3.1 Introduction

Mercury and lead are transition and post-transition metals with atomic no. 80 and 82 respectively. Mercury is the only metal that exists in liquid state at room temperature while lead is soft, malleable and exists in solid form. Mercury exists in three oxidation states: Hg (elemental or metallic mercury), Hg (I) (mercurous or monovalent mercury), and Hg (II) (mercuric or divalent mercury), which further exist in several physical and chemical forms. Most of Hg (I) compounds are diamagnetic and exists in dimeric cationic form ($\text{Hg}_2^{2+}$) while most common oxidation state of mercury is +2. On the other hand, lead exists in mainly +2 and +4 oxidation states.

Both of these heavy metals have some potential uses. Because of high density and high rate of thermal expansion, mercury is used in barometers, manometers and thermometers. Also, it is used in mercury vapor lamps, which emit light rich in UV radiations, used as electrodes in production of chlorine and sodium hydroxide. Mercury compounds like calomel (mercurous chloride) utilized for standard electrochemical measurements. Mercuric oxide and mercurochrome are used in skin ointments and in some antiseptics creams, respectively. Mercuric sulfate is used as catalyst in organic chemistry. In the same way, because of corrosion resistant nature and high density, lead can be easily molded and shaped. Lead is used as electrode in electrolysis, in solder for electronic purposes, in high voltage cables, as a sheathing material in order to prevent in-flow of water into insulation. It is also used as a shielding from radiations especially in X-ray rooms. Lead in molten state can be used as a coolant. It plays important role in construction industry, in statues and sculptures. $^{210}\text{Pb}$ has been used as dating material from marine sediment cores by various radiometric methods. Lead pigments were also used in paints for white, yellow and red. But now use of such paints has been discontinued because of lead poisoning.

In spite of such potential uses of lead and mercury, both of these are global pollutants as both of them being heavy metals affect human and ecosystem health [1]. Studies have revealed that high exposure to mercury lead to changes in central nervous system; it results in certain symptoms as irritability, fatigue, behavioral changes, hearing and cognitive loss, hallucinations and even death [2, 3]. Mercury exposure also
leads to various cardiovascular problems. A very harmful effect of exposure of mercury, which drew the attention of scientific society, was observed in Japan as Minamata Bay incident. A serious accident occurred resulting from deposition of industrial waste with large quantity of mercury in Minamata Bay [4]. Mercury poisoning occurred in Iraq in 1971, when wheat grains were treated with fungicides containing organic mercury. Mercury is so much toxic because of soft acid nature. It can bind strongly to proteins and enzymes that contain S and N containing groups at active sites thus inhibiting the metabolic reactions taking place inside the body [5]. Mercury is now considered as environmental pollutant because of its high toxicity and mobility in ecosystems.

In the same way, lead being heavy metal poses environmental problems. Distribution of lead in environment varies from place to place as in lead paints and older buildings, contamination of lead in food during production, processing, packaging and storage. Lead may occur in drinking water through leaching from lead containing pipes, faucets and solders. Through these sources, lead mainly affects the central nervous system in both adults and children. Children’s brain is very sensitive to lead and they are high risk to problems like lower class rank, poor vocabulary, grammatical reasoning scores, longer reaction time, poor hand and eye coordination [6]. Lead exposure can also lead to blood pressure. It can damage kidneys, brain in adults and children and ultimately lead to death [7]. Lead is readily absorbed in blood stream and can adversely affect the immune system. Therefore, level of these pollutants need to be estimated as both mercury and lead are hazardous to environment and public health.

Silver is a white lustrous metal which is known for its decorative beauty and electrical conductivity. It belongs to 11th group of periodic table between copper and gold and its physical and chemical properties are intermediate between these two metals. Silver is found in the environment in four different oxidation states; 0, +1, +2 and +3. Out of these 0 and +1 are the most common while +2 and +3 states rarely exist. Silver is present in the form of sulfides in soil and monovalent silver is commonly present in surface waters in the form of sulfides, bicarbonates and may also form complex ions with sulfates and chlorides.

Silver has some unique properties that make it desirable for various industrial uses. On exposure to certain wavelength of light and X-rays, silver halide crystals form
metallic silver nuclei. This phenomenon is used for photographic and imaging applications. Silver possess properties such as strength, heat stability and electrical conductance. Due to these properties, silver finds a valuable role in electrical industry. Because of its brilliant white color, malleability, ductility and resistance to atmospheric oxidation; it is used for the manufacture of coins, jewellery and ornaments. Some of industries use metallic silver in solders, bearings, dental and medical applications. Silver is not harmful in less concentration because animal and human cells have thick cell walls. Due to its antibacterial properties, silver has been increasingly used for purification of water in place of chlorine, bromine etc.

As a result of its wide application range, silver can easily enter the environment through the waste discharge and disposal of various products. Ionic form of silver is much more toxic to aquatic environment as compared to non ionic form. Ionic form is potentially hazardous as it has been rapidly found to react with natural chemical ligands in sewer systems, sewage treatment plants and also in environment [8]. Over exposure of silver nanoparticle’s can lead to impairment of tolerance to hypoxia. As nanomolar amount of silver goes to gills of fishes along with water, this reduces the diffusion conductance leading to internal hypoxia during low partial pressure of oxygen in water. Silver is practically not much toxic but silver deposited around nerves and in skin layers can cause permanent skin damage [9]. Soluble salts of silver are lethal. They are absorbed by tissues leading to continuous bluish or blackish pigmentation of skin; condition called as argyria, and can also cause corneal injury if eyes are exposed to it. It can cause other toxic effects like kidney, eyes, lungs, liver damages and can lead to changes in blood cells also [10]. So, the detection of silver in the ecological system is necessary. For this purpose, the close monitoring of trace amount of silver in environmental samples is of considerable importance.

There are number of methods such as cold vapour atomic fluorescence spectrometry (CV-AFS), cold vapour atomic absorption spectrometry (CV-AAS), cathodic stripping differential pulse voltammetry (CSDPV), anodic stripping voltammetry (ASV), inductively coupled plasma mass spectrometry (ICP-MS) and X-ray fluorescence spectrometry can be applied for determination of trace amount of mercury, lead and silver in different samples. However, these methods shows excellent detection
limit and selectivity for different metal ions but these methods are time consuming, costly, required personal skills and complicated instrumental setup make it difficult to employ for routine speciation analysis.

Potentiometric sensors based on ion selective electrodes (ISEs) are today well understood and can be optimized for quantification of various ions. Ion selective electrodes can effectively overcome above said complications associated with various methods for analysis of these metal ions with advantages in term of selectivity, sensitivity, high precision, simple instrumentation, ease of preparation, relatively fast response, lower detection limit, portability and rapid determination of these metal ions in different type of samples. Keeping in view of these advantages, many research groups all over the world are engaged to develop the mercury, lead and silver ion selective electrodes by employing the potential and novel ion carriers. Short and quick review of work done by some active groups is given below:

A mercury (II) ion selective sensor based on PVC membrane was reported by Rofouei et al. [11] in which 1, 3-bis(2-methoxybenzene)triazene (MBT) was used as an ionophore. Electrode was found to exhibit Nernstian slope (30.2±0.3mV/decade) over Hg$$^{2+}$$ ions concentration range of 1.0×10$$^{-2}$$-1.0×10$$^{-7}$$M. The detection limit of sensor was also low i.e. 5.0×10$$^{-8}$$M. Selectivity coefficient values were calculated for mono-, di- and trivalent metal ions and electrode was highly selective for Hg$$^{2+}$$ ions especially with respect to Ag$$^{+}$$ ions (Log $$K_{Hg^{2+}Ag^{+}}^{Pot}$$ = -2.01). Shawish [12] studied potentiometric response towards Hg$$^{2+}$$ ions by developing Hg$$^{2+}$$ ion selective electrode based on N,N’-bis(salicylaldehyde)-phenylenediamine as an ion carrier. Developed sensor exhibited Nernstian response for Hg$$^{2+}$$ ions over a concentration range of 3.2×10$$^{-4}$$-3.2×10$$^{-7}$$M. The proposed sensor worked well within the pH range of 3.8-7.8 and displayed a low detection limit of 1.5×10$$^{-7}$$M. The proposed sensor was employed as indicator electrode in potentiometric titration and was successfully used to determine Hg$$^{2+}$$ content in different water samples.

Ethyl-2-benzoyl-2-phenylcarbamoylacetate was employed as a sensing material in the preparation of sensor for selective determination of Hg$$^{2+}$$ as reported by Hassan et al. [13]. Electrode worked well in the wide concentration range (1.0×10$$^{-3}$$-1.0×10$$^{6}$$M)
and showed the Nernstian behavior towards Hg$^{2+}$ ions. The developed sensor exhibited high selectivity for Hg$^{2+}$ ions over a variety of alkali, alkaline and transition metal ions especially Ag$^+$ ions (Log $K_{Hg^{2+},Ag^+}^{Pot}$ = -5.26). The developed ion selective electrode was employed for the determination of Hg$^{2+}$ ion in amalgam alloys. Calix[4]arene derivatives, salicylaldehyde thiosemicarbazone and 1-furan-2-yl-4-(4-nitrophenyl)-2-phenyl-5H-imidazole-3-oxide were used as potential ionophores as described by Mahajan et al. [14-16] for the preparation of Hg$^{2+}$ ion selective electrodes. Potentiometric responses of proposed sensors were investigated by detailed study of experimental parameters such as effect of additives, composition of membrane, amount and nature of added plasticizers. Moreover, pH and concentration of internal solution was found to significantly affect the response of these developed Hg$^{2+}$ ion selective electrodes.

The suitability of 5,11,17,23-tetra-tert-butyl-25, 27-dihydroxy-26,28-bis(o-methyl glycylcarbonylmethoxy) thiacalix [4]-arene as Hg$^{2+}$ ion carrier for the selective determination of Hg$^{2+}$ was reported by Gupta et al. [17]. Electrode exhibited Nernstian slope of 29.5mV/decade over a wide concentration range of 1.0×10$^{-2}$-5.0×10$^{-8}$M with a lower detection limit of 1.0×10$^{-8}$M. The proposed sensor showed a short response time of 10s between pH range of 2.0-4.0. The developed potentiometric sensor was able to discriminate Hg$^{2+}$ ions from other cations. Same group used the 1-(2-ethoxyphenyl)-3-(3-nitrophenyl)triazene (ENTZ) as ion carrier to develop the potentiometric sensor for selective determination of Hg$^{2+}$ ions. Electrode worked in wide concentration range of 1.0×10$^{-4}$-5.0×10$^{-9}$M and exhibited the Nernstian slope of 29.3±0.2 mV/decade with a detection limit of 2.5×10$^{-9}$M for Hg$^{2+}$ ions. The developed Hg$^{2+}$ ion selective electrode was successfully used as an indicator electrode for direct estimation of Hg$^{2+}$ amount in dental amalgam and water samples.

A series of calix[4]arene-dithiacrown-5 and crown-6 derivatives were employed as ionophores for preparation of Hg$^{2+}$ ion selective electrode demonstrated by Yang et al. [18]. Selectivity coefficient values were calculated and it was reported that proposed ion selective electrode was very much selective for Hg$^{2+}$ ions as compare to other transition metal and heavy metal ions. The suitability of heterogeneous poly(Hg(II)-4-
vinyl pyridine) as ionophore for the preparation of PVC membrane based electrode has been investigated by Mashhadizadeh group [19]. The developed ion selective electrode was found to exhibit Nernstian response for Hg$^{2+}$ ions with lower detection limit of 5.0×10$^{-8}$ M. Considerable interferences from other cations were not found with exception of Ag$^+$ ions (Log $K_{Hg^{2+},Ag^+}^{Pot}$ = 1.32). Another PVC membrane based potentiometric sensor in which calixarene derivatives containing thiazole azo moiety acted as ion carrier was reported by Lu et al. [20]. The slope of the proposed Hg$^{2+}$ ion selective electrode was dependent upon the pH of test solution. The electrode was found to exhibited super Nernstian slope of 61.1mV/decade at pH 6.5 while it showed a Nernstian slope of 28.7mV/decade at pH 4.0 over the wide concentration range of 1.0×10$^{-2}$-5.0×10$^{-6}$M for Hg$^{2+}$ ions.

Gupta et al. [21] constructed Pb$^{2+}$ ion selective sensor based on PVC membrane. N,N”-dibenzyl-1,4,10,13- tetraoxa-7,16-diazacyclooctadecane was employed as an ionophore for selective determination of Pb$^{2+}$ ions. The sensor was found to work well over a concentration range of 1.0×10$^{-1}$-8.2×10$^{-6}$M within pH range of 2.0-6.8. High selectivity was demonstrated by the proposed sensor towards Pb$^{2+}$ ions in presence of variety of soft and hard metal ions (Log $K_{Pb^{2+},Ag^+}^{Pot}$ = -0.28, Log $K_{Pb^{2+},Ca^{2+}}^{Pot}$ = -0.42).

Anastasova et al. [22] reported the use of carbon screen printed substrates for the optimized preparation of Pb$^{2+}$ solid contact ion-selective electrodes (SC-ISEs). Excellent and reproducible results in terms of calibration characteristics such as slope, limit of detection were obtained for Pb$^{2+}$ ions by proper control over fabrication procedures. The detection limit was obtained in the nanomolar range which provided a very good opportunity for trace estimation of Pb$^{2+}$ in environmental samples. A new calixarene derivative based ion selective sensor for detection of Pb$^{2+}$ was reported by Kulesza et al. [23]. This ionophore was used to prepare PVC- membranes based sensor, plasticized by either BBPA or o-NPOE and displayed potentiometric slopes of 29.2 and 27.5mV/decade towards Pb$^{2+}$ ions, respectively. The potentiometric selectivity coefficient values for Pb$^{2+}$ ion over other interfering ions were Log $K_{Pb^{2+},M^{n+}}^{Pot}$ < -3.9 which demonstrated that this ionophore can be successfully employed for the estimation of Pb$^{2+}$ ions in various environmental samples. Polymeric
membrane Pb\(^{2+}\) ion selective electrodes based on N,N"-dimethylcyanodiaza-18-crown-6 as ionophores were prepared by Ganjali et al. [24]. The Nernstian response for Pb\(^{2+}\) ions with wide concentration range (1.0\(\times\)10\(^{-2}\)-1.0\(\times\)10\(^{-7}\)M) and a lower detection limit of about 7.0\(\times\)10\(^{-8}\)M was revealed by the sensors. The constructed electrodes were used as indicator electrodes in the potentiometric titrations of Pb\(^{2+}\) ions and were also successfully used for monitoring Pb\(^{2+}\) content in edible oil, water samples and human hair.

A new Pb\(^{2+}\) ion selective electrode based on polyphenylenediamine as a receptor was developed by Huang et al. [25]. The developed electrode was highly sensitive towards Pb\(^{2+}\) over the concentration range of 3.16\(\times\)10\(^{-2}\)-3.16\(\times\)10\(^{-6}\)M within pH range 3.0-5.0. The electrode was found to exhibit Nernstian slope of 29.8mV/decade for Pb\(^{2+}\) ions with a lower detection limit of 6.31\(\times\)10\(^{-7}\)M. The fixed interference method (FIM) was used to calculate potentiometric selectivity coefficients and data suggested that there was hardly any interference by other metal ions in the determination of Pb\(^{2+}\) except high concentrations of Hg\(^{2+}\) ions. Pb\(^{2+}\) carbon paste electrode based on a derivative of multi-walled carbon nanotubes as ionophore was reported for first time by Guo et al. [26]. The constructed electrode exhibited an excellent response towards Pb\(^{2+}\) ion with Nernstian slope of 29.5\(\pm\)0.3mV/decade over concentration range of 1.0\(\times\)10\(^{-2}\)-5.9\(\times\)10\(^{-10}\)M. The detection limit was found to be 3.2\(\times\)10\(^{-10}\)M. High selectivity was observed for Pb\(^{2+}\) ions over all studied alkali, alkaline and transition metals cations as indicated by selectivity coefficients (Log \(K_{Pb^{2+},M^{n+}}^{Pot}\) < -3.5). The electrode worked well over wide pH range (2.5-6.5) with a fast response time of 25s. Importantly, AC impedance technique was used to investigate the response mechanism of proposed sensor. The developed sensor was successfully employed for analysis of Pb\(^{2+}\) ions in various samples, e.g. soils, waste waters, lead accumulator waste and black tea.

Selective properties of Pb\(^{2+}\) ion selective electrodes incorporating two podand derivatives, 1,5- bis(2’-hydroxy-4’-nitrophenoxy)-3-thiapentane (L1) and 1,5-bis(8’-oxybenzopyridine)-3-thiapentane (L2), as ion carriers were established by Singh et al. [27]. The potentiometric selectivity coefficient values were found to lie in the range of -3.4 and -7.3 for most of metal ions except Cu\(^{2+}\) ions, which found to be cause
significant interference ($\log K_{pot}^{Pb_{2+},Cu^{2+}} = -1.2$) with $Pb^{2+}$ ions. The developed electrode successfully worked for determination of $Pb^{2+}$ ions in natural samples and results obtained were found to have good experimental correlation with that to AAS and ICP-MS methods. Another $Pb^{2+}$ selective electrode was developed with platinum wire coated with phenyl hydrazone derivative by Abbaspour et al. [28]. The Nernstian slope of 29.46mV/decade for $Pb^{2+}$ ions was found over a wide concentration range with a low detection limit of $3.2 \times 10^{-7}$M. The sensor showed a short response time of 6s within the pH range of 3.7-6.3 and the electrode was selective for $Pb^{2+}$ ions relative to other metal ions. The developed electrode was found to function well in partial water-alcohol mixture and was successfully used for the analysis of lead content in mineral rocks.

Recently, a novel nanographene carbon composite was used as ion carrier in the construction of potentiometric sensor for the trace analysis of $Ag^+$ ion by Afkhami et al. [29]. The suggested $Ag^+$ ion selective electrode exhibited Nernstian slope of 59.70mV/decade with observed response time of 6s. The electrode worked linearly over the concentration range of $1.0 \times 10^{-2}$-$8.0 \times 10^{-9}$M and has detection limit of $4.17 \times 10^{-9}$M. The proposed sensor was reported to be unaffected by interference from heavy metal ions especially with $Hg^{2+}$ ($\log K_{pot}^{Ag^{+},Hg^{2+}} = -2.61$) and $Pb^{2+}$ ($\log K_{pot}^{Ag^{+},Pb^{2+}} = -2.55$) ions. $Ag^+$ ion selective electrode was prepared by Gupta et al. [30] using membrane containing strong $Ag^+$ complex with Schiff-base lariat ether chelates based on 4,13-diaza-18-crown ether. Electrode was found to exhibit Nernstian slope (59.3mV/decade) for $Ag^+$ ions in the concentration range of $1.0 \times 10^{-1}$-$5.6 \times 10^{-8}$M. Developed electrode was applied successfully for analysis of silver ions in blood samples of occupationally exposed persons.

Derivatized silica-coated multi-walled carbon nanotubes (MWCNTs@SiO2) nanocomposites was designed as a neutral carrier for the preparation of novel carbon paste electrode (CPE) as reported by Zhao et al. [31] for the trace analysis of $Ag^+$ ions. This proposed electrode worked within concentration range of $1.0 \times 10^{-1}$-$8.6 \times 10^{-8}$M with quite low detection limit of $8.0 \times 10^{-8}$M. It was found to exhibit a Nernstian slope of 60.8±0.2mV/decade. Meanwhile, it also demonstrated a good selectivity and a fast response time (~20 s). The life time of the sensor was also long (1month) and it was
found to work well over a wide pH range (4.0-9.0). Zhang et al. [32] prepared Ag⁺ ions selective electrodes based on monoazathiacrown ether based receptors as ionophores. Among all receptors, the 2,2'-thiodiethanethiol derivative based sensor demonstrated high selectivity towards Ag⁺ ions in presence of number of interfering cations. With the Hg²⁺ ions, selectivity coefficient (Log $K^\text{Pot}_{Ag^+,Hg^{2+}}$) value found to be -2.5. The proposed ISE was found to exhibit lower detection limit of $2.2 \times 10^{-10}$M. The proposed ISE was found to work well within concentration range of $1.0 \times 10^{-5}$-$1.0 \times 10^{-11}$M and exhibited near-Nernstian slope of 54.5mV/decade.

Glassy carbon electrode based Ag⁺ ISE was prepared by Evtugyn et al. [33] by making use of thiacalix[4]arene (containing pyridine fragments in the lower rim) as an ionophore. The sodium fluoride was used as a masking agent in this work, which could fully eliminate the effect of Hg²⁺ and Fe³⁺ ions as interferents and therefore, the proposed sensor was employed for the determination of Ag⁺ ion content in sulfathiazole cream. Another Ag⁺ ion selective potentiometric sensor was reported by Hassouna et al. [34]. For the membrane preparation, N,N'-bis(3-methyl-1-phenyl-4-benzylidene-5-pyrazolone)propylene diamine was incorporated as an ion carrier. The proposed sensor was found to work well in terms of Nernstian slope (59.3mV/decade) ranging from $1.0 \times 10^{-1}$-$1.0 \times 10^{-6}$M with pH range of 4.0-10.0. Electrode was very much selective for Ag⁺ ions against the interfering ions such as Hg²⁺ and Cu²⁺. The suitability of Schiff base derivative of p-tert-butyl calix[4]arene as Ag⁺ ion carrier was used for the construction of Ag⁺ ion selective electrodes as demonstrated by Mahajan et al. [35]. The constructed electrode exhibited Nernstian behavior towards Ag⁺ ions in pH range of 1.0-6.5 and observed detection limit was $3.98 \times 10^{-6}$M. Electrode was found to show better selectivity for Ag⁺ ions against variety of other interfering ions.

Heterocycle functionalized p-tert-butylcalix[4]arene was used as ion carrier by Yan et al. [36] to prepare the Ag⁺ ion selective electrode. The Nernstian response slope of 59.8mV/decade was exhibited by proposed sensor in a linear range of $1.0 \times 10^{-3}$-$5.0 \times 10^{-7}$M for Ag⁺ ions. Selectivity of electrode towards Ag⁺ ion was very much high over variety of metal ions with some common interferents (Log $K^\text{Pot}_{Ag^+,Hg^{2+}}$ = -2.51, Log $K^\text{Pot}_{Ag^+,Pb^{2+}}$ = -5.34, Log $K^\text{Pot}_{Ag^+,Cu^{2+}}$ = -4.16). The developed sensor was successfully
employed as indicator electrode for the estimation of Ag\(^+\) and Cl\(^-\) ions in water samples and in vitamin B6 tablets. Yang et al. [37] incorporated the novel graphene oxide (NGO) nanosheets covalently grafted 2-thiophenecarboxylic (TPC) hybrid material for the preparation of ion selective electrode for the estimation of Ag\(^+\) ions. The proposed electrode displayed an excellent Nernstian slope of 59.3mV/decade over a concentration range of \(1.0 \times 10^{-1} - 8.4 \times 10^{-7}\)M. The observed low detection limit of sensor was \(6.3 \times 10^{-7}\)M. The proposed sensor helped in solving the universal problem of leaching of membrane components in analyte solution from ion-selective electrode.

3.2 Present work

In continuation to our efforts in the field of ion selective electrodes (ISEs), in the present work, we have explored the sensing properties of three different organic compounds as a potential ion carrier to construct the ISEs for qualitative and quantitative analysis of mercury (II), lead (II) and silver (I) ions. The structure and binding properties of these ionophores have been already explained in chapter 2 of thesis in detail. The compounds are:

- 1,3-alternate thiacalix[4]crown derivative as ion carrier for mercury (II) ISEs
- Naphthalene-sulfonamide (NS) derivative as ionophore for lead (II) ISEs
- Isoquinoline-1,3-dione derivatives as ionophore for silver (I) ISEs

These ion carriers displayed excellent binding affinity towards their respective metal ion. Initially, the ISEs constructed using these ionophores were employed to investigate the potentiometric response towards various metal ions and after that the response characteristics of optimized electrode towards their selective metal ion was studied in detail. Selectivity of developed Hg (II), Pb (II) and Ag (I) ISEs were checked towards various alkali, alkaline earth and transition metal ions and results revealed the remarkable selectivity of these ISEs towards Hg (II), Pb (II) and Ag (I) ions. Electrodes analytical applicability was tested by utilizing them as indicator electrode for the monitoring of potentiometric titrations as well as Hg (II), Pb (II) and Ag (I) ions content in various sample matrices. The results of these ISEs based on above mentioned ion carriers are discussed in detail in upcoming sections under following headings:
3.3 Mercury (II) ion selective electrodes based on 1, 3-*alternate* thiacalix[4]crown

3.4 Lead (II) solid contact ion selective electrodes based on naphthalene-sulfonamide derivative

3.5 Silver (I) ion selective electrodes based on isoquinoline-1,3-dione derivatives

3.3 Mercury (II) ion selective electrode based on 1, 3-*alternate* thiacalix[4]crown

Among the calixarene family, calix[4]arenes are most admired because they have rigid structures, which make them perfect contender for the complexation with various metal ions. Both the lower and upper rims of the calixarene can be tailored depending on the necessity and these tailored calixarenes provide a well preorganized architecture for the assembling of binding sites. The ionophore (1,3-*alternate* thiacalix[4]crown) used in the present work for construction of ISEs is insoluble in water. The lower rim of the 1,3-alternate thiacalix[4]crown consists of the two imine groups in which two nitrogen atoms are trivalent, with each one having pair of electrons, and also two ethereal oxygen having two electron pairs per oxygen atom which are capable of making coordinate bond with the vacant d-orbital of Hg (II) ions. Therefore, 1, 3-*alternate* thiacalix[4]crown based receptor I (Fig. 3.1) was employed as an ion carrier for development of Hg (II) ion selective polymeric and coated graphite electrodes.

![Fig. 3.1 Structure of 1, 3-*alternate* thiacalix[4]crown (receptor I)](image-url)
3.3.1 Potentiometric response

(a) Potentiometric response for various metal ions employing polymeric membrane electrodes (PMEs)

In the preliminary experiments, PVC based polymeric membrane electrodes (PMEs) for wide variety of mono-, di-, and trivalent metal ions were prepared by incorporating 100.0mg PVC, 200.0mg 2-nitrophenyl octyl ether (2-NPOE) as plasticizer, 2.0mg sodium tetraphenyl borate (NaTPB) as additive and 6.2mg of receptor I as ionophore. These PMEs were conditioned in the respective metal ion solution of concentration 1.0×10^{-2}M for 48h and their potential response was noted over the concentration range from 1.0×10^{-1}-1.0×10^{-8}M for different metal ions (Fig. 3.2). It can be seen from the Fig. 3.2 that except of Hg^{2+} ions, the slopes for the linear part of the potential responses of different PMEs for most of the tested metal ions such as K^+, Na^+, Li^+, Mg^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+}, NH_4^+, Cu^{2+}, Fe^{3+}, and Ag^+ are much lower than as expected as by Nernst equation. Preliminary results thus indicate that receptor I have preferential affinity toward Hg (II) ions and can be employed as ionophore for the development of Hg (II) ion selective electrodes.

![Fig. 3.2 Potentiometric response of receptor I based polymeric membrane electrodes (PMEs) for various metal ions](image-url)
(b) Potentiometric response for Hg (II) ions with polymeric membrane electrode (PME-1)

Based on results obtained from preliminary investigation on receptor I, it was decided to employ receptor I as ion carrier for the development of Hg (II) ion selective electrodes. Potentiometric response curve for polymeric membrane electrode (PME-1) based on receptor I have been shown in Fig. 3.3. PME-1 exhibited Nernstian slope of 29.16mV/decade over the concentration range from 1.0×10⁻¹-5.0×10⁻⁶M for Hg (II) ions with lower detection limit of 9.77×10⁻⁶M (Table 3.1). This preferential affinity of receptor I towards Hg (II) ions can be attributed to the presence of oxygen and nitrogen as donor atoms in the receptor I. Electrochemical cell assembly used for the study of polymeric membrane electrode was:

| Ag/AgCl | 3.0 M KCl | 1.0×10⁻¹M Hg(NO₃)₂ | PVC membrane | Test Solution | 3.0 M KCl | Ag/AgCl |

All the potential measurements were made with an EQUIPTRONICS MODEL EQ-602 potentiometer. The pH measurements were made using Elico LI model-120 pH meter.

![Fig. 3.3 Potential response curves of receptor I based Hg (II) ion selective electrodes PME-1 and CGE-1](image-url)
(c) **Potentiometric response for Hg (II) ions with coated graphite electrode (CGE-1)**

It is well known that replacement of the internal solution of polymeric membrane electrodes with some solid contact like graphite rods results into the improvement of electrode characteristics properties such as Nernstian slope, working concentration range, lower detection limit and selectivity etc. So it was decided to prepare the coated graphite electrode (CGE-1) employing the receptor I as ion carrier. CGE-1 was prepared by employing 40.0mg of PVC, 80.0mg of 2-NPOE as plasticizer, 2.0mg NaTPB as ionic additive and 3.5mg of ionophore. CGE-1 prepared was conditioned in 1.0×10⁻²M solution of respective metal ions for 72h. The potentiometric measurements of the coated graphite electrode were done by using following electrochemical cell assembly:

<table>
<thead>
<tr>
<th>Graphite surface</th>
<th>PVC membrane</th>
<th>Test Solution</th>
<th>3.0 M KCl</th>
<th>Ag/AgCl</th>
</tr>
</thead>
</table>

The external reference electrode used to carry out potential measurements was Ag/AgCl electrode with 3.0M KCl as salt bridge. The coated graphite electrode (CGE-1) exhibited Nernstian slope of 30.39mV/decade over the concentration range of 1.0×10⁻¹-5.0×10⁻⁷M for Hg (II) ions with lower detection limit of 7.76×10⁻⁷M (Fig. 3.3). The response characteristics properties of PME-1 and CGE-1 based on receptor I were analyzed and compared (Table 3.1). CGE-1 exhibits the better electrode characteristics in terms of wide concentration range and lower detection limit as compared to PME-1.

### 3.3.2 Effect of membrane composition on response characteristics of Hg (II) ISEs

It is now well established that potentiometric response behavior of ion selective electrodes is extensively affected by the amount (in ratio) and nature of the membrane constituents. In order to optimize the electrode response, we have investigated the influence of various parameters such as internal solution, additive content, ionophore content and nature of plasticizer on the response characteristics of the constructed Hg (II) ion selective electrodes.
(a) Influence of internal solution

Effect of concentration of internal solution on the potential response of the proposed electrodes PME-1 for Hg (II) ions was studied. Internal solution concentration of Hg (II) ion varied from \(1.0 \times 10^{-1}\)-\(1.0 \times 10^{-3}\)M (PME-1 to PME-3) and then potential response characteristics of each electrode was noted (Table 3.1). It was found that the PME-2 and PME-3 containing \(1.0 \times 10^{-2}\) & \(1.0 \times 10^{-3}\)M internal solution exhibited super Nernstian slope of 44.56 & 38.56mV/decade, respectively. Conversely, PME-1 which have \(1.0 \times 10^{-1}\)M internal solution showed Nernstian slope of 29.16mV/decade over wide concentration range of \(1.0 \times 10^{-1}\)-\(5.0 \times 10^{-6}\)M with lower detection limit of \(9.77 \times 10^{-6}\)M. Thus, \(1.0 \times 10^{-1}\)M solution was considered quite appropriate for the smooth functioning of proposed PME-1.

**Table 3.1** Composition and response characteristics of receptor I based Hg (II) ion sensors

<table>
<thead>
<tr>
<th>S. No.</th>
<th>PVC (mg)</th>
<th>Plasticizer (mg)</th>
<th>NaTPB (mg)</th>
<th>Ionophore (mg)</th>
<th>Internal Solution (M)</th>
<th>Linear Range (M)</th>
<th>Detection Limit (M)</th>
<th>Slope (mV/decade)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PME-1</td>
<td>100.0</td>
<td>200.0 2-NPOE</td>
<td>2.0</td>
<td>6.2</td>
<td>1.0 \times 10^{-1}</td>
<td>1.0 \times 10^{-1}, 5.0 \times 10^{-6}</td>
<td>9.77 \times 10^{-6}</td>
<td>29.16</td>
</tr>
<tr>
<td>CGE-1</td>
<td>40.0</td>
<td>80.0 2-NPOE</td>
<td>2.0</td>
<td>3.5</td>
<td></td>
<td>1.0 \times 10^{-1}, 5.0 \times 10^{-7}</td>
<td>7.76 \times 10^{-7}</td>
<td>30.39</td>
</tr>
<tr>
<td>PME-2</td>
<td>101.0</td>
<td>200.1 2-NPOE</td>
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<td>6.0</td>
<td>1.0 \times 10^{-2}</td>
<td>1.0 \times 10^{-1}, 5.0 \times 10^{-5}</td>
<td>1.55 \times 10^{-5}</td>
<td>44.56</td>
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<td>PME-3</td>
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<td>200.12-NPOE</td>
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<td>6.1</td>
<td>1.0 \times 10^{-3}</td>
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<td>8.86 \times 10^{-5}</td>
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<td>PME-4</td>
<td>101.0</td>
<td>200.0 2-NPOE</td>
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<td>1.0 \times 10^{-1}, 5.0 \times 10^{-6}</td>
<td>1.31 \times 10^{-6}</td>
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<td>PME-5</td>
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<td>199.8 2-NPOE</td>
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<td>1.0 \times 10^{-1}, 5.0 \times 10^{-5}</td>
<td>2.18 \times 10^{-5}</td>
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<td>PME-6</td>
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<td>200.0 2-NPOE</td>
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<td>4.2</td>
<td>1.0 \times 10^{-1}</td>
<td>1.0 \times 10^{-1}, 5.0 \times 10^{-6}</td>
<td>6.45 \times 10^{-6}</td>
<td>47.22</td>
</tr>
<tr>
<td>PME-7</td>
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<td>200.8 2-NPOE</td>
<td>2.1</td>
<td>8.2</td>
<td>1.0 \times 10^{-1}</td>
<td>1.0 \times 10^{-1}, 5.0 \times 10^{-5}</td>
<td>1.69 \times 10^{-5}</td>
<td>39.04</td>
</tr>
<tr>
<td>PME-8</td>
<td>99.8</td>
<td>201.0 DOS</td>
<td>2.0</td>
<td>6.0</td>
<td>1.0 \times 10^{-1}</td>
<td>1.0 \times 10^{-1}, 5.0 \times 10^{-5}</td>
<td>6.45 \times 10^{-5}</td>
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</tr>
<tr>
<td>PME-9</td>
<td>100.5</td>
<td>200.2 TBP</td>
<td>2.2</td>
<td>6.2</td>
<td>1.0 \times 10^{-1}</td>
<td>5.0 \times 10^{-2}, 1.0 \times 10^{-5}</td>
<td>9.55 \times 10^{-6}</td>
<td>47.44</td>
</tr>
<tr>
<td>PME-10</td>
<td>101.0</td>
<td>199.0 DOP</td>
<td>1.9</td>
<td>6.0</td>
<td>1.0 \times 10^{-1}</td>
<td>1.0 \times 10^{-1}, 5.0 \times 10^{-5}</td>
<td>1.05 \times 10^{-4}</td>
<td>82.34</td>
</tr>
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<td>PME-11</td>
<td>100.8</td>
<td>200.0 DOA</td>
<td>1.9</td>
<td>6.1</td>
<td>1.0 \times 10^{-1}</td>
<td>1.0 \times 10^{-1}, 5.0 \times 10^{-5}</td>
<td>1.23 \times 10^{-5}</td>
<td>52.09</td>
</tr>
<tr>
<td>PME-12</td>
<td>100.1</td>
<td>201.0 DBP</td>
<td>2.2</td>
<td>6.2</td>
<td>1.0 \times 10^{-1}</td>
<td>5.0 \times 10^{-2}, 5.0 \times 10^{-5}</td>
<td>3.89 \times 10^{-5}</td>
<td>63.44</td>
</tr>
</tbody>
</table>

NaTPB: Sodium tetraphenylborate, 2-NPOE: 2-Nitrophenyl octyl ether, DOS: Dioctylsebacate, TBP: Tributylphosphate, DOP: Dioctylphthalate, DOA: Dioctyladipate, DBP: Dibutylphthalate
(b) Influence of additive content

Presence of lipophilic negatively charged additive improves the potential response of cation-selective electrodes and enhances the membrane sensitivity of the ionophores whose extraction capability is poor [38]. In our studies, sodium tetrphenylborate (NaTPB) was incorporated as an additional membrane component to construct polymeric membrane ion-selective electrodes. Response characteristics for the PME-1, 4, 5 incorporating different amounts of NaTPB have been given in Table 3.1. It is clear from Table 3.1 that 2.0mg of NaTPB as an additive is the optimum content for the preparation of proposed PME-1 ion-selective electrode because it exhibited the best response characteristics in terms of Nernstian slope (29.16mV/decade), wide concentration range (1.0×10^{-1}-5.0×10^{-6}M) with lower detection limit (9.77×10^{-6}M). It may be that 2.0mg of NaTPB is an appropriate amount to charge compensation of counter ion in the membrane as well as facilitate the process of ion charge transduction. On the other hand, PME-4 & PME-5, which contained 1.0 & 0.0mg amount of lipophilic additive, showed sub-Nernstian slopes of 18.31 and 25.90mV/decade, respectively. That may be due to the presence of anionic impurities with the polymeric membrane matrix [39].

(c) Influence of ion carrier

The extraction equilibrium at the vicinity of interface between the membrane and aqueous layer and concentration of the ionophore in the PVC membrane affects the potential response mechanism of the neutral carriers incorporated for construction of ion-selective electrodes. The effect of the amount of ionophore incorporated in the membrane on proposed sensor characteristics was also investigated and results are compiled in Table 3.1 (PME-1, 6, 7). The best response characteristics were obtained with 6.2mg amount of ionophore in membrane (PME-1) which showed Nernstian slope of 29.16mV/decade over the wide concentration range of 1.0×10^{-1}-5.0×10^{-6}M with detection limit of 9.77×10^{-6}M.

On the other hand, the electrodes PME-6 and PME-7 exhibited super-Nernstian slope of 47.22 and 39.04mV/decade over relatively narrow concentration range with lower detection limits of 6.45×10^{-6} and 1.69×10^{-5}M, respectively. The deviation in the
Chapter-3

electrode characteristics at the higher amount of ionophore (PME-7) may be due to loss of selectivity and increase in the interference of the lipophilic counter ions of the test solution as presumed in the phase boundary potential model of carrier based ion-selective electrodes [40]. So, further studies were made by incorporating 6.2mg of ionophore for membrane preparation.

(d) **Influence of nature of plasticizer**

Plasticizers are expected to play key role in determining the characteristics properties of ion-selective electrodes. Plasticizer is responsible for ionophore salvation and distribution in the membrane matrix which influences the detection limit, selectivity, sensitivity, and provides the elasticity and strength to the membrane [41]. The effect of plasticizer on potential response of Hg (II) ion selective electrode was studied by preparing different polymeric membrane containing plasticizer of different polarity such as 2-NPOE, DOS, TBP, DOP, DOA, and DBP and results are summarized in Table 3.1.

The electrodes PME-(8-12) prepared by incorporating DOS, TBP, DOP, DOA and DBP exhibited super-Nernstian slopes of 32.14, 47.44, 82.34, 52.09 and 63.44mV/decade, respectively. The response of membrane sensor PME-1 incorporating 2-NPOE as plasticizer were found to be better in terms of Nernstian slopes (29.16mV/decade) with wide linear concentration range of 1.0×10^{-1}-5.0×10^{-6}M for Hg (II) ions. Here, 2-NPOE may act as the perfect solvate having the capability to extract the number of cations in the ionophore-membrane matrix. Therefore, 2-NPOE plasticizer was more compatible with membrane matrix of proposed Hg (II) ions sensors.

3.3.3 **Influence of pH on response characteristics of Hg (II) PME-1 and CGE-1**

The effect of pH on potential response of Hg (II) ion selective electrodes PME-1 and CGE-1 was studied over a pH range from 1.0-8.0 at the Hg (II) ions concentration of 1.0×10^{-2}M. The pH of the solution was adjusted with concentrated nitric acid and hexamine. **Fig. 3.4** shows the effect of pH variation on the potential response of PME-1 and CGE-1.
Fig. 3.4 Effect of pH on potential response of receptor I based Hg (II) ion-selective electrodes PME-1 and CGE-1

Potential response of the PME-1 and CGE-1 remain constant with pH range of 2.0-6.0 and 1.5-6.5, respectively. Sharp increase in potential at lower end of the pH range may be attributed due to interference of hydrogen ion whereas potential decrease at higher end of pH range may be due to formation of hydroxyl complexes of Hg (II) ions in the solution from the hydrolysis of Hg(NO$_3$)$_2$ salt.

3.3.4 Response time and life time of Hg (II) PME-1 and CGE-1

The response time of an ion selective electrode is the average time it required to attain the equilibrium value of the potential (±1mV) when dipped in the successive Hg (II) ions solution; each having a tenfold difference in concentration. The measurements were carried out with Hg(NO$_3$)$_2$ solutions from lower (1.0×10$^{-5}$M) to higher (1.0×10$^{-1}$M) concentrations.

Response time curves obtained for Hg (II) ion selective electrodes PME-1 and CGE-1 are represented in Fig. 3.5. The static response time of the Hg (II) ion-selective electrode PME-1 was nearly 20s while static response time for CGE-1 was less than 10s. The lifetimes of PME-1 and CGE-1 are found to be 3 and 4months, respectively. During this period, the slope of electrodes showed only slight change from 29.45 to 28.10mV/decade for PME-1 and 30.55 to 29.55mV/decade for CGE-1. After this period, the response characteristic of electrodes gradually deteriorates; this may be because ionophore gets started to be leached from the membrane.
Fig. 3.5 Response time of Hg (II) ion-selective electrodes PME-1 and CGE-1, based on receptor I as ionophore for step changes in concentration of Hg (II) ions [A] 1.0×10^{-1}M, [B] 1.0×10^{-2}M, [C] 1.0×10^{-3}M, [D] 1.0×10^{-4}M, [E] 1.0×10^{-5}M

3.3.5 Selectivity of Hg (II) PME-1 and CGE-1

Selectivity is one of the most important characteristics features of ion selective electrodes. It shows the preferential response of an ion-selective electrode towards primary analyte ions in the presence of different secondary ions. From the selectivity behavior, one can conclude whether proposed electrode can be used for analyte ion estimation in different samples. In the present work, fixed interference method (FIM) based on semi empirical Nikolsky-Eiseman equation [42] was employed to determine selectivity coefficient (Log $K_{A,B}^{f}$) of proposed Hg (II) ion selective electrodes PME-1 and CGE-1. In this method, the concentration of primary ion, Hg (II) ion (A) is varied whereas the concentration of secondary ions (B) is kept constant at 1.0×10^{-2}M. Comparative potentiometric selectivity plots of PME-1 and CGE-1 are shown in Fig. 3.6. It is clear from Fig. 3.6 that univalent ions (Li^{+}, Na^{+}, K^{+}, NH_{4}^{+}) exhibit selectivity coefficient with in range of -3.20 to -4.12 for PME-1 and -3.49 to -4.25 for the CGE-1. Similarly, different divalent and trivalent cations (Zn^{2+}, Cu^{2+}, Pb^{2+}, Mg^{2+}, Ca^{2+}, Co^{2+}, Fe^{3+}, Cd^{2+}) except Ag^{+} ions exhibit selectivity coefficient with in range of -2.10 to -4.09 for PME-1 and -1.75 to -4.25 for CGE-1. It can also be seen from the selectivity diagram that the selectivity coefficient of PME-1 for Ag^{+} ions is
slightly positive \((\log K_{Hg^{2+},Ag^+}^{Pot} = +0.25)\) and \(Ag^+\) ion shows small interference in the determination of Hg (II) ions. On comparison between selectivity studies of PME-1 and CGE-1, it can be observed that selectivity of CGE-1 \((\log K_{Hg^{2+},Ag^+}^{Pot} = -0.95)\) is negative and therefore there is no interference of \(Ag^+\) ions is observed in smooth functioning of CGE-1 for Hg (II) ions. It is observed that \(\log K_{Hg^{2+},Ag^+}^{Pot}\) value for \(Ag^+\) ions decreased from +0.25 (PME-1) to -0.95 (CGE-1). This improvement in selectivity of CGE-1 behavior can be explained by the ion flux mechanism. In case of CGE-1, the internal solution get replace by the solid graphite rod due to which diffusion of ion across the PVC membrane get eliminated and also the probability of the Hg (II) ions to get leached from membrane get completely stopped. The replacement of the internal reference of Hg (II) ions solution by graphite rod resulted in enhancement of selectivity of Hg (II) ion selective electrodes toward Hg (II) ions in comparison to \(Ag^+\) and other secondary ions.

![Selectivity diagram of Hg (II) ion selective electrodes PME-1 and CGE-1 based on receptor I](image-url)

**Fig. 3.6** Selectivity diagram of Hg (II) ion selective electrodes PME-1 and CGE-1 based on receptor I
3.3.6 Analytical applications

Due to small interference of Ag\(^+\) ion with PME-1, it is decided to use the CGE-1 for all quantitative estimation of Hg (II) ions in different variety of samples. Practical significance of the sensor was tested by using them as indicator electrode for monitoring the potentiometric titration of mercuric nitrate (1.0×10\(^{-2}\)M) versus EDTA (1.0×10\(^{-2}\)M) as shown in Fig. 3.7. The plot is sigmoidal shape and the inflexion point of the plot corresponds to 1:1 stoichiometry of EDTA complex, while the potential response after the end point remains almost constant due to low concentration of free Hg (II) ions in solution. Therefore, the end point and the amount of Hg (II) ions in the solution can be accurately determined by extrapolation of the three linear portion of titration plot.

![Fig. 3.7](image)

**Fig. 3.7** Potentiometric titration of 1.0×10\(^{-2}\)M Hg (II) ions solution with 1.0×10\(^{-2}\)M EDTA using CGE-1, based on receptor I. **Inset:** Corresponding first derivative plot

Proposed CGE-1 sensor has been used for the determination of Hg (II) ions in different water samples such as well, river, and waste water samples. Firstly, these samples are filtered; then after, the pH of these samples solutions was brought within working pH range (1.5-6.5) of the electrode by adding adequate amount of nitric acid or hexamine. The estimation of Hg (II) ions in these samples was also estimated by
volumetrically using EDTA method of titration (reference method). Results obtained for Hg (II) ions content in different water samples using both volumetric and ion-selective electrode method of analysis have been given in Table 3.2. Results obtained from both the methods on comparison were found to be quite in agreement with each other.

Some ayurvedic medicines (rasa-shastra) manufactured in South Asian countries especially in India contain high quantity of Hg (II) as in form of HgS (Cinnabar or Ras-sindoora). There are a number of analytical techniques used for quantification of mercury in ayurvedic medicines, but with the best of our knowledge, there is still no ion-selective electrode that is directly applied for determination of mercury in ayurvedic medicines. So, we decided to do the quantitative analysis of Hg (II) content in some Indian-made ayurvedic medicines purchased from local bazaar of India, in which cinnabar is the main ingredient like vasant kusumaker ras (antidiabetic), agnitundi vati (digestion improver), and ekangveer ras (immune system booster) with proposed CGE-1 sensor.

Table 3.2 Estimation of Hg (II) ions in various sample matrices by using CGE-1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hg (II) content in water samples (M)</th>
<th>Volumetric method</th>
<th>Ion selective electrode (CGE-1)</th>
<th>% age compatibility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Well water</td>
<td></td>
<td>5.72×10^{-6}</td>
<td>5.70×10^{-6}</td>
<td>100.35</td>
</tr>
<tr>
<td>River water</td>
<td></td>
<td>2.84×10^{-5}</td>
<td>2.87×10^{-5}</td>
<td>98.95</td>
</tr>
<tr>
<td>Waste water</td>
<td></td>
<td>9.60×10^{-3}</td>
<td>9.67×10^{-3}</td>
<td>99.27</td>
</tr>
<tr>
<td>Vasant kusumaker ras</td>
<td></td>
<td>1.41×10^{-4}</td>
<td>1.37×10^{-4}</td>
<td>102.92</td>
</tr>
<tr>
<td>Agnitundi vati</td>
<td></td>
<td>1.14×10^{-5}</td>
<td>1.10×10^{-5}</td>
<td>103.63</td>
</tr>
<tr>
<td>Ekangveer ras</td>
<td></td>
<td>8.66×10^{-4}</td>
<td>8.70×10^{-4}</td>
<td>99.54</td>
</tr>
</tbody>
</table>

For sample preparation, firstly, sample tablets were crushed into fine powder with the help of mortar and pestle. Then, powder were weighed out accurately about 1.0g of the each sample and dissolved into 10 to 15ml of freshly mixed concentrated HNO₃ and concentrated HCl (aqua regia) in the volume ratio of 1:3, respectively, in 100mL conical flask. It was shaken vigorously and warmed gently until the sample is
completely dissolve. This solution was made to 100mL by adding requisite amount of double distilled water. After filtration, these samples were analyzed for estimation of Hg (II) content by employing CGE-1 ion-selective electrode (Table 3.2). From Table 3.2, it is clear that estimation of Hg (II) content in ayurvedic medicines by using CGE-1 give compatible results with the volumetric methods using EDTA as titrant.

3.3.7 Statistical test of CGE-1 significance

Results obtained by CGE-1 and traditional volumetric methods are statistically compared to see whether results obtained from CGE-1 are reliable or not. A good agreement is obtained since line regression of CGE-1 vs volumetric method yielded a correlation of R=0.9974 for n=9 degree of freedom (total no of samples minus 1) with comparable line y=0.9821x+0.00022. Here, R value represent that both methods are undistinguished to each other. Similarly, if the paired Student’s t test is performed, the calculated t value found to be 0.00511 for CGE-1 vs volumetric method which is quite less than tabular critical value (t =2.26) (9 degree of freedom with 5% level of significance). These t values demonstrate that there is no significant difference between these two methods to determine Hg (II) ion in different samples. So, results obtained from CGE-1 are reliable.

3.3.8 Conclusions

1,3-alternate thiacalix[4]crown (receptor I) has been found to be potential carrier of Hg (II) ions in the PVC based PME-1 and CGE-1. The PME-1 based on membrane composition ionophore (6.2mg), PVC (100.0mg), 2-NPOE (200.0mg), and NaTPB (2.0mg) exhibited Nernstian slope of 29.16mV/decade and wide concentration range of 1.0×10^{-1}-5.0×10^{-6}M with lower detection limit of 9.77×10^{-6}M. It has a response time of 20s and it can work within pH range of 2.0-6.0. All the electrode properties of PME-1 were compared with CGE-1. It concluded that CGE-1 was superior to PME-1 with regard to concentration range (1.0×10^{-1}-5.0×10^{-7}M), lower detection limit (7.76×10^{-7}M), response time of less than 10s, and its ability to work within pH range of 1.5-6.5. The selectivity coefficient value obtained by using CGE-1 showed better sensitivity and selectivity as compare to PME-1 where Ag^{+} ions cause small interference with Hg (II) ions. Proposed CGE-1 was successfully applied as indicator
electrode in potentiometric titration of Hg (II) ions solution with EDTA solution. The high selectivity of CGE-1 made it possible to determine Hg (II) content in water and ayurvedic medicine samples.

3.4 Lead (II) solid contact ion selective electrodes based on naphthalene-sulfonamide derivative

Naphthalene-sulfonamide (NS) derivative (receptors II) shown in Fig. 3.8 on account of their distinctive architecture and presence of two donor nitrogen atoms was utilized as potential and new ionophore for the construction of Pb (II) solid contact ion selective electrodes.

![Structure of naphthalene sulfonamide (NS) derivative (receptor II)](image)

**Fig. 3.8** Structure of naphthalene sulfonamide (NS) derivative (receptor II)

3.4.1 Preliminary complexation study of receptor II

(a) Conductivity study

In order to obtain knowledge about the stability and stoichiometry of receptor II with the various alkali, alkaline earth, and transition metal ions, the receptor II complexation studies were investigated conductometrically in acetonitrile solutions at 298K by the method reported in the literature [43]. 25mL metal ion solution ($1.0 \times 10^{-4}$M) were titrated with receptor II ($L = $ liganad) and the conductance of the mixture, after each addition of titrate was measured. The **Fig. 3.9** showed the conductance variation plots with various metal ions ($M^{n+} = \text{Hg}^{2+}, \text{Ni}^{2+}, \text{Co}^{2+}, \text{Cd}^{2+}, \text{Fe}^{3+}, \text{Ca}^{2+}$ and $\text{Zn}^{2+}$) in addition to Pb (II) ions. The conductance decreases in the beginning on addition of receptor II which shows that the metal ions interact with the receptor II to
form a complex. At a particular point, the conductance becomes constant with further addition of receptor II which indicates the complete complexation. Break in the plot represent the stoichiometry of metal complex and found to be 1:1.

![Graph showing conductivity vs ligand/metal ratio for different metal ions](image)

**Fig. 3.9** Plot of conductivity vs ligand/metal ratio for different metal ions

(b) **Determination of stability constants**

The formation constant of the metal-ionophore complex within the membrane phase is an important parameter that indicates the selectivity of the sensor. The metal-ionophore complex formation constants were evaluated by potentiometric method [44, 45]. In this method, a sandwich membrane is prepared by fusing two membranes, with only one containing the ionophore (receptor II). This membrane electrode was brought in contact with the aqueous solution, having identical concentration on both sides, and cell potential was measured. On the other hand, the cell potential of another membrane having no ionophore was measured. The membrane potential (E_M) is determined by subtracting the cell potential of membrane without ionophore from the sandwich membrane. The formation constant is then calculated from the following equation:

$$\beta_{II_n} = \left( L_T - \frac{nR_T}{Z_1} \right)^{-n} \exp \left( \frac{E_M Z_1 F}{RT} \right)$$

Where $L_T$ is the total concentration of ionophore in the membrane segment, $R_T$ is the concentration of lipophilic ionic sites additive, $n$ is the metal-ionophore complex...
stoichiometry, and $R$, $T$, and $F$ are gas constants, the absolute temperature, and Faraday constant, respectively, $Z_1$ is the charge on metal ion.

**Table 3.3** The formation constant of receptor II-M$^{n+}$ complexes using sandwich method

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Formation constant $(\log \beta_{\text{II}} \pm \text{SD})$</th>
<th>Metal ion</th>
<th>Formation constant $(\log \beta_{\text{II}} \pm \text{SD})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb$^{2+}$</td>
<td>5.75 ± 0.05</td>
<td>Mg$^{2+}$</td>
<td>2.65 ± 0.04</td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>3.43 ± 0.03</td>
<td>Hg$^{2+}$</td>
<td>4.20 ± 0.08</td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>3.89 ± 0.05</td>
<td>Li$^+$</td>
<td>2.43 ± 0.07</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>4.01 ± 0.08</td>
<td>Ca$^{2+}$</td>
<td>3.30 ± 0.04</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>3.22 ± 0.02</td>
<td>K$^+$</td>
<td>3.05 ± 0.03</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>2.89 ± 0.01</td>
<td>Na$^+$</td>
<td>2.95 ± 0.05</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>1.76 ± 0.06</td>
<td>Ni$^{2+}$</td>
<td>3.68 ± 0.02</td>
</tr>
</tbody>
</table>

*aMean value ± standard deviation (three measurements)*

The values of stability constants of different metal complexes calculated by the sandwich method are given in **Table 3.3**. The formation constant $(\log \beta_{\text{II}})$ for receptor II-Pb (II) complex is maximum (5.75) which indicates that receptor II shows maximum affinity toward Pb (II) ions. On the other hand, the stability constants for other metal ions are less than Pb (II) ions, which indicate the less affinity of receptor II toward these metal ions. Because of this affinity difference, it is expected that the receptor II will facilitate the transport of Pb (II) ions in preference to other metal ions. Therefore, the receptor II can be used as potential ionophore for preparing solid-contact Pb (II) ion selective electrode.

(c) **Preparation and surface characterization of membrane**

The procedure for preparation of PVC membrane was to mix thoroughly PVC, 2-NPOE as plasticizer, NaTPB as additive and varying amount of receptor II as ionophore in about 5mL of tetrahydrofuran (THF). Mixture was shaken vigorously and a clear solution was poured into petridish (50mm diameter). Solvent was allowed to evaporate at room temperature. The resulting membrane of 0.4mm thickness was cut to
size and conditioned with Pb (II) ion solution \((1.0\times10^{-2}\text{M})\) for about 48 hours. After that, the membrane takes out from the conditioned solution and let them dry for 5 hours.

One of the important aspects of ion selective electrode is the microstructure of the membrane material, which determines the distribution of carrier as well as metal ion in the polymer matrix that further affect the response characteristics of proposed sensor. With the development of the new surface analysis technique such as scanning electron microscopy (SEM), it is possible to image the surfaces of some non-conducting sample like PVC membrane to distinguish their surface characteristics.

**Fig. 3.10** SEM images of the membrane at different stages \((1000\times)\) (A) PVC membrane (B) PVC/2-NPOE/ionophore membrane. EDX spectra of (C) PVC/2-NPOE membrane without ionophore (D) PVC/2-NPOE membrane with ionophore conditioned in \(10^{-2}\text{M}\) Pb (II) ions for 48 hours
In order to investigate the surface morphology of proposed Pb (II) ion selective membrane, SEM studies were carried out at different magnification (Fig. 3.10). In Fig. 3.10, image (A) shows the pure PVC membrane exhibited high porous polymer matrix with a relatively uniform pore size in the sub-micrometer range and physically tight structure in the polymer matrix. The image (B) shows that after the addition of 2-NPOE and receptor II as ionophore, the pores of pure PVC membrane vanishes and a new layer has been formed that has tiny channel to diffuse the Pb (II) ions. In order to check the selectivity of the receptor II toward the Pb (II) ions, the energy dispersive X-ray (EDX) spectra of the conditioned membranes PVC/2-NPOE membrane without ionophore (image C) and PVC/2-NPOE membrane with ionophore (image D) conditioned in 1.0×10⁻²M Pb (II) solution have been taken. It’s clear from image C that no Pb (II) content has been detected in the PVC/2-NPOE membrane without ionophore. It shows only PVC membrane constituents such as C, O, and Cl. But on the other hand, the PVC/2-NPOE membrane with ionophore (image D) shows PVC membrane constituents C, O, Cl as well as Pb (II) content. These results reveal that the receptor II is efficient and selective to form the complex with Pb (II) ions.

3.4.2 Potentiometric response

(a) Potentiometric response for multiple ions using solid contact modified with PEDOT/PSS coated graphite electrodes (SC-PEDOT/PSS-CGEs)

In the preliminary experiments, PVC-based SC-PEDOT/PSS-CGEs for a wide variety of mono-, di-, and trivalent metal ions were prepared by incorporating 40.0mg PVC, 80.0mg 2-NPOE as plasticizer, 2.0mg potassium tetrakis (p-chlorophenyl) borate (KTpClB) as additive, and 3.0mg of receptor II as ionophore. These SC-PEDOT/PSS-CGEs were conditioned in respective metal ion solution at 1.0×10⁻²M concentration for 72h, and its potential response was noted over the concentration range of 1.0×10⁻¹-1.0×10⁻⁹M for different metal ions (Table 3.4). It can be seen from Fig. 3.11 that except Pb (II) ions, the slopes for the linear part of the response of different SC-PEDOT/PSS-CGEs for most of tested metal ions are much lower than as expected by Nernstian equation. Results obtained from conductivity, SEM and preliminary potentiometric studies indicate that receptor II has preferential affinity towards Pb (II) ions and can be
employed as an ionophore for the development of Pb (II) solid-contact ion-selective electrodes.

![Figure 3.11](image)

**Fig. 3.11** Potentiometric responses of receptor II based SC-PEDOT/PSS-CGEs for various metal ions

**(b) Potentiometric response for Pb (II) ions with SC-PEDOT/PSS-CGE-1**

On the basis of results obtained from preliminary investigations on receptor II, it was decided to employ receptor II as an ion carrier for the development of Pb (II) solid-contact electrodes. Potentiometric response curve and composition for the SC-PEDOT/PSS-CGE-1 have been shown in **Fig. 3.12** and **Table 3.4**, respectively. Polymeric based SC-PEDOT/PSS-CGE-1 for Pb (II) containing receptor II as ionophore exhibited Nernstian slope of 29.21mV/decade over wide concentration range of $1.0 \times 10^{-1}$-$1.0 \times 10^{-7}$ M with lower detection limit of $5.62 \times 10^{-8}$ M (‘x’ in **Fig. 3.12**). The potentiometric measurements were carried out using following electrochemical cell assembly:

<table>
<thead>
<tr>
<th>Graphite Surface</th>
<th>PEDOT/PSS Film</th>
<th>PVC Membrane</th>
<th>Test Solution</th>
<th>3.0M KCl</th>
<th>Ag/AgCl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
All the measurements of electrode potential were made with an Equip-tronics model EQ-602 potentiometer. The pH measurements were carried out with Elico LI model-120 pH meter.

**Fig. 3.12** Potential response curves of receptor II based SC-PEDOT/PSS-CGE-1 for Pb (II) ions

3.4.3 *Effect of membrane composition on response characteristics of Pb (II) SC-PEDOT/PSS-CGEs*

(a) **Effect of additive content**

The properties of ion-selective electrodes (ISEs) based on neutral ionophores are strongly influenced by the ionic sites in their membranes. Although neutral carrier-based ISEs membranes may work properly even when they contain only a small amount of ionic sites, the addition of a salt of lipophilic ion is advisable and beneficial for various other reasons as well. Their main function is to render the ion selectivity and to reduce the bulk membrane impedance [46]. In our study, potassium tetrakis(4-chlorophenyl)borate (KTpClB) was incorporated as an additional membrane component. It is clear from **Table 3.4** that decrease in the amount of KTpClB from SC-PEDOT/PSS-CGE-1 (2.0mg) to SC-PEDOT/PSS-CGE-3 (0.0mg), the Nernstian slopes and linear range decreases and detection limits change from 5.62×10^{-8} to 9.20×10^{-5}M. So, it revealed that 2.0mg amount of KTpClB was found to be optimum for the smooth functioning of SC-PEDOT/PSS-CGE-1 for Pb (II) ions.
Table 3.4 Composition and response characteristics of receptor II based SCPEDOT/PSS-CGEs for Pb (II) ions

<table>
<thead>
<tr>
<th>S. No.</th>
<th>SC-PEDOT/PSS (mg)</th>
<th>PVC (mg)</th>
<th>Plasticizer (mg)</th>
<th>KTpClB (mg)</th>
<th>Ionophore (mg)</th>
<th>Linear Range (M)</th>
<th>Detection Limit (M)</th>
<th>Slope (mV/decade)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CGE-1</td>
<td>40.0</td>
<td>80.0</td>
<td>2-NPOE</td>
<td>2.0</td>
<td>3.0</td>
<td>1.0×10⁻¹-1.0×10⁻⁷</td>
<td>5.62×10⁻⁸</td>
<td>29.21</td>
</tr>
<tr>
<td>CGE-2</td>
<td>40.0</td>
<td>80.1</td>
<td>2-NPOE</td>
<td>1.0</td>
<td>3.1</td>
<td>1.0×10⁻¹-5.0×10⁻⁷</td>
<td>2.09×10⁻⁷</td>
<td>24.14</td>
</tr>
<tr>
<td>CGE-3</td>
<td>40.6</td>
<td>80.2</td>
<td>2-NPOE</td>
<td>0.0</td>
<td>3.0</td>
<td>5.0×10⁻¹-5.0×10⁻⁶</td>
<td>9.20×10⁻⁴</td>
<td>11.61</td>
</tr>
<tr>
<td>CGE-4</td>
<td>41.0</td>
<td>80.0</td>
<td>2-NPOE</td>
<td>2.1</td>
<td>5.0</td>
<td>1.0×10⁻¹-5.0×10⁻⁷</td>
<td>1.07×10⁻⁷</td>
<td>35.39</td>
</tr>
<tr>
<td>CGE-5</td>
<td>40.6</td>
<td>81.0</td>
<td>2-NPOE</td>
<td>2.2</td>
<td>1.0</td>
<td>1.0×10⁻¹-1.0×10⁻⁸</td>
<td>7.92×10⁻⁶</td>
<td>17.12</td>
</tr>
<tr>
<td>CGE-6</td>
<td>40.5</td>
<td>81.0</td>
<td>2-NPOE</td>
<td>1.9</td>
<td>0.0</td>
<td>1.0×10⁻¹-1.0×10⁻⁸</td>
<td>6.95×10⁻³</td>
<td>8.21</td>
</tr>
<tr>
<td>CGE-7</td>
<td>39.8</td>
<td>80.2</td>
<td>2-NPOE</td>
<td>2.0</td>
<td>7.0</td>
<td>1.0×10⁻¹-1.0×10⁻⁸</td>
<td>2.81×10⁻⁶</td>
<td>46.39</td>
</tr>
<tr>
<td>CGE-8</td>
<td>40.8</td>
<td>79.7</td>
<td>DOS</td>
<td>2.2</td>
<td>5.1</td>
<td>1.0×10⁻²-1.0×10⁻⁶</td>
<td>5.33×10⁻³</td>
<td>19.26</td>
</tr>
<tr>
<td>CGE-9</td>
<td>40.2</td>
<td>79.9</td>
<td>TBP</td>
<td>2.1</td>
<td>5.1</td>
<td>1.0×10⁻²-1.0×10⁻⁸</td>
<td>9.0×10⁻⁶</td>
<td>22.91</td>
</tr>
<tr>
<td>CGE-10</td>
<td>41.0</td>
<td>80.4</td>
<td>DOP</td>
<td>1.9</td>
<td>4.8</td>
<td>5.0×10⁻²-5.0×10⁻⁷</td>
<td>7.79×10⁻⁷</td>
<td>15.78</td>
</tr>
<tr>
<td>CGE-11</td>
<td>40.0</td>
<td>80.8</td>
<td>DOA</td>
<td>1.8</td>
<td>4.9</td>
<td>1.0×10⁻¹-5.0×10⁻⁶</td>
<td>1.11×10⁻⁶</td>
<td>20.50</td>
</tr>
<tr>
<td>CGE-12</td>
<td>40.8</td>
<td>80.3</td>
<td>DBP</td>
<td>2.0</td>
<td>5.2</td>
<td>1.0×10⁻²-5.0×10⁻⁶</td>
<td>4.29×10⁻⁶</td>
<td>12.36</td>
</tr>
</tbody>
</table>

KTpClB: Potassium tetrakis (p-chlorophenyl) borate, 2-NPOE: 2-Nitrophenyl octyl ether, DOS: Dioctylsebacate, TBP: Tributylphosphate, DOP: Dioctylphthalate, DOA: Dioctyladipate, DBP: Dibutylphthalate

(b) Effect of ionophore content

Effect of ionophore content on the response characteristics of Pb (II) solid-contact ISEs incorporating different content of receptor II as an ion carrier was studied by preparing membrane electrodes SC-PEDOT/PSS-CGE-1 (3.0mg), SC-PEDOT/PSS-CGE-4 (5.0mg), SC-PEDOT/PSSCGE-5 (1.0mg) and SC-PEDOT/PSS-CGE-7 (7.0mg). Composition and response characteristics for these electrodes are given in Table 3.4. The SC-PEDOT/PSS-CGE-1 containing 3.0mg of ionophore exhibited Nernstian slope of 29.21mV/decade over wide concentration range of 1.0×10⁻¹-1.0×10⁻⁷ M for Pb (II) ions with lower detection limit of 5.62×10⁻⁸ M. SC-PEDOT/PSS-CGE-5 containing 1.0mg of receptor II exhibited sub-Nernstian slope of 17.12mV/decade for Pb (II) ions over concentration range of 1.0×10⁻¹-1.0×10⁻⁶ M with the detection limit of 7.92×10⁻⁶ M. On the other hand, SC-PEDOT/PSS-CGE-4 and SC-PEDOT/PSS-CGE-7 containing 5.0 and 7.0mg of receptor II shows super-Nernstian slopes of 35.39 and 46.39mV/decade for Pb (II) ions over concentration ranges of 1.0×10⁻¹-5.0×10⁻⁷ M and 1.0×10⁻¹-1.0×10⁻⁷ M.
5 M with the detection limits of $1.07 \times 10^{-7}$ and $2.81 \times 10^{-6}$ M, respectively. The performance of membrane without receptor II (dummy membrane) (SC-PEDOT/PSS-CGE-6) was also investigated, and sub-Nernstian slope (8.21 mV/decade), narrow concentration range ($1.0 \times 10^{-1}$-1.0 $\times 10^{-4}$ M) with high detection limit (6.95 $\times 10^{-4}$ M) was observed. This clearly demonstrated the need of carrier in the fabrication of Pb (II) ISEs. So, the best result was obtained with SC-PEDOT/PSS-CGE-1 containing 3.0 mg content of receptor II as ionophore.

(c) **Effect of nature of plasticizer**

Choosing an appropriate plasticizer is essential for the construction of an ion-selective electrode with high analytical performances, such as Nernstian slope, selectivity, fast response, long life, and lower detection limit. Compatibility with polymer and electrod component (ionophore), low solubility in aqueous solution, low viscosity, low cost, and low toxicity are the desirable properties of the plasticizers [47]. Plasticizers embedded itself between chains of the polymer and spaces them apart, so free volume increases which is responsible for the flexibility and durability of the membrane. In the present work, six plasticizers of different dielectric constants ($\varepsilon$) and chemical structures such as 2-NPOE, DOS, TBP, DOP, DOA, and DBP were studied on Pb (II) ISEs based upon receptor II.

From the data in Table 3.4, it is clear that 2-NPOE is proved to be most suitable plasticizer, which shows Nernstian slope of 29.21 mV/decade with detection limit of 5.62 $\times 10^{-8}$ M (SC-PEDOT/PSS-CGE-1). The plasticizers of different dielectric constant ($\varepsilon$) such as DOS (4.6), TBP (3.5), DOP (5.1), DOA (4.0), and DBP (6.4) {SC-PEDOT/PSS-CGEs 8-12} exhibited sub-Nernstian slopes of 19.26, 22.91, 15.78, 20.50, and 12.36 mV/decade, respectively. All of these imply that the plasticizer 2-NPOE with high dielectric constant ($\varepsilon$=24) showed best response characteristics seem to be favorable environments for the complexation between Pb (II) and receptor II, whereas the plasticizers with moderate or lower dielectric constants were not considered so appropriate for construction of Pb (II) SC-PEDOT/PSS-CGE-1. So, 2-NPOE was selected as the plasticizer for further investigation.
3.4.4 Influence of pH on response characteristics of SC-PEDOT/PSS-CGE-1

The potential response of ISEs is affected by the pH of analyte ion solution employed. The pH dependent of SC-PEDOT/PSS-CGE-1 has been tested over the pH range of 1.0-9.0 with 1.0×10^{-2}M Pb (II) ions solution. The pH values were adjusted using conc. nitric acid or hexamine and potential was measured after each addition. The potential response remains constant over pH range of 2.0-7.0 as shown in Fig. 3.13. The noticeable decrease in potential response observed at lower pH can be due to interference of hydrogen ions, and potential response decreasing sharply at higher pH may be due to the formation of some hydroxyl complexes of Pb (II) ions in solution from hydrolysis of Pb (II) nitrate salt.

![Fig. 3.13](image)

**Fig. 3.13** Effect of pH on potential response of receptor II based SC-PEDOT/PSS-CGE-1 for Pb (II) ions

3.4.5 Aqueous layer test: potential stability of Pb (II) SC-PEDOT/PSS-CGE-1

It has been realized that the thin water layer can form between the PVC membrane and its solid contact. The stability of the proposed electrode was tested using the protocol developed by Fibbioli et al. [48]. The studied electrode modified with PEDOT/PSS was initially immersed in 1.0×10^{-2}M Pb(NO_3)_2 solution. After 1.5 hours, the solution was changed to 1.0×10^{-2}M NaNO_3 solution (diverse ion). After 3h, diverse ion solution was replaced by again 1.0×10^{-2}M Pb(NO_3)_2 solution. Its clear from **Fig. 3.14** that no potential drift was observed for Pb (II) SC-PEDOT/PSS-CGE-1 upon
changing the analyte in sample solution from primary ions to the diverse ions and again to primary ions.

![Diagram](image.png)

**Fig. 3.14** Water layer test of Pb (II)-selective electrodes with SC-PEDOT/PSS-CGE-1 and SC-CGE recorded in (A) 1.0×10^{-2} M of Pb (NO₃)₂ (B) 1.0×10^{-2} M NaNO₃.

On the other hand, at similar conditions, the electrode (SC-CGE) without PEDOT/PSS polymer modification exhibits significant potential drift as shown in Fig. 3.14. So, these results revealed that no aqueous layer was formed in between membrane and solid contact, when the solid contact was modified with PEDOT/PSS polymer.

### 3.4.6 Response, life time, reproducibility of proposed Pb (II) SC-PEDOT/PSS-CGE-1

The response time of an ISE is the average time required for attaining the equilibrium value of the potential when dipped in successive Pb (II) ion solution, each having the ten-fold difference in concentration. To measure the dynamic response time of proposed SC-PEDOT/PSS-CGE-1, the Pb (II) ions concentration of the test solution was successively changed from lower (1.0×10^{-5} M) to higher (1.0×10^{-1} M). A potential vs time trace plot for SC-PEDOT/PSS-CGE-1 is shown in Fig. 3.15. It is evident from Fig. 3.15 that potential response reached the equilibrium in very short time of <10s. The potential generated by the developed sensor remain stable for more than 4-minute after which divergence was recorded. Short response time of SC-PEDOT/PSS-CGE-1 may be due to high conductivity of the conducting polymer casted on the graphite rod. SC-
PEDOT/PSS-CGE-1 can be used over the period of 4 months without any significant change in Nernstian slope, lower detection limit, linear range, and response time. During this period, slope of electrodes shows slight change from 29.21 to 27.96 mV/decade for SC-PEDOT/PSS-CGE-1 and that after more than 4 months time, the selectivity and sensitivity of SC-PEDOT/PSS-CGE-1 get degrading. It may be due to leaching out of the ionophore from the membrane.

![Image of Fig. 3.15: Response times of SC-PEDOT/PSS-CGE-1 for Pb (II) ions based on receptor II for step changes in concentration of Pb (II) ions]

**Fig. 3.15** Response times of SC-PEDOT/PSS-CGE-1 for Pb (II) ions based on receptor II for step changes in concentration of Pb (II) ions [A] 1.0×10^(-1) M, [B] 1.0×10^(-2) M, [C] 1.0×10^(-3) M [D], 1.0×10^(-4) M, [E] 1.0×10^(-5) M

### 3.4.7 Selectivity of proposed Pb (II) SC-PEDOT/PSS-CGE-1

The selectivity coefficient \(K_{A,B}^{Pot}\) is the very important source of information concerning interference on the electrode response. In the present work, fixed interference method (FIM) based on semi-empirical Nikolsky-Eiseman equation was employed to determine logarithmic selectivity coefficient (Log \(K_{A,B}^{Pot}\)) of proposed Pb (II) SC-PEDOT/PSS-CGE-1.

\[
K_{A,B}^{Pot} = \left(\frac{a_A}{a_B}\right)^{z_A z_B}
\]

Emf of the cell is measured for solution containing constant activity \(a_B\) of diverse ions with charge \(Z_B\) and varying activity \(a_A\) of the primary ions with charge \(Z_A\).

The values of logarithmic selectivity coefficients Log \(K_{Pb^{2+},B}^{Pot}\) obtained by FIM for proposed electrode are shown in Table 3.5. As it is evident from Table 3.5, the Pb
(II) SC-PEDOT/PSS-CGE-1 is very selective to Pb (II) ions over all diverse ions but among all of them, Hg (II) ions have high selectivity coefficient \( \log K_{Pb^{2+},Hg^{2+}}^{pot} = -2.53 \) which indicate that the tolerance level of the proposed Pb (II) SC-PEDOT/PSS-CGE-1 toward Hg (II) is low as compare to other diverse metal ions. Taking account to the lower detection limit and response time, the observed tolerable Hg (II) concentration was up to \(1.0 \times 10^{-2} \text{M} \). Below this concentration, the Hg (II) ions show no interference in the normal functioning of Pb (II) SC-PEDOT/PSS-CGE-1.

**Table 3.5** Selectivity coefficients of various diverse ions (B) for receptor II based Pb (II) SC-PEDOT/PSS-CGE-1

<table>
<thead>
<tr>
<th>Diverse Ions (B)</th>
<th>( \log K_{Pb^{2+},B}^{pot} \pm SD )</th>
<th>Diverse Ions (B)</th>
<th>( \log K_{Pb^{2+},B}^{pot} \pm SD )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(^{2+})</td>
<td>-3.05 ± 0.06</td>
<td>Mg(^{2+})</td>
<td>-4.20 ± 0.03</td>
</tr>
<tr>
<td>Hg(^{2+})</td>
<td>-2.53 ± 0.02</td>
<td>Ag(^{+})</td>
<td>-3.39 ± 0.08</td>
</tr>
<tr>
<td>Cd(^{2+})</td>
<td>-3.94 ± 0.07</td>
<td>Li(^{+})</td>
<td>-3.49 ± 0.09</td>
</tr>
<tr>
<td>Cu(^{2+})</td>
<td>-2.98 ± 0.07</td>
<td>Ca(^{2+})</td>
<td>-4.10 ± 0.08</td>
</tr>
<tr>
<td>Zn(^{2+})</td>
<td>-4.25 ± 0.05</td>
<td>K(^{+})</td>
<td>-4.20 ± 0.03</td>
</tr>
<tr>
<td>Fe(^{3+})</td>
<td>-3.15 ± 0.04</td>
<td>Na(^{+})</td>
<td>-4.36 ± 0.06</td>
</tr>
<tr>
<td>NH(_4^+)</td>
<td>-3.00 ± 0.05</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{b}\)Mean value ± standard deviation (three measurements)

### 3.4.8 Analytical applications

Due to the high selectivity toward Pb (II) ion, Pb(II)-PEDOT/PSS-CGE-1 was employed to monitor Pb (II) ion concentration in various samples, while atomic absorption spectrophotometer (AAS) and volumetric methods were used as reference methods. Proposed Pb (II)-PEDOT/PSS-CGE-1 was found to work well under laboratories conditions. Practical utility of the this electrode was tested by using them as indicator electrode for potentiometric titration of Pb (II) ion solution \((1.0 \times 10^{-2} \text{M})\) with EDTA solution \((1.0 \times 10^{-2} \text{M})\), and corresponding titration curve is shown in **Fig. 3.16**. The plot is sigmoid in shape, and the inflexion point of the plot corresponds to 1:1 stoichiometry of EDTA complex, while the potential response after the end point remains almost constant, due to low concentration of free Pb (II) ions in solution.
Therefore, the end point and the amount of Pb (II) ions in the solution can be accurately determined by extrapolation of the three linear portion of titration plot.

Fig. 3.16 Potentiometric titration of $1.0 \times 10^{-2}$M Pb (II) solution with $1.0 \times 10^{-2}$M EDTA using Pb (II) SC-PEDOT/PSS-CGE-1 based on receptor II. Inset: Corresponding first derivative plot

| Table 3.6 Estimation of Pb (II) ions in various sample matrices by Pb (II) SC-PEDOT/PSS-CGE-1 |
|---------------------------------------------|---------------------------------|-----------------|-----------------|-----------------|
| Sample | Pb (II) content in samples ± SD (M) | % compatibility | (CGE-1 with AAS) |
| | | | |
| Tap water | $3.50 \times 10^{-2}$ | $3.45 \pm 0.04 \times 10^{-2}$ | $3.70 \pm 0.04 \times 10^{-2}$ | $3.20 \pm 0.07 \times 10^{-2}$ | 93.24 ± 0.04 |
| Well water | $1.50 \times 10^{-4}$ | $1.61 \pm 0.01 \times 10^{-4}$ | $1.55 \pm 0.06 \times 10^{-4}$ | $1.11 \pm 0.08 \times 10^{-4}$ | 103.24 ± 0.03 |
| River water | $4.50 \times 10^{-6}$ | $4.55 \pm 0.07 \times 10^{-6}$ | $4.69 \pm 0.08 \times 10^{-6}$ | - | 97.0 ± 0.07 |
| Industrial waste water | - | $9.22 \pm 0.02 \times 10^{-5}$ | $8.90 \pm 0.03 \times 10^{-5}$ | - | 103.59 ± 0.08 |
| Lead acid batteries | - | $4.98 \pm 0.05 \times 10^{-4}$ | $4.98 \pm 0.01 \times 10^{-4}$ | $4.70 \pm 0.07 \times 10^{-4}$ | 100.00 ± 0.08 |
| Naga bhasma | - | $5.00 \pm 0.07 \times 10^{-2}$ | $5.25 \pm 0.02 \times 10^{-2}$ | $4.35 \pm 0.08 \times 10^{-2}$ | 95.24 ± 0.07 |
| Basant kasumkar ras | - | $5.06 \pm 0.06 \times 10^{-4}$ | $4.68 \pm 0.01 \times 10^{-4}$ | $5.20 \pm 0.08 \times 10^{-4}$ | 108.12 ± 0.04 |
| Ekangveer ras | - | $7.96 \pm 0.03 \times 10^{-6}$ | $7.23 \pm 0.04 \times 10^{-6}$ | - | 110.10 ± 0.03 |

*Mean value ± standard deviation (three measurements)
Pb (II) SC-PEDOT/PSS-CGE-1 has been used to determine the Pb (II) content in different samples such as tap, well, river, industrial waste water, lead acid batteries and some Indian manufactured ayurvedic medicines such as naga bhasma, basant kasumkar ras and ekangveer ras. Tap, well, and river water samples were analyzed by Pb (II) SC-PEDOT/PSS-CGE-1 to detect Pb (II) concentration by using its spiked samples; otherwise, it is very difficult to determine Pb (II) content in these samples. All others samples have been prepared by the method reported from our laboratory [49]. From the Table 3.6, it is clear that estimation of Pb (II) in various sample matrices by using Pb (II) SC-PEDOT/PSS-CGE-1 gives compatible result with the atomic absorption spectrophotometer (AAS) and also with volumetric method using EDTA as titrant except those samples where Pb (II) concentration is lower than 1.0×10^{-5}M.

3.4.9 Statistical treatment of Pb (II) SC-PEDOT/PSS-CGE-1

To check the reliability of proposed electrode, the results obtained by Pb (II) SC-PEDOT/PSS-CGE-1 and AAS are statistically compared with each other and observed that very satisfactory results have been obtained. Linear regression line of Pb (II) SC-PEDOT/PSS-CGE-1 vs AAS yields a correlation coefficient of $R=0.999$ (approx. equal to 1) and 7 degree of freedom with comparison line $y = 1.05x+0.012$. It is clear from the value of R that regression line was indistinguishable from the theoretical $y=x$ comparison line. Similarly, if the paired Student’s $t$ test is performed for Pb (II) SC-PEDOT/PSS-CGE-1 vs AAS, the calculated value of $t$ was found to be 1.37, whereas the tabular $t$ value is 2.365 (7 degree of freedom with 95 % confidence level). The calculated $t$ value is less than tabular $t$ value, which demonstrated that there are no significant difference between results obtained with both the methods Pb (II) SC-PEDOT/PSS-CGE-1 and AAS. So, we can say that results obtained from Pb (II) SC-PEDOT/PSS-CGE-1 are reliable, reproducible, and acceptable.

3.4.10 Conclusions

New graphite contact modified with PEDOT/PSS conducting polymer coated with PVC membrane electrode (SC-PEDOT/PSS-CGE-1), which is highly selective to Pb (II) ions, has been developed using naphthalene-sulfonamide (NS) derivative (receptor II) as ion carrier. It shows Nernstian slope of 29.21mV/decade and wide
concentration range $1.0 \times 10^{-1} - 1.0 \times 10^{-7}$M with lower detection limit of $5.62 \times 10^{-8}$M. Its response time is <10s and has ability to work within pH range of 2.0-7.0. Developed electrode exhibited excellent selectivity, sensitivity, and large concentration range with no interference observed from diverse ions. It is successfully applied as an indicator electrode in potentiometric titration of Pb (II) ion solution with EDTA. Its high selectivity permits the direct measurement of Pb (II) ions in different environmental and ayurvedic medicine samples. The reliability of proposed electrode has been checked statistically by using paired Student’s $t$ test.

3.5 Silver (I) ion selective electrodes based on isoquinoline-1,3-dione derivatives

The four derivatives of isoquinoline-1,3-dione based on β-lactum receptors III-VI (Fig. 3.17), were explored as ion carrier for constructing PVC based polymeric membrane electrodes (PME) selective to Ag (I) ions.

![Fig. 3.17 Structures of Isoquinoline-1, 3-dione receptors III-VI](image)

3.5.1 Potentiometric response

(a) Potentiometric response for multiple-ions using polymeric membrane electrodes (PMEs)

In preliminary experiments, different PVC-based ion selective membrane sensors, using isoquinoline-1,3-dione based receptor III as ion carrier, were prepared by
mixing 100.1mg PVC, 201.1mg DOS, 1.5mg NaTPB and 9.2mg receptor III. Membranes so prepared were conditioned with 10^{-2}M solution of different metal ions for 24h. Their potential responses were noted against 1.0 \times 10^{-1} to 1.0 \times 10^{-8}M solutions of respective analyte ions to determine their potentiometric response for different metal ions (Fig. 3.18). Ag (I) ions were found to give better response in terms of slope, working concentration range and lower detection limit as compared to other metal ions. Results obtained indicate that electrode based on receptor III has preferential affinity for Ag (I) ions and it can be employed as an ionophore for the preparation of Ag (I) ion selective electrodes. The preferential affinity of receptor III for Ag (I) ions can be due to the presence of nitrogen and oxygen as donor atoms.

![Figure 3.18](image)

**Fig. 3.18** Potentiometric response of polymeric membrane electrodes (PMEs) based on receptor III for various metal ions

(b) **Potential response for Ag (I) ions using PMEs**

Based on the results obtained from the preliminary investigation with receptor III, it was decided to employ isoquinoline-1,3-dione based receptors III-VI as ion carrier for the preparation of Ag (I) ion selective electrodes. Response curves of polymeric membrane electrodes PMEs 1-4 incorporating receptors III-VI, respectively,
as ion carriers are shown in Fig. 3.19. The composition and the response characteristics obtained for the polymeric membrane electrodes PMEs 1-4 are shown in Table 3.7. The Ag (I) ion ISEs PME-2, PME-3 and PME-4 exhibited Nernstian slopes of 52.72, 49.62 and 67.47 mV/decade, respectively, in the concentration range of $1.0 \times 10^{-1}$ - $1.0 \times 10^{-5}$ M for Ag (I) ions and produced lower detection limits of the order of $9.54 \times 10^{-6}$ M, $1.15 \times 10^{-5}$ M and $1.07 \times 10^{-5}$ M, respectively. Electrode PME-1 based on receptor III shows Nernstian slope of 58.44 mV/decade over concentration range of $1.0 \times 10^{-1}$ - $5.0 \times 10^{-6}$ M of Ag (I) ions with $5.83 \times 10^{-6}$ M as lower detection limit. Therefore, it was decided to employ receptor III as ion carrier for preparation of Ag (I) ISEs.

**Fig. 3.19** Potentiometric responses of silver (I) selective polymeric membrane electrodes based on receptors III-VI as ionophores

Electrochemical cell assembly used for the study was:

<table>
<thead>
<tr>
<th>Ag/AgCl</th>
<th>3.0 M KCl</th>
<th>$1.0 \times 10^{-2}$ M AgNO$_3$</th>
<th>PVC membrane</th>
<th>Test Solution</th>
<th>3.0 M KCl</th>
<th>Ag/AgCl</th>
</tr>
</thead>
</table>

All the measurements of electrode potential were made with an EQUIPTRONICS MODEL EQ-602 potentiometer. The pH measurements were made using Elico LI MODEL-120 pH meter. Ag/AgCl electrodes with 3M KCl as salt bridge were used as internal and external reference electrodes.
Table 3.7 Composition and response characteristics of silver (I) ion selective electrodes based on receptors III-VI as ionophores

<table>
<thead>
<tr>
<th>S. No</th>
<th>PVC (mg)</th>
<th>Plasticizer (mg)</th>
<th>NaTPB (mg)</th>
<th>Ionophore</th>
<th>Internal Solution (M)</th>
<th>Linear Range (M)</th>
<th>Detection Limit (M)</th>
<th>Slope (mV/decade)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PME-1</td>
<td>100.1</td>
<td>201.1 DOS</td>
<td>1.5</td>
<td>9.2 III</td>
<td>1.0×10⁻³</td>
<td>1.0×10⁻⁴-5.0×10⁻⁶</td>
<td>5.83×10⁻⁵</td>
<td>58.44</td>
</tr>
<tr>
<td>PME-2</td>
<td>100.0</td>
<td>199.8 DOS</td>
<td>1.5</td>
<td>9.0 IV</td>
<td>1.0×10⁻³</td>
<td>1.0×10⁻⁴-1.0×10⁻⁵</td>
<td>9.54×10⁻⁵</td>
<td>52.72</td>
</tr>
<tr>
<td>PME-3</td>
<td>100.0</td>
<td>201.7 DOS</td>
<td>1.6</td>
<td>9.2 V</td>
<td>1.0×10⁻³</td>
<td>1.0×10⁻⁴-1.0×10⁻⁵</td>
<td>1.15×10⁻⁵</td>
<td>49.62</td>
</tr>
<tr>
<td>PME-4</td>
<td>100.3</td>
<td>199.6 DOS</td>
<td>1.6</td>
<td>8.9 VI</td>
<td>1.0×10⁻³</td>
<td>1.0×10⁻⁴-1.0×10⁻⁵</td>
<td>1.07×10⁻⁵</td>
<td>67.47</td>
</tr>
<tr>
<td>PME-5</td>
<td>100.2</td>
<td>201.0 DOS</td>
<td>1.5</td>
<td>9.2 III</td>
<td>1.0×10⁻³</td>
<td>1.0×10⁻⁴-1.0×10⁻⁵</td>
<td>1.01×10⁻⁵</td>
<td>53.20</td>
</tr>
<tr>
<td>PME-6</td>
<td>100.0</td>
<td>201.2 DOS</td>
<td>1.5</td>
<td>9.2 III</td>
<td>1.0×10⁻³</td>
<td>1.0×10⁻⁴-5.0×10⁻⁶</td>
<td>8.12×10⁻⁵</td>
<td>44.96</td>
</tr>
<tr>
<td>PME-7</td>
<td>100.0</td>
<td>201.0 DOS</td>
<td>1.5</td>
<td>7.0 III</td>
<td>1.0×10⁻²</td>
<td>1.0×10⁻⁵-1.0×10⁻⁶</td>
<td>3.16×10⁻⁵</td>
<td>44.50</td>
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<tr>
<td>PME-8</td>
<td>100.5</td>
<td>200.2 DOS</td>
<td>1.6</td>
<td>5.2 III</td>
<td>1.0×10⁻²</td>
<td>1.0×10⁻⁵-1.0×10⁻⁶</td>
<td>1.07×10⁻⁵</td>
<td>49.09</td>
</tr>
<tr>
<td>PME-9</td>
<td>101.0</td>
<td>201.5 DOS</td>
<td>1.5</td>
<td>3.2 III</td>
<td>1.0×10⁻³</td>
<td>1.0×10⁻⁴-5.0×10⁻⁶</td>
<td>6.45×10⁻⁶</td>
<td>27.52</td>
</tr>
<tr>
<td>PME-10</td>
<td>100.4</td>
<td>200.7 DOS</td>
<td>3.0</td>
<td>9.0 III</td>
<td>1.0×10⁻²</td>
<td>1.0×10⁻⁵-1.0×10⁻⁶</td>
<td>1.05×10⁻⁵</td>
<td>50.31</td>
</tr>
<tr>
<td>PME-11</td>
<td>100.8</td>
<td>200.3 DOS</td>
<td>0.0</td>
<td>9.1 III</td>
<td>1.0×10⁻²</td>
<td>1.0×10⁻⁵-5.0×10⁻⁶</td>
<td>4.36×10⁻⁵</td>
<td>38.09</td>
</tr>
<tr>
<td>PME-12</td>
<td>100.0</td>
<td>200.0 DBP</td>
<td>1.5</td>
<td>9.2 III</td>
<td>1.0×10⁻³</td>
<td>1.0×10⁻⁴-1.0×10⁻⁶</td>
<td>1.90×10⁻⁵</td>
<td>29.25</td>
</tr>
<tr>
<td>PME-13</td>
<td>100.0</td>
<td>200.3 DOA</td>
<td>1.5</td>
<td>9.2 III</td>
<td>1.0×10⁻²</td>
<td>1.0×10⁻⁴-5.0×10⁻⁶</td>
<td>8.91×10⁻⁶</td>
<td>71.86</td>
</tr>
<tr>
<td>PME-14</td>
<td>99.9</td>
<td>200.1 TBP</td>
<td>1.6</td>
<td>9.0 III</td>
<td>1.0×10⁻²</td>
<td>1.0×10⁻⁴-1.0×10⁻⁶</td>
<td>5.01×10⁻⁶</td>
<td>77.56</td>
</tr>
<tr>
<td>PME-15</td>
<td>100.6</td>
<td>201.4 DOP</td>
<td>1.6</td>
<td>9.1 III</td>
<td>1.0×10⁻²</td>
<td>1.0×10⁻⁴-1.0×10⁻⁶</td>
<td>1.77×10⁻⁵</td>
<td>17.39</td>
</tr>
</tbody>
</table>

NaTPB: Sodium tetraphenylborate, 2-NPOE: 2-Nitrophenyl octyl ether, DOS: Dioctylsebacate, TBP: Tributylphosphate, DOP: Dioctylphthalate, DOA: Dioctyladipate, DBP: Dibutylphthalate

3.5.2 Effect of membrane composition on response characteristics of Ag (I) ISEs

(a) Effect of internal solution

The effect of the concentration of internal solution on the potential response of the PME-1, PME-5 and PME-6 for Ag (I) ion based on receptor III was studied. The internal solution concentration of Ag (I) ion was varied from 1.0×10⁻¹ to 1.0×10⁻³M and their potential responses observed were shown in Table 3.7. The concentration of internal solution has been found to affect the slope and the working range of the electrode. PME-5 and PME-6 which have internal solutions 1.0×10⁻³ & 1.0×10⁻¹M exhibited sub-Nernstian slopes of 53.20 & 44.96mV/decade, respectively. Whereas, PME-1 which contains 1.0×10⁻²M internal solution displayed best response characteristics such as near Nernstian slope (58.44mV/decade), wide working concentration range (1.0×10⁻¹-5.0×10⁻⁶M) and lower detection limit (5.83×10⁻⁶M). Thus,
1.0×10⁻²M solution was found to be quite appropriate for the smooth functioning of the proposed polymeric electrode PME-1.

(b) Effect of ionophore content

The influence of the ionophore content on the response behavior of Ag (I) ion selective electrode incorporating receptor III as an ion carrier was studied by preparing membrane electrodes PME-1, PME-7, PME-8 and PME-9, using varying amount of receptor III (Table 3.7). Polymeric membrane electrode PME-1 containing 9.2mg of receptor III exhibited Nernstian slope of 58.44mV/decade over the wide concentration range of 1.0×10⁻¹-5.0×10⁻⁶M with lower detection limit of 5.83×10⁻⁶M. Whereas, polymeric membrane electrodes PME-7, PME-8 and PME-9, containing 7.0mg, 5.2mg and 3.2mg of receptor III, exhibited sub-Nernstian slopes over comparatively narrow concentration range with lower detection limit of 3.16×10⁻⁵M, 1.07×10⁻⁵M and 6.45×10⁻⁶M, respectively (Table 3.7). The best result was obtained in case of PME-1 containing 9.2mg content of receptor III.

(c) Effect of additive content

The presence of lipophilic negatively charged additive improve the potentiometric behavior of cation-selective electrodes by reducing ohmic resistance, increasing the membrane sensitivity in case of ionophore whose extraction capability is poor and by catalyzing the exchange kinetics. Thus the presence of lipophilic negatively charged additive improves the response behavior and selectivity of ion selective electrodes. In our study sodium tetra phenyl borate (NaTPB) was incorporated as an additional membrane component (Table 3.7). Polymeric membrane electrodes PME-1 and PME-10 were prepared by using 1.5mg and 3.0mg of NaTPB and PME-11 was prepared without any additive (NaTPB). Response characteristics for the polymeric membrane electrodes PME-1, PME-10 and PME-11 incorporating varying amount of NaTPB are given in Table 3.7. It is clear from Table 3.7 that 1.5mg NaTPB is the optimal content required for proper functioning of receptor III based Ag (I) ion selective electrode. It may be due to the fact that 1.5mg of NaTPB is the appropriate amount for the charge compensation of counter ion in the membrane and thus facilitates the process of the ion charge transduction. On the other hand, PME-10 & PME-11
which contains 3.0 & 0.0mg content of lipophilic additive shows sub-Nernstian slopes of 50.31 & 38.09mV/decade, respectively. In case of PME-11, the bad response characteristics may be due to the presence of anionic impurities within the polymer matrix [50].

(d) **Effect of nature of plasticizer**

The dielectric constant of the membrane phase, the mobility of ionophore molecules and the state of ligands are dependent on the nature of the plasticizer incorporated in the membrane. The selectivity and the sensitivity of the selective electrode strongly depend on the membrane composition and the nature of plasticizer used [51]. The effect of plasticizer on the potential response of Ag (I) ISE incorporating receptor III as an ion carrier was studied by preparing different membrane sensors containing plasticizer such as DOS, DBP, DOA, TBP, DOP and the results are summarized in **Table 3.7**. The electrodes PME-13 and PME-14, prepared by incorporating DOA and TBP, exhibited super-Nernstian slopes (71.86, 77.56mV/decade), while DBP and DOP incorporating electrodes PME-12 and PME-15 exhibited sub-Nernstian response of 29.25 and 17.39mV/decade, respectively. The response of membrane sensor PME-1 incorporating DOS as a plasticizer was found to be relatively better in terms of Nernstian slope of 58.44mV/decade and wide linear concentration range of 1.0×10⁻¹-5.0×10⁻⁶M. Therefore, incorporation of DOS as plasticizer is most appropriate for smooth functioning of proposed Ag (I) PME-1.

**3.5.3 Effect of pH on response characteristics of Ag (I) PMEs**

The potential response of an ion selective electrode is affected by pH of the analyte ion solution. The pH dependence of the polymeric membrane electrodes PMEs 1-4 containing receptors III-VI as ionophores were examined at 1.0×10⁻²M concentration of Ag (I) ions (Fig. 3.20). The pH values were adjusted using conc. nitric acid and hexamine and the potential was measured after each addition. The electrode potential for all four electrodes remained constant over a pH range 1.0-5.5, which was the working pH range of the proposed Ag (I) ion electrode. At lower pH<1 deviation in potential may be due to the hydrogen error of the proposed electrode, and the sharp
change at higher pH values may be due to the formation of some hydroxyl complexes of the charge transport process by the membrane, thereby causing interference.

Fig. 3.20 Effect of pH on potential response of silver (I) ion selective polymeric membrane electrodes PME 1-4 based on receptors III-VI as ionophores

Fig. 3.21 Response time of silver (I) ion selective electrode PME-1, based on receptor III for step changes in concentration of silver (I) ion (A) 1.0×10⁻⁵M, (B) 1.0×10⁻⁴M, (C) 1.0×10⁻³M, (D) 1.0×10⁻²M, (E) 1.0×10⁻¹M
3.5.4 Response time and life time of PME-1

The response time of an ion selective electrode is the average time required for attaining the equilibrium value of the potential. In this study the practical response time was recorded from lower to higher successive concentrations of Ag (I) ions solutions (10^{-5} to 10^{-1}M). A potential vs time trace for electrode PME-1 is shown in Fig. 3.21. It is evident that the electrode reached the equilibrium response in a very short time of less than 12s and no change was observed up to 5min. The life time of the present electrode was more than three months and electrode potentials were reproducible. After more than three months the selectivity and sensitivity of polymeric membrane started degrading. It may be due to the leaching out of ionophores from the membrane.

3.5.5 Electrode selectivity

The most important characteristic of any ion-selective sensor is its response to the primary ion (A) in the presence of secondary ions (B) present in solution, which is expressed in terms of the potentiometric selectivity coefficients ($\log K_{A,B}^{Pot}$). In the present work the selectivity coefficients ($\log K_{A,B}^{Pot}$) have been determining using fixed interference method (FIM) based on the semi empirical Nikolsky-Eisenman equation. In FIM, the selectivity coefficient was evaluated from potential measurement in solutions containing a fixed concentration of interfering cation (1.0×10^{-2}M) and varying amount of Ag (I) ions. The potential values obtained are plotted versus the activity of the primary Ag (I) ions. The potentiometric selectivity coefficients for proposed Ag (I) ion selective electrodes PMEs 1-4 were evaluated by FIM as shown in Fig. 3.22. On comparing selectivity data of polymeric membranes PMEs 1-4, it has been found that the $\log K_{Ag^{+},B}^{Pot}$ values for most of secondary ions are better with PME-1. As seen from Fig. 3.22, the Ag (I) ion electrode (PME-1) is significantly selective to Ag (I) ions over all the interfering ions. Although, the selectivity coefficients value for Hg (II) ion is higher than the values for other secondary metal ions ($\log K_{Ag^{+},Hg^{2+}}^{Pot} = -2.81$), but still, it has been found that Hg (II) ion does not interfere in the normal functioning of the proposed Ag (I) ion selective electrode PME-1. Moreover, it is found that most of the studied cations such as K^+, Zn^{2+}, Fe^{3+}, Cu^{2+}, Co^{2+}, Pb^{2+}, NH_4^+, Al^{3+}, Mg^{2+}, Na^+, Li^+ and Cd^{2+} does not cause any interference in the estimation of silver ions even if present in large amount.
Fig. 3.22 Selectivity of silver (I) ion sensors (PME-1 to 4) based on receptors III-VI

3.5.6 Analytical applications

The optimized proposed polymeric membrane sensor PME-1 was found to work well under laboratory conditions. Practical utility of the proposed sensor (PME-1) was tested by using it as an indicator electrode for potentiometric titration of silver solution (1.0×10^{-2}M) with 1.0×10^{-2}M sodium chloride solution (Fig. 3.23). The plot is of sigmoidal shape and the inflexion point of the plot corresponds to 1:1 stoichiometry of the AgCl precipitation. Therefore, the end point and the amount of Ag (I) ions in the solution can be accurately determined by extrapolation of the three linear portions of the titration plot.

Further, PME-1 was employed for the quantitative determination of Ag (I) ion content in synthetic water (1 and 2), silver foil (3) and dental amalgam (4) samples. In case of silver foil, the sample was prepared by dissolving it in diluted nitric acid (3ml of double distilled water and 5ml of conc. HNO₃), and then diluted to 100ml by adding
double distilled water. Ag (I) ion content in these samples was also determined volumetrically. The results summarized in Table 3.8 make it clear that both of these methods of analysis give compatible results providing the practical significance of proposed electrode.

![Graph](image)

**Fig. 3.23** Potentiometric titration of $1.0 \times 10^{-2} \text{M}$ silver (I) solution with $1.0 \times 10^{-2} \text{M}$ NaCl using PME-1, based on receptor III

**Table 3.8** Quantitative estimation of silver (I) ion content in water samples, silver foil and dental amalgam

<table>
<thead>
<tr>
<th>Sample</th>
<th>Silver content (M) in different samples</th>
<th>% age compatibility</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Volumetric method</td>
<td>Estimated using PME-1</td>
</tr>
<tr>
<td>Water sample (1)</td>
<td>$3.72 \times 10^{-3} \text{M}$</td>
<td>$3.86 \times 10^{-3} \text{M}$</td>
</tr>
<tr>
<td>Water sample (2)</td>
<td>$6.69 \times 10^{-4} \text{M}$</td>
<td>$6.58 \times 10^{-4} \text{M}$</td>
</tr>
<tr>
<td>Silver foil (3)</td>
<td>$9.13 \times 10^{-3} \text{M}$</td>
<td>$9.23 \times 10^{-3} \text{M}$</td>
</tr>
<tr>
<td>Dental amalgam(4)</td>
<td>$1.67 \times 10^{-2} \text{M}$</td>
<td>$1.61 \times 10^{-2} \text{M}$</td>
</tr>
</tbody>
</table>

3.5.7 **Conclusions**

Isoquinoline-1,3-dione based receptor III has been found to be novel carrier of Ag (I) ions in the PVC based polymeric membrane PME-1. The main advantage of the electrode is the simplicity of construction. It shows good response properties and performance, with Nernstian response (58.44mV/decade) in the concentration range of...
the $1.0 \times 10^{-1} - 5.0 \times 10^{-6}$M and detection limit of $5.83 \times 10^{-6}$M. The sensors have working pH range of 1.0-5.5 with fast response time of less than 12s. The selectivity coefficient indicated that PME-1 sensor is significantly selective to Ag (I) ion over many different secondary ions. Even Hg (II) ions were not found to interfere in normal functioning of the proposed PVC membrane PME-1. Additionally, the life time of this electrode longer than three months could be of importance as well. The electrode was successfully applied as an indicator electrode for potentiometric titration of Ag (I) ion solution against sodium chloride solution and it can be used for determination of Ag (I) ion content in different real samples.

References


