

Mercury selective membrane electrode based on dithio derivatized macrotricyclic compound

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Abstract A novel dithio derivatized macrotricyclic compound (cryptand) has been synthesized using high dilution technique by condensation of diaminodibenzo18-crown-6 with 2, 2'-dithiobenzoyl chloride. The compound was characterized by elemental analysis, ^1H NMR, ^{13}C NMR and FAB-MS. PVC membrane electrode based on this macrotricyclic compound showed good selectivity for Hg^{2+} ion with a wide linear range of 1.0×10^{-6} to 1.0×10^{-1} M and a lower detection limit of 5.0×10^{-6} M with a calibration slope of $30.2 \text{ mV decade}^{-1}$. The electrode response was stable in pH range 3–6. Electrode showed good selectivity for Hg^{2+} over other interfering metal ions. The electrode was then applied to direct determination of Hg^{2+} in water samples.

Keywords Ion-selective electrode · Hg^{2+} · PVC-membrane · Cryptand · Potentiometry

Introduction

The flourishing field of supramolecular chemistry was launched by the discovery of an important class of macro polycyclic polyethers called cryptands. They have demonstrated excellent complexing ability towards metal ions [1], making them a topic of considerable attention within the scientific community. These molecules are three-

dimensional analogues of crown ethers but are more selective and complex the guest ions more strongly. This amazing property of cryptands has been described by Lehn and co-workers as the “Cryptate Effect”. Over the past two decades a variety of cryptands have been developed which have found application as potentiometric and optical sensors for the determination of cations [2, 3]. Ion selective electrodes based on these sensors works on the principle that the activity of the specific ion dissolved in solution is converted to electrical potential, which can be determined by voltmeter or pH meter. The design of these ion-selective electrodes are based on the structure and cavity size of the ligand, the stability and selectivity of its metal ion complex, its solubility and the ability to extract the metal ion into the membrane phase. Ion selective electrodes provide a simple, highly selective and economic method for monitoring the concentration of selected species without any pretreatment. Hence the ion selective electrode based on macrocyclic compounds provides an easy and highly efficient method to determine the concentration of heavy metals and transition metals [4–10], which are hazardous to health of human beings. Even at low concentrations, mercury can cause ill effects on the nervous system, gastrointestinal tract and kidney [11, 12]. Because of expensive instrumentation and pretreatment involved in low level determination of mercury by AAS, it becomes necessary to develop a simpler and inexpensive method without sacrificing the efficiency. Ion selective electrodes for mercury have shown great promise to achieve the desired result. Although several ion selective electrodes for mercury have been developed recently [13–16], many problems like interference of other metal ions and longer response time have been encountered. Hence the development of ion selective electrode for mercury is still a subject of research in analytical chemistry. Several organic

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and inorganic compounds have been tested as ionophores in producing ion selective electrodes, which includes Schiff bases [17], amides, crown ethers [18–22], salicylaldehyde thiosemicarbazone, oxamides, thiosemicarbazone, calix derivatives [23–29], calix-crowns derivatives, mercapto compounds [30] and acyclic carriers.

Cryptands have found application as neutral carriers in preparation of ion selective electrodes for many cations. However there are very few reports wherein cryptands have found application as ion selective electrode for mercury. A mercury ion-selective electrode finds application in environmental monitoring and waste water analysis. In this paper, we report the synthesis and application of a novel dithia cryptand as an excellent neutral carrier for construction of mercury ion sensor. Some of the earlier reported works have shown that the presence of soft coordination sites of sulfur offers great affinity toward Hg^{2+} [31]. Hence as expected the synthesized dithia based cryptand showed good selectivity and response for mercury ion over alkali, alkaline and some other transition metal ions. The potentiometric selectivity for various ions and the effect of pH were also investigated. In addition to this, the electrode was also applied for determination of mercury ion by potentiometric titration with EDTA.

Experimental

Reagents and materials

All reagents and chemicals used were of analytical grade. Milli-Q water was used for preparing the stock solution of metal salts. Dilutions of the stock solution were also done by Milli-Q water. Sodium tetraphenyl borate (NaTPB) and dioctylphthalate(DOP) were purchased from Merck. Polyvinyl chloride (PVC) was obtained from G.S.C (India) and mercury (II) was used as mercuric nitrate for membrane sensor studies.

Apparatus

The FT-IR spectra were recorded on Bruker Tensor 27 FT-IR spectrometer as KBr pellets. The FAB-MS were recorded on a Jeol/SX/102/Da-600 mass spectrometer data system using Argon/Xenon as the accelerating gas. M-Nitro benzyl alcohol (NBA) was used as a matrix with the peak at m/z 136, 137, 154, 289 and 307. EI-MS were recorded on GC-MS SHIMADZU QP 5050. 1H NMR spectra were recorded on a 400 MHz FT-NMR Bruker DRX 300 spectrophotometer in $CDCl_3$ with tetra methyl silane(TMS) as a internal standard. A MeterLab Model PHM 95 pH/ION Meter with a saturated calomel electrode as reference electrode was used for potential measurements.

Synthesis

Preparation of 2,2'-dithiodibenzoyl chloride (1)

A mixture of (5 g, 16 mmol) of 2, 2' dithiodibenzoic acid and excess of thionyl chloride (4 mL, 45 mmol) was placed in a single neck flask equipped with a reflux condenser. After refluxing the mixture for 6–7 h excess thionyl chloride was distilled off under vacuum using rotary evaporator to get compound **1**. Yield 4.3 g mp 140 °C. 1H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 7.4–8.0 (m, 8H, Ar-H) EI-MS m/z 344 (M+1)

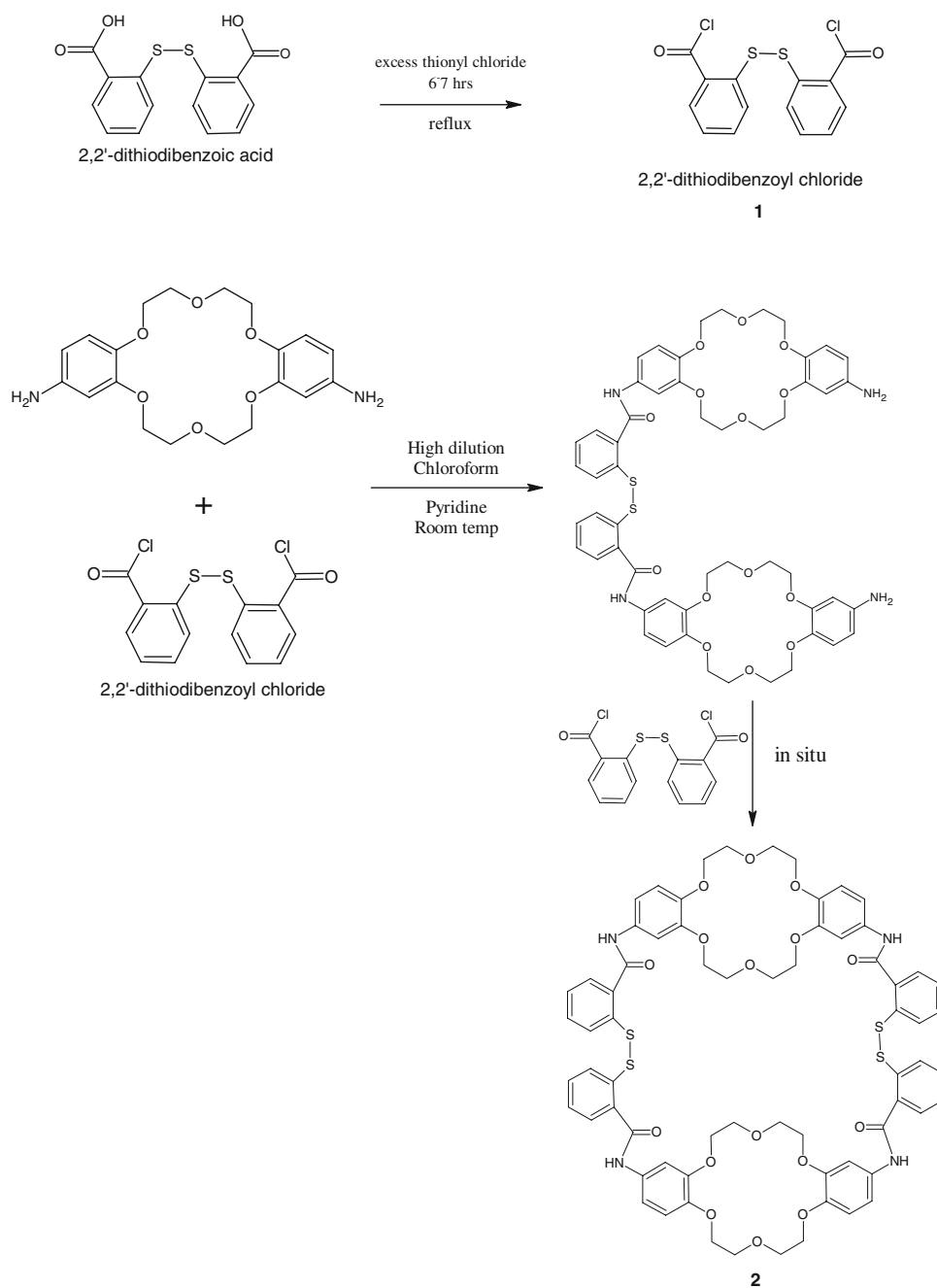
Preparation of di thio based macrotricyclic compound (2)

The novel macrotricyclic compound was synthesized using high dilution method by condensation of 4, 4' di aminodibenzo-18-crown-6 with 2, 2'dithiodibenzoyl chloride.

To a solution of 4, 4'diaminodibenzo-18-crown-6 (20 g, 5 mmol) dissolved in 700 mL chloroform was added pyridine in a one liter three neck flask equipped with a mechanical stirrer. The solution of 2, 2'dithiodibenzoyl chloride (0.85 g, 2.5 mmol) in 50 mL chloroform was then added drop wise with vigorous stirring for a period of 30 min to this solution and allowed to stir for further 2 h. The second portion of 2, 2'dithiodibenzoyl chloride (0.85 g, 2.5 mmol) in chloroform was then added drop wise with vigorous stirring in a span of 30 min followed by stirring for about 6 h at room temperature (25 °C). After completion of reaction, the reaction mixture was washed with 0.1 M HCl solution. The organic layer was separated and chloroform was distilled off from the reaction mixture. The resulting mixture was then subjected to column chromatography using toluene: methanol (9:1) as the eluant. The product **2** obtained was recrystallized in DMF. Yield 3.2 g (52.2%) mp 235 °C. Elemental analysis calculated for $C_{68}H_{64}N_4O_{16}S_4$ %C 61.81, %H 4.84%N 4.24 Found %C 62.03%H 4.87%N 4.22. 1H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 10.08 (s, 4H, CONH), 7.4–8.2 (m, 16H, ArH), 7.1 (d, 4H, ArH), 7.0 (s, 4H, ArH), 6.6(d, 4H, ArH), 4.17–4.0 (m, 16H, OCH_2), 3.4–3.2 (m, 16H, OCH_2) ^{13}C NMR (125 MHz, $CDCl_3$, Me_4Si): δ 165.2 (CONH), 145.3, 140.1, 134.2, 132.2, 130.4, 129.3, 127.6, 125.4, 115.0, 112.6, 106.7, 73.3, 70.5 FT-IR(KBr) 3250, 1636, 1127 cm^{-1} FAB-MS observed m/z 1321 (M+) The synthetic protocol is given in Scheme 1.

Electrode preparation

The examination carried out on a number of membranes for Hg^{2+} selective sensor (**2**) showed good performance in the terms of characteristics and reproducibility with following ingredients. They were prepared by dissolving 6% ionophore,

Scheme 1 Synthetic protocol of dithio derivatized macrotricyclic compound

28% PVC, 56% dioctylphthalate and 10% NaTPB in 6 mL of THF. The suspension was stirred until all the PVC was dissolved. The resulting solution was carefully cast into a slide glass and left standing for 24 h in a Petri dish to allow THF to evaporate slowly. Membranes of appropriate size were cut from this master membrane. In order to avoid drastic variation in the thickness and morphology of the membrane, the viscosity of the solution and solvent evaporation was carefully controlled. Membranes that gave reproducible results as well as fast response time were selected for further studies.

Potential measurement

The membranes were cut to size and attached to PVC tube with araldite. The tube was filled with $1.0 \times 10^{-2} \text{ mol L}^{-1} \text{ Hg} (\text{NO}_3)_2$ solution. Ag/AgCl was used as internal reference electrode. The sensor was conditioned with $10^{-2} \text{ mol L}^{-1} \text{ Hg} (\text{NO}_3)_2$ solution for 24 h and stored in the same solution when not in use. The following cell assemble was set up for electrochemical measurement.

Ag-AgCl/KCl/ 1.0×10^{-2} M Hg (NO₃)₂/PVC membrane/
test solution/KCl/Hg-Hg₂Cl₂

All the measurements were made at 25 ± 1 °C.

Result and discussion

In preliminary investigation, the synthesized dithia cryptand was used as neutral ion carrier to prepare PVC membrane ion-selective electrodes for a variety of metal ion including alkali, alkaline earth and transition metal ions. The presence of dithia linkage in the cryptand and high affinity of sulphur towards Hg²⁺ made it selective for mercury ion as compared to other cations.

Effect of membrane composition

It is recognized that sensitivity and selectivity of the ion selective electrode depend not only on the nature of the carrier used but also extensively on its membrane composition as well as plasticizer/polyvinyl chloride (PVC) ratio. The presence of the lipophilic site in composition of membrane reduces the ohmic resistance; improve extraction capacity of the membrane. We investigated the influence of membrane composition on the potential response of the Hg²⁺ sensor. Different aspects of membrane were optimized and results were summarized in the Table 1. Among the different composition studied, the membrane in absence of ionophore displayed insignificant selectivity towards anion. Whereas in the presence of ionophore the membrane showed remarkable selectivity for Hg²⁺. The membrane optimized with ingredients 6% ionophore, 28% PVC, 56% dioctylphthalate and 10% NaTPB gave the best response characteristics. The potential response of the all the membrane sensors were measured in the range 1.0×10^{-1} M to 1.0×10^{-8} M

The measurements were performed in the concentration range of 1.0×10^{-8} to 1.0×10^{-1} M HgNO₃ as shown in Fig. 1. The electrode showed linear response in the range from 1×10^{-6} to 1.0×10^{-1} M with Nernstian slope close to 30.2 mV decade⁻¹. The detection limit obtained was 5.0×10^{-6} M

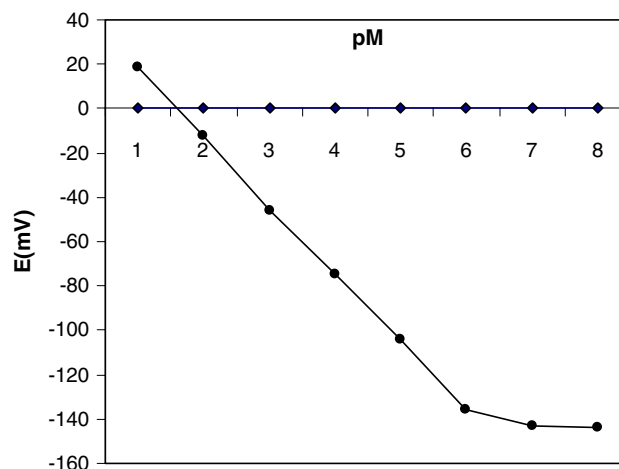


Fig. 1 Potential response of Hg²⁺ ion selective electrode

The pH dependence of the membrane sensor has been investigated at two different concentrations 1.0×10^{-2} M (Series 2) and 1.0×10^{-3} M (Series 1) for the membrane electrode. pH was adjusted using dilute nitric acid and dilute sodium hydroxide. Figure 2 shows that the potential response remains almost unvarying over the pH range 4.0 to 6.0, which is a wider range as compared to other mercury selective electrode.

The working of the electrode in different solvent was studied using methanol–water, ethanol–water combinations. The results are summarized in Table 2. The studies revealed that the slope and working concentration was found to decrease on increasing the content of non-aqueous medium above 40% (v/v)

Life time of ion selective electrode

The response of the prepared mercury ion selective electrode was examined at regular intervals to check the reproducibility and life time. Results obtained are summarized in the Table 3 which indicates that during the long time of 90 days, sensor slope was reduced from 30.2 to 28.6 mV decade⁻¹ and the effect on limit of detection on sensor was also negligible.

Table 1 Composition (%) of membranes and response characteristics of the electrode

No	Ionophore	DOP	NaTPB	PVC	Slope (mV · decade ⁻¹)	Linear range (mol L ⁻¹)
1	6	56	10	28	30.2	5.0×10^{-6} to 1.0×10^{-1}
2	3	60	7	30	29.2	3.2×10^{-5} to 1.0×10^{-1}
3	5	62	5	28	28.6	3.9×10^{-5} to 1.0×10^{-1}
4	9	56	7	28	29.8	7.0×10^{-6} to 1.0×10^{-1}
5	6	35	4	55	27.5	5.0×10^{-5} to 1.0×10^{-1}

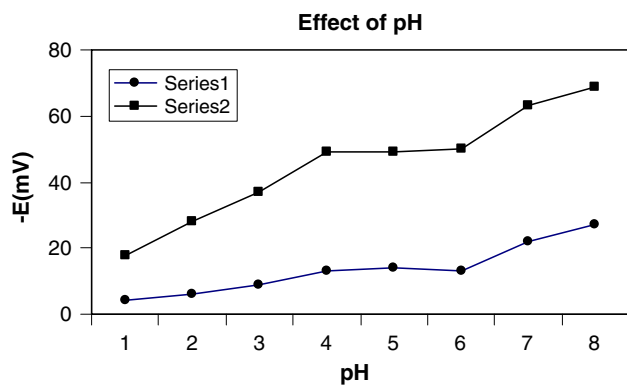


Fig. 2 Effect of pH on the potential response of the Hg²⁺ ion selective electrode

Table 2 Performance of Hg²⁺-selective electrode in partially non aqueous medium

Non aqueous content % (v/v)	Working concentration range M	mV · decade ⁻¹
0	1.0 × 10 ⁻⁶ –1.0 × 10 ⁻¹	30.2 ± 0.4
Ethanol		
10	1.0 × 10 ⁻⁶ –1.0 × 10 ⁻¹	30.2 ± 0.4
20	1.0 × 10 ⁻⁶ –1.0 × 10 ⁻¹	30.2 ± 0.4
30	1.0 × 10 ⁻⁶ –1.0 × 10 ⁻¹	30.2 ± 0.4
40	1.0 × 10 ⁻⁶ –1.0 × 10 ⁻¹	29.9 ± 0.4
50	2.0 × 10 ⁻⁵ –1.0 × 10 ⁻¹	27.8 ± 0.4
Methanol		
10	1.0 × 10 ⁻⁶ –1.0 × 10 ⁻¹	30.2 ± 0.4
20	1.0 × 10 ⁻⁶ –1.0 × 10 ⁻¹	30.2 ± 0.4
30	1.0 × 10 ⁻⁶ –1.0 × 10 ⁻¹	30.2 ± 0.4
40	1.0 × 10 ⁻⁶ –1.0 × 10 ⁻¹	29.4 ± 0.4
50	1.3 × 10 ⁻⁵ –1.0 × 10 ⁻¹	26.2 ± 0.4

Table 3 Lifetime behavior of Hg²⁺ion selective electrode

Time (day)	Slope(mV · decade ⁻¹)	Linear range(M)
1	30.2 ± 0.4	1.0 × 10 ⁻⁶ –1.0 × 10 ⁻¹
15	30.2 ± 0.4	1.0 × 10 ⁻⁶ –1.0 × 10 ⁻¹
30	30.2 ± 0.4	1.0 × 10 ⁻⁶ –1.0 × 10 ⁻¹
45	30.2 ± 0.4	1.0 × 10 ⁻⁶ –1.0 × 10 ⁻¹
60	29.9 ± 0.6	2.8 × 10 ⁻⁶ –1.0 × 10 ⁻¹
75	29.1 ± 0.6	2.8 × 10 ⁻⁶ –1.0 × 10 ⁻¹
90	28.6 ± 0.7	4.5 × 10 ⁻⁶ –1.0 × 10 ⁻¹

Response time of the electrode

Response time is the one of the most important characteristic of the ion selective electrodes. To measure response time, the electrode was first dipped in to 0.1 to 0.01 M concentration solution of Hg²⁺ and was then immediately shifted to another solution in which the concentration of the ion solution was tenfold. After dipping in the second

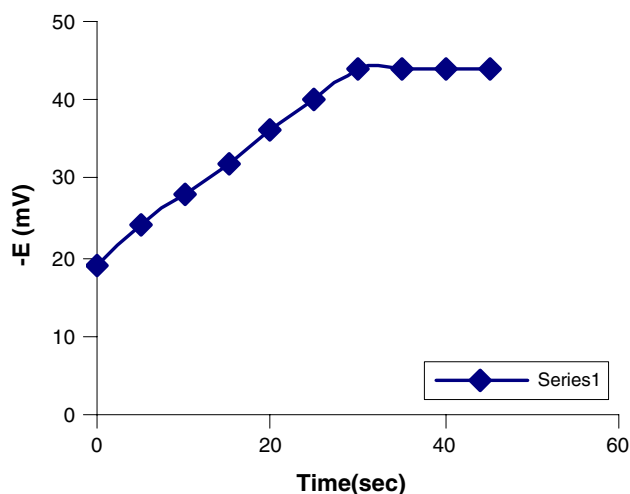


Fig. 3 Dynamic response of Hg²⁺ ion selective electrode

solution the potential was noted in the interval of 5 s and the graph of potential against time was plotted as shown in Fig. 3. The time taken by the electrode to obtain stable potential is the response time of the electrode.

Interference study

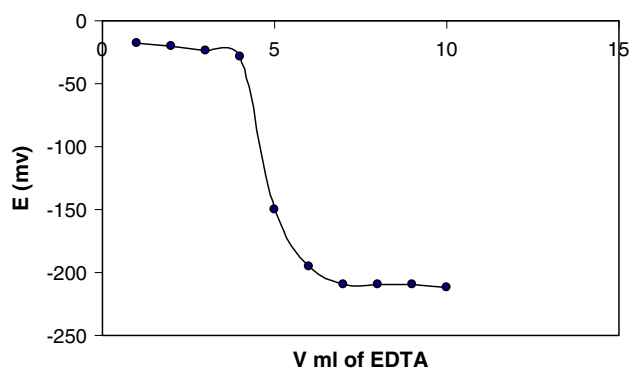
The most important characteristic of an ion selective electrode is the effect of interferences on its response, which is usually expressed in the terms of selectivity coefficient which is evaluated using Match Potential Method (MPM) [32]. According to this method the selectivity coefficient is defined as the activity ratio of the primary ion and interfering ions that give the same potential change under ideal condition. Its value can be determined from the following equation

$$K_{A,B}^{Pot} = \frac{\Delta aA}{aB} = \frac{a'A - aA}{aB}$$

Specific activity (concentration) of the primary ion (a_{Hg} = 1.0 × 10⁻⁶ M) is added to reference solution (a'_{Hg} = 5.0 × 10⁻⁶ M) and potential change (ΔE) is measured. In a separate experiment the interfering ion activity (concentration) (a_B = 1.0 × 10⁻⁵ to 1.0 × 10⁻¹ M) was added to an identical reference solution until the same potential change (ΔE) is recorded. The resulting selectivity coefficients for different interfering ions are given in the Table 4. The results indicate that except Ag⁺ (selectivity coefficient in order 0.2) all diverse ions showed selectivity coefficients in the order of 6.2 × 10⁻³ or smaller indicating negligible disturbance on the functioning of the Hg²⁺ membrane sensor. The working concentration range, slope, response time of our electrode is compared with earlier reported mercury selective electrodes (Table 6).

Table 4 Selectivity coefficient values for Hg^{2+}

Diversion ions	$K_{\text{HgM}}^{\text{Pot}}$
Ag^+	2.0×10^{-1}
Pb^{2+}	6.4×10^{-2}
Cd^{2+}	6.2×10^{-3}
Ni^{2+}	4.2×10^{-3}
Co^{2+}	6.9×10^{-3}
Mg^{2+}	7.3×10^{-4}
Fe^{2+}	8.2×10^{-4}

**Fig. 4** Potentiometric titration curve of 20 mL of 1×10^{-3} M Hg^{2+} with 0.01 M EDTA solution at pH 6**Table 5** Potentiometric determination of Hg^{2+} ion in the different samples

No	Sample	Spectroscopy method (ppm)/SD($n = 5$)	ISE(ppm)/SD($n = 5$)
1	10 ppm	9.9/0.4	9.6/0.3
2	20 ppm	19.8/0.6	19.5/0.4
3	30 ppm	29.6/0.4	29.3/0.4
4	Mercury lamp	58.6/0.5	58.2/0.5

Table 6 Comparison of the proposed Hg^{2+} -selective electrode with the reported electrode

Reference number	Ionophore	Linear range (mol L^{-1})	Slope ($\text{mV} \cdot \text{decade}^{-1}$)	Response time (s)
[33]	Bis[5-((4-nitrophenyl)azo salicyladehyde	7.0×10^{-7} – 5.0×10^{-2}	30.0 ± 1	10
[34]	p-tert-Butyl Calix [4] crowns	5.0×10^{-5} – 1.0×10^{-1}	27.3	20
[35]	$\text{H}_2\text{NCHMeCH}_2\text{NH}_2$ (H_2O) HgCl_2	1.3×10^{-5} – 1.0×10^{-1}	25 ± 0.1	10
[15]	1,3-diphenylthiourea	6.0×10^{-6} – 5.0×10^{-4}	58.6 ± 0.8	20
[36]	6,7:13,14-dibenzo–2,4,9,11-tetra-phenyl-1,5,8,12-tetraazacyclotetradeca-1,4,6,8,11,13-hexaene	8.9×10^{-6} – 1.0×10^{-1}	30 ± 1	10
	dithio derivatized macrotricyclic compound 2	1.0×10^{-6} – 1.0×10^{-1}	30.2	30

Potentiometric titration

In addition to the direct determination of Hg^{2+} , the mercury ion selective electrode can also be used for the titration of Hg^{2+} with complexing agent. It was successfully applied as an indicator electrode for the potentiometric titration of 20 mL 1×10^{-3} M Hg^{2+} with 0.01 M EDTA solution at pH 6. Results are summarized in Fig. 4. The amount of Hg^{2+} ions in the solution can be accurately determined from the titration curve.

The applicability of the proposed Hg^{2+} selective electrode for direct potentiometric determination of Hg^{2+} in doubly distilled deionised water spiked with 10, 20 and 30 ppm Hg^{2+} and also from high intensity mercury lamp was also investigated. The lamp was crushed to small pieces and digested with nitric acid. The obtained results were compared with those obtained from spectrophotometry method which is summarized in the Table 5 and as can be seen, the recovery of mercury from different samples is almost quantitative.

Conclusion

The mercury ion selective electrode based on dithia cryptand gave better results and reproducibility as compared to earlier reported electrodes for mercury. The prepared mercury ion electrode showed a response range of 1.0×10^{-6} to 1.0×10^{-1} M and detection limit of 5.0×10^{-5} M with a short response time of 30 s. The electrode showed good selectivity for Hg^{2+} as compared to other ions such as Ag^+ , Pb^{2+} , Cd^{2+} , Ni^{2+} , Co^{2+} , Mg^{2+} and Fe^{2+} . It can further be used for end point determination in potentiometric titration of Hg^{2+} with EDTA and also for direct determination of mercury in different samples.

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