

# A highly selective mercury electrode based on a diamine donor ligand

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## Abstract

(H<sub>2</sub>NCHMeCH<sub>2</sub>NH<sub>2</sub>)(H<sub>2</sub>O)<sub>2</sub>HgCl<sub>2</sub> (**I**) was synthesised, characterised and used for the fabrication of a potentiometric sensor for Hg<sup>2+</sup> 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<sup>2+</sup> ions in a concentration range of 1.25 × 10<sup>-5</sup> to 1.0 × 10<sup>-1</sup> M having a detection limit of 8.9 × 10<sup>-6</sup> 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<sup>2+</sup> ions over a large number of mono-, bi-, and trivalent cations. Normal interferents like Ag<sup>+</sup> and Cd<sup>2+</sup> 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* = ±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.

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## 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 borondipyromethane-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  $\text{Hg}^{2+}$  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  $\text{Hg}^{2+}$  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)

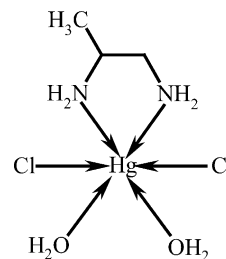


Fig. 1. Proposed chemical structure for I.

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,  $\text{cm}^{-1}$ ):  $\nu$  (CH,  $\text{CH}_2$ ) = 2953, 2866  $\text{cm}^{-1}$ ;  $\delta$  (CH,  $\text{CH}_2$ ) = 1454  $\text{cm}^{-1}$ ;  $\nu$  (NH) = 3324  $\text{cm}^{-1}$ ;  $\nu$  (OH) = 3255, 3460  $\text{cm}^{-1}$ . Bands at 430  $\text{cm}^{-1}$  may be attributed to the Hg-Cl vibration.

Elemental analysis: calcd. for  $\text{C}_3\text{H}_{14}\text{N}_2\text{O}_2\text{Cl}_2\text{Hg}$ , C: 9.4; H: 3.6; N: 7.3; found: C: 9.8; H: 2.8, N: 7.6. NMR:  $^1\text{H}$  NMR (DMSO):  $\delta$  (ppm): 1.04 (d, 3 H,  $\text{CH}_3$ ,  $3J_{\text{HH}} = 6.4$  Hz); 2.24 (m, 1 H, CH); 2.79 (m, 2 H,  $\text{CH}_2$ ); 3.93 (bs, 4 H, NH).

$^{13}\text{C}\{^1\text{H}\}$  NMR (DMSO):  $\delta$  (ppm): 20.5 ( $\text{CH}_3$ ); 45.7, 47.0 ( $\text{CH}_2$ , 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.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded with a Bruker Advance 250 spectrometer, operating in the Fourier transform mode.  $^1\text{H}$  NMR spectra were recorded at 250.130 MHz (internal standard relative to DMSO,  $\delta = 2.50$  ppm);  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded at 62.902 MHz (internal standard relative to DMSO,  $\delta = 39.5$  ppm). Chemical shifts are reported in  $\delta$  units (ppm) downfield from  $\text{SiMe}_4$ . 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  $25 \pm 0.1$  °C with the help of ceramic junction calomel electrodes and the cell set-up was the same as reported in earlier publications [17,18].  $1.0 \times 10^{-1}$  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.

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