

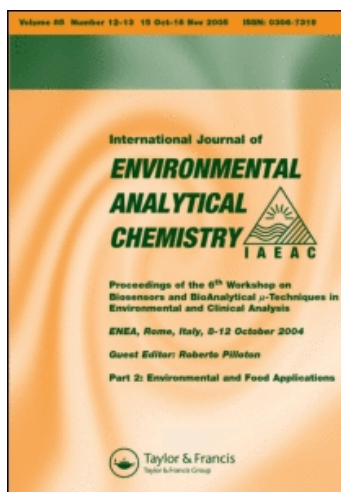
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Morteza Hosseini^a; Mohammad Rahimi^b; Hayedeh Bagheri Sadeghi^b; Saeed Taghvaei-Ganjali^c; Shiva Dehghan Abkenar^a; Mohammad Reza Ganjali^{de}

^a Department of Chemistry, Islamic Azad University, Savadkooh Branch & Young Researcher Club, Iran ^b Department of Chemistry, Islamic Azad University, Tehran Central Branch, Tehran, Iran ^c Department of Chemistry, Islamic Azad University, North Tehran Branch, Tehran, Iran ^d Center of Excellence in Electrochemistry, Department of Chemistry, University of Tehran, Tehran, Iran ^e Endocrine & Metabolism Research Center, Tehran University of Medical Sciences, Tehran, Iran

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Determination of Hg(II) ions in water samples by a novel Hg(II) sensor, based on calix[4]arene derivative

Morteza Hosseini^{a*}, Mohammad Rahimi^b, Hayedeh Bagheri Sadeghi^b, Saeed Taghvaei-Ganjali^c, Shiva Dehghan Abkenar^a and Mohammad Reza Ganjali^{de}

^aDepartment of Chemistry, Islamic Azad University, Savadkooh Branch & Young Researcher Club, Iran; ^bDepartment of Chemistry, Islamic Azad University, Tehran Central Branch, Tehran, Iran; ^cDepartment of Chemistry, Islamic Azad University, North Tehran Branch, Tehran, Iran; ^dCenter of Excellence in Electrochemistry, Department of Chemistry, University of Tehran, Tehran, Iran; ^eEndocrine & Metabolism Research Center, Tehran University of Medical Sciences, Tehran, Iran

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A PVC membrane electrode for Hg(II) ions, based on a new cone shaped calix[4]arene (L) as a suitable ionophore was constructed. The sensor exhibits a linear dynamic in the range of 1.0×10^{-6} – 1.0×10^{-1} M, with a Nernstian slope of 29.4 ± 0.4 mV decade⁻¹, and a detection limit of 4.0×10^{-7} M. The response time is quick (less than 10 s), it can be used in the pH range of 1.5–4, and the electrode response and selectivity remained almost unchanged for about 2 months. The sensor revealed comparatively good selectivity with respect to most alkali, alkaline earth, and some transition and heavy metal ions. It was successfully employed as an indicator electrode in the potentiometric titration of Hg²⁺ ions with potassium iodide, and the direct determination of mercury content of amalgam alloy and water samples.

Keywords: mercury; membrane electrode; calix[4]arene; potentiometric; sensor

1. Introduction

Mercury is a toxic element of great environmental concern. Mercury is widely used in industry and agriculture that causes the pollution of air and water [1,2]. Compounds containing mercury, especially methyl mercury, whose target organ is the brain in humans, disrupts the blood-brain barrier upsetting the metabolism of the nervous system. Inorganic mercury, especially soluble mercury species, can be transformed into methyl mercury under anaerobic conditions. Organomercury compounds have a strong tendency to accumulate as they pass through the food chain. Because of the great impact of mercury and its compounds on environment, there is an imperious need for developing new methods for determination of mercury at low concentrations [3–6].

Analysis of trace metals in environmental samples is still a challenging task due to both the low levels of metals in the samples and the complexity of the matrices.

*Corresponding author. Email: hossiny54@yahoo.com

Thus, the development of reliable methods for the determination of mercury in environmental and biological materials is of particular significance. The available methods for low-level determination of mercury include thermolysis coupled with atomic absorption spectrometry, cold vapour atomic fluorescence spectrometry, gas chromatography, neutron activation analysis and isotope mass spectrometry. However, all of them involve long analysis time and considerable volume samples. Conversely, carrier-based ion-selective electrodes have long been in routine analytical use, yet they still attract an important focus for further research, trying to push their capabilities into new dimensions. Potentiometric sensors based on ion-selective electrodes are especially suited for such determination because they offer advantage such as selectivity, sensitivity, good precision, simplicity and low cost [7–9]. All the sensors show insufficient limits of detection and are very sensitive towards speciation of the mercury in the environment (pH dependent hydrolytic instability, inorganic and organic complexes, lack of sensitivity toward methyl mercury, etc.).

Due to the lack of efficient commercial Hg(II)-electrodes and even quite sparse literature reports on such electrodes, there has been great interest to investigate new ionophores as receptor molecules in the preparation of mercury sensors.

Calixarene derivatives have been widely used as building blocks for the construction of artificial molecular receptors in the past two decades. The structures of this type of 3-D macrocyclophanes largely benefit their receptor properties for neutral molecules and ionic species [10–12]. One's aim is to construct calix[4]arene-based receptor molecules with or without soft donors, which are sensitive to transition metal ions in analytical chemistry due to their medical, environmental and industrial significance.

The interaction between sulphur atoms and Hg^{2+} ion is much stronger than that of ion-dipoles present between a metal ion and oxygen atoms. This often brings about slow metal-ion exchange equilibria in the membrane interface that is the cause of some of the disadvantages of the thio compound-based ion sensors (such as slow response time and relatively poor sensitivity).

Hg^{2+} as a soft acid can interact with π -coordinate groups. This interaction is quite selective and relatively weak [13–16]. In this work we used a new calix[4]arene (L) (Figure 1) containing a π -coordinate group in construction of a PVC membrane, Hg^{2+} ion-selective electrode for sensitive, and selective determination of mercury ions in different samples.

2. Experimental

2.1 Reagents

The Aldrich and the Merck Chemical Co. supplied the following reagents; nitrate and chloride salts of all the cations, reagent-grades of 2-nitrophenyl octyl ether (NPOE), dibutyl phthalate (DBP), benzylacetate (BA), sodium tetraphenyl borate (NaTPB), tetrahydrofuran (THF) and relatively high molecular weight PVC. Moreover, all reagents were used without any purification. As far as the nitrate and chloride salts are concerned, they were of the highest available purity and were P_2O_5 vacuum dried. During the experiments, triply distilled deionised water was used.

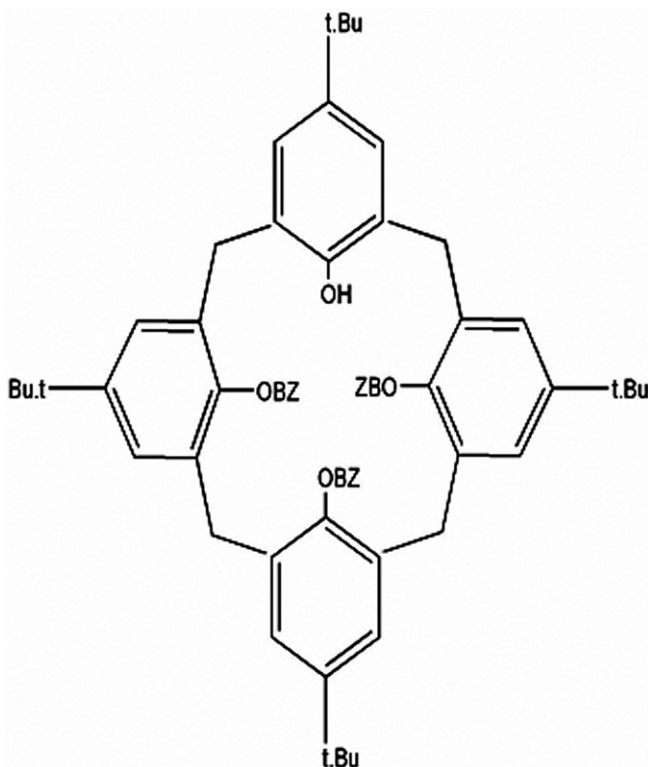


Figure 1. Calix[4]arene derivative structure.

2.2 Synthesis of ligand L

The cone shaped asymmetrically substituted calix[4]arene 26,27,28-*tris*-benzyloxy-25-hydroxy-5,11,17,23-tetra-*tert*-butyl-calix[4]arene (L) was synthesised by the following procedure:

Para-tert-butyl calix[4]arene (5.0 g, 7.7 mmol) and benzyl chloride (17.5 mL, 152.0 mmol) were dissolved in acetonitrile (100.0 mmol) [17,18]. The solution was stirred for 6 h in the presence of barium hydroxide (8.5 g, 49.6 mmol) and barium oxide (8.0 g, 52.2 mmol). The reaction mixture was diluted with water (1000.0 mL) and extracted with dichloromethane. The organic layer was then separated, dried over magnesium sulphate, filtered and evaporated to yield a white solid, which crystallised from dichloromethane–methanol, to give L in 63% yield: m.p. 210–214°C, IR ν_{\max} (KBr)/ cm^{-1} : 3550, 3454, 2961, 1481, 1198, 694. ^1H NMR (CDCl_3 , 500 MHz) (δ , ppm): 7.18–7.47 (15H, m, ArH), 7.08 (2H, s, ArH), 6.99 (2H, s, ArH), 6.57 (2H, d, $J=2.1$ Hz, ArH), 6.50 (2H, d, $J=2.1$ Hz, ArH), 6.31 (1H, s, OH), 4.93 (2H, s, OCH_2 Ph), 4.60, 4.67 (4H, 2d, $J=15$ Hz OCH_2 Ph), 3.03, 4.17 (4H, 2d, $J=15$ Hz, ArCH_2Ar), 2.97, 4.15 (4H, 2d, $J=15$ Hz, ArCH_2Ar), 1.31 [9H, s, $\text{C}(\text{CH}_3)_3$], 1.28 [9H, s, $\text{C}(\text{CH}_3)_3$], 0.84 [18H, s, $\text{C}(\text{CH}_3)_3$]. ^{13}C NMR (CDCl_3 , 125 MHz) (δ , ppm): 31.01, 31.3, 31.6, 31.7, 31.8, 33.7, 34.1, 76.0, 124.8, 124.9, 125.5, 127.1, 127.6, 127.7, 127.8, 128.2, 128.6, 128.7, 128.8, 129.3, 129.4, 132.2, 132.5, 135.8, 137.5, 138.5, 141.1, 145.4, 145.6, 150.9, 151.0, 153.3.

2.3 Electrode preparation

The required amount of the membrane ingredients (30 mg powdered PVC and 64 mg NPOE as plasticiser) were mixed and dissolved in 5 mL of THF. To this mixture, 1.5 mg NaTPB and 4.5 mg ionophore L were added, and the solution was mixed well. The resulting mixture was transferred into a glass dish of 2 cm in diameter. The THF content of the mixture was evaporated slowly, until an oily concentrated mixture was obtained. A Pyrex tube (3–5 mm i.d.) was dipped into the mixture for about 10 s, so that a transparent membrane of about 0.3 mm in thickness was formed [19–21]. Afterwards, the tube was removed from the solution, kept at room temperature for 12 h and filled with an internal solution (1.0×10^{-3} M $\text{Hg}(\text{NO}_3)_2$). The electrode was finally conditioned for 36 h by soaking in a 1.0×10^{-3} M solution of $\text{Hg}(\text{NO}_3)_2$. A silver/silver chloride coated wire was used as an internal reference electrode.

2.4 EMF measurements

The potential measurements were performed by means of a Corning ion analyser with a 250 pH mV^{-1} meter at room temperature.

Moreover, a cell assembly of:

$\text{Ag-AgCl} \mid 1.0 \times 10^{-3}$ M $\text{Hg}(\text{NO}_3)_2 \mid$ PVC membrane: test solution $\mid \text{Hg-Hg}_2\text{Cl}_2$, KCl (satd.)

was used to carry out all the needed potential measurements. The emf observations were made relative to a double-junction saturated calomel electrode (SCE, Philips), with its chamber filled with an ammonium nitrate solution. The activities of all species were calculated with respect to the Debye–Hückel procedure [22].

2.5 Procedure of conductance study

Conductivity measurements were carried out with a Metrohm 660 conductivity meter. A dip-type conductivity cell made of platinum black with a cell constant of 0.83 cm^{-1} was used. In all measurements, the cell was thermostated at the desired temperature of 25.0°C , using a Phywe immersion thermostat. In typical experiments, 25 mL of a metal-nitrate solution (1.0×10^{-4} M) in acetonitrile was placed in a water-jacketed cell equipped with a magnetic stirrer, and connected to the thermostat that was circulating water at the desired temperature. In order to keep the electrolyte concentration constant during the titration, we assured that both the starting solution and the titrant had the same cation concentration. Then, a known amount of the ligand L (1.0×10^{-2} M) solution was added in a stepwise manner using a calibrated micropipette. The conductance of the solution was measured after each addition. Addition of the ligand L was continued until the desired ligand L-to-cation mole ratio was achieved. The 1:1 binding of the cations with ligand L can be expressed by the following equilibrium:



The corresponding equilibrium constant, K_f , is given by

$$K_f = \frac{[\text{ML}^{n+}]}{[\text{M}^{n+}][\text{L}]} \times \frac{f_{(\text{ML}^{n+})}}{f_{(\text{M}^{n+})}f_{(\text{L})}} \quad (2)$$

Here $[ML^{n+}]$, $[M^{n+}]$, $[L]$ and f represent the equilibrium molar concentration of complexes, free cation, free ligand L and the activity coefficient of the species indicated, respectively. Under dilute conditions we used, the activity coefficient of the unchanged ligand $f_{(L)}$ which can be reasonably assumed to be in unity [23]. The use of the Debye–Hückel limiting law of 1:1 electrolytes [22] leads to the conclusion that $f_{(M^{n+})} \approx f_{(ML^{n+})}$, so the activity coefficient in Equation (2) is cancelled out. Hence, the complex formation constant in term of the molar conductance can be expressed as [24]:

$$K_f = \frac{[ML^{n+}]}{[M^{n+}][L]} = \frac{(\Lambda_M - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_{ML})[L]} \quad (3)$$

where

$$K_f = C_L - \frac{C_M(\Lambda_M - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_{ML})} \quad (4)$$

Here Λ_M is the molar conductance of the cation before addition of ligand L, Λ_{ML} is the molar conductance of the complexes, Λ_{obs} the molar conductance of the solution during titration, C_L the analytical concentration of the ligand L added, and C_M the analytical concentration of the cation salt. The complex formation constant, K_f , and the molar conductance of complex, Λ_{ML} , were obtained by computer fitting of Equations (3) and (4) to the molar conductance–mole ratio data using a nonlinear least-squares program KINFIT [25].

2.6 Determination of mercury in amalgam

A sample amalgam (50% Mercury, 35% Silver, 15% Tin) was prepared from shahid faghihi company Tehran iran. A 0.050 g of amalgam was dissolved in 10 mL 6 M nitric acid and the resulted solution was evaporated to dryness. The residue was dissolved in 10 mL of 1% (w/w) HNO_3 and filtered. The clear solution was quantitatively transferred into a 25 mL volumetric flask and diluted with 1% (w/w) HNO_3 to the mark. The mercury content determined by present ion-selective electrode and by inductively couple plasma (ICP).

Proper sample solutions were prepared by appropriate dilution of the mother solution. The mercury content of the sample solution was determined by the proposed mercury selective electrode using the calibration method.

2.7 Determination of mercury in water samples

The proposed potentiometric procedure was also successfully applied to assay of mercury in spiked water samples. The water samples were then acidified to the optimal pH range with nitric acid, and the resultant samples were stored at 4°C. Different amounts of mercury ions (0.12, 0.16, 0.25, 0.54, 0.70 $\mu g mL^{-1}$) are added to water samples. The mercury content of the sample solution was determined by the proposed mercury selective electrode using the calibration method.

Table 1. The formation constants of L-Mⁿ⁺ complexes.

Cation	log K_f
La ³⁺	2.33 ± 0.11
Ag ⁺	3.35 ± 0.11
Cr ³⁺	<2.0
Cu ²⁺	<2.0
Hg ²⁺	4.75 ± 0.11
Sn ²⁺	2.26 ± 0.17
Pb ²⁺	2.86 ± 0.17
Cs ⁺	2.68 ± 0.17
Co ²⁺	<2.0
Ni ²⁺	2.74 ± 0.18
Cd ²⁺	<2.0

3. Results and discussion

3.1 Complexation of ligand L with some metal ions in acetonitrile

In primary experiments, interaction of ligand L with a number of metal ions was investigated in acetonitrile solution by conductometric method. The results showed that in all cases, the ligand-to-cation mole ratio is 1. The formation constants (K_f) of the resulting 1:1 complexes was evaluated by the computer fitting of the molar conductance–mole ratio data to appropriate equations, the results are summarised in Table 1. The results presented above suggest a significant contribution to the complex stability by π -interactions between Hg²⁺ and the electron-rich aromatic rings in the calixarene framework [7–10,26]. The obtained formation constants revealed that ligand L could be used as an excellent ion carrier for preparation of a selective Hg²⁺ membrane sensor.

3.2 The electrode response to the Hg(II) ions

In order to examine the calix[4]arene suitability as an ion carrier for the Hg²⁺ ion, several PVC membrane ion-selective electrodes were constructed for a wide variety of cations, including alkali, alkaline earth and transition metal ions. The potential response for the ion-selective electrodes is depicted in Figures 2 and 3. Figure 3 shows slopes of the potential responses, except for Hg²⁺, in all cases the slopes are much lower than expected for: mono, di and trivalent metal ions. Actually, the Hg²⁺ sensor exhibits a Nernstian response across the range of 1.0×10^{-6} – 1.0×10^{-1} M.

3.3 Membrane composition effect on the potential response of the ligand L-based Hg(II) sensor

Since the sensitivity and selectivity for a given ionophore depend significantly on the membrane ingredients, the nature of the solvent mediator and the nature of the additive [26–28], the membrane composition influences were investigated on the potential responses of the Hg(II) sensor.

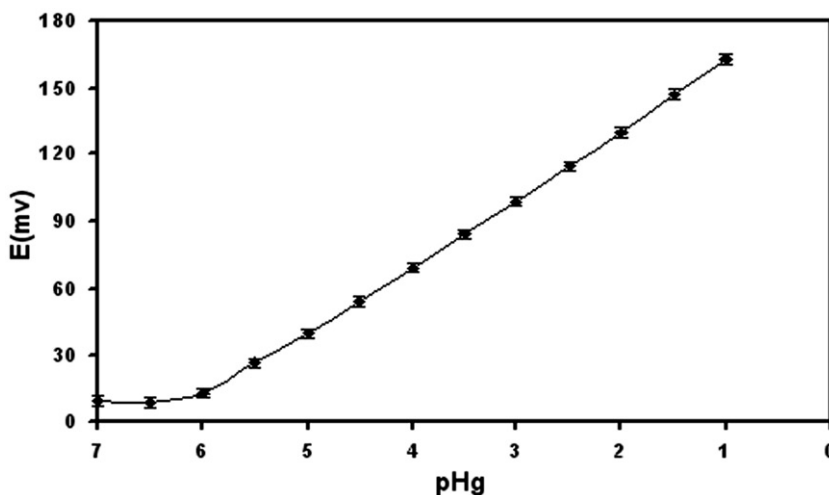


Figure 2. Calibration curve of the mercury electrode, based on calix[4]arene derivative with the composition of the membrane no. 9.

The results are summarised in Table 2. It is seen that the membrane number 9 with the PVC:NPOE:L1:NaTPB ratio of 30:64:4.5:1.5 presents a Nernstian behaviour for an extensive concentration range of the Hg^{2+} ions.

In addition, Table 2 displays among three different solvent mediators used, NPOE with higher polarity than DBP and BA exhibits better sensitivity. This is due to the NPOE ability as a polar solvent to extract mercury ions with relatively high charge density from the aqueous solution to the organic membrane phase.

The data from the same table revealed that in the absence of NaTPB in the membrane, the slope of the sensor is lower than the Nernstian (No. 4 with a slope of 16.8 mV per decade). The membrane, containing NaTPB, presents a Nernstian response (No. 9 with a slope of 29.4 mV per decade).

Noticeably, the presence of lipophilic and immobilised ionic additives could influence the membrane resistance and in some cases, the selectivity pattern of the ion-selective PVC membranes, resulting in a good working performance. It has been clearly illustrated that the presence of lipophilic additives in ion-selective electrodes is necessary to induce permselectivity, so that without these additives the electrodes do not respond properly [28]. The presence of such additives not only reduces the ohmic resistance [27] and improves the response behaviour and selectivity, but it also increases the sensitivity of the membrane electrode when the extraction capability of an ionophore is poor [27–31].

3.4 Calibration graph and statistical data

The EMF *versus* pHg^{2+} plot for optimal membrane ingredients indicates that it has a Nernstian behaviour over a broad concentration range of Hg^{2+} ions (Figure 2). The slope and the linear range of the resulting calibration graph were 29.4 ± 0.4 mV per decade and 1.0×10^{-6} – 1.0×10^{-1} M, respectively. The limit of detection (LOD), defined as the Hg^{2+} ion concentration obtained when the linear region of the calibration graph was extrapolated to the base line potential, was 4.0×10^{-7} M. The standard deviation of 10 replicate potential measurements for the proposed electrode was ± 0.4 mV at most.

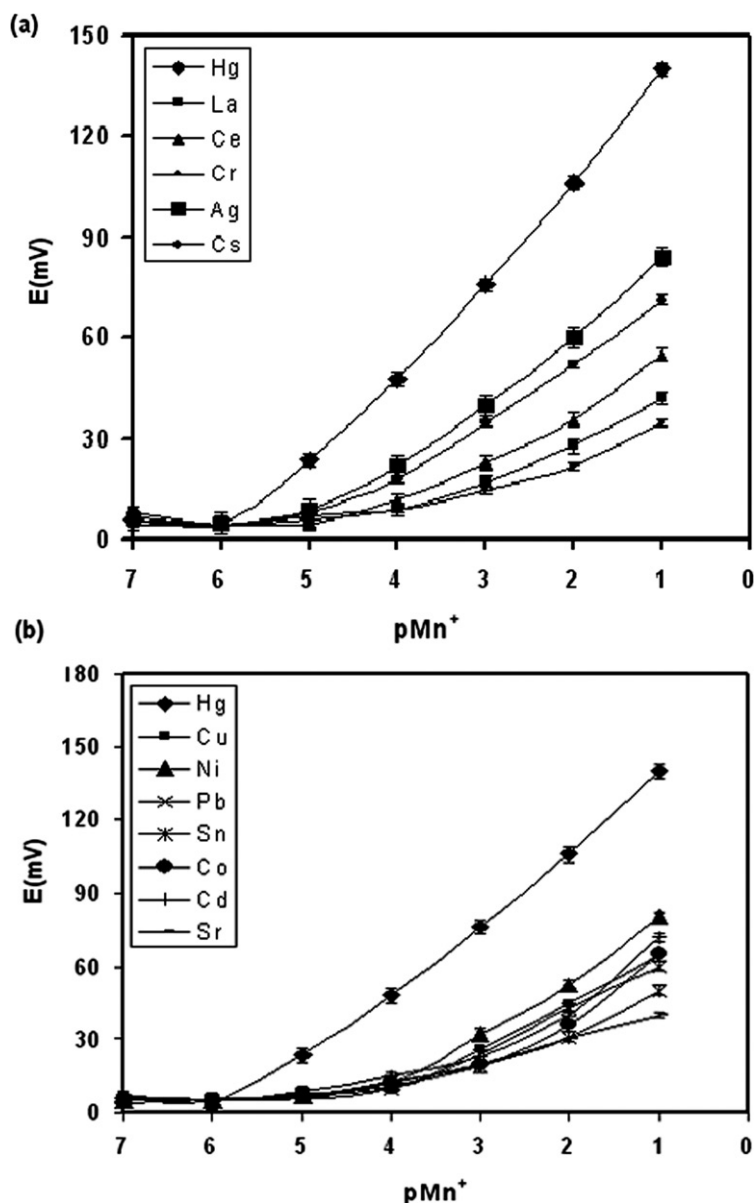


Figure 3. Potential responses of various ion-selective electrodes based on calix[4]arene derivative.

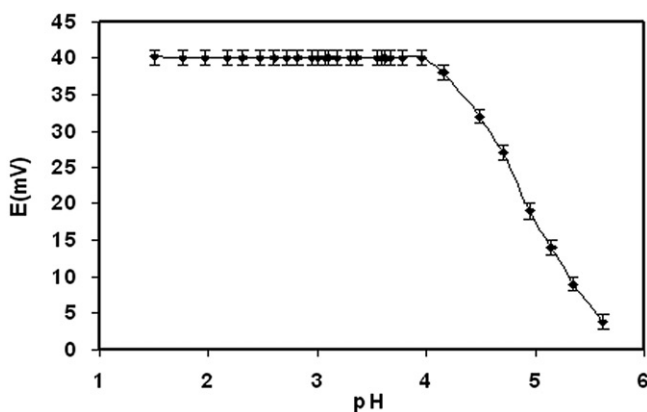
This certain electrode was satisfactorily stable, and it could be used for at least 2 months without observing any change in its response characteristics.

3.5 pH effect

The pH dependence of the membrane sensor was tested from the pH value of 1.5 up to 10 in a 1.0×10^{-4} M Hg^{2+} solution. The pH was adjusted by dropwise addition of a 0.1 M solution of either HCl or NaOH, and the emf of the electrode was measured at each

Table 2. Optimisation of membrane ingredients of the Hg^{2+} ion-selective electrode based on caix[4]arene derivative.

Sensor No.	Composition (wt%)				Slope (mV decade ⁻¹)	Concentration range (M)
	Calix	NaTPB	Plasticizer	PVC		
1	1	0	NPOE, 69	30	6.7 ± 0.4	6.5×10^{-3} – 5.0×10^{-1}
2	2	0	NPOE, 68	30	9.4 ± 0.5	8.7×10^{-3} – 4.6×10^{-1}
3	3	0	NPOE, 67	30	14.1 ± 0.3	1.0×10^{-3} – 1.0×10^{-1}
4	4.5	0	NPOE, 65	30	16.8 ± 0.4	8.3×10^{-4} – 1.0×10^{-1}
5	5.5	0	NPOE, 64	30	15.7 ± 0.6	7.3×10^{-4} – 1.0×10^{-1}
6	7	0	NPOE, 63	30	14.4 ± 0.4	1.0×10^{-4} – 1.0×10^{-1}
7	4.5	0.5	NPOE, 65	30	15.4 ± 0.7	1.0×10^{-5} – 1.0×10^{-1}
8	4.5	1	NPOE, 64.5	30	23.6 ± 0.3	5.2×10^{-5} – 1.0×10^{-1}
9	4.5	1.5	NPOE, 64	30	29.4 ± 0.5	1.0×10^{-6} – 1.0×10^{-1}
10	4.5	1.5	DBP, 64	30	20.4 ± 0.6	4.0×10^{-4} – 1.0×10^{-1}
11	4.5	1.5	BA, 64	30	23.2 ± 0.5	1.0×10^{-5} – 1.0×10^{-1}
12	–	1	NPOE, 69	30	5.1 ± 0.5	1.0×10^{-3} – 1.0×10^{-1}

Figure 4. The pH effect of the test solution (1.0×10^{-4} M) on the potential response of the mercury sensor.

pH value. The associated resulting data are illustrated in Figure 4, where it can be seen that the potential remains fairly constant in the pH range of 1.5–4. Beyond this range, a gradual change in the potential was detected. The observed potential drift at higher pH values could be caused by the formation of some Hg^{2+} hydroxyl complexes in the solution. At lower pH values, the potentials increased, indicating that the membrane sensor responded to hydrogen ions, too.

3.6 Dynamic response time

For analytical purposes, response time is one of the most important factors that are taken into account. In this work, the practical response time was recorded by immediate and successive Hg^{2+} concentration changes from 1.0×10^{-6} to 10×10^{-1} M. The reported

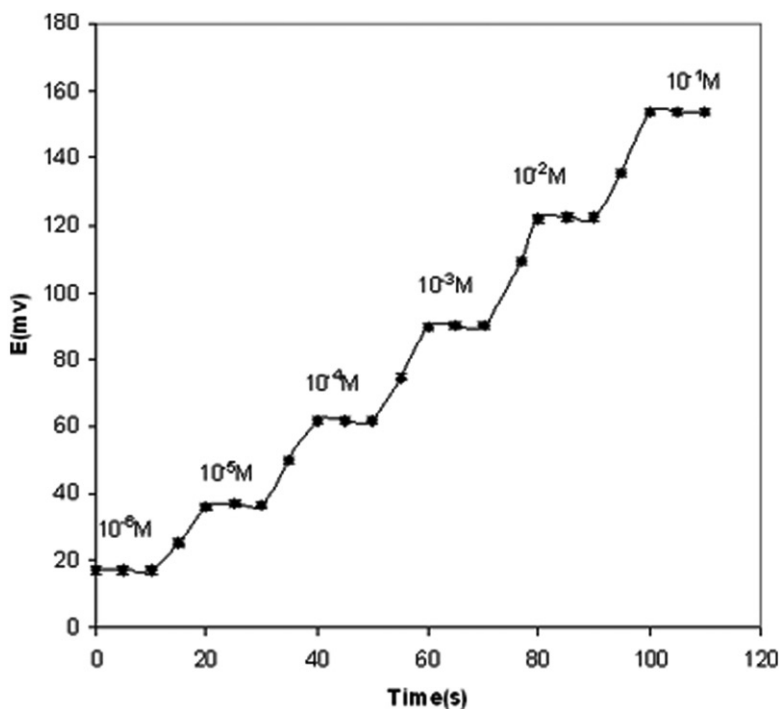


Figure 5. Dynamic response time of the mercury electrode for step changes in the Hg^{2+} concentration: (A) 1.0×10^{-6} M, (B) 1.0×10^{-5} M, (C) 1.0×10^{-4} M, (D) 1.0×10^{-3} M, (E) 1.0×10^{-2} M, (F) 1.0×10^{-1} M.

results in Figure 5 exhibit that in the whole concentration range the electrode reaches to its equilibrium response in a short time (< 10 s).

3.7 Reversibility of the electrode response

To evaluate the reversibility of the electrode, a similar procedure with opposite direction was adopted. The measurements were performed in the sequence of high-to-low sample concentrations, and the results are shown in Figure 6. It shows that the potentiometric responses of the sensor was reversible and had no memory effect, although the time needed to reach equilibrium values were longer than that of low-to-high sample concentration. It is noteworthy, that in the case of high-to-low concentrations, the time needed to attain a stable potential is somewhat 60 times larger than that required for the case of low-to-high concentrations (for a 10 times change in the cation concentration) [30].

3.8 Hg(II) -electrode selectivity

The potentiometric selectivity coefficients, which reflects the relative response of the membrane sensor towards the primary ion over other ions present in solution, is perhaps the most important characteristic of an ion-selective electrode. In this research, the potential responses of the recommended Hg^{2+} membrane sensor to a wide variety of

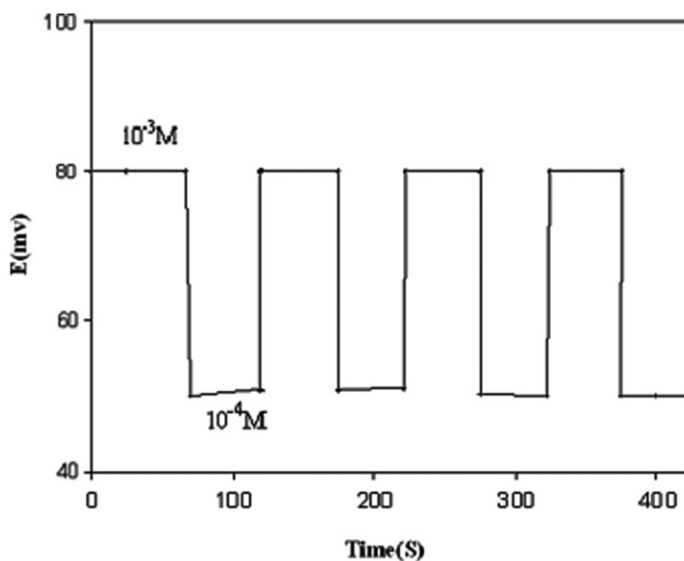


Figure 6. Dynamic response characteristics of the Hg(II)-electrode for several high-to-low sample cycles.

cations were investigated through the matched potential method (MPM) and the separation solution method (SSM) [30–32]. According to matched potential method, a specified activity (concentration) of primary ions ($A = 1.0 \times 10^{-6}$ to 1.0×10^{-3} M of mercury ions) is added to a reference solution (1.0×10^{-6} M of mercury ion) and then the potential is measured. In a separate experiment, the interfering ions ($B = 1.0 \times 10^{-4}$ to 1.0×10^{-1} M) are successively added to an identical reference solution, until the measured potential matches the one obtained before the primary ion addition. The matched potential method selectivity coefficient K_{AB}^{MPM} , is then given by the resulting primary ion to the interfering ion activity (concentration) ratio, $K_{AB}^{\text{MPM}} = a_A/a_B$ (Table 3).

In the separation solution method (SSM), the cell concentration is adjusted. The cell consists of an ion-selective electrode and a reference electrode (ISE cell). For the concentration adjustment of this cell, two solutions are required. The first contains the ion A (but no B) of a_A activity, whereas the second contains the ion B (but no A) of a_B activity, being as high as required to achieve the same measured cell voltage. From any pair of the a_A and a_B activities, giving the same cell voltage, the value of K_{AB}^{SSM} is calculated from the equation:

$$K_{AB}^{\text{SSM}} = \frac{a_A}{a_B^{Z_A/Z_B}}$$

The resulting values are given in Table 3. As it is seen, for all alkaline and alkaline earth metal ions used, the selectivity coefficients are in the order of 7.4×10^{-2} or smaller, indicating they would not disturb the functioning of the mercury electrode. As seen from Table 3 for the monovalent cations tested (with the exception Ag^+), the selectivity coefficients are in the range (6.1×10^{-3} – 4.7×10^{-4}). Table 3 illustrates the case of a divalent transition and heavy metal ions used. The selectivity coefficients are smaller than 10^{-2} (in the range 7.4×10^{-2} – 3.8×10^{-4}). The selectivity coefficients for the lanthanide

Table 3. Selectivity coefficients of various interfering ions.

M^{n+}	K_{AB}^{MPM}	K_{AB}^{SSM}
Li ⁺	4.7×10^{-4}	2.3×10^{-5}
Na ⁺	5.7×10^{-4}	4.1×10^{-5}
K ⁺	6.1×10^{-3}	2.0×10^{-4}
Ag ⁺	1.3×10^{-2}	8.7×10^{-3}
Ca ²⁺	5.3×10^{-3}	2.4×10^{-3}
Sr ²⁺	3.8×10^{-4}	2.0×10^{-4}
Ba ²⁺	1.9×10^{-3}	7.6×10^{-3}
Co ²⁺	3.5×10^{-3}	6.2×10^{-3}
Zn ²⁺	1.3×10^{-3}	2.2×10^{-3}
Pb ²⁺	5.1×10^{-3}	3.8×10^{-3}
Cd ²⁺	4.7×10^{-3}	4.3×10^{-3}
Ni ²⁺	7.4×10^{-2}	7.5×10^{-2}
Cu ²⁺	5.9×10^{-3}	1.2×10^{-3}
Sn ²⁺	1.2×10^{-3}	8.9×10^{-3}
Cr ³⁺	2.5×10^{-3}	2.7×10^{-2}
La ³⁺	3.9×10^{-2}	1.7×10^{-2}
Ce ³⁺	5.9×10^{-3}	7.0×10^{-2}

Note: Reference solution (1.0×10^{-6} M of Hg²⁺), primary ion (1.0×10^{-6} – 1.0×10^{-3} M of Hg²⁺), interfere ring ion (1.0×10^{-4} – 1.0×10^{-1} M).

ions in their trivalent state, are relatively small (1.7×10^{-2} – 5.9×10^{-3}), thus indicating they would not significantly disturb the functioning of the Hg²⁺ electrode.

In Table 4 the serious interfering ions, linear dynamic range, slope and detection limit of different Hg²⁺ ion-selective electrodes based on derivatives of calix[4]arenes and other ionophores are compared with those of this work. As can be seen from the table, the proposed sensor in term of selectivity coefficient (specially, for Ag⁺, Li⁺, Na⁺, Cu²⁺, Pb²⁺) is better than that of all previously reported Hg²⁺ sensors based on calixarenes.

There are some differences between the obtained result by conductance study and selectivity coefficient, especially in the case of lanthanum and nickels ions. This is due to the environment of the complexation and number of phases. The formation constant was obtained from acetonitrile solution and in single phase, while in the selectivity coefficient determination; there are two phases with different polarity. This kind of behaviour has been reported by some researchers [19–21].

3.9 Effect of temperature

Trend of changes of electrode performance with temperature, at test solution temperatures: 25, 30, 35, 40 and 50°C for the Hg(II)-electrode was studied. The electrode exhibits good Nernstian behaviour in the temperature range (20–45°C). At higher temperatures, the slope of the electrode did not show a good Nernstian behaviour. This behaviour may be due to the following reason: at such high temperatures, the phase boundary equilibrium at the gel layer-test solution interface is disturbed by the thermal agitation of the solution [33,34]. The standard cell potentials (E_{cell}^0), were determined at different temperatures from the respective calibration plots as the intercepts of these plots

Table 4. Comparison of the characteristics of the proposed sensor with those of the previously reported Hg²⁺ sensor.

	Detection limit (M)	Dynamic Range (M)	Serious interfering (Selectivity coefficients)	Slope	Ref.
Ionophore with calixarene					
Calixarene (containing thiazole azo group)	5×10^{-6}	5×10^{-6} – 10^{-2}	Ag ⁺ (3.98), Cu ²⁺ (0.11)	28.7	[33]
Calixarene (containing nitrogen, oxygen)	2.63×10^{-6}	5.0×10^{-6} – 10^{-2}	Li ⁺ (0.72), Ag ⁺ (5623) Na ⁺ (5.3×10^{-2}), K ⁺ (5.8×10^{-2})	26.1	[9]
Calixarene (containing sulfur, oxygen)	7.76×10^{-6}	1.0×10^{-5} – 10^{-2}	Li ⁺ (0.91), Na ⁺ (0.11), Ag ⁺ (5400) K ⁺ (6.6×10^{-2})	29.6	[9]
Calixarene (containing nitrogen, oxygen, sulfur)	2.24×10^{-5}	5×10^{-5} – 10^{-1}	Li ⁺ (2.08), Ag ⁺ (5400), Na ⁺ (0.1) K ⁺ (4.4×10^{-2})	31.9	[9]
Calixarene (L)	4.0×10^{-7}	1×10^{-6} – 10^{-1}	–	29.4	This work
Another ionophores					
2-Amino-6-purinethiol	4.4×10^{-8}	7.0×10^{-8} – 10^{-1}	Ag ⁺ (1.5×10^{-2}), Cu ²⁺ (3.1×10^{-2})	30	[7]
4-(4- <i>N,N</i> -Dimethylphenyl)-2,6-diphenylpyrillium	1.0×10^{-8}	1.0×10^{-8} – 10^{-3}	Pb ²⁺ (5.0×10^{-2}) Ag ⁺ (2.2×10^{-2})	34	[5]
tetrafluoroborate					
Tribromomercurate–rhodamine B	2.4×10^{-6}	10^{-5} – 10^{-2}	Ag ⁺ (1.0×10^{-2})		[6]
Bis(2-hydroxybenzophenone)butane-2,3-dihydrazone	4.4×10^{-7}	1×10^{-6} – 10^{-1}	–	29.7	[16]

at $p\text{Hg(II)}=0$, and were used to determine the isothermal temperature coefficient (dE^0/dT) of the cell with the aid of the following equation [35]:

$$E_{\text{cell}}^0 = E_{\text{cell}(25^\circ\text{C})}^0 + (dE^0/dt)_{\text{cell}} (t - 25) \quad (5)$$

Plot of E^0 cell *versus* $(t - 25)$ produced a straight line. The slope of this line was taken as the isothermal temperature coefficient of the cell. It amounts to $0.00082 \text{ V}^\circ\text{C}^{-1}$. The standard potentials of the reference electrode (Ag/AgCl; KCl (saturated)) were calculated using the following equation:

$$E_{\text{Ag/AgCl}}^0 = 0.23695 - 0.000485 (t - 25) \quad (6)$$

The values of the standard potentials of Hg(II)-electrode were calculated at the different temperatures from the following relation:

$$E_{\text{cell}}^0 + E_{\text{reference}}^0 = E_{\text{electrode}}^0 \quad (7)$$

Plot of $E_{\text{electrode}}^0$ *versus* $(t - 25)$ gave a straight line. The slope of the line was taken as the isothermal temperature coefficient of the Hg(II)-electrode. It amounts to $0.00014 \text{ V}^\circ\text{C}^{-1}$. The small values of $(dE^0/dT)_{\text{cell}}$ and $(dE^0/dT)_{\text{electrode}}$ reveal the high thermal stability of the electrode within the investigated temperature range.

3.10 Analytical application

Apart from application of the introduced mercury-selective membrane electrode in the direct determination of the Hg^{2+} ions, the sensor was found useful in the titration of Hg^{2+} with different chelating and precipitating agents. For example, it was applied to the titration of 10.0 mL Hg^{2+} ion solution ($1.0 \times 10^{-4} \text{ M}$), with potassium iodide ($1.0 \times 10^{-2} \text{ M}$). The resulting titration curve is depicted in Figure 7 as can be seen from Figure 6, the endpoint of the titration curve is sharp and the amount of Hg^{2+} ions in solution can be accurately determined with the proposed sensor.

The proposed Hg^{2+} -selective electrode was found to work well under laboratory conditions. It was successfully applied to the determination of mercury content of amalgam alloy [36] and spiked waters samples – the results are shown in Table 5. As can be seen from Table 5, there is a good agreement between the amount of mercury ion added and the amount of mercury found. Table 5 shows the obtained mercury content of amalgam sample by the proposed Hg^{2+} -sensor. It is in satisfactory agreement with that obtained by ICP measurement. This is due to the low selectivity coefficient of Sn^{2+} , Ag^+ .

4. Conclusion

The use of the calix[4]arene L with NPOE as plasticiser shows the best response characteristics with Nernstian behaviour across the concentration range of 1.0×10^{-6} – $1.0 \times 10^{-1} \text{ M Hg}^{2+}$, and a fast response time of 10 s. The sensor works well in a pH range of 1.5–4 and it can be successfully employed for the estimation of Hg^{2+} in different solution samples. Thus, the suggested sensor is superior to the existing sensors in terms of response time and lifetime. For actual analysis, this sensor is comparable with the other sensors regarding parameters such as slope, concentration range and selectivity.

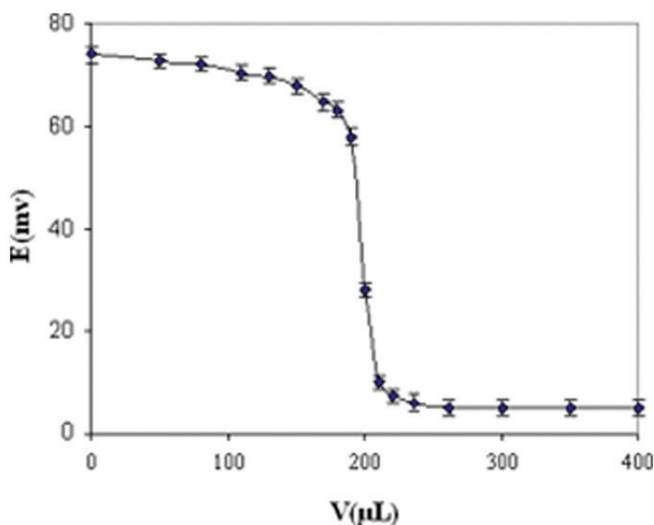


Figure 7. Potentiometric titration curve of 10.0 mL of a 1.0×10^{-4} M Hg^{2+} solution with 1.0×10^{-2} M of potassium iodide.

Table 5. Recovery of mercury from different water samples.

Sample	Hg(II) ($\mu\text{g mL}^{-1}$)		Recovery (%)
	Added	Found	
Laboratory water	0.12	0.123(0.003)	102.5
	0.25	0.256(0.002)	104
River water (Telar)	0.16	0.168(0.001)	105
Well water	0.54	0.543(0.003)	100.5
	0.70	0.702(0.005)	100.2
Amalgam alloy		0.335(0.003)% (ISE)	
		0.328(0.002)% (ICP)	

Note: Values in parentheses are RSDs based on four replicate analysis.

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