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ORIGINAL ARTICLE

Mercury(II) ion recognition by newly synthesized oxadiazaphosphepine based receptors: coated graphite and polymeric membrane electrodes

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Abstract Oxadiazaphosphepine based receptors were synthesised and their ion sensing properties have been investigated. Polymeric membrane electrodes (PMEs) and coated graphite electrodes (CGEs) based on these receptors exhibited selective response for mercury(II) ions and the response characteristics of CGEs were found to be comparatively better. 2,2,2,4,7-Pentaphenyl-5-o-tolyl-2,5-dihydro-2l5-[1,3,5,2]oxadiazaphosphepine based coated graphite electrode (CGE-1) exhibited Nernstian response (29.39 mV/decade) for mercury(II) ions over a wide concentration range (1.0×10^{-1} M–1.0×10^{-6} M) with lower detection limit of 7.24×10^{-7} M. The proposed electrodes possess high selectivity for mercury(II) ions with respect to alkali, alkaline and heavy metal ions especially silver(I) ions ($\log K^{\mathrm{Pot.}}_{\mathrm{Hg}^{2+},\mathrm{Ag}^{+}} = -0.35$) and have wide functional pH range (0.95–4.50) with fast response time of less than 10 s. These electrodes have been successfully used as indicator electrodes during the potentiometric titrations of mercury.

Keywords Oxadiazaphosphepine derivatives · Mercury(II) ion selective electrodes · Coated graphite electrodes · Polymeric membrane electrodes · Potentiometric sensors

Introduction

Mercury is a common contaminant of ambient air, soil, water and food and has lethal effects on living systems. Mercury and its salts cause irreparable neurological damage to human health [1]. Mercury is toxic as on entering the living systems it reacts with metabolic proteins and enzymes and inhibits the catalysis of basic metabolic reactions [2]. Due to its toxic effects and the associated environmental problems [3, 4], trace level estimation of mercury in different environmental and industrial samples requires modern methods. In literature there are number of reports regarding trace level estimation of mercury(II) ions using different spectroscopic or electrochemical methods [5–11]. However, these methods have shortcomings in practical use owing either to high instrumentation cost or the use of hazardous materials. Development of new approaches that allow mercury detection with more simplicity and selectivity is thus urgently required and ion sensing electrodes are especially appealing in this direction.

In literature, number of reports are available on the mercury(II) ion selective electrodes employing carriers like crown ethers, amides, oxamides, metalloporphyrines, schiff bases etc. [12–20]. The interference of silver(I) ions in the performance of these mercury(II) ion-selective electrodes is a major problem except for few reports, where ligands have highly selective binding tendency towards mercury(II) ions [21–24]. The interference of silver(I) ions is on account of the similarity in size with mercury(II) ions along with the ion flux effects [25–30]. This interference can be eliminated by the following either of the two approaches. First approach seeks the synthesis of newer and novel ionophores that are more selective for mercury(II) ions in comparison to silver(I) ion. Earlier, our group has successfully employed a variety of calixarenes, thiosemicarbazone derivatives, metal-porphyrinate complexes and related compounds as ionophores to develop PVC membrane based ion-selective electrodes for a variety of cations and anions [31–36]. In this work, we have synthesised the novel oxadiazaphosphepine based receptors

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and investigated their use as carriers for mercury(II) ions in ion selective electrodes. Oxadiazaphosphepine based receptors have attracted our interest owing to their properties of versatile chelating tendency for metal ions and formation of selective complexes with metal ions.

The second approach to eliminate the silver(I) ion interference is by reducing the leaching of primary ions from across the PVC membrane of polymeric membrane electrodes and different groups have attempted in this direction by strongly reducing the primary ion activity of the internal solution [37], increasing the PVC content in the membrane [38], covalently attaching the ionophore to the polymer matrix [39, 40], or incorporating lipophilic additive in the membrane [41]. More recently, ISEs with solid internal contact, i.e., without an inner solution, have been reported to produce better values of lower detection limits and selectivity values than conventional electrodes with optimized inner solutions [42–44]. Our group has also reported the coated graphite based electrodes for selective estimation of mercury(II) ions, silver(I) ions, bismuth(III) ions and chloride ions and reported that these have better electrode characteristics properties compared to the corresponding polymeric membrane electrodes [45–47]. In present work, apart from synthesising the newer and novel oxadiazaphosphepine receptors for use as ionophores in mercury(II) ion selective polymeric membrane electrodes, we have also attempted to enhance their sensitivity and selectivity towards mercury(II) ions by developing coated graphite electrodes (CGE) based on these ionophores.

The resulting mercury(II) ion-selective electrodes have been characterized in terms of slope, linear range, lower detection limit, selectivity and response time. From the comparative studies of these electrodes, CGEs have been found to be performing better than PMEs in terms of lower detection limit and better selectivity for mercury(II) ions. The proposed electrodes have also been successfully used as indicator electrodes in titration experiments.

Experimental

Chemicals and reagents

All reagents used were of Analytical-Reagent grade. Oxadiazaphosphepine based receptors **I** and **II** were synthesized in the laboratory as per the scheme given in Fig. 1. Various plasticizers like dioctylsebacate (DOS), dioctylphthalate (DOP), dioctyladipate (DOA), dibutylphosphate (DBP) and tributylphosphate (TBP) alongwith high molecular weight poly(vinylchloride) (PVC) were obtained from Fluka. Sodium tetraphenyl borate (NaTPB) was obtained from Aldrich. Mercuric nitrate and other metal ion nitrates received from Merck were used without any further purification. Doubly distilled deionised water was used to prepare solutions.

Synthesis of oxadiazaphosphepine derivatives based receptors

The treatment of N-imidoyliminophosphoranes with substituted α-bromoacetophenones in the presence of triethylamine in dry dioxane at room temperature resulted in very good yields of the products which were characterized as 5,7-diaryl-2,2,2,4-tetraphenyl-1-oxo-3,5-diazaphosphepines (Scheme 1 in Fig. 1).

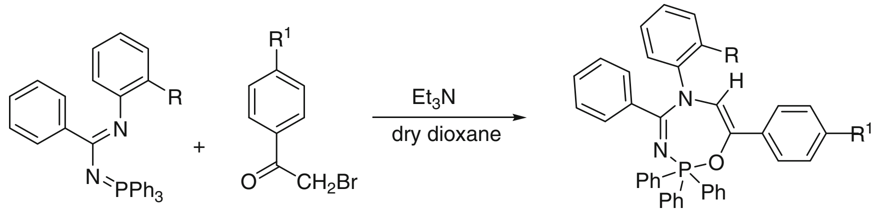
The ^{1}H NMR spectrum confirmed the presence of triphenylphosphine group as indicated by the number of protons in the aromatic region. The number of carbon atoms in ^{13}C spectrum further corroborated its presence. The above reactions were also examined in the presence of a number of bases viz sodium bicarbonate, 1,8-diazabicyclo(5,4,0)undec-7-ene (DBU), pyridine and in different solvents like benzene, dichloromethane and dioxane and all these combinations invariably resulted in the isolation of same product as confirmed from their mixed melting points and super imposable IR spectra. However, best yields were obtained in dioxane-triethylamine and dioxane-pyridine combinations. The plausible mechanism for the formation of oxadiazaphosphepines is as shown in Scheme 2 (Fig. 1) and involves an initial attack of N-1 of N-imidoyliminophosphorane on methylene carbon of α-bromoacetophenone resulting in the formation of the corresponding bromide salt, the cyclisation of which via its enolic form yields oxadiazaphosphepines (Scheme 2 in Fig. 1).

General procedure for the reaction of N-imidoyliminophosphoranes with α-bromoacetophenones

To a well stirred solution of N-imidoyliminophosphorane and pyridine in dry dioxane was slowly added phenacyl bromide at room temperature. The reaction mixture was allowed to stir for 1.5–2 h and the progress of the reaction mixture was monitored by TLC. The reaction mixture was then worked up in benzene and water mixture. The organic layer was removed, dried over anhydrous magnesium sulphate and the solvent was removed under reduced pressure so as to concentrate the reaction mixture. The product was then crystallized by trituration and re-crystallized by using hexane: benzene mixture (10:1) to yield finely crystalline product.

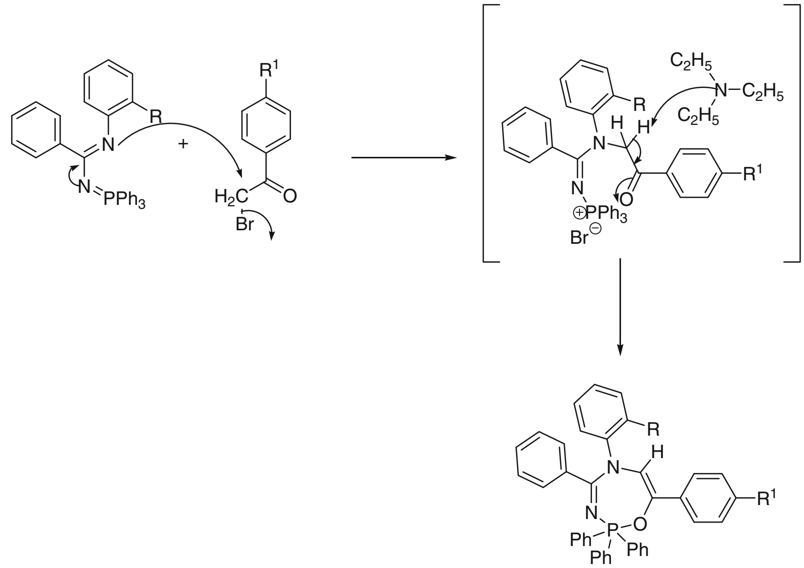
Receptor I (2,2,2,4,7-pentaphenyl-5-o-tolyl-2,5-dihydro-2l5-[1,3,5,2]oxadiazaphosphepine)

m.p.: 212–213°C ν_{max}: 1110, 1343, 1435, 1548 cm^{-1} Anal. Calcd. For $C_{40}H_{33}N_2OP$: C, 81.61; H, 5.65; N, 4.76: Found



	R	R^1	%age yield
I	$-CH_3$	H	77
II	$-CH_3$	$-CH_3$	71

Scheme 1



Scheme-2

Fig. 1 Method of synthesis of functionalised oxadiazaphosphepine. *Scheme 1* Reaction of N-imidoyliminophosphorane with substituted phenacyl bromides. *Scheme 2* Plausible mechanism of formation of functionalised oxadiazaphosphepine

C, 81.78; H, 5.57; N, 4.67 δ_H (200 MHz) 2.18 (s, 3H, $-CH_3$); 6.22–6.25 (m, 1H, ArH); 6.80–6.84 (m, 1H, ArH); 7.22–7.29 (m, 5H, ArH); 7.40–7.56 (m, 15H, ArH); 7.68–7.94 (m, 8H, ArH): ^{13}C (50.4 MHz) 20.1, 121.6, 123.0, 126.1, 127.0, 127.2, 127.5, 127.8, 128.0, 128.1, 128.2, 128.5, 128.8, 128.9, 129.3, 131.8, 133.0, 135.8, 168.0, 168.2 *m*/*z* 588.

Receptor II (2,2,2,4-tetraphenyl-5,7-di-o-tolyl-2,5-dihydro-2l5-[1,3,5,2]oxadiazaphosphepine)

m.p.: 185–187°C ν_{max}: 1107, 1340, 1438, 1550 cm^{-1} Anal. Calcd. For $C_{41}H_{35}N_2OP$: C, 81.71; H, 5.85; N, 4.65. Found C, 81.57; H, 5.94; N, 4.70 δ_H (200 MHz) 2.16 (s, 3H, $-CH_3$); 2.19 (s, 3H, $-CH_3$); 6.21–6.24 (m, 1H, ArH); 6.78–6.82 (m, 1H, ArH); 7.19–7.27 (m, 4H, ArH); 7.36–7.52 (m, 15H, ArH); 7.65–7.91 (m, 8H, ArH): ^{13}C (50.4 MHz) 20.3, 20.7, 121.8, 123.2, 126.2, 127.1, 127.2, 127.3, 127.9, 128.0, 128.1, 128.2, 128.3, 128.7, 128.9, 129.4, 131.6, 133.2, 135.4, 168.1, 168.2 *m*/*z* 602.

Preparation of PVC membrane based potentiometric sensors

The membrane was prepared by dissolving PVC, plasticizer, additive and varying amounts of ionophore in about 5.0 mL of tetrahydrofuran (THF). The mixture was shaken vigorously and a clear solution was poured into a petridish (50.0 mm in diameter). The solvent was allowed to evaporate at room temperature. The resulting membrane of 0.4 mm thickness was cut to the size, attached to the PVC tube with the help of PVC glue and conditioned with 1.0×10^{-2} M metal ion solution for about 24 h till it gave reproducible and stable potential. Electrochemical cell assembly used for the study was as follows:

Ag–AgCl	3.0 M KCl	1.0×10^{-3} M $Hg(NO_3)_2$	PVC membrane	Test solution	3.0 M KCl	Ag–AgCl

Preparation of coated graphite based potentiometric sensors

Spectroscopic grade graphite rods (10.0 mm in length and 3.0 mm in diameter) were used to prepare the coated graphite electrodes. A shielded copper wire was glued to one end of the graphite rod and the electrode was sealed into the end of a glass tube of about the same diameter with epoxy resin. Working surface of the electrode was polished with fine alumina slurry on a polishing cloth, sonicated in distilled water and dried in air. Membrane solution was prepared by thoroughly dissolving appropriate amounts of ionophore, powdered PVC, DOS and NaTPB in 3.0 mL THF. The resulting clear solution was evaporated slowly at room temperature until an oily concentrated mixture was obtained. The polished graphite electrode was then 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 was allowed to stabilize overnight. Electrode was finally conditioned by soaking in 1.0 × 10^{-3} M solution of $Hg(NO_3)_2$ for 48 h. Potentiometric measurements were carried out using following electrochemical cell assembly:

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

All the electrode potential measurements were made with an EQUIPTRONICS model EQ-602 potentiometer. The pH measurements were made using an Elico LI-MODEL-120 pH meter. Silver/silver chloride electrode along with 3.0 M KCl as salt bridge was used as internal and external reference electrode in case of polymeric membrane electrode. Internal reference electrode was not used in coated graphite electrode.

Results and discussion

Membrane composition

Oxadiazaphosphepine derivative based receptor I was employed as an ionophore for the preparation of a variety of mono-, di- and tri-valent metal ion-selective electrodes. Among different cations tested for the preparation of ion selective electrodes, mercury(II) ion was found to provide better sensitivity and selectivity with the PVC based polymeric membrane (PME) of oxadiazaphosphepine derivative based receptor I. Potential response slopes for other ion-selective electrodes were found much lower than the values expected from Nernstian equation and were in a limited concentration range (Fig. 2). On optimization, Nernstian slope (30.47 mV/decade) for mercury(II) ions over a concentration range of 1.0 × 10^{-1} M to 5.0 × 10^{-6} M was observed in case of membrane (PME-1) containing 1.9 mg NaTPB and 5.5 mg receptor I (Table 1). The observed Nernstian response of the electrode towards mercury(II) ions is due to rapid and reversible complex formation between nitrogen and oxygen donor atoms of the ionophore and mercury(II) ions.

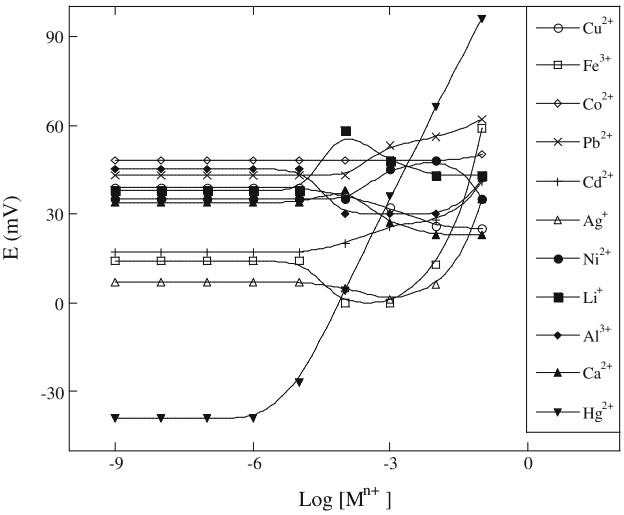


Fig. 2 Potentiometric response of oxadiazaphosphepine receptor I based polymeric membrane electrodes (PMEs) for various metal ions

In order to study the effect of plasticizer on response behaviour of the proposed ion selective electrode, several plasticizers such as DOS, TBP, DOA, DBP and DOP were employed for the membrane preparation (Table 1). The mercury(II) ion-selective polymeric membrane electrode (PME-1) based on DOS as a plasticizer displayed better properties compared to the polymeric membrane electrodes (PMEs: 3–6) containing other plasticizers. It shows better Nernstian slope (30.47 mV/decade) over a wide concentration range of 1.0 × 10^{-1} M to 5.0 × 10^{-6} M with lower detection limit of 3.80 × 10^{-6} M. The mercury(II) ion-selective electrodes (PME: 3–6) based on TBP, DOA, DBP and DOP as plasticisers exhibited super-Nernstian slopes (55.65, 37.54, 54.84 and 44.80 mV/decade, respectively) for mercury(II) ions (Table 1).

On the basis of results obtained for receptor I, it was decided to employ oxadiazaphosphepine based receptor II as an ion carrier for the development of mercury(II) ion selective electrode. The mercury(II) ion-selective polymeric membrane electrode PME-2 based on receptor II as an ionophore exhibited Nernstian slope (30.09 mV/decade) for mercury(II) ions over a concentration range of 1.0 × 10^{-1} M to 5.0 × 10^{-6} M with lower detection limit of the value 4.17 × 10^{-6} M (Fig. 3).

Table 1 Composition and response characteristics of oxadiazaphosphepine receptors based mercury(II) ion selective electrodes

S. no.	PVC (mg)	Plasticizer (mg)	NaTPB (mg)	Ionophore (mg)	Linear range (M)	Detection limit	Slope (mV/dec)
PME-1	100.7	200.3 DOS	1.9	5.5 (**I**)	1.0×10^{-1}–5.0×10^{-6}	3.80×10^{-6}	30.47
PME-2	100.7	200.1 DOS	1.9	5.6 (**II**)	1.0×10^{-1}–5.0×10^{-6}	4.17×10^{-6}	30.09
PME-3	100.6	200.8 TBP	1.9	5.6 (**I**)	1.0×10^{-1}–5.0×10^{-5}	1.99×10^{-5}	55.65
PME-4	100.4	200.4 DOA	1.9	5.6 (**I**)	1.0×10^{-1}–5.0×10^{-5}	4.46×10^{-5}	37.54
PME-5	100.4	200.6 DBP	1.9	5.5 (**I**)	1.0×10^{-1}–5.0×10^{-5}	3.63×10^{-5}	54.84
PME-6	100.8	200.3 DOP	1.9	5.7 (**I**)	1.0×10^{-1}–5.0×10^{-5}	1.38×10^{-5}	44.80
CGE-1	20.0	40.2 DOS	1.8	4.7 (**I**)	1.0×10^{-1}–1.0×10^{-6}	7.24×10^{-7}	29.39
CGE-2	20.0	40.0 DOS	1.8	4.7 (**II**)	1.0×10^{-1}–1.0×10^{-6}	5.62×10^{-7}	30.42

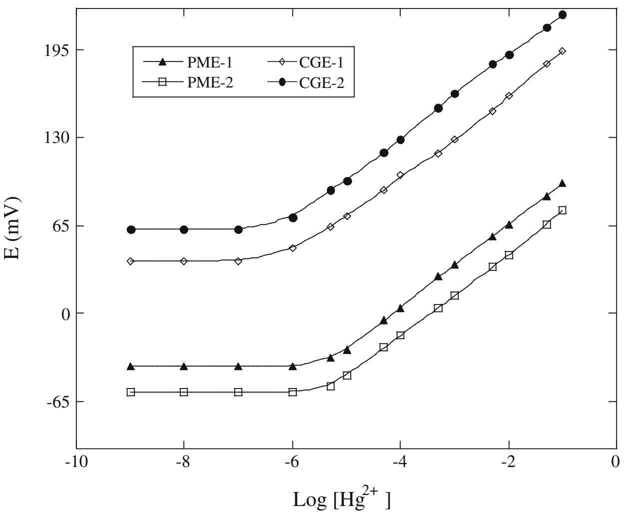


Fig. 3 Potential response curves of oxadiazaphosphepine receptors I and II based mercury(II) ion-selective electrodes (PMEs: 1, 2 and CGEs: 1, 2)

It has already been reported in literature that the replacement of internal reference solution of polymeric membrane based electrode with some solid substrate like graphite rod results into the improvement of characteristic properties such as slope, working concentration range, lower detection limit and selectivity etc. of the electrode [45–47]. Therefore, it was decided to prepare the coated graphite electrodes employing oxadiazaphosphepine based receptors I and II as ionophores. The coated graphite electrode CGE-1 employing receptor I as an ionophore displayed Nernstian response (29.39 mV/decade) for mercury(II) ions over a wide concentration range (1.0 x 10^{-1} M to 1.0×10^{-6} M) with lower detection limit of the order 7.24×10^{-7} M. The corresponding coated graphite electrode CGE-2 employing receptor II as an ionophore displayed Nernstian response of 30.42 mV/decade for mercury(II) ions over a wide concentration range (1.0×10^{-1} M to 1.0×10^{-6} M) with lower detection limit of the order 5.62×10^{-7} M.

Effect of pH on response characteristics of mercury(II) ion selective electrodes

The potential response of ion selective electrodes is affected by the pH of the analyte ion solution employed. The effect of pH on potential response of the proposed ion selective electrodes was studied over a pH range of 0.80 to 7.20 at the mercury(II) ion concentration of 1.0×10^{-3} M. Potential response of the PVC based polymeric membrane electrodes (PMEs: 1 and 2) remain constant within pH range of 1.2 to 3.75 and 1.2 to 3.60 respectively, Whereas the potential response of the corresponding coated graphite electrodes (CGEs: 1 and 2) remain constant within pH range of 0.95 to 4.50 and 1.05 to 4.35 respectively (Fig. 4). The potential variation at lower end of functional pH range may be attributed to the interference by H^+ ions and the potential variation at higher end of the pH range may be due to the formation of some hydroxyl complexes of mercury(II) ions in solution from the hydrolysis of mercuric nitrate salt.

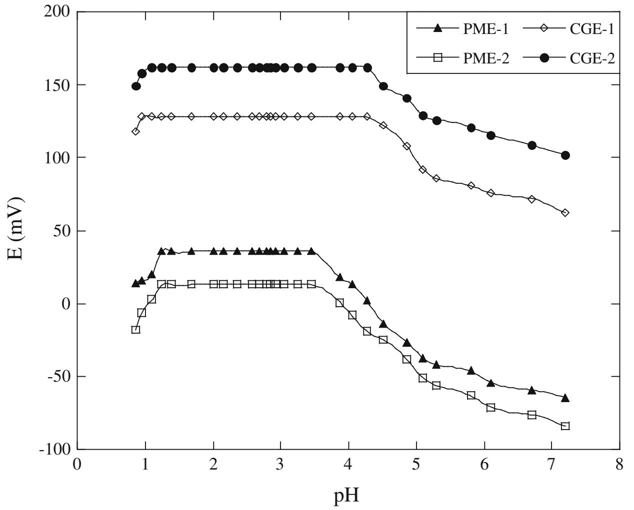


Fig. 4 Effect of pH on potential response of oxadiazaphosphepine receptors I and II based mercury(II) ion-selective electrodes (PMEs: 1, 2 and CGEs: 1, 2)

Response time and lifetime of mercury(II) ion selective electrodes

Response time of an ion selective electrode is the average time required by it for attaining the equilibrium value of potential when dipped in successive mercury(II) ion solutions, each having a tenfold difference in concentration. The static response time of the mercury(II) ion selective electrodes (PMEs: 1, 2 and CGEs: 1, 2) was less than 10 s (Fig. 5). The lifetime of the proposed electrodes was at least 2 months. During this time, their electrode behaviour such as concentration range, detection limit and slope remained almost constant.

Electrode selectivity

Selectivity of an ion selective electrode is one of the important characteristic properties that measure the response of the electrode towards the primary ion (A) in the presence of secondary ions (B) present in the test solution. It is measured in terms of the potentiometric selectivity coefficients ($\log K^{\text{Pot.}}_{\text{A,B}}$). In the present work, selectivity coefficients have been determined using fixed interference method (FIM) based on the semi empirical Nikolsky-Eisenman equation. In this method, the concentration of primary ion, mercury(II) ion, is varied, whereas the concentration of secondary ion is kept constant at 1.0×10^{-2} M. The potentiometric selectivity data of polymeric membrane electrodes (PMEs: 1, 2) and coated graphite electrodes (CGEs: 1, 2) for different secondary ions is shown in selectivity diagram (Fig. 6). It is clear from the selectivity diagram that the $\log K^{\text{Pot.}}_{\text{Hg}^{2+},\text{B}}$ values in case of polymeric membrane electrodes (PMEs: 1, 2) are of the order of ~ -2.6 to -3.22 for alkaline earth (Mg^{2+}, Ca^{2+}) and some heavy metal ions (Zn^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+}, etc.), which indicate that these divalent metal ions do not cause much interference in the normal functioning of mercury(II) ion selective polymeric membrane based electrodes even when present at a high concentration of 1.0×10^{-2} M in the test solution. Although, the $\log K^{\text{Pot.}}_{\text{Hg}^{2+},\text{B}}$ values of the monovalent ions (Na^+, K^+, $NH_4{}^+$) have been found to be comparatively higher than those of the divalent ions, they also do not disturb the normal functioning of the proposed mercury(II) ion selective polymeric membrane based electrodes and the electrodes possess high mercury(II) ion selectivity with respect to these secondary ions.

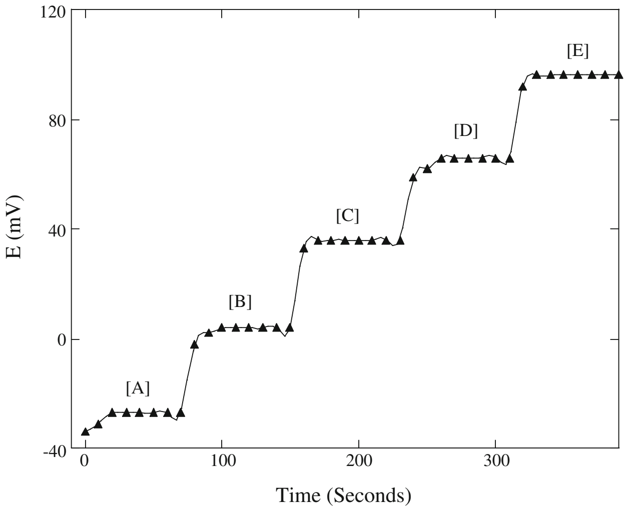


Fig. 5 Response time obtained with electrode PME-1 based on oxadiazaphosphepine receptor I. [*A*] 1.0×10^{-5} M mercury(II) ion solution. [*B*] 1.0×10^{-4} M mercury(II) ion solution. [*C*] 1.0×10^{-3} M mercury(II) ion solution. [*D*] 1.0×10^{-2} M mercury(II) ion solution [*E*] 1.0×10^{-1} M mercury(II) ion solution

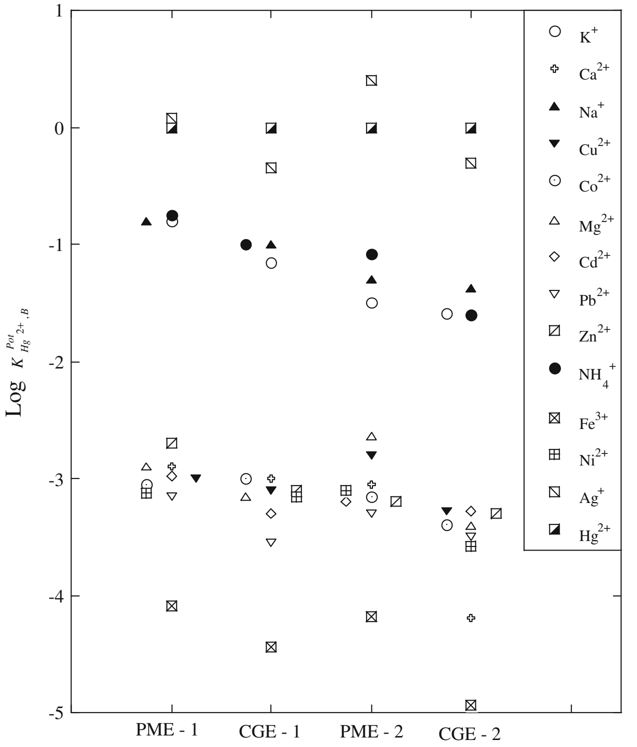


Fig. 6 Selectivity diagram of oxadiazaphosphepine receptors I and II based mercury(II) ion-selective electrodes (PMEs: 1, 2 and CGEs: 1, 2)

On comparing the selectivity data of polymeric membrane electrodes (PMEs: 1, 2) and coated graphite electrodes (CGEs: 1, 2), it has been found that the $\log K^{\text{Pot.}}_{\text{Hg}^{2+},\text{B}}$ values for most of the secondary ions are better in case of corresponding coated graphite electrodes (CGEs: 1, 2). The better selectivity behavior is more pronounced in case of the major interferent silver(I) ion. The selectivity coefficient values ($\log K^{\text{Pot.}}_{\text{Hg}^{2+},\text{Ag}^{+}}$) for PME-1 and CGE-1 are

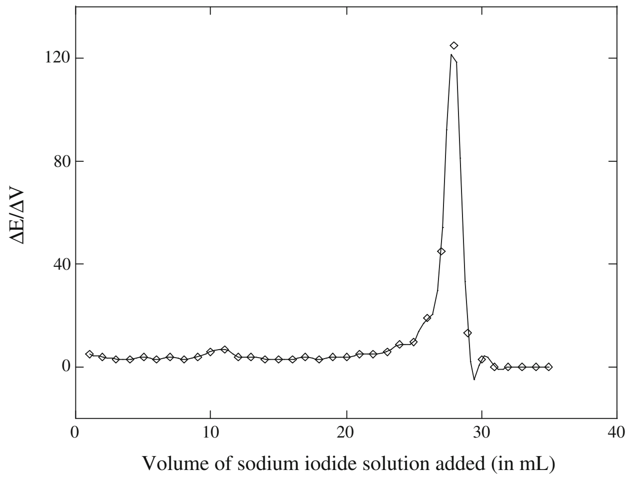


Fig. 7 Derivative plot for titration of 1.0×10^{-2} M mercury(II) ion solution with 1.0×10^{-2} M sodium iodide solution using the electrode CGE-1 as an indicator electrode

+0.08 and −0.35 respectively and corresponding values for PME-2 and CGE-2 are +0.40 and −0.30, which shows that there is manifold increase in the selectivity of CGEs in comparison to PMEs. This increase in selectivity in case of CGEs in comparison with the corresponding PMEs is attributed to the ion flux mechanism. In case of PME based electrodes, solution of mercury(II) ions is employed as an internal reference solution and there is probability that mercury(II) ions are being constantly leached from across the PVC membrane resulting into the change in concentration of ions near the membrane surface. This concentration change of mercury(II) ions in test solution in the vicinity of membrane results in inferior values of characteristic electrode properties like lower detection limit and selectivity coefficients for PMEs in comparison to that of the corresponding CGEs. In case of CGE based electrodes, the internal solution gets replaced with solid graphite rod and the phenomenon of diffusion of ions across the PVC membrane gets eliminated. This replacement of internal reference mercury(II) ion solution by graphite rod resulted in the enhanced selectivity of mercury(II) ion selective electrodes toward silver and other secondary ions.

Analytical applications

The practical significance of the proposed electrodes has been tested by using them as the indicator electrodes for the potentiometric titration of a mercuric nitrate solution with sodium iodide solution (Fig. 7). Before the end point, the potential shows usual logarithmic change with the volume of the titrant added, while the potential response after the end point remains almost constant, due to the low concentration of free mercury(II) ions in the solution.

Conclusion

Oxadiazaphosphepine based receptors I and II have been found to be novel carriers of mercury(II) ions in the PVC based polymeric membrane (PMEs: 1, 2) and coated graphite electrodes (CGEs: 1, 2). The proposed mercury(II) ion selective electrodes exhibit Nernstian response with lower detection limits of the order 7.24×10^{-7} M. The sensors have working pH range of ~0.95 to 4.50 with the fast response time of less than 10 s. Selectivity coefficient values show the high preference of the proposed electrodes for mercury(II) ions compared to different secondary ions. Even, silver(I) ions have not been found to be interfering in the normal functioning of the proposed coated graphite electrodes (CGEs: 1 and 2). The electrodes have also been successfully applied as indicator electrodes for potentiometric titration of mercury(II) solution against sodium iodide solution.

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