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A highly selective mercury electrode based on a diamine donor ligand

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Abstract

$(H_2NCHMeCH_2NH_2)(H_2O)_2HgCl_2$ (**I**) was synthesised, characterised and used for the fabrication of a potentiometric sensor for Hg^{2+} metal ions. Membrane having **I** as electroactive material, sodium tetraphenyl borate (NaTPB) as an anion excluder, dibutylamine (DBA) as plasticizer in PVC matrix in the percentage ratio of 10:3:150:150 (**I**:NaTPB:DBA:PVC) (w/w) exhibits a linear response to Hg^{2+} ions in a concentration range of 1.25×10^{-5} to 1.0×10^{-1} M having a detection limit of 8.9×10^{-6} with a slope of 25 ± 0.1 mV over the pH range 6.6–9.3. Selectivity coefficients for Hg(II) relative to a number of interfering ions were investigated. The electrode 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 electrode. The electrode has also been used successfully in mixtures having a 10% (v/v) methanol and acetone content without showing any considerable change in working concentration range or slope. These electrodes have been found to be chemically inert showing a fast response time of 10 s and were used over a period of 4 months with good reproducibility ($s = \pm 0.2$). The electrode was used for determination of mercury in binary mixtures with 100% recovery and thus the proposed sensor can be used for real sample analysis.

Keywords: Chemical sensor; Mercury; PVC; Diamine donor; Ion selective electrodes

1. Introduction

The determination of mercury is important, due to its toxicity even in low concentration. The available method for low-level determination of mercury and other heavy metals in solutions includes AAS, but it involves expensive instrumentation and sample pre-treatment, which is time consuming and inconvenient. Ion-selective electrodes (ISEs) have taken firm roots as convenient tools for measuring ion activity or concentration in various fields of chemical analysis. For the detection of mercury ions using ISE, there are two kinds of electrodes described in the literature [1]. One is a liquid-state electrode [2], which is one of the most common techniques applied in routine analysis, but the application of the electrode is strongly limited by the conditions used in many factories. The other one is a solid-state membrane electrode [3], which is one of the most important types of chemical sensors. These electrodes are prepared with a poly(vinyl chloride) (PVC) immobilized carrier deposited directly on the conductive composite [4].

The procedure for the construction of the PVC membrane electrode is easy to implement, inexpensive and reliable [5]. These electrodes show good stability and their responses are acceptable for analytical applications [6].

Thus, the development of a selective electrode for mercury has been a subject of investigation to analytical chemists. So far, it has not been possible to have a good electrode for this ion and efforts in this direction are called for. To improve the analytical selectivity, it is essential to search carrier compounds that would react with mercury with high selectivity. Many organic and inorganic compounds have been tested as

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ionophore in producing ISEs, including crown ethers [7] and acyclic compounds, such as dithiocarbamate and their metal ion complexes [8], amides [9] and oxamides [10]. Examples of recent advances along this line have been the synthesis of some new Hg(II) carriers including a borondipyrromethane-type dye [11] and a macrocyclic ligand with 8-hydroxyquinoline moieties [12]. Hexathia-18-crown-6-tetraone has been reported [13] as an ionophore for Hg^{2+} ions, with a Nernstian response of 30 mV per decade between pH 0.5–2.0 in a similar concentration range. Plaschke et al. [14] reported a fluorometric method for Hg(II) assay with tetra(*p*-sulfonatophenyl) and a sol–gel film optochemical sensor based on this compound, though the response characteristics of the sensor were not described in detail.

The availability of improved highly selective materials has opened up new channels for developing specific sensors. Efforts were initiated by us to develop selective electrodes for Hg^{2+} ions using a diamine donor ligand as sensor material. The most important requirement for an ionophore to act as a good electroactive material in membranes is its ability to act as a selective extractant, or to form strong complexes, preferentially with only few metal ions.

The recognition of small molecules in binding with heavy metals has gained importance in the field of research [15,16]. The newly synthesised diamine with two donating nitrogen atoms, low molecular weight and flexible structure was expected to act as a suitable ionophore in the preparation of PVC membrane sensors for transition and heavy metal ions of proper size and charge.

In this paper, we report on the electroanalytical applicability of a diamine donor ligand as mercury ion sensor. The results presented in this paper show that the sensor developed for Hg(II) ion using the above system as electroactive phase in a PVC matrix has a wide working concentration range and a fast response time with reproducible results.

2. Experimental

2.1. Reagents

Mercuric chloride and mercuric nitrate were obtained from Loba Chemie (India). Propylenediamine was purchased from Aldrich. High molecular weight PVC was obtained from Fluka and used as such. Anion excluder, sodium tetraphenyl borate (NaTPB) from BDH (England) and dioctyl phthalate (DOP) from Reidal (India), chloronaphthalene (CN), tris(2-ethyl hexyl)phosphate (TEP) and tributylphosphate (TBP) from Merck. Dibutylamine (DBA) and diphenylether (DPE) were obtained from Aldrich.

2.2. Synthesis of *I*

A methanolic solution of propylenediamine (20 mL, 0.25 mol) was mixed with mercuric chloride (33.9 g, 0.125 mol) and stirred at room temperature. The reaction mixture is then heated to reflux for 4 h. Then methanol (10 mL) is added to quench the reaction followed by addition of water. The solvent is removed by oil-pump vacuum and the remaining material is washed with water (20 mL) and ethanol (5 mL) to give silvery coloured crystals of **I**; yield: 35 g (65% based on mercuric chloride), m.p.: 188 °C. IR (KBr, cm^{-1}): ν (CH, CH_2) = 2953, 2866 cm^{-1}; δ (CH, CH_2) = 1454 cm^{-1}; ν (NH) = 3324 cm^{-1}; ν (OH) = 3255, 3460 cm^{-1}. Bands at 430 cm^{-1} may be attributed to the Hg-Cl vibration.

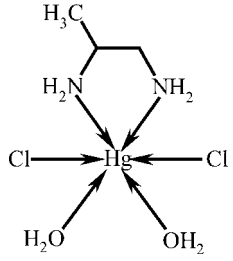

Fig. 1. Proposed chemical structure for **I**.

Elemental analysis: calcd. for $C_3H_{14}N_2O_2Cl_2Hg$, C: 9.4; H: 3.6; N: 7.3; found: C: 9.8; H: 2.8, N: 7.6. NMR: ^{1}H NMR (DMSO): δ (ppm): 1.04 (d, 3 H, CH_3, $3J_{HH}$ = 6.4 Hz); 2.24 (m, 1 H, CH); 2.79 (m, 2 H, CH_2); 3.93 (bs, 4 H, NH).

$^{13}C\{^1H\}$NMR (DMSO): δ (ppm): 20.5 (CH_3); 45.7, 47.0 (CH_2, CH) (Fig. 1).

2.3. Apparatus

The potential measurements were carried out on a pH 5652 digital pH meter/millivoltmeter (ECIL, India) and 301 Century microvoltmeter (Century Instruments, India). pH measurements were made with a digital pH meter (glass electrode as pH electrode and calomel as reference electrode). IR spectra were recorded with a Perkin-Elmer FTIR 1000 Spectrometer as films between KBr plates. ^{1}H and $^{13}C\{^1H\}$ NMR spectra were recorded with a Bruker Advance 250 spectrometer, operating in the Fourier tansform mode. ^{1}H NMR spectra were recorded at 250.130 MHz (internal standard relative to DMSO, δ = 2.50 ppm); $^{13}C\{^1H\}$NMR spectra were recorded at 62.902 MHz (internal standard relative to DMSO, δ = 39.5 ppm). Chemical shifts are reported in δ units (ppm) downfield from $SiMe_4$. C,H,N—microanalysis was performed in the Organic Department at Chemnitz, The Technical University, using a Foss Heraeus Vario EL analyser. Melting point is measured using a Gallenkamp (Type MFB 595010 M) instrument.

2.4. Potential measurements

Potentials were measured by direct potentiometry at 25 ± 0.1 °C with the help of ceramic junction calomel electrodes and the cell set-up was the same as reported in earlier publications [17,18]. 1.0×10^{-1} M mercuric nitrate was taken as inner reference solution and saturated calomel electrodes (SCE) were used as reference electrodes. All pH adjustments were made with appropriate acid or base.

2.5. Electrode preparation

A number of membranes incorporating the ionophore, anion excluder and plasticizers in different compositions in PVC matrix were fabricated by the method reported earlier [17,18]. Since the ionophore was insoluble in THF, it was dissolved in cyclohexanone and then added to the solution containing PVC, NaTPB, and plasticizers in THF. A number of membranes were fabricated by varying the composition of all the components using DBP, DOP, CN, TEP, DBA, TBP and DPE as solvent mediators. After complete dissolution of all the components and thorough mixing, the resulting solution were poured into acrylic rings placed on a smooth glass plate and allowed to evaporate at room temperature. After 48 h, transparent membranes of 0.5 mm thickness were obtained. A 5 mm-diameter pieces were cut out and attached to one end of a pyrex tube with Araldite (Ciba-Geigy, India). Membranes were equilibrated for 3 days in a 0.5 M Hg^{2+} solution.

Proper equilibration of membranes is essential to have a sensor showing good response characteristics. The ratio of various membrane ingredients, time of contact and the concentration of equilibrating solution were optimized first so that the membranes develop reproducible, stable and noiseless potentials. Membrane to membrane and batch to batch reproducibility was assured carefully following the optimum conditions of fabrication.

3. Results and discussion

3.1. Potentiometric measurements

A number of characteristics are required for a membrane ISE to be considered a suitable sensor for quantitative measurement of ions. Of these, slope, selectivity, working concentration range, response time, and electrode life time are most important. These characteristics have been taken into account in order to ascertain the utility of **I** as ionophore for the preparation of mercury-selective electrodes.

Investigation revealed that proper equilibration of the membranes was achieved, when these were dipped in a solution of 0.5 M for Hg^{2+} for 3 days. Potential studies on the membrane sensors were carried out with the varying Hg^{2+} concentration (1.0×10^{-6} to 1.0×10^{-1} M). Potentials generated with blank membranes (containing only PVC, NaTPB and solvent mediators) were insignificant (5–10 mV). As such, the potentials generated in the proposed sensor are ascribed to the uptake of mercury ions on the diamine donor ligand. Since the nature of solvent mediators influences the dielectric constant of the membrane, the mobility of the ionophore molecule and state of ligand [18], it is expected that the solvent mediators play a key role in determining the ion selective characteristics. So various solvent mediators, viz., DBP, DOP, CN, TEP, DBA, TBP, DPE, were added in varying amounts to the membranes and ion-selective characteristics were studied (Table 1). Also, the optimization of permselectivity of the membrane sensor is known to be highly dependent on the incorporation of additional components [18], therefore, NaTPB was also added to the membrane components for better results. Of the various membranes prepared using **I** as the ion-active phase, the one having DBA as plasticizers and NaTPB as anion excluder (membrane number 6) exhibited the best working concentration range of 1.25×10^{-5} to 1.0×10^{-1} M with a slope of 25 mV/decade of activity. The limit of detection for this membrane calculated as recommended by IUPAC from the intersection of the two extrapolated segments of the calibration curve was 8.9×10^{-6} M. Membrane number 2 with DPE showed linearity in the concentration range 2.5×10^{-5} to 1.0×10^{-1} M with a slope of 26.6 mV/decade of activity. The membranes with DOP, CN, TEP and TBP as plasticizers gave poor performance with regard to the working concentration range, slope and response time. Hence, membrane number 6 having composition 10:150:3:150 (**I**:PVC:NaTPB:DBA) was chosen for further electroanalytical studies. Periodic monitoring of potentials (10 measurements) at a fixed concentration gave a standard deviation of ±0.2 mV. The deviation for slope value was found to be ±0.3–0.5 mV, which shows good reproducibility. The sensing behaviour of the membranes did not change, when potentials were recorded from lower to higher concentrations or vice-versa.

3.2. Response and life time

The response time of the Hg^{2+}-ISE was defined as t_{95} for a 10^{-2} M Hg^{2+} solution when the mercury ion concentration

Table 1
Composition and response characteristics of PVC based $(H_2NCHMeCH_2NH_2)(H_2O)_2HgCl_2$ (**I**) membrane sensor for Hg^{2+} ions

Membrane number	Components in membranes (w/w)									Working concentration range (M)	Slope (mV/decade of activity)	Response time t_{95} (s)
	I	PVC	DPE	DOP	CN	TEP	DBA	TBP	NaTPB			
1	10	150	–	–	–	–	–	–	3	8.9×10^{-4} to 1.0×10^{-1}	45.0	30
2	10	150	150	–	–	–	–	–	3	2.5×10^{-5} to 1.0×10^{-1}	26.6	12
3	10	150	–	150	–	–	–	–	3	5.0×10^{-4} to 1.0×10^{-1}	21.4	15
4	10	150	–	–	150	–	–	–	3	5.0×10^{-5} to 1.0×10^{-1}	22.0	17
5	10	150	–	–	–	150	–	–	3	2.2×10^{-4} to 1.0×10^{-1}	30.0	15
6	10	150	–	–	–	–	150	–	3	1.25×10^{-5} to 1.0×10^{-1}	25.0	10
7	10	150	–	–	–	–	–	150	3	1.12×10^{-4} to 1.0×10^{-1}	24.0	18

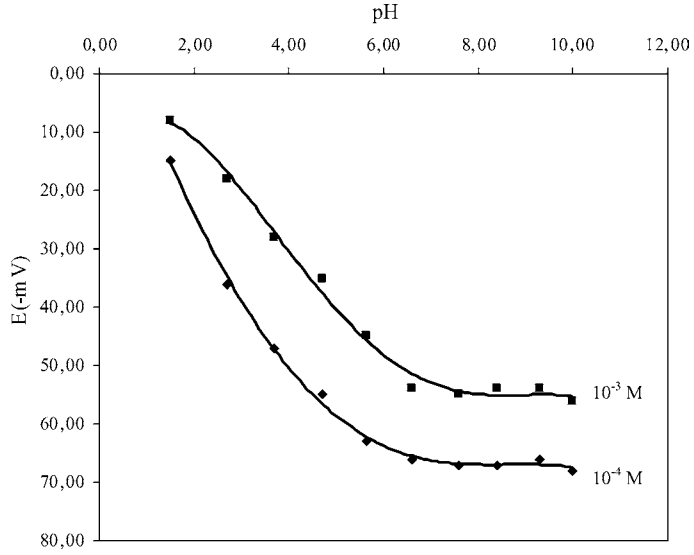

Fig. 2. Effect of pH on potential; $[Hg^{2+}] = 10^{-3}$ and 10^{-4} M for membrane number 6.

was rapidly increased from 10^{-3} to 10^{-4} M, where t_{95} is the time required for the electrode to reach 95% of the steady-state potentiometric value. The membrane without plasticizers (number 1), but with NaTPB showed a response time of 30 s. It could significantly be reduced by 12–20 s, when the solvent mediators were added. The best response time of 10 s was recorded for membrane having DBA as solvent mediator. The potentials generated by this membrane remained stable for more than 3 min after which it started deviating.

The lifetime of electrodes based on ionophore in solvent polymeric membranes depends on the distribution coefficient of the ionophore and the plasticizer between the aqueous and membrane phases [19]. Hence, the lifetime of electrodes must depend on the components of the solution and the measured specimens with electrodes. The lifetime of the electrodes was worked out by performing calibrations periodically with standard solutions and calculating the response, slope over the range 1.0×10^{-6} to 1.0×10^{-1} M $Hg(NO_3)_2$ solution. The experimental results show that the lifetime of the present electrode was over 120 days. During this time, the detection limit and the slope of the electrode remained almost constant. Subsequently the electrochemical behaviour of the electrode gradually deteriorated which may be due to ageing of the polymer (PVC), plasticizers and ionophore. However, the assembly can be used further for another 1 month after reequilibrating with 0.5 M solution of Hg^{2+} for 2 days.

3.3. pH and solvent effect

The effect of pH of the mercury nitrate test solutions (1.0×10^{-3}, 1.0×10^{-4} M) on the sensor potential was investigated by following the potential variation over the pH range 1– 12. The pH was adjusted by introducing small drops of hydrochloric acid (0.1 M) and sodium hydroxide (0.1 M). The influence of pH on the response of PVC membrane electrode is shown in Fig. 2. Potentials remain constant from pH 6.6–9.3 and the same may be taken as the working pH range of the assembly.

Chemical equilibrium for Hg^{2+} [20,21],

$$Hg^{2+} + OH^- \rightleftharpoons HgOH^+ + OH^- \rightleftharpoons Hg(OH)_2.$$

Under more acidic conditions, the ligand may be protonated and thereby losing its capacity to form a complex with the metal, but, when the pH is nearly neutral, the fundamental

Table 2
Effect of partially non-aqueous medium on the working of Hg^{2+} sensor (number 6)

Non-aqueous content (%, v/v)	Slope (mV/decade of activity)	Working concentration range (M)
0	25.0	1.25×10^{-5} to 1.0×10^{-1}
Methanol		
10	25.0	1.25×10^{-5} to 1.0×10^{-1}
15	28.0	7.0×10^{-4} to 1.0×10^{-1}
20	33.3	2.8×10^{-4} to 1.0×10^{-1}
Acetone		
10	25.0	1.25×10^{-5} to 1.0×10^{-1}
15	29.0	7.9×10^{-4} to 1.0×10^{-1}
20	30.0	3.1×10^{-4} to 1.0×10^{-1}

Table 3
Selectivity coefficient values for mercury selective membrane electrode (number 6) for various interfering ions (B) using the fixed interference method (FIM) and the matched potential method (MPM)

Interfering ions (B)	Selectivity coefficient ($K^{Pot}_{A,B}$)		
	FIM		MPM
	With superscript	Without superscript	
Ag^+	3.16×10^{-1}	3.16×10^{-3}	0.14
Na^+	7.07	7.07×10^{-2}	0.15
NH_4^+	6.3	6.3×10^{-2}	0.14
Cd^{2+}	7.9×10^{-2}	7.9×10^{-2}	0.12
Mg^{2+}	2.1×10^{-2}	2.1×10^{-2}	0.11
Pb^{2+}	5.0×10^{-2}	5.0×10^{-2}	0.14
Zn^{2+}	5.0×10^{-2}	5.0×10^{-2}	0.13
Cu^{2+}	3.5×10^{-2}	3.5×10^{-2}	0.13
Mn^{2+}	4.4×10^{-2}	4.4×10^{-2}	0.12
Co^{2+}	8.9×10^{-2}	8.9×10^{-2}	0.14
Fe^{3+}	1.2×10^{-2}	5.6×10^{-2}	0.13
Cr^{3+}	3.0×10^{-2}	1.4×10^{-1}	0.13
Al^{3+}	2.5×10^{-2}	1.1×10^{-2}	0.13

cation is $[HgOH]^+$, which reacts with the ligand. The drift of potential values at pH > 9.5 are attributed to the formation of mercury(II) hydroxide.

The performance of the membrane (number 6) was investigated in partially non-aqueous medium using methanol–water and acetone–water mixtures. The membrane worked satisfactorily in solutions having a maximum of 10% (v/v) non-aqueous content (Table 2). Above 10% non-aqueous content, slope and working concentration range was reduced and potentials showed a drift. It is worth mentioning that the life time of the membranes did not alter in non-aqueous solutions.

3.4. Potentiometric selectivity

The selectivity behaviour is obviously one of the important characteristics of the ion-selective electrodes, determining whether reliable measurement in the target sample is possible. To investigate the selectivity of the potentiometric electrodes proposed, their potential responses were investigated in the presence of a wide variety of interfering foreign cations using the fixed interference method (FIM) [21] as well as matched potential method (MPM) [22], the values of which are presented in Table 3.

Table 5
Determination of mercury ions in binary mixtures

Hg^{2+} (M)	Added cations (M)	Determination of Hg^{2+}
3.2×10^{-4}	–	3.2×10^{-4}
3.2×10^{-4}	Na^+ (2.0×10^{-3})	3.18×10^{-4}
3.2×10^{-4}	NH_4^+ (1.5×10^{-3})	3.18×10^{-4}
3.2×10^{-4}	Ag^+ (2.0×10^{-3})	3.20×10^{-4}
3.2×10^{-4}	Cd^{2+} (1.6×10^{-3})	3.19×10^{-4}
3.2×10^{-4}	Mg^{2+} (1.5×10^{-3})	3.21×10^{-4}
3.2×10^{-4}	Pb^{2+} (2.0×10^{-3})	3.22×10^{-4}
3.2×10^{-4}	Zn^{2+} (2.4×10^{-3})	3.18×10^{-4}
3.2×10^{-4}	Cu^{2+} (1.4×10^{-3})	3.19×10^{-4}
3.2×10^{-4}	Mn^{2+} (2.7×10^{-3})	3.19×10^{-4}
3.2×10^{-4}	Co^{2+} (1.8×10^{-3})	3.20×10^{-4}
3.2×10^{-4}	Fe^{3+} (1.8×10^{-3})	3.19×10^{-4}
3.2×10^{-4}	Cr^{3+} (2.4×10^{-3})	3.20×10^{-4}
3.2×10^{-4}	Al^{3+} (2.4×10^{-3})	3.18×10^{-4}

MPM is a recently recommended procedure by IUPAC [23] that gets rid of the limitations of the corresponding methods based on the Nicolsky–Eisenmann equation for the determination of potentiometric selectivity coefficients [24]. These limitations include non-Nernstian behaviour of interfering ions and inequality of charges of primary and interfering ions. According to MPM, the selectivity coefficient is defined as the activity ratio of the primary ion and interfering ion that gives the same potential change in a reference solution [22]. Thus, the change in potential upon changing the primary ion activity is measured. Then the interfering ion is added to an identical reference solution until the same potential change is obtained. The selectivity coefficient, $K^{Pot}_{A,B}$, is determined as $K^{Pot}_{A,B} = \Delta a/a_B$ ($\Delta a = a'_A - a_A$; a_A is the initial primary ion activity and a'_A is the activity of A in the presence of interfering ion, a_B). The concentration of Hg^{2+} used, as primary ion in this study was 6.7×10^{-5} M. The resulting selectivity coefficients are summarised in Table 3.

It is clear that the proposed mercury sensor is highly selective with respect to other common cations. Normal interferents, Ag^+ and Cd^{2+} has no effect on the functioning of the Hg(II) electrode.

It is interesting to note that a comparison of the selectivity coefficients obtained with the proposed sensor along with those reported before [25–30] (Table 4), clearly indicated a tremendous enhancement in the behaviour of the proposed Hg^{2+} electrode in terms of the working concentration range,

Table 4
Comparison of the reported electrodes with the proposed assembly

Serial number	Working concentration range	Lifetime	pH range	Response time	Slope (mV/decade)	Reference
1	10^{-5} to 10^{-1}	NM	NM	NM	58.0	25
2	10^{-4} to 10^{-1}	NM	2.0–12.8	NM	27.0	26
3	10^{-5} to 10^{-1}	5 weeks	1.0	4 min	NM	27
4	10^{-5} to 10^{-1}	5 weeks	0–2.0	Less than 3 min	28.5	28
5	10^{-5} to 10^{-1}	3 months	2.8–3.9	30–40 s	29.0	29
6	10^{-4} to 10^{-1}	4 months	2.8–4.2	30–40 s	28.0	30
7	10^{-6} to 10^{-1}	4 months	6.6–9.3	10 s	25.0	Proposed assembly

response time, lifetime, pH range and potentiometric selectivity.

3.5. Analytical application

The sensor was used for the determination of Hg^{2+} in the presence of various cations (Table 5). The results show that the recovery of mercury ions in binary mixtures is about 100% and thus the proposed sensor can be used for real sample analysis.

4. Conclusions

The mercury(II) ion selective sensor, based on the use of a diamine donor ligand exhibits a high selectivity and sensitivity to mercury(II) ions and fast potential response. The functional pH range of the proposed electrode is 6.6–9.3. The selectivity of the electrode towards Hg^{2+} is very good over other cations and also does not show interference from Ag^{+} and Cd^{2+}. The life time of the assembly is 4 months in aqueous and 10% methanol–water and acetone–water mixtures. Besides selectivity, the electrode also shows better stability and response time (<10 s) in comparison to the other Hg^{2+} selective electrodes reported in literature (Table 4).

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