

Highly Selective Potentiometric Membrane Sensor for Hg(II) Based on Bis(Benzoyl Acetone) Diethylene Triamine

Ali A. Ensafi, S. Meghdadi, and Alireza R. Allafchian

Abstract—A new ion selective PVC membrane sensor is described based on bis(benzoyl acetone) diethylene triamine as a potentiometric sensor for Hg²⁺ ions. The membrane having bis(benzoyl acetone) diethylene triamine as an electroactive material, sodium tetraphenyl phthalate (NaTPB), and dibutyl phthalate (DBP) as an anion excluder in PVC matrix in the percentage ratio of 4.21:2.11:60.25:33.43 (Ionophore:NaTPB:DBP:PVC) (w/w) exhibits a linear response to Hg²⁺ ions in a concentration range of 1.0×10^{-6} to 1.0×10^{-1} M with a limit of detection of 3.7×10^{-7} M and with a slope of 29.8 ± 1.0 mV/decade over the pH range of 2.0–11.5. Selectivity coefficients for Hg(II) relative to a numbers of potential interfering ions were investigated. The sensor is highly selective for Hg²⁺ ions over a large number of mono-, bi-, and trivalent cations. Normal interferents like Ag⁺ and Cd²⁺ do not interfere in the working of the sensor. The sensor has been found to be chemically inert to other ions and showing a fast response time of 1 s and was used over a period of three months with a good reproducibility. The sensor was successfully applied to determine mercury(II) in water samples with satisfactory results.

Index Terms—Bis(benzoyl acetone) diethylene triamine, membrane sensor, mercury(II), potentiometry.

I. INTRODUCTION

MERCURY IS A toxic persistent bioaccumulative pollutant that affects the nervous system. It is found as industrial waste because of its growing area in production of some batteries, thermometers, cameras, cathode tubes, calculators, medical laboratory chemicals, and have been used as a catalyst in production of urethane polymers for plastics, a cathode in electronic production of chlorine and caustic soda, mercury vapor lamps and barometers. Thus, it is very important to determine mercury at lower levels in our environments. Various common methods are used to determine mercury such as complexometry [1], spectrophotometry, flame and atomic absorption spectrometry (AAS), inductively coupled plasma (ICP), fluorimetry, X-ray fluorescence, voltammetry, and potentiometry [2]. The available method for low-level determination of Hg(II) in solutions include flameless AAS and ICP, but it

Manuscript received August 8, 2007; revised October 3, 2007; accepted October 24, 2007. This work was supported in part by the Isfahan University of Technology Research Councils and the Center of Excellence in Sensors. The associate editor coordinating the review of this paper and approving it for publication was Prof. Michael Schoening.

The authors are with the College of Chemistry, Isfahan University of Technology, Isfahan 84156-83111, Iran (e-mail: Ensafi@cc.iut.ac.ir; smeghdad@cc.iut.ac.ir; allafchian@ch.iut.ac.ir).

Digital Object Identifier 10.1109/JSEN.2007.913146

involves expensive instrumentation and sample pretreatment, which is time consuming and inconvenient.

Potentiometric detection based on ion-selective electrodes (ISEs), offers several advantages such as speed and ease of preparation and procedures, simple instrumentation, relatively fast response, wide dynamic range, reasonable selectivity, and low cost [3]. Thus, the development of a selective sensor for mercury(II) has been a subject of investigation to analytical chemists. Several organic and inorganic compounds have been tested as an ionophore in producing ISEs. Table I shows most of the previously reported potentiometric method for determination of Hg(II). However, those ISEs have a short lifetime, and/or are prone to interference by a number of metal ions such as silver, iron, and cadmium ions. Recently, Gupta *et al.* ([26, Table I]) has reported an Hg(II) ISE based on diamine donor ligand with a linear range of 1.2×10^{-5} to 1.0×10^{-1} M. The sensor has a thin linear dynamic range and sodium and ammonium ions are also interfered. In this paper, we have reported an Hg(II) membrane sensor based on bis(benzoyl acetone) diethylene triamine (BBDT) as an ionophore. The developed sensor is selective to Hg(II), has a wide working concentration range, and a fast response time with reproducible results. The present ISE based on BBDT is comparable and superior in many results than those reported in literature (Table I).

II. EXPERIMENTAL

A. Reagents

PVC of high relative molecular weight, dibutyl phthalate (DBP), dioctyl phthalate (DOP), sodium tetraphenyl borate (NaTPB) and tetrahydrofuran (THF), and all other chemicals were of highest purity available from Merck, and were used without further purifications, except THF, which was distilled before using. All solutions were prepared by dissolving the salts of the metal nitrates in distilled deionized water.

Bis(benzoyl acetone) diethylene triamine (BBDT) is used as an ionophore which was prepared according to the reported method [4]. The ligand was synthesis according to the following procedure: a solution of 1.032 g (0.010 mole) of diethylenetriamine in 20 ml of methanol was added to a stirring solution containing 3.24 g (0.020 mole) of benzoylacetone in a minimum amount of diethyl ether. The result solution was stirred for 1 h at room temperature, and the volume was then reduced to 1/3 by slow evaporation. The concentration solution was then added dropwise to 240 ml of water with constant stirring. The resulting white crystals was filtered off and dried in the open air. Elemental analysis ($C_{24}H_{29}N_3O_2$,