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Development of a highly sensitive and selective mercury optical sensor based on immobilization of bis(thiophenal)-4,4′-methylenedianiline on a PVC membrane

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ABSTRACT

A reversible optical sensor was fabricated for highly sensitive and selective determination of Hg(II) ions. The optode was prepared using a newly synthesized ionophore, bis(thiophenal)-4,4′-methylenedianiline, and ETH-5294 as a lipophilic H^+-selective indicator in a plasticized PVC membrane. Different variables affect the optical signal such as pH and compositions of the membrane components were optimized. The spectrophotometric method (λ_{max} 662 nm) was used for the determination of Hg(II). Under the optimum conditions, the optode has a wide linear dynamic range of 2.51×10^{-13} to 1.02×10^{-5} mol L^{-1} Hg(II) with a detection limit as low as 3.43×10^{-14} mol L^{-1} and a response time of 90 s (for a highly diluted solution). The influence of potential interference ions on the Hg(II) determination was studied. The results showed that the prepared optical sensor was highly selective to Hg(II) ions so that it had no significant response to a wide variety of common metal ions. The response of the optode to Hg(II) is completely reversible and was lucratively applied for the determination of Hg(II) in different real samples.

1. Introduction

Mercury is a potentially poisonous environmental contaminant that is among the most highly bio-concentrated trace metals in the human food chain, and several international committees have targeted mercury for special notice with regard to its emissions and effects on human health [1]. The toxicity of heavy metals, such as Cd(II) and Hg(II), is attributed to their hurtful and even poisonous effects on the human body, mainly on the central nervous system, which can cause cerebral disorders or neuropsychiatric disorders [2].

Several methods have been reported for mercury determination, including cold vapor atomic absorption spectrometry [3], atomic fluorescence spectrometry [4], voltammetry [5,6], inductively coupled plasma atomic emission spectrometry [7], inductively coupled plasma-mass spectrometry (ICP-MS) [8] and X-ray fluorescence spectrometry [9]. Most of these methods have important limitations and problems, among them are time consuming, expensive and/or complicated equipment, boring, and hard to operate. In addition, they are not appropriate for out of laboratory or field monitoring.

Optical sensors have received significant notice in recent decades. Optical sensors have many advantages such as simplicity of production, affordability, good selectivity and sensitivity, high dynamic concentration range and also low detection limit [10–13]. Numerous optodes have been reported to determine Hg(II) in the literature based spectrophotometric and/or fluorimetric detections [14–33]. Many of them are not sensitive enough to detect ultra trace amount (less than 1.0×10^{-10} mol L^{-1}) of Hg(II) [14–30]. In addition, many of them have response time longer than 5 min [14–18,20,21,23,25–29]. Recently, we have introduced new ionophores to prepare PVC-based optodes to detect Hg(II) as low as 3.5×10^{-13}.

In this project, we selected bis(thiophenal)-4,4′-methylenedianiline [34] as a suitable ionophore for fabrication of a highly sensitive optical sensor for the determination of Hg(II). For preparation of the optode, bis(thiophenal)-4,4′-methylenedianiline as an ionophore, ETH-5294 as a chromoionophore plus sodium tetraphenyl borate as an ionic liophilic additive, works by an ion-exchange mechanism, in a PVC-based membrane have been selected. The procedure for construction of the PVC-membrane is easy to implement, inexpensive and reliable. This optode shows good stability and sensitive response for detection of ultra trace amounts of Hg(II) with regeneration ability, short response time and high dynamic concentration range. Selectivity of the optode is good, and it can be used for the determination of Hg(II) ions in environmental samples. This sensor can detect very low concentrations of mercury(II) ions without any preconcentration steps. The detection limit of this

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optode is superior to all reported optodes [14–33]. The optode can be easily regenerated.

2. Experimental

2.1. Chemicals

Analytical reagent grade chemicals with the highest purity available and tetrahydrofuran (THF) were purchased from Merck. Deionized water was used throughout. ETH5294 and polyvinyl chloride (PVC) were purchased from Fluka. Dioctylsebacate (DOS), dibutylphthalate (DBP), dioctylphthalate (DOP) and sodium tetraphenyl borate (NaTPB) were purchased from Aldrich. A stock solution (0.010 mol L^{-1}) of Hg(II) ions was prepared by dissolving $Hg(NO_3)_2 \cdot H_2O$ in water in a 100-mL volumetric flask in the presence of 0.5 mL of 1.0 mol L^{-1} HNO_3. More dilute solutions were prepared by appropriate dilution of the stock solution with buffer.

Bis(thiophenal)-4,4′-methylenedianiline (BTMD) was synthesized and purified as reported elsewhere [34].

2.2. Apparatus

UV/Vis absorption spectra were recorded on a double beam spectrophotometer (Cary 500 UV–vis-near-IR Varian) with 1.0-cm quartz cells.

Atomic emission measurements were taken by inductively coupled plasma (Perkin–Elmer, OPTIMA 7300-DV). The pH of the solutions was checked by a pH-meter (Metrohm, Herisau, Switzerland).

2.3. Preparation of bis(thiophenal)-4,4-methylenedianiline

Bis(thiophenal)-4,4-methylenedianiline was synthesized by reaction of 4,4-methylenedianiline with thiophene-2-carbaldehyde in a 1:2 mol ratio in methanol as follows: 4,4-methylenedianiline (0.02 mol, 3.96 g) and thiophene-2-carbaldehyde (0.04 mol, 1.48 g) were placed in a100-mL round-bottom flask equipped with a condenser and a magnetic bar. Then 60 mL of methanol was added to the mixture and the mixture was refluxed for 4 h while stirring. The solvent was evaporated and the viscous material was kept under vacuum while heating gently. The viscous ligand was then solidified upon standing for a few days to obtain a brown product quantitatively. ^{1}H NMR($CDCl_3$): $\delta =$ 4.03 (2H, s), 7.15 (1H, dd $J = 4.8$ Hz, $J = 3.6$ Hz), 7.18–7.25 (10H, m), 7.49–7.53 (3H, d), 8.60 (2H, s). IR(KBr, cm^{-1}): 3067, 3017, 2910, 1893, 1615, 1585, 1494, 1427, 1318, 1192, 1040, 846, 825, 700. The results of the CHSN chemical analysis were as follow: analytically calculated: C23H18N2S2: H, 4.69%; C, 71.47%; N, 7.25% and S, 16.59%; the experimental values were H, 4.59%; C, 71.38%; N, 7.30%, and S, 16.73%.

2.4. Membrane preparation

A mixture of 31.0 mg PVC, 62.0 mg DOS, 2.0 mg NaTPB, 2.5 mg ionophore, and 1.5 mg ETH5294 was dissolved in 1.0 mL of THF. The membrane solution was homogenized with a magnetic stirrer for 15 min. A Plexiglas slides with 9 mm × 50 mm dimensions were cut to fit into standard spectrophotometer cells. The slides were cleaned with ethanol, then water and finally dried in an oven at 60 °C. The membranes were cost by pipetting 25 μL of the membrane solution onto a Plexiglas slide and spread it with a capillary glass tube rapidly. The estimated thickness of the prepared films was about 6.7–7.0 μm.

2.5. Measurement procedure

The membrane was conditioned by inserting it into a cell including 3 mL of phosphate buffer (pH 7.5). After 240 s the membrane absorbance was measured at 662 nm. Then, the cell was filled with the Hg(II) standard solution and after 90 s its absorbance was measured in the same wavelength. The membrane response is defined as the ratio of the concentration of the unprotonated form of the chromoionophore [C] to the total amount present in the membrane [C_{tot}], i.e. $\alpha = [C]/[C_{tot}]$. Then, the α value was calculated by the absorbance measurements at the λ_{max} of the protonated form of the chromoionophore as: $\alpha = (A_P - A)/(A_P - A_D)$, where A_p is the absorbance value of the membrane containing completely protonated chromoionophore (i.e., at $\alpha = 0$), A_D is the absorbance value for the membrane containing the completely deprotonated chromoionophore (i.e., at $\alpha = 1$), and A is the absorbance measured at any time during the titration procedure. Then, the calibration curve was obtained by plotting of $(1 - \alpha)$ *vs.* log[Hg(II)]. The optode was regenerated in 0.1 mol L^{-1} H_2SO_4 solution for 90 s and was ready to use several times.

2.6. Sample preparation

Zayanderood river water was collected in a polyethylene container and two drops of concentrated nitric acid were added. The sample was filtered to eliminate any solid particles before analysis, and then the water sample was buffered with the citrate buffer (pH 7.5) prior to the measurement.

3. Results and discussion

3.1. Principle of the operation

Bis(thiophenal)-4,4′-methylenedianiline (BTMD) contains a sulfur donor atom which could form internal bonds with soft metal ions such as mercury(II). BTMD (Fig. 1) has high affinity to make a complex with mercury(II) ions.

The organic membrane contains ionophore, chromoionophore (acid–base indicator), and anionic additive stabilized in plasticized polyvinylchloride by DOS. Mercury(II) ions form a complex with the ionophore when the organic membrane contacts with the aqueous solution; therefore, the following ion-exchange reaction takes place:

$$Hg^{2+}{}_{(aq)} + nL_{(org)} + 2HIn^{+}{}_{(org)} + 2R^{-} \leftrightarrow HgL_n{}^{2+}{}_{(org)} + 2In_{(org)} + 2H^{+}{}_{(aq)} + 2R^{-} \quad (1)$$

In this equation, ‘*n*’ is the stoichiometric coefficient of the ionophore in the complex, ‘L’ is the ionophore, In and HIn^+ are the neutral and charged chromoionophores, respectively. R^- is the lipophilic anionic site that ensures the presence of a sufficiently negative charge to attractive Hg(II) ions and restraint to entrance anions into the membrane. The color of the chromoionophore in the acidic form ($HIn^{+}{}_{(org)}$) and in the basic form ($In_{(org)}$) is completely different. It can be seen that by the addition of mercury ions into the aqueous solution, the chromoionophore in the organic membrane is more deprotonated. Fig. 2 shows the absorption spectra of the optode with different concentrations of Hg(II) in the range 1.0×10^{-15} to 1.0×10^{-4} mol L^{-1}. This figure indicates that by addition of Hg(II) to the solution, the absorption of the membrane at 662 nm decreased. The response of the membrane is defined as the ratio of the concentration of the unprotonated form of the

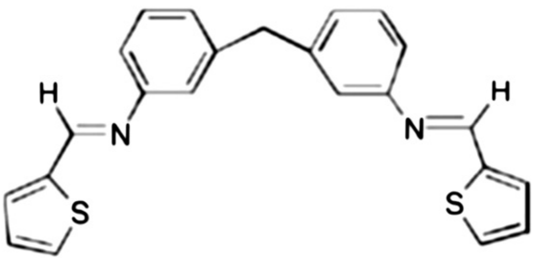

Fig. 1. Structure of bis(thiophenal)-4,4′-methylenedianiline (BTMD).