RESEARCH ARTICLE

Selective sensing of mercury(II) using PVC-based membranes incorporating recently synthesized 1,3-alternate thiacalix[4] crown ionophore

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Abstract The construction and electrodes characteristics of poly(vinylchloride) (PVC)-based polymeric membrane electrode (PME) and coated graphite electrode (CGE), incorporating 1,3-alternate thiacalix[4]crown as ionophore for estimation of Hg(II) ions, are reported here. The best potential response was observed for PME-1 having membrane composition of: ionophore (6.2 mg), PVC (100.0 mg), 2-nitrophenyl octyl ether (2-NPOE; 200.0 mg), and sodium tetraphenyl borate (NaTPB; 2.0 mg); for CGE-1 with the membrane composition: ionophore (3.5 mg), PVC (40.0 mg), 2-NPOE (80.0 mg), and NaTPB (2.0 mg). The electrodes exhibits Nernstian slope of 29.16 mV/decade with PME-1 and 30.39 mV/decade with CGE-1 for Hg(II) ions over wide concentration range, i.e., 1.0×10^{-1} to 5.0×10^{-6} M with PME-1 and 1.0×10^{-1} to 5.0×10^{-7} M with CGE-1. Lower detection limits were found to be 9.77×10^{-6} M for PME-1 and 7.76×10^{-7} M for CGE-1 with response time varying from 10 to 20 s. Also, these electrodes work within pH range of 2.0–6.0 for PME-1 and 1.5–6.5 for CGE-1. Overall, CGE-1 has been found to be better than PME-1. CGE-1 has been used as indicator electrode for the potentiometric titration of Hg(II) ions with EDTA as well as successfully applied for determination of Hg(II) content in wastewater, insecticide, dental amalgam, and ayurvedic medicines samples with very good performance (0.9974 correlation coefficient in the comparison against volumetric method).

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Introduction

Mercury exists in various chemical forms such as methyl mercury, elemental mercury, and organic and inorganic mercury. Each form show specific mercury poisoning, the methyl mercury and inorganic mercury form are the most toxic among these forms. Mercury exposure can occur from contaminated air or using mercury-containing products such as mercury thermometer, fluorescent light bulb, pesticides, paints, dental amalgam, cosmetics, pharmaceutical, and laboratory chemicals. But the main and common culprit for mercury poisoning to human health (especially population residing in coastal area) is consumption of fish which is contaminated with methyl mercury. The World Health Organization (WHO) has set the guideline value for inorganic mercury in drinking water at 6 μg^{-1} (WHO 2005). Still in many countries, mercury-containing pesticides are used freely; as a result, mercury may be deposited in lake, indigested by fish, and, by this route, reach humans and wildlife. Also, many ayurvedic medicines specially manufactured in South Asian countries contains high level of mercury as mercuric sulfide (rasa shastra; Saper et al. 2008; Dargan et al. 2008). Kidney failure, sensory impairment, disturbed sensation, lack of coordination, acrodynia (pink disease), allergic reactions, negative reproductive effects, and Minamata diseases are mainly caused by mercury poisoning. In the past years, the detection of mercury has forced particular scientific attention due to their biological and environmental toxicities. So, it is necessary to determine mercury at trace

level in our environment especially in drinking water. There are a number of methods such as cold vapor atomic fluorescence spectrometry (Roulet et al. 2000), cold vapor atomic absorption spectrometry (Hight and Cheng 2005), cathodic stripping differential pulse voltammetry (Ju and leech 2000), anodic stripping voltammetry (Berchmans et al. 2000), inductively coupled plasma mass spectrometry (Ugo et al. 2001), and X-ray fluorescence spectrometry (Bennun and Gomez 1997) that were applied for determination of trace amount of mercury in different samples. However, these methods show excellent detection limit and selectivity for different metal ions; these methods are time consuming, costly, require personal skills, and instrumental setup is complicated making it difficult to employ for routine speciation analysis.

Potentiometric sensors based on ion-selective electrodes are sufficiently well understood today and optimized for estimation of various ions. Ion-selective electrodes (ISEs) can successfully overcome the said complications above associated with different methods for analysis of various metal ions with advantages in terms of selectivity, sensitivity, high precision, simple instrumentation, ease of preparation, relatively fast response, lower detection limit, portability, and rapid determination of variety of ions in different type of samples (Gupta et al. 2002a, b; Jain et al. 1997; Srivastava et al. 1995; Gupta 2002a, b, 2006a, b, 2007a, b, 2011a, b). Many ionophores have been employed for preparation of Hg(II) ISEs including diamine (Gupta et al. 2005), 2-amino-6-purinethiol (Gupta et al. 2007a, b), crown ether (Gupta et al. 1997, 2003a, b), Schiff base (Xu et al. 2005), macrocycle (Singh et al. 2004), calixarene derivative (Lu et al. 2003), furanphenylimidazoleoxide (Mahajan et al. 2009a, b), oxadiazaphosphepine (Puri et al. 2011), calixthienopyrrole (Abbas 2012), poly(Hg (II)-4-vinyl pyridine) complex (Bakhtiarzadeh and Ghani 2008), salophen (Shawish 2009), pyrylium perchlorate (Yari and Papi 2009), and cyclic thioether derivative (Lon et al. 2009). But the major problem associated with some of Hg(II) ion-selective electrodes (Lu et al. 2003; Gismera et al. 2007) are interference of Ag(I) ions that can be attributed due to similarity in their size, soft nature, and other characteristics of both ions along with ion flux effects (Gyurcsanyi et al. 2001; Ceresa et al. 2002). The ISEs with solid contact has attributed a lot of attention due to their advantages over the conventional ISEs with an internal solution (Bator 2012; Jain et al. 1996). Recently, our research group employed polymeric membrane and coated graphite electrode for Hg(II) ion as well as variety of other cations (Puri et al. 2011; Mahajan et al. 2008, 2009a, b, 2010) and anions (Babu et al. 2008, 2009). Thiacalix[4] arenes is considered as a second-generation calixarene (Kumagai et al. 1997). The presence of sulfur groups instead of methylene group provide additional opportunity to tune the ring size, conformational, and binding properties of the thiacalix[4]arene (Gupta et al. 2008). Taking into account the highly desirable attributes of thiacalix[4]arene, it was employed as an ionophore for preparations of Hg(II) ion-selective electrodes. So in continuation to our work, an attempt has been made to improve the sensitivity, selectivity, and detection limit of Hg(II) ions selective electrode specially with coated graphite electrode (CGE) toward various secondary ions particularly Ag(I) ions based on newly synthesized 1,3-alternate thiacalix[4]crown as ionophore. Ionophores incorporated in the ISEs should have properties like highly lipophilicity, complexation properties, and minimum conformational change when coordinated to analyte ion. The chemical and structural properties of ionophore depend upon the different hard and soft donor sites present in the structure of chelating ring (Gupta et al. 2012) 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 (Fig. 1a) consists of the two imine groups in which two nitrogen atoms are trivalent, with each having one remaining pair of electrons, and also two ethereal oxygen having two electron pairs per oxygen atom that are capable of making coordinate bond with the vacant d-orbital of mercury(II) ions (Fig. 1b). So receptor 1A can be used as ionophore for construction of ISEs (Kumar et al. 2011).

Experimental

Materials

All reagents used were of analytical grade and doubly distilled deionized water was used to prepare solutions. The ionophore 1,3-alternate thiacalix[4]crown, synthesized as reported in literature (Kumar et al. 2011), and its structure are shown in Fig. 1a. The plasticizers 2-nitrophenyl octyl ether (2-NPOE), bis(2-ethylhexyl) sebacate (DOS), bis(2-ethylhexyl) phthalate (DOP), bis(2-ethylhexyl) adipate (DOA), dibutylphthalate (DBP), tributylphosphate (TBP), and high molecular weight poly(vinylchloride) (PVC) were used as received from Fluka. Anion excluder sodium tetraphenyl borate (NaTPB) was obtained from Aldrich while mercuric nitrate and other metal
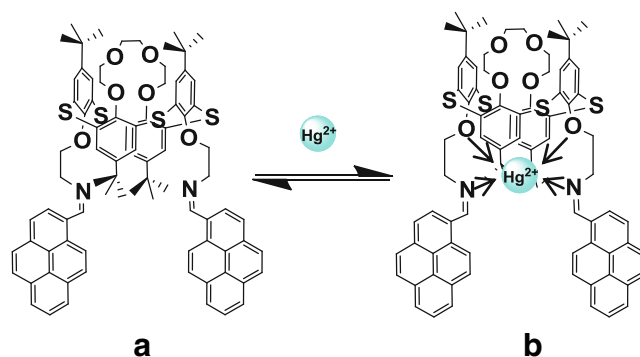

Fig. 1 Structure of 1,3-alternate thiacalix[4]crown (**a**) and its coordination with Hg(II) ion (**b**)

nitrates received from Merck were used without any further purification.

Preparation of PVC polymeric membrane based Hg(II) ion-selective electrodes (PMEs)

The general procedure for preparation of PVC membrane was to mix thoroughly PVC, plasticizer, additive, and varying amount of 1,3-alternate thiacalix[4]crown-based ionophore (composition given in Table 1) in about 5 mL of tetrahydrofuran (THF). The mixture was shaken vigorously and a clear solution was poured into a Petri dish (50 mm in diameter). The solvent was allowed to evaporate at room temperature. The resulting 0.4-mm thickness membrane was cut to size, attached to PVC tube with the help of PVC glue, and conditioned with metal ion solution (1.0×10^{-2} M) for about 48 h till it gave reproducible and stable potential. Electrochemical cell assembly used for the study was:

Ag– AgCl	3.0 M KCl	1.0×10^{-1} M Hg (NO$_3$)$_2$	PVC membrane	Test Solution	3.0 M KCl	Ag– AgCl

Preparation of coated graphite-based Hg(II) ion-selective electrodes (CGEs)

Spectroscopic grade graphite rods 20.0 mm in length and 3.0 mm in diameter were used for the preparation of coated graphite electrodes. At one end of the coated graphite, a shielded copper wire was glued and the electrodes were sealed into the other end of a glass tube having the same diameter with epoxy resin (Araldite). The working surface of the electrodes was polished with fine alumina slurry on the polishing cloth, washed with double-distilled water, and then dried in air. Membrane solution was prepared by thoroughly dissolving PVC, plasticizer, ionophore, and additive in 3.0 mL THF (composition given in Table 2). Resulting clear solution was evaporating slowly at room temperature until an oily concentrate mixture was obtained. Then, polished graphite was coated with the prepared membrane solution and the solvent was allowed to evaporate at room temperature. A membrane was formed on the graphite surface and electrode was allowed to stabilize overnight. The electrode was finally conditioned by soaking in 1.0×10^{-2} M mercuric nitrate solution for 72 h until it give stable reproducible potential. The potentiometric measurements were carried out using the following electrochemical cell assembly:

Graphite surface	PVC membrane	Test solution	3.0 M KCl	Ag– AgCl

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.

Table 1 Composition and response characteristics of 1,3-alternate thiacalix[4]crown based Hg(II) polymeric membrane electrodes (PMEs)

S. No.	PVC (mg)	Plasticizer (mg)	NaTPB (mg)	Ionophore (mg)	Internal solution (M)	Linear range (M)	Detection limit (M)	Slope (mV/dec.)
PME-1	100.0	200.0[a]	2.0	6.2	1.0×10^{-1}	1.0×10^{-1} to 5.0×10^{-6}	9.77×10^{-6}	29.16
PME-2	101.0	200.1[a]	2.0	6.0	1.0×10^{-2}	1.0×10^{-1} to 5.0×10^{-5}	1.55×10^{-5}	44.56
PME-3	100.3	200.1[a]	2.1	6.1	1.0×10^{-3}	5.0×10^{-2} to 1.0×10^{-6}	8.86×10^{-5}	38.56
PME-4	101.0	200.0[a]	1.0	6.3	1.0×10^{-1}	1.0×10^{-1} to 5.0×10^{-6}	1.31×10^{-6}	18.31
PME-5	100.0	199.8[a]	0.0	6.2	1.0×10^{-1}	1.0×10^{-1} to 1.0×10^{-5}	2.18×10^{-5}	25.90
PME-6	99.8	200.0[a]	2.0	4.2	1.0×10^{-1}	1.0×10^{-1} to 5.0×10^{-6}	6.45×10^{-6}	47.22
PME-7	100.0	200.8[a]	2.1	8.2	1.0×10^{-1}	1.0×10^{-1} to 1.0×10^{-5}	1.69×10^{-5}	39.04
PME-8	99.8	201.0[b]	2.0	6.0	1.0×10^{-1}	1.0×10^{-1} to 5.0×10^{-5}	6.45×10^{-5}	32.14
PME-9	100.5	200.2[c]	2.2	6.2	1.0×10^{-1}	5.0×10^{-2} to 1.0×10^{-5}	9.55×10^{-6}	47.44
PME-10	101.0	199.0[d]	1.9	6.0	1.0×10^{-1}	1.0×10^{-1} to 5.0×10^{-5}	1.05×10^{-4}	82.34
PME-11	100.8	200.0[e]	1.9	6.1	1.0×10^{-1}	1.0×10^{-1} to 1.0×10^{-6}	1.23×10^{-5}	52.09
PME−12	100.1	201.0[f]	2.2	6.2	1.0×10^{-1}	5.0×10^{-2} to 5.0×10^{-5}	3.89×10^{-5}	63.44

[a] 2-NPOE

[b] DOS

[c] TBP

[d] DOP

[e] DOA,P

[f] DBP

Table 2 Composition and response characteristics of 1,3-alternate thiacalix[4]crown-based Hg(II)-coated graphite electrodes (CGEs)

S.No.	PVC (mg)	Plasticizr (mg)	NaTPB (mg)	Ionophore (mg)	Linear range (M)	Detection limit (M)	Slope (mV/dec.)
CGE-1	40.0	80.0[a]	2.0	3.5	1.0×10^{-1} to 5.0×10^{-7}	7.76×10^{-7}	30.39
CGE-2	40.0	79.8[a]	2.2	3.4	1.0×10^{-1} to 5.0×10^{-6}	2.32×10^{-6}	37.92
CGE-3	40.5	80.1[a]	2.1	3.5	1.0×10^{-1} to 1.0×10^{-5}	5.60×10^{-5}	46.20
CGE-4	40.1	80.2[a]	1.0	3.6	1.0×10^{-1} to 1.0×10^{-6}	2.51×10^{-6}	41.83
CGE-5	40.0	79.9[a]	0.0	3.5	1.0×10^{-1} to 1.0×10^{-6}	1.01×10^{-6}	17.02
CGE-6	40.3	79.5[a]	2.1	1.5	1.0×10^{-1} to 5.0×10^{-6}	6.02×10^{-6}	68.28
CGE-7	40.0	80.0[a]	2.2	5.5	1.0×10^{-1} to 5.0×10^{-7}	3.16×10^{-7}	24.29
CGE-8	39.9	80.1[b]	2.0	3.6	1.0×10^{-2} to 5.0×10^{-6}	2.69×10^{-6}	50.54
CGE-9	40.2	80.3[c]	1.9	3.4	1.0×10^{-1} to 5.0×10^{-6}	5.33×10^{-6}	41.40
CGE-10	40.1	80.0[d]	1.9	3.5	1.0×10^{-1} to 1.0×10^{-6}	2.18×10^{-6}	77.99
CGE-11	40.6	79.8[e]	2.0	3.4	1.0×10^{-3} to 5.0×10^{-7}	7.24×10^{-6}	37.89
CGE-12	39.8	80.1[f]	2.2	3.5	1.0×10^{-2} to 1.0×10^{-6}	1.07×10^{-5}	69.45

[a] 2-NPOE

[b] DOS

[c] TBP

[d] DOP

[e] DOA

[f] DBP

Results and discussion

Potentiometric response for multiple ions using PMEs and CGEs

In the preliminary experiments, PVC-based PMEs for a wide variety of mono-, di-, and trivalent metal ions were prepared by incorporating 100.0 mg PVC, 200.0 mg 2-NPOE as plasticizer, 2.0 mg NaTPB as additive, and 6.2 mg of receptor 1A as ionophore. These PMEs were conditioned in the respective metal ion solution at 1.0×10^{-2} M concentration for 48 h and its potential response was noted over the concentration range 1.0×10^{-1} to 1.0×10^{-8} M for different metal ions. It can be seen from Fig. 2 that except Hg(II) ions, the slopes for the linear part of the potential responses of different PMEs for most of the tested cations are much lower than as expected as by Nernst equation. It is well known that replacement of the internal solution of polymeric membrane electrodes with some solid contact like graphite rods results into improvement electrode characteristics properties such as Nernstian slope, working concentration range, lower detection limit, and selectivity, etc. So it is decided to prepare the CGEs employing the receptor 1A as ionophore. CGEs were prepared by employing 40.0 mg of PVC, 80.0 mg of 2-NPOE as plasticizer, 2.0 mg NaTPB as ionic additive, and 3.5 mg of ionophore. Different CGEs were prepared for a variety of metal ions and CGEs prepared were conditioned in 1.0×10^{-2} M solution of its respective metal ions for 72 h and its potential response was measured over concentration range of 1.0×10^{-1} to 1.0×10^{-8} M of its corresponding metal ion solution. The potential response obtained for different metal ions by these coated graphite electrodes are shown in Fig. 3. It is clear from Fig. 3 that among different metal ions tested for the development of coated graphite electrodes, Hg(II) ions were found to be most suitable for the development of coated graphite electrodes based on receptor 1A as ionophore. Results thus indicate that receptor 1A has preferential affinity toward Hg(II) ions and can be employed as ionophore for the development
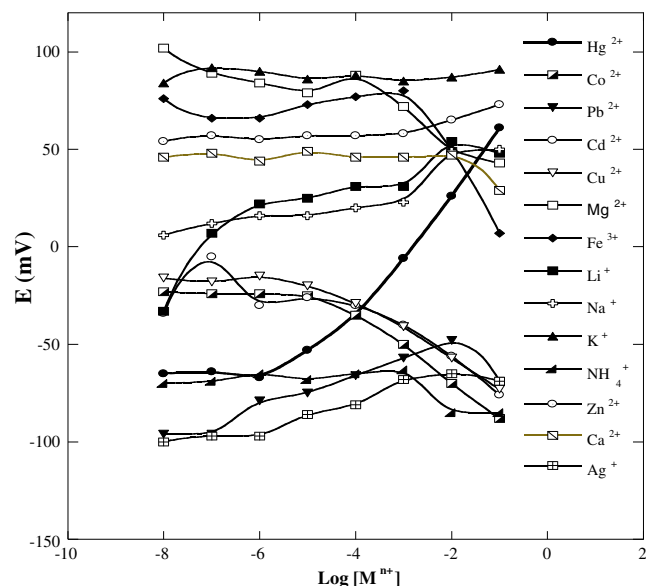
Fig. 2 Potentiometric response of 1,3-alternate thiacalix[4]crown-based PMEs for various metal ions
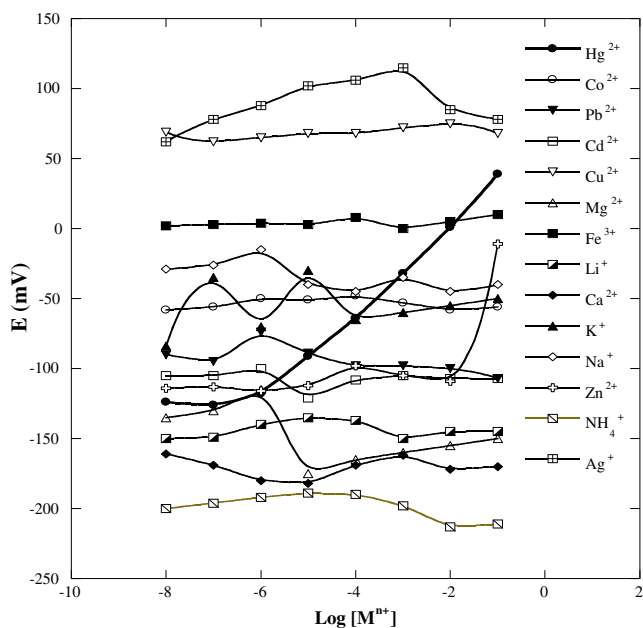
Fig. 3 Potentiometric response of 1,3-alternate thiacalix[4]crown-based CGEs for various metal ions

of Hg(II) ions PMEs and coated graphite ion-selective electrodes CGEs.

Potentiometric response for Hg(II) ions using PMEs and CGEs

Based on results obtained from preliminary investigation on receptor 1A, it was decided to employ 1,3-alternate thiacalix[4]crown as ion carrier for the development of Hg(II) ion-selective electrodes. Potentiometric response curves for PME-1 and CGE-1 based on receptor 1A have been shown in Fig. 4 and Tables 1 and 2 show composition and response
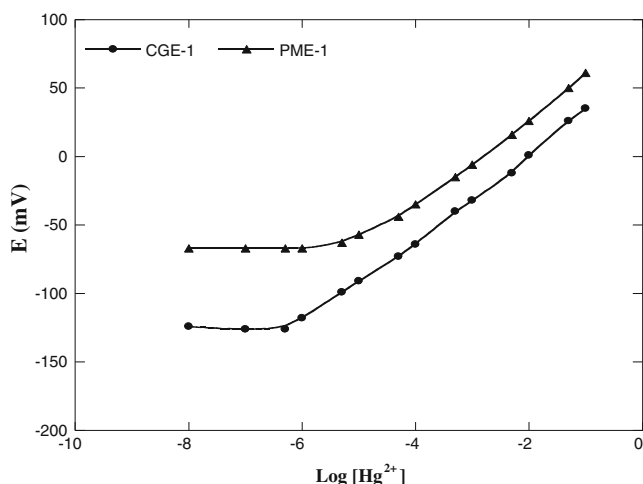

Fig. 4 Potential response curves of 1,3-alternate thiacalix[4]crown-based Hg(II) ion-selective electrodes PME-1 and CGE-1

characteristics of PME-1 and CGE-1, respectively. PME-1 exhibited Nernstian slope of 29.16 mV/decade over the concentration range of 1.0×10^{-1} to 5.0×10^{-6} M for Hg(II) ions with lower detection limit of 9.77×10^{-6} M (Table 1). Whereas in case of CGE-1, it exhibited Nernstian slope of 30.39 mV/decade over the concentration range of 1.0×10^{-1} to 5.0×10^{-7} M with lower detection limit of 7.76×10^{-7} M (Table 2). In case of CGE-1, electrode characteristics are highly improved as compare to PME-1.

Effect 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 was varied from 1.0×10^{-3} to 1.0×10^{-1} M and then potential response of PME-1 has been observed as shown in Table 1. It is found that the concentration of internal solution has an important effect on the Nernstian slope and working concentration range of electrodes. Further, it was found that with internal solution of concentration 1.0×10^{-1} M, the best results are obtained in terms of Nernstian slope and working concentration range. Thus, 1.0×10^{-1} M solution was considered quite appropriate for the smooth functioning of proposed PME-1.

Effect of additive content

Presence of lipophilic negatively charged additive improves the potential response of cation-selective electrodes, by minimizing Ohmic resistance, enhance the membrane sensitivity of the ionophores whose extraction capability is poor (Gehrig et al. 1990; Gupta et al. 2009a, b, c). In our studies, NaTPB was incorporated as an additional membrane component to construct both polymeric membrane and coated graphite ion-selective electrodes. Response characteristics for the PME-1, 4, 5 and CGE-1, 4, 5 incorporating different amounts of NaTPB have been given in Tables 1 and 2. It is clear from Tables 1 and 2 that 2.0 mg of NaTPB as an additive is the optimum content for the preparation of proposed PME-1 and CGE-1 ion-selective electrodes. It may be that 2.0 mg 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-5 and CGE-5, which contain no lipophilic additive, show sub-Nernstian slopes. That may be due to the presence of anionic impurities with the polymeric membrane matrix (Anker et al. 1981).

Effect of ionophore content

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 neural 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 1 (PME-1, 6, 7) and Table 2 (CGE-1, 6, 7). In case of PME-1, the best result was obtained with 6.2 mg of ionophore whereas 3.5 mg content of ionophore show best response in case of CGE-1. The ionophore amount for construction of CGE-1 was less than required in PME-1. The deviation in the electrode characteristics at the higher amount of ionophore (PME-7 and CGE-7) may be due to loss of selectivity and increase in the interference of the lipophilic counter ions of the test solution as the presumed in the phase boundary potential model of carrier-based ion-selective electrodes (Gupta and D'Arc 2001). So therefore, further studies were carried out using 6.2 mg of ionophore for PME-1 and 3.5 mg of ionophore for CGE-1.

Effect 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 (Bakker et al. 1994; Gupta et al. 2003a, b, 2006a, b, 2009a, b, c). The effect of plasticizer on potential response of Hg(II) ion-selective electrode was studied by preparing different polymeric membrane and coated graphite electrodes containing plasticizer of different polarity such as 2-NPOE, DOS, TBP, DOP, DOA, and DBP and results are summarized in Tables 1 and 2. The electrodes PME-8, 9, 11 and CGE-8, 9, 11 prepared by incorporating DOS, TBP, and DOA exhibited sub-Nernstian slopes [32.14, 47.44, 52.09, 50.53, 41.40, 37.89 mV/decade] while DOP and DBP incorporating electrodes PME-10, 12 and CGE-10, 12 exhibited super-Nernstian slopes (82.34, 63.44, 77.99, 69.45 mV/decade). The response of membrane sensor PME-1 and CGE-1 incorporating 2-NPOE as plasticizer were found to be better in terms of Nernstian slopes (29.16 and 30.39 mV/decade) with wide linear concentration range of 1.0×10^{-1} to 5.0×10^{-6} M and 1.0×10^{-1} to 5.0×10^{-7} M, respectively. Less amount of plasticizer is required for preparation of CGE-1 as compared to PME-1, this may be due to the graphite surface acting as a good transducer and help in electron transfer process between heterogeneous phases. As compared to other studied plasticizer, 2-NPOE is more of a polar mediator which influence the formation constant of the ionophore with mercury(II) ions which further influence the selectivity and mobility of electro active cation in the membrane. 2-NPOE may be the perfect solvate here having the capability to extract the number of cations in the ionophore–

membrane matrix. Also, its salvation energy for the free and complex ions may also be optimum for the binding constant in addition to possible changes in complex stoichiometry. So, 2-NPOE plasticizer may be more compatible with membrane matrix of proposed mercury(II) ions sensors.

Effect of pH

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 to 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. Figure 5 shows the effect of pH variation on the potential response of PME-I 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 mercury(II) nitrate salt.

Response time and life time of Hg(II) ion-selective electrodes

The response time of an ion-selective electrode is the average time it required to attain the equilibrium value of the potential (±1 mV) when dipped in the successive Hg(II) ions solution; each having a tenfold difference in concentration. The measurements were carried out with mercuric nitrate 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
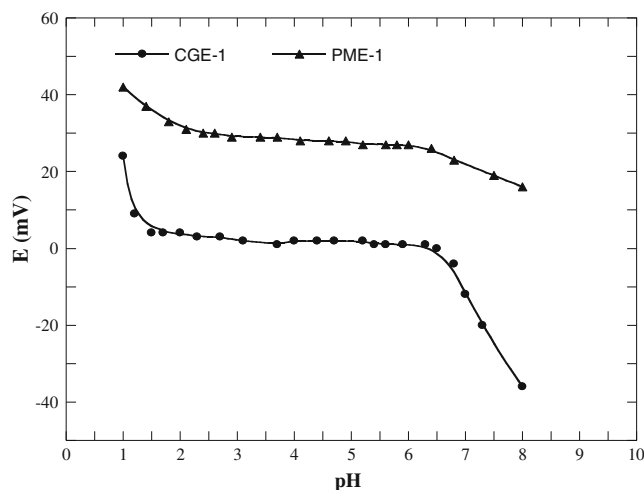
Fig. 5 Effect of pH on potential response of 1,3-alternate thiacalix[4] crown-based Hg(II) ion-selective electrodes PME-1 and CGE-1
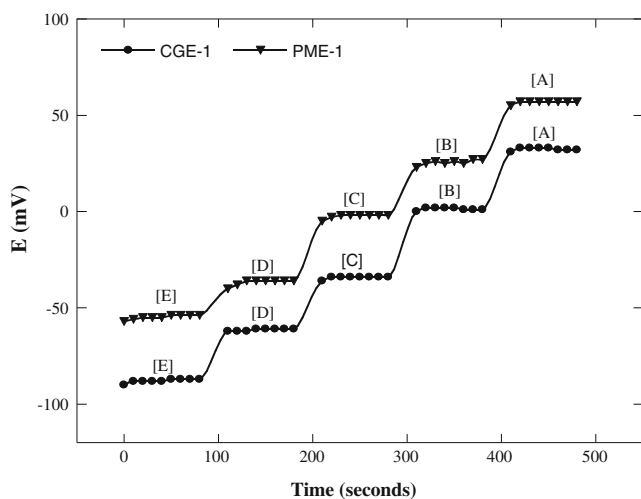
Fig. 6 Response time of Hg(II) ion-selective electrodes PME-1 and CGE-1, based on 1,3-alternate thiacalix[4]crown ionophore for step changes in concentration of Hg(II) ions. *[A]* 1.0×10^{-1} M, *[B]* 1.0×10^{-2} M, *[C]* 1.0×10^{-3} M, *[D]* 1.0×10^{-4} M, *[E]* 1.0×10^{-5} M

in Fig. 6. The static response time of the Hg(II) ion-selective electrode PME-1 was nearly 20 s while static response time for CGE-1 was less than 10 s. It can also be seen from Table 3 that the lifetimes of PME-1 and CGE-1 are found to be 3 and 4 months, respectively. During this period, the

**Table 3** Lifetime behavior of Hg(II) ion-selective electrodes PME-1 and CGE-1

Days	Slope (mV/decade)	Linear range (M)	Detection limit (M)
PME-1			
3	29.45	1.0×10^{-1} to 5.0×10^{-6}	2.77×10^{-6}
15	29.14	1.0×10^{-1} to 4.2×10^{-6}	3.99×10^{-6}
30	28.80	1.0×10^{-1} to 5.6×10^{-6}	4.37×10^{-6}
45	28.75	1.0×10^{-1} to 5.8×10^{-6}	4.50×10^{-6}
70	28.30	1.0×10^{-1} to 6.0×10^{-6}	6.77×10^{-6}
90	28.10	1.0×10^{-1} to 6.7×10^{-6}	7.77×10^{-6}
100	23.21	1.0×10^{-1} to 5.0×10^{-5}	2.77×10^{-5}
110	16.85	1.0×10^{-1} to 7.0×10^{-5}	8.77×10^{-5}
CGE-1			
3	30.55	1.0×10^{-1} to 5.0×10^{-7}	7.75×10^{-7}
15	30.36	1.0×10^{-1} to 5.5×10^{-7}	7.95×10^{-7}
30	30.32	1.0×10^{-1} to 6.2×10^{-7}	8.10×10^{-7}
45	30.10	1.0×10^{-1} to 7.1×10^{-7}	8.50×10^{-7}
70	30.15	1.0×10^{-1} to 8.5×10^{-7}	8.62×10^{-7}
90	30.00	1.0×10^{-1} to 8.7×10^{-7}	8.95×10^{-7}
110	29.85	1.0×10^{-1} to 9.0×10^{-7}	9.41×10^{-7}
120	29.55	1.0×10^{-1} to 9.8×10^{-7}	9.85×10^{-7}
130	24.66	1.0×10^{-1} to 1.6×10^{-6}	1.75×10^{-6}
140	18.55	1.0×10^{-1} to 5.6×10^{-6}	4.75×10^{-6}

slope of electrodes showed only slight change from 29.45 to 28.10 mV/decade for PME-1 and 30.55 to 29.55 mV/decade for CGE-1. After this period, the electrochemical behavior of electrodes gradually deteriorates; this may be because ionophore gets started to be leached from the membrane.

Selectivity of proposed ion-selective electrodes

Selectivity is the 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, we can conclude whether proposed electrode can be used for analyte ion estimation in different samples. In the present work, fixed interference method based on semi-empirical Nikolsky–Eiseman equation was employed to determine selectivity coefficient $\left(Log\, K_{A,B}^{Pot.} \right)$ of proposed Hg(II) ion-selective electrodes PME-1 and CGE-1 (Gupta et al. 2009a, b, c). In this method, the concentration of primary ion, Hg(II) ion, is varied whereas the concentration of secondary ions is kept constant at 1.0×10^{-2} M. Comparative potentiometric selectivity plots of PME-1 and CGE-1 is shown in Fig. 7. It is clear in Fig. 7 that univalent ions (Li^+, Na^+, K^+, and $NH4^+$) exhibit selectivity coefficient within the 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+}, and Cd^{2+}) except Ag(I) ions exhibit selectivity coefficient within the range of −2.10 to −4.09 for PME-1 and −1.75 to −4.25 for CGE-1. It can be also seen from the selectivity diagram the selectivity coefficient of PME-1 for Ag(I) ions is slightly positive $\left(Log\, K_{Hg^{2+},Ag^+}^{Pot.} = +0.25 \right)$ and Ag(I) ion is found to 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 $\left(Log\, K_{Hg^{2+},Ag^+}^{Pot.} = -0.95 \right)$ is negative and therefore there is no interference of Ag(I) ions $\left(Log\, K_{Hg^{2+},Ag^+}^{Pot.} \right)$ is observed in smooth functioning of CGE-1 for Hg(II) ions. It can be observed that $Log\, K_{Hg^{2+},Ag^+}^{Pot.}$ value for Ag(I) 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 is replaced by the solid graphite rod due to which diffusion of ion across the PVC membrane is eliminated and also the probability of the Hg(II) ions to get leached from membrane is 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(I) and other secondary ions.

Fig. 7 Selectivity diagram of Hg(II) ion-selective electrodes PME-1 and CGE-1 based on 1,3-alternate thiacalix[4]crown
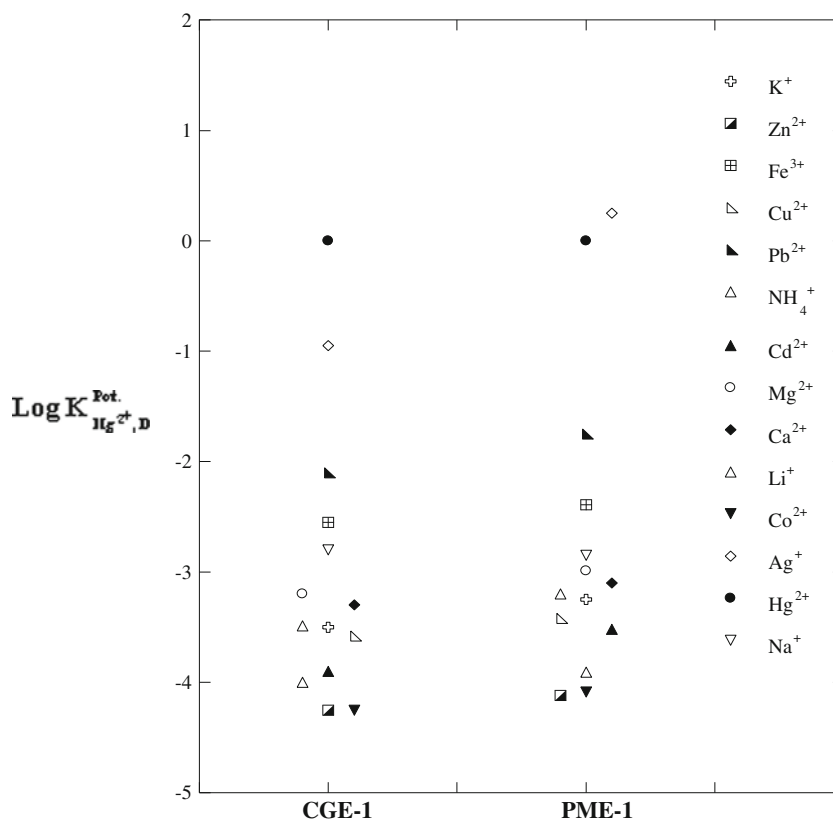
Comparison with recently reported ion-selective electrodes

From the comparative study of proposed Hg(II) ion-selective electrodes PME-1 and CGE-1 and those which are recently reported in literature, the proposed electrodes based on 1,3-alternate thiacalix[4]crown, especially the coated graphite electrode CGE-1, has been found to be better in terms of its wide concentration range, lower detection limit, wide pH range, short response time, and improved selectivity with respect to various secondary ions specially with Ag(I) ions,

which has been reported to be the major interference in the recently reported ion-selective electrodes (Table 4) and the interference of Ag(I) has been completely eliminated by CGE-1 proposed sensor in the present work.

Analytical applications

Due to small interference of Ag(I) 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.

Table 4 Comparison of response characteristic of PME-1 and CGE-1 with previously reported electrodes

| Ionophore	Linear range (M)	Detection limit (M)	Slope (mV/dec.)	pH range	$Log\ K_{Hg^{2+},Ag^+}^{Pot.}$	Response time (s)	Reference no.
1-Furan-2-yl-4-(4-nitrophenyl)-2-phenyl-5 H-imidazole-3-oxide	1.0×10^{-1} to 1.0×10^{-6}	8.91×10^{-7}	32.60	1.0–4.0	-0.10	<20	Mahajan et al. (2009a, b)
Oxadiazaphosphenpine derivatives	1.0×10^{-1} to 1.0×10^{-6}	7.24×10^{-7}	29.39	0.9–4.5	-0.35	<10	Puri et al. (2011)
Calix[2]thieno[2]pyrrole	1.0×10^{-2} to 1.0×10^{-6}	–	27.80	1.0–6.0	0.63	20	Abbas (2012)
Poly(Hg(II)-4-vinyl pyridine)	1.0×10^{-2} to 1.0×10^{-7}	0.50×10^{-7}	30.00	3.0–4.0	0.048	<25	Bakhtiarzadeh and Ghani (2008)
N,N′-bis(salicylaldehyde)-phenylenediamine	1.0×10^{-4} to 1.0×10^{-7}	1.50×10^{-7}	58.80	3.8–7.8	0.097	10–60	Shawish (2009)
1,3-Alternate thiacalix[4]crown (PME-1)	1.0×10^{-1} to 5.0×10^{-6}	9.77×10^{-6}	29.16	2.0–6.0	0.25	20	This work
1,3-Alternate thiacalix[4]crown (CGE-1)	1.0×10^{-1} to 5.0×10^{-7}	7.76×10^{-7}	30.39	1.5–6.5	-0.90	<10	This work
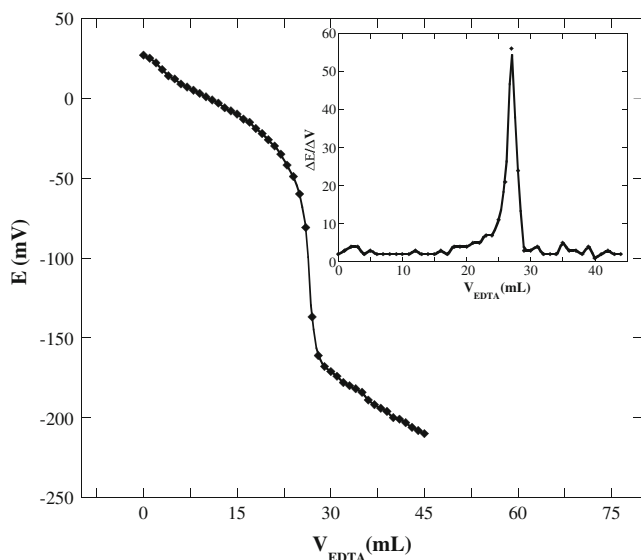
Fig. 8 Potentiometric titration of 1.0×10^{-2} M Hg(II) solution with 1.0×10^{-2} M EDTA using CGE-1, based on 1,3-alternate thiacalix[4] crown

Potentiometric titration

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. 8. 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 mercury(II) ions in solution. Therefore, the end point and the amount of mercury(II) ions in the solution can be accurately determined by extrapolation of the three linear portion of titration plot.

Estimation of Hg(II) in water samples

Proposed CGE-1 sensor has been used for the determination of Hg(II) ions in different water samples such as well, river, and wastewater 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. Result 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 5. Results obtained from both the methods on comparison were found to be quite in agreement with each other.

Table 5 Estimation of Hg(II) ions in water samples by using CGE-1

Sample	Hg(II) content in water samples (M)		
	Volumetric method	Ion-selective electrode (CGE-1)	Percentage compatibility
Well water	5.72×10^{-6}	5.70×10^{-6}	100.35
River water	2.84×10^{-5}	2.87×10^{-5}	98.95
Waste water	9.60×10^{-3}	9.67×10^{-3}	99.27

Estimation of Hg(II) in synthetic samples

Hg(II) ions content in synthetic samples like synthetic water (1 and 2), dental amalgam, and parad tablets (insecticide) were quantitatively determined by using proposed CGE-1 sensor. In case of dental amalgam and parad tablets, 1.0 g of each sample to be tested was dissolved in minimum amount of concentrated nitric acid upon mild heating for 15 min. Sample solutions thus prepared were diluted to 100.0 mL using double-distilled water. After filtration, these samples were employed for determination Hg(II) content using proposed CGE-1 sensor. Hg(II) content in synthetic samples was also determined by employing volumetric methods using EDTA as the titrant. Results of both the methods are compared in Table 6 and results compatibility indicate that proposed sensor are efficiently used for estimation of Hg(II) content in synthetic samples.

Estimation of Hg(II) in traditional Indian made ayurvedic medicines

As discussed in the "Introduction" section, 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, in

Table 6 Estimation of Hg(II) ions in synthetic water samples by using CGE-1

Sample	Hg(II) content in water in synthetic samples (M)		
	Volumetric method	Ion-selective electrode (CGE-1)	Percentage compatibility
Synthetic water (1)	6.31×10^{-2}	6.28×10^{-2}	100.47
Synthetic water (2)	1.81×10^{-5}	1.86×10^{-5}	97.31
Dental amalgam	4.79×10^{-2}	4.68×10^{-2}	102.35
Parad tablets (insecticide)	7.79×10^{-3}	7.79×10^{-3}	100.00

Table 7 Estimation of Hg(II) ions in ayurvedic medicines samples by using CGE-1

Sample	Hg(II) content in ayurvedic medicines samples (M)		
	Volumetric method	Ion-selective electrode (CGE-1)	Percentage compatibility
Vasant kusumaker ras	1.41×10^{-4}	1.37×10^{-4}	102.92
Agnitundi vati	1.14×10^{-5}	1.10×10^{-5}	103.63
Ekangveer ras	8.66×10^{-4}	8.70×10^{-4}	99.54

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 available in a local bazaar of India. Firstly, sample tablets were crushed into fine powder with the help of mortar and pestle. Then, powder were weighed out accurately about 1.0 g of the each sample and dissolved into 10–15 ml of freshly mixed concentrated HNO_3 and concentrated HCl (aqua regia) in the volume ratio of 1:3, respectively, in 100 mL conical flask. It should be shaken vigorously and warmed gently if the sample is not dissolved completely. Make the solution 100.0 mL by adding 90.0 mL double-distilled water to a conical flask. After filtration, these samples are ready for estimation of Hg(II) content by employing CGE-1 ion-selective electrode. From Table 7, 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.

Test of CGE-1 significance

Result obtained by CGE-1 and traditional volumetric methods are statistically compared to see that result obtained from CGE-1 are reliable and acceptable. A good agreement is obtained, line regression of CGE-1 vs. volumetric method yielded a correlation of $R=0.9974$ for $n=9°$ of freedom (total no of samples minus 1) with comparable line $y=0.9821 \times + 0.00022$. Here, R value represent that both method are undistinguished to each other. Similarly, if the paired Student's t test is performed, calculated value of $t=0.00511$ for CGE-1 vs. volumetric method. Here, t-calculated value is quite less than tabular critical value of $t=2.26$ ($9°$ of freedom with 5 % level of significance). These values of t 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.*

Conclusion

1,3-Alternate calix[4]crown has been found to be novel carrier of Hg(II) ions in the PVC based PME-1 and CGE-1.

The PME-1 based on membrane composition ionophore (6.2 mg), PVC (100.0 mg), 2-NPOE (200.0 mg), and NaTPB (2.0 mg) exhibited Nernstian slope of 29.16 mV/decade and wide concentration range of 1.0×10^{-1} to 5.0×10^{-6} M with lower detection limit of 9.77×10^{-6} M. It has a response time of 20 s 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} to 5.0×10^{-7} M), lower detection limit (7.76×10^{-7} M), response time of less than 10 s, 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(I) ions cause small interference with Hg(II) ions. CGE-1 sensor is superior to other recently reported ion-selective electrode for Hg(II) ions (Table 4). 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, synthetic, and ayurvedic medicines samples.

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