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Development of a mercury optical sensor based on immobilization of 4-(2-pyridylazo)-resorcinol on a triacetylcellulose membrane

Ali A. Ensafi*, Masoud Fouladgar

College of Chemistry, Isfahan University of Technology, Isfahan 84156, Iran

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Abstract

A new optical sensor for mercury(II) ions is developed based on immobilization of 4-(2-pyridylazo)-resorcinol (PAR) on a triacetylcellulose membrane. Chemical binding of Hg^{2+} ions in solution with a PAR immobilized on the triacetylcellulose surface could be monitored spectrophotometrically at 525 nm. The optode shows excellent response over a wide concentration range of 5–3360 μM Hg(II) with a limit of detection of 1.5 μM Hg(II). The influence of factors responsible for the improved sensitivity of the sensor were studied and identified. The response time of the optode was 20 min for a stable solution, and was 15 min for a stirrer solution. The influence of potential interfering ions on the determination of 5×10^{-5} M Hg(II) was studied. The sensor was applied for determination of Hg(II) in water samples.

Keywords: PAR; Optical sensor; Triacetylcellulose; Mercury(II)

1. Introduction

The determination of trace amounts of heavy metal ions are of interest in several fields including environmental analysis, process control, biology and medicine. Environmental contamination of Hg(II), a widely known toxic heavy metal can result in death or severe damage to the brain [1]. Over recent decades, considerable progress has been made in analytical methodology for mercury detection, including voltammetry, mass spectrometry, atomic absorption or emission spectrometry and chromatography. Although the methods are sensitive and accurate, most require a tedious sample pre-treatment, sophisticated performance and/or expensive equipment. Two types of polymeric support have been used for determination of ions. One of them is based on the non-transparence polymers such as cellulose papers, and silica [2–5] and the other is based on the transparence support such as glass, PVC, and/or triacetylcellulose [6–10].

Recent decades have seen an increase in the development of optical chemical sensors for heavy metals, because of easy fabrication, low cost, good selectivity and sensitivity. Most optical sensor for determination of heavy metal ions are based on either conventional indicator dyes, neural ionophores or on biological recognition components [7]. From the above compounds, organic indicator dyes and the immobilization technique play important roles in the development and design of the optode. The immobilization of the organic dye by chemical bonding is the best, because its prevent leaching of indicator, long life time of the sensor and the response time. Many of the reported optical sensors for mercury determination is based on incorporating of the dye (ionophor) and plasticized in polyvinyl chloride [8–13]. A common weakness of all these membranes is the leakage of the reagent into aqueous solution in contact with them. A few works on the development of optode for mercury ions sensing have been reported recently, based on immobilization of dithizone on the optical membrane such as XAD-7 and using reflectance spectroscopy [14–16] or triacetylcellulose with absorbance measurement.

A 4-(2-pyridylazo)-resorcinol (PAR) is a reagent, has been known as a selective solvent extraction for heavy metal ions and the complexation reactions can be monitored easily by its sensitive color change. In this paper, we discuss fabrication of

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* Corresponding author. Tel.: +98 311 3912351; fax: +98 311 3912350.
E-mail address: ensafi@cc.iut.ac.ir (A.A. Ensafi).

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a new optode for determination of mercury(II) in which PAR immobilization on triacetylcellulose membrane. The method has longer linear dynamic range relative to the other existence reported paper [14–16].

2. Experimental

2.1. Reagents

All of the chemicals used were of analytical reagent grade (Merck). Doubly distilled water was used throughout.

Hg(II) stock solution (0.010 M) was prepared by dissolving of 0.3426 g $Hg(NO_3)_2 \cdot H_2O$ in water and 0.5 ml of 1 M HNO_3 and diluted to 100 ml in a standard flask. Sample solutions were prepared by appropriate dilution.

PAR solutions, 0.020 g/100 ml, were prepared daily by dissolving 0.020 g of the reagent in a 100 ml standard flask by 1:1 water–ethanol solution.

2.2. Apparatus

A Spectronic 20 (Genesys) UV–vis spectrophotometer was used to measure the absorbance of fix wavelength. UV–vis spectra were measured with a Jasco, Model V-570, double beam spectrophotometer.

A homemade cell holder was used with a special frame with a size of 8.5 mm × 35 mm, as shown in Fig. 1.

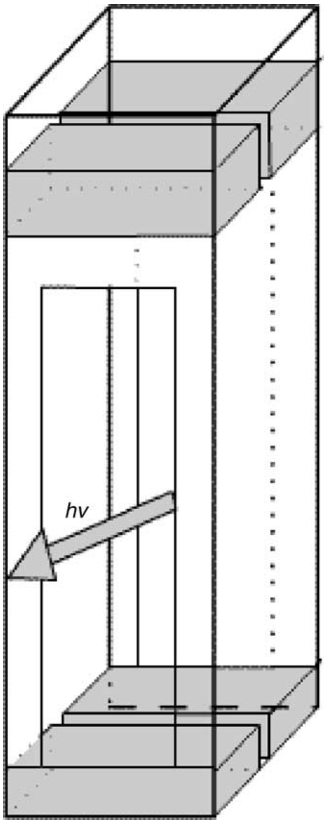

Fig. 1. Schematic diagram of the homemade cell.

2.3. Membrane preparative

The triacetyl cellulose film was hydrolyzed in order to de-esterify the acetyl groups and to increase the porosity of the membrane by treating the membrane into 0.20 M KOH solution for 24 h and then, the film was washed with distilled water and immersed in 0.6% (w/v) thiourea and 0.5% (w/v) polyvinyl alcohol solution. It was found that further activation processes [17,18] were not necessary. The membrane was immediately treated with a 0.02 g/100 ml PAR at 30 °C for 4 h. Then the membrane was washed with distilled water until there was no absorption at the wavelength of the ligand during rising. Then the film was dried.

2.4. Recommended procedure

The membrane was immersed into mercury(II) solution in acetate buffer (pH 5.0) for 20 min. Then the membrane was washed with water and dried. The absorbance of the membrane was measured spectrophotometrically at 525 nm.

3. Results and discussion

PAR, 4-(2-pyridylazo)-resorcinol (Fig. 2), is a photometric reagent for mercury(II) ions at a suitable pH. Fig. 3 shows the absorbance spectra of the reagent and the Hg(II)–PAR complex in the solution and Fig. 4 shows the absorbance spectra for Hg(II)–PAR complex as immobilized in triacetylcellulose membrane. These figures show that the formation of the complex on the surface of membrane causes to appear as a new peak at 525 nm, whereas for the soluble form appears at 515 nm. The absorption spectra of the complex as immobilized in triacetylcellulose membrane are red shifted in comparison to those of their soluble form. This can suggest that the structural conformation of the immobilized indicators is more planar than that of its soluble analogue [19]. According to the structure of PAR, and the fact that only reagents with amino groups could be linked chemically with triacetylcellulose [20], we used thiourea plus polyvinyl alcohol as a bridge between PAR and triacetylcellulose film. Possible scheme for the reaction of PAR with activated cellulose acetate film is shown in Fig. 5.

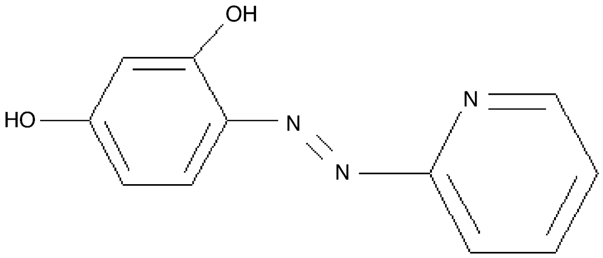

Fig. 2. Structure of PAR.