



Mercury selective potentiometric sensor based on low rim functionalized thiacalix [4]-arene as a cationic receptor

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ABSTRACT

A novel potentiometric mercury(II) sensor based on the use of cation receptor 5,11,17,23-tetra-*tert*-butyl-25,27-dihydroxy-26,28-bis(O-methyl glycerylcarbonylmethoxy) thiacalix [4]-arene in poly(vinyl chloride) (PVC) matrix for detection of Hg^{2+} has been developed. The sensor exhibits best performance with a membrane composition of PVC:*o*-NPOE:ionophore:NaTPB of 60:120:5:10 (% w/w). The sensor selectively used for determination of mercury ions is in the concentration range 5.0×10^{-8} – 1.0×10^{-2} M with a lower detection range of the order 1.0×10^{-8} M and a Nernstian compliance of (29.5) within pH range 6.0 to 7.5 and fast response time of 10 s. Influence of the membrane composition and possible interference of other ions have also been investigated on the response properties of the sensor. Fast and stable response, good reproducibility and long-term stability of the sensor are demonstrated. It has been observed that the developed sensor satisfactorily works in partially non-aqueous media up to 10% (v/v) content of methanol and acetonitrile and could be used for a period of 2.5 months. Selectivity coefficients determined with fixed interference method (FIM) and match potential method (MPM) indicate high selectivity towards mercury(II) ions. The proposed electrode shows fairly good discrimination of mercury from other cations. The developed mercury ion-selective electrode can be successfully employed as an indicator electrode in potentiometric titration with EDTA.

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1. Introduction

Mercury is an extremely rare element in the earth's crust but it has been widespread in the environment as a result of disposal of industrial and agricultural waste [1,2]. Its concentration is continuously increasing in the environment due to its extensive industrial applications. Mercury is used in lamps, batteries, thermometers, dental amalgams, explosives, electrolytic manufacture of chlorine and sodium hydroxide, catalysts, fungicides, herbicides, disinfectants, pigments and pharmaceuticals. It is considered by the Environmental Protection Agency (EPA) as a highly dangerous element because of its accumulative and persistent character in the environment and biota [3]. The tendency of mercury to accumulate in the food chain has resulted in many outbreaks of its toxicity. Chronic exposure to mercury leads to an insidious form of toxicity that is manifested by neurological effects which are referred to as asthenic vegetative syndrome. The syndrome is characterized by tremor, psychological depression, irritability, insomnia, emotional instability, vasomotor disturbances and autism [4].

Thus, mercury is an environmentally and toxicologically important element. Its toxicity from environmental pollution and occupational exposure continues to be an area of concern throughout the world. Thus, the need for its determination has generated increasing interest in the development of ion-selective electrodes for measurement of this analyte. In past years, a diverse range of mercury selective sensors has been developed [5–24] using PVC membrane and coated wire electrode. These sensors have a limited use for the determination of mercury ions due to their poor detection limit and narrow concentration range.

Calixarenes are well known for their relationship between design and selective complexation of metal ions because the size of their cavity is large enough to accumulate metal cation and they also have a sufficient number of donor atoms for coordination. Therefore, the calixarenes are used as an ionophore for selective determination of metal ions in electrochemical sensors [25]. In the last decade the calixarenes are recognized to form stable complexes with metals and act as ion carriers in the polymeric membrane. Almost all metals form 1:1 metal complexes with calixarenes. The geometric and cavity control of host–guest complexation and modulation of lipophilicity in calixarenes and calixarene derivatives provide remarkable selectivity, sensitivity and stability for specific ion. Thus, calixarene complexes have attracted increasing attention for determining cations such as Hg^{2+} [13,20], Sr^{2+} [26], Ag^+ [27,28], and

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Na⁺ [29–31]. The present work focuses on the use of 5,11,17,23-tetra-*tert*-butyl-25,27-dihydroxy-26,28-bis(O-methyl glycylicarbonylmethoxy) thiacalix [4]-arene as electroactive material for the fabrication of mercury selective electrode. It has been verified that these hosts adopt a pinched cone conformation in the solid as well as in the solution state. An investigation of hydrogen bonding in the solid state indicates a rather unusual involvement of bridging sulfur atoms in intramolecular hydrogen bonding interactions. Due to the complexity of hydrogen bonding interactions in the disubstituted molecule, an unusual crossover of the two tethered strands were noticed. These structural features make the ionophore selective towards cations. Also, the UV–vis and ¹H NMR spectroscopic studies of this compound carried out by Sreeja et al. [32] prefigure that receptor 5,11,17,23-tetra-*tert*-butyl-25,27-dihydroxy-26,28-bis(O-methyl glycylicarbonylmethoxy) thiacalix [4]-arene selectively binds with Hg²⁺ ion. Thus it was thought worthwhile to explore the newly synthesized cation receptor as potential material for preparing membranes, which may show selective potential response to mercury(II) ion.

2. Experimental

2.1. Reagents

All reagents used were of analytical grade. High molecular weight poly(vinyl chloride) (PVC), sodiumtetrphenylborate (NaTPB), and 2-nitrophenyloctyl ether (*o*-NPOE) were purchased from Fluka (Buchs, Switzerland) and used as received. Chloronaphthalene (CN), and tri-*n*-butyl phosphates (TBP) were obtained from High Media Laboratories (Mumbai); dibutyl phthalate (DBP), dioctyl phthalate (DOP) and EDTA were obtained from SD-Fine Chem. Limited (Mumbai, India). Analytical reagent-grade tetrahydrofuran (THF), methanol and acetonitrile (MECN) were obtained from Ranbaxy (New Delhi, India). Nitrate and chloride salts of all metals were purchased from Merck/Fluka and used without further purification except vacuum drying over P₂O₅.

2.2. Synthesis of ionophore

The ionophore 5,11,17,23-tetra-*tert*-butyl-25,27-dihydroxy-26,28-bis(O-methyl glycylicarbonylmethoxy) thiacalix [4]-arene (Fig. 1) was synthesized [32] by taking a solution of amino acid methyl ester hydrochloride (86 mg, 0.618 mmol) in dichloromethane (20 ml) at 0 °C, triethylamine (0.2 ml, 0.93 mmol) was added and stirred for 30 min. Then the acid chloride of thiacalix [4]-arene di-acetic acid (135 mg, 0.155 mmol) in dry CH₂Cl₂ was syringed out at once. The reaction mixture was then washed with NaOH (1.0 M), hydrochloric acid, brine and column chromatography using 100% distilled ethyl acetate as eluent. The product obtained was a white powdery material.

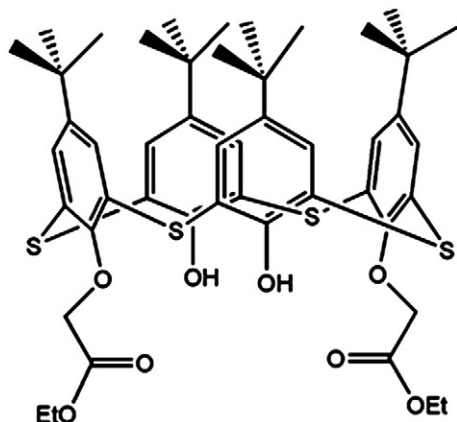


Fig. 1. Structure of 5,11,17,23-tetra-*tert*-butyl-25,27-dihydroxy-26,28-bis(O-methyl glycylicarbonylmethoxy) thiacalix [4]-arene.

The compound was stable at room temperature. Anal. Calc. for [C₅₀H₆₂N₂O₁₀S₄]: C, 61.32, H, 6.38, N, 2.86, O, 16.34, S, 13.10%. Found: C, 60.80, H, 6.32, N, 3.40, O, 16.50, S, 12.5%. IR: 3360 (broad) (NH, OH), 1740 (COOMe), 1650 (CONH, amide I) 1525 CM⁻¹ (CONH II).

2.3. Preparation of PVC membranes

The PVC membranes were prepared by dissolving 5,11,17,23-tetra-*tert*-butyl-25,27-dihydroxy-26,28-bis(O-methyl glycylicarbonylmethoxy) thiacalix [4]-arene, anion excluder NaTPB and PVC in 15 ml THF and the plasticizers CN, DOP, DBP, TBP and *o*-NPOE were added to get membranes of different compositions. The mixture was shaken vigorously with a glass rod and the THF was allowed to evaporate up to 5 ml. The homogenous mixture was concentrated by evaporating THF and then poured gently (so that bubbles are not formed) into polyacrylate rings placed on a smooth glass plate. After 24 h of evaporation when all THF had evaporated, a transparent membrane of ~0.5 mm thickness was formed and was removed carefully from the glass plate and cut to size and glued to one end of a Pyrex glass tube with araldite. The composition of membranes was optimized so that best performance characteristics are obtained. The quality of the membrane was controlled by taking the same composition and casting membranes slowly and carefully.

2.4. Apparatus and potential measurement

The ¹H NMR spectra of cation receptor were recorded on a Bruker AC 500 MHz spectrophotometer and elemental analysis was performed with a Vario ELIII instrument. The prepared PVC membranes were equilibrated for 24 h in 1.0 × 10⁻³ M Hg²⁺ solution. The potential measurements were carried out at 25 ± 0.1 °C with a digital potentiometer (model 5652 A, ECIL, India) by setting up the following cell assembly, employing saturated calomel electrodes (SCE) as a reference electrode.

Internal reference electrode (SCE)	Internal solution	Membrane	Test solutions	External reference electrode (SCE)
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The cell potentials were measured by varying the concentration of Hg²⁺ in the test solution in the range 1.0 × 10⁻¹⁰ to 1.0 × 10⁻² M.

3. Results and discussion

3.1. The effect of membrane composition on potential response of membrane

The selectivity and accuracy obtained for a sensor depends on the nature of the ionophore or receptor, membrane composition and the nature of the plasticizer. It is reported that the best commonly used composition for preparation of PVC membrane was ionophore or receptor 1–7%, PVC 25–34%, plasticizer 60–80% and other lipophilic additive 0.02–2%. The potential of sensors was measured by using different prepared membranes of the receptor as function of mercury ion free concentration and the potential response plots are shown in Fig. 2. From these plots the working concentration range, the slope and the response time have been evaluated and given in Table 1 along with the response for each sensor. It is seen from Table 1 that the response of the membrane (sensor no. 0) without plasticizer is poor in terms of short concentration range, non Nernstian slope, poor detection limit and high response time. It is therefore necessary to improve the performance of the membranes. It is documented that the addition of plasticizer and lipophilic additive [33,34] to the membrane tends to improve the performance of the membranes. Table 1 shows that the addition of plasticizers (CN, DOP, DBP, TBP and *o*-NPOE) improves the performance of the membranes in terms of near Nernstian slope, wider linear working concentration range, better detection limit and smaller response time. Further it is seen from Table 1 that out of the five plasticizers investigated

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