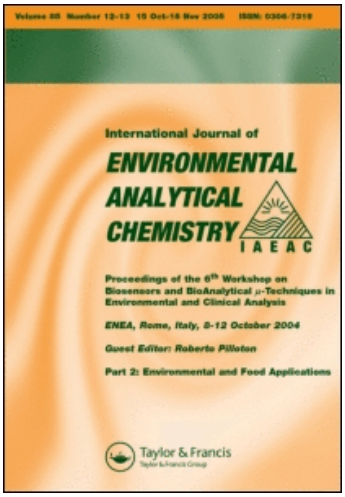

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Conductometric Hg sensor based on polyaniline as transducer

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Mercury is a common pollutant in natural water. Several chelating agents have been used to treat mercury poisoning. Among these agents British-anti-Lewisite (dimercaprol, 2,3-dimercapto-1-propanol, BAL) is a particularly successful antidote to inorganic mercury poisoning. In the present study a conductometric electrochemical sensor for Hg^{2+} ions was developed using polyaniline as the transducer as well as the immobilization matrix and BAL as the receptor for the heavy metal ion determination. There is a release of H^+ ions in solution when Hg–BAL complex is formed causing an increase in the conductance of the polyaniline film. The study was performed using Hg^{2+} solutions of varying concentrations prepared in 10^{-2} M HCl solution as the supporting electrolyte. The polyaniline conductance was measured in the presence of different concentrations of Hg^{2+} ions. The study showed an increase in the conductance of the polyaniline film in the presence of increasing concentrations of Hg^{2+} ions at -0.2 V gate potential *vs.* SCE. This conductometric sensor showed a good sensitivity in concentrations as low as 10^{-12} M of Hg^{2+} ions.

Keywords: Environment; Conducting polymers; Electrochemical sensors; Heavy metals

1. Introduction

Mercury is a common pollutant in natural water and is of great environmental concern because of its toxicity. Over recent decades, considerable progress has been made in analytical techniques for mercury detection which include atomic absorption or emission spectrometry, mass spectrometry and voltammetry. Although these methods are sensitive and accurate, most of them require a tedious sample pretreatment, sophisticated performance and/or expensive equipment.

Organic conducting polymers have emerged as promising materials in the development of compact and portable probes for the detection of biologically significant molecules [1, 2]. Early reports of using conducting polymer matrix for the immobilization of biological substrates used polypyrrole for the amperometric detection

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of glucose [3]. Since then, various research pursuits have resulted in a variety of sensors based on different conducting polymers. Among various conducting polymers, polyaniline has a unique position due to its easy synthesis, environmental stability and reversible acid–base chemistry in aqueous solution. The application of polyaniline in biosensors is very promising. Polyaniline has been used both as an immobilization matrix and as a physicochemical transducer to convert a chemical signal into an electrical signal. A change in the pH of the microenvironment or a change in the conformation of the polymer caused by a binding event in the polymer matrix results in a change in the electronic conductivity of the polymer. This property of polyaniline has been explored in the fabrication of conductometric sensors for the determination of various biomolecules/ions in our laboratory [4–7]. Using the same approach a Hg sensor was developed and is described in this article. The receptor used for Hg^{2+} ion determination was 2,3-dimercapto-1-propanol (BAL). BAL is generally used in the treatment of mercury poisoning to help in removal of mercury from the body [9]. BAL forms a 1 : 1 complex with Hg^{2+} ion and the stability constant (K) for Hg^{2+}–BAL complex is several orders of magnitude larger than that found for the Hg^{2+}–EDTA complex (though EDTA has three times as many effective donor groups as BAL) [8]. This shows great preference of mercapto groups for coordination to Hg^{2+}. Hg^{2+}–BAL complex is unaffected by alkali–alkaline earth metals like Na, K, Ca, Mg, etc. There is an increase in the $[H^+]$ ions in the microenvironment of the polyaniline film when Hg^{2+}–BAL complex is formed [9] according to the reaction:

$$HgCl_2 + BALH_3 \rightarrow HgBALH + 2HCl$$

This increase in $[H^+]$ causes increase in the conductance of the PANI film and this can be used for detection of Hg^{2+} ion quantitatively.

2. Experimental

Freshly vacuum distilled aniline (Merck) was used for preparing monomer solution. The sulfuric acid used was MOS grade with 99.9% purity. 2,3-dimercapto-1-propanol with 95% purity was obtained from sigma-aldrich. $HgCl_2$ from Thomas Baker was used as received. Hydrochloric acid used was of analytical grade. All solutions were prepared from water obtained from Milli-Q water purification system. Track-etched polycarbonate membranes having a pore diameter of 1.2 μm and thickness of 10 μm were obtained from the Millipore Inc. The average pore densities in these membranes were found to be 1.2×10^7 pores cm^{-2}.

2.1 *Fabrication of sensor devices*

Track-etched polycarbonate membranes were used for the fabrication of sensor electrodes. Gold films were deposited on the two sides of the membrane by vacuum evaporation [10]. The mask was made by cutting equidistant lines of 1 mm on an aluminium sheet. The two gold lines at the opposite faces of the membrane exactly overlapped with each other and were used as electrodes for the growth of the polyaniline. The electrodes were held by a plastic clip holder with platinum contacts

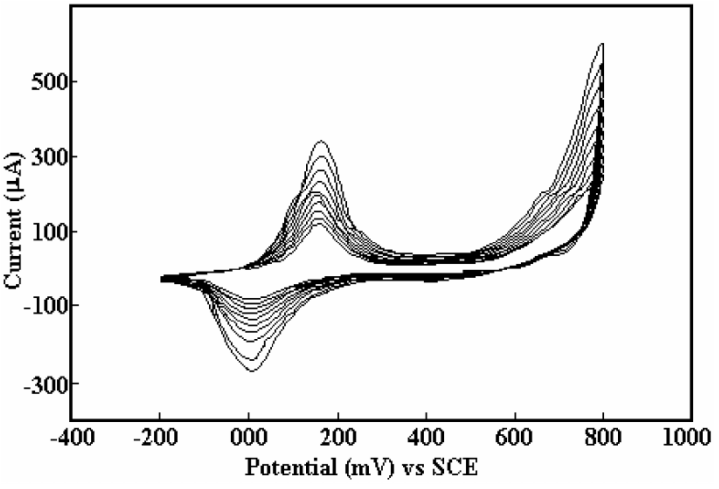

Figure 1. CV of growth of polyaniline from 0.1 M aniline in 0.5 M H_2SO_4.

from which connections to a bi-potentiostat were made. Polyaniline (PANI) was synthesized by electropolymerization of 0.1 M aniline monomer in 0.5 M H_2SO_4 within the pores (1.2 μm) of gold coated polycarbonate membranes. For electropolymerization the scanning was done between −0.2 and 0.8 V *versus* SCE at a scan rate of 50 $mV\,s^{-1}$. The sensor device was fabricated by immobilization of 2,3-dimercapto-1-propanol (prepared in 95% ethanol) by physical adsorption after polymerization in the same manner as described earlier [4, 5].

2.2 *Characterization of the polymer*

PANI films were characterized by cyclic voltammetry and *in situ* conductance measurements. Cyclic voltammograms of the polymer were recorded with the help of computer controlled EG & G PAR 273 potentiostat/galvanostat. Figure 1 illustrates a typical cyclic volammogram of polyaniline showing two prominent peaks due to oxidation and reduction of the polymer. *In situ* conductance measurements were carried out on the polymer formed on gold coated 1.2 μm pore diameter polycarbonate membranes in the transistor mode. The two sides of the membrane electrode act as 'source' and 'drain' of the electrochemical transistor. The charge flowing between source and drain was modified by the analyte which is analogous to the gate voltage in the conventional transistor. An AFRDE4 Pine bi-potentiostat coupled with a Philips multimeter was used for carrying out the conductance measurements.

2.3 *Sensor measurements*

Sensor response for Hg^{2+} ion is represented by $\Delta g/g_0$, where g_0 is the conductance of the sensor in the absence of the substrate and $\Delta g = g - g_0$, where g is the conductance in the presence of the substrate. Representing the response in this manner normalizes it for variations in conductance from sensor to sensor.

3. Results and discussion

3.1 *Sensor response*

The responses of the membrane devices were measured by dc conductance measurements as described earlier [10]. The sensor respone was measured at −0.2 V *versus* SCE with a 20 mV drain voltage, since the sensitivity (defined as change in response of the sensor per millimolar change in the concentration of the substrate in the linear region of response) was found to be highest at this potential for PANI based sensors. The experiment was repeated several times with films prepared under identical conditions. The conductance of the PANI film with the immobilized 2,3-dimercapto-1-propanol was measured in supporting electrolyte 10^{-2} M HCl at −0.2 V and 0.2 V to check the quality of the polymer. Normally polyaniline shows a three- to four-order change in conductance when it is switched from neutral state to oxidized state. Then it was exposed to various concentrations of Hg^{2+} ion prepared in 10^{-2} M HCl solution and conductance was measured. There was an increase in the conductance of the PANI film on exposure to increasing concentrations of Hg^{2+} ions and at higher concentrations it became saturated. The sensor response $\Delta g/g_0$ was plotted against the concentration of the Hg^{2+} ion. The sensor response is shown in figure 2. Using this method Hg^{2+} ion concentration as low as 10^{-12} M could be detected. The upper range selected was up to 10^{-7} M according to WHO limits in portable water for Hg^{2+} ion. To confirm that sensor response is due to binding of Hg^{2+} with 2,3-dimercapto-1-propanol a control experiment was also performed without immobilizing 2,3-dimercapto-1-propanol receptor in PANI matrix and in presence of varying concentrations of Hg^{2+} ion at the −0.2 V gate potential. Figure 2(b) shows that there was hardly any change in the sensor response in the absence of the receptor.

3.2 *Sensitivity*

The present polyaniline based conductometric sensor is sensitive to Hg^{2+} ion concentrations of as low as 10^{-12} M. This shows the high sensitivity of present sensor towards Hg^{2+} ion. In the present approach we are exposing the sensor to varying concentrations of standard Hg^{2+} ion solutions.

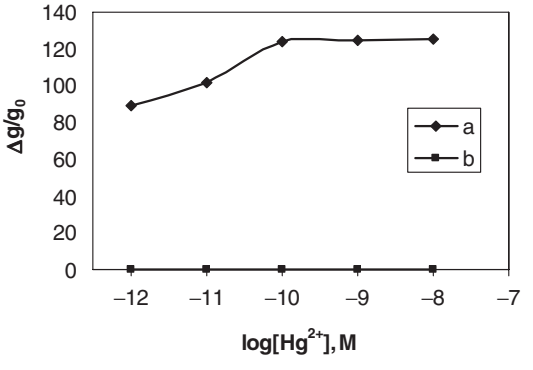

Figure 2. Sensor response of Hg^{2+} at $V_g = -0.2$ V *vs.* SCE; (a) when 100 mM of receptor (BAL) was immobilized in the polymer, (b) blank (without any receptor).

3.3 *Reproducibility*

This sensor is not reproducible. It gets saturated at higher Hg^{2+} ion concentrations.

3.4 *Accuracy*

Accuracy of the present sensor for different concentrations of Hg^{2+} ions is very good except that for each experiment we need to use a new sensor since it is not reproducible because of problems due to saturation at higher concentrations of Hg^{2+} ion.

3.5 *Interferences*

The main interferences are due to other heavy metals in Hg group for, e.g. As, Cd and Pd. The BAL receptor interferes with these metal ions. To find the interferences due to these metal ions we performed the identical experiments using the BAL receptor and other heavy metal ions as analytes. We found that though this sensor interferes with these metal ions it is not specific and hence sensor response is very low for these ions. Also since stability constant of BAL is maximum with Hg^{2+} ion it responds specifically to Hg^{2+} ion as compared to other heavy metal ions.

3.6 *Lifetime*

Since polyaniline is a very stable conducting polymer, sensors based on it are also stable. The present sensor can be stored for one or two weeks without any change in its sensitivity.

4. Conclusions

In this report, it has been shown that a conductometric Hg^{2+} sensor can be fabricated using 2,3-dimercapto-1-propanol as receptor and polyaniline as transducer as well as immobilization matrix. Using this approach, concentrations of Hg^{2+} ion as low as 10^{-12} M could be detected.

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References

[1] D. McQuade, A.E. Pullen Tyler, T.M. Swager. *Chem. Rev.*, **100**, 2537 (2000).
[2] P.N. Bartlett, Y. Astier. *Chem. Commun.*, **2**, 105 (2000).
[3] M. Umana, J. Waller. *Anal. Chem.*, **58**, 2979 (1984).
[4] D.T. Hoa, T.N. Suresh Kumar, R.S. Srinivasa, R. Lal, N.S. Punekar, A.Q. Contractor. *Anal. Chem.*, **64**, 2645 (1992).
[5] H. Sangodkar, S. Sukeerthi, R. Lal, R.S. Srinivasa, A.Q. Contractor. *Anal. Chem.*, **68**, 779 (1996).
[6] S. Sukeerthi, A.Q. Contractor. *Anal. Chem.*, **71**, 2231 (1999).
[7] R.B. Dabke, G.D. Singh, A. Dhanabalan, R. Lal, A.Q. Contractor. *Anal. Chem.*, **69**, 724 (1997).
[8] R.L. Coates, M.M. Jones. *J. Inorg. Nucl. Chem.*, **39**, 677 (1977).
[9] A.J. Canty, R. Kishimoto. *Nature*, **253**, 123 (1975).
[10] S. Sukeerthi, A.Q. Contractor. *Chem. Mater.*, **10**, 2412 (1998).