Potentiometric Studies on Some Zinc Selective Ionophores

A

Thesis submitted

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in

Chemistry

Under the supervision of	Submitted By
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Date: 18 July, 2012

Place: Patiala

Candidate's Declaration

I, hereby declare that the work being presented in the thesis entitled **"Potentiometric Studies on Some Zinc Selective Ionophores"**, in partial fulfillment of the requirements for the award of the degree of Masters in Chemistry, School of Chemistry and Biochemistry, Thapar University, Patiala, is my own work during the period of Jan 2012 to July 2012, under the supervision of Dr. Susheel Mittal, Senior Professor, School of Chemistry and Biochemistry, Thapar University, Patiala. I have not submitted the matter embodied in this thesis for the award of any other degree.

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This is to certify that the above statement made by the candidate is correct and true to the best of our knowledge.

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This is to certify that the thesis entitled **"Potentiometric Studies on Some Zinc Selective Ionophores",** being submitted by Ms. Manjot Kaur in partial fulfillment of the requirements for the award of degree of Master of Science in the School of Chemistry and Biochemistry, Thapar University, Patiala, is a bonafide work carried out under the supervision of Dr. Susheel Mittal and that no part of this thesis has been submitted for the award of any other degree.

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LIST OF CONTENTS

1 INTRODUCTION

Sensors are the devices which detect target species present in the sample. Human beings also have five of these which include nose, eye, ear, skin and tongue. Sensors are of three types:-physical, chemical and biosensors. Chemical sensors are those analytical devices, which can detect the presence of specific ions in samples. Firstly an analyte recognition process occurs and then conversion of chemical information into an electrical or optical signal takes place. Various techniques are used for determination of specific ions in the sample. One of those techniques is titrimetric analysis, but this is not very much selective and laborious. Both gravimetric and volumetric analysis require large amount of analyte. In real life, for many purposes there is need for trace level analysis in the systems and it led to the development of chromatographic methods, spectrophotometric methods and electroanalysis. Chromatography is used as a separation technique.

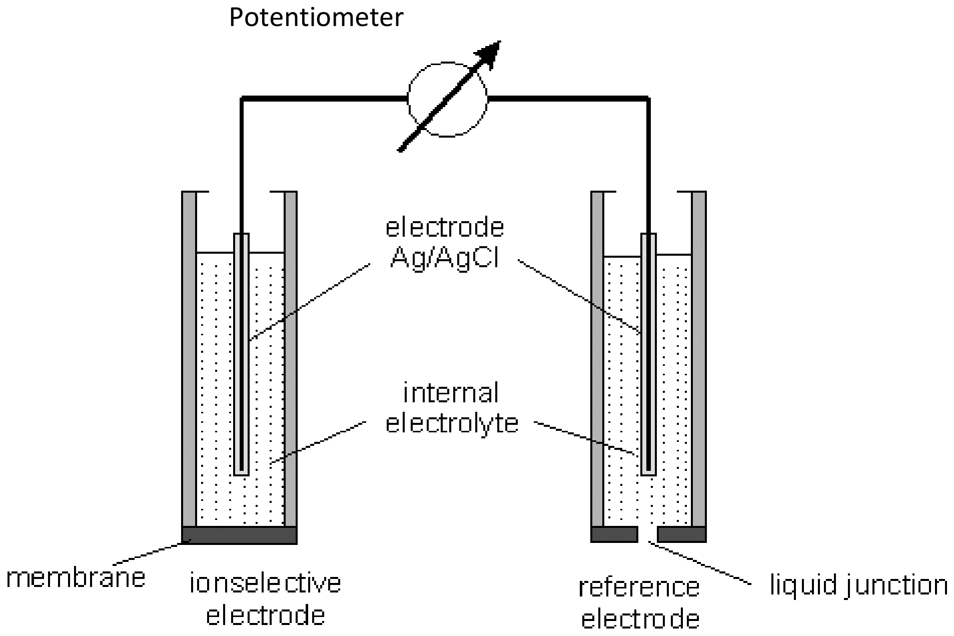
Various techniques have developed which are based on absorption / emission spectroscopy and they involve the use of a spectrophotometer including flame emission spectroscopy (FES), atomic absorption spectroscopy (AAS), atomic fluorescence spectroscopy (AFS), inductively coupled plasma atomic emission spectroscopy (lCP AES). Electroanalytical techniques can also be used for trace level analysis and these are complementary to other analytical techniques. There are many advantages of electrochemical monitoring. One of them is the achievement of lower detection limits which makes it a better technique as compared to the existing analytical techniques. Also, it is able to differentiate between various oxidation states of the analyte. Those situations where other analytical techniques cannot be applied because they require complex and large equipment, electroanalysis give simple and better solutions. Electroanalytical monitoring is of three types which include conductimetry, potentiometry, amperometry and voltammetry. Potentiometry is an analytical technique and it involves the measurement of electrode potential of a system at equilibrium. It helps in determination of concentration of an ion by the use of Nernst equation. There are various classes of chemical sensors among which ion-selective electrodes (ISEs) are one of the most widely used potentiometric sensors for environmental monitoring, clinical analysis and laboratory analysis as well as in industry analysis. It generally responds to one particular ion rather than others and it operates on the principle of concentration cell. For many applications, ion selective electrodes substitute various existing analytical methods. This is due to the reason that ion-selective electrodes have relatively high accuracy, low cost, simple instrumentation, good selectivity, low detection limits, non destructive analysis, adaptable to small volume changes and can also be applied to coloured solutions.

1.1 Ion selective electrodes

Working principle: Electrode potential is developed due to the concentration difference of electrolyte solutions across the membrane and it is measured between two identical reference electrodes which are placed in the two phases. In general, EMF is measured between an ion selective electrode and a reference electrode. If ions of only one type are exchanged between the two phases, then the potential difference developed between these phases is given only by the activities of the target ion. When solution across the membrane has different ionic activities i.e. a_1 and a_2, then the potential difference (E) across the membrane is described by the Nernst equation:-

$$E = RT / zF \times \ln (a_2 / a_1)$$

A set-up for the measurement of electromotive force (EMF) is shown in the figure given below. Potential difference is measured at zero current i.e., under equilibrium conditions. Measured EMF is sum of the different potentials which are developed at solid-solid, solid-liquid and liquid-liquid interfaces.



1.2 Characteristics of ion-selective electrodes

The performance of ISEs is determined by various factors given below:

(i) Selectivity: Selectivity is one of the most important characteristics of an electrode and it is determined by selectivity coefficient (K). It gives information about capability of ISE to distinguish the ion of interest from other interfering ions. Smaller the value of selectivity coefficient, smaller is the interference from other ions. The effect of interfering ions on EMF is given by Nicolsky-Eisenman equation:

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

(ii) Slope: It is calculated from linear part of the calibration curve. According to Nernst equation, the theoretical value of slope for monovalent ion is 59.16 mV/decade, for divalent 29.58 mV/decade and for trivalent, it is 19.72 mV/decade.

(iii) Working range: At high and very low activities of the target ion, deviation from linearity in the curve occurs. Usually, the electrode calibration curve exhibits linear response from 10^{-5} to 10^{-1} M range.

(iv) Detection limit: The detection limit is given by the cross-section of the two extrapolated linear parts of the calibration curve.

(v) Response time: It is defined as the average time for the sensor to reach the potential within ± 1 mV of its final equilibrium value.

1.3 Types of Ion Selective Electrodes

1.3.1 Glass membrane electrodes: The best known example of this type of electrode is pH electrode. In this, cationic vacancies are created by non silicon constituents of glass and those of anionic ones are made by imperfections in the SiO_2 membrane. Membrane with composition 22% Na_2O, 6% CaO and 72% SiO_2 shows good selectivity towards hydrogen ions. Hydrated layer is formed due to the exposure of this electrode to water and this improved the mobility of ions. During the interaction of this glass hydrated membrane with sample solution, diffusion and ion-exchange process takes place. Other example of this type of electrode is sodium-selective electrode.

1.3.2 Solid membrane electrodes: These types of membranes can be either homogeneous or heterogeneous. Homogeneous membranes contain fixed sites of single crystals of sparingly soluble salts and in heterogeneous membranes insoluble salt is dissolved in suitable inert binder. The sensitivity to ions by these electrodes arises due to the dissolution equilibria at the membrane surface. When membranes are directly attached to wire, they are called coated-wire electrodes.

1.3.3 Liquid membrane electrodes: In this class of electrodes, a substance capable of exchanging ion is dissolved in water-immiscible solvent. This electro active component which may be a neutral or a charged compound and is able to bind ions reversibly is called as an ionophore. It has molecule–sized dimensions. It has cavities to surround the target ions. It forms reversible, selective and strong complexes only with target ion. It is mobile both in free and complexed forms. These mobile binding sites are dissolved in a suitable solvent and incorporated in a matrix of some organic polymer. The main components of PVC based polymeric membranes are polymer matrix, plasticizer, lipophilic salt and ionophore. Polymer matrix provides elasticity and mechanical strength to the membrane. PVC is the most widely used matrix material. Plasticizer is added to increase the mobility of the free and complexed ionophore. It also determines polarity of the membrane. Lipophilic salt improves the performance of a membrane.

1.3.4 Other Membrane Electrodes: In gel immobilised and chemically modified enzyme membranes, an enzyme is bonded to the solid surface and it catalyses a specific chemical reaction to form product ions. Detection of these ions is carried out by an internal ion-selective membrane. For the determination of various gases such as carbon dioxide, ammonia potentiometric gas sensors are used.

1.4 Advantages and Applications

Some of the advantages and applications of ISEs are given below:

(i) Ion-Selective Electrodes have several advantages like simple instrumentation, inexpensive, high selectivity, low detection limit, good accuracy and precision, non destructive analysis and can also be applied to viscous and coloured solutions.

(ii) They are particularly useful for trace level analysis in many samples.

(iii) These are used for the detection of end point in the potentiometric titrations by indicating the rapid change in the potential developed in the electrode system.

(iv) They are very useful in biological applications as they measure directly the activity of ions in place of concentration.

(v) ISEs are one of the few techniques which can measure both cations and anions.

2 LITERATURE REVIEW

2.1 Development of ISEs

The history of ISEs started from 1906, when pH-sensitive glasses were discovered by Max Cremer which led to the development of first commercial pH glass electrode in the 1930s. Then crystalline compounds like silver chloride, lanthanum fluorides were introduced in the early 1960s as detecting elements and after this the number of ions that could be detected with ISEs increased suddenly. Fluoride and halide selective electrodes were the most important ISEs of this type. Then modification in the glass composition detected some ions like sodium, but even then the selectivities of electrodes based on glasses were not enhanced. Also these materials had poor ionic conductivity. So, due to this further development of ISEs based on glasses and crystalline materials was hindered. A major breakthrough came with the discovery of ion binding receptors. The introduction of ionophores and the concept of host-guest chemistry completely changed ISEs field. The earliest work with ISEs based on ionophores was inspired by the observation of Moore and Pressman in 1964 who observed the uptake of K^+ in mitochondria by the antibiotic valinomycin and this led to the development of electrically neutral ionophores. During 1960s, Ross and Frant made the discovery of calcium selective electrodes.

In 1966, Simon and Stefanac showed that thin films formed by water-immiscible organic solvents and doped with antibiotics showed responses to monovalent cations. The earliest work on such ISEs was based on ammonium-selective ionophores, nonactin and monactin. Then pressed powdered ISEs based on sparingly soluble salt was developed. Liquid membrane electrodes were introduced in 1967 and further development occurred in 1970 when a polymer film was produced by immobilizing the ionophore in poly (vinyl chloride). Electrodes based on spectral grade graphite powder and low soluble metal salts were introduced by Mesaric and Dahmen in 1973. Heineman et al introduced the first chemically modified carbon paste electrode in 1980.

During 1960s, invention of crown ethers by Pederson made significant advancement in the field of host–guest chemistry. After that, development of synthetic ionophores was done on a large scale. Due to this, ISEs replaced flame atomic emission spectroscopy for detection of ions in blood samples in 1980s. With time, there was development in

ISE techniques with the introduction of microelectrodes, integrated enzyme layer ISEs, gas-permeable ISEs for the detection of gases such as ammonia and carbon dioxide.

2.2 Alkali metal ion selective electrodes

Earliest work in this class includes use of natural compounds such as antibiotics valinomycin, monactin and nonactin. Valinomycin was selective for K^+ and possessed good selectivity over Na^+. But it was not much soluble in polymeric matrices of low polarity and hydrophobicity. Then synthetic ionophores like crown ethers were used to bind with K^+. Bis-15-crown-5 ethers were also useful and bound K^+ in sandwich like fashion and exhibited good selectivity over Na^+. 15-crown-5 macrocycles were not capable in binding K^+ to their centre and thus K^+ lie in between the two 15-crown-5 macrocyclic rings. The use of bis-15-crown-5 ethers was limited by the large conformational freedom of these and after that the development of bridged calix [4] arene crown-5 compounds was important.

For Na^+ macrocyclic crown ethers were used as ionophores. Na^+ fits well into 15-crown-5 due to its small size. The bis crown ether ionophores like 12-crown-4 macro cyclic rings were successfully used in which Na^+ is bound and associated with eight ion–ether interactions. Due to limited conformational freedom bridged calix [4] arenes had been proposed.

For lithium ion, diamide was used as ionophore which forms 1:2 complexes with Li^+ and was used for successful measurements in blood. First commercial clinical analyser for Li^+ came in 1987. For lower interferences from other alkali metal ions like sodium, 1, 4, 8, 11-tetraoxacyclotetradecane with bulky substituents was used as ionophore and thus it hindered the formation of 1:2 complexes and inhibited the binding of larger ions. From all alkali metal cations, Cs^+ possess the lowest free energy of hydration, so ionophore-free ion exchanger membrane was also selective for Cs^+ over the other alkali metal cations.

Table 1. Electrode characteristics of Ionophores for alkali metal ions.

Ionophore	Selected Metal Ion	Slope (mV/decade)	Working Range (M)	Reference No.
Lipophilic crown-4 derivatives	Li(I)	58	$10^{-4} - 10^{-1}$	1
1-methyl-1-vinyl-14-crown-5	Na(I)	55	$3.16\times10^{-6} - 1.0 \times 10^{-1}$	2
Bis(crown ether)with two benzo-15-crown-5 moieties	K(I)	57	$5.0\times10^{-6} - 1.0\times10^{-1}$	3
dibenzo-21-crown-7(DB21C7)	Rb(I)	57.8	$1.0\times10^{-5} - 5.0\times10^{-2}$	4
1,3-alternate thiacalix	Cs(I)	57.6	$1\times10^{-6} - 3.2\times10^{-2}$	5

2.3 Alkaline earth metal ion selective electrodes

Not much work was carried out on Be^{2+}, Sr^{2+} and Ba^{2+}selective ionophores, but there was large interest in Mg^{2+} and Ca^{2+} ISEs due to their applications in clinical analysis and other fields. So, tremendous work was done with these metal ions. Smaller size Mg^{2+} has stronger hydration and any hypothetical ionophore which can bind both of these ions to the same extent would bind selectively Ca^{2+} than Mg^{2+}. In 1994, Mg^{2+} based ISEs were introduced in clinical analysers. Since, stability constant determinations were not available, so much work was supported only by experimentally determined potentiometric selectivities alone. The non cyclic amide ionophores (ETH1001 and ETH 129) were used for Ca^{2+}. Ca^{2+} was also bound with diaza crown ethers, the metal ion is present in the crown ring, and the two pendants from top and bottom bind to Ca^{2+}. Mg^{2+} ionophores have structurally similar appearance as those of Ca^{2+} ionophores. Diamide as ionophores for Mg^{2+} was also used and amongst from non cyclic ionophores, most successful were triamides.

Table 2. Electrode characteristics of Ionophores for alkaline earth metal ions.

Ionophore	Selected metal ion	Slope (mV/decade)	Working range (M)	Reference No.
2,3,5,6,8,9-hexahydronap-hto[2,3-b]- [1,4,7,10] tetraoxacyclododecine	Be(II)	29.8	10^{-8} - 10^{-2}	6
dibenzo-18-crown-6 (DB18C6)	Ca(II)	28	10^{-5}- 10^{-1}	7
benzo-15-crown-5	Mg(II)	31	10^{-5} - 10^{-1}	8
dimethyl1-acetyl-8-oxo-2,8-dihydro-1H-pyrazolo[5,1-a]iso-indole-2,3-dicarboxy-late	Ba(II)	29.7	10^{-6} - 10^{-1}	9
benzo-substituted macrocyclic diamides	Sr(II)	30	3.2×10^{-5} - 1.0×10^{-1}	10

2.4 Transition metal and lanthanide ion selective electrodes

Earlier work on ISEs for heavy metal cations used ionophores based on inorganic chemistry like chelating reagents. Lanthanides have attracted attention over the past years. The ionophores which were used for lanthanide ions generally possessed semi cavity and contained heteroatoms like S and N. These ionophores were able to form stronger complex with a particular cation rather than with others. This is due to the presence of flexible donor atoms and also due to the size and the charge density of the cation. This field possess large potential to develop more and to perform much better from the past.

Table 3. Electrode characteristics of Ionophores for transition metal ions

Ionophore	Selected metal ion	Slope (mV/decade)	Working range (M)	Reference No.
N,N´-bis(3-methyl-1-phenyl-4-benzylidine-5-pyrazolone)propylenediam-ine	Ag(I)	59.3	10^{-6} - 10^{-1}	11
5-((4-nitrophenyl)azo)-N-(2’,4’-dimethoxyphenyl)salicylaldimine	Co(II)	29	9.0×10^{-7} - 10^{-2}	12
benzo-18-crown-6 crown ether	Fe(III)	15.7 ± 1	10^{-6} - 10^{-1}	13
Dibenzo[*e*,*k*]-2,3,8,9-tetraphenyl-1,4,7,10-tetraazacyclododeca-1,3,5,7,9,11-hexaene	Ni(II)	29.5	3.98×10^{-6} - 10^{-1}	14
Bis(2-hydroxyacetophenone)butane-2,3-dihydrazone (BHAB)	Cu(II)	29.6	5.0×10^{-8} - 10^{-2}	15
tetrathia-12-crown-4	Cd(II)	29.0±1.0	4×10^{-7} - 10^{-1}	16
bis(2-hydroxybenzophenone) butane-2,3-dihydrazone (HBBD)	Hg(II)	29.7	10^{-6} - 10^{-1}	17

Table 4. Electrode characteristics of Ionophores for lanthanide metal ions.

Ionophore	Selected metal ion	Slope(mV/ decade)	Working range (M)	Reference No.
2,9-dihydroxy-1,10-diphenoxy-4,7-dithiadecane (DHDPDTD)	Ce(III)	19.3	10^{-8} - 10^{-1}	18
3-{[2-oxo-1(2*H*)-acenaphthylenyliden]amino}-2-thioxo-1,3-thiazolidin-4-one	Sm(III)	19.3	10^{-6} - 10^{-1}	19
8-amino-N-(2-hydroxybenzylidene) naphthylamine (AIP)	La(III)	20.3 ± 0.3	10^{-7} - 10^{-1}	20
N-(pyridine-2-yl-methylene)Benzohydrazi-de	Pr(III)	21.1	10^{-6} - 10^{-2}	21
2-{[(6-aminopyridin-2yl) imino]methyl}phenol	Nd(III)	19.6	10^{-5} - 10^{-2}	22
bis(thiophenol)butane2,3-dihydrazone	Eu(III)	19.8	10^{-5} - 10^{-2}	23
N'-(2-Hydroxy-1,2-diphenyl-ethylidene) benzohydrazide	Er(III)	21	10^{-7} - 10^{-2}	24
N,N-bis(pyrrolidene) benzene-1,2- diamine	Tb(III)	19.8	10^{-5} - 10^{-1}	25
bis(thiophenal) pyridine-2,6- diamine (BPD)	Gd(III)	19.4 ± 0.4	10^{-6} - 10^{-1}	26
N-(1-thien-2-yl-methylene)-1,3-benzothiazol-2-amine	Ho(III)	19.7	10^{-5} - 10^{-2}	27
N-(thien-2-yl-methylene)-pyridine-2,6-diamine	Lu(III)	20.5 ± 0.4	10^{-6} - 10^{-2}	28

2.5 Zinc selective electrodes

Use of cryptands as ionophores in the construction of zinc selective electrodes was reported by Srivastava et al in 1996. They reported PVC-based 2, 2, 2-cryptand sensor for the determination of zinc ions. The electrode exhibited a slope of 22.0 mV / decade and showed working range from 2.06 ppm to 6.54×10^3 ppm. The response time of the sensor was less than 10 s and it could be used for more than 3 months without any observed divergence in potential. The proposed sensor exhibited very good selectivity for Zn (II) over other cations and could be used in a wide pH range (2.8- 7.0) [29]. Another PVC membrane electrode for zinc was reported by Shamsipur et al in 1999 which was based on a benzo-substituted macrocyclic diamide (1,13-diaza-2,3;11,12;15,18-tribenzo-4,7,10-trioxacyclononaoctane-14,19-dione). The electrode showed the Nernstian behaviour over a wide concentration range of $1.0 \times 10^{-1} – 9.0 \times 10^{-5}$M. It could be used for at least 3 months without any significant change in performance and had a response time of about 20 s. The working pH range for proposed membrane was 3.0–7.0 and possessed good selectivities for zinc over other metal ions. It was also used as an indicator electrode for direct determination of zinc [30].

A PVC membrane for zinc based on Sulipride drug N-[(ethyl-1 pyrrolidinyl-2) methyl] methoxy-2 sulfamoyl-5 benzamide was reported by Saleh et al in 2001. The PVC electrode exhibited a Nernstian slope of 29.3 mV per decade and a fast response time of 20 s with working concentration range of10^{-5} - 10^{-1} M. The working pH range for electrode was 4.0 ± 6.5. The electrode exhibited very good selectivity over other metal ions. The electrode was applied to determine zinc contents in some rock materials and was also used as an indicator electrode in potentiometric titration of Zinc against EDTA [31].

In 2002, Fakhari et al reported a new PVC electrode based on tetra (2-aminophenyl) porphyrin (TAPP) for Zn (II). The electrode exhibited a slope of 26.5 mV/decade with detection limit of 3.0×10^{-5} M and showed a linear stable response over a wide concentration range (5.0×10^{-5} to 1.0×10^{-1} M). It had a fast response time of about l0 s and could be used for at least 8 months without any significant divergence in response characteristics. It also showed very good selectivities for Zn (II) over a wide variety of other metal ions. It could be used in the pH range of 3.0 – 6.0. It was used as an indicator electrode in potentiometric titration of zinc and also for the direct determination of zinc in pharmaceutical samples [32]. V. K. Gupta et al in 2005 proposed dibenzo-24-crown-8 as a carrier for Zn (II) ions. Effect of different anion excluders and plasticizers was studied. This electrode exhibited a Nernstian slope of 29.0 ± 0.5 mV/decade with a wide working concentration range of 9.2×10^{-5} to 1.0×10^{-1} M. Response time of electrode was also fast (about 12s) and it possessed good selectivity over a number of mono, bi, and trivalent cations. This sensor could be used in the pH range of 4.8 - 6.2 and can also be employed for the estimation of zinc ions in partially non-aqueous medium [33]. PVC sensor based on N, N´-bis (acetylacetone) ethylenediimine as an ionophore, sodium tetraphenylborate (NaTPB) as an anion excluder and *o*-nitrophenyl octyl ether (NPOE) as a plasticizer was reported by Gupta et al in 2006. Effect of various plasticizers was investigated on the membrane performance. The electrode showed a Nernstian response of 30.0 mV/decade with working range of 1.0×10^{-6} to 1.0×10^{-1} M and detection limit of 8.9×10^{-7}M. It could be used in the pH range of 3.2 – 7.1. The sensor had been successfully used in the potentiometric titration of zinc with EDTA [34].

Gupta et al in 2006 reported a PVC membrane electrode based on 4-tert-butyl calix [4] arene for Zn (II) ions. Sodium tetraphenylborate (NaTPB) as an anion excluder and tri-butylphosphate (TBP) as a plasticizer was used for membrane preparation. The sensor exhibited a near-Nernstian slope of 28.0 ± 1.0 mV/decade with the detection limit of 5.0×10^{-7} mol dm^{-3} and also showed a stable response over a wide working range of 9.8×10^{-6} to 1.0×10^{-1} mol dm^{-3}. It could be used in the pH range of 2.5 – 4.3 and works well in partially non-aqueous medium. The response time of the electrode was about 30 s and could be used for more than four months without any significant divergence in response characteristics. It possessed excellent selectivity for Zn (II) over other mono, bi and trivalent cations. It could be used as an indicator electrode in the potentiometric titration of Zn (II) against EDTA and also for determination of zinc in industrial waste waters [35]. In 2006, Zamani et al reported a PVC membrane electrode based on 5,6-benzo-4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8,8,8]hexacos-5-ene (BHDE) as an ionophore for the detection of zinc ion. Sodium tetraphenylborate (NaTPB) as an anion excluder and nitrobenzene (NB) as a plasticizer was used for membrane preparation. The proposed sensor exhibited a Nernstian slope of 29.1 ± 0.4 mV per decade with a wide concentration range from 1.0×10^{-6} to 1.0×10^{-1} mol L^{-1}. The detection limit of electrode was 6.3 ×10^{-7} mol L^{-1}. It showed a fast response time and working pH range of 2.8 - 7.3. The lifetime of the electrode was of 10 weeks. The proposed sensor was used as an indicator electrode in titration of zinc with EDTA and also for the determination of zinc ion in waste water [36].

PVC based membrane electrode using 1, 12, 14-triaza-5, 8-dioxo-3(4), 9 (10)-dibenzoylcyclopentadeca-1, 12, 14-triene as an ionophore was developed by Chandra et al in 2010. The electrode exhibited a Nernstian behaviour with a slope of 29.2 ± 0.4 mV/ decade and a working range of 1.3 × 10^{-7} – 1.0 × 10^{-1} mol L^{-1} with a detection limit of 1.0 × 10^{-8} mol L^{-1}. It possessed a fast response time of 7 s and could be used for at least 100 days without any significant change in response characteristics. It showed stable potential response over a pH range of 3.5–9.2. The proposed electrode was directly used for determination of zinc in human hair and waste water samples [37]. PVC sensor based on two macrocyclic ligands 6,7:14,15-Bzo2-10,11-(4-methylbenzene)-[15]-6,8,12,14-tetraene-9, 12-N2-1,5-O2 (L1) and 6,7:14,15-Bzo2-10,11-(4-methylbenzene)-[15]-6,14-diene-9,12-dimethylacrylate- 9,12-N2-1,5-O2 (L2) for Zn (II) determination was reported by Singh et al in 2011. The detection limit of electrode was found to be of the order of 3.3×10^{-7}mol L^{-1} for PME and 7.9×10^{-8} mol $l^{-1}$for CGE, respectively. It exhibited Nernstian slope with response time of 12 s and 10 s for PME and CGE, respectively. The electrode showed stable response in the pH range of 3.0 – 8.0 for PME and 2.5 – 9.0 for CGE. CGE could be used as an indicator electrode in potentiometric titration of EDTA with Zn (II) solution and could also be used for the determination of Zn (II) in various samples like water, milk, biological and tea samples [38].

Another Zn (II) selective membrane was developed by Asousi et al in 2012 which was based on dibenzo-24-crown-8 (DBC) as an electroactive material, dioctyl phthalate (DOP) as a plasticizer, and potassium tetrakis (p-chlorophenyl) borate (KTpClPB) or the halogen-free ionic liquid tetraoctylammonium dodecylbenzene sulphonate [TOA][DBS] as an additive. For each additive a membrane was prepared and the surfaces of two membranes were investigated by using, ion-scattering spectroscopy, X-ray photoelectron and atomic force microscopy. The comparison of the two surfaces indicated the high selectivity was achieved when [TOA][DBS] was used as an additive. The proposed sensor had a detection limit of 1.53μg Zn (II) / mL with working range from 3.4 ×10^{-5} to 3.8 × 10^{-2} M [39]. For zinc, a new optical sensor based on fluorescence enhancement of a disperse azo dye (parared, PR) was reported by Shamsipur et al in 2012. The optode showed the concentration range of $5.0 \times 10^{-3} – 1.0 \times 10^{-6}$ M for zinc. This was used for the determination of zinc in zinc sulphate tablets and in zinc oxide cream and also used as an indicator electrode in titration of zinc [40].

3 EXPERIMENTAL SECTION

3.1 Reagents

Reagent grade o-nitrophenyl octyl ether (o-NPOE), sodium tetraphenylborate (NaTPB), tetrahydrofuran (THF) and high molecular weight PVC were purchased from Sigma Aldrich. Hydrated salts like $Zn(NO_3)_2$, $Cu(NO_3)_2$, $Co(NO_3)_2$, $Ni(NO_3)_2$, $Hg(NO_3)_2$, $Cd(NO_3)_2$, $Pb(NO_3)_2$, $Ca(NO_3)_2$, $MgSO_4$, $Fe(SO_4)_2(NH_4)_2$, $AgNO_3$, $Ga(NO_3)_3$ and $Al(NO_3)_3$ (analytical grade) were purchased from Sigma Aldrich and were used as such. Lanthanide salt $Ce(NO_3)_3$ was purchased from s.d. fine- Chemicals. Double distilled deionised water was used through the experiments.

3.2 Preparation of zinc (II) nitrate stock solution

Zinc nitrate hexahydrate was weighed accurately and transferred to a measuring flask to prepare 0.1 M solution of zinc nitrate. Then solutions of various concentrations (10^{-2} to 10^{-8}M) were prepared by further dilutions.

3.3 Membrane preparation

Five membranes with four different ionophores were prepared by the standard procedure. PVC, o-NPOE, lipophilic salt and ionophores (I-1, I-2, I-3, I-4) were dissolved separately in THF at room temperature. The solvent was allowed to evaporate slowly so as to get viscous solution. Each solution thus obtained was poured in glass rings which were placed on glass plates. Again the solutions were allowed to evaporate slowly at room temperature. The prepared membranes were removed from the glass plate and fixed to one end of the glass tubes by using an epoxy resin as adhesive. Then each membrane was equilibrated with Zn^{2+} solution (0.1M) for about 5 to 6 days.

3.4 EMF measurements

Membrane electrodes were filled one-fourth with zinc (II) nitrate solution and immersed in a beaker containing the test solution of varying concentrations of zinc. The level of inner filling solution was kept higher than the test solution so as to avoid reverse diffusion of the electrolyte. Potentiometric measurements were made by using digital potentiometer (Equiptronics EQ – 602, Mumbai, India). All the measurements were done by using the following cell assembly:

$$\mathbf{SCE\ |\ Zn^{2+}\ (0.1M)\ ||\ Membrane\ ||\ Zn^{2+}\ (test\ solution)\ |\ SCE}$$

3.5 pH adjustment of solution

pH of the salt solution was adjusted by the introduction of small addition of nitric acid (0.1 M) or sodium hydroxide (0.1 M) as per requirements. For the adjustment of pH, buffer solutions were not used for preparing calibration curves as they change the ionic strength of the solution.

3.6 Buffer solution

For the potentiometric titration of 50 ml of 10^{-3} M Zn (II) solution against 10^{-2} M EDTA, buffer solution was used to maintain pH. The solution was prepared by adding 73.2 mL of 0.1 M NaOH solution to 100 mL of 0.1 M potassium hydrogen phthalate solution.

3.7 Interference studies

The effect of interfering ions on the potentiometric response of the electrode was measured in the terms of selectivity coefficients, $K_{A,B}$. These were determined by fixed interference method (FIM). In FIM, the potential of the system containing an ion selective electrode and a reference electrode is measured by changing activity of the primary ions but the activity of interfering ions remain fixed throughout the experiment. The potential values were plotted against logarithm of primary ion concentration. The intersection of the extrapolated linear portions of the curve corresponds to the value of a_A i.e., primary ion concentration and this is applied in Nikolsky - Eisenmann equation to find the selectivity coefficient values.

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

Here, a_A is activity of the primary ion A and a_B is activity of interfering ion B, and z_A and z_B are the respective charges. The concentration of the primary ion was varied from 10^{-8} M to 10^{-1}M but the concentration of interfering ion was fixed i.e. 10^{-3} M for all membranes which were studied.

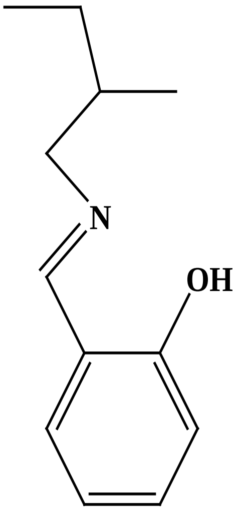
4 RESULTS AND DISCUSSION

4.1 Membrane composition

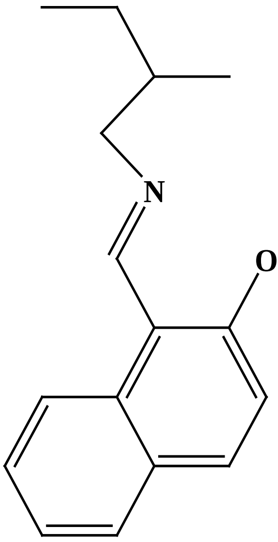
Membranes with different amounts of ionophore in the different range of ratios were prepared and used for studying electrode response for the primary ions. However, the best results were obtained with membrane having composition Ionophore: PVC: Plasticiser: Lipophilic additive in the percent ratio of 10: 29: 56: 5.

o-nitrophenyl octyl ether (o - NPOE) was used as a plasticizer and sodium tetraphenyl borate (NaTPB) was used as a lipophilic additive for the preparation of membranes. The presence of lipophilic additives generally improves the performance characteristics of various cation selective electrodes with the minimisation of ohmic resistance. The membranes were prepared with the plasticizer/ PVC ratio of approximately 2.

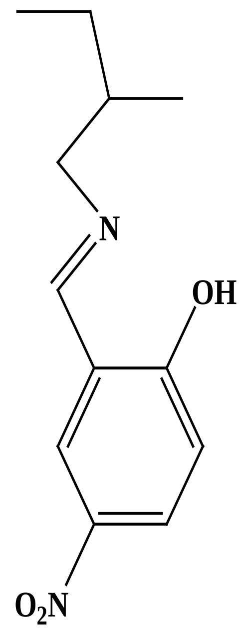
Experiments were conducted to study electrode response with four different ionophores having partial structures of which are given below:



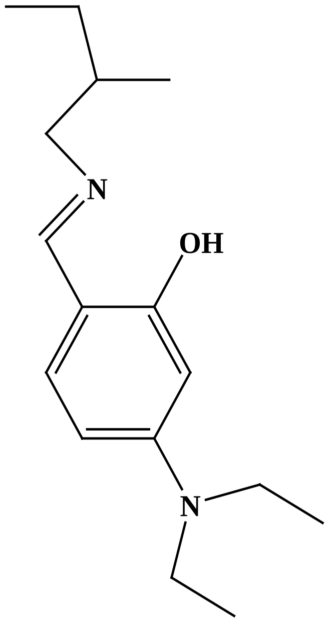
IONOPHORE 1



IONOPHORE 2



IONOPHORE 3



IONOPHORE 4

4.2 Calibration curve

PVC based membrane electrodes were equilibrated with Zn $(NO_3)_2$ solution for about 5 days so as to saturate the cavities of ionophores with zinc ions. Potentiometric readings were recorded with the electrode immersed in different concentrations of zinc ions as the primary ion in the concentration range of 10^{-8} to 10^{-1} M. The obtained data was plotted as electrode potential (E) against logarithm of primary ion concentration, as shown in Figures 1 and 2.

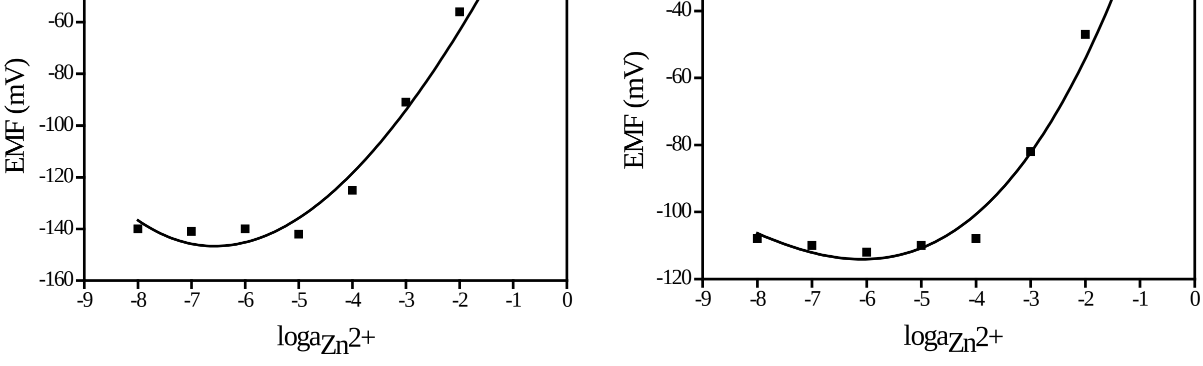


Figure 1. Calibration curves for Zn^{2+} ion using electrode with (a) ionophore I-1 and (b) ionophore I-2

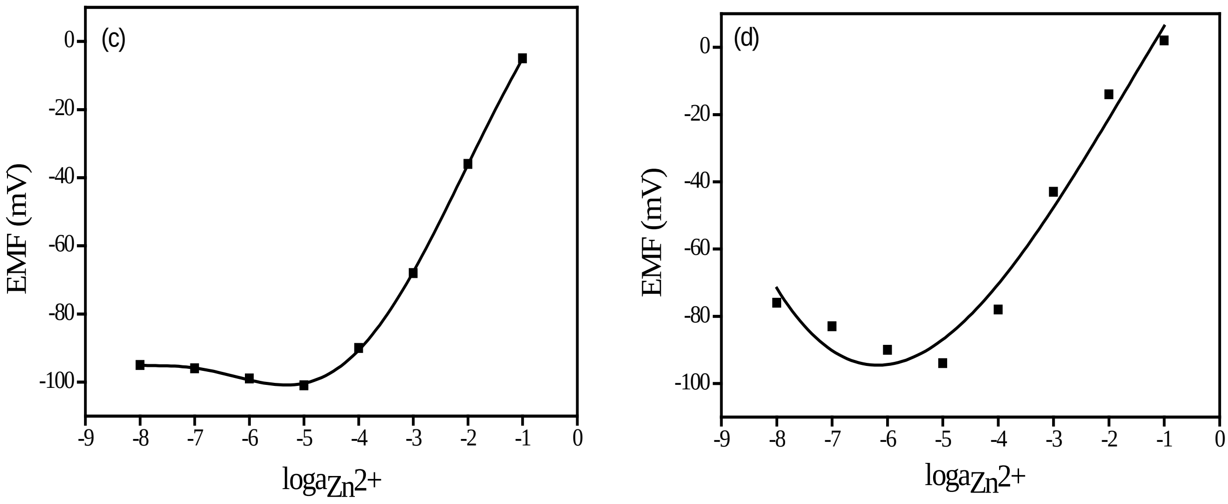


Figure 2. Calibration curves for Zn^{2+} ion using electrode with (c) ionophore I-3 and (d) ionophore I-4

Slopes of calibration curves for Zn^{2+} ion using electrodes with ionophores i.e. I-1, I-2, I-3, I-4 were calculated as shown in Table 5. From the graphs, it is observed that all electrodes with ionophores exhibited near Nernstian slopes with working range from 10^{-5} to 10^{-1} M and the detection limit obtained is 10^{-5} M.

Table 5. Slopes of calibration curves for Zn^{2+} ions using electrodes with ionophores I-1, I-2, I-3, I-4.

S. No.	**Slope (mV/decade)**			
	Ionophore, I-1	**Ionophore, I-2**	**Ionophore, I-3**	**Ionophore, I-4**
1.	33	32	27	29
2.	30	30	29	27
3.	32	29	27.5	27
4.	33	30	29	27
Mean	32 ± 2.0	30.2 ± 1.5	28.1 ± 1.0	27.5 ± 1.0

4.3 Interference studies

The effect of interfering ions on the potentiometric response of the electrode was measured by fixed interference method. The concentration of the primary ion was varied from 10^{-8} M to 10^{-1} M but the concentration of interfering ion was fixed i.e. 10^{-3} M. The selectivity coefficient values of Zn^{2+} selective electrodes prepared with ionophores I-1, I-2, I-3 and I-4 for different interfering ions is shown in Table 6.

Table 6. Selectivity coefficient values of Zn^{2+} selective electrodes prepared with ionophores I-1, I-2, I-3, I-4 for different interfering ions (1×10^{-3}M) by fixed interference method.

S. No.	Interfering ions	Selectivity coefficient, log k			
		I-1	I-2	I-3	I-4
1.	Ca^{2+}	-1.0	-0.2	-0.4	-0.5
2.	Mg^{2+}	0.0	0.4	-0.3	-0.2
3.	Fe^{2+}	0.5	-	-	-
4.	Co^{2+}	-0.4	-0.3	-0.3	-0.4
5.	Ni^{2+}	0.7	-0.3	-0.3	-0.4
6.	Cu^{2+}	-0.4	-0.6	-	-0.5
7.	Pb^{2+}	-1.3	-0.4	-1.0	-1.1
8.	Cd^{2+}	-0.4	-0.4	-0.5	-
9.	Ga^{3+}	-1.4	-1.4	-	-1.3
10.	Al^{3+}	-	-1.3	-1.3	-1.3
11.	Ce^{3+}	-1.3	-1.2	-1.3	-1.3

It can be concluded from the values of selectivity coefficients that the ions having values less than one show limited interference with the working of the proposed electrode for Zn^{2+} determination.

4.4 Effect of pH

pH response of the electrode was studied by the use of 1× 10^{-2} M Zn (II) solution over the pH range 2 - 11. The adjustment of pH was done by the dropwise addition of 10^{-1} M HNO_3 or 10^{-1}M NaOH solution. The graphs of electrode potential (E) against pH of electrode with different ionophores are shown in Figures 3 and 4.

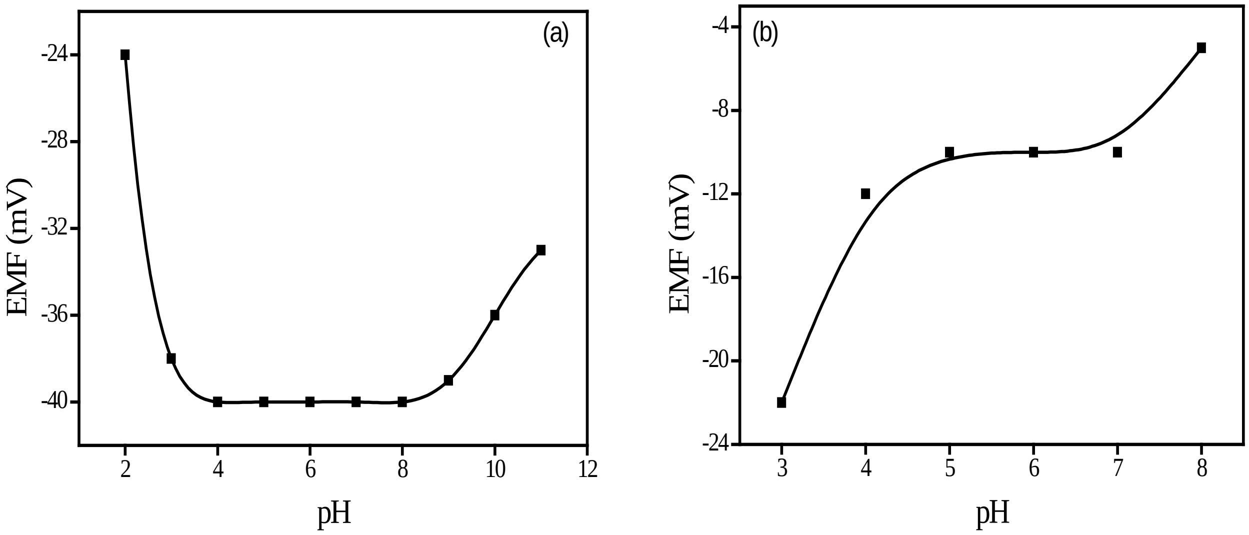


Figure 3. Working pH range of electrodes with (a) ionophore I-1 and (b) ionophore I-2

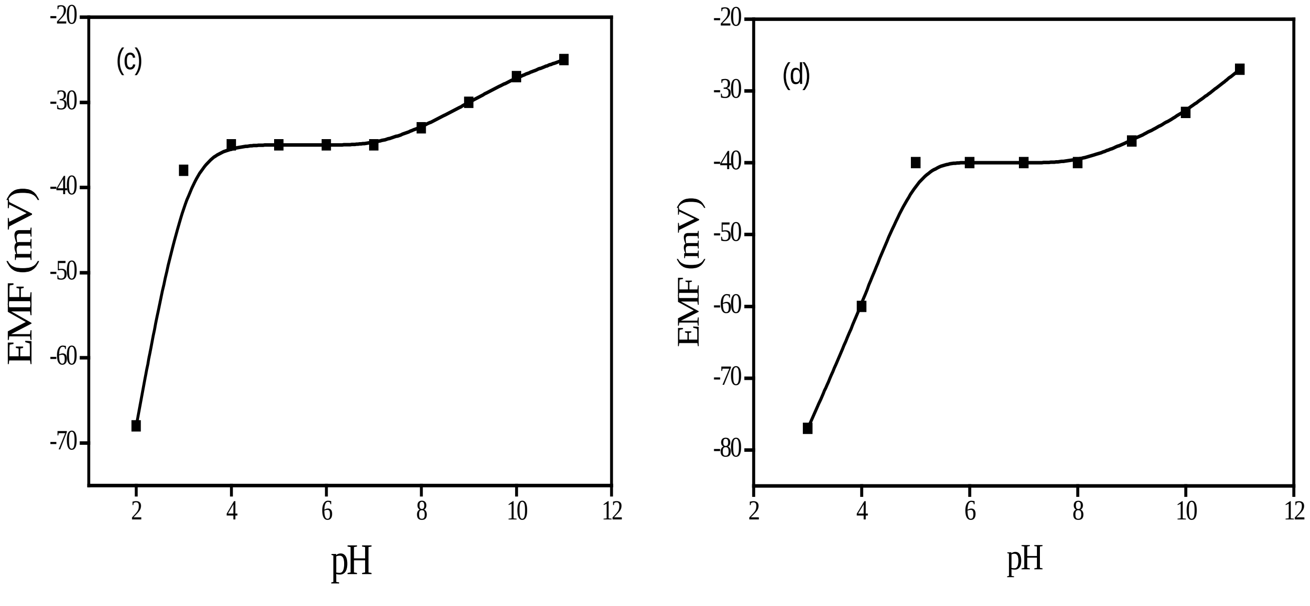


Figure 4. Working pH range of electrodes with (c) ionophore I-3 and (d) ionophore I-4

Table 7. Working pH range of electrode with different ionophores I-1, I-2, I-3 and I-4.

S.No.	Ionophores	Working pH range
1.	I-1	4 - 8
2.	I-2	5 - 7
3.	I-3	4 - 7
4.	I-4	5 - 8

Table 7 shows that the potential remains constant in different pH ranges for different ionophores. So, the corresponding ranges are considered as the working pH range of the electrode. At lower and higher pH, change in potential is observed. At lower pH electrodes respond to H^+ ions and at higher to OH^- ions due to the formation of $Zn(OH)_2$.

4.5 Potentiometric titration

The proposed electrodes were also used as indicator electrodes for the titration of 50 ml of 10^{-3} M Zn (II) solution against 10^{-2} M EDTA. The pH of solution was adjusted to 5 - 6 with the use of an appropriate volume of buffer which was made from potassium hydrogen phthalate and sodium hydroxide solution. The graphs between electrode potential against volume of EDTA used for ionophores are shown below in Figures 5 and 6.

From the figures 5 and 6, it can be concluded that with all ionophores i.e., I-1, I-2, I-3 and I-4 sharp end point is obtained which corresponds to the 1:1 stoichoimetry of the Zn(II)-EDTA complex.

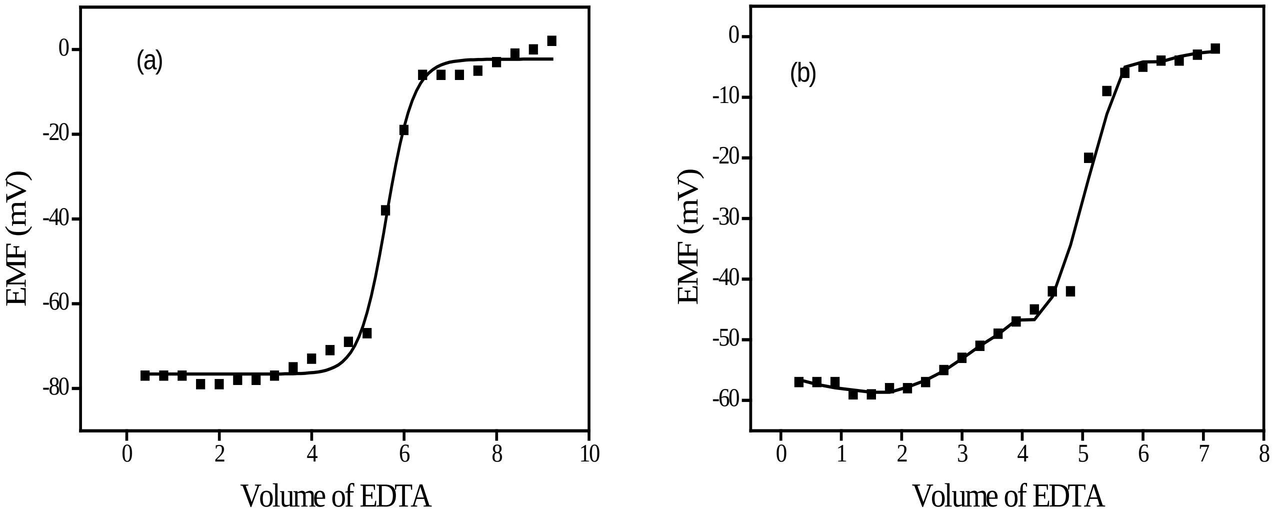


Figure 5. Potentiometric titration curves for electrodes with (a) ionophore I-1 and (b) ionophore I-2

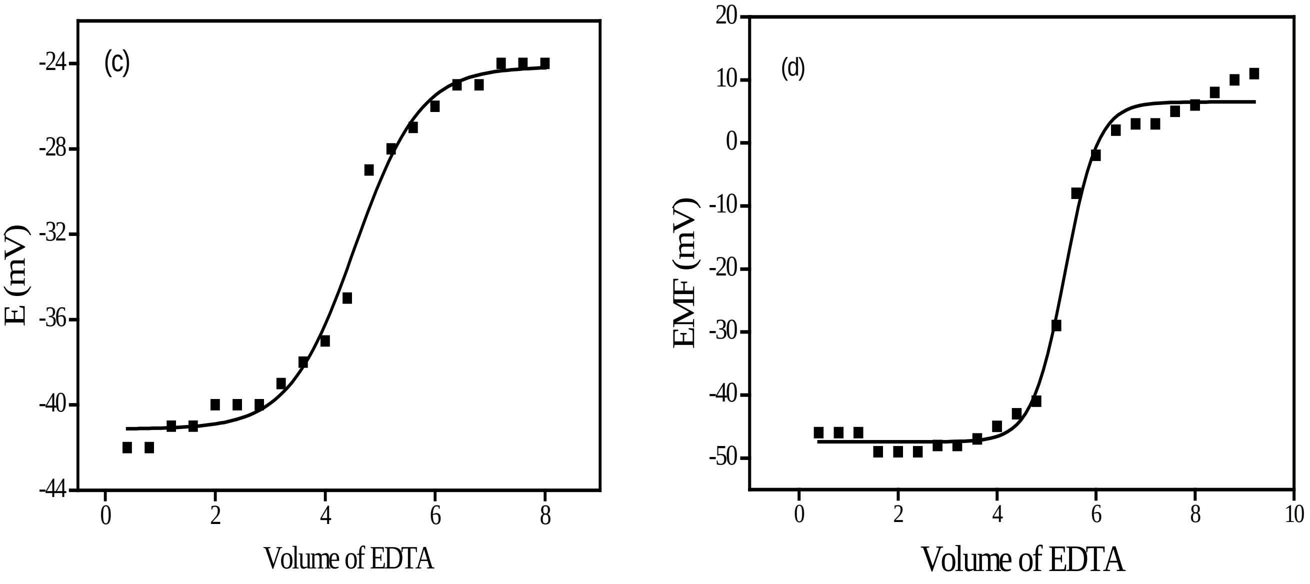


Figure 6. Potentiometric titration curves for electrodes with (c) ionophore I-3 and (d) ionophore I-4

5 CONCLUSION

The membrane electrodes incorporating ionophores I-1, I-2, I-3 and I-4 can be used to determine zinc in the concentration range of 10^{-5} to 10^{-1} M. All these electrodes exhibited near Nernstian slopes with the detection limit of 10-5 M.

These electrodes possessed good selectivity over other transition metal ions like Ni(II), Cu(II), Cd(II), Hg(II), Co(II), Pb(II) and also over trivalent metal ions like Ga(III), Al(III) and Ce (III). The proposed electrodes worked well over wide pH ranges and could also be used for determination of zinc by potentiometric titrations.

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