

Full Paper

Mercury Recognition: A Potentiometric Membrane Sensor based on 4-(Benzylidene amino)-3,4-dihydro-6-methyl-3-thioxo-1,2,4-triazin-5(2H)one

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Abstract- In this study, a Hg²⁺ potentiometric membrane sensor was prepared based on the highly selective complexation between 4-(benzylidene amino)-3,4-dihydro-6-methyl-3-thioxo-1,2,4-triazin-5(2H)one as ionophore and Hg²⁺ ion. The electrode exhibits a Nernstian response for Hg²⁺ over a concentration range (1.0×10⁻² to 1.0×10⁻⁶ M) with a slope of 29.06±0.4 mV per decade. The limit of detection of the sensor is 6.0×10⁻⁷ M. The sensor has a relatively fast response time (~10 s) and a useful working pH range of 3.5–6.5. Interference of some cations was also evaluated. It was used as an indicator electrode in potentiometric titration of Hg²⁺ ion with EDTA and in direct determination of Hg²⁺ in water and wastewater samples. The results indicate that this electrode is sensitive for determination of Hg²⁺ ion.

Keywords- Hg²⁺, 4-(Benzylidene Amino)-3,4-dihydro-6-methyl-3-thioxo-1,2,4-triazin-5(2H)one, Potentiometric Membrane Sensor

1. INTRODUCTION

Mercury has specific characteristics that are largely employed for different industrial purposes, such as in thermometers, batteries and lamps. In addition, this element is toxic elements that can be found as contaminant in many different chemical forms, which can be easily inter-converted and transported through geochemical processes and pollute the environment [1]. Its neurotoxicity has been reported to result in hearing loss, mental deterioration, speech difficulty, impaired vision, vestibular dysfunction and autism. It is considered by the Environmental Protection Agency (EPA) as a highly dangerous element because of its accumulative and persistent character in the environment and biota [2]. The common techniques for detection of mercury ion, such as thermolysis coupled with atomic absorption spectrometry, cold vapor atomic fluorescence spectrometry, gas chromatography, neutron activation analysis and isotope mass spectrometry are often expensive, complex and unsuitable for on-site analyses. Also, all of them need long analysis time and considerable sample volumes. A low-cost, easy-to-use and reliable device is still much needed for environmental monitoring and green chemistry of mercury.

Development of potentiometric sensors for detection of hazardous metal ions is of great interest in the environmental fields. Potentiometry by ion selective electrodes are simple, low cost, accurate and rapid method which is the reason behind the increasing interest of their uses [3-17]. The main problem in the field of ion potentiometric membrane sensors is finding a suitable and selective sensing material for use in the membrane. Low selectivity of many ionophores, which have been introduced to Hg^{2+} monitoring in previous reports [18-23], confirms the necessity of more investigation to finding more suitable ionophores.

Therefore, in this work, 4-(benzylidene amino)-3,4-dihydro-6-methyl-3-thioxo-1,2,4-triazin-5(2H)one (Fig. 1) was used as a selective sensing material in the PVC membrane for the first time. The proposed sensor was successfully applied for direct determination of the mercury ions in environmental samples without any separation or purification.

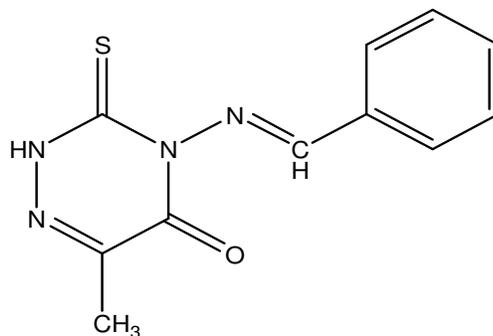


Fig. 1. The structure of 4-(benzylidene amino)-3,4-dihydro-6-methyl-3-thioxo-1,2,4-triazin-5(2H)one

2. EXPERIMENTAL SECTION

2.1. Apparatus

The glass cell, where the Hg^{2+} ion-selective electrode was placed, consisted of two Ag/AgCl reference electrodes (Azar electrode, Iran) as the internal and external reference electrodes. Both electrodes were connected to a Corning ion analyzer with a 250 pH/mV meter with ± 0.1 mV precision

2.2. Reagents and Materials

Reagent grade dibutyl phthalate (DBP), nitrobenzene (NB), high relative molecular weight polyvinyl chloride (PVC), sodium tetraphenyl borate (NaTPB) and tetrahydrofuran (THF) were purchased from Merck and used as received. 4-(benzylidene amino)-3,4-dihydro-6-methyl-3-thioxo-1,2,4-triazin-5(2H)one was synthesized and purified as described elsewhere [24]. Nitrate salts of the cations used (from Merck and Aldrich) were all of the highest purity available, and used without any further purification except for vacuum drying over P_2O_5 . Doubly distilled deionized water was used throughout.

2.3. Electrode Preparation

The general procedure to prepare the PVC membrane was as followed: Different amounts of the 4-(benzylideneamino)-3,4-dihydro-6-methyl-3-thioxo-1,2,4-triazin-5(2H)one (ionophore) along with appropriate amounts of additive were weighed. Then, known amounts of PVC and plasticizer were added to the mixture. The mixture was dissolved in 2 mL of tetrahydrofuran (THF), and the solution was mixed well. The resulting mixture was transferred into a glass dish of 2 cm diameter. The solvent was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (3-5 mm o.d.) was dipped into the mixture for about 10 s so that a transparent membrane of about 0.3 mm thickness was formed. The tube was then pulled out from the mixture and kept at room temperature for about 24 h. The tube was then filled with an internal filling solution (1.0×10^{-3} M $\text{Hg}(\text{NO}_3)_2$). The electrode was finally conditioned for 24 h by soaking in a 1.0×10^{-3} M $\text{Hg}(\text{NO}_3)_2$ solution.

2.4. Emf Measurements

The following cell was assembled for the conduction of the emf (electromotive force) measurements; Ag–AgCl, KCl (satd.) | internal solution, 1.0×10^{-3} M $\text{Hg}(\text{NO}_3)_2$ | PVC membrane | sample solution | Ag–AgCl, KCl (satd.)

A Corning ion analyzer 250 pH/mV meters was used for the potential measurements at 25.0 ± 0.1 °C. Activities were calculated according to the Debye- Hückel procedure.

3. RESULTS AND DISCUSSION

3.1. Membrane Composition Effect on the Potential Response of the Sensor

Because the degree of sensitivity and selectivity for a certain ionophore is greatly related to the membrane ingredients, the influence of membrane composition on the potential responses of the Hg^{2+} sensor was inspected [25,26]. In this study, different membrane compositions, as shown in Table 1, were tested. As can be seen, the membrane with the composition of 33% PVC, 5% ionophore, 2% NaTPB and 60% DBP (no. 7) was the optimum one in the development of this sensor.

The Hg^{2+} ion extraction into the liquid membrane is a result of the high concentration of the ligand in the membrane. From Table 1, it was obvious that in the absence of ionophore (no. 1), the response of the recommended electrode was low (slope of 5.80 ± 0.4 mV per decade).

Table 1. The optimization of the membrane ingredients

Membrane No.	Composition (%)				Slope (mV per decade)
	PVC (%wt.)	Plasticizer (%wt.)	Ionophore (%wt.)	NaTPB (%wt.)	
1	30	DBP, 70	----	-----	5.80 ± 0.4
2	36	DBP, 60	3	1	24.82 ± 0.4
3	30	DBP, 65	3	2	21.15 ± 0.3
4	35	DBP, 60	5	-----	23.63 ± 0.4
5	34	DBP, 60	5	1	25.77 ± 0.3
6	30	DBP, 64	5	1	24.10 ± 0.3
7	33	DBP, 60	5	2	29.06 ± 0.4
8	31	DBP, 62	5	2	27.62 ± 0.2
9	28	DBP, 65	5	2	26.47 ± 0.3
10	30	DBP, 61	7	2	20.87 ± 0.3
11	33	NB, 60	5	2	25.63 ± 0.4

The second factor which helps the extraction of the Hg^{2+} ion is plasticizer. After the evaluation of two solvent mediators (NB and DBP), it was observed that the DBP displays the better sensitivity than NB (no. 7 and 11), because NB presented higher dielectric constant values than DBP, leading to the extraction of the polar interfering ions, which may have negative effects on the selectivity behavior of the sensor.

The presence of lipophilic anions in a cation-selective membrane was also considered. Actually, the presence of such anions in a cation-selective membrane, which is based on a neutral carrier, decreases the ohmic resistance and improves the response behavior and selectivity. Furthermore, when the extraction capability is poor, it increases the membrane electrode sensitivity [27-29]. Here, a NaTPB addition of 2% as an additive led to the slope increase of the potential sensor response from the sub-Nernstian value of 23.63 ± 0.4 mV per decade (no. 4) to the Nernstian value of 29.06 ± 0.4 mV per decade (no. 7).

3.2. Internal Solution

The concentration of the internal solution ($\text{Hg}(\text{NO}_3)_2$) of the electrode was changed from 1.0×10^{-2} M to 1.0×10^{-4} M and the potential response of the Hg^{2+} selective electrode was obtained (Fig. 2). It was found that the variation of concentration of the internal solution does not cause any significant differences in potential response, except for an expected change in the intercept of the resulting Nernstian plot. A 1.0×10^{-3} M concentration $\text{Hg}(\text{NO}_3)_2$ solution is quite appropriate for smooth functioning of the electrode system.

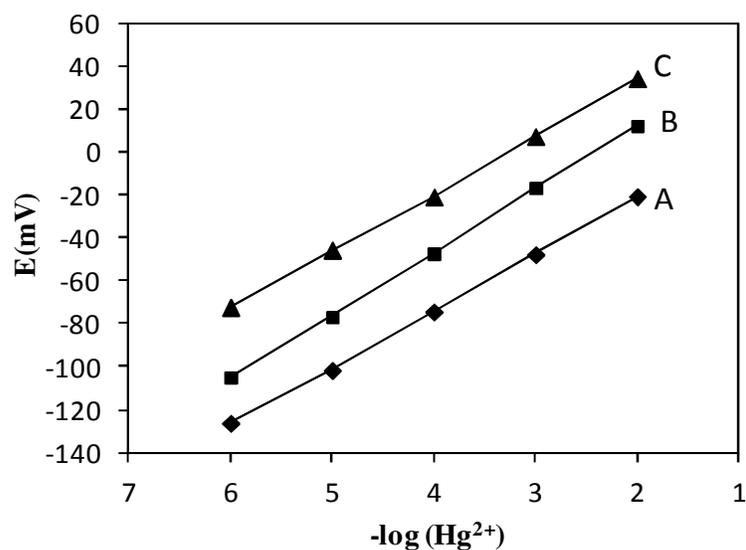


Fig. 2. The effect of concentration of internal reference solution concentration on the electrode response; (A) 1.0×10^{-2} M, (B) 1.0×10^{-3} M, (C) 1.0×10^{-4} M of Hg^{2+} ion

3.3. pH Effect on the Electrode Response

The influence of the pH of the test solution on the potential response of Hg^{2+} sensor investigated at 1.0×10^{-4} M Hg^{2+} concentration, in the pH value of 2.0 up to 11.0 (concentrated NaOH or HCl solutions were employed for the pH adjustment). In agreement with the resulting data (Fig. 3), the potential remained constant despite the pH change in the range of 3.5 to 6.5, indicating the applicability of this electrode in this specific pH range.

On the contrary, relatively noteworthy fluctuations in the potential vs. pH behavior took place below and above the formerly stated pH limits. In detail, the fluctuations above the pH value of 6.5 might be justified by the formation of the Hg^{2+} ion hydroxy complexes in the solution. On the other hand, the fluctuations below the pH value of 3.5 were attributed to the partial protonation of the employed ionophore.

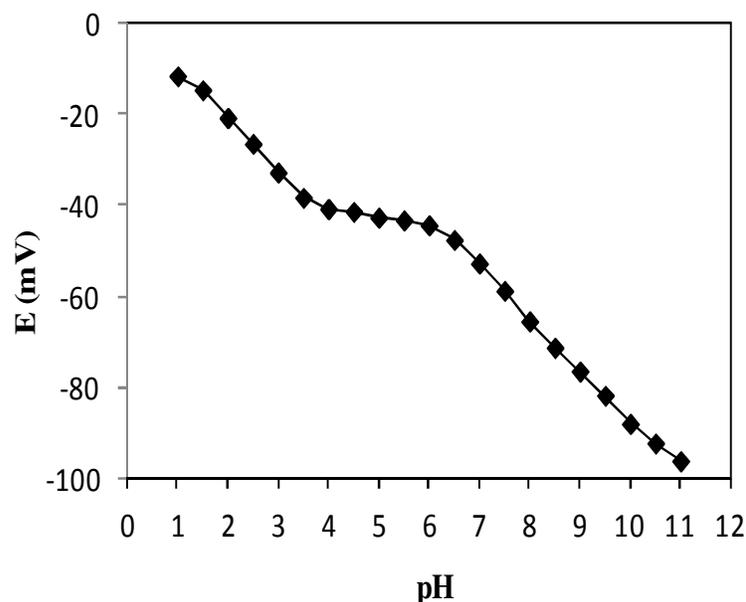


Fig. 3. The effect of the pH of the test solution (1.0×10^{-4} M Hg^{2+}) on the potential response of the mercury sensor

3.4. Response Time

The response time of an electrode is evaluated by measuring the average time required to achieve a potential within ± 0.1 mV of the final steady-state potential, upon successive immersion of a series of interested ions, each having a ten-fold difference in concentration. It is notable that the experimental conditions-like the stirring or flow rate, the ionic concentration and composition of the test solution, the concentration and composition of the solution to which the electrode was exposed before experiment measurements were

performed, any previous usages or preconditioning of the electrode, and the testing temperature have an effect on the experimental response time of a sensor [30].

In this work, dynamic response time was obtained by changing the Hg^{2+} concentration in solution, over a concentration range 1.0×10^{-6} to 1.0×10^{-2} M. The actual potential versus time traces is shown in Fig. 4. As can be seen, in whole concentration range the electrode reaches its equilibrium response in a relatively short time (~ 10 s).

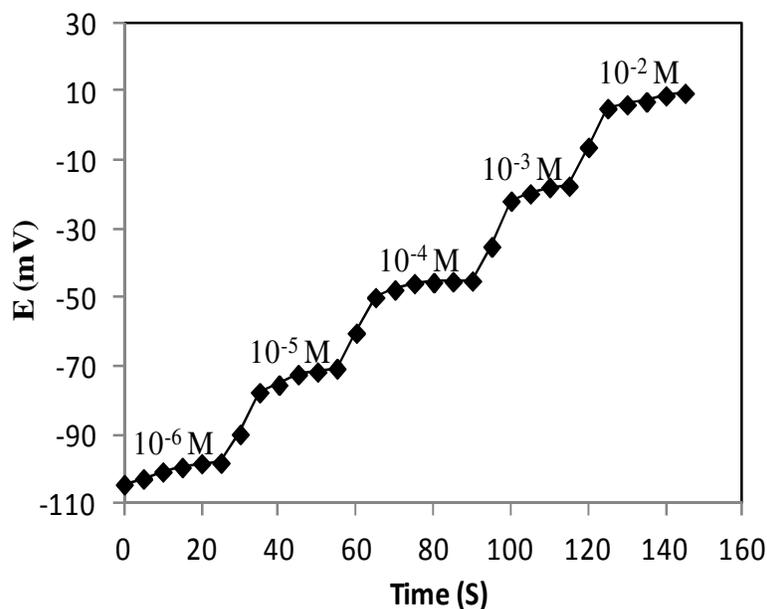


Fig. 4. Dynamic response of mercury sensor for step changes in concentration of Hg^{2+}

3.5. Measuring Range and Detection Limit

The measuring range of an ion-selective electrode includes the linear part of the calibration graph as shown in Fig. 5. The applicable measuring range of the proposed sensor is between 1×10^{-6} and 1×10^{-2} M.

In practice, detection limits for the most selective electrodes are in the range of 10^{-5} – 10^{-6} M. In this work the detection limit of the proposed membrane sensor was 6.0×10^{-7} M which was calculated by extrapolating the two segments of the calibration curve.

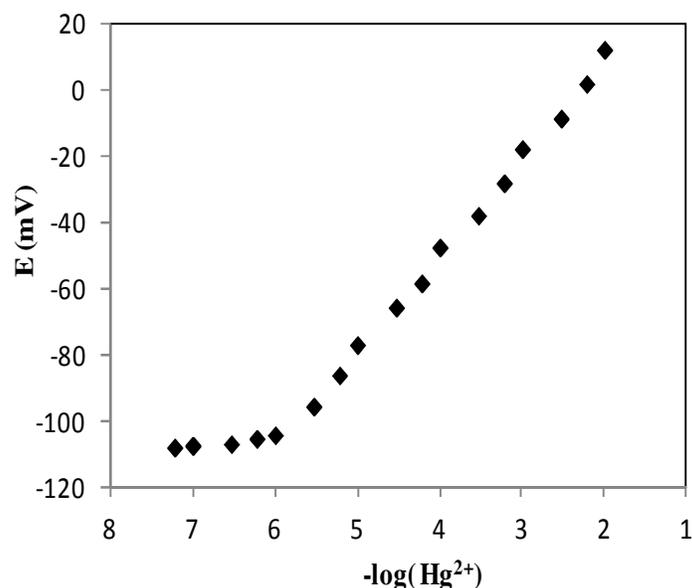


Fig. 5. The calibration curve of the Hg²⁺ membrane sensor

3.6. Selectivity

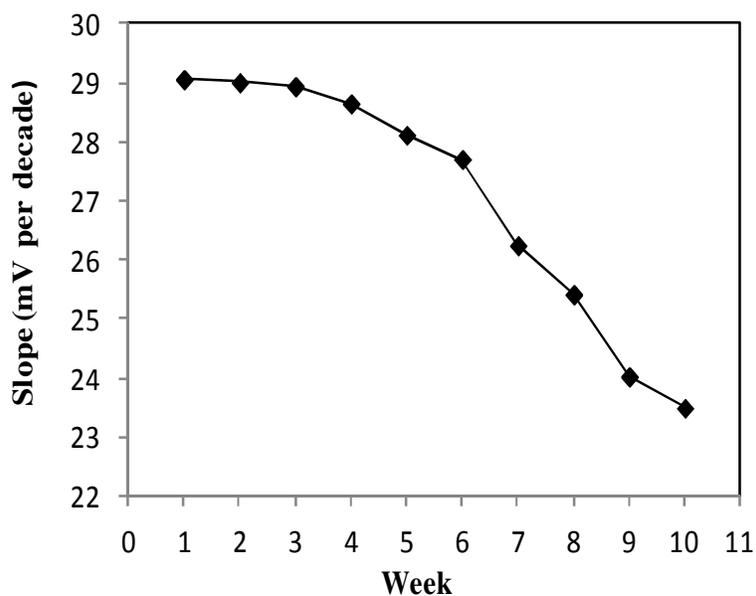
The potentiometric selectivity coefficients of the Hg²⁺ sensor were evaluated by the matched potential method (MPM) [31]. The resulting values of the selectivity coefficients are given in Table 2. The selectivity coefficients clearly indicate that the electrode is more selective to Hg²⁺ than to a number of other mono and bivalent metal ions. The selectivity coefficients seems to indicate negligible interferences in the performance of the electrode assembly.

3.7. Lifetime

It is well established that the loss of plasticizer, carrier, or ionic site from the polymeric film due to leaching into the sample is a primary reason for the limited lifetimes of the sensors. The average lifetime for most of the reported ion-selective sensors is in the range of 4–10 weeks. The average lifetime of this sensors was investigated by monitoring the changes in sensor slope with time. The sensors were tested for 10 weeks, during which time the electrodes were used extensively (one hour per day). Fig. 6 shows the changes in the slope of this sensor with time. The proposed sensors can be used for 6 weeks. There is a slight gradual decrease in the slopes (from 29.06 to 27.71 mV per decade) .

Table 2. The selectivity coefficients of various interfering cations for the membrane

Ion	K_{MPM}
Na^+	1.8×10^{-3}
Mg^{2+}	8.8×10^{-4}
Co^{2+}	1.9×10^{-2}
Pb^{2+}	1.6×10^{-3}
Ni^{2+}	8.9×10^{-3}
Cu^{2+}	5.7×10^{-2}
Zn^{2+}	2.5×10^{-3}
Cd^{2+}	1.2×10^{-3}
Ag^+	9.1×10^{-2}
Cr^{3+}	1.1×10^{-3}

**Fig. 6.** The lifetime of the Hg^{2+} membrane sensor

3.8. Analytical Application

Ion-selective electrodes tend to be; low in cost, simple to use, easily automated for rapid sampling, with low interferences from the matrix and can be applied to small volumes. These characteristics make them an ideal choice for environmental measurements.

The practical utility of the proposed membrane sensor was tested by its use as an indicator electrode for the titration of 50.0 mL of 1.0×10^{-5} M of Hg^{2+} ion solution with EDTA 1.0×10^{-3} M. The resulting titration curve is shown in Fig. 7. As can be seen, the amount of Hg^{2+} ions in solution can be accurately determined with the electrode.

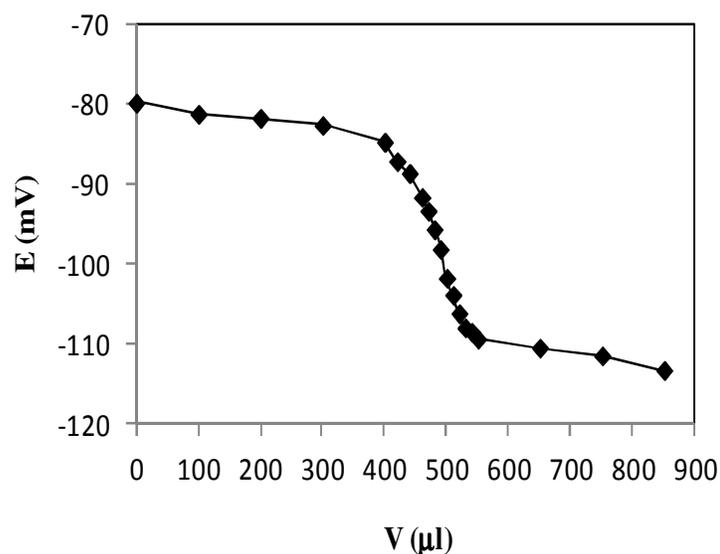


Fig. 7. Potentiometric titration curve of 50 mL 1.0×10^{-5} M Hg^{2+} ion with 1.0×10^{-3} M EDTA, using the proposed sensor as an indicator electrode

To assess the applicability of proposed electrode in real samples an attempt was made to determine Hg^{2+} ions in water and wastewater sample. The electrode was applied to the direct measurement of Hg^{2+} ion in Islamic Azad university of Shahre Rey laboratory wastewater and well water samples. All of the samples were filtered using a $0.45\text{-}\mu\text{m}$ pore size membrane filter to remove suspended particulate matter. To 100 mL of the some sample solutions were added 0.05 and 0.1 mg of the Hg^{2+} ions and to some of solutions were added nothing. All of the samples were adjusted to pH of about 5 and their potentials were measured by direct potentiometry. As shown in Table 3, the proposed method could be applied successfully for the direct determination of Hg^{2+} ions in water and wastewater samples.

3.9. Comparison of the proposed Hg²⁺ sensor and some of the best previously reports

The Nernstian slope, linearity range, detection limit, selectivity coefficients and response time of proposed Hg²⁺ sensor with some of the best previously reports are compared in Table 4. As is obvious, the results clearly indicate that the proposed sensor is superior to the previously reported ones in: Nernstian slope, response time and selectivity coefficients. In linearity range and detection limit, proposed sensor is closed to the best previously reports.

Table 3. Determination results of Hg²⁺ ions in various samples

Sample	added amount (mg L ⁻¹)	Measured with proposed sensor (mg L ⁻¹)
Well water	0	< LOD
Well water	0.5	0.61(±1.1) ^a
Well water	1.0	1.09(±1.4)
Wastewater	0	0.24(±1.0)
Wastewater	1.0	1.23(±1.3)

^a % RSD based on three replicate analysis

Table 4. Comparison of the proposed Hg²⁺ sensor and some of the previously reports

Ionophore	Slope mV/decade	Linear range(M)	Detection limit(M)	Interferences ions	Response time (S)	Ref.
Hexathia -18-crown-6-tetranone	29	1×10 ⁻⁶ -1×10 ⁻³	1.3×10 ⁻⁶	Tl ⁺ , Ag ⁺	<45	[18]
Dibenzodiazathia-18-crown-6-dione	29	8×10 ⁻⁶ -1×10 ⁻²	6×10 ⁻⁶	Ag ⁺ , Pb ²⁺ , Cd ²⁺	10	[19]
2-mercaptobenzimidazole	28.5	1×10 ⁻⁵ -1×10 ⁻¹	6×10 ⁻⁷	Ag ⁺ , NH ₄	20-100	[20]
Bis [5-((4- nitrophenyl) azo salicyladehyde)]	28.5	7×10 ⁻⁷ -5×10 ⁻²	2×10 ⁻⁷	----	10	[15]
N-(O,O-di isopropyl thio phosphoryl)- thiobenzamide	29	5×10 ⁻⁵ -1×10 ⁻²	4.7×10 ⁻⁶	Fe ²⁺	----	[21]
1,4-Dithia-12-crown-4	30	1×10 ⁻⁶ -1×10 ⁻³	----	Pb ²⁺ , Cd ²⁺	60	[22]
Calix-[4]- crown	27.3	5×10 ⁻⁵ -1×10 ⁻¹	----	Pb ²⁺ , Zn ²⁺ , Cd ²⁺ , Ni ²⁺	<20	[23]
4-(Benzylidene amino)-3,4-dihydro-6-methyl-3-thioxo-1,2,4-triazin-5(2H)one	29.1	1×10 ⁻⁶ -1×10 ⁻²	6.0×10 ⁻⁷	----	10	This work

4. CONCLUSIONS

Mercury is toxic elements that can be found as contaminant in many different chemical forms, which can be easily inter-converted and transported through geochemical processes and pollute the environment. A low-cost, easy-to-use and reliable device is much needed for environmental monitoring of mercury. On the other hand, potentiometry by ion selective electrodes are simple, low cost, accurate and rapid method. Therefore, in this study, the Hg^{2+} potentiometric membrane sensor was constructed by 4-(benzylidene amino)-3,4-dihydro-6-methyl-3-thioxo-1,2,4-triazin-5(2H)one as ionophore. The electrode exhibits a Nernstian response for Hg^{2+} over a concentration range (1.0×10^{-6} to 1.0×10^{-2} M) with a slope of 29.1 ± 0.4 mV per decade. This electrode was shown a fast response time (~ 10 s), a lower detection limit of 6.0×10^{-7} M, pH independent potential responses across the range of 3.5–6.5 and relatively long lifetime. Its selectivity towards the mercury ions was not influenced by the presence of the common alkali, alkaline earth, or transition and heavy metal ions, since the interference of these substances was low. It was used as an indicator electrode in potentiometric titration of Hg^{2+} ion with EDTA and in direct determination of Hg^{2+} in water and wastewater samples.

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