Potentiometric Studies on Neutral Carrier Based Ion Selective Electrodes for Aluminium ions : Effect of CNTs in the Liquid Membrane Electrode

A

Thesis submitted

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Under the Supervision of

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Manisha Sharma

Date: 10/7/13

Place: Patiala

ii

Candidate's Declaration

I, hereby declare that the work being presented in the thesis entitled **"Potentiometric Studies on Neutral Carrier Based Ion Selective Electrodes for Aluminium ions : Effect of CNTs in the Liquid Membrane Electrode",** 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 2013 to July 2013, 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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iii

Certificate

This is to certify that the thesis entitled **"Potentiometric Studies on Neutral Carrier Based Ion Selective Electrodes for Aluminium ions : Effect of CNTs in the Liquid Membrane Electrode",** being submitted by Ms. Manisha Sharma 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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iv

List of contents

Abstract

Potentiometric chemical sensors for aluminium ion based on T_4, T_5, T_6 as neutral ionophores has been prepared. o-Nitrophenyl octyle ether (o-NPOE) was used as plasticiser and sodium tetraphenyl borate (NaTPB) was used as lipophilic additive for the preparation of membranes. These electrodes have been studied for the detection of aluminium ions in different concentration range of 10^{-5} to 10^{-1}. The electrodes have been studied for interference from metal ions other than aluminium by using fixed interference method. The electrode show reasonably good selectivity for aluminium ions in the presence of interfering ions like Fe^{3+}, Cr^{3+}, Tb^{3+}, Sm^{3+}, La^{3+}, Ce^{3+}, Co^{2+}, Zn^{2+}, Cu^{2+}, Mg^{2+} and Ca^{2+}. The proposed electrodes also showed stable behaviour in different pH ranges. The membranes containing T_4, T_5, T_6 as ionophores doped with CNTs and these electrodes were also studied for detection limits, interference studies and in different pH ranges. Performance of the electrodes containing CNTs was better than other electrodes, not containing CNTs.

Overall performance of all the electrodes was very good and stable for aluminium ions.

1 Introduction

Chemical sensors consist of a recognition element that is sensitive to stimuli produced by various chemical compounds (analyte) and a transduction element that generates a signal whose magnitude is functionally related to the concentration of the analyte [1]. These sensors are miniaturized analytical devices, which can deliver real-time and on-line information on the presence of specific compounds or ions in complex samples. Ion selective electrode (ISEs) are one of the most successful chemical sensors, which can be used to determine the concentration of selected ions by comparatively simple measurements of electrical potentials with a voltmeter. Various techniques are used for determination of specific ion in the given sample. One of these is titrimetric analysis, but this is laborious and not very much selective. Practicaly, for many purposes there is a need for trace level analysis and it leads to the development of different methods like chromatography, spectrophotomety and electroanalysis.

Electroanalytical techniques are complementary to other various techniques based on absoption /emission spectroscopy and they involve the use of a spectrophotometer including flame emission spectroscopy (FES), atomic absorption spectroscopy (AAS), atomic fluorescence spectroscopy (AFS). There are many advantages of electrochemical monitoring, main by the achievement of lower detection limit. This achievement makes it a better technique than the other existing techniques. Electroanalysis gives a simple and better solution of those situations where other analytical techniques require complex and large equipments. Electroanalytical monitoring include techniques like conductometry, amperometry, potentiometry and voltammetry. Potentiometry involves the measurment of electrode potential of the system at equilibrium. In this method, the Nernst equation is used for the determination of concentration of an ion. There are various classes of chemical sensors among which ion selective electrodes (ISEs) is one of the most widely used for monitoring the environment clinical analysis and laboratory analysis as well as industrial analysis. It generally responds to one particular ion rather than others and it operates on the principle of concentration cell. For wide range of applications, ion selective electrodes subtitute various existing analytical methods. This is due to the reason that ion selective electrodes have relatively high accuracy, low cost, simple intrumentation good selectiviy, low detection limit, non destructive analysis, adaptable to small volume changes and can be applied to the coloured solutions.

1.1 Types of ion selective electrodes: For all kinds of electrodes used in potentiometric ion measurements is an ion-sensitive membrane. This membrane can be prepared as:

Solid membrane (fixed ion exchange sites)

(i) Glass membrane (ii) Crystal membrane

Liquid membrane (mobile ion exchange sites)

(i) Neutral (ii) Charged carrier

Membrane in a special electrode

(i) Gas-sensing (ii) Enzyme electrode

The binding sites are incorporated in the membrane matrix, which basically determines the internal polarity, lipophilicity, transport and other mechanical properties of the membrane of the ion selective electrode.

Glass membrane electrode: pH electrode is the best known example of this type of electrode, in these electrodes the anionic fixed sites are created by defects in the SiO_2 membrane and the cationic vacancies are created by the nonsilicon constituents of glass. This membrane shows good selectivity towards hydrogen ion with the composition : Na_2O 22%, 6% CaO and 72% SiO_2. When the glass membrane is exposed to water it exhibits improved mobility of the ions due to formation of hydrated layer. Two processes occur when there is interaction of glass hydrated membrane and the sample solution : ion-exchange and diffusion of all participating ions. These two processes influence the value of selectivity coefficient.

Liquid membrane electrode : These electrodes belong to the class in which a substance which is capable of exchanging ion is dissolved in water-immisible solvent. In these membranes the electro-active component which can be a neutral or a charged compound and is able to bind ion reversibly is called ionophore or an ion exchanger. It has the dimensions of molecule size. Ionophore contain a cavity which surrounds the target ion and form reversible, selective and strong complexes. There are two kinds of ionophores: charged one and neutral carriers. They are mobile in free as well as complexed forms, thus the mobilities of all species are part of the selectivity coefficient together with ion-exchange equilibrium. The mobile binding sites are dissolved in a suitable solvent and

usually trapped in a matrix of organic polymer. Ion activity measurements are performed mainly in aqueous media, thus all membrane components are lipophilic. Main components of PVC based polymeric membranes are polymer matrix, plasticizer, lipophilic salt and ionophore. It contain approximately 66% of an plasticizer and 33% of PVC. In order to ensure the mobility of the free and complexed ionophore an appropriate plasticizer is added to a membrane. It determines the membrane polarity and provides suitable mechanical properties of the membrane. Polymer matrix provides elasticity and mechanical strength to the membrane PVC is the most widely used matrix material. Lipophilic salt is added to improve the performance of the membrane in the aqueous media.

Solid membrane electrode: These type of membranes can be of two type : homogeneous and heterogeneous. Membranes with fixed sites including single crystals of sparinly soluble salt are the homogeneous membranes and the heterogeneous membranes are those in which the insoluble salt is dissolved in some suitable inert binder. It is necessary to use saturated solutions in order to get the equilibrium. Practically these electrodes are applied in non-saturated solutions so that the insoluble membrane slowly dissolves in this case. Insoluble inorganic materials such as Ag_2S, CuS, CdS, PbS, LaF_3, AgCl, AgBr, AgI and AgSCN are tested as cation exchange membranes. Sensors for the detection of ions like Ag^+, Cu^{2+}, Cd^{2+}, Pb^{2+}, S^{2-}, F^-, Br^-, I^-, SCN^- and CN^- ions can be prepared from such membranes. When the membrane film of PVC containing an ion-exchanger is simply attached to the wire, then they are called as coated-wire electrode. Example of coated wire electrode is silver-selective electrode.

Membrane in special electrode: In the last few years, development of new ion selective mainly directed towards the special electrodes:

Gas sensing electrode: Ion selective electrodes can be modified as potentiometric gas sensors. The original concept was made for sensing carbon dioxide. But this electrode operates on general principle which is applicable for other gas sensors for the detection of: NH_3, SO_2, NO_2, HCN etc. These electrodes are based on the measurement of variation in local ion-cativity, caused by permeation of gas molecules to the inner electrode compartment and their subsequent interaction with an internal solution. The pH change is detected by an internal pH electrode. It is important to note, that if the detected species is

hydrogen ion, then all acid/base species will interfere. Improved selectivity is obtained by an appropriate choice of the internal electrode.

Enzyme sensing electrode: By using composite membranes additional selectivity can be attained, in which an enzyme present in the outer part of the membrane catalyses a specific chemical reaction to generate product ions. These ions can be detected by an internal ion-selective membrane. Detection of urea using urease as the enzyme catalyst is the well-known example of these type of membranes [55].

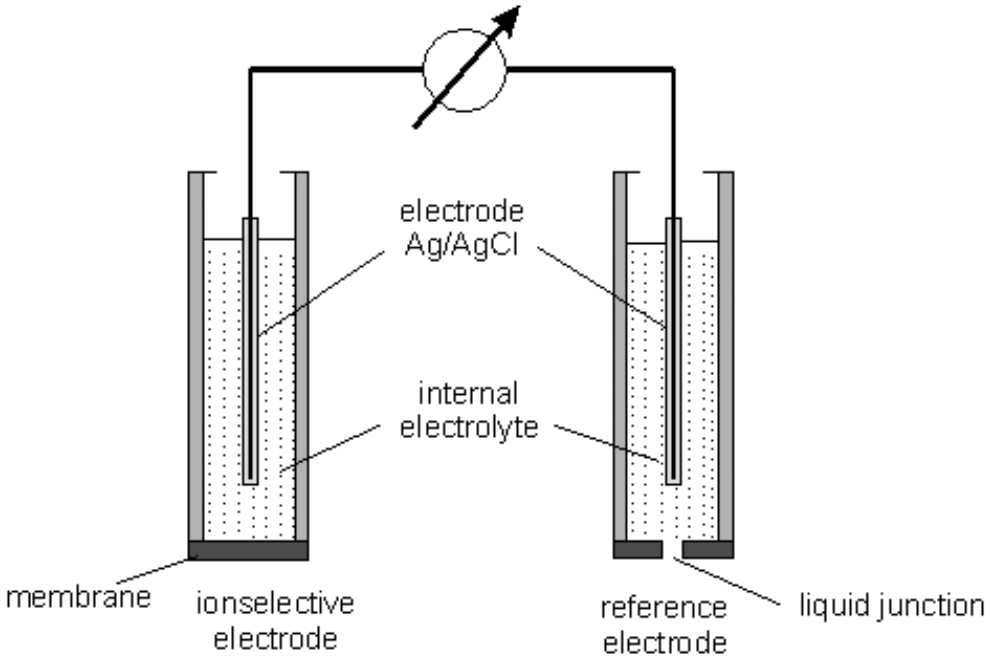


Fig 1. Measurement set-up of ion selectiveelectrode (ISE)

1.2 Ion selective electrode

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

$$\mathbf{E = RT/zF \cdot \ln (a_2/a_1)}$$

Potential difference is mearsured at zero current i.e, under equilibrium conditions. Measured electromotive force (EMF) is the sum of different potentials which are developed at solid-solid, solid-liquid and liquid-liquid interfaces. A set-up for electromotive force (EMF) measurement is shown in the figure given above (fig:1) .

1.3 Characteristics of ion selective electrode There are different factors which determine the performance of ISE.

Selectivity: Selectivity is one of the most important characteristics of an electrode, as it often determines whether there is possibility or not in the sample for reliable measurement. The selectivity coefficient (K) determines the selectivity of an ISE. It gives the information about capability of ISE to distinguish the ion of interest from other interfering ions. Most often it is expressed as the logarithm of K. Negative values indicate a preference for the target ion relative to the interfering ion. Positive values of log K indicate the preference of an electrode for the interfering ion. The experimental selectivity coefficients depend on the activity and a method of their determination. The effect of interfering ions on EMF is given **by Nicolsy-Eisenman equation:**

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

Slope: It is calculated from the linear part of calibration curve of the EMF measurement. The theoretical value of slope according to the Nernst equation is: 59.16 mv/decade for a single charged ion or 59.16/2 = 29.58 mV /decade for a double charged ion and for triple charged ion it is 19.72 mv/decade.

Working range: There are deviations from linearity at high and very low activities of target ion. Typically, the electrode calibration curve exhibits linear response range between 10^{-5}M and 10^{-1}M.

Detection limit: According the IUPAC recommendations the detection limit is defined by the cross-section of the two extrapolated linear parts of the ion-selective calibration curve. In practice, detection limit on the order of 10^{-5} to10^{-6}M is measured for most of ion-selective electrodes. The observed detection limit is often affected by the presence of other interfering ions or impurities.

Response time: It was defined as the time between the instant at which the ion-selective electrode and a reference electrode are dipped in the sample solution and the first instant at which the potential of the cell becomes equal to its steady-state value within 1 mV or has reached 90% of the final equilibrium value value.

1.4 Ion selective electrode doped with carbon nanotubes (CNTs)

Carbon nanotubes (CNT) were first reported by Iijima in 1991, and the first polymer nanocomposite using carbon nanotubes as a filler was reported in 1994 by Ajayan et al. The intoduction of carbon nanotubes has constituted a significant milestone in modern analytical sciences [57]. Carbon nanotubes are the cylinders of covalently bonded carbon molecules with novel properties like outstanding mechanical, electrical, thermal and chemical properties. These properties make them potentialy useful in wide variety of applications for example: optics, conductive polymers, sensors. CNTs are of two types, namely single-walled carbon nanotubes (SWCNTs), multi-walled nanotubes (MWCNTs) [58].

The electronic behaviour of CNTs shows that they have the ability to promote electron transfer reactions when used as electrode materials. Carbon nanotube surfaces shows enhanced electron transfer rates when used as an electrode in the electrochemical reaction . Scientist named Dai and Shiu demostrated that MWCNT-modified electrode could be employed as an amperometric oxygen sensitive electrode to construct a glucose biosensor offering a good performance for glucose determination. CNTs act as sensing materials in pressure, flow, thermal, gas, optical, mass, position, chemical and biological sensors. Some applications of CNTs based sensors are given below:

(1) **Biomedical industry**: CNT based nanosensors are highly suitable as implantable sensors, these can be used for monitoring pulse, temperature, glucose detection.

(2) **Food industry:** Various kinds of sensors and biosensors are being employed in the food industry to provide safety and quality control. CNT-based biosensors are being used for meat freshness monitoring. CNT-based chemical sensors can be used to detect undesired chemical residues resulting from food additives, animal drugs, pesticides, herbicides and other environmental contaminants in raw and processed foods.

(3) **Agriculture and fishing industry**: The MWCNT-coated quartz crystal microbalance humidity sensor can be used to monitor relative humidity over the range of 5-97%.CNT-

based pH sensors are highly useful for maintaining proper pH balance of water quality for fishing industries.

(4) **Manufacturing industry**: To make strain and pressure measurements in manufacturing industries, CNT based strain and pressure sensors are useful [58].

1.5 Advantages and Applications of Ion selective electrodes

Some of the advantages and applications of ion selective electrodes are given below:

1. Ion selective electrodes have several advantages like inexpensive, high selectivity, simple instrumentation, low detection limit, good accuracy and precision, non- destructive analysis and can also be applied to coloured and viscous solutions.
2. These are used for the detection of end point in the potentiometric titration by indicating the rapid change in the potential developed in the electrode system.
3. In many samples ISEs are useful for trace level analysis, thus ideal for monitoring environmental pollution or water quality.
4. This is the technique which can measure both cation and anion.
5. They are useful in biological applications as they measure directly the activity of ions in place of concentration.
6. These are ideal for long term monitoring of changes in ion concentration i.e, for measuring the rate of the reaction or nutrient uptake [56].

2 Literature Review

2.1 Development of ion selective electrodes

In 1906 Max Cremer discovered pH-sensitive glasses which started the history of the ion selective electrode, this further led to the the development of the first commercial pH glass electrodes in the 1930s. After that a wave of sensing materials evolved in 1960 by the introduction of crystalline compounds such lantanum fluorides, silver chloride as detecting materials. This considerably expanded the number of ions that could be detected. Most important ISEs of this type are the fluoride and halide selective electrodes. The ISEs based on glasses and the crystalline materials are useful for many applications, but further enhancement of ISEs based on these materials was hindered by the poor ionic condutivity of these materials, then the ISEs based on ionophore (ion binding receptor) come in to light, which completely transformed the field of ion selective electrodes. A major breakthrough came with introduction of ionophore and concept of host-guest chemistry.

A significant advancement was made in the field of host-guest chemistry by Pederson who invented the crown ethers in 1960s. After that a large scale development of synthetic polymer took place, which replaced the atomic emission spectroscopy for the detection of ions, specially in blood sample [44]. During 1960s, the discovery of calcium selective electrode was made by Ross and Frant. In 1966 Simon and Stefanac showed that a thin film responded to monovalent cations which is formed by water immiscible organic solvent doped with antibiotics. The best known example of these type of electrode is potassium selective electrode based on antibiotic valinomycin. Because of its high ion selectivity it is used to detect the potassium ion in the biological samples. Before this the first known example of such ISEs is ammonia selective electrode in which nonactin and monactin act as the receptor. In 1967 liquid membrane electrodes were introduced by immobilizing the ionophore in polyvinyl chloride. During the last two decades, a large number of neutral ionophores for specific metal ions with high selectivities have been developed and have found numerous applications in potentiometric and optical sensors for the determination of the particular metal ions in a variety of real samples [43].

2.2 Alkali metal ion selective electrodes

Since alkali metal are generally present in significant amounts in all natural and biological fluids, together with several inorganic and organic ligands, thus a large amount of work has been done on alkali metal ion selective electrode. Crown ethers are the macrocyclic ethers compounds containing several oxygen atoms, with each oxygen atom being bound between two of the carbon atoms and arranged in a ring. These crown ethers have more stable complex formation stability than the acyclic ligand. Through this ability of cavities in crown ethers, the detection of metal ion can be achieved. Thus these can be used as ionophores in the ion selective electrodes. As the cavity size of the crown ethers are very specific, so a particular size metal ion can form the complex with that crown ether. 12-crown-4 is specific for lithium ion, sodium ion is fit for cavity size of 15-crown-5 and 18-crown-6 cavity can form stable complex with potassium ion. For alkali metal ion it is difficult to form complex with other ligand. Thus crown ethers became the best choice as netural ionophores for these type of metal ions [18].

Reinhoudt and co-workers have synthesised a new 1,3-alternate calix[4]arene-crown-5 derivative which shows the selectivity of potassium and sodium ion higher than valinomycin. An inverse potassium and sodium ion selectivity in ISEs has been reported by Sinkai and Yamamoto. They used a calix[4]arene dialkyl ether which contain four oxygen atoms in the glycol chain. Selectivity for larger alkali metal ions such as rubidium and caesium has been obtained with calix[4]arene-crown-6 [38].

Table 1. Electrode characteristrics of ionophores for alkali metal ions

Ionophore	Selected metal ion	Slope (mv/decade)	Working Range(M)	Reference No
N,*N*'dicyclohexyl-*N'*,*N'*-diisobutyl-cis-cyclohexane-1,2-dicarboxamide	Li(I)	58.7	2×10^{-6} to 1	2
1-methyl-1-vinyl-14-crown-5	Na(I)	55.0	3.16×10^{-6} to10^{-1}	3
calix[4]crown-5-azacrown-5	K(I)	55.2	10^{-5} to 10^{-1}	4
indanopyrazolo[1,5-*a*]pyrimidines	Rb(I)	59.0	10^{-1} to 10^{-4}	5
calix[6]arene tetraester	Cs(I)	55.7	10^{-6} to 10^{-1}	6

2.3 Alkaline earth metal ion selective electrode

As Mg^{2+} and Ca^{2+} have their applications in clinical analysis and other field so, a large number of work was done with these metal ions. Because of small size of the Mg^{2+} the hydration energy of Mg^{2+} is higher than Ca^{2+}, so an ionophore which can bind with both, will preferably bind to the Mg^{2+}. Mg^{2+} based ISEs were introduced in 1994 as clinical analyzers. Much work was supported only by experimentally determined potentiometric selectivities alone, as stability constant determination were not available . The Ca^{2+} ionophores currently being used are PVC based containing (ETH1001 and ETH 129) [6]. Ca^{2+} was bound with diaza crown ethers, the metal ion is present in the crown ring and the two pendents from top and bottom bind to Ca^{2+}. Mg ion ionophores are similar in appearances structurally with Ca ion ionophores. Literature survey shows that very little work has been done on the development of ISEs for Be^{2+}, Sr^{2+} and Ba^{2+}. In 1998, first time a highly selective Be^{2+} membrane-sensor based on benzo-9-crown-3 was introduced [39]. The membranes of an epoxy-resin binder were found suitable for Ba^{2+} sensors by Lal and coworkers. Nakamura and Rechnitz reported a Ba^{2+} selective electrode based on immobilized dibenzo-18- crown-6 ionophore. Recently, Saleh reported neutral bidentate organophosphorus compounds as ionophores for potentiometric membrane sensors for Ba^{2+} [40]. In comparison with other alkali and alkaline earth metal cations, only a few Sr^{2+} selective sensors have been reported which suffer from various limitations [41]. The performance of the Sr^{2+}electrodes using three synthesized lipophilic diamides with pyridine ring as neutral Carriers have been reported in 1998 [42].

Table 2. Electrode characteristics of ionophores for alkaline Earth metal ion

Ionophore	Selected metal ion	Slope (mV/decade)	Working range (M)	Reference no
dibenzo(perhydrotriazino)aza-14-crown-4 ethers	Be(II)	30.7	7.6×10^{-6} to 10^{-1}	7
Benzo-15-crown-5	Mg(II)	31.0	10^{-5} to 10^{-1}	8
Calix[4]arene tetraphosphine oxide	Ca(II)	26.3	10^{-1} to 10^{-4}	9
2,3,4-pyridine-1,3,5,7,12-pentaazacyclopentadeca-3-ene	Ba(II)	30.0	1.41×10^{-6} to 10^{-1}	10
N,*N*,*N*',*N*'-tetracyclohexyl-2,6-pyridine-bis(methyleneoxy acetamide)	Sr(II)	29.0	2×10^{-5} to 1×10^{-1}	11

2.4 Transition metal ion selective electrode

During the past two decades, a large number of efforts have been made in the synthesis and characterization of neutral ionophores with high selectivities for specific metal ions which can develop new potentiometric and optical sensors for the determination of the respective metal ions in real samples [12]. Calixarenes are the examples of these type of ionophores with high selectivity for specific metal ions. Recently, thiacalix[4]arenes have been reported as well known member of calixarenes family. These thiacalixarenes shows the properties like large cavity, oxidizability of bridging sulphur and coordination to transition metals, thus because of these properties these ionophores show their selectivity towards Cu(II), Co(II), Ni(II), Zn(II) metal ions. For Cu(II) these shows highest selectivity. A polymeric thiacalixarenes which is derived from terephthaloyldichloride shows better selectivity for Cu(II), Cd(II), Hg(II), Pd(II), Co(II) and Ni(II) transition metal ions [13].

The Porphyrin rings also form stable complex with many metal ions, thus these can be used as ionophores to realize selective and sensitive complex formation with specfic ions. Frequently, the reports on their use as ionophore for copper and cobalt ions in ion selective electrode have been found. In recent years is is found that the porphyrin was used as lead ISEs [14]. Reports show that very little work has been done on the development of ion-selective electrodes for cobalt(II) ions and several number of sensor materials such as Schiff base, chelates, macrocycles, variety of other ligands have been used for the past years [15]. Iron(III)-selective PVC membrane electrodes based on formylsalicylic acid derivatives has been reported which shows a high selectivity for iron(III) in comparison with alkali, alkaline earth and heavy metal ions [16]. In copper ion selective electrode carriers include small size thia-crown ethers and acyclic neutral ionophores with dithiocarbamate groups and with nitrogen atoms, calix[4]arenes, macrocyclic diamides and Schiff bases. However, most of these copper-selective sensors suffer from the interfering effect of such cations as Zn^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+} and Ag^{1+} [17]. In 1996 the use of cryptands as ionophores in the construction of Zn(II) selective electrode was reported.

Table 3. Electrode characteristics of ionophores for Transition metal ion

Ionophore	Selected metal ion	Slope (mV/decade)	Working range (M)	Reference no.
4-amino-3-hydrazino-6-methyl-1,2,4-triazin-5-one	Cr(III)	19.7	$10^{-6\ to}\ 10^{-1}$	17
p-chloroaniline-3-formylsalicylic acid	Fe(III)	20.0	10^{-1} to 5×10^{-5}	16
(2-mercapto-4-methylphenyl)-2-benzamido-3-phenyl-thiopropenoate	Co(II)	30.0	1.0×10^{-2} to 4.0×10^{-7}	19
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} to 1.0×10^{-1}	20
2-picolyl armed 1,3-alternate calix [4] azacrown ether	Cu(II)	24.5	$10^{-4.5}$ to $10^{-2.5}$	21
N,*N*'bis(acetylacetone)ethylenediimine	Zn(II)	30.0	10^{-6} to10^{-1}	22
N,N'-bis(3-methyl-1-phenyl-4-benzylidine-5-pyrazolone)propylenediamine	Ag(I)	59.3	10^{-6} to10^{-1}	23
[1,1'-bicyclohexyl]-1,1'-2,2'-tetrol	Cd(II)	27.8	10^{-1} to 10^{-5}	24
4-(4-*N*,*N*-dimethylphenyl)-2,6-diphenylpyrilium tetrafluoroborate	Hg(II)	34.0	10^{-8} to 10^{-3}	25

2.5 Lanthanides ion selective electrodes

Lanthanides have attracted attention over the past few years. The ionophores which are used for lanthanide ion generally possessed semi cavity and contained S, N and other hetero atoms. These ionophores are selective for particular cations. Thus these were able to form stronger complexes with a specific cation rather than with others. This is due to the size and the charge density of the cation. Recently a large number of of lanthanide selective membrane sensors for La(III), Ce(III), Gd(III), Sm(III), Eu(III), Dy(III), Tb(III)

and Yb(III) ions based on different noncyclic and macrocyclic ionophores have been introduced.

Table 4. Electrode characteristics of ionophores for Lanthanides metal ion

Ionophore	Selected metal ion	Slope (mV/decade)	Working range	Reference no
N'-[(2-hydroxyphenyl)methylidene]-2-furohydrazide	Ce(III)	19.4	1.0×10^{-5} to 1.0×10^{-1}	26
N-[2-[4-[[[(cyclohexyle amino) carbonyl]amino]sulphonyl] phenyl]ethyl]-5-methyl pyrazine carboxamide (glipizid)	Sm(III)	19.8	1.0×10^{-1} to 1.0×10^{-6}	27
bis(thiophenal)phenylen-1,3-diamine (TPD)	La(III)	19.6	1.0×10^{-7} to 1.0×10^{-1}	28
N'-(pyridin-2-ylmethylene)benzohydrazide (PBA)	Pr(III)	21.1	1.0×10^{-2} to 1.0×10^{-6}	29
N,N'-bis((1H-pyrrol-2-yl)methylene)cyclohexane-1,2-Diamine	Nd(III)	19.8	5.0×10^{-7} to 1.0×10^{-2}	30
N-pyridine-2-carboxamido-8-aminoquinoline (PCQ)	Eu(III)	19.8	1.0×10^{-2} to 1.0×10^{-6}	31
N'-(2-Hydroxy-1,2-diphenylethylidene) benzohydrazide (HDEBH)	Er(III)	21.0	1.0×10^{-7} to 1.0×10^{-2}	32
3,4,5:12,13,14-dipyridine-2,6,11,15-tetramethyl-1,7,10,16-tetrame thylacrylate-1,4,7,10,13,16-hexaazacyclooctadeca-3,13-di ene	Tb(III)	19.8	8.7×10^{-8} to 1.0×10^{-1}	33
2-(4-phenyl-1,3-thiazol-2-yliminomethyl)phenol	Gd(III)	19.5	9.38×10^{-7} to 10^{-2}	34
N-phenyl-2-(thiophen-2-ylmethylene)hydrazinecarbothioamide (PHC)	Ho(III)	20.4	10^{-6} to 10^{-2}	35
1-((Dimethylamino)(phenylimino)methyl)-3,3-dimethyl-1- phenylthiourea (DPDP)	Dy(III)	20.5	1.0×10^{-7} to 5.0×10^{-1}	36
2-amino-4-(4 aminophenyl)thiazole	Lu(III)	18.7	1.0×10^{-6} to 1.0×10^{-1}	37

2.6 Aluminium selective electrodes

A poly(vinyl chloride) matrix membrane electrode in which 7-ethylthio-4-oxa-3-phenyl-2-thioxa-1,2-dihydropyrimido-[4,5-d]pyrimidine (ETPTP) acts as an ionophore was introduced in 2001 by Mohamed B.Saleh. The electrode exhibits good potentiometric response for Al^{3+} over a wide concentration range (10^{-5} to 10^{-1} M) with a slope of 19.5mV per decade. It exibits good selectivity for Al^{3+} in comparison with alkali, alkaline earth, transition and heavy metal ions. The proposed sensor is used for potentiometric titration of HPO_4^{2-} with Al^{3+} and for direct potentiometry of Al^{3+} content of some rocks [47].

In 2002, A.Abbaspour reported a PVC membrane electrode for aluminium ion based on bis(5-phenyl azo salicylaldehyde) 2,3-naphthalene diimine (5PHAZOSALNPHN) as an ion carrier. The electrode exhibited a Nernstian slope of 19.3 mV per decade and a linear range of 5.0×10^{-6} to 1.0×10^{-2} M for $Al(NO_3)_3$. The proposed membrane sensor revealed good selectivity for Al^{3+} over a wide variety of other metal ions and could be used in pH range of 2.9–5.0 [46]. The suitability of a xanthone derivative, 1-hydroxy-3-methyl-9H-xanthen-9-one (HMX) as a neutral ionophore for the preparation of a polyvinylchloride (PVC) membrane electrode for aluminum(III) ions was investigated by Abdollah Yari in 2005. The prepared electrode exhibits a Nernstian response for Al^{3+} ions over a wide concentration range (1.0×10^{-6} to 1.6×10^{-1} M). The proposed membrane electrode revealed very good selectivity for Al^{3+} ions over a wide variety of other cations and could be used at a working pH range of 3.0–8.5 [49]. An ion-selective PVCmembrane selective for Al(III) ions based on 6-(4-nitrophenyl)-2-phenyl-4-(thiophen-2-yl)-3,5-diaza-bicyclo[3.1.0]hex-2-ene (NTDH) as a new ionophore has been reported by M. Arvand in 2008. The electrode exhibited a good response for aluminum ion over concentration range of 1.0×10^{-6} to 1.0×10^{-1} mol L^{-1} with a Nernstian slope of 19.6±0.4mV per decade and low detection limit of 6.3×10^{-7} mol L^{-1}. NTDH-based electrode was suitable for aqueous solutions of pH 3. The proposed membrane electrode showed good selectivity for Al(III) ions over a wide variety of other cations [45].

In 2009, a potentiometric aluminium sensor based on the use *N*,*N*'-bis(salicylidene)-1,2-cyclohexanediamine (NBSC) as a neutral carrier, in poly(vinyl chloride) (PVC) matrix, is reported by Vinod K. Gupta. The sensor exhibited significantly enhanced selectivity toward Al^{3+} ions over the concentration range 1.0×10^{-8} to1.0×10^{-1}M with a lower

detection limit of 5.0×10^{-9}M and a Nernstian slope of 20.3±0.1mV/decade. It shows fast and stable response, good reproducibility and long-term stability . Selectivity coefficients determined by matched potential method (MPM) indicate high selectivity for aluminium (III) ion. The proposed electrode showed fairly good differentiation of aluminium (III) from many metal ions. It was successfully applied for direct determination of aluminium (III) in biological, industrial and environmental samples [50].

First time in 2010 a coated wire electrode (CWE) for Al(III) ions is described based on 2-(1H-benzo[d]imidazole-1-yl)-1-phenylethanoneoxime as a new ionophore in carbon–PVC composite by A. Abbaspour. The sensor exhibits significantly enhanced selectivity toward Al^{3+} ions over the concentration range 4.3×10^{-7} to 5.0×10^{-2} M with a lower detection limit of 2.5×10^{-7}M and a Nernstian slope of 19.41±0.52mVdecade of aluminium activity. This proposed CWE which is designed for the first time revealed good selectivity for Al(III) over a wide variety of other cations [48].

A potentiometric aluminium sensor, based on the use AlMCM- 41(mesoporous aluminosilicates) as a neutral carrier, in poly (vinyl chloride) matrix, is reported in 2010 by Majid Arvand. It exhibited significantly enhanced selectivity toward Al^{+3} ions over the concentration range 1.0×10^{-7} to 1.0×10^{-1}M with a Nernstian slope of 19.5±0.4 mV/decade of activity. It showed fast and stable response, good reproducibility and long-term stability. It was used to determine Al^{3+} in drugs and food products [51].

2.7 Electrodes doped with Carbon nanotubes(CNTs)

In 2009, negatively charged multi-walled carbon nanotubes (MWCNTs) were used as dopants in the electrochemical synthesis of the conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT) by Zekra Mousavi. The resulting electroactive film, PEDOT(CNT), was used as ion-to-electron transducer (solid contact) in potassium ion-selective electrodes (K^+ ISEs) based on plasticized PVC membrane containing valinomycin as neutral ionophore. Potentiometric measurements were carried out to study the analytical performance of solid-contact K^+ ISEs, the influence of dissolved O_2 and CO_2 on the potential of the electrodes, and the formation of the interfacial aqueous film. These electrodes, based on PEDOT(CNT) as ion-to-electron transducer, showed high sensitivity and selectivity to K^+ ion which can be related to the plasticized PVC-based ion-selective membrane containing valinomycin. The stability of the electrode potential however, was

found to depend on the conducting substrate used for deposition of the PEDOT (CNT) film [54].

In 2010 M.R. Ganjali reported that based on the conductometric studies of the binding properties of the macromolecule (1-[({2-[2-(2-hydroxy-1-naphtyl)-3-(2-{[(E)-1-(2-hydroxy-1-naphtyl)methylidene] amino}ethy l)- 1 -imidazolidinyl] ethyl} imino) methyl] - 2 - naphthol) (HHN) and a series of main group, transition and lanthanide cations it was expected to have good potentials as a proper ionophore for constructing an ion selective electrode (ISE) for La^{3+} ions. The compound was hence used as an ionophore in a membrane of a new composite carbon paste electrode comprising acetyl grafted multi-walled carbon nano tube (MWCNT-COOH), graphite and a room temperature ionic liquid (RTIL), 1-n-butyl-3-methylimidazolium tetrafluoroborate [bmim] BF_4. The capability of the ionic liquid and paraffin were also compared and it was observed that membranes comprising 60-65% wt of graphite, 15-20% wt of the RTIL, The best performance for nano-composite sensor was obtained with electrode with composition of 10% HHN, 20% [bmim] BF_4, 60% graphite powder, and 10% MWCNT-COOH. The electrode exhibited a Nernstian response (19.7±0.3 mV decade-1) toward La^{3+} ions in the range of 1.0×10^{-9} to 1.0×10^{-2} mol L^{-1} with a detection limit of 8.0×10^{-9} mol L^{-1} [52].

A sensitive amperometric sensor for the selective detection of hydroquinone in cosmetics was developed by Guiyun Xu in 2012, which was based on the excellent electrocatalytic property of carbon nanotube (CNT) doped poly(3,4- ethylenedioxythiophene) (PEDOT) conducting polymer toward the oxidation of hydroquinone. The oxidation potential of hydroquinone on the PEDOT/CNT modified carbon paste electrode was much lower than that on the electrode without CNTs, and the charge transfer rate constant for the oxidation of hydroquinone was significantly increased from 0.45 to 1.84 s^{-1} after the modification with PEDOT/CNT. Under optimal conditions, the differential pulse voltammetry current of the sensor was linear with hydroquinone concentration across a 1.1–1.25 M range and associated with a detection limit of 0.3 M. Significantly, the detection limit is comparable or better than many current electrochemical hydroquinone assays, and the sensor is potentially much cheaper and easier for fabrication. The sensor was capable not only of comfortably quantifying hydroquinone in the presence of common interferences but also doing this in real cosmetics samples with satisfaction and accuracy [53].

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 $Al(NO_3)_3$, $Cu(NO_3)_2$, $Ca(NO_3)_2$, $Zn(NO_3)_2$, $Co(NO_3)_2$, $Mg(NO_3)_2$, $Fe_2(SO_4)_3$ (analytical grade) were purchased from Sigma Aldrich and were used as such. Salts like $Ce(NO_3)_3$, $Cr(NO_3)_3$, $Sm(NO_3)_3$, $Pr(NO_3)_3$, $Tb(NO_3)_3$, $La(NO_3)_3$, were purchased from CDH (central drug house). Doubly distilled deionised water was used through the experiments.

3.2 Preparation of Al(III) nitrate stock solution

Aluminium nitrate hexahydrate was weighed accurately and transferred to measuring flask to prepare 0.1 M solution of aluminium nitrate. Then solution of various concentration (10^{-2} to 10^{-8}) were prepared with further dilutions.

3.3 Membrane preparation

Six membranes with three different ionophores were prepared by standared procedure. PVC, o-NPOE, lipophilic salt and ionophores (T4, T5, T6, without CNTs and with CNTs) 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 the glass rings which were placed on the glass plates. Again the solutions were allowed to evaporate slowly at room temperature the prepared membrane was removed from the glass plate and fixed to one end of the glass body by using an epoxy as adhesive. Then each membrane was equilibrated with Al(III) solution (0.1M) for about 4-5 days.

3.4 EMF Measurements

Membrane electrodes were filled one fourth with Al(III) nitrate solution and immersed in the beaker containing the test solution of different concentration of aluminium. The level of inner filling solution was kept higher than the test solution so as to avoid reverse diffusion of the electrolyte. The potentiometric measurment were made by using digital potentiometer. All the measurement were done by using the following cell assembly :

SCE|Al^{3+}(0.1)M||Membrane||Al^{3+} (Test solution) |SCE

3.4 pH adjustment of solution

pH of salt solution was adjusted by the introduction of small additions 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 changed ionic strength of the solution.

3.5 Interference studies

The effect of interfering ions on the potentiometric response of the electrode was measured in terms of selectivity cofficients, $K_{A,B.}$ 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 primary ion but the activity of interfering ion remain fixed throughout the experiment. The potential values were plotted against logarithm of primary ion concentration. The intersection of the extraploted 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.

$$K_{A,B} = a_A / (a_B)^{Z_A/Z_B}$$

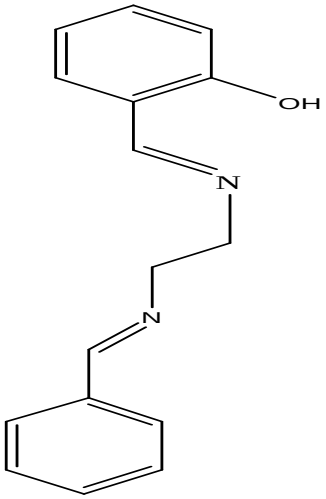
Here, a_A is the activity of the primary ion A and a_B is the activity of interfering ion B and Z_A and Z_B are the respective charges. The concentration of the primary ion was varied from 10^{-8} M to 10^{-1} M, but the concentration of interfering ion was fixed i.e 10^{-3} M for all membranes which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

4 Result and Discussion

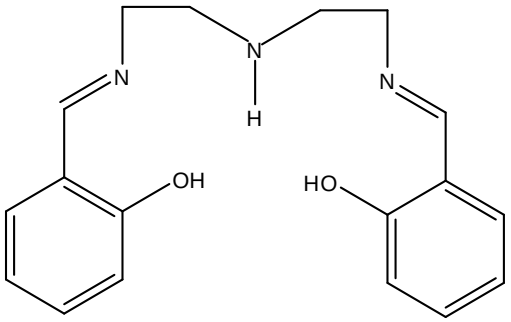
4.1 Membrane composition

Membranes with different amounts of the ionophore in the different range of ratios were prepared and used for studying electrode response for primary ions. However, the best result were obtained with membrane having composition ionophore : PVC:Plasticiser:Lipophilic additive in the percent ratio 3:33:63:1.

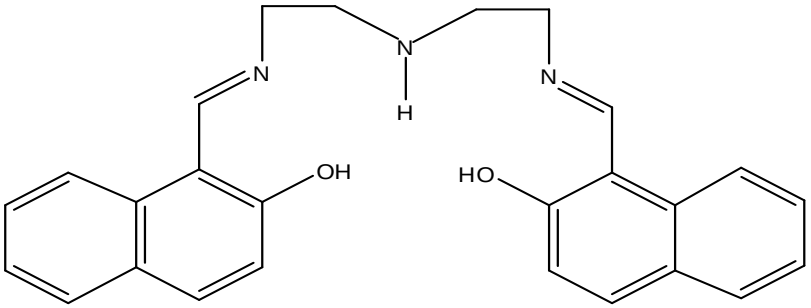
o-nitrophenyl octyle ether (o-NPOE) was used as plasticiser and sodium tetraphenyl borate (NaTPB) was used as lipophilic additive for the prearation of membranes. The presence of lipophilic additives generally improves the performance characteristics of various cation selective electrodes with the minimization of ohmic resistance. Experiments were conducted to study electrode responses with three different ionophores with CNTs and without CNTs having partial structures of which are given below:



Ionophore T_4



Ionophore T_5



Ionophore T_6

Fig 2. Structures of ionophores T_4, T_5, T_6

4.2 Calibration curves

PVC membrane electrodes were equilibrated with $Al(NO_3)_3$ for about 5 days so as to saturate the cavities of ionophore with aluminium ions. Potentiometric readings were recorded with the electrode immersed in the different concentration of aluminium ion 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:

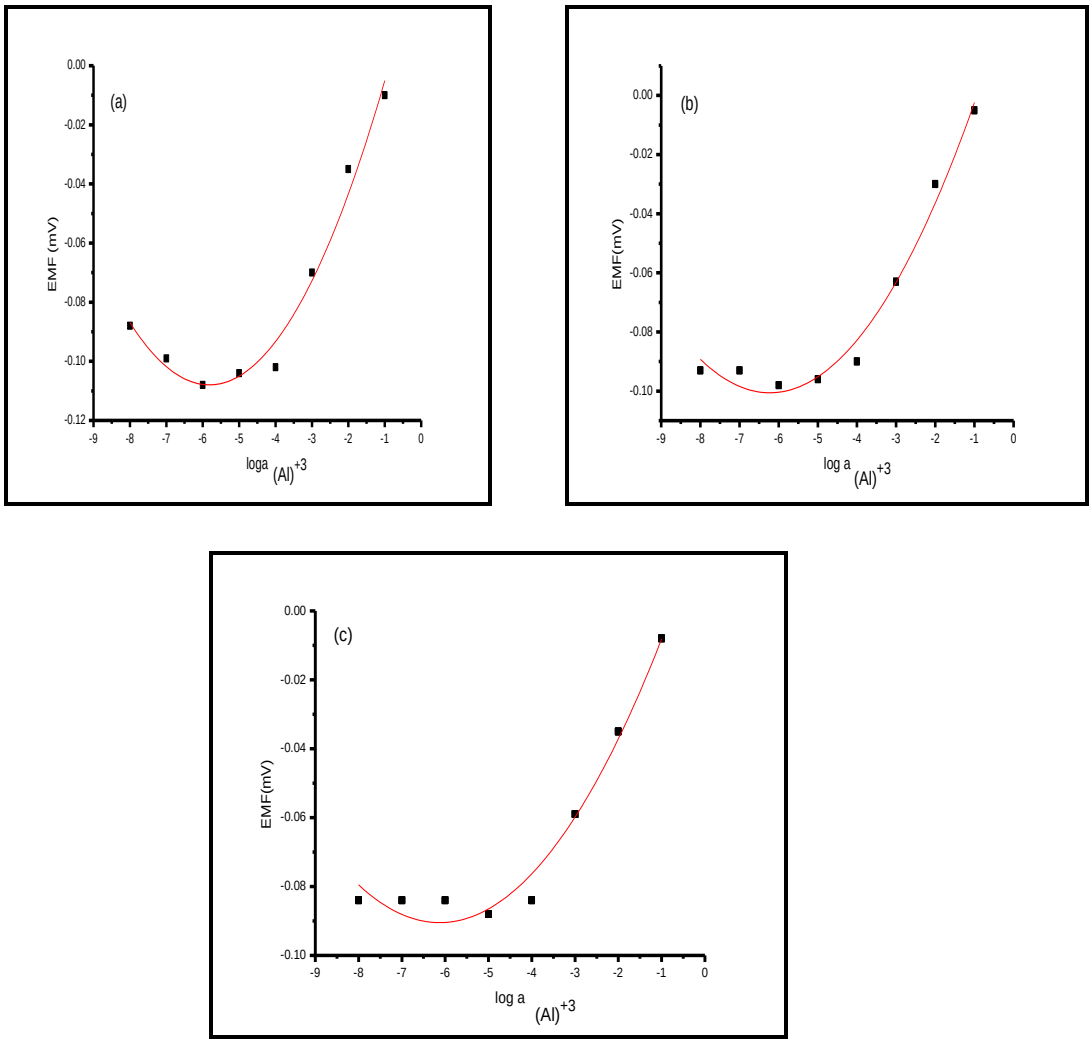


Fig 3. Calibration curves for Al^{3+} ion using electrode with (a) Ionophore T_4 (b) Ionophore T_5 (c) Ionophore T_6

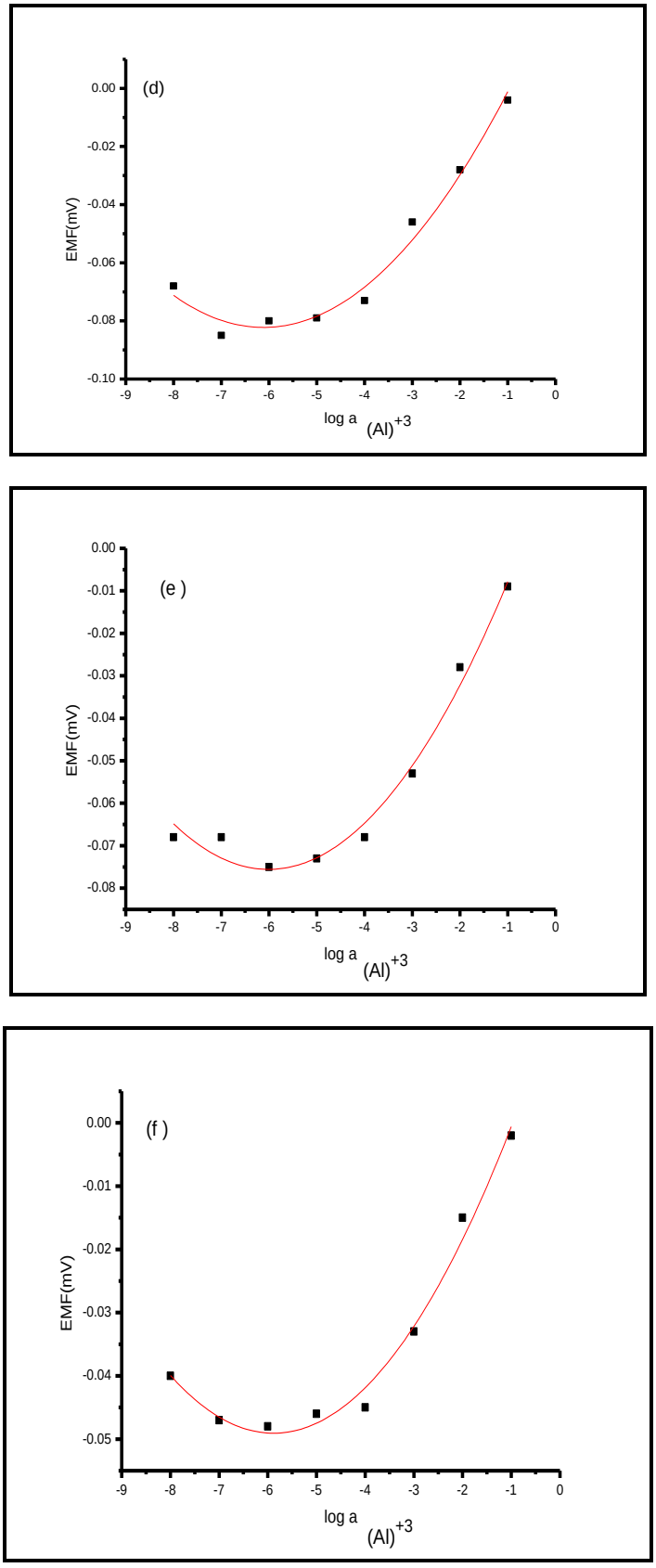


Fig 4. Calibration curves for Al^{3+} ion using electrode with (d) Ionophore T_4 with CNTs (e) Ionophore T5 with CNTs (f) Ionophore T_6 with CNTs

Slopes of calibration curves for Al^{+3} ion using electrode with ionophore i.e. T_4, T_5,T_6 without CNTs and with CNTs, were calculated and given in table 5. From the graphs, it is observed that all the electrodes with ionophores exibited near Nernstian slopes with working range from 10^{-5} to 10^{-1}.

Table 5. Slopes of the calibration curves for Al^{+3} ions using electrodes with ionophores T_4,T_5,T_6

S.No.	Slope (mV)/ decade					
	Ionophore T_4	Ionophore T_5	Ionophore T_6	Ionophore T_4 with CNTs	Ionophore T_5 with CNTs	Ionophore T_6 with CNTs
1.	17.0	16.5	19.0	16.5	18.0	22.0
2.	18.0	17.5	22.0	18.0	19.0	19.0
3.	16.5	17.0	17.0	18.0	16.3	19.0
4.	18.0	19.0	19.5	19.0	19.4	17.0
Mean	17.3$\pm$1.0	17.5$\pm$1.5	19.3$\pm$1.0	17.8$\pm$2.0	18.1$\pm$1.0	19.25$\pm$2.0

Table 6. Detection limits by calibration curves for Al^{3+} ions using electrodes with Ionophores T_4,T_5,T_6

S.No.	Detection limit (M L^{-1})					
	Ionophore T_4	Ionophore T_5	Ionophore T_6	Ionophore T_4 with CNTs	Ionophore T_5 with CNTs	Ionophore T_6 with CNTs
1.	2×10^{-5}	1×10^{-5}	1×10^{-5}	1×10^{-6}	6×10^{-5}	5×10^{-5}

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} to 10^{-1} but the concentration of the interfering ion was fixed i.e 10^{-3} M. The selectivity coefficient values of Al^{3+} selective electrode prepared with ionophores T_4,T_5,T_6 for different interfering ion is shown in Table 7.

Table 7. Selectivity coefficient values of Al^{3+} selective electrodes with T_4, T_5, T_6

S.No	Interfering ions	Selectivity coefficient ,log K		
		T_4	T_5	T_6
1.	Mg^{2+}	-0.04	0.39	-0.15
2.	Co^{2+}	0.20	0.38	0.01
3.	Zn^{2+}	0.44	0.54	0.30
4.	Cu^{2+}	1.43	1.15	1.18
5.	Ca^{2+}	0.30	0.69	0.59
6.	Fe^{3+}	-2.21	-1.10	-1.60
7.	Cr^{3+}	-0.80	-1.13	-1.61
8.	Tb^{3+}	-1.50	-1.39	-1.50
9.	Pr^{3+}	-1.51	-2.52	-1.73
10.	Sm^{3+}	-1.22	-1.69	-1.37
11.	La^{3+}	-0.89	-2.39	-1.38
12.	Ce^{3+}	-1.19	-1.60	-1.52

For ionophores with CNTs the interference studies were same. From the above table it can be concluded from the values of selectivity coefficients that ions having values less than one show limited interference with the working of the propsed electrode for Al^{3+} determination. As Al is as tripositive ion so the above values will be less than one only for tripositive ions(it is the limitation of fixed interference method). The electrodes show reasonably good selectivity for aluminium ion in the presence Fe^{3+}, Cr^{3+}, Tb^{3+}, Sm^{3+}, La^{3+} and Ce^{3+} while it suffers interference from Co^{2+}, Zn^{2+}, Cu^{2+}, Mg^{2+} and Ca^{2+}. The membrane electrodes containing CNTs in the matrix along with the ionophore did not show much difference in their performance except for a little less interference from the above listed metal ions.

4.4 Effect of pH

pH response of the electrode was studied by the use of 1×10^{-4} M Al^{+3} solution over the range 2-10. The adjustment of pH was done by the drosp wise 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 ionophore are shown in Figures 5, 6 and 7:

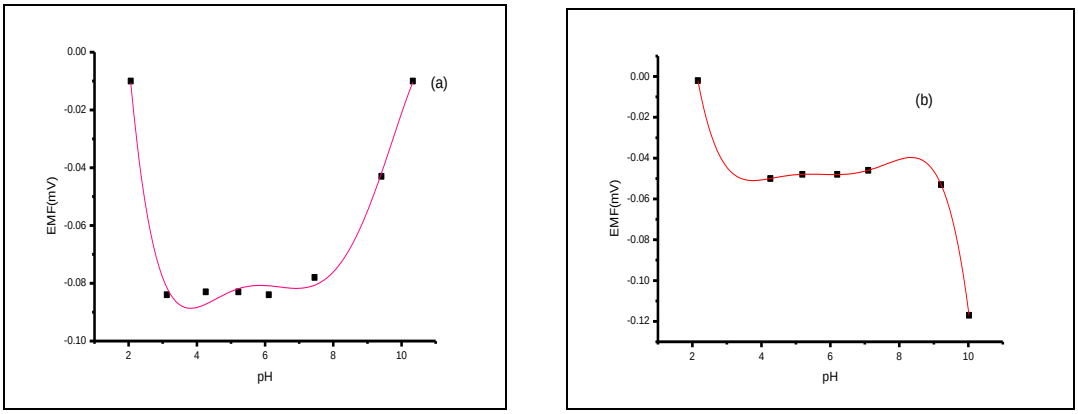


Fig 5. Working pH range of electrodes with (a) Ionophore T_4 and (b) Ionophore T_5

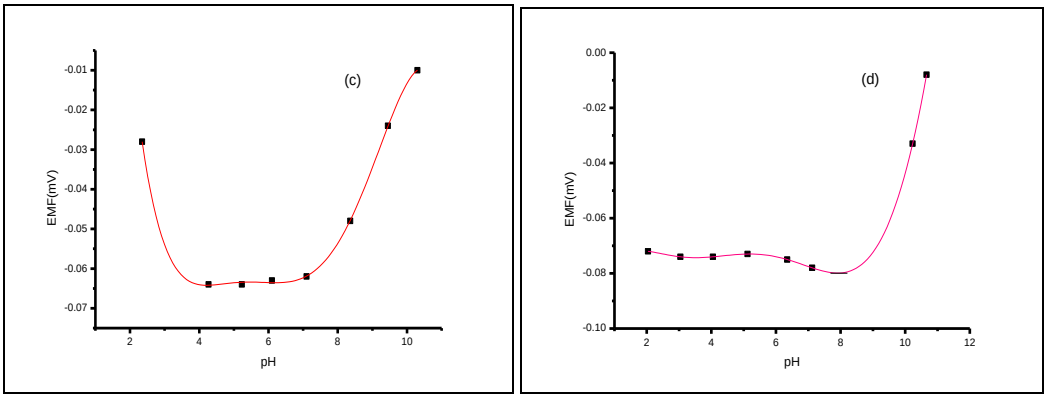


Fig 6. Working pH range of electrodes with (c) Ionophore T_6 and (d) Ionophore T_4 with CNTs

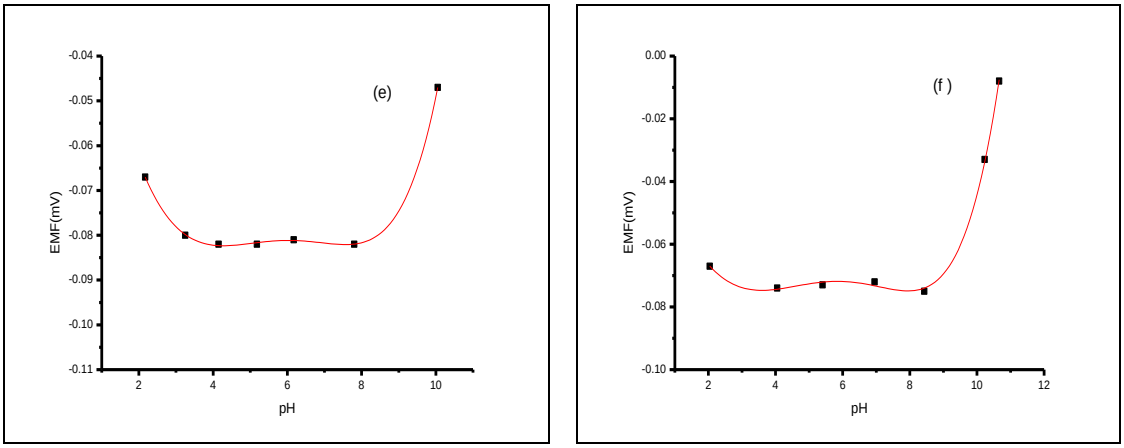


Fig 7. Working pH range of electrodes with (e) Ionophore T_5 with CNTs and (f) Ionophore T_6 with CNTs

Table 8. Working pH range of electrode with different Ionophore T_4,T_5,T_6 with CNTs and without CNTs.

S.NO	Ionophores	Working pH range	
		With CNTs	Without CNTs
1.	T_4	2-6	3-6
2.	T_5	3-7	4-7
3.	T_6	4-8	3-7

Table 8 shows that the potential remains stable in different pH ranges for different ionophores. The working pH range for electrodes with CNTs show better pH range than those without CNTs. Thus, the corresponding ranges are considered as the working pH range of the electrode.

4.5 Conclusion

1. The electrodes containing ionophores T_4, T_5, T_6 as the neutral carriers can be used in different concentration range of 10^{-5} to 10^{-1} M for the detection of aluminium ion.
2. All these electrodes exibited near Nernstian slopes and detection limits are 2×10^{-5}, 1×10^{-5}, 1×10^{-5}, 1×10^{-6}, 6×10^{-5}, 5×10^{-6} for T_4, T_5, T_6 without CNTs and with CNTs respectively.
3. The proposed electrodes shows good selectivity for aluminium ion over other transition metal ions like Co^{2+}, Zn^{2+}, Cu^{2+}, Ca^{2+}, Fe^{3+}, Cr^{3+} and also over lanthanides metal ions like Tb^{3+}, Pr^{3+}, Sm^{3+}, La^{3+}, Ce^{3+}.
4. These electrodes worked well over wide pH ranges, with better range in presence of CNTs.
5. These ion selective electrodes when doped with CNTs showed improved detection limits and senstivity.

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