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Fabrication of a highly sensitive and selective sensing element based on Curcuminthe natural pigment of Curcumaforoptical determination of toxic mercury(II) in aqueous solutions

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ABSTRACT

In this paper, we are reporting the application of Curcumin, a natural diketon and an anticancer compound, to develop and construct a novel optical sensor that is highly selective to Hg^{2+} ion in aqueous solution. The sensing element, incorporated into a plasticized poly(vinyl chloride) membrane, is capable of determining mercury(II) over a wide dynamic range from 4.07×10^{-8} to 3.47×10^{-1} M at pH5.0 with a lower detection limit of 1.01×10^{-8} M. The optode membrane's response to $Hg^{2+}$was fully reversible and revealed a very good selectivity towards Hg^{2+} ion over a wide variety of other metal ions in solution at a response-time less than two min. The results of experimental measurements by the proposed optical sensor were significantly suitable for applications in direct determination of mercury(II) in environmental real samples and satisfactorily was comparable with the data from cold-vapor atomic absorption spectrometry.

KEYWORDS

Curcumin;
Mercury(II);
Optical sensor;
PVC-membrane;
Sensor fabrication.

INTRODUCTION

There is currently great interest in the construction and development of optical sensors as an emerging frontier in analytical chemistry. The need for fast, easy, and economical monitoring of environmental samples especially for heavy metal ions in real time is why they have gained scientific interest. They have the advantages of size, cost-effectiveness, simplicity, no necessity of the reference solution, and fieldwork applicability[1–5]. The sensing element of an optical sensor can selectively reacts with the analyte and shows spectral change in absorption (or emission) caused by the analyte either itself, or the analyte reacting with a specific indicator. This change could be followed as a function of analyte concentration or to gain some qualitative information about the species of the system tested. No further samplings, addition of reagents or dilutions are normally required, so chemical sensors based on optical signal measurements are those of the advanced techniques in analytical chemistry[2,3,6].

Because of effects of heavy metals on the ecosystem and the human health, the determination of their trace amounts in aquatic environment is of tremendous interest. Nowadays determination of trace amounts of one of these heavy metal ions, mercury (II), in environmental samples is of great importance due to its high toxicity, accumulative and persistent character in the environment and living organisms. It may cause kidney toxicity, neurological damage, paralysis, chromosome breakage, and birth defects since it readily be absorbed by humans and other organisms[7–13]. So far, a variety of methods have thus been used for measuring of Hg(II) concentration in aqueous solutions. The most common methods are atomic spectrometry[14–16], molecular spectrophotometry[1–3,17], and voltammetric methods[18–20].

Curcumin,(1E,6E)-1,7-bis(4-hydroxyl-3-methoxyphenyl)-1,6-heptadiene-3,5-dione,is a yellow natural phenolic pigment extracted from the rhizome of *Curcuma longa* Linn[21] (Figure 1). Recent years, considerableattention has been paid to Curcumin due to its attractive biological, pharmacological and some helpful properties including anti-inflammatory, anticancer, antibacterial and antiviral characteristics[22–29]. Recently, we have studied the chemiluminescence of Curcumin in a peroxyoxalate system[30] and also found that Curcumin can selectively reacts toward mercury(II) ion in solution.

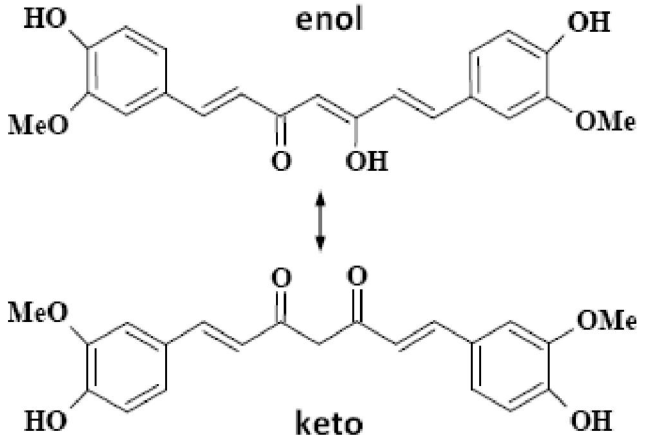

Figure 1 : The tautomericstructural "enol" and "keto" forms of C, incorporated into the membrane as the sensing material.

Here, we are going to introduce a novel optical sensor based on thenatural compoundCurcumin,which demonstrates significant change oflight absorptionwhen exposures to a solution containing mercury(II) ion. Therefore, we will discuss the selectivity, response time, reversibility, and lifetime of the proposed optode in details.

EXPERIMENTAL

Materials and reagents

All reagents (all from Merck) were of analytical reagent grade and used as received, except for vacuum drying over P_2O_5. Curcumin (C), which was selected as sensing material,was also purchased from Merck. High molecular weight PVC, plasticizers Teris (2-Ethylhexyl Butyl) Phosphate (TEBP), Tri(methylhexyl)phthalate (TMHP), Bis(2-ethylhexyl)phosphate (BEHP), Di(ethylhexyl)sebacate (DEHS), Diisodecylphthalate (DIDP), and freshly distilled Tetrahydrofuran (THF) were used for membrane preparations. The cationic additive, potassium tetrakis(para-chlorophenyl)borate (KTpClPB),was used where needed. Tetraethylammoniumperchlorate (TEAP) was used as the ionic strength stabilizer in the spectrophotometric solution studies. The metal cations tested were of their nitrate salts. Doubly distilled and deionized water was used throughout.

Instrumentation

Spectrophotometric measurements were made by using a Shimadzu UV-76 1650PC UV-Vis spectrophotometer with 1.0-cm quartz cells. pHs of solutions were measured by aJenway 3020 (UK) pH-meter. A hydride-generation cold-vapor atomic absorption spectrometry system (CV-AAS) including an AA 670 Shimadzu atomic absorption spectrometer was used for measurement of mercury contents of the samples.

General procedureof sensor fabrication and measuring method

The general procedure is as we have already described elsewhere[4]. A clear and homogenous oily solution was prepared from a mixture containing appropriate amounts of active components, 1 mg C, 1 mg KTpClPB, 50 mg PVC and 100 mg of BEHP (see TABLE 1) by dissolving in 3.0 ml of freshly distilled THF. An aliquot of 0.2 ml of this solution was transferredon top of the surface of a 14×25 mm^2 thin quartz plate, which was mounted on a platform under a THF-saturated atmosphere[31]. In this way, a clear and homogenous membrane of approximately 4 ?m thick[32] was coated onto the plate and allowed to stand in ambient air for 2 h before use.

The film was mounted in the diameter direction of a measuring cell (Figure 2). A stock solution of $1.0 \times 10^{"3}$ M Hg^{2+} was prepared by dissolving exactly weighted

TABLE 1 : Construction of different membranes to find the best membrane composition based on C

	Composition (mg)				Response	
No.	Ionophore (C)	PVC	Plasticizer(100 mg)	Additive (KTpClPB)	Responsetime(min)	Linear range(M)
1	1	50	DIDP	1	3	$3.68\times10^{-5} – 3.33\times10^{-2}$
2	1	50	DEHS	1	4	$3.21 \times10^{-5}– 2.39\times10^{-2}$
3	1	50	TMHP	1	4	$6.81\times10^{-5} – 1.81 \times10^{-1}$
4	1	50	TEBP	1	4	$9.11 \times10^{-6} – 1.45\times10^{-2}$
5	1	50	BEHP	1	<2	$4.07\times 10^{-8}– 3.\times4710^{-1}$
6	2	50	BEHP	1	3	$6.21 \times10^{-7} – 9.31 \times10^{-2}$
7	3	50	BEHP	1	3	$3.87\times10^{-7} – 1.31 \times10^{-1}$
8	1	40	BEHP	1	3	$8.15 \times10^{-7} – 2.51 \times10^{-2}$
9	2	60	BEHP	1	2	$1.27\times10^{-7} – 1.11\times10^{-2}$
10	1	50	BEHP	2	2	$8.21 \times10^{-8} – 7.31\times10^{-2}$
11	1	50	BEHP	4	3	$4.01 \times10^{-7} – 1.18\times10^{-1}$
12	0	50	BEHP	1	6	$8.51 \times10^{-4} – 7.51\times10^{-3}$

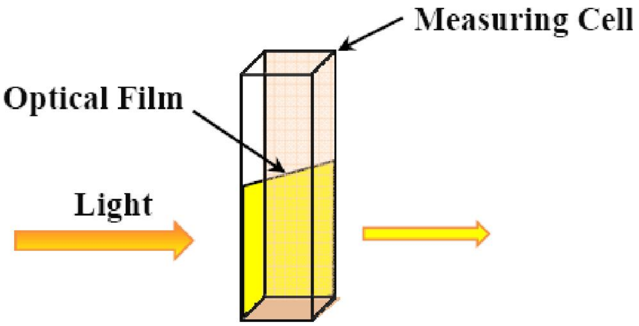

Figure 2 : Mountingand the position of optical sensing film in the measuring cell.

amount ofHg$(NO_3)_2.2H_2O$ inwater. The standard mercury(II) solutions were added sequentially into the system by a micropipette (with 2-µl step) and the absorbance data was recorded at $\lambda_{max} = 420$ nm. The limiting absorbencies A_0 and A_c were determined with the optode membrane in contact with $(1.0\times10^{-3}$ M) and without Hg^{2+}. By plotting the response values versus the logarithmic concentrations of mercury(II) ion (pHg), the unknown mercury(II) concentrationswereevaluated. All measurements were carried out at room temperature.

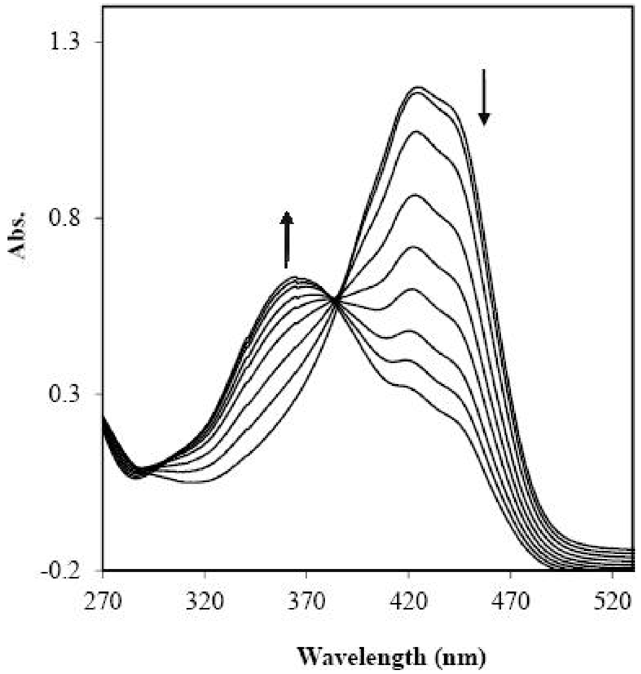

Figure 3 : Absorption spectra for a solution containing 1.20×10^{-4} M of the ligand C at a fixed ionic strength of 0.05 M (TEAP) and varying amounts of Hg^{2+} ions (0.00 to 3.52) × 0^{-4} M.

RESULTS AND DISCUSSION

Solutionspectrophotometric study

To explore the spectral properties of C to use as an optically sensing material for mercury(II) ion, we tested various metal ions in a preliminary experiment. It was found that addition of proper amounts of Hg^{2+} to a solution of Cin ethanol (EtOH)results in a fast change in the absorption of the solution indicative the complex formation from the reaction of C with Hg(II). Figure 3

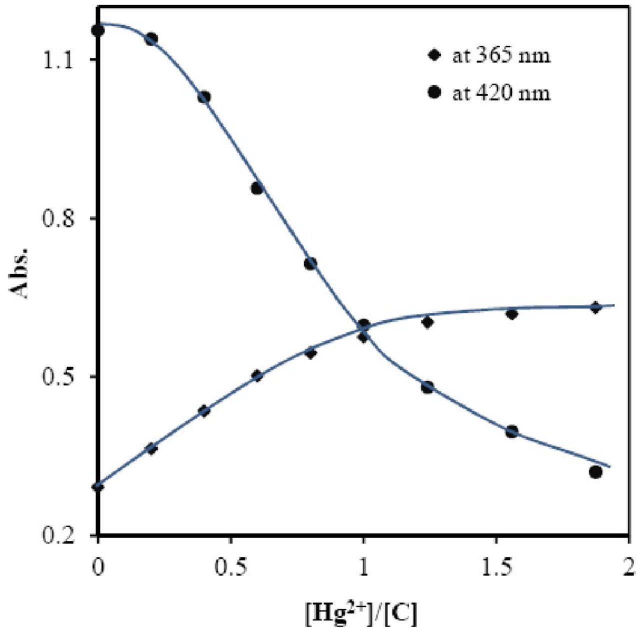

Figure 4 : The absorbance versus [Hg^{2+}]/[C] mole ratio plots, obtained at 420 and 365 nm (points) and the corresponding program-predicted values (solid line)in EtOH solution.

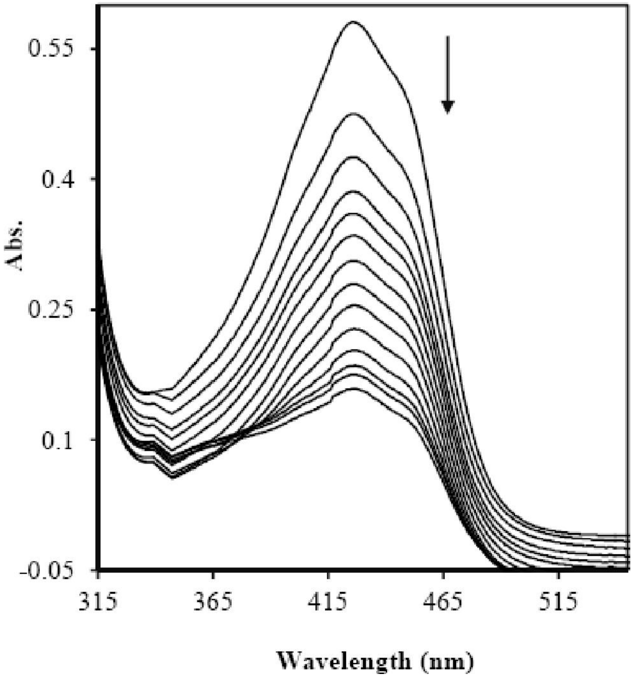

Figure 5 : Absorption spectra for the ligand C, incorporated into the membrane, at the presence of varying amounts of Hg^{2+} ion (0.0 to 1.0 × 10^{-4}) M in aqueous solution.

demonstrates the absorption spectra of a solution of C(1.20×10^{-4} M, at a fixed ionic strength of 0.05 M TEAP) after addition of varying amounts of the Hg(II) (0.00 to 3.52×10^{-4} M) solution. As can be seen, the complexation was accomplished by creating a clear isobestic point at 382 nm and a relatively strong shift of absorption band of the ligand C($\lambda_{max} = 420$ nm) towards a shorter wavelength 365 nm for the complex, where the ligand showed no distinct peak. Such a pronounced effect on the electronic spectra of the ligand can be related to effective change in the conjugation of the ligand molecule brought about by its complexation with the Hg^{2+} ion.

The absorbance versus[Hg^{2+}]/[C] mole ratio plots, obtained at 420and 365 nm in EtOH solution, are shown in Figure 4. The plot reveals a clear inflection point at [Hg^{2+}]/[C] mole ratio of about 1 emphasizing formation of a 1:1 (metal-to-ligand) complex in the solution. The formation constant of the resulting complex was evaluated by computerized fitting of the corresponding mole ratio data to proper mass balance equation[33] by using a non-linear curve-fitting program, KINFIT[34]. The output of the program comprises the refined parameters, the sum-of-squares, and the standard deviations of the data.

The program'spredicted values (solid line) best fitted on the experimentally obtained data (points) for a 1:1 (metal:ligand) model. The resultsare also shown in Figure 4. The resulting formation constant value, K_1, was$(2.44 \pm 0.01) \times 10^5$. The sum-of-square value for this computation was less than 0.0001 that is so reasonable.

As can be seen in Figure 5, after C was incorporated in the PVC membrane, the spectral pattern of the ligand-metal interaction in the membrane remained similar to that occurred in the organic solvent. This fact showed us the way, on which we could use the ligand as a sensing material in a membrane as a novel sensing element to construct an optical sensor for mercury(II) ion measurement in solution. This is the basis of the optical sensing device in this investigation. Therefore, wavelength 420 nm was used in all subsequent absorbance measurements.

Measuring principle

When a mercury(II) ion is extracted into the optical membrane, it forms a complex with C and decreases its absorption at $\lambda_{max} = 420$ nm considerably, as the concentration of Hg^{2+} increases. This illustrates that the optode membrane can be used for the assay of Hg^{2+} in aqueous solution.

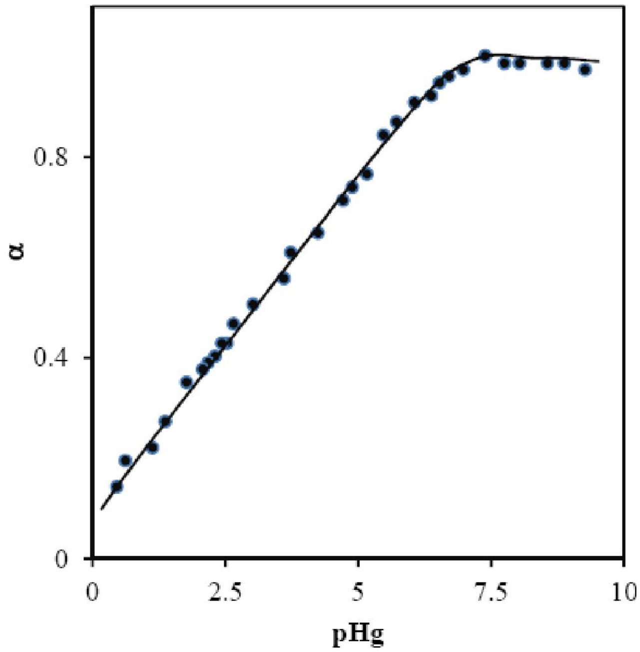

Figure 6 : The predicted data curve plot (line) for the optimized membrane (No. 5, Table 1) is best fitting to the experimental data (points) indicative a 1:1 nature of the complex exists between Hg^{2+} and the ligand (C) in the membrane with $K_{exch}(7.81\pm0.01) \times 10^2$.

As we have already shown in Figure 1, C involves in an enol–ketotautomeric reaction, in which complexes Hg(II) via the "keto" form[35]. Neglecting charge balance, the overall equilibrium is expressed as follows (Eq. 1):

$$mHg^{2+}_{(aq)} + nC_{(org)} + 2mKR_{(org)} \Leftrightarrow R_{2m}Hg_mC_{n(org)} + (2m)K^{+}_{(aq)} \qquad (1)$$

KR is the cationic additive. The law of mass action can describe the corresponding equilibrium constant, K_{exch}, of the system for Hg^{2+} ions that is expressed in Eq. 2, in which it is assumed that the concentrations of species in the membrane are proportional to their activities:

$$K_{exch} = \frac{[R_{2m}Hg_mC_n]_{org}.[K^+]^{2m}_{aq}}{[Hg^{2+}]^{m}_{aq}.[C]^{n}_{org}.[KR]^{2m}_{aq}} \qquad (2)$$

K_{exch} depends on the complex formation constant, on the distribution coefficient of the Hg^{2+}ions between the aqueous sample solution and the organic membrane phase, and pH of the tested solution.

It is obvious from Eq. 2 that a plot of α,which is the ratio of the concentration of free Hg(II)–C complex to the total amount of C (C_C) in the organic phase, versus pHg should give complicate relationships by altering the ratio of *m*:*n* and adjusting the overall equilibrium constant K_{exch}. In order to study the composition effect, different stoichiometric ratios of *m*:*n*and equilibrium constant K_{exch} were used for different membranes. There were no good agreements between the experimental data and those from the theoretical calculations except for the 1:1 model (*m*=*n*).

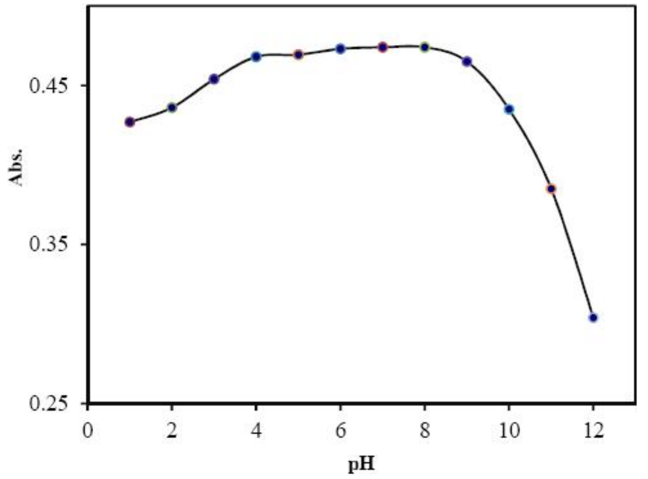

Figure 7 : The effect of pH on the response of the proposed optical sensor to the metal ion in the presence of 4.0×10^{-4} M Hg^{2+} ion. The response curve data was obtained by measuring the absorbance values for Hg^{2+} at different pH values from 1.0 to 12.0.

The solution study revealed a 1:1 complex is formed from the reaction of C with Hg^{2+} ion, from which if we also assumesuch a complex is formed in the optode membrane then Eqs. (1)and (2)are simplified to Eqs. (3) and (4), respectively. The extraction of Hg^{2+} from aqueous sample solution into the membrane phase and its complexation by C proceeds with the exchange of twoK^+.

$$2KR_{(org)} + C_{(org)} + Hg^{2+}_{(aq)} \leftrightarrow R_2HgC_{(org)} + 2K^{+}_{(aq)} \qquad (3)$$

$$K_{exch} = \frac{[R_2HgC]_{org}.[K^+]^{2}_{aq}}{[C]_{org}.[Hg^{2+}]_{aq}.[KR]^{2}_{org}} \qquad (4)$$

From Eq. 4, we can obtain the relationship between α and $[Hg^{2+}]$:

$$\alpha = \frac{[HgC]_{org}}{C_C} \Rightarrow [HgC]_{org} = \alpha C_C, [C]_{org} = (1-\alpha)C_C$$

Then the response function for such a membrane could be denoted by Eq. 5.

$$K_{exch}=\frac{\alpha C_C.[K^+]_{aq}^2}{(1-\alpha)C_C.[Hg^{2+}]_{aq}.[KR]_{org}^2}$$

$$=(\frac{\alpha}{1-\alpha}).\frac{[K^+]_{aq}^2}{[KR]_{org}^2}.\frac{1}{[Hg^{2+}]} \quad (5)$$

In this equation, at a constant pH, αwould be a function of Hg^{2+} concentration in the solution, if we assume the term $[K^+]^2/[KR]^2$ is nearly constant because the total concentration of KR is low and not changed considerably.

Here, the response curve of the optical sensor is usually depicted as the normalized absorption α as a logarithmic function of the metal-ion concentration. The measured absorption is converted into α by Eq. 6, in which A_0 is the absorption of the free ligand, A_c the absorption of the complex, and A is the measured absorbance at 420 nm. From Beer's law, we assume the normalized absorbance value α, whichindicates the molar fraction of the complex, is related to the measured absorbance as follows:

$$a=\frac{(A-A_0)}{(A_c-A_0)} \quad (6)$$

Eq. 5 can be used to find the theoretical data, to fit observed absorptions and to calculate K_{exch}[36]. In addition, Eq. 5 is the basis of quantitative determination of mercury(II) using the optical membrane. Using Excel® and different reasonablevalues for K_{exch}, we predicted the corresponding data for the experimentally obtained values of measured responses of the optode in the presence of different concentrations of Hg^{2+} in the solution. As is clear from Figure 6,the predicted data (curve line) is best fitting to the experimental data (points) indicative a 1:1 nature of the complex exists between Hg^{2+} and the ligand (C) in the membrane and the corresponding$K_{exch}$was$(7.81\pm0.01)\times10^2$.

Although, it has been reported that the addition of a salt with a highly lipophilic anion in the membrane phase may ensure a sufficiently high amount of cations in the organic phase[37] we found that the membraneabsorption was not varied considerably in the presence of KTpClPB. However, a lipophilic anion is necessary to facilitate the cation extraction from the aqueous solution. Experimentally, we optimized the amount of KTpClPB (see TABLE 1).

Effect of pH

Apparently, from Eq. 3, the sensitivity of the sensing film not depends on the pH of the aqueous solution, while the complexation reaction involves a proton transfer in enol-ketotautomericprocess of C. Certainly, this process could be affected by pH of the surrounding solution thataffects the response function of the membrane. This implies that the response values for Hg^{2+} should be measured in pH-buffered solutions. Figure 7 shows the effect of pH on the response of the proposed optical sensor to the metal ion in the presence of 4.0×10^{-4} M Hg^{2+} ion. The response curve data were obtained by measuring the absorbance values for Hg^{2+} at different pH values from 1.0 to 12.0, which adjusted with minor amounts of concentrated NaOH and HCl solutions. At the pH values in the range of 4.0–8.0, the working response did not vary. At pH values lower than 4.0, the sensing material is totally protonated in the massive presence of hydrogen ion, so its absorbance would extremely decreases. After the pH reaches a relative high value (higher than 8), the keto form deprotonated and the hydrogen transferring process stops. On the other hand, the mercury(II) ion precipitate as a hydroxide form and the exchange reaction would also be inhibited. Among some buffer solutions tested, the best working function was seen when the membrane was used in the presence of acetate-buffer (pH= 5). In subsequent experiments, a pH 5.0 acetic acid/sodium acetate (0.01 M) buffer solution was used as a good experimental condition in which the ionic strength was also kept constant through the work.

The membrane composition

As it was expected,the nature of plasticizer could play a key role in determining the ion selectivity of the membrane[38]. Here, five different plasticizers were investigated and the results are shown in TABLE 1 (Nos. 1–5). As can be seen for the case of BEHP, the membrane response towards Hg^{2+} ion gives the widest working dynamic range (4.07×10^{-8}– 3.47×10^{-1} M at pH 5.0 with a lower detection limit of 1.01×10^{-8} M).

In addition, the amount of PVC (Nos. 5,8 and 9 in TABLE 1) can influence the response of the membrane.

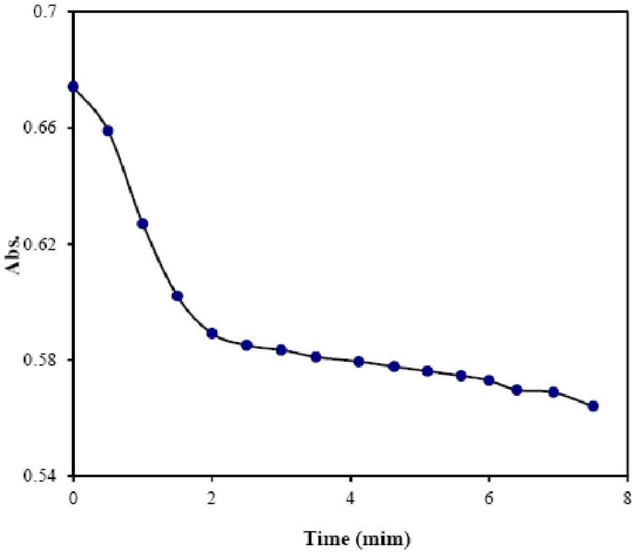

Figure 8 : The time-dependent response characteristics of the optical membrane, which immersed in an acetate buffer solution containing 4.0 × 10^{-4} M Hg^{2+}, at λ_{max} = 420 nm.

Membranes 5, 6 and 7 indicate the effects of concentration of the ligand incorporated into the composition.

The other parameter of the membrane composition, which has to be investigated, is the ligand-to-additive ratio. The results are summarized as Nos. 5, 10 and 11. Finally, in order to show the capability of the optimized membrane (No. 5 in TABLE 1) toward the Hg^{2+} ion without the ionophore (white membrane), we investigated the composition No. 12 which showed that the response characteristics of the system are not useful. In the end, the optode (No. 5) with the optimized composition 1:1:50:100 (mg) of C:KR:PVC:BEHP was selected as the best one for subsequent measurements.

Response time and reversibility

From the literature[39] and our preliminary experiments, the response time value ($t_{95\%}$) of the sensor when reaches to 95% of its final value (steadystate), depends on the sensing membrane composition. Figure 8 shows the time-dependent response characteristics of the optical membrane, which immersed in a buffer solution containing 4.0 × 10^{-4} M Hg^{2+}. We found that a very thin, homogenous and reproducible PVC-based membrane including 50 mg PVC and100 mg plasticizer BEHP(No. 5) shows the shortest response time for each membrane (<2 min), in which the sensor is able to monitor the mercury(II) ions reversibly.

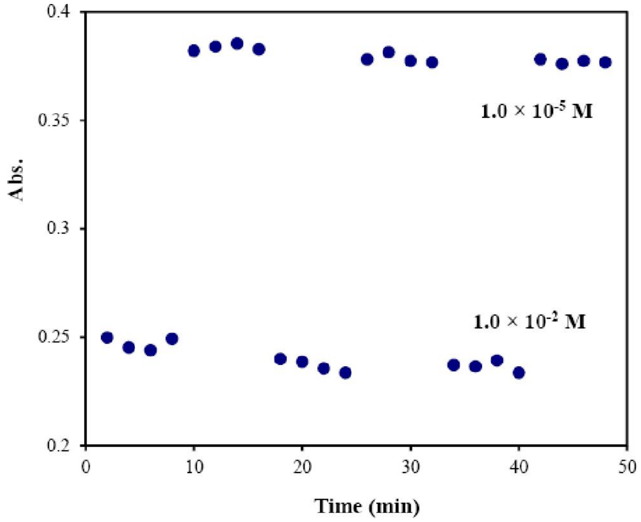

Figure 9 : The reversibility of the optical membrane calculated from the absorption values collected from the alternative measurements of the buffer solutions containing 1.0 × 10^{-5} and 1.0 × 10^{-2} M Hg^{2+} at λ_{max} = 420 nm, top and bottom, respectively.

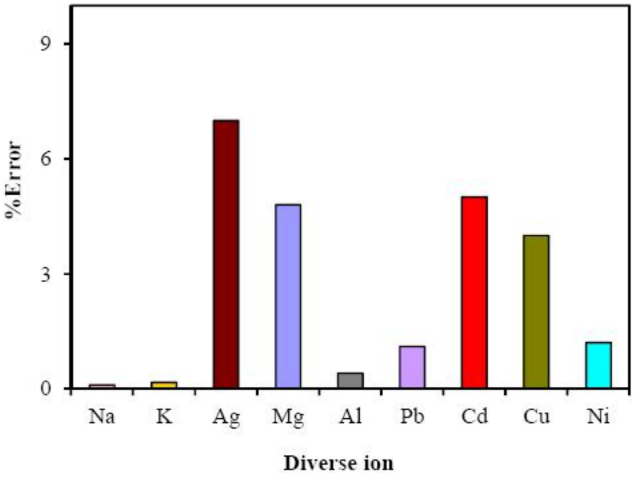

Figure 10 : Effect of some diverse cations on the optode response to the mercury(II) ion. The plot shows the deviations (%) of the optode response in the presence of 0.01 M of the diverse ions, Al(III), Cu(II), Pb(II), Cd(II), Ni(II), Mg(II), Ag(I), Na^+ and K^+.

The reversibility of the optical membrane was calculated from the absorption values collected from the alternative measurements of the buffer solutions containing 1.0 × 10^{-5} and 1.0 × 10^{-2}M Hg^{2+}. The results are shown in Figure 9. As can be seen from this Figure, the system is highly reversible. The evaluated %RSDs were of ±0.02 and ±0.03 for the lower and the upper Hg^{2+} concentrations, respectively.

Stability and lifetime

The optimized membrane was kept unused over a

TABLE 2 : Application of the optode to determine the mercury(II) contents (ppb) of some real samples by using standard addition methodof six replicate measurements

Sample	CV-AAS	Proposed Sensor
Tap water	1.32 ± 0.02	1.36± 0.05
Fountain	2.61 ± 0.02	2.68± 0.06
Khorramabad River	1.86 ± 0.03	1.78± 0.06
Cyanidic garbage	3.88 ± 0.03	3.79 ± 0.05
Resinic black mud	1.16 ± 0.03	1.22 ± 0.04

period of 2 months. The membrane exhibited a good stability with a dynamic range deviation of less than 1.0%, when the mercury(II) ion solutions were measured. Then, over a period of 3 months, using the optode in contact with a mercury(II) solution (1.0×10^{-5} M) for 1 h per day, the absorbance signal of the optical membrane not changed more than 3%.

Washing by distilled water regenerated the membrane and no detectable leach of the ligand into the solution was seen during the measurements of sample solutions over this period. The overall lipophilic property of ionophore (C) and itslong-chain structure would provide long lifetime and no leaching from the membrane into the solution.

Detection limit and selectivity

In order to assess the possible analytical application of the sensing membrane, the limit of detection 1.01×10^{-8}M was obtained from the intersection of two segments of the calibration graph of the membrane response at its lowest part of the response calibration curve.

Substances that can take part in formation of the membrane and react with the probe may influence the measurements. In order to clue the influence of other cations, we used the calibration curve for the membrane in the presence of 0.01 M of some potential interfering ions such as Al(III), Cu(II), Pb(II), Cd(II), Ni(II), Mg(II), Ag(I), Na^+ and K^+ then plotted each deviation(Error %). The results are summarized in Figure 10. This Figure clearly shows that the optode does not have a significant selectivity towards other ions, but had shown a highly selective response to the Hg^{2+} ion.

Determination of Hg^{2+} concentrations in aqueous samples

The best-fitted curve, which has the widest working dynamic range (from 4.07×10^{-8} to 3.47×10^{-1} M at pH 5.0 with a lower detection limit of 1.01×10^{-8} M. see TABLE 1 No. 5 and Figure 6), can serve as a calibration curve for the determination of Hg^{2+} in aqueous solution.

To test the practical application of the presented sensor, applications for direct determination of mercury(II) in cyanidic garbage,resinic black mud and water samples fromTap, Fountain and Khorramabad River (west of Iran) were carried out. The collected samples were first acidified with HNO_3, filtered through a packed filter to remove oils and other organic impurities, and then prepared according to literatures. Under the optimal conditions for the proposed optode, the obtained data were collected. The real samples wereanalyzed by following the standard addition calibration method. As shown in TABLE 2, which summarizes six repeated measurements for each case, the results were in good agreement with data obtained by CV-AAS. In addition, the proposed mercury(II)-selective optode was found to work well under laboratory conditions where mercury ions (1.0×10^{-3} M) were accurately determined with the proposed membrane when it was used as an indicator device for the titration of a solution of Hg^{2+} with standard EDTA solution.

CONCLUSIONS

The numbers of natural ion-carriers for sensing purposes are not so much. The useful ability of C to selectively embracemercury(II) ion led in using as a proper ionophore for construction anovel optical sensor for Hg(II).

The results reported in this work clearly demonstrate the ability of Curcumina natural ligand containing a diketoncrampon to coordinate Hg(II) metal ion in aPVC-derived film. The constructed optical sensordemonstrates a high selectivity toward mercury(II) ion, the most important advantage of the sensor, over many other potentially divers ions in the solution. In addition to a wide range of concentrations measured, the sensor is easy to use in acidic conditions that can prevent the system from interfering of conjugate bases of weak acids in the solution. Furthermore, the solution studies about the complexation of mercury(II) with C actually reveals that this comestible compound could swept mercury infections from living organisms.

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