# Highly Selective Potentiometric Membrane Sensor for Hg(II) Based on Bis(Benzoyl Acetone) Diethylene Triamine

Ali A. Ensafi, S. Meghdadi, and Alireza R. Allafchian

***Abstract*—A new ion selective PVC membrane sensor is described based on bis(benzoyl acetone) diethylene triamine as a potentiometric sensor for $Hg^{2+}$ ions. The membrane having bis(benzoyl acetone) diethylene triamine as an electroactive material, sodium tetraphenyl phthalate (NaTPB), and dibutyl phthalate (DBP) as an anion excluder in PVC matrix in the percentage ratio of 4.21:2.11:60.25:33.43 (Ionophore:NaTPB:DBP:PVC) (w/w) exhibits a linear response to $Hg^{2+}$ ions in a concentration range of $1.0 \times 10^{-6}$ to $1.0 \times 10^{-1}$ M with a limit of detection of $3.7 \times 10^{-7}$ M and with a slope of 29.8 $\pm$ 1.0 mV/decade over the pH range of 2.0–11.5. Selectivity coefficients for Hg(II) relative to a numbers of potential interfering ions were investigated. The sensor is highly selective for $Hg^{2+}$ ions over a large number of mono-, bi-, and trivalent cations. Normal interferents like $Ag^{+}$ and $Cd^{2+}$ do not interfere in the working of the sensor. The sensor has been found to be chemically inert to other ions and showing a fast response time of 1 s and was used over a period of three months with a good reproducibility. The sensor was successfully applied to determine mercury(II) in water samples with satisfactory results.**

***Index Terms*—Bis(benzoyl acetone) diethylene triamine, membrane sensor, mercury(II), potentiometry.**

## I. Introduction

MERCURY IS A toxic persistent bioaccumulative pollutant that affects the nervous system. It is found as industrial waste because of its growing area in production of some batteries, thermometers, cameras, cathode tubes, calculators, medical laboratory chemicals, and have been used as a catalyst in production of urethane polymers for plastics, a cathode in electronic production of chlorine and caustic soda, mercury vapor lamps and barometers. Thus, it is very important to determine mercury at lower levels in our environments. Various common methods are used to determine mercury such as complexometry [1], spectrophotometry, flame and atomic absorption spectrometry (AAS), inductively coupled plasma (ICP), fluorimetry, X-ray fluorescence, voltammetry, and potentiometry [2]. The available method for low-level determination of Hg(II) in solutions include flameless AAS and ICP, but it involves expensive instrumentation and sample pretreatment, which is time consuming and inconvenient.

Potentiometric detection based on ion-selective electrodes (ISEs), offers several advantages such as speed and ease of preparation and procedures, simple instrumentation, relatively fast response, wide dynamic range, reasonable selectivity, and low cost [3]. Thus, the development of a selective sensor for mercury(II) has been a subject of investigation to analytical chemists. Several organic and inorganic compounds have been tested as an ionophore in producing ISEs. Table I shows most of the previously reported potentiometric method for determination of Hg(II). However, those ISEs have a short lifetime, and/or are prone to interference by a number of metal ions such as silver, iron, and cadmium ions. Recently, Gupta *et al.* ([26, Table I]) has reported an Hg(II) ISE based on diamine donor ligand with a linear range of $1.2 \times 10^{-5}$ to $1.0 \times 10^{-1}$ M. The sensor has a thin linear dynamic range and sodium and ammonium ions are also interfered. In this paper, we have reported an Hg(II) membrane sensor based on bis(benzoyl acetone) diethylene triamine (BBDT) as an ionophore. The developed sensor is selective to Hg(II), has a wide working concentration range, and a fast response time with reproducible results. The present ISE based on BBDT is comparable and superior in many results than those reported in literature (Table I).

## II. Experimental

### A. Reagents

PVC of high relative molecular weight, dibutyl phthalate (DBP), dioctyl phthalate (DOP), sodium tetraphenyl borate (NaTPB) and tetrahydrofuran (THF), and all other chemicals were of highest purity available from Merck, and were used without further purifications, except THF, which was distilled before using. All solutions were prepared by dissolving the salts of the metal nitrates in distilled deionized water.

Bis(benzoyl acetone) diethylene triamine (BBDT) is used as an ionophore which was prepared according to the reported method [4]. The ligand was synthesis according to the following procedure: a solution of 1.032 g (0.010 mole) of diethylentriamine in 20 ml of methanol was added to a stirring solution containing 3.24 g (0.020 mole) of benzoylacetone in a minimum amount of diethyl ether. The result solution was stirred for 1 h at room temperature, and the volume was then reduced to 1/3 by slow evaporation. The concentration solution was then added dropwise to 240 ml of water with constant stirring. The resulting white crystals was filtered off and dried in the open air. Elemental analysis ($C_{24}H_{29}N_3O_2$,

Manuscript received August 8, 2007; revised October 3, 2007; accepted October 24, 2007. This work was supported in part by the Isfahan University of Technology Research Councils and the Center of Excellence in Sensors. The associate editor coordinating the review of this paper and approving it for publication was Prof. Michael Schoening.

The authors are with the College of Chemistry, Isfahan University of Technology, Isfahan 84156-83111, Iran (e-mail: Ensafi@cc.iut.ac.ir; smeghdad@cc.iut.ac.ir; allafchian@ch.iut.ac.ir).

Digital Object Identifier 10.1109/JSEN.2007.913146

1530-437X/$25.00 © 2008 IEEE

TABLE I
COMPARISON STUDIES OF THE PROPOSED ISE WITH PREVIOUSLY REPORTED IN LITERATURE

| *Ionophore* | *Response time (sec)* | *Linearity (M)* | $logK^{POT}_{I,J}$ | | | | *Reference* |
|---|---|---|---|---|---|---|---|
| | | | $Co^{2+}$ | $Pb^{2+}$ | $Cd^{2+}$ | $Mg^{2+}$ | |
| Salicylaldehyde thiosemicarbazone | 30 | $1.8\times10^{-6}$-$1.0\times10^{-1}$ | -3.5 | -3.23 | -0.4 | -2.70 | [21] |
| 1,4-Dithia-12-crown-4calixarene derivative containing the thiazole azo group | Not reported | $5.0\times10^{-6}$-$1.0\times10^{-2}$ | -3.8 | -2.6 | -4.6 | -4.5 | [22] |
| Tetrathia-diazacyclotetradeca-2,9-diene | 18 | $1.4\times10^{-6}$-$1.0\times10^{-1}$ | -3.16 | -1.70 | -3.50 | -4.53 | [23] |
| Bis[5-((4-nitrophenyl)azo salicylaldehyde)] | 10 | $7.0\times10^{-7}$-$5.0\times10^{-2}$ | -4.49 | -4.29 | -4.30 | -5.12 | [24] |
| Ethyl-2-benzoyl-2-phenylcarbamoyl acetate | Not reported | $1.0\times10^{-6}$-$1.0\times10^{-3}$ | <-6 | <-6 | <-6 | <-6 | [25] |
| $(H_2NCHMeCH_2NH2)(H_2O)_2HgCl_2$ | 10 | $1.3\times10^{-5}$-$1.0\times10^{-1}$ | -1.05 | -1.30 | -1.10 | -1.67 | [26] |
| Bis(benzoylacetone) diethylene triamine | 1 | $1.0\times10^{-6}$-$1.0\times10^{-1}$ | -4.50 | -4.74 | -5.80 | -4.50 | This work |

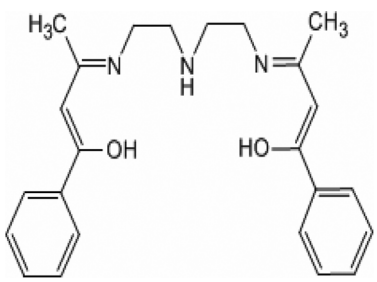


Fig. 1. Structure of BBDT.

$\mathrm{MW} = 391\ \mathrm{g/mol}$) showed that C, 73.26 (calculated, 73.66), N, 10.60 (calculated 10.74), H, 7.40 (calculated 7.42). IR (KBr, $\mathrm{cm}^{-1}$) spectra showed $\upsilon_{\max}$: O-H (3400–3500), N-H (3337), $\mathrm{C} = \mathrm{N}$ (1603.52), and C-H (2975–3057). UV-VIS spectra in dichloromethane showed $\lambda$, nm ($\varepsilon$, $\mathrm{M}^{-1}\ \mathrm{cm}^{-1}$): 245, (16743); 343, (35266). $^1\mathrm{H} - \mathrm{NMR}$ ($\mathrm{CDCl_3}$, 300 MHz) showed NH (1.57 ppm, s, 1H), $\mathrm{H_c}$ (2.12 ppm, s, 6H), $\mathrm{H_a}$ (3.46–3.52 ppm, dt, 4H), $\mathrm{H_b}$ (2.93–2.97 ppm, t, 4H), $\mathrm{H_d}$ (5.69 ppm, s, 2H), $\mathrm{H_e}$ (7.84–7.87 ppm, dd, 4H), $\mathrm{H_f}$, $\mathrm{H_g}$ (7.368–7.456 ppm, m, 6H), OH (11.49 ppm, s, 1H). The structure of the ligand is shown in Fig. 1.

### B. Apparatus

Potentials were measured by direct potentiometry at $25 \pm 0.1\ ^\circ\mathrm{C}$ with the help of ceramic junction calomel electrodes and the cell setup was as follows:

$$\mathrm{Hg/Hg_2Cl_2, KCl(sat'd)|Internal\ electrolyte(0.010\ M)\ Hg^{2+}|Membrane|Sample\ solution|Hg/Hg_2Cl_2, KCl(sat'd)}.$$

All potentiometric measurements were made with a pH/mV meter (Corning, Model 140). All emf measurements were carried out in a 50-ml double walled glass cell with a constant magnetic stirring of the test solution. Activities were calculated according to Debye–Huckel procedure [5]. Response times were determined after the potential of a mercury solution had become constant, and similar measurements were carried out in another solution of 100-fold lower concentration. The response time was defined as the time taken to reach a potential of 95% of the potential difference in the two measurements.

A Perkin–Elmer (Waltham, MA) Model 2380 furnace atomic absorption spectrometer furnished with an Hg-hollow cathode lamp was used. The instrument was set at a wavelength of 228.8 nm and all of other parameters were adjusted according to the standard recommendation.

A pH-meter (Corning, Model 140) with a double junction glass electrode was used to check the pH of the solutions.

### C. Electrode Preparation

A number of membranes incorporating the ionophore, plasticizers, and ion excluder in different compositions in PVC matrix fabricated as follow: a mixture of 28.20 mg of PVC, 60.25 mg of DBP as a plasticizer, 2.11 mg of NaTPB, and 4.21 mg of BBDT was added in 5 ml of THF and the mixture was shaken well to dissolve and produce a clear solution. The resulting homogeneous mixture was then poured into a 20 mm Petri dish, covered with a filter paper, and the solvent was allowed to evaporate at room temperature. Semitransparent PVC membranes were obtained with an average thickness of about 0.2 mm. A Pyrex tube (3 mm i.d.) was dipped into the mixture for about 10 s so that a membrane was formed. The tube was then pulled out from the mixture and kept at room temperature for 12 h. The tube was filled with the internal solution [0.010 M Hg(II)]. The filled electrode was conditioned by soaking in 0.010 M Hg(II). The first conditioning time was approximately 24 h and then was about 30 min for successive uses. A calomel electrode was used as an internal reference electrode. The lifetime of the sensor is at least three months when conditioned by soaking in 0.010 M $\mathrm{Hg(NO_3)_2}$ solution for 30 min before measurements and stored in air when not in use.

## III. RESULTS AND DISCUSSION

Bis(benzoyl acetone) diethylene triamine (BBDT) (Fig. 1) is a ligand with three nitrogen and two hydroxyl group. This compound could make complex with soft metal ions such as Hg(II). In preliminary experiments, the derivative was used to prepare a PVC membrane ISE for a wide variety of metal ions, including alkali, alkaline earth, transition, and heavy metal ions. Among

TABLE II
OPTIMIZED MEMBRANE COMPOSITIONS AND THEIR POTENTIOMETRIC RESPONSE PROPERTIES FOR THE MERCURY(II) MEMBRANE SENSOR

| Number | Composition (%) | | | | Slope (mV/decade) | Dynamic range (M) |
|---|---|---|---|---|---|---|
| | PVC | L | NaTPB | DBP/DOP | | |
| 1 | 31.07 | 0.52 | 3.92 | 64.49, DBP | No response | No response |
| 2 | 31.01 | 3.63 | 0.00 | 65.36, DOP | No response | No response |
| 3 | 30.70 | 3.78 | 2.06 | 60.76, DBP | 25.71 | $1.0 \times 10^{-1}$ - $1.0 \times 10^{-6}$ |
| 4 | 33.19 | 3.89 | 3.35 | 59.57, DOP | 23.20 | $1.0 \times 10^{-1}$ - $1.0 \times 10^{-6}$ |
| 5 | 33.68 | 4.09 | 1.47 | 60.76, DOP | 28.68 | $1.0 \times 10^{-1}$ - $1.0 \times 10^{-6}$ |
| 6 | 33.43 | 4.21 | 2.11 | 60.25, DBP | 29.80 | $1.0 \times 10^{-1}$ - $1.0 \times 10^{-6}$ |
| 7 | 29.86 | 4.73 | 3.35 | 62.06, DBP | 34.45 | $1.0 \times 10^{-1}$ - $1.0 \times 10^{-5}$ |
| 8 | 28.21 | 4.75 | 2.47 | 64.57, DBP | 17.70 | $1.0 \times 10^{-1}$ - $1.0 \times 10^{-5}$ |
| 9 | 33.40 | 5.06 | 3.16 | 58.38, DBP | 30.10 | $1.0 \times 10^{-1}$ - $1.0 \times 10^{-6}$ |
| 10 | 30.41 | 5.20 | 4.00 | 60.57, DBP | 29.03 | $1.0 \times 10^{-1}$ - $1.0 \times 10^{-6}$ |
| 11 | 29.30 | 5.70 | 2.13 | 62.87, DBP | 27.60 | $1.0 \times 10^{-1}$ - $1.0 \times 10^{-6}$ |
| 12 | 28.73 | 7.26 | 4.81 | 59.20, DOP | 16.65 | $1.0 \times 10^{-1}$ - $1.0 \times 10^{-6}$ |

these cations, Hg(II) shows more sensitive potential responses than the others. A number of characteristics are required for a sensor to be considered as a suitable sensor for determination of ions, including selectivity and lifetime. Those characteristics have been taken into account in order to assertion the utility of BBDT as an ionophore, membrane composition, and the properties of the additives employed.

Preliminary experiments were carried out to obtain an optimum membrane composition. The optimized membrane was used to test the performance of the membrane characteristics.

### A. Influence of Membrane Composition

In a preliminary experiment, membranes with and without carrier were constructed. The membrane with no carrier displayed insignificant selectivity toward mercury(II) and their response was not reliable. However, in the presence of BBDT, the optimized membrane demonstrated Nernstian response and remarkable selectivity for Hg(II) over several common inorganic cations. The preferential response of the membrane toward Hg(II) is believed to be associated with coordination of Hg(II) with the ligand. Besides the critical role of the nature of the ion-carrier in preparing membrane-selective sensors, some other important features of the PVC membrane such as amount of the ionophore, nature of the solvent mediator (plasticizer), amount of plasticizer to PVC ratio, and especially the nature of additives used are known to significantly influence the sensitivity and selectivity of ion selective electrodes [6]–[8]. Thus, several membrane compositions were investigated by varying the ratio of PVC, plasticizer, and the ionophore (Table II). The potentiometric response of the membrane was greatly improved in the presence of ionophore. The presence of lipophilic ionic sites is beneficial for both neutral carrier and charged carrier-based ion-selective electrodes [9], [10]. Neutral carrier based cation-selective electrodes require lipophilic ionic sites with a charge sign opposite to that of the primary ion for obtaining Nernstian responses [11], [12]. However, for the charged carrier-based ion-selective electrodes, the charge sign of the ionic sites that gives the highest potentiometric selectivities depends on the charge of the ionophore, charge of the primary and interfering ions, as well as on the stoichiometry of their complexes with the ionophore [13]. Therefore, from the different effect that the charge of the added ionic sites has on neutral and charged carrier-based ion-selective electrodes, the carrier mechanism may be evaluated by investigating membranes that contain ionic sites of opposing charges [14], [15].

As it is obvious from Table II, among the two different plasticizers used, DBP was a more effective solvent mediator in preparing the Hg(II) membrane sensor. It should be noted that the nature of the plasticizer influences both the dielectric constant of the membrane and the mobility of the ionophore and its complex. Initially, plasticizers were applied to the polymer matrix in order to decrease its viscosity and provide mobility of the membrane constituents within the membrane phase. In relation to the role of plasticizer in a PVC membrane, it should be noted that plasticizer acts as a membrane solvent, affecting membrane selectivity through both extraction of ions into organic phase, and influencing their complexation with the ionophore [16]. The drastic influence of the dielectric constant on the membrane selectivity stems from the contribution of the dielectric medium to the free energy of transfer. The introduction of polar or polarizable groups prevents these plasticizers from being exuded but they all have somewhat worse selectivities than the analogues because of the lack of such groups. The critical response characteristics of the proposed electrode were investigated according to IUPAC recommendations [13], [14]. The membrane with a composition of 2.11% NaTPB, 60.25% DBP, 33.43% PVC, and 4.21% BDDA (No. 6 in Table II) generated a stable potential response in solutions containing Hg(II) after conditioning for 24 h in a 0.010 M Hg(II) solution.

### B. pH Effect

The effect of pH of the test solutions [$1.0 \times 10^{-3}$, $1.0 \times 10^{-4}$, and $1.0 \times 10^{-6}$ M Hg(II)] on the sensor potential was investigated by following the potential variation of the sensor over a pH range of 1.5–12. The pH was adjusted by introducing small drops of hydrochloric acid (0.10 M) and/or sodium hydroxide (0.10 M) to the sample solution. The influence of pH on the response of the membrane sensor is shown in Fig. 2. The results show that the potentials of the sensor remain constant from pH of 2.0 to 11.5. Under more acidic conditions, the ligand may be protonated and thereby losing its capacity to form a complex with the metal ions. When the pH is nearly neutral, the fundamental cation is $[HgOH]^+$, which reacts with the ligand. The drift of potential values at pH $> 11.5$ is attributed to the formation of mercury(II) hydroxide [17], [18].

TABLE III
ANOVA TEST METHOD FOR THE REPRODUCIBILITY AND REPEATABILITY OF THE SENSOR FOR Hg(II) CONCENTRATION OF $1.0 \times 10^{-5}$ M

| | Day 1 | Day 2 | Day 3 | Day 4 |
|---|---|---|---|---|
| Electrod 1 | 29.90 | 29.80 | 29.89 | 30.02 |
| Electrod 2 | 30.03 | 30.04 | 30.06 | 30.14 |
| Electrod 3 | 28.10 | 28.70 | 28.70 | 29.80 |
| Electrod 4 | 30.30 | 30.57 | 31.20 | 31.30 |
| RSD (%) | 3.39 | 2.64 | 3.49 | 2.21 |
| Repeatability of preparation sensors on any day (%) | 96.60 | 97.36 | 96.51 | 97.79 |
| Reproducibility of preparation sensors (%) | 97.20 | | | |
| Between-sample mean square | 1.1856 | | | |
| Within-sample mean square | 9.3655 | | | |
| $F_{cal(3,12)}$ | 0.506 | | | |
| $F_{tab(3,12)}$ | 3.490 | | | |

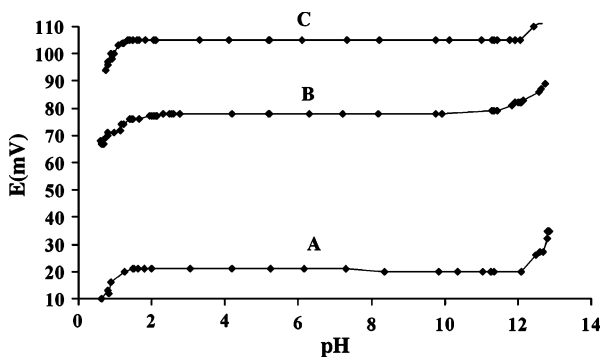


Fig. 2. Influence of pH on the response of the membrane: (a) $1.0 \times 10^{-6}$ M, (b) $1.0 \times 10^{-4}$ M, and (c) $1.0 \times 10^{-3}$ M Hg(II).

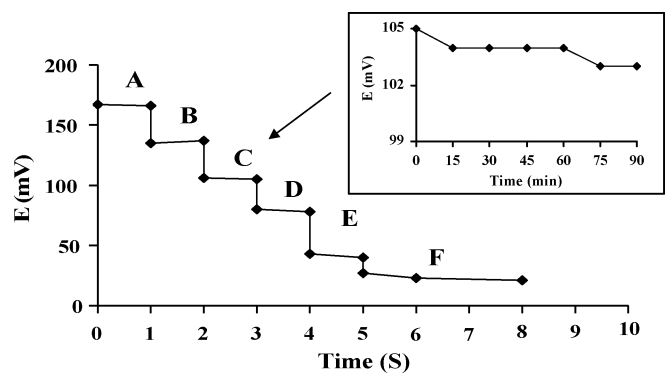


Fig. 3. Response time of the electrode: (a) 0.10 M, (b) $1.0 \times 10^{-2}$ M, (c) $1.0 \times 10^{-3}$ M, (d) $1.0 \times 10^{-4}$ M, (e) $1.0 \times 10^{-5}$ M, and (f) $1.0 \times 10^{-6}$ M Hg(II).

### C. Response, Reproducibility, and Lifetime

The response time of the $Hg^{2+}$-ISE was defined as $t_{95}$ for a $1.0 \times 10^{-6}$ M $Hg^{2+}$ solution when the mercury ion concentration was rapidly increased from $1.0 \times 10^{-6}$ to $1.0 \times 10^{-1}$ M, where $t_{95}$ is the time required for the sensor to reach 95% of the steady-state potentiometric value. The best response time of 1 s was recorded for membrane having the optimized conditions. The potentials generated by this membrane remained stable for more than 60 min after which it started deviating (Fig. 3).

The stability and reproducibility of the electrodes were also tested using analysis of variance (ANOVA) with a test of null hypothesis (F-test) was used. The standard deviation of ten replicate measurements at several mercury concentrations over periods of 20 min and 2 h were $\leq$0.5%. ANOVA test method used to show the reproducibility and repeatability of the sensor for Hg(II) concentration of $1.0 \times 10^{-5}$ M. The results are given in Table III. The results of the calculations showed that $F_{cal(3,12)}(= 0.506)$ was less than that $F_{tab(3,12)}(= 3.490)$, meaning that there was not any significant difference between the sensor responses signals during measurements, and confirmed the stability and reproducibility.

The lifetime of sensors is based on ionophore in solvent polymeric membranes, distribution coefficient of the ionophore and also to the plasticizer [19]. The lifetime of the sensors was worked out by performing calibrations periodically with standard solutions and calculating the slopes over the concentration ranges of $1.0 \times 10^{-6}$ to $1.0 \times 10^{-1}$ M of $Hg(NO_3)_2$ solutions. The experimental results showed that the lifetime of the present sensor was over 90 days (Table IV). During this time, the detection limit and the slope of the electrode remained almost constant. Subsequently, the electrochemical behavior of

TABLE IV
RESPONSE OF THE SENSOR DURING 90 DAYS

| Time (day) | Slope (mV/decade) | Dynamic range (M) | Detection Limit (M) |
|---|---|---|---|
| 1 | +29.8 ±1. 0 | $1.0\times10^{-6}$- $1.0\times10^{-1}$ | $3.7 \times 10^{-7}$ |
| 5 | +29.8 ±1. 0 | $1.0\times10^{-6}$- $1.0\times10^{-1}$ | $3.7 \times 10^{-7}$ |
| 12 | +29.8 ± 1.0 | $1.0\times10^{-6}$- $1.0\times10^{-1}$ | $3.7 \times 10^{-7}$ |
| 20 | +29.8 ± 1.0 | $1.0\times10^{-6}$- $1.0\times10^{-1}$ | $3.7 \times 10^{-7}$ |
| 35 | +29.8 ± 1.0 | $1.0\times10^{-6}$- $1.0\times10^{-1}$ | $3.7 \times 10^{-7}$ |
| 50 | +29.8 ± 1.0 | $1.0\times10^{-6}$- $1.0\times10^{-1}$ | $3.7 \times 10^{-7}$ |
| 70 | +29.8 ±1. 0 | $1.0\times10^{-6}$- $1.0\times10^{-1}$ | $3.7 \times 10^{-7}$ |
| 80 | +29.7 ± 1.0 | $1.0\times10^{-6}$- $1.0\times10^{-1}$ | $4.1 \times 10^{-7}$ |
| 90 | +29.7 ± 1.0 | $1.0\times10^{-6}$- $1.0\times10^{-1}$ | $4.2 \times 10^{-7}$ |

TABLE V
VALUES OF SELECTIVITY COEFFICIENTS OF $Hg^{2+}$-SELECTIVE ELECTRODE

| Interfering ion | $\log K_{I,J}^{POT}$ |
|---|---|
| $Cd^{2+}$ | -5.80 |
| $Hf^{4+}$ | -6.91 |
| $La^{3+}$ | -5.59 |
| $Ag^{+}$ | -3.12 |
| $Co^{2+}$ | -4.50 |
| $Mg^{2+}$ | -4.50 |
| $Pt^{4+}$ | -2.54 |
| $K^{+}$ | -3.31 |
| $Sr^{2+}$ | -5.45 |
| $Ti^{3+}$ | -6.67 |
| $Fe^{2+}$ | -3.92 |
| $V^{3+}$ | -6.08 |
| $Al^{3+}$ | -4.52 |
| $Li^{+}$ | -4.13 |
| $Na^{+}$ | -3.01 |
| $Th^{4+}$ | -5.83 |
| $Ca^{2+}$ | -6.63 |
| $Ni^{2+}$ | -4.74 |
| $Cr^{3+}$ | -5.82 |
| $Cu^{2+}$ | -5.44 |
| $Zn^{2+}$ | -3.79 |
| $Tl^{+}$ | -3.30 |
| $Cs^{+}$ | -3.29 |
| $Pb^{2+}$ | -4.74 |
| $Zr^{4+}$ | -6.89 |
| $U^{6+}$ | -5.83 |
| $Y^{3+}$ | -5.96 |
| $Mn^{2+}$ | -4.03 |

the sensor gradually deteriorated which may be due to ageing of the polymer (PVC), the plasticizers, and the ionophore. Therefore, the sensor can be used for at least 3 months, without a considerable change in their response characteristic towards $Hg^{2+}$.

### D. Potentiometric Selectivity

The selectivity behavior is obviously one of the important characteristics of membrane sensors in which reliable measurement of the target sample is determined to be possible or not. Potentiometric selectivity coefficients ($K_{potHg}$) describing the preference of the membrane for an interfering ion $M^{n+}$ relative to Hg(II) were determined by the separate solution method (SSM) [20]. Table V lists the potentiometric selectivity coefficient data of the sensor for several cations relative to Hg(II). The selectivity coefficients clearly indicate that the sensor is highly selective to Hg(II) over a numbers of other cations, and therefore the sensor has been found to be chemically inert to other ions. The response of the sensor for different cations is shown in Fig. 4(a) and (b), shows the best selectivity to Hg(II).

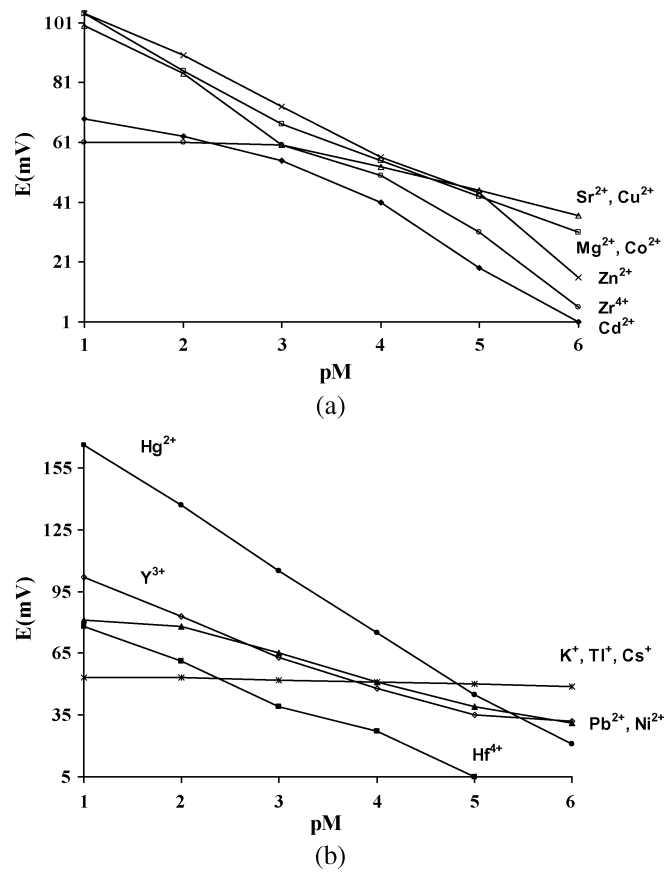


Fig. 4. The response of the sensor for two different cations groups as (a) and (b).

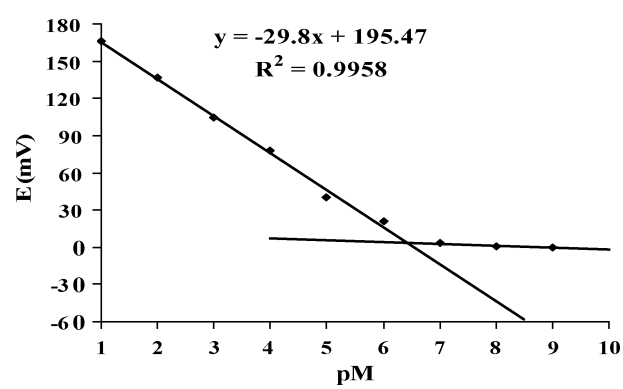


Fig. 5. Potentiometric response of the sensor.

### E. Calibration Range

Using the optimized membrane composition described above, the potentiometric response of the sensor was studied for $Hg^{2+}$ in the concentration range of $1.0\times10^{-9}$ to $1.0\times10^{-1}$ M at 25 °C. The calibration curve of the electrode is shown in Fig. 5. The results show a Nernstian response of 29.8 mV/decade of $Hg^{2+}$ concentration, and the wide linear range within the concentration range from $1.0 \times 10^{-6}$ to $1.0 \times 10^{-1}$ M Hg(II), and with a slope of 29.8 mV/decade.

The limit of detection defined as the concentration of mercury obtained when extrapolating the linear region of the calibration curve to the baseline potential was $3.7\times10^{-7}$ M Hg(II) (Fig. 5).

TABLE VI
RECOVERY OF MERCURY IONS FROM DIFFERENT WATER SAMPLE

| Sample type | $Hg^{2+}$ added (M) | $Hg^{2+}$ found (M) | Recovery(%) | FAAS[b] |
|---|---|---|---|---|
| Tap water[a] | — | <LOD | — | <LOD |
| Tap water | $5.00\times10^{-5}$ | $5.30(\pm0.02)\times10^{-5}$ | 100.6 | $5.20(\pm0.04)\times10^{-5}$ |
| Tap water | $3.15\times10^{-5}$ | $3.10(\pm0.07)\times10^{-5}$ | 98.4 | $3.20(\pm0.09)\times10^{-5}$ |
| River water (Zayandehrood)[a] | — | <LOD | — | <LOD |
| River water (Zayandehrood) | $5.00\times10^{-5}$ | $5.06(\pm0.06)\times10^{-5}$ | 98.0 | $5.01(\pm0.08)\times10^{-5}$ |
| River water (Zayandehrood) | $4.00\times10^{-5}$ | $3.85(\pm0.04)\times10^{-5}$ | 97.5 | $3.95(\pm0.08)\times10^{-5}$ |
| Waste water | — | <LOD | — | <LOD |
| Waste water | $5.00\times10^{-5}$ | $5.12(\pm0.09)\times10^{-5}$ | 102.4 | $5.20(\pm0.09)\times10^{-5}$ |
| Waste water | $3.00\times10^{-5}$ | $3.11(\pm0.02)\times10^{-5}$ | 103.7 | $3.05(\pm0.08)\times10^{-5}$ |

a) Isfahan city.
b) Furnace atomic absorption spectrometry.

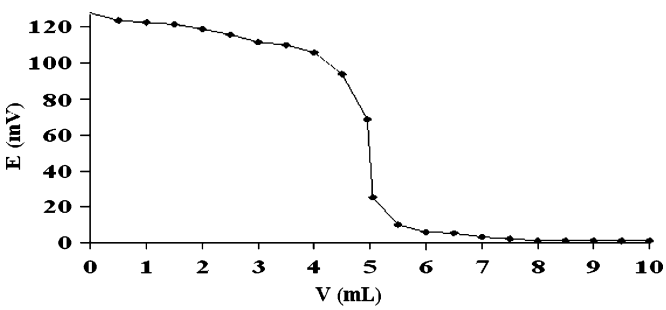


Fig. 6. Application of the mercury membrane sensor to the potentiometric titration of 50.0 ml 0.0010 M $Hg^{2+}$ with 0.010 M EDTA.

## IV. ANALYTICAL APPLICATIONS

The proposed membrane sensor was found to work well under laboratory conditions. It can be seen that the amount of Hg(II) ions can be accurately determined using the proposed sensor. To assess the applicability of the proposed sensor to real samples, an attempt was made to determine Hg(II) an industrial wastewater, river water, and some synthetic samples. The samples were collected by a routine technique, preserve by acidification with $HNO_3$, and stored in polyethylene bottles and analyzed within 12 h of collection. Each sample was analyzed in triplicate, using the sensor by standard addition method and also using flameless atomic absorption spectrometry as a standard method. The results are given in Table VI, which shows that the amount of mercury recovered with the help of the sensor are in good and the accuracy also is well, thereby reflecting the utility of the proposed method.

The sensor was also successfully applied as an indicator electrode in the potentiometric titration of $Hg^{2+}$ solution with EDTA. Typical results for the titration of a 50 ml of $1.0 \times 10^{-3}$ M Hg(II) solution with 0.010 M EDTA is shown in Fig. 6 with a very good inflection point, showing perfect stoichiometry, is observed in the titration plot. This titration was repeated three times with end point volume of $4.98 \pm 0.03$ ml of EDTA solution. The resulting titration curve is unsymmetrical. Before the titration end point, the measured potential shows a usual logarithmic change with amount of the titrant added, while the potential response after the end point was almost constant, due to the low concentration of free Hg(II) ions in the solution could be determined accurately by extrapolation of the two linear portions of the titration plot.

## V. CONCLUSION

The proposed potentiometric sensor has good operating characteristics including Nernstian response, reasonable detection limit, relatively high selectivity, wide dynamic range, and fast response. These characteristics and the typical applications presented in this paper make the sensor suitable for measuring Hg(II) content in real samples without a significant interaction from concomitant cationic or anionic species.

## REFERENCES

[1] P. Shetty and N. Shetty, "Complexometric method for the determination of mercury using metabisulphite as selective masking reagent," *Indian J. Chem. Tech.*, vol. 11, pp. 163–165, 2004.
[2] S. S. M. Hassan, M. B. Saleh, A. A. Abdel Gaber, R. A. H. Mekheimer, and N. A. Abdelkream, "Novel mercury(II) ion-selective polymeric membrane sensor based on ethyl-2-benzoyl 2-phenylcarbamoyl acetate," *Talanta*, vol. 53, pp. 285–293, 2000.
[3] P. Buhlmann, E. Pretsch, and E. Bakker, "Carrier-based ion-selective electrodes and bulk optodes. 2, Ionophores for potentiometric and optical sensors," *Chem. Rev.*, vol. 98, pp. 1593–1687, 1998.
[4] S. Megdadi, M. Amirnasr, and H. Mhamoudkhani, "[N, N′-bis(1-benzoylethylidene) proplenediiminato(2-)]diprrolidineccobalt(III) percholorate," *Acta Cryst.*, vol. E62, pp. m69–m71, 2006.
[5] R. P. Buck and V. V. Cosofret, "Recommended procedure for calibration of ion-selective electrode," *Pure Appl. Chem.*, vol. 65, pp. 1849–1858, 1993.
[6] M. Shamsipur, G. Khayatian, and S. Tangestaninejad, "Thiocyanate-selective membrane electrode based on octabromo-tetraphenylporphyrinato manganese(III) chloride," *Electroanalysis*, vol. 11, pp. 1340–1344, 1999.
[7] A. Rouhollahi and M. Shamsipur, "Highly selective triiodide PVC membrane electrode based on a charge-transfer complex of iodine with 2,4,6,8-tetraphenyl-2,4,6,8-tetraazabicyclo[3.3.0]octane," *Anal. Chem.*, vol. 71, pp. 1350–1353, 1999.
[8] K. H. Farhadi, R. Maleki, and M. Shamsipur, "Triiodide ion selective polymeric membrane electrode based on a ketoconazole-triiodide ion pair," *Electroanalysis*, vol. 14, pp. 760–766, 2002.

[9] U. Schaller, E. Bakker, U. E. Spichiger, and E. Pretsch, "Ionic additives for ion-selective electrodes based on electrically charged carriers," *Anal. Chem.*, vol. 66, pp. 391–398, 1994.
[10] E. Bakker, E. Malinowska, R. D. Schiller, and M. E. Meyerhoff, "Anion-selective membrane electrodes based on metalloporphyrins: The influence of lipophilic anionic and cationic sites on potentiometric selectivity," *Talanta*, vol. 41, pp. 881–890, 1994.
[11] P. Buhlmann, S. Yajima, K. Tohda, K. Umezawa, S. Nishizawa, and Y. Umezawa, "Studies on the phase boundaries and the significance of ionic sites of liquid membrane ion-selective electrodes," *Electroanalysis*, vol. 7, pp. 811–816, 1995.
[12] S. Yajima, K. Tohda, P. Buhlmann, and Y. Umezawa, "Donnan exclusion failure of neutral ionophore based ion-selective electrodes studied by optical second-harmonic generation," *Anal. Chem.*, vol. 69, pp. 1919–1924, 1997.
[13] S. Amemiya, P. Buhlmann, E. Pretsch, B. Rusterholz, and Y. Umezawa, "Cationic or anionic sites selectivity optimization of ion-selective electrodes based on charged ionophores," *Anal. Chem.*, vol. 72, pp. 1618–1631, 2000.
[14] E. Bakker, P. Buhlmann, and E. Pretsch, "Carrier-based ion-selective electrodes and bulk optodes. 1. General characteristics," *Chem. Rev.*, vol. 97, pp. 3083–3132, 1997.
[15] U. Schaller, E. Bakker, and E. Pretsch, "Carrier mechanism of acidic ionophores in solvent polymeric membrane ion-selective electrodes," *Anal. Chem.*, vol. 67, pp. 3123–3132, 1995.
[16] D. Ammann, *Ion-Selective Electrodes*. New York: Springer-Verlag, 1986.
[17] F. A. Cotton and G. Wilkinson, *Quimica Inorganica Avanzada*, 4th ed. Limusa, Mexico: , 1996, pp. 73–732.
[18] E. Lindner, F. Behm, P. Oggenfuss, D. H. Welti, D. Ammann, and W. E. Morf, "Lead-selective neutral carrier based liquid membrane electrode," *Anal. Chem.*, vol. 56, pp. 1127–1131, 1984.
[19] U. Oesch and W. Simon, "Lifetime of neutral carrier based ion-selective liquid-membrane electrodes," *Anal. Chem.*, vol. 52, pp. 700–704, 1980.
[20] E. Bakker, E. Pretsch, and P. Buhlmann, "Selectivity of potentiometric ion sensors," *Anal. Chem.*, vol. 72, pp. 1127–1133, 2000.
[21] R. K. Mahajan, I. Kaur, and T. S. Lobana, "A mercury(II) ion-selective electrode based on neutral salicylaldehyde thiosemicarbazone," *Talanta*, vol. 59, pp. 101–105, 2003.
[22] J. Lu, X. Tong, and X. He, "A mercury ion-selective electrode based on a calixarene derivative containing the thiazole azo group," *J. Electroanal. Chem.*, vol. 540, pp. 111–117, 2003.
[23] A. K. Singh, G. Bhattacharjee, and R. Singh, "Mercury(II)-selective membrane electrode using tetrathia-diazacyclotetradeca-2,9-diene as neutral carrier," *Sens. Actuators B*, vol. 99, pp. 36–41, 2004.
[24] M. H. Mashhadizadeh and I. Sheikhshoaie, "Mercury(II) ion-selective polymeric membrane sensor based on a recently synthesized Schiff base," *Talanta*, vol. 60, pp. 73–80, 2003.
[25] S. S. M. Hassan, M. B. Saleh, A. A. A. Gaber, R. A. H. Mekheimer, and N. A. Abdel Kream, "Novel mercury (II) ion-selective polymeric membrane sensor based on ethyl-2-benzoyl-2-phenylcarbamoyl acetate," *Talanta*, vol. 53, pp. 285–293, 2000.
[26] V. K. Gupta, S. Chandra, and H. Lang, "A highly selective mercury electrode based on a diamine donor ligand," *Talanta*, vol. 66, pp. 575–580, 2005.

**Ali A. Ensafi** received the Degree in chemistry and the Ph.D. degree from Shiraz University, Shiraz, Iran, in 1988 and 1991, respectively.

Then, he joined the College of Chemistry, Isfahan University of Technology, Isfahan, Iran. He became a Full Professor in 2001. His research interest comprises the development of new electrochemical or chromogenic chemosensors and molecular probes for anions, cations, and neutral chemical species.

**S. Meghdadi** received the M.Sc. degree from the Isfahan University of Technology, Isfahan, Iran, in 1998. Then, she joined the College of Chemistry, Isfahan University of Technology, Isfahan, Iran, as a Lecturer.

**Alireza R. Allafchian** received the B.S. and M.S. degrees from the Isfahan University of Technology, Isfahan, Iran, in 2005 and 2007, respectively.