A fast response cadmium-selective polymeric membrane electrode based on N,N′-(4-methyl-1,2-phenylene)diquinoline-2-carboxamide as a new neutral carrier

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Abstract

A new polyvinylchloride membrane sensor for Cd^{2+} ions based on N,N′-(4-methyl-1,2-phenylene)diquinoline-2-carboxamide (Mebqb) as a new and excellent neutral ionophore has been prepared. The sensor shows a Nernestian response for cadmium ions over a wide concentration range (1.0×10^{-6} to 1.0×10^{-1} M) with the determination coefficient of 0.9964 and slope of 29.9 ± 0.5 mV decade^{-1}. The limit of detection is 8×10^{-7} M. It has a fast response time of 3–8 s and can be used for at least 8 weeks without any divergence in potential. The electrode can be used in the pH range from 4.0 to 9.0. The proposed sensor shows a very good discriminating ability towards Cd^{2+} ion in comparison to some alkali, alkaline earth, transition and heavy metal ions. It was successfully applied for the direct determination of Cd^{2+} in standard and real sample solutions.

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1. Introduction

There is a challenge for analytical chemists to develop new sensors for the fast, accurate, reproducible, and selective determination of various species in the fields of environmental, agricultural and medicinal analysis. During the past two decades, many efforts has been done in the synthesis and characterization of neutral ionophore with high selectivity for specific metal ions to develop new potentiometric and optical sensors for the determination of the respective metal ions in real samples [1–3]. In modern world, the pollution of heavy metal ions is becoming more and more severe. Cadmium is a toxic heavy metal that appears in the environment mainly due to industrial processes. Besides natural exposure from soils or earth crust with high content of cadmium, anthropogenic processes like combustion of coal and mineral oil, smelting, mining, alloy processing, paint industries, etc. are the major sources of lead and cadmium to the people in the vicinity of the industrial areas.

Human uptake of cadmium takes place mainly through food. Foodstuffs that are rich in cadmium can greatly increase the cadmium concentration in human bodies. Examples are liver, mushrooms, shellfish, mussels, cocoa powder and dried seaweed. Another important source of cadmium emission is the production of artificial phosphate fertilizers. Cadmium strongly adsorbs to organic matter in soils. United States Environmental Protection Agency (EPA) has found cadmium to potentially cause the following health effects when people are exposed to it at levels above the minimum concentration level (MCL) for relatively short periods of time: nausea, vomiting, diarrhea, muscle cramps, salivation, sensory disturbances, liver injury, convulsions, shock and renal failure and in long-term cadmium has the potential to cause the following effects from a lifetime exposure at levels above the MCL: kidney, liver, bone and blood damage [4]. Recently, several techniques including; flame atomic absorption spectrometry (FAAS), electrothermal atomic absorption spectrometry (ETAAS), inductively coupled plasma mass spectrometry (ICP-MS) and atomic fluorescence spectrometry (AFS) [5–12] have been used for the determination of trace elements in different samples, but the wide utilization of these methods is limited by the expensive equipment. At the same

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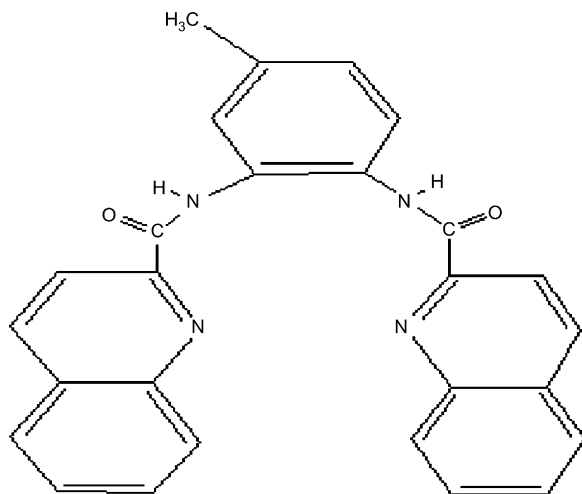
Scheme 1. The Mebqb structure.

time, numerous voltammetric methods especially using chemically modified electrodes (CME) have been developed [13,14]. Because of some imperfectness of these methods for application to routine analysis, considerable efforts have been directed towards the design and synthesis of highly selective ionophore [15]. Since less than three decades ago the solid-state ISE based on a mixed CdS/Ag$_2$S membrane has been commercially available [16]. Polymeric carrier-based ion-selective electrodes (ISEs) for determining the alkali metal cations such as sodium [17,18], potassium and lithium [19] have been studied numerously. The efforts are needed to make ion-selective electrodes for heavy metal ions in very low concentration [20,21], so we were interested in preparation of a new solvent polymeric membrane electrode for selective and fast monitoring of cadmium ion in solutions. The most important advantages of proposed polymeric carrier-based ISE over solid-state ISE based on a mixed CdS/Ag$_2$S membrane are their required fine conditioning, near-Nernestian slope and short response time [16]. In the present work, we use Mebqb, synthesized recently in our laboratories, as an excellent neutral ion carrier in construction of novel cadmium(II)–PVC membrane electrode [22]. The ionophore is shown in Scheme 1.

2. Materials and methods

2.1. Reagents

Reagent grade dibutyl phthalate (DBP), dioctyl phthalate (DOP), sodium tetraphenyl borate (NaTPB), tetrahydrofuran (THF) were purchased from Merck and polyvinylchloride (PVC) with high molecular weight from Fluka were used as received.

A 0.1 M stock solution of cadmium nitrate was prepared by dissolving an appropriate, accurate amount of Cd(NO$_3$)$_2$·4H$_2$O (Merck). A 1.0×10^{-6} to 1.0×10^{-1} M solution of cadmium ion was prepared daily by sequential dilution of the appropriate stock solution with doubly distilled water. Nitrate salts of cations (all from Merck) were of the high-

est purity available. All other reagents used were of analytical reagent grade, and doubly distilled water was used throughout. Mebqb as an ionophore was synthesized recently in our laboratories.

2.2. Construction and calibration of electrodes

Membranes with different PVC/plasticizer ratios were studied for finding the most suitable membrane composition. The optimum composition was 31% of powdered PVC, 59% of a plasticizer (DOP), 4% of an additive (NaTPB) and 6% of the corresponding ionophore. These were mixed in 5 mL THF. The resulting clear mixture was evaporated at room temperature slowly until an oily concentrated mixture was obtained. A Pyrex tube (3 mm o.d.) was dipped into the mixture for about 10 s, so that a non-transparent membrane of about 0.3 mm thickness was formed. The tube was then pulled out from the mixture and kept at room temperature for about 24 h. The tube was then filled with an internal filling solution (1.0×10^{-3} M Cd(NO$_3$)$_2$·4H$_2$O). The electrode was finally conditioned by soaking for 24 h in a 0.01 M solution of cadmium nitrate. An SCE electrode was used as the reference internal electrode. The compositions of the membrane electrode are summarized in Table 1.

2.3. Apparatus and emf measurements

A cadmium-selective PVC electrode and a saturated calomel electrode (SCE) were used as an indicating electrode and a reference electrode, respectively. The emf measurements were carried out at room temperature with a Fanavary Tajhizat Sanjesh pH meter Model 162, a double junction SCE reference electrode. The electrode cell assembly of the following type was used: (SCE) internal solution (1.0×10^{-3} M Cd(NO$_3$)$_2$·4H$_2$O) sensor membrane (sample solution) (SCE).

The potential reading of each solution was recorded when it became stable, and then plotted as a logarithmic function of Cd(II) cation activity. The activities of metal ions were based on the activity coefficient g, data calculated from the modified form of the Eq. (1) (Debye–Huckel Eq.), which is applicable to any ion:

$$\text{Log}\,\gamma = -0.511 Z^2 [\mu^{1/2}/(1 + 1.5\mu^{1/2}) - 0.2\mu] \tag{1}$$

where μ is the ionic strength and Z is the valency. All measurements were carried out at $25 \pm 0.1\,^\circ\text{C}$.

2.4. Procedure for the determination of Cd Ion in the real samples

Spiked and real water and waste water samples containing different cadmium concentrations for standard addition method were prepared by adding known amounts of cadmium to the samples. The cadmium selective and reference electrodes were immersed in the samples and the cadmium concentrations were determined by direct potentiometry and using the standard addition technique.