

4-(4-Methoxybenzilidenimin) Thiophenole as Neutral Carrier for Construction of Highly Mercury Selective Electrode

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Abstract

Highly selective poly (vinyl chloride) (PVC) membrane electrode based on 4-(4-methoxybenzilidenimin) thiophenole as new carrier for mercury-selective electrode has been reported. The electrode was prepared by coating the membrane ingredient on the surface of graphite electrode. The effect of various parameters including, the membrane composition, pH and possible interfering ions on the response properties of the electrode were examined. The sensor exhibited Nernstian responses toward mercury over a wide concentration range from 2×10^{-6} to 0.1 M, with slopes of 29.24 ± 0.82 mV per decade of mercury concentration, over a wide pH range of 1.3 – 2.9. The limit of detection for electrode was 8×10^{-7} M. The sensor has stable responses times of ≤ 10 s after conditioning in 0.05 M Hg (NO₃)₂ for 18 h and can be used for at least 2 months without any considerable divergence in the potential response characteristics. The proposed electrode show fairly good discrimination of mercury over several inorganic ions. The electrodes were successfully applied to direct determination of mercury in some real sample with complicated matrix and as indicator electrode in complexation titrations.

Keywords: mercury-selective electrode, potentiometry, poly (vinyl Chloride) (PVC) membrane, 4-(4-Methoxybenzilidenimin) thiophenole (MBITP).

1. Introduction

Mercury is a toxic element that can be absorbed readily by humans and other organisms. It is well known that mercury ion inactivates sulfhydryl enzymes and also combines with amine. The need for highly sensitive and selective mercury determination arises from its wide application in industry and its long term toxicity toward human beings. Over the last two decades, the need has increased for the determination of extremely low concentrations of mercury in various samples because it accumulates in living tissues, thereby causing many harmful effects [1-3]. It has been shown that the presence of soft donor atoms in ligands results in a considerable increase in stability of their complexes with soft cations such as mercury and silver ions, while diminishing the stability of their alkali, alkaline earth metal ions and hard transition metal ion complexes [4, 5]. In this respect, thio-containing compounds have attracted widespread attention owing to the unique properties of these compounds and their use as carrier in ISEs, is expected to increase their selectivity toward mercury and silver over those of alkali, alkaline earth and several other metal ions.

The need for monitoring of toxic heavy metal ions such as Hg²⁺ in the environmental samples, in one hand, and the lack of efficient commercial mercury (II) ion selective electrodes, on the other hand, have made the development of new Hg²⁺ ion-selective electrodes a challenging problem in addition to potentiometric detection based on ion-selective sensors, as a simple method, offers great advantages such as speed and ease of preparation and procedure, non destructive analysis and wide dynamic range and low cost that these days widely have been applied for important ion determination. For a truly ion-selective electrode, a strong interaction between the ionophore and the ion is required in order to complex it in a selective fashion and therefore, there has been much focus on the construction of ion selective electrodes that function on the basis of chemical recognition principle. It was pointed out that the soft coordination sites of sulfur offer great affinity toward Ag⁺ and especially Hg²⁺ as soft transition metal ions [6].

Metal ions classified into so called soft acids such as Hg (II), Au (III) and Ag (I) etc. can be selectively and effectively interact with compounds containing sulphur

Table 1. Characteristic Performance of Some Mercury Ion Selective Electrodes

Ref.	L. T (day) ^a	I. ^b	R. T. (s) ^c	D.L. ^d	pH ^e	L. R. ($\mu\text{M-M}$) ^f	Slope ^g	Ionophore
7	90	Fe ³⁺ , Ag ⁺	20	22.4	1.3-4.0	50-0.1	27.3	PTBCC
8	--	Fe ³⁺	60	---	2-5	1-0.001	30.0	DTC
9	90	---	45	1.3	0.5-2.0	10-0.001	29.0	HTCT
10	60	Ni ²⁺ , Pb ²⁺ , Ag ⁺	20-100	6	1-4	10-0.1	28.5	MBI
10	60	Ni ²⁺ , Ag ⁺	20-100	6	1-4	10-0.1	29.6	HTCOD
10	--	Ag ⁺	--	-	4	5-0.01	28.7	CD
11	--	Ag ⁺	--	--	6.5	7.5-0.05	61.1	CD
12	-	Fe ³⁺ , Ag ⁺	120	0.7	2-4.5	1-0.001	30.0	EBPCA
13	60	--	<30	1	1-3	1.78-0.1	29.0	SATSC
14	120	--	18	--	2.5 or 5	---	30.0	DPDATTCTDD
15	--	Ag ⁺	20	--	2	50-0.01	29.0	DIPTPTB
16	90	--	<10	---	1-3.5	0.7-0.05	29-31	BNAS
17	90	Cd ²⁺ , Pb ²⁺ , Ag ⁺	10	6	0.5-2.5	8-0.01	28.5-29.5	DBCD
18	42	Ag ⁺	20	1	4.0	2-0.00021	30.8	DPT
19	42	Ag ⁺	20		2.7-5	25.1-0.1	32.1	PTC
20	42	Ag ⁺	--	--	--	10-0.001	29.0	DACE
21	--	Ag ⁺ , Pb ²⁺	---	--	3-5.5	10-0.01	28.4	ACE

a) Life Time b) Interference c) Response Time d) Detection Limit (μM) e) Applicable pH Range f) Linear Range g) slope (mV/decade)

Abbreviation: PTBCC (p-tert-ButylCalix[4]crowns); DTC (1,4-Dithia-12-Crown-4); HTCT (Hexa-18-Crown-6-tetrone); MBI (2-mercaptobenzimidazole); HTCOD (Hexathiacyclooctadecane), CT (calixarene derivative containing thiazole azo group); EBPCA (ethyl-2-benzoyl-2-phenylcarbamoyl acetate); SATSC (salicylaldehyde thiosemicarbazone); DPDATTCTDD (tetrathia-diazacyclotetradeca-2,9-diene); DIPTPTB (N-(O,O-diisopropylthiophosphoryl) thiobenzamide); BNAS (bis[5-((4-nitrophenyl)azo salicylaldehyde)]); DBCD (Dibenzo-diazathia-18-crown-6-dione); DPT (1,3-diphenylthiourea); EVBM (ethyl violet bromomercurate); PTC (pentathia-15-crown-5);

as donor atom. There are several articles dealing with the introduction of new mercury ion selective electrodes based on different neutral ion carriers, which their characteristic performances are presented in Table 1 [7-21]. These electrodes exhibited linear response for Hg (II) ion over nearly 3 or 4 orders of magnitudes and have disadvantages including long response time, long equilibration time, and short life time and suffer interferences by a number of metal ions.

Therefore, we were prompted to investigate the design MBITP as new sulfur-containing ligand in the construction of PVC based for evaluation of mercury concentration.

2. Experimental

2.1. Reagents

PVC of high relative molecular weight, dibutyl phthalate (DBP), dioctyl phthalate (DOP), 4-nitrophenyl octyl ether (NPOE) and bis(2-ethylhexyl) sebacate (BEHS), benzyl acetate (BA) were used as received from Aldrich. Reagent grade tetrahydrofuran (THF), sodium tetraphenylborate (NaTPB), methyltrioctylammonium chloride (MTOAC) and all other chemicals were of

highest purity available from Merck, and were used without further purification. All aqueous solutions were prepared with deionized, distilled water. The pH adjustments were made with dilute nitric acid or sodium hydroxide solutions as required.

2.2. Preparation of Electrode

The coated-graphite electrodes were prepared according to a previously reported method.²² Graphite rods (3 mm diameter and 10 mm long) were prepared from spectroscopic grade graphite. A shielded copper wire was glued to one end of the graphite rod with silver loaded epoxy resin, and the rod was inserted into the end of a PVC tube. The working surface of the electrode was polished with a polishing cloth. The electrode was rinsed with water and methanol and allowed to dry. A mixture of PVC, plasticizer and the membrane additive (MTOAC) to give a total mass of 100 mg, was dissolved in about 4 mL of THF. To this mixture was added the electro-active material, MBITP, and the solution was mixed well. The polished graphite electrode was then coated, by repeated dipping (several times, a few minutes between dips), into the membrane solution. A membrane was formed on the graphite surface, which

was allowed to set overnight. The electrode was rinsed with water and conditioned for ~18 h in 0.05 M mercury nitrate solution.

2.3. Potential Measurement

The response characteristics of the prepared coated-graphite electrodes were determined by recording potential across the membrane as a function of mercury-concentration at a constant temperature of 25 °C. All the potential measurements were carried out with a digital pH/ion meter, model 691 Metrohm. The potential build up across the membrane electrodes were measured using the galvanic cell of the following type: Ag/AgCl/KCl (sat'd.) || test solution | PVC membrane | graphite electrode. Potentials were measured relative to a saturated Ag/AgCl reference electrode. The pH of the sample solutions was monitored simultaneously with a conventional glass pH electrode, while in all cases, 0.01 M HNO₃ was used as electrolytic solution. The performance of each electrode was investigated by measuring its potential in mercury nitrate solutions prepared in the concentration range $1.0 \times 10^{-1} - 1.0 \times 10^{-7}$ M by serial dilution of the 0.1 M stock solution at constant pH. The solutions were stirred and potential readings recorded when they reached steady state values. The data were plotted as observed potential versus the logarithm of the mercury ion-concentration.

2.4. Synthesis of 4-(4-methoxybenzylideneimin) thiophenole

To 0.2 mmol (0.2501 g) 4-amino thiophenole in 10 mL methanol, 0.2 mmol (0.2724 g) of 4-methoxybenzaldehyde was added and reaction mixture was stirred at room temperature. The progress of reaction was monitored by TLC. After 4 hour the yellowish precipitate (product) was appeared. The reaction mixture was filtered and precipitate washed by methanol (twice) and dried under vacuum and 0.340 g product was obtained (~70%). The compound was identified by IR, ¹HNMR. The MBITP information are as follow:

IR (cm⁻¹, in KBr): 2996(w), 2962(w), 2928(w), 2831(w), 2563(w), 1617(vs), 1600(vs), 1577(vs), 1514(s), 1486(s), 1457(s), 1400(m), 1309(s), 1246(vs), 1195(s), 1161(vs), 1104(m), 1035(s), 967(m), 933(w), 881(m), 842(vs), 819(vs), 807(vs), 867(m), 728(m), 539(m), 568(m).

¹HNMR (CDCl₃): (8.37ppm, s, 1H), (7.52ppm, d, 2H), (7-7.2 ppm, dd, 4H), (6.79ppm, d, 2H), (3.71ppm, s, 3H), (2.9ppm, s, 1H).

2.5. General Extraction Procedure

An aliquot of solution containing 1-500 µg of Hg (II) ion was taken in separator funnel. To this 2 mL of 0.01 M HNO₃ was added and the total volume was made up to 20 mL with distilled water. This solution was

then equilibrated with 20 mL of chloroform containing various amount of MBITP and stirred for 70 s. After allowing 2 min for phase separation, the absorbance of organic phase containing the complex was measured at 390 nm against a reagent blank. After extraction procedure, the pH of aqueous phase changes to acidic that is an indication of this idea.

2.6. Determination of Hg (II) in Amalgam Alloys

An accurately weighed 2.0 g of each amalgam alloy (0.6–0.8% Hg(II)) sample was dissolved in 20 mL of 60% nitric acid. The solution was heated to near dryness. Acid treatment and evaporation were repeated two times, the residue dissolved in the least volume of water, the clear solution was quantitatively transferred into 25-mL volumetric flask and the pH of the solution was adjusted to 2. The solution was brought to the mark with distilled water, filtered and an mercury evaluation using of proposed electrode has been carried out.

2.7. Pretreatment of Natural Water Samples

Analysis of the real samples for determination of its Hg²⁺ ion content was carried out as follow: to 400 mL of sample in a beaker, 24 mL of concentrated HNO₃ and 10 mL of H₂O₂ (30%) were added. The elimination of interference of organic compound were carried out by irritating the samples with a high pressure mercury lamp for 2 hr. Then, the volume of mixture while stirring by heating was reduced to half and 3 mL of concentrated HNO₃ was added and the solution was filtrated. After adjustment of pH to 2, mercury determination using developed electrode has been carried out.

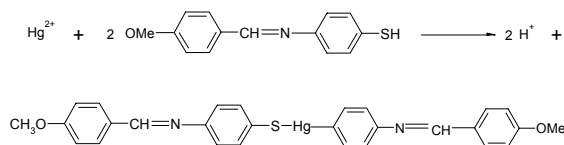
2.8. Pretreatment of Soil Samples

Analysis of the soil samples for determination of its Hg²⁺ ion content was carried out as following: to 40 g of soil sample in a beaker, 50 mL of distilled water, 24 mL of concentrated HNO₃ and 10 mL of H₂O₂ (30%). The elimination of interference of organic compound were carried out by irritating the samples with a high pressure mercury lamp for 2 hr. Then, the volume of mixture while stirring and heating was reduced to 0.1 volume and 3 mL of concentrated HNO₃ was added and the solution was filtrated. After adjustment of pH at 2, mercury determination using developed electrode has been carried out.

3. Results and Discussion

Among the various solid electrodes (Au, Pt, Ag and Graphite), because of appearance stable potentials, wide linear range, fast response time and near-Nernstian response, graphite was chosen for further studies.

Ligands for use as ionophores in such a mercury ion-selective electrode should ideally fulfill certain conditions. They should be selective for mercury over other ions, have rapid exchange kinetics and be sufficiently lipophilic to prevent leaching of the ligand into the solutions surrounding the membrane electrode.



Scheme 1. Schematic diagram of complexation between mercury ion and MBITP

In preliminary experiments complexation between Hg (II) ion and MBITP in acetonitrile and chloroform was examined, and the nature of complex was investigated using the mole ratio method under the established experimental conditions. An increase in absorbance of ligand solution with addition of mercury ion in acetonitrile can be attributed to the strong binding and interaction of mercury ion with MBITP (Fig.1) and complexation are presented in scheme 1. In order to confirm this result and ascertain the nature and structure of the extracted species, fixed amount of Hg²⁺ ion was extracted with various amounts of MBITP dissolved in a fixed value of chloroform and the distribution constant (D) of was calculated at different concentration of them. Further, log D vs. Log [MBITP] which are plotted in Fig.2 illustrate a linear relation with approximate slope of 2, indicating the association of two MBITP molecules with the extracted Hg²⁺ species into organic phase i.e. the composition of extracted species is Hg (MBITP)₂, that due to its neutral structure it can be extracted with high efficiency in short time in organic phase. Due to the stric hindered and linear structure of the ligand, coordination numbers more than two

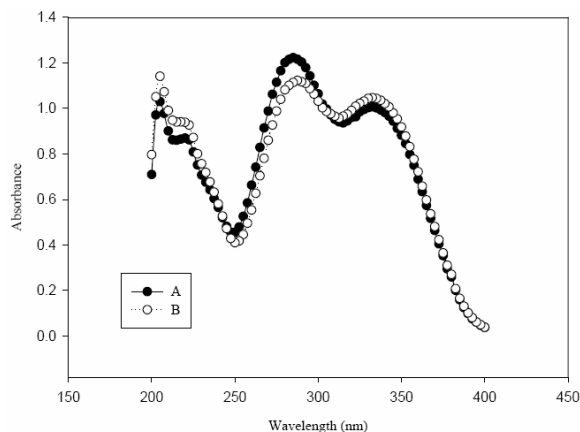


Figure 1. Spectra of 0.4 mM of MBITP (A) and 0.4 mM of MBITP with 0.2 mM of Hg²⁺ (B) in acetonitrile

and linkage via nitrogen atoms of ligand seem to be impossible. This ligand is very insoluble in aqueous acidic media, which ensures a very low leaching rate of the membrane active component into the sample solution and suitable for construction of a truly mercury ion-selective electrode.

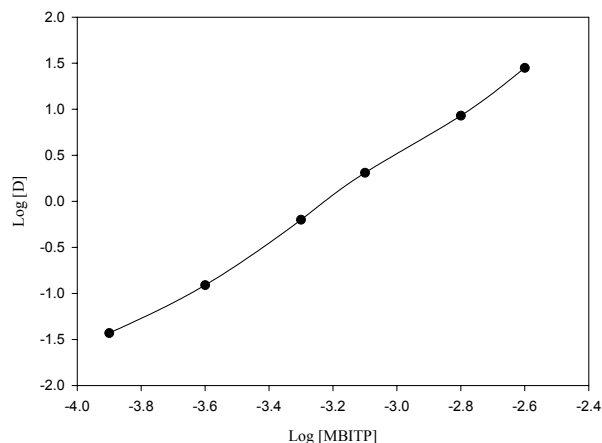


Figure 2. Normalized Plot of Log D versus Log [MBITP] (M), Conditions: sample, 20 mL of 5 μg mL⁻¹ Hg²⁺ in pH 2.9; organic phase, 10 mL chloroform containing various amount of MBITP

3.1. Optimization of variables

The plasticized PVC-based membrane electrode containing the MBITP carrier responds to mercury according to Nernstian response. Therefore, we studied in detail the performance of the membrane electrodes based on this carrier for mercury in aqueous solutions. It is well known that the sensitivity, linear dynamic range, and selectivity of the ISEs depend not only on the nature of the carrier used, but also significantly on the membrane composition and the properties of the additives employed.

In preliminary experiment, membranes, with and without ionophore was constructed, the results showed that in absence of carrier the membrane displayed insignificant selectivity toward mercury, although its response is not reliable, whereas, in the presence of the ionophore, the membrane shows Nernstian and remarkable selectivity for mercury over most common inorganic and organic ions. The preferential response toward mercury is believed to be associated with the coordination of mercury to the carrier and lead to a change in symmetry of compound and appearance of new maximum. This is due the fact that soft ions such as mercury is expected to interact with the soft sulfur atom in ligand. Increasing in absorbance and change in the UV spectra of the carrier with and without mercury is an indication of strong interaction, which can be related to mercury coordination with the mercury center of the ligand.

3.2. Influence of the membrane composition

It is well known that the sensitivity and selectivity of the ion selective electrodes depend not only on the nature and amount of ionophore used but also significantly on the properties of the plasticizer employed as well as the PVC/plasticizer ratio used.²⁴⁻³⁰

Since the nature of plasticizer influences the dielectric constant of the membrane phase, the mobility of the ionophore molecules and the state of ligand³¹⁻³³ it is expected to play an important role in determining the ion selective characteristics. The influence of the plasticizer type on the characteristics of the mercury ion-selective electrodes was investigated by using plasticizers with different polarities including DBP, DOP, NPOE, BA and BEHS. The electrodes containing DOP and DBP as a low polarity compounds among the plasticizers investigated, provide more appropriate conditions for incorporation of the mercury ion into the membrane prior to its coordination with the soft sulfur atom in the ligand generally showed better potentiometric responses, i.e., sensitivity and linearity of the calibration plots. Therefore, we used DOP as a suitable plasticized for further studies.

The response characteristics of the electrode are strongly dependent on amount of ionophores, therefore, the membranes with different amounts of MBITP with a constant ionophore-additive site ratio were prepared and their response performances were investigated. The working range and sensitivity of the electrode response were improved on increasing the concentration of carrier up to 5.0%. Further addition of the ionophores concentrations worsened the electrode response, most probably due to saturation of the membrane or due to some non-uniformity of the membrane.^{23, 24}

It is well known that, the presence of lipophilic additive in cations-selective membrane electrodes not only diminishes the ohmic resistance and enhance the response behavior and selectivity but also, in cases where the extraction capability is poor, increases the sensitivity of the membrane electrodes.³²⁻³⁵ Therefore, the influence of the type and concentration of the membrane additives were also investigated by incorporating MTOAC or NaTPB at NaTPB/carrier mole ratios of ca. 0.5 into the membranes. The potentiometric response of the electrode was greatly improved in the presence of the lipophilic anionic additive, NaTPB, compared to the membranes with no additive at all, but no response was observed when the cationic additive, MTOAC, was incorporated into the membranes. The effect of NaTPB concentration in the membranes was investigated at several additive/carrier mole ratios at 5% ionophore. The electrodes with NaTPB/carrier mole ratios of ca. 0.51 showed near-Nernstian responses in a wide range of mercury concentration. The response of the blank membranes containing additives but no carrier at all was far from Nernstian. The compositions and characteristics of the plasticized PVC membranes based on MBITP in construction of coated graphite mercury electrodes are summarized in Table 2.

3.3. Response Characteristics and Selectivity of the Electrodes

The best equilibration time and concentration of the conditioning solution for generating stable potential of the electrode was ~18 h in 0.05 M Hg (NO₃)₂ solution. The response time (the time elapsed to attain a response that is within ± 1 mV of steady state potential after successive immersion of the electrodes

Table 2. Response Performance of the mercury ion-selective electrodes based on MBITP carriers, conditions: various membrane composition, conditioned 18 h in 0.05 M Hg (NO₃)₂, pH 2.8

No	Plasticizer	PVC	MBITP	NaTPB	MTOACI	L. R. ^a	D. L. ^b	Slope ^c	R.T (S) ^d	L. T (day) ^e
1	60.9 (DBP)	30.5	5.0	3.6	----	2.0–0.1	0.8 μM	29.24	<10	60
2	60.9 (DOP)	30.5	5.0	3.6	----	2.0–0.1	0.8 μM	29.3	<10	60
3	60.9 (NPOE)	30.5	5.0	3.6	----	2.0–0.01	1.6 μM		15	54
4	60.9 (DMS)	30.5	5.0	3.6	----	5.0–0.1	2.1 μM		20	50
5	60.0 (DBP)	30.0	5.0	----	5.0	Low Linear	---	-5.4	35	60
6	63.3 (DBP)	31.7	5.0	0	----	9.0–0.07	5.6 μM	24.4	<15	52
7	62.5 (DBP)	31.3	5.0	1.2	----	4.0–0.01	3.3 μM	25.9	<18	59
8	61.7 (DBP)	30.9	5.0	2.4	----	3.0–0.05	1.8 μM	26.8	<30	58
9	60.1 (DBP)	30.1	5.0	4.8	----	2.0–0.05	0.8 μM	27.4	<15	55
10	64.9 (DBP)	32.4	0.0	3.7	----	30–0.004	10.8 μM	26.3	<10	58
11	65.1 (DBP)	32.5	1.4	1	----	10–0.01	6.8 μM	27.5	<10	57
12	63.8 (DBP)	31.9	2.5	1.9	----	5.0–0.01	3.2 μM	28.1	<10	60
13	62.3 (DBP)	31.1	3.8	2.8	----	3.0–0.06	1.8 μM	28.6	<10	60
14	59.1 (DBP)	29.6	6.5	4.8	----	3.0–0.05	1.5 μM	29.3	<10	60
15	65.3 (DBP)	26.1	5.0	3.6	----	12–0.04	6.8 μM	30.9	<25	50
16	54.9 (DBP)	36.5	5.0	3.6	----	6.0–0.05	3.8 μM	29.9	<25	44
17	45.7 (DBP)	45.7	5.0	3.6	----	20–0.005	12.6 μM	29.24	<30	38

a) linear Range (μM-M) b) Detection Limit c) Slope (mV per decade concentration) d) Response Time (s) e) Life times (day) all value for membrane composition are (W/W %)

in a series of mercury solutions with each having a 10-fold difference in concentration from 1.0×10^{-5} to 1.0×10^{-2} M was investigated. Electrode has reasonably fast and stable potential within 10 s and no change is normally observed up to 5 min that a typical response time was shown in Fig. 3. Life time studies were based on monitoring the change in electrode slope and linear range with time. A decrease in slope was a symptom of loss of the normal characteristics of the electrodes. During the whole operational life of the membrane, calibration parameters of the electrode were very stable. The membrane electrode prepared could be used for at least 2 months without considerable change in potential of the electrodes.

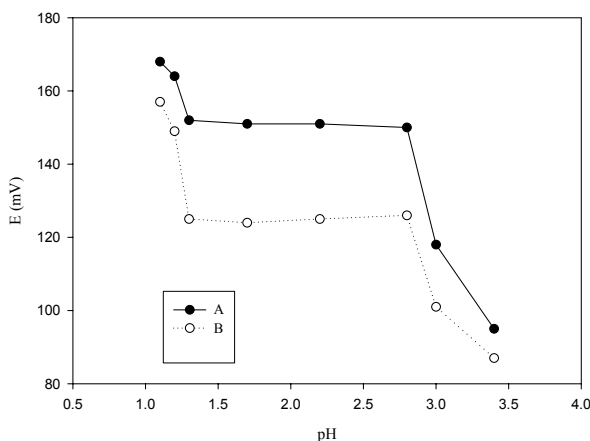


Figure 3. The influence of pH on the potential response of the membrane electrode based on MBITP at (A) 1×10^{-3} and (B) 1×10^{-4} , conditions: membrane, DOP: PVC: NaTPB: MBITP % is 60.9: 30.5: 3.6: 5.0 conditioned 18 h in 0.05 M Hg (NO_3)₂, (A) 1×10^{-3} and (B) 1×10^{-4} , Hg^{2+} in various pH

The influence of pH of the test solution on the potential response of the membrane sensor was tested in the pH range 1.1–3.4 (for 1.0×10^{-3} and 1.0×10^{-2} M mercury solutions, where the pH was adjusted with dilute hydrochloric acid and sodium hydroxide solutions as required) and the results are shown in Fig. 3. As can be seen, potential remains constant from pH 1.3–2.9, beyond which the potential changes considerably. The diminished electrodes potential at lower and higher pH values could be most probably due to the simultaneous response of the electrode to Hg^{2+} ion and hydrogen ions, respectively. The observed drift in potential at higher pH values may be attributed to the hydrolysis of Hg^{2+} and formation of some hydroxyl complexes of mercury (II) ion in solution.³⁴ It should be noted that according to Baes and Mesmer, the hydrated Hg^{2+} exist only at low pH values; therefore all measurement in this study was carried out at pH 2.0. The response of the electrodes was examined in the concentration range 1.0×10^{-7} – 1.0×10^{-1} M. The calibration plots for both

carriers are shown in Fig. 4, which show linearity over the concentration range of 2.0×10^{-6} – 1.0×10^{-1} M with a detection limit of 8×10^{-7} M, and sensitivities of 29.24 ± 0.82 mV/decade of mercury concentration ($n=5$).

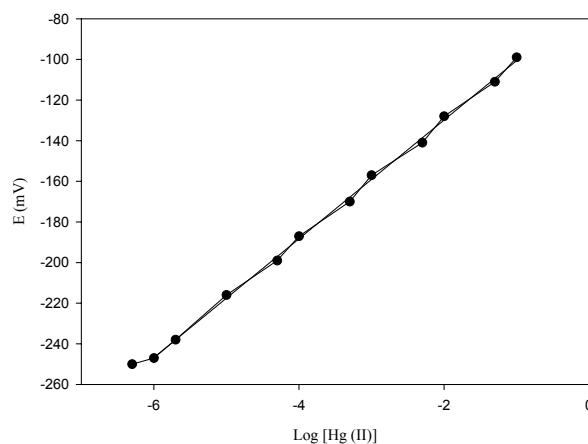


Figure 4. Calibration plots of the electrode slope 29.24 $r=0.9987$, conditions: membrane, DOP: PVC: NaTPB: MBITP % is 60.9: 30.5: 3.6: 5.0 conditioned 18 h in 0.05 M Hg (NO_3)₂, various concentration of Hg^{2+} in pH 2.0

Dynamic response time is an important factor for an ion sensitive electrode. In this study, the practical response time was recorded by changing solution with different low-to-high Hg^{2+} concentrations. The actual potential vs. time traces is shown in Fig. 5. As can be seen, in whole the concentration range, the electrode reaches the equilibrium response in a very short time (approx. 60 s). To evaluate the reversibility of the electrode, a similar procedure at the opposite direction was adopted. This time, measurements were performed in the sequence of high-to-low sample concentrations and the similar results were obtained.

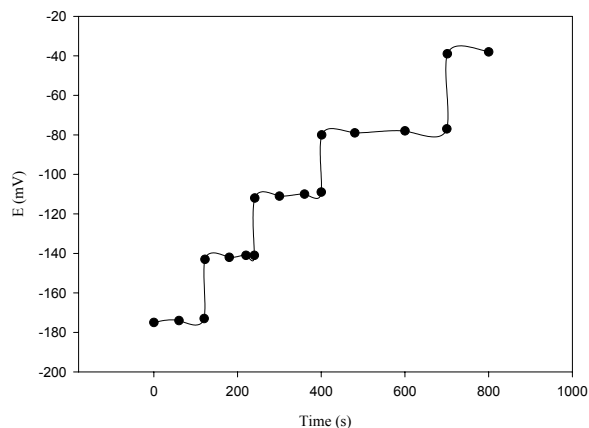


Figure 5. Typical potential-time recorder trace of the electrode based on MBITP conditions: membrane, DOP: PVC: NaTPB: MBITP % is 60.9: 30.5: 3.6: 5.0 conditioned 18 h in 0.05 M Hg (NO_3)₂ various concentration of Hg^{2+} in pH 2.0

The long-term stability of the electrodes were studied by direct periodically re-evaluating mercury electrode characteristic performances in standard solutions ($\text{Hg}(\text{NO}_3)_2$ or out of solution) and calculating the response slope over the range of 1.0×10^{-5} to 1.0×10^{-1} mercury ion. The slopes of the electrode responses were reproducible to within 1.0 mV/decade over a period of 2 months, but life time studies for more than this period have not been done. Therefore, these membrane electrodes can be used for at least 2 months, without a considerable change in their response characteristics towards mercury ion.

The most important characteristics of any ion sensitive sensors are its response to the primary ion in the presence of other ions in solution, which is expressed in term of selectivity coefficient. The selectivity behavior is obviously one of the most important characteristics of an ion-selective electrode, determining whether a reliable measurement in the target sample is possible. In order to assess the selectivity of the proposed mercury ion-selective electrodes over other anions the method of fix interference method [FIM] and separate solution method [SSM] was employed.^{35,36}

Table 3. Selectivity coefficients of the mercury coated-graphite electrodes based on MBITP carrier, conditions: membrane, DOP: PVC: NaTPB: MBITP % is 60.9: 30.5: 3.6: 5.0 conditioned 18 h in 0.05 M $\text{Hg}(\text{NO}_3)_2$, pH 2.8, (FIM, 0.01 M or 0.001 M Hg^{2+} and various amount of interfering ion, SSM 0.01 M Hg^{2+} or different interfering ions

Ion	-Log $K_{\text{Hg},i}$	
	SSM	FIM
K^+	4.06	3.76
Na^+	4.11	2.85
Cr^{3+}	3.68	3.43
Sn^{2+}	4.26	4.05
Ba^{2+}	3.74	3.03
Pb^{2+}	3.42	2.86
Co^{2+}	3.69	3.21
Ni^{2+}	3.78	3.38
Fe^{3+}	2.1	1.9
Cd^{2+}	3.35	3.53
Zn^{2+}	3.76	3.32
Mg^{2+}	3.97	3.78
Mn^{2+}	3.84	3.51
Cu^{2+}	3.43	3.16
Ag^+	0.95	1.67

According to this method, the potentiometric selectivity coefficients, $K_{\text{pot Hg}}$, can be evaluated from the potential measurements on solutions containing a

fixed concentration (0.01 M or 0.001 M) of mercury ion and varying concentration of interfering ion (respective nitrate salts) in FIM and in SSM potential of different solution containing same amount of mercury or interfering ion (0.01 M). As it is evident from Table 3, most of the interfering ions show low values of selectivity coefficient, indicating no interference in the performance of the membrane electrode assembly. Such remarkable selectivity of the proposed mercury ion-selective electrode over other ions reflects the high affinity of the sulfur coordination sites of the ligand toward the mercury ions.

4. Applications

The new mercury-selective electrode was satisfactorily applied to the determination of mercury in various samples from different sources. The analyses were performed by direct potentiometry using the standard additions technique. The high degree of mercury selectivity exhibited by the electrodes based on MBITP carrier, makes it potentially useful for monitoring concentration levels of mercury in biological samples, so, the optimized coated-wire electrodes were successfully applied as an indicator electrode in the direct potentiometric method for determination of mercury in water sample. In addition, the sensors were used as indicator electrodes for potentiometric titration of mercury with potassium iodide and EDTA solution. The titration curves showed good inflection point at the equivalence point. Typical results for the titration of potassium iodide with mercury nitrate using the electrodes is shown in Fig. 6 and Table 4.

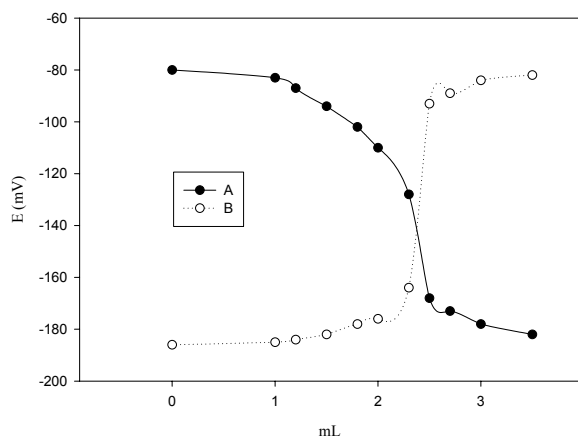


Figure 6. Application of the electrode based on MBITP for potentiometric titration of (A) 50 mL 0.005 M Hg^{2+} with 0.1 M EDTA and (B) 50 mL 0.005 M iodide with 0.01 M Hg^{2+} , conditions: membrane, DOP: PVC: NaTPB: MBITP % is 60.9: 30.5: 3.6: 5.0 conditioned 18 h in 0.05 M $\text{Hg}(\text{NO}_3)_2$, pH 2.8.

Table 4. Application of the electrodes based on MBITP carriers for determination of mercury in real samples, conditions: membrane, DOP: PVC: NaTPB: MBITP % is 60.9: 30.5: 3.6: 5.0 conditioned 18 h in 0.05 M Hg (NO₃)₂, various real sample treated according experimental section in pH 2.8,

Sample	Added	Founded	Recovery %	AAS
Soil sample ^a	0	1.23 ± 0.03	---	1.35 ± 0.04
	1.0	2.27 ± 0.03	104	2.20 ± 0.05
Waste water ^a	0.0	0.48 ± 0.04	----	0.51 ± 0.04
	1.0	1.51 ± 0.06	103	1.54 ± 0.06
River Water ^a	0	0.35 ± 0.04	---	0.38 ± 0.04
	0.75	1.13 ± 0.08	104.0	1.16 ± 0.07
Amalgam ^b	0	3.22 ± 0.04	---	01.01 ± 0.03
	1	4.26 ± 0.03	104	2.04 ± 0.06
	2	5.28 ± 0.03	103	3.04 ± 0.08
Synthetic Mixture ^a (1.5) Pb ²⁺ , (3.0) Cu ²⁺ , (5.0) Ca ²⁺ , (6.0) Na ⁺ , (2.0) Hg ²⁺ , (5) Cd ²⁺	-----	2.08 ± 0.03	104	2.04 ± 0.03

a) Number are in μg mL⁻¹ for n=4 measurements b) values are μg g⁻¹

5. Conclusions

The electrode has been shown to have good operating characteristics (Nernstian response; reasonable detection limit; relatively high selectivity with respect to the alkali and alkaline-earth cations; wide dynamic range; fast response; applicability over a wide pH range). These characteristics and the typical applications presented in this paper, make the electrode suitable for measuring the mercury content in a wide variety of samples, without a significant interaction from concomitant anionic species. The results show that there was a coordination interaction between Hg (II) ion and the proposed carrier, which played an important role in the response characteristics and selectivity of the electrode. The proposed electrode permits the direct determination of mercury ion in water without prior separation steps.

Coated type electrodes are very easy to construct and handle, and offer much higher mechanical resistance, compared to their liquid membrane counterparts.

As can be seen in Tables 2-5 in comparison to Table 1, the proposed electrode is superior to those

reported mercury (II) ion-selective electrodes in term of selectivity,^{7, 10, 12, 17, 21} linear range,^{7-12, 15-21} detection limit,^{7-10, 17} applicable pH range,^{9-11, 14-18} and response time.^{8-10, 12}

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7. References

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Povzetek

Pripravili smo selektivno elektrodo na osnovi polivinil klorida s 4-(4-metoksibenzilidenimin)tiofenolom kot nevtralnimi nosilcem, ki smo ga nanjali na površino grafitne elektrode. Preverili smo vpliv različnih parametrov, kot so sestava membrane, pH in prisotnosti možnih motečih ionov. Senzor izkazuje linearen naklon v koncentracijskem intervalu 2×10^{-6} do 0,1 M ($29,24 \pm 0,82$ mV na dekada koncentracije živega srebra), v območju pH 1,3–2,9. Meja detekcije je 8×10^{-7} M. Odzivni čas senzorja je ≤ 10 s po osemnajsturnem kondicioniranju v 0,05 M $\text{Hg}(\text{NO}_3)_2$. Uporabnost je najmanj 2 meseca. Elektrodo smo uspešno uporabili za neposredno potenciometrično določitev živega srebra v nekaterih realnih vzorcih in kot indikatorsko elektrodo pri kompleksometričnih titracijah.