Mercury(II) Selective Membrane Electrode Based on Calix[2]thieno[2]pyrrole

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Abstract

The construction, performance, and applications of mercury(II) ion selective electrode based on calix[2]thieno[2]pyrrole receptor are described. The influences of membrane composition and pH on the potentiometric response of the electrode were investigated. The electrode exhibits Nernstian response (27.8 mV per decade) for Hg^{2+} ion over a wide concentration range (1.0×10^{-6} to 1×10^{-2} M). The response time of the electrodes is 20 s for the solution of Hg^{2+} ions in the concentration range of $1 \times 10^{-6} - 1 \times 10^{-2}$ M. The selectivity coefficient values showed better sensitivity and selectivity of this sensor for mercury(II) ions over various mono-, di, and trivalent cations studied. The sensor was also applied as indicator electrode in the potentiometric titrations.

Keywords: Calix[2]thieno[2]pyrrole, Ion selective electrode, Selectivity, Potentiometric titration

1. Introduction

Mercury is a toxic element that can be absorbed readily by humans and other organisms. It is well known that mercury ion inactivates sulfhydril enzymes and also combines with amine. The need for highly sensitive and selective mercury determination arises from its wide application in industry and its long term toxicity toward human beings. Over the last two decades, the need has increased for the determination of extremely low concentrations of mercury in various samples because it accumulates in living tissues, thereby causing many harmful effects (Baird & Freeman, 1995; Hill, 1974).

Toxicity of mercury and the need for its determination in clinical analysis and environmental monitoring has generated increasing interest in the development of ion-selective electrodes for measurement of this analyte. Dithiacrown ethers (Shih & Lai, 1986), antimony(III) arsenate (Gupta, Jain, & Singh, 1996), hexathia-18-crown-6-tetraone (Shamsipur, Fakhari, & Ganjali, 1997), bis[5-(4-nitrophenyl)azo salicylaldehyde] (Mashhadizadeh, & Sheikhshoaie, 2003) and thiosemicarbazone derivatives (Mahajan, Kaur, & Lobana, 2003) have been studied as ion-carriers in the preparation of PVC membrane electrodes for mercury(II) ions.

It has been shown that the presence of soft donor atoms in ligands results in a considerable increase in stability of their complexes with soft cations such as mercury and silver ions, while diminishing the stability of their alkali, alkaline earth metal ions and hard transition metal ion complexes (Izatt, Bradshaw, Pawlak, Bradshaw, & Bruening, 1991; Izatt, Bradshaw, Nielsen, Lamb, Christian, & Sen, 1985). In this respect, thio-containing compounds have attracted widespread attention owing to the unique properties of these compounds and their use as carrier in ISEs, is expected to increase their selectivity toward mercury and silver over those of alkali, alkaline earth and several other metal ions. The production of highly selective cation receptors is an area of great interest for researchers, particularly those that are able to enter selective interaction with heavy metal cations. The scope of supramolecular chemistry for the design of selective receptors opens the way for the development of new technological approaches for the detection and removal of toxic metal cations from contaminated sources. Calixpyrroles, a class of hetero-calixarenes, are a topic of considerable current interest in supramolecular chemistry because of their ability to act as receptors for anions (Danil de Namor & Shehab, 2003; Danil de Namor, Shehab, Abbas, Withams, & Zvietcovich-Guerra, 2006; Danil de Namor & Shehab, 2005; Danil de Namor & Shehab, 2004; Danil de Namor, Abbas, & Hammud, 2006) cations (Danil de Namor, Abbas, & Hammud, 2007; Danil de Namor & Abbas, 2007) and neutral molecules (Gale, Sessler, & Anzenbacher, 2001).

The applications of calixpyrroles are versatile ranging from the attachment of these macrocycles to silica for anion extraction purposes to the most recent studies on the use of these macrocycles for the development of fluorescence and optical sensors (Woods, Camiolo, Light, Coles, Hursthouse, King, Gale, & Essex, 2002; Gale, 2001).

So far no data concerning detection of mercury(II) cation by the calix[4]pyrrole derivatives have been published. In the light of the results reported (Danil de Namor, & I. Abbas, 2007) for Calix[2]thieno[2]pyrrole which shows its unique interaction with Hg(II) cation, this ligand is now utilized in the construction of Hg(II) ion selective electrode.

In the present work, we have explored the ability of calixpyrrole derivative to selectively detect mercury(II) ions in aqueous media. Polymeric ion-selective membrane sensor was investigated for various metal ions and the electrode characteristics of the optimized mercury(II)- selective electrode were studied in detail. The selectivity of this sensor was also examined with respect to variety of cations and the electrode was used as indicator electrode.

2. Experimental Work

2.1 Chemicals

All of the chemicals used were of analytical reagent grade (Merck). Doubly distilled water was used throughout. The calix[2]thieno[2]pyrrole was recently synthesized and its structure has been approved (Danil de Namor & I. Abbas, 2007). Dioctylsebacate (DOS), tetrahydrofuran (THF), sodiumtetraphenylborate (NaTPB) and high relative molecular weight poly (vinyl chloride) (PVC) were obtained from Merck or Sigma and used without any further purification. Also, the nitrate salts of all cations used (all from Merck) were of the highest purity available and were used without any further purification except for vacuum drying over P_2O_5.

2.2 Preparation of the electrode

Poly(vinyl chloride)-based Hg^{2+} membrane sensors were prepared as described in literature (Gholivand, Babakhanian, & Joshaghani, 2007) by thoroughly mixing 1 mg of ionophore (calix[2]thieno[2]pyrrole), 1 mg of additive (NaTPB), 33 mg of powdered PVC and 65 mg of plasticizer DOS in a glass dish of 2 cm diameter. The mixture was then completely dissolved in 5 mL of fresh THF. The mixture was shaken vigorously and the clear solution was poured into a petridish and allowed to evaporate overnight. A flexible, transparent membrane so obtained was cut to size and fixed onto the PVC tube with the help of PVC glue. The tube was then filled with internal filling solution of 1.0×10^{-3} mol L^{-1} of $Hg(NO_3)_2$. The electrodes were then conditioned for 24 h by soaking in a 1.0×10^{-3} mol L^{-1} solution of Hg(II). The electrodes were kept in 1.0×10^{-6} mol L^{-1} solution of Hg(II) when not in use.

2.3 EMF measurements

The response characteristics of the prepared electrodes were determined by recording potential across the membrane as a function of mercury- concentration at a constant temperature of 25 ℃. All the potential measurements were carried out with a digital pH/ion meter, model 692 Metrohm. A cell assembly of the following type was used: Ag/AgCl, KCl (3 mol L^{-1})| internal solution: $Hg(NO_3)_2$ (1.0×10^{-3} mol L^{-1}) PVC membrane|test solution|Hg/Hg_2Cl_2, KCl (satd.). The performance of each electrode was investigated by measuring its potential in mercury nitrate solutions prepared in the concentration range $1.0 \times 10^{-1} – 1.0 \times 10^{-7}$ M by serial dilution of the 0.1 M stock solution at constant pH. All pH adjustments were made with appropriate acid or base. The solutions were stirred and potential readings recorded when they reached steady state values. The data were plotted as observed potential versus the logarithm of the mercury ion- concentration.

3. Results and Discussion

3.1 Complex formation

The interaction between Hg(II) ion and calix[2]thieno[2]pyrrole (Figure 1) in acetonitrile was examined, and the nature of complex was investigated by ^{1}H NMR, conductometric and calorimetric titrations (Danil de Namor, Abbas, & Hammud, 2007). The results obtained from conductometric and calorimetric titrations showed the formation of 1:1 Hg^{2+}/calix[2]thieno[2]pyrrole complex with moderate stability (log K_s = 4.00). ^{1}H NMR and conductometric studies showed that calix[2]thieno[2]pyrrole interacts selectively with mercury(II) cation in preference to other cations. This was attributed to the presence of two alternative sulphur atoms of the thiophene rings in the cavity of the ligand. The importance of this ligand appears in its ability to interact with mercury only without any interference from other cations that may exist in solution. This unique interaction of

calix[2]thieno[2]pyrrole with Hg^{2+} cation encourages us to design mercury-responsive sensor for the potentiometric monitoring of Hg^{2+} cations in aqueous media. The results are described in the next sections.

3.2 Potentiometric measurements

The plasticized PVC-based membrane electrode containing the calix[2]thieno[2]pyrrole carrier responds to mercury according to Nernstian response. Therefore, we studied in details the performance of the membrane electrodes based on this carrier for mercury in aqueous solutions. A number of characteristics are required for a membrane ISE to be considered a suitable sensor for quantitative measurement of ions. Of these, slope, selectivity, working concentration range, response time, and electrode life time are most important. These characteristics have been taken into account in order to ascertain the utility of calixpyrrole derivative as ionophore for the preparation of mercury-selective electrode.

In preliminary experiment, membranes, with and without ionophore were constructed, the results showed that in absence of carrier the membrane displayed insignificant selectivity toward mercury, whereas in the presence of the ionophore, the membrane shows near Nernstian and remarkable selectivity for mercury over most common inorganic ions. As such, the potentials generated in the proposed sensor are ascribed to the uptake of mercury ions on the calix[2]thieno[2]pyrrole receptor. The preferential response toward mercury is believed to be associated with the pre-organisation and complementarity of the receptor upon interaction with Hg(II) ions in solution. Investigations revealed that proper equilibration of the membrane was achieved, when this was dipped in a solution of 1×10^{-3} M for Hg^{2+} cation for 24 hrs. Potential studies on the membrane sensors were carried out with the varying Hg^{2+} cation concentration (1.0×10^{-7} to 1.0×10^{-1} M).

A plasticizer is an important component of the membrane used in ion-selective electrodes. Membranes with a high amount of plasticizer ensure relatively high mobilities of their constituents owing to the low specific membrane resistance. The plasticizers used in the present study were dioctylsebacate (DOS). Also, the optimization of permselectivity of the membrane sensor is known to be highly dependent on the incorporation of additional components (Mazloum, Amini, & Mohammadpoor, 2000), therefore, NaTPB was also added to the membrane components for better results. This electrode exhibited the best working concentration range of 1.0×10^{-6} to 1.0×10^{-2} M with a slope of 27.8 mV per decade of activity (Figure 2). The limit of detection for this membrane calculated as recommended by IUPAC from the intersection of the two extrapolated segments of the calibration curve was 1.0×10^{-6} M.

3.3 Response time and effect of pH

The response time, an important factor of an ion-selective membrane sensor, was recorded at different concentrations of $Hg(NO_3)_2$ in the sample solution. The potentiometric response of sensor was recorded by changing the solution from lower (1.0×10^{-7} M $Hg(NO_3)_2$) to higher (1.0×10^{-1} M $Hg(NO_3)_2$) concentration. The response time of the sensor was found to be 20 s at various concentrations of the test solution and found to remain stable for several days without much drift in potentials. The electrode potentials were reproducible, and the standard deviation of four identical measurements was ±1.3 mV at various concentrations of mercury(II) ions. In terms of lifetime, this electrode gave stable potentials over the period of six months without any significant divergence in its Nernstian behavior.

The influence of pH of the test solution on the potential response of the membrane sensor was tested in the pH range 1.0-12.0 (for 1.0×10^{-3} M mercury solution) and the results are shown in Figure 3. It was observed that the potential response of the electrode is pH dependent. The potential was constant from pH 1.0-6.0 beyond which the potential decreases sharply. The observed drift in potential at higher pH values may be attributed to the hydrolysis of Hg^{2+} and formation of some hydroxyl complexes of mercury(II) ion in solution.

3.4 Selectivity

The selectivity is one of the most important characteristics of a sensor, as it often determines whether a reliable measurement in the sample solution, in the presence of interfering ions, is possible or not. It is measured in terms of potentiometric selectivity coefficients $K_{Hg^{2+},M^{n+}}^{Pot}$. In the present work, the selectivity coefficients have been determined using the fixed interference method (FIM) based on semi-empirical Nicolsky-Eisenman equation at 1.0×10^{-3} M concentrations of interfering ions. Table 1 gives the potentiometric selectivity data of mercury(II) sensor for various interfering ions. Very low values of log $K_{Hg^{2+},M^{n+}}^{Pot}$ for alkali, alkaline-earth, and some

heavy metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+}) indicate that these metal ions do not cause much interference, even when present at a high concentration of 1.0×10^{-3} M in the test solution.

However, although a soft metal ion, Ag^+, is a significant interfering ion, the logarithmic value of the corresponding selectivity coefficient for Hg^{2+} against Ag^+ is small, which is 0.628. Although the interference of Ag(I) still exists, it is insignificant, and as such the prepared electrode is suitable for analysis of Hg(II) ions in environmental waters. Therefore, the selectivity of the present ion-selective electrode is good enough to assure analytical application.

3.5 Comparison with other Hg(II) electrodes

A comparison with other Hg^{2+} ion-selective electrode based on various ionophores reported in the literatures (Mashhadizadeh & Sheikhshoaie, 2006; Zka & Pietraszkiewicz, 1991; Lai & Shih, 1986; Siswanta, Kin, Hisamoto, & Suzuki, 1996; Javanbakht, Ganjali, Eshghi, Sharghi, & Shamsipur, 1991) was made. Table 2 presents the potentiometric selectivity coefficients and slope of some mercury(II) ion-selective electrodes. The proposed electrode based on calix[2]thieno[2]pyrrole ionophore exhibits superior in many respects than those reported ionophores, such as response time (20 s) and potentiometric selectivity over other metal ions. Meanwhile, relatively cheap and easily synthesis method indicate the proposed electrode will be used widely in the future.

4. Application

The sensor was used as an indicator electrode to determine the end point in potentiometric titrations of mercury(II) ions with EDTA solution. A typical titration curve of a 25 ml 2.4×10^{-3} mol l^{-1} Hg^{2+} solution with 1.7×10^{-2} mol l^{-1} EDTA solution is shown in Figure 4. A very good inflection point is observed in the titration plot. Before the end point, the potential shows a usual logarithmic change with the volume of titrant added, while the potential response after the end-point remains almost constant, which may be due to the low concentration of free Hg^{2+} ions in the solution (Fakhari, Ganjali, & Shamsipur, 1997).

5. Conclusion

An Hg-ISE based on calix[2]thieno[2]pyrrole has been prepared. The electrode exhibits good Nernstian response and linearity range, fast potential response, high selectivity and reasonable life time. The only drawback is the rather narrow pH range obtained. The proposed electrode functions well either as ISE or indicator electrode.

Acknowledgements

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Table 1. Selectivity coefficient of various ions with Hg(II) sensor based on calix[2]thieno[2]pyrrole

Interfering Ion	$-\log K^{Pot}_{Hg^{2+},M^{n+}}$
Ag^+	0.628
K^+	0.147
Na^+	0.056
Cu^{+2}	-2.960
Cd^{+2}	-9.960
Ni^{+2}	-2.930
Pb^{+2}	-3.020
Mg^{+2}	-2.930
Ca^{+2}	-2.940

Table 2. Some Hg-ISE based on various organic ionophores

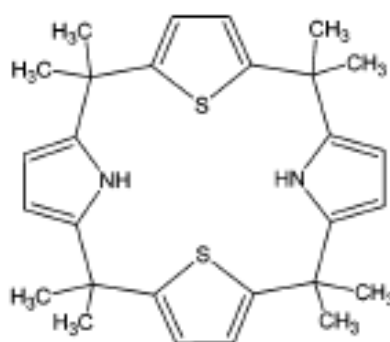| Ionophore	Slope (mV/decade)	$-\log K^{Pot}_{Hg^{2+},Ag^+}$	Reference
Calix[2]thieno[2]pyrrole	27.8	0.628	This work
Bis[5-(4-nitrophenyl)azo] salicylaldehyde	30.0	4.10	22
Diaza-18-crown-6	41	-2.60	23
Dithia-12-crown-4	30	3.40	24
N,N-dibenzyl oxysebacic acid diamide	70	3.90	25
Dibenzodiazathia-18-crown-6-dione	29	1.82	26

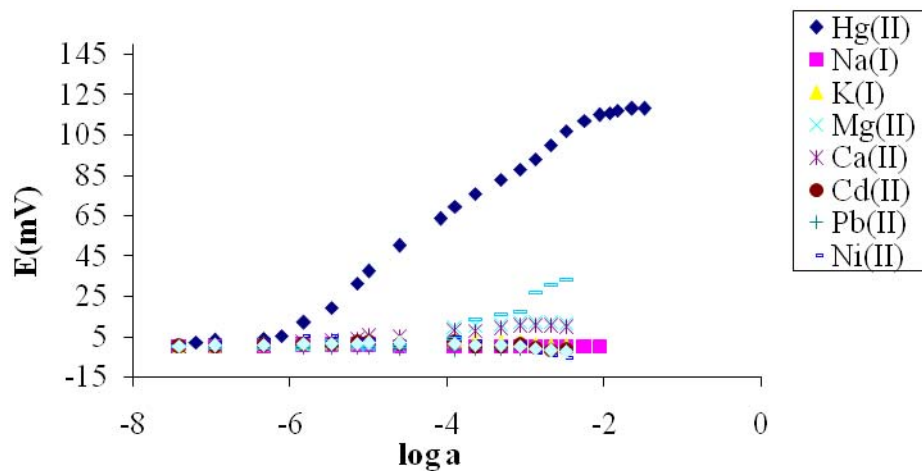Figure 1. Chemical structure of calix[2]thieno[2]pyrrole

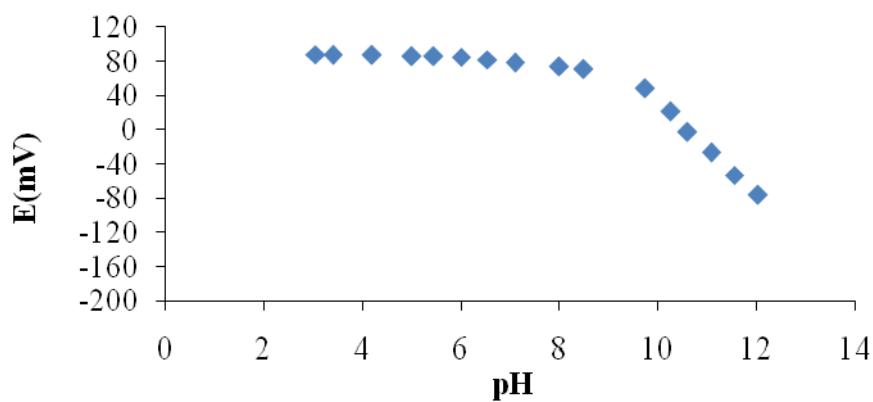Figure 2. Potentiometric response of ionophore electrode for various metal ions

Figure 3. The pH response of Hg^{2+} - selective electrode based on calix[2]thieno[2]pyrrole
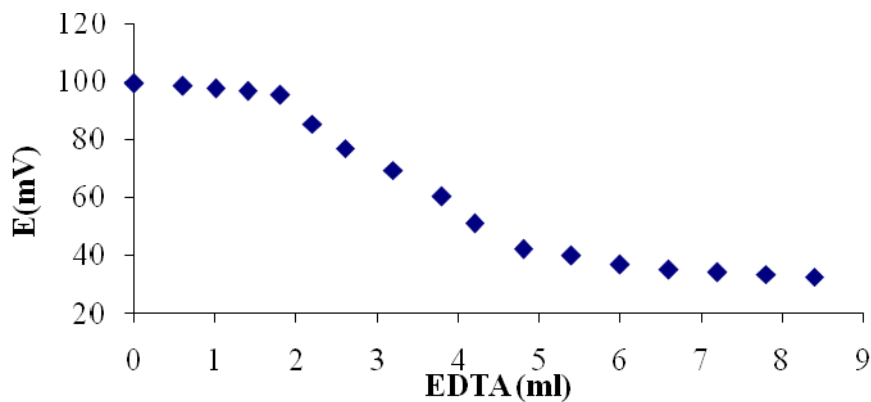

Figure 4. Application of the Hg^{2+} - ISE for potentiometric titration of 25 ml 2.4×10^{-3} mol l^{-1} Hg^{2+} solution with 1.7×10^{-2} mol l^{-1} EDTA