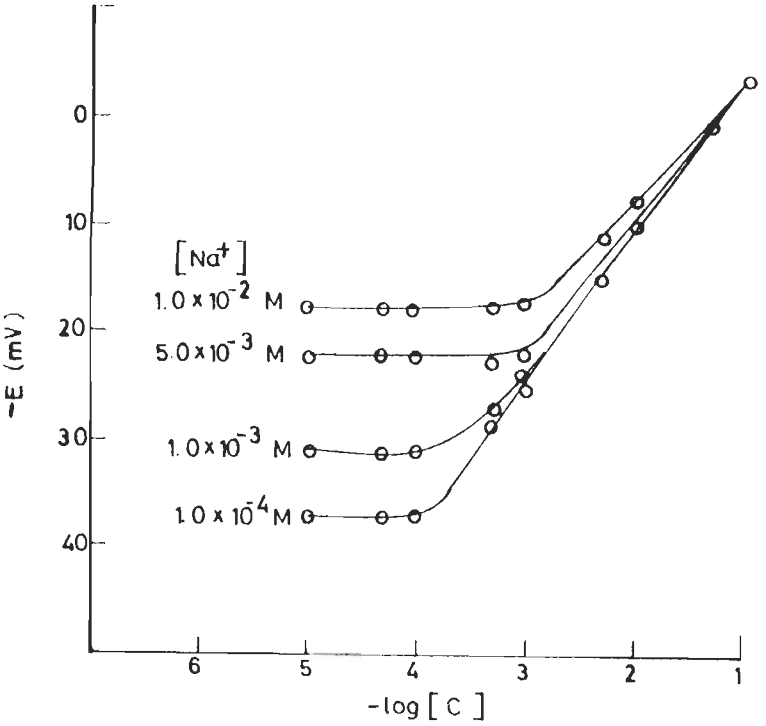

Fig. 38(a) Potential vs log$[Zn^{2+}]$ plot in the presence of Na^+ of varying concn.

Polystyrene based membrane of 2-Salicylaldene aminothio phenol formaldehyde

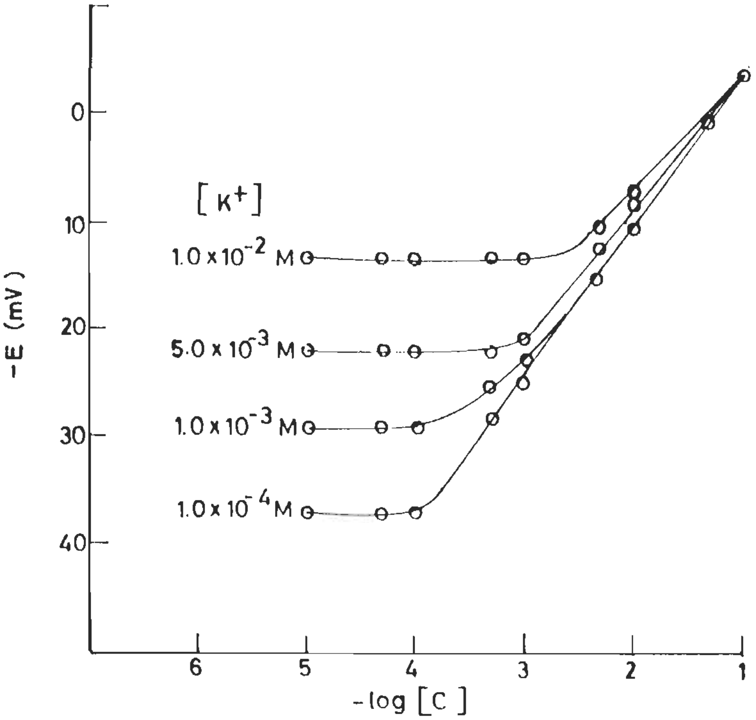

Fig. 38(b) Potential vs log$[Zn^{2+}]$ plots in the presence of K^+ of varying concn.

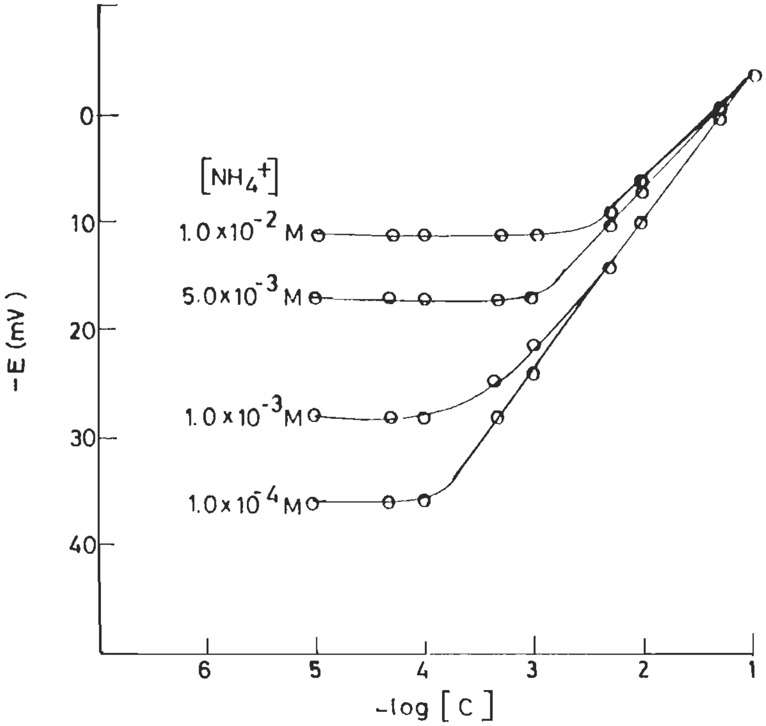

Fig. 38(c) Potential vs log$[Zn^{2+}]$ plots in the presence of NH_4^+ of varying concn.

Polystyrene based membrane of 2-Salicylaldene aminothio phenol formaldehyde

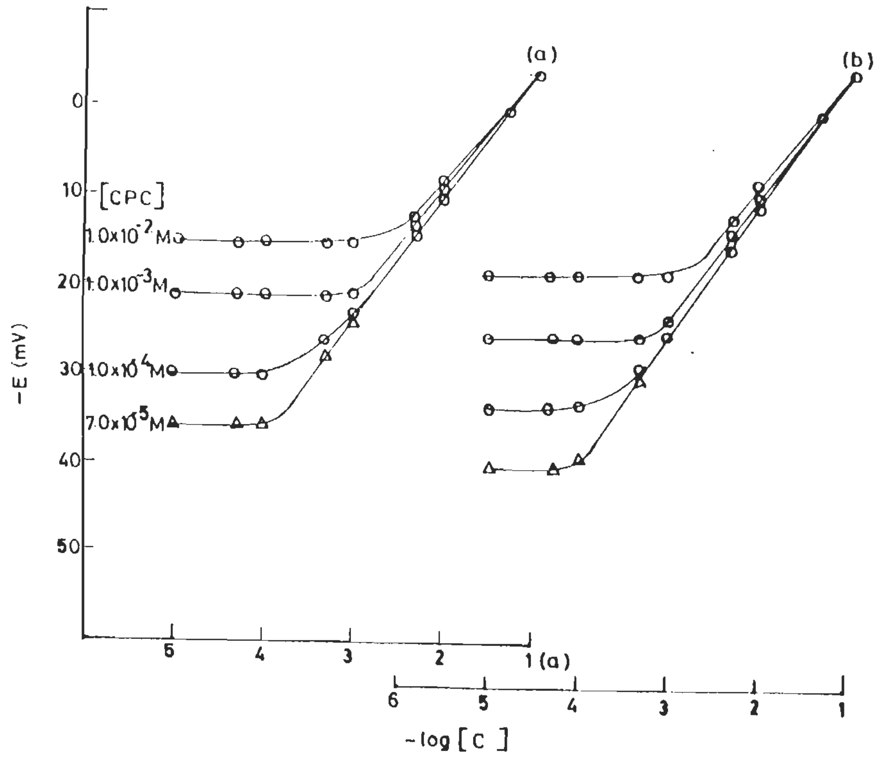

Fig.39 Potential vs log$[Zn^{2+}]$ plots in the presence of CPC of varying concn. with untreated membranes (a) and treated membranes (b)

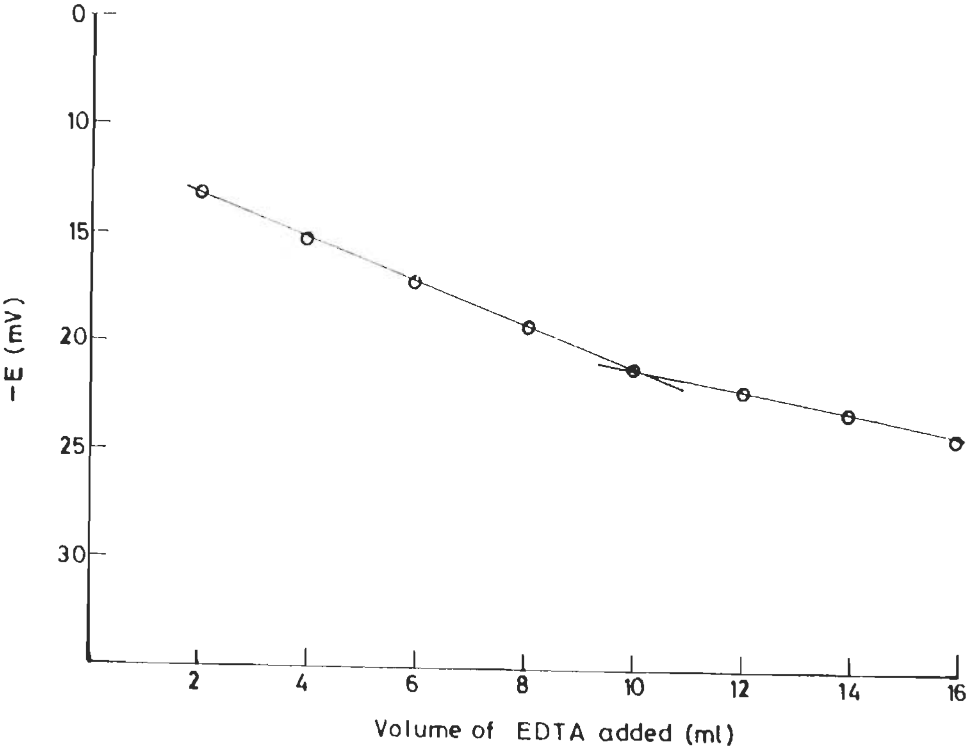

Fig. 40 Titration plot of 10ml of 1.0×10^{-2} M Zn^{2+} ions with 1.0×10^{-2}M EDTA solution

Polystyrene based membrane of 2-Salicylaldene aminothio phenol formaldehyde

The plots in 15% non-aqueous medium reveal perfect linearity with a slight change in working concentration range and slope of the plot and a further increase in non-aqueous content quite clearly shows the interference in the functioning of this sensor (Table-22). Even the response time also increased in non-aqueous solutions. As such it can only be used in pure aqueous solutions.

Interferences of other cations, if present, along with the primary ion, are estimated by the Fixed Interference and Mixed Solution methods and reported in terms of selectivity coefficient values (Table-23). Potentials are observed at a fixed concentration of interfering ions (1.00×10^{-2}M). Selectivity coefficient values for a number of interfering ions, as computed from the potential data, are given in Table-23. Selectivity coefficient pattern (as calculated by Fixed Interference method) indicates significant interference of monovalent cations where as bivalent and multivalent ions do not seem to disturb the working of this electrode assembly. Selectivity coefficients as obtained by Mixed Solution method are, in general, lower in comparison to the one obtained by Fixed Interference method. There is a marked difference in the values obtained by these two methods in the case of monovalent ions. The monovalent ions seem to record lesser interference if the values obtained by Mixed Solution method are taken into consideration.

In order to assess the working feasibility of the membrane sensor, in presence of monovalent cations some mixed runs are also made with primary ions along with different level of interference of monovalent cations. Potential vs concentration plots observed at various interfering level of Na^+, K^+ and NH_4^+ are shown in Fig.38(a), to 38(c).

It is evident that these ions do not cause any disturbance upto a concentration of 1.00×10^{-4}M or less. Beyond this concentration the sensor can not be used in the presence of monovalent cations. Other multivalent ions would normally not interfere unless present in very large concentration - a situation which is hardly met with.

Interference of anions on the working of the electrode assembly has also been seen. Potentials vs concentration plots in Hence different anionic solutions can be easily used without any interference.

Quite often the proposed assembly may be required to estimate the metal ions is presence of detergents. As such the working of the membrane sensor has also been checked in presence of surfactant ions. Fig. 39 and Table-24(a) show the complete tolerance of a cationic surfactant, cetyl pyridinium chloride (CPC), upto a concentration level of 7.00×10^{-5}M. But higher concentrations of this surfactant cause serious interference in the working of the membrane sensor.

Efforts were also made to condition the membrane by treating it with the surfactant ions at 1.00×10^{-3}M concentration to make it immune to the disturbances caused by the presence of higher concentrations of the same. Although the sensor does not develop immunity to the disturbing effect of detergent, at higher concentrations, one interesting feature is the enhancement of the working concentration range of the treated membrane

(1.26×10^{-4}-1.00×10^{-1}M to 1.00×10^{-4}-1.00×10^{-1}M) (Table-24). The level of interference, at larger concentrations of detergent, also goes down.

This sensor could also be used successfully for potentiometric titrations of zinc ions. The titration plot of 10 ml of 1.00×10^{-2}M zinc sulphate with 1.00×10^{-2}M EDTA is shown in Fig.40. The inflexion point is quite sharp and may be taken as the equivalence point.

IV.7.b. PVC based membranes

PVC based membranes of the same compound 2-salicylaldene aminothiophenol formaldehyde were also tried for the estimation of Zn^{2+} ions. These were equilibrated with 1.0M zinc sulphate solution for five days a precondition for the membrane to generate stable potentials. Potentials were measured at 30±1 °C against saturated calomel electrodes proceeding from lower to higher concentrations (10^{-6}-10^{-1}M).

The membrane potentials (Fig.41) exhibit linearity in the range 2.51×10^{-4} to 1.00×10^{-1}M concentration of zinc ions and the trend is non Nernstian with a slope of 12 mV per decade of concentration. The membrane electrode under discussion can thus be used to estimate zinc ions in the concentration range mentioned above. In dilute solutions the response of the electrode deviates from the linear behaviour and the potentials stay constant below a concentration of 1.00×10^{-4}M.

The electrode assembly is found to function best with 1.00×10^{-1}M reference solution. It is evident by observing the potentials with reference solutions of varying concentration.

Table-25

Working concentration range of the PVC based membrane sensor for zinc ions with reference solution of varying concentration.

Reference solution concentration (M)	Slope mV/decade of concentration	Working concentration range (M)
1.00×10^{-1}	12	2.51×10^{-4} - 1.00×10^{-1}
5.00×10^{-2}	12	3.16×10^{-4} - 1.00×10^{-1}
1.00×10^{-2}	11	3.16×10^{-4} - 1.00×10^{-1}

Table-26

Performance of electrode system in 15, 30 and 50% (volume by volume) non-aqueous medium.

percentage	Slope mV/decade of concentration	Working concentration range (M)
x	12	2.51×10^{-4} - 1.00×10^{-1}
Ethanol		
15	15	3.16×10^{-4} - 1.00×10^{-1}
30	17	3.98×10^{-4} - 1.00×10^{-1}
50	18	4.46×10^{-4} - 1.00×10^{-1}
Methanol		
15	15	3.16×10^{-4} - 1.00×10^{-1}
30	16	5.62×10^{-4} - 1.00×10^{-1}
50	18	5.62×10^{-4} - 1.00×10^{-1}

Table-27

Selectivity of the electrode system for zinc ions in the presence of 1.00×10^{-2}M concentration of interfering ions (as calculated by Fixed Interference and Mixed Solution methods).

Interfering ion	Selectivity coefficient $[K^{Pot}_{A,B}]$	
	Fixed Interference Method	Mixed Solution Method
Na^+	25.17	9.04
K^+	31.62	11.38
Tl^+	28.18	10.15
Li^+	39.81	14.33
Ag^+	39.81	14.33
NH_4^+	31.62	11.38
Mn^{2+}	3.16×10^{-1}	1.14×10^{-1}
Pb^{2+}	5.62×10^{-1}	2.02×10^{-1}
Cd^{2+}	5.01×10^{-1}	1.80×10^{-1}
Ba^{2+}	4.47×10^{-1}	1.61×10^{-1}
Sr^{2+}	3.98×10^{-1}	1.43×10^{-1}
Co^{2+}	5.01×10^{-1}	1.80×10^{-1}
Ca^{2+}	3.98×10^{-1}	1.43×10^{-1}
Cu^{2+}	3.51×10^{-1}	1.28×10^{-1}
Mg^{2+}	2.82×10^{-1}	1.01×10^{-1}
Al^{3+}	8.91×10^{-2}	3.21×10^{-2}
La^{3+}	6.31×10^{-2}	2.27×10^{-2}
Fe^{3+}	9.78×10^{-2}	3.52×10^{-2}

Table-28(a)

Performance of the electrode system in presence of the detergent cetyl pyridinium chloride (CPC).

Untreated membrane

Concentration of CPC (M)	Slope mV/decade of concentration	Working concentration range (M)
x	12	2.51×10^{-4} - 1.00×10^{-1}
5.00×10^{-5}	12	2.51×10^{-4} - 1.00×10^{-1}
1.00×10^{-3}	12	7.94×10^{-4} - 1.00×10^{-1}
5.00×10^{-3}	11	1.00×10^{-3} - 1.00×10^{-1}
1.00×10^{-2}	10	3.16×10^{-3} - 1.00×10^{-1}

Table-28(b)

Performance of the membrane conditioned with 1.00×10^{-3}M cetyl pyridinium chloride (CPC).

Concentration of CPC (M)	Slope mV/decade of concentration	Working concentration range (M)
x	15	1.41×10^{-4} - 1.00×10^{-1}
5.00×10^{-5}	15	1.41×10^{-4} - 1.00×10^{-1}
1.00×10^{-3}	15	3.55×10^{-4} - 1.00×10^{-1}
5.00×10^{-3}	13	7.08×10^{-4} - 1.00×10^{-1}
1.00×10^{-2}	12	1.00×10^{-3} - 1.00×10^{-1}

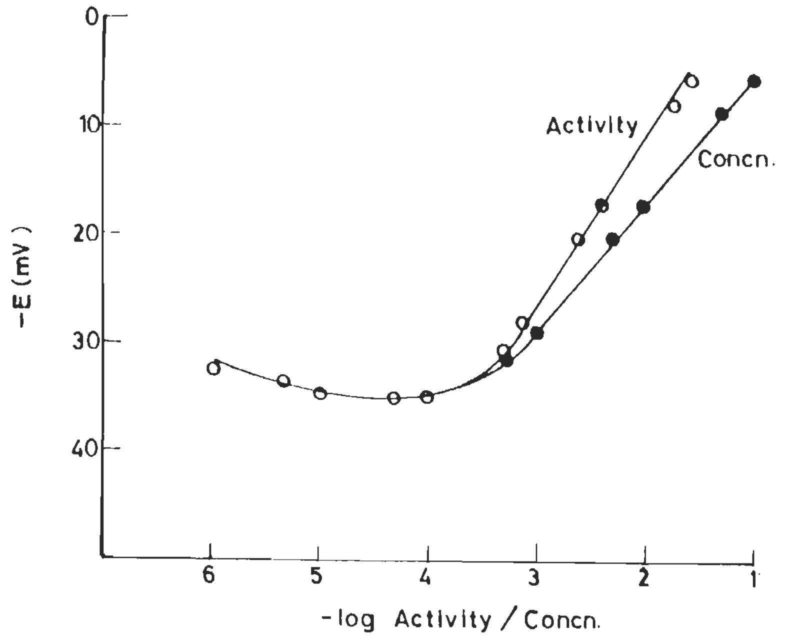

Fig. 41 Potential vs log $[Zn^{2+}]$ plots

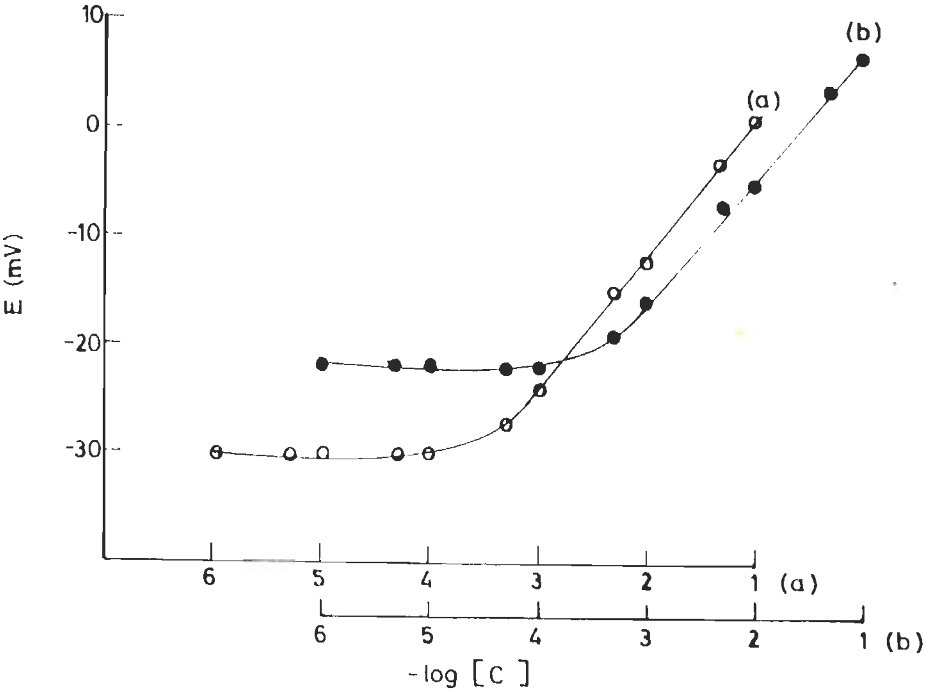

Fig. 42 Potential vs log $[Zn^{2+}]$ plots with reference solution concn. (a) 5.0×10^{-2} M (b) 1.0×10^{-2} M

PVC based membrane of 2-Salicylaldene aminothio phenol formaldehyde

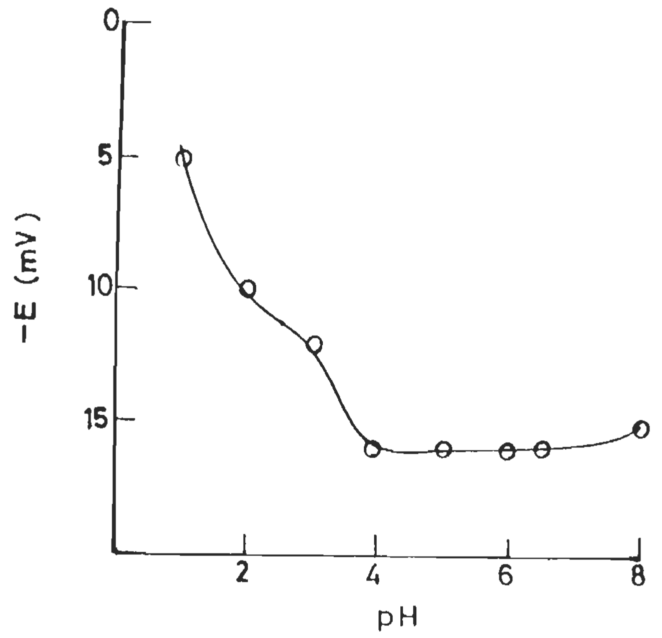

Fig. 43 Potential vs pH plot $[Zn^{2+}$ concn. $= 1.0 \times 10^{-2}$ M$]$

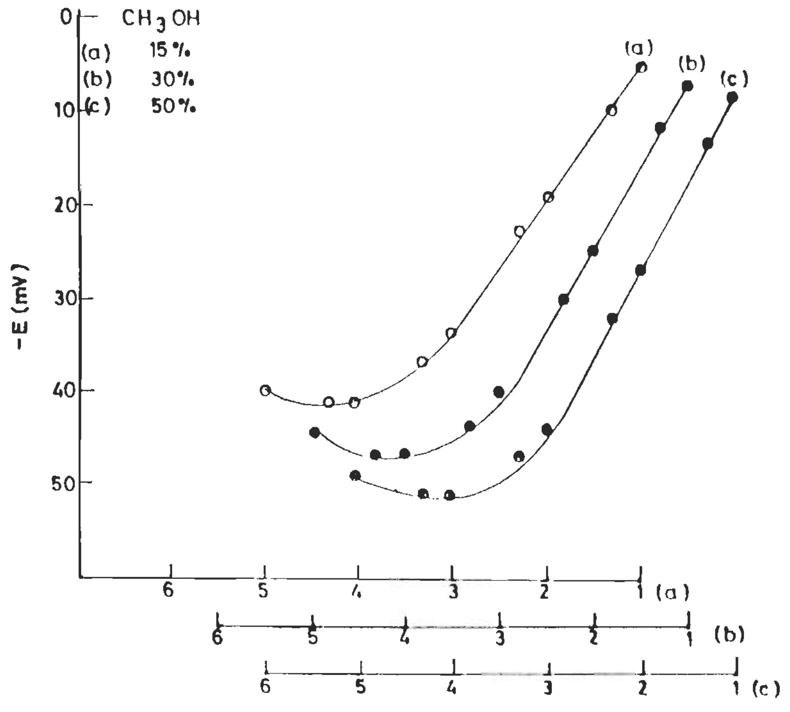

Fig. 44 Potential vs log $[Zn^{2+}]$ plots in partially non-aqueous medium

PVC based membrane of 2-Salicylaldene aminothio phenol formaldehyde

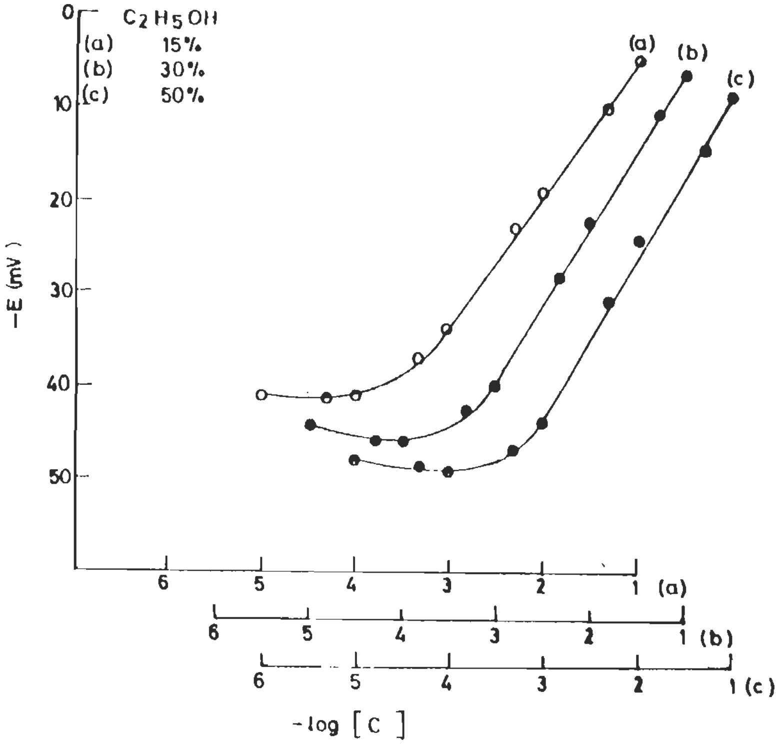

Fig. 45 Potential vs log $[Zn^{2+}]$ plots in partially non-aqueous medium

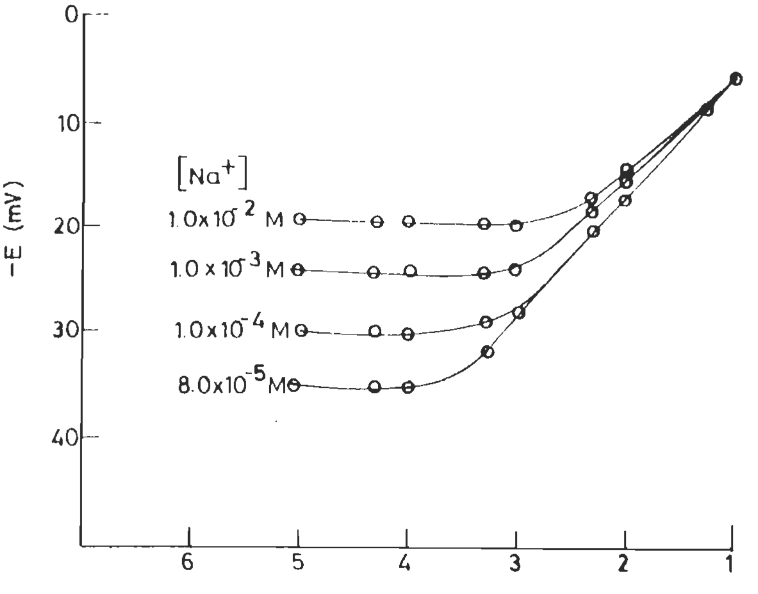

Fig. 46 (a) Potential vs log $[Zn^{2+}]$ plots in the presence of Na^+ of varying concn.

PVC based membrane of 2-Salicylaldene aminothio phenol formaldehyde

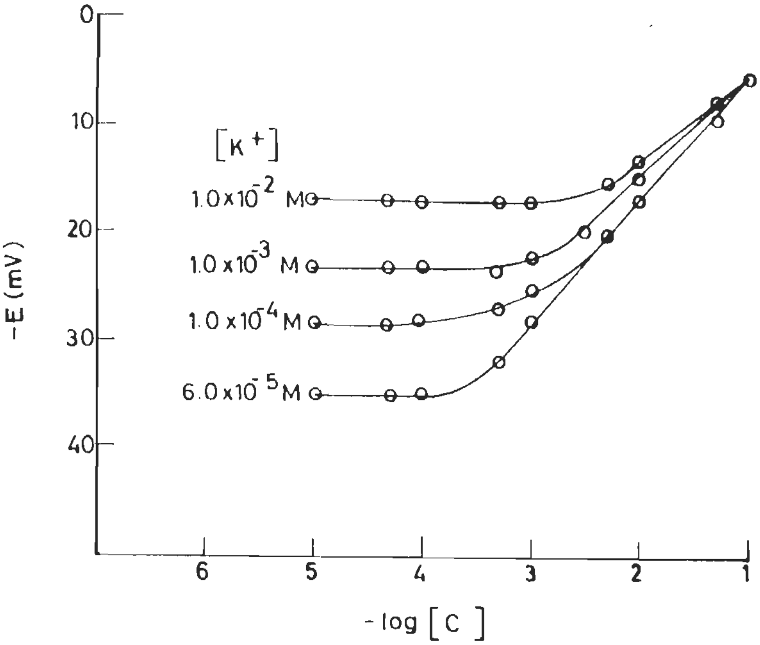

Fig. 46 (b) Potential vs log$[Zn^{2+}]$ plots in the presence of K^+ of varying concn.

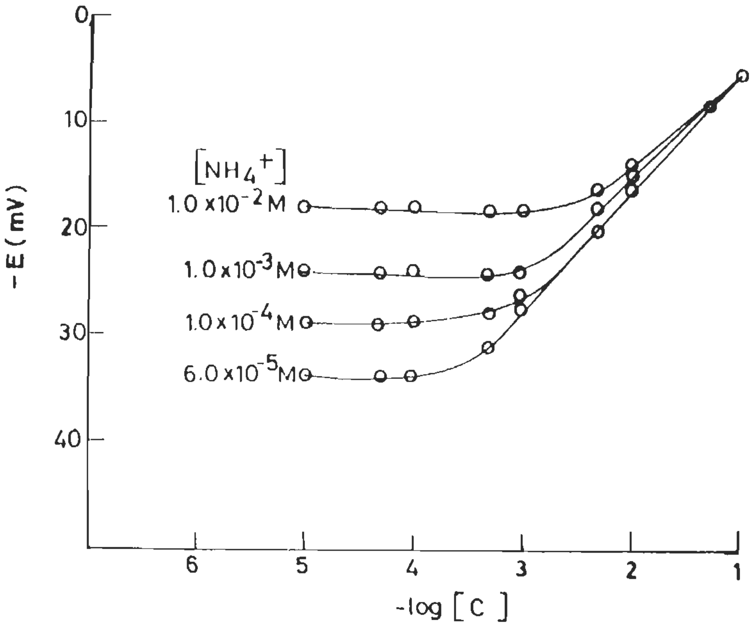

Fig. 46 (c) Potential vs log$[Zn^{2+}]$ plots in the presence of NH_4^+ of varying concn.

PVC based membrane of 2-Salicylaldene aminothio phenol formaldehyde

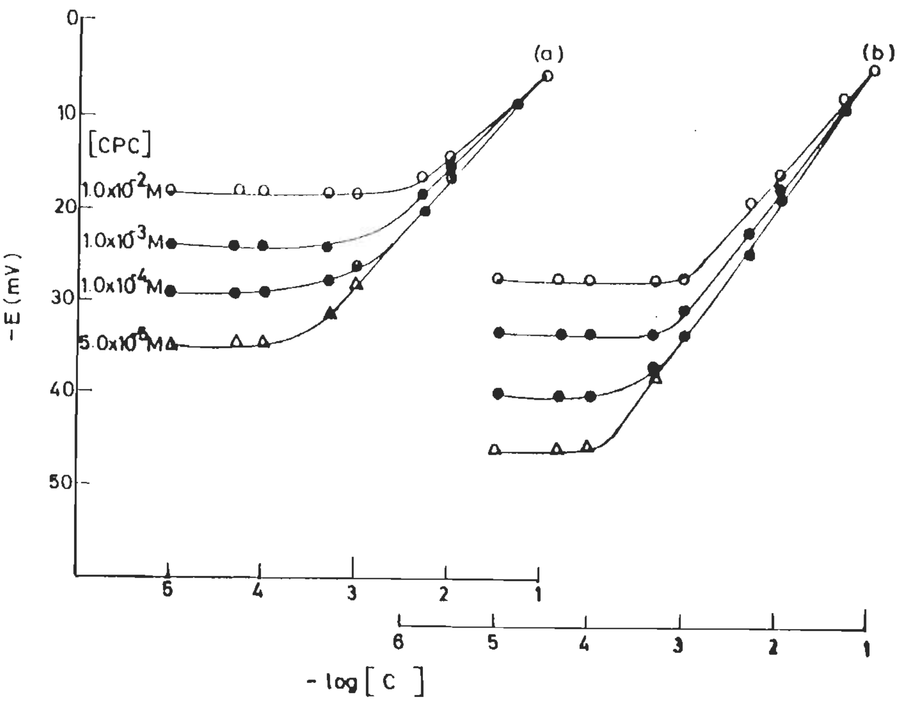

Fig. 47 Potential vs log $[Zn^{2+}]$ plots in the presence of CPC of varying concn. with untreated membranes (a) and treated membranes (b)

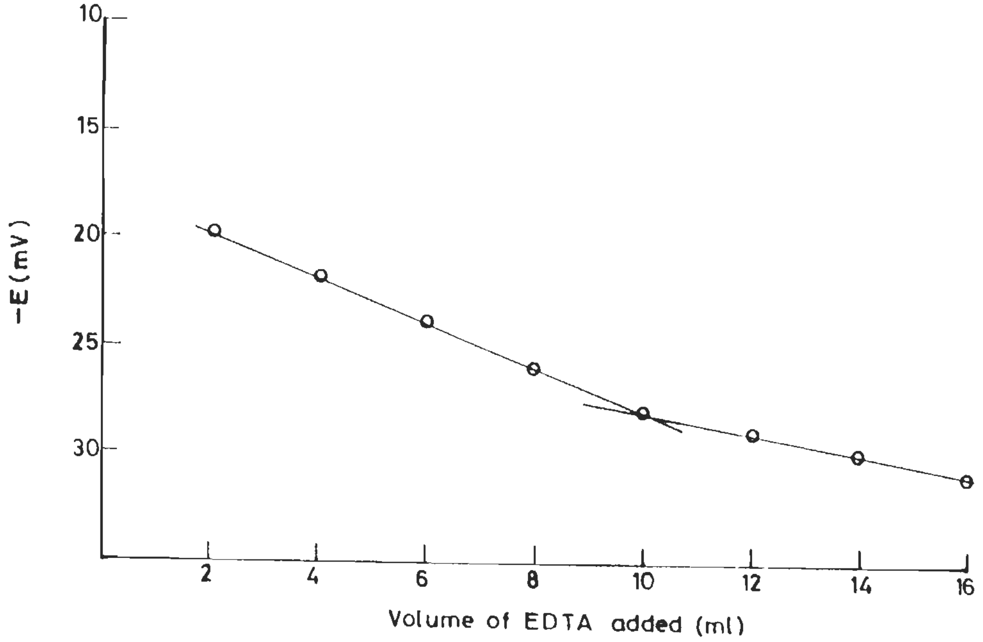

Fig. 48 Titration plot of 10ml of 1.0×10^{-2} M Zn^{2+} ions with 1.0×10^{-2} M EDTA solution

PVC based membrane of 2-Salicylaldene aminothio phenol formaldehyde

Potential vs concentration plots (Fig.42) with 5.00×10^{-2} and 1.00×10^{-2}M reference solutions of Zn^{2+} ions generate potentials of lower order and the working concentration range also changes (Table-25). Thus the entire investigations with this electrode assembly, as well, were performed with 1.00×10^{-1}M zinc sulphate as reference solution.

The response time of the said membrane is 72 seconds. The same response time is obtained whether the measurements are made from low to high concentration or vice versa. Potentials stay constant for more than 3 minutes and are quite reproducible. Reliability of the electrode is determined by periodically monitoring the potentials at 1.00×10^{-2}M concentration of zinc ions and the standard deviation of almost 20 measurements is ±0.2mV.

Potential vs pH plot (Fig.43) reveal the working range of the sensor as 4 to 6.5. A sharp change in potential at low pH may be attributed to the interference by hydrogen ions.

The utility of the electrode assembly has also been investigated in partially non-aqueous medium. Potential vs concentration plots in 15, 30 and 50% ethanolic and methanolic solutions are shown in Figs.44 & 45. Although the response is linear in partially non-aqueous medium, the working concentration range of the sensor goes down with simultaneous increase in slope of the plot (Table-26). Along with it, the response time of membrane sensor also increases. As such the electrode assembly has almost no validity even in partially non-aqueous medium.

In order to investigate the selectivity of this sensor, the response of the electrode was examined in the presence of various foreign ions. Potentiometric selectivity coefficient (Table-27) are obtained by both the Fixed Interference and Mixed Solution methods. The value of the parameter is generally quite low for polyvalent cations. As such these ions do not interfere. High selectivity coefficient values (as calculated by Fixed Interference method) suggest that monovalent cations do interfere in the working of the sensor but at the same time even in case of monovalent cations comparatively low values of this parameter are obtained by Mixed Solution method. To assess the actual interference level of monovalent ions some mixed runs are made in the presence of these ions. Plots in case of Na^+, K^+ and NH_4^+ ions are shown in Fig.46(a)-(c). Potential vs log $[Zn^{2+}]$ plots at a level of interference of 8.00×10^{-5}M almost completely overlap the plot obtained in solutions without any interference. As the concentration of monovalent ions increases, a divergence from the original plot is quite apparent. Thus the electrode system can be safely operated in the presence of 8.00×10^{-5}M concentration of monovalent cations.

Besides the cations, the effect of some anions on the working of membrane sensor has also been observed. The working concentration range and the slope of the plot is found to be almost same when membrane electrode is used in contact with $ZnSO_4$, $Zn(NO_3)_2$ and $ZnCO_3$. Thus anions do not interfere in the working of the assembly.

The working of membrane sensor has also been checked in presence of a cationic surfactant cetyl pyridinium chloride. The plots of potential vs log $[Zn^{2+}]$ in presence of varying concentration of cetyl pyridinium chloride is shown in Fig. 47 and the results are depicted in Table-28. Surfactant ion does not cause any disturbance up to a concentration of 5.00×10^{-5}M. Beyond this concentration the surfactant ions causes significant interference. Efforts made to make the electrode immune to the disturbing effects of the surfactant ions failed.

Even the PVC based sensor can be used as an end point indicator in potentiometric titrations involving Zn^{2+} ions. The titration of 10 ml of 1.00×10^{-2}M $ZnSO_4$ solution with 1.00×10^{-2}M EDTA is shown in Fig.48. The inflexion point in the plot corresponds to the stoichiometric ratio of EDTA required to neutralize the zinc sulphate solution.

IV.7.c. Comparative evaluation

A comparative assessment of the polystyrene and PVC based membranes for zinc ions shows that the performance of the electrode assembly having polystyrene as binder material is better even in this case (reference Cd^{2+} ions).

IV.8 A. comparative evaluation of polystyrene and PVC membranes

An overview of the data recorded during the estimation of cadmium and zinc with the help of 2-salicylaldene aminothiophenol membranes shows that the proposed electrode assembly displays a better selectivity for cadmium in comparison to zinc ions.

In general the polystyrene based membranes are found to be much better than the one supported by PVC. A detailed step wise comparison of the two sensors is given below.

Polystyrene based membranes show response for cadmium in a wide concentration range 1.00×10^{-4}-1.00×10^{-1}M with a slop of 15 mV/decade of concentration. The performance is better than those of PVC based membranes where the range is $1.79 \times 10^{-4}-1.00 \times 10^{-4}$ M and the slope of the plot is 12 mV/decade of concentration. Similarly for zinc ions the working concentration range and the slope of the plot is found to be better for polystyrene supported membranes.

The response time of polystyrene based membranes is generally faster in comparison to PVC based membranes in both the cases (i.e., for Cd^{2+}, Zn^{2+}).

Cd^{2+} can be estimated in solutions having a 15% non-aqueous content with a polystyrene based membrane sensor while the PVC based membrane does not function in non-aqueous mediums. Estimation of zinc, in partially non-aqueous medium, is not possible at all.

The selectivity coefficient in the case of Cd^{2+} ion suggests the superiority of polystyrene supported membranes over the PVC based ones. Even in the case of zinc ions, polystyrene based membrane electrodes are superior. Polystyrene supported membranes, during the estimation of Cd^{2+} ions, have higher tolerance limit of monovalent cations and surfactants. Thus the organic resin, under investigation, would form a better membrane electrode for cadmium in comparison to zinc and the performance of polystyrene based membrane is superior to the one prepared with the help of PVC.

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CHAPTER - V

PRACTICAL APPLICATIONS

V.1. Introduction

Ion-selective electrodes allow the specific and quantitative determination of an almost unimaginable number of substances, varying from simple inorganic ions through amino acids to complex organic molecules. The wide range of applications, low material requirements and simplicity of analytical procedure make this technique handy for analytical chemists, physiologists, material researchers, biologists, geologists and environmental protection specialists. Because of these undisputed advantages, ion-selective electrodes are used in industrial processes, electroplating, toxicology, Industrial hygiene and water and air pollution.

Concern for maintaining the quality of life by the preservation of clean environment has further given a boost for the development of selective membrane sensors which could be successfully used for the monitoring of environment. The need to have continuously monitoring gadgets and field monitoring devices has led to the development of some elegant sensing electrodes. Many reviews have been devoted to practical applications of ion-selective electrodes (1,2). Besides this many specialized reviews (3-5) deal with the application of ISEs in environmental monitoring.

Several papers have been published on the analysis of water by using ISEs. Fluoride has been determined with ion-selective electrode in presence of water soluble organic substances (6). Srivastava and co-workers (7) estimated sulphate ion concentration in water and industrial wastes.

The level of nitrates is increasing dangerously in virtually all kinds of water. In the presence of ammonical nitrogen and sulphur dioxide emissions, ammonium sulphate can be formed in the atmosphere in addition to sulphuric acid, which adversely affects human health. Hence, the determination of ammonical nitrogen in waste water is important. Many monitors of ammonia in water operate in industrially developed countries and are based on the ammonia gas probe.

Evanse and Patridge (8) determined it's content in various water samples and the results were in good agreement with those of spectrophotometric determinations. Ruzicka (9) demonstrated the use of air-gap electrode on the determination of ammonical nitrogen in waste water.

Potable and waste waters as well as water in swimming pools, are commonly disinfected by chlorination. To determine the residual chlorine and its ability to oxidise iodide can be exploited. Moody et al. (10), reported a chloride selective electrode with a Nernstian response down to 3.5 ppb of Cl_2.

Recently an ion-selective electrode (11) based on tetra(p-tolyl) vinylenediphosphine oxide was reported for the estimation of water hardness. The total Ca and Mg content of water sample acidified to pH 5-6 was determined down to 0.1mM concentration.

Several commercial ISEs are available for heavy metal cations (e.g., Pb^{2+}, Cd^{2+}, Hg^{2+} etc.). These are chiefly being used for the speciation of heavy metals i.e., for studying the distribution of the metals among various chemical forms in water.

Determination of various metal ions, in sea water using ISEs is discussed by Takashi (12). Cupric ion is of great environmental concern in natural waters, owing to it's high toxicity towards aquatic organisms. Potentiometry with a cupric ion-selective electrode is the only technique that allows selective determination of cupric ion activity without disturbing equilibria in the sample. Paper by Hoyer (13) demonstrate that it is possible to obtain Nernstian calibration slopes for a Cu-ISE in the range of cupric ion buffers with high chloride content. Another example of such an application is given by Stella (14). The author separates the colloidal particles from the solution and measure its cupric ion activity using a Cu-ISE.

The overall concentration of some metals can also be determined indirectly. The toxicity of mercury is utilized for the determination of mercury on the basis of urease inhibition (15). For monitoring the concentration of cyanide in waste waters, analysers containing ISEs, have been constructed by Frant and co-workers (16). Srivastava and co-workers (17) also reported a membrane sensor for the estimation of Cr(VI) as chromate in water tannery and plating wastes.

The commercially available electrodes are all imported stuff and cost wise these are beyond the reach of small scale entrepreneurs. The stringent financial regulations regarding the availability of foreign currency further adds to the difficulties of those who can afford to purchase it. Naturally, in national context, it becomes imperative to develop reasonably cheap and selective sensors for monitoring some species in a particular situation.

Some of the sensors developed in this project and described in this dissertation have been applied to assess metal ions in waste waters. Experiments conducted in this regard are described in subsequent paragraphs.

V.2. Geographical locations and other details of the samples collected for analysis.

The upper part of the Hindon river (a local river) basin in Saharanpur district, Uttar Pradesh, India, has a number of industries related to paper, milk products, distillery and many small scale cottage industries dealing with electroplating, paper board, chemicals and rubber etc. The waste effluents generated from these industries are released on the low lands and tributaries of the Hindon river system passing through this area. Hindon river has two perennial tributaries viz. Dhamola nala* and Nagdeo nala . Nagdeo nala confluences with Padli nala and Indana nala near Naugaja before merging into the river Hindon near Ghogreki village (Fig.1).

Samples, collected from three different nalas namely Padli nala , Nagdeo nala and Indana nala shown in Fig.1. by SW2, SW3 & SW4, were obtained from the Deptt. of Hydrology, University of Roorkee, Roorkee. The Department of Hydrology of this University, under some Govt. of India sponsored programme, has undertaken exhaustive investigations and analysed the waste water coming out of the above mentioned industries and have observed the water quality of Hindon river at strategic points. Important

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* A `nala is a vernacular word meaning a rivulet, which may be tributary to a stream or river.

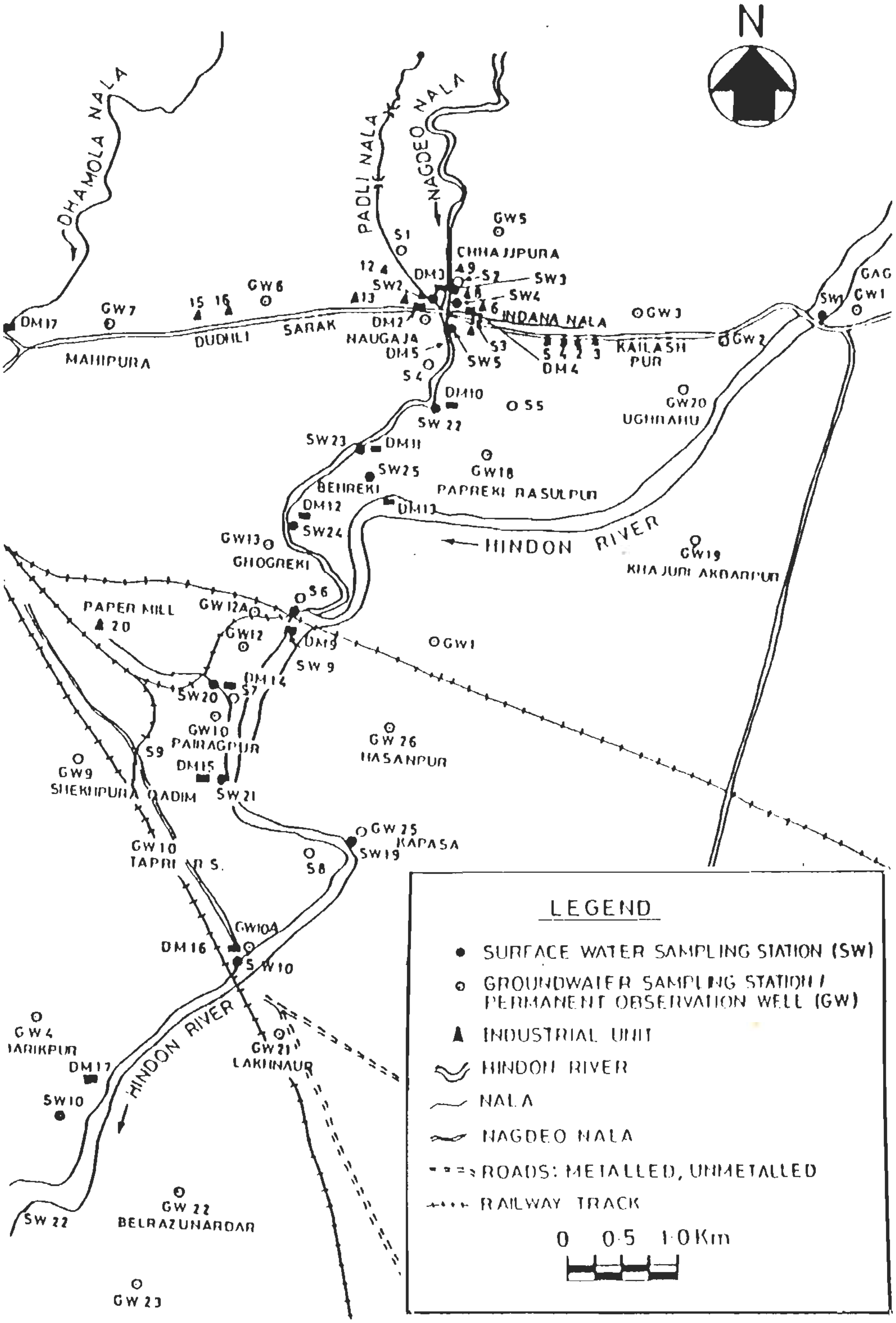

FIG. 1 LOCATION MAP

contaminants of concern have been evaluated and presented in a project report entitled "Hydrological aspects of waste disposal of upper Hindon basin, U.P.". Some of the features are as follows :

pH of the waste waters of the three nalas varied between 7.0 to 9.0. The discharge from all the nalas is quite rich in metal concentrations like Pb^{2+}, Zn^{2+}, Cd^{2+}, Cr^{3+}, Mn^{2+} etc. The contaminants mentioned above cause concern and cast adverse effects to human health. Besides other ingredients the concentration of two metal ions Cd^{2+} and Zn^{2+} in three different samples (SW3, SW3, & SW4) are given below. These values were initially obtained by using a highly sensitive water analyzer and then confirmed by an Inductively Coupled Plasma spectrophotometer.

Table - I

Sample	Cd^{2+} mg l^{-1}	Zn^{2+} mg l^{-1}
SW2	17.875	8.256
SW3	15.798	9.125
SW4	17.955	8.215

The membrane sensors described in chapter III section III.3.a and chapter IV section IV.5.a of this dissertation were also tried to estimate the two metal ions (Cd^{2+} & Zn^{2+}) in the three samples (SW2, SW3 & SW4) and the process as well as results obtained are given below :

V.3.a Pretreatment of electrodes

Prior to the determination of concentration of metal ions of interest, the electrodes were equilibrated and tested by repeated measurements in standard solutions till the electrode's response was rapid, precise and reproducible

V.3.b. Temperature adjustment

The slope of the calibration graph is dependent upon the temperature (slope=2.303 RT/ZF). Thus, all standards and samples must be at the same temperature for accurate analysis. Thermostating is not required, if all solutions are allowed to be equilibrated at room temperature.

V.3.c. Sample pretreatment

Water samples were boiled, filtered and stored for analysis. There after these were subjected to pH adjustment, with reference to the electrode's optimum pH range and the emf of each sample was recorded using ISE/reference electrode assembly and the metal concentration was obtained from previously drawn calibration curves. This gives the estimated amounts of metal ions is waste water samples as obtained by the help of ISEs developed in this Lab. (Tables II & III).

Table - II

Polytungstoantimonate membrane used for the estimation of Zn^{2+} ions in water samples. (Working pH range of the electrode is 4-6).

Sample	Original pH	pH after adjustment	emf (-mV)	Concentration (M)
SW2	7.5	5.6	63	1.26×10^{-4}
SW3	7.9	5.3	62	1.41×10^{-4}
SW4	8.2	5.4	63	1.26×10^{-4}

Table - III

Polystyrene based 2-salicylaldene amino thiophenol formaldehyde membrane used for the estimation of Cd^{2+} ions in water samples (Working pH range 4-6)

Sample	Original pH	pH after adjustment	emf (-mV)	Concentration (M)
SW2	7.5	5.7	40	1.58×10^{-4}
SW3	7.9	5.8	41	1.41×10^{-4}
SW4	8.2	5.7	40	1.58×10^{-4}

The values obtained with the help of ion-selective electrodes are compared (Table IV) with the one determined by other more sophisticated techniques (Table I). A comparison of the two values

Table - IV

Sample	Cd^{2+} (mg l^{-1})		Zn^{2+} (mg l^{-1})	
	Observed values	Reported values	Observed values	Reported values
SW2	17.816	17.875	8.237	8.256
SW3	15.876	15.798	9.218	9.125
SW4	17.816	17.955	8.237	8.215

(observed and reported) proves, beyond doubt, the utility of the two sensors used for these investigations. Maximum error obtained in the two estimations is not more than 0.5% . In any case the two sensors can be used for a quick estimation of the said metal ions in specific situations.

V.4. References

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