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Mercury(II) ion-selective electrode. Study of 1,3-diphenylthiourea as ionophore

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A new liquid membrane, mercury(II) ion-selective electrode (ISE) based on 1,3-diphenylthiourea as a neutral carrier was developed. In solubility tests of 1,3-diphenylthiourea in six different plastizicers, tris(2-ethylhexyl) phosphate (TEHP) showed the best performance and was selected for the membrane. Several ISEs were conditioned and tested for the selection of seven metal ions (Hg^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Ca^{2+}, Mg^{2+} and Ag^{+}). The best Nernstian response was obtained for Hg^{2+} with an experimental slope of 58.6 ± 0.8 mV per decade in the concentration range 6.0×10^{-6}–5.0×10^{-4} mol l^{-1}; the presence of the complex $Hg(OH)^{+}$ ion explains the slope of the response curve. The ISE showed stable detection reproducibility during 6 weeks, with a practical detection limit of 10^{-6} mol dm^{-3} and a high selectivity for Cd^{2+}, Pb^{2+}, Co^{2+}, Cu^{2+}, Sr^{2+}, Zn^{2+}, Ca^{2+}, Mg^{2+}, Mn^{2+}, K^{+}, Na^{+} and NH_4^{+} ions. Only one interference for Ag^{+} was found. A second linear response curve for Hg^{2+} was obtained at pH 4 with a slope of 30.8 mV per decade in the concentration range 2.0×10^{-6}–2.1×10^{-4} mol l^{-1}.

Introduction

Analytical chemists have long been concerned with developing selective electrodes for the detection of mercury ions. Solid state mercury(II) sulfide electrodes have been described in many papers.[1] These ion-selective electrodes (ISEs) respond to mercury(II) ion activity in solution. Good linear response limits have been reported for these ISEs; many factors strongly influence the characteristics and quality of the sensors, for example high purity of sulfides, mechanical properties, temperature and pressure used in making pellets. Liquid-membrane ISEs are one of the most important groups of chemical sensors, and recent reviews have been published.[2–4] Those electrodes are currently prepared with the PVC immobilized carrier deposited directly on the conductive composite, without an internal reference solution.[5,6] The composite material is generally prepared with a mixture of graphite, epoxy resin and hardener in suitable ratios.[7] The procedure for the construction of the PVC membrane electrode is easy to implement, inexpensive and reliable.[8,9] These electrodes show good stability and their responses are acceptable for analytical applications.[9]

Many organic and inorganic compounds have been tested as ionophores in producing ISEs, including crown ethers[10] and acyclic compounds such as dithiocarbamates and their metal ion complexes,[11] amides[12] and oxamides.[13,14] However, there is no efficient commercial mercury(II) ISE available and there have been few literature reports. Dithia crown ethers have been tested in Hg^{2+}-selective PVC membrane electrodes[15] with a good linear response of 30 mV per decade at pH 2–5 within the concentration range of 10^{-2}–10^{-6} mol l^{-1} and high ion selectivity. Recently, hexathia-18-crown-6-tetraone has been reported[16] as a very selective ionophore for Hg^{2+} ion, with a Nernstian response of 30 mV per decade at pH 0.5–2 in a similar concentration range; this ISE does not have a conductive composite as membrane support, but has an inner reference solution, and it can detect Hg^{2+} in the pH range 0.5–5. However, this ISE is not successful at pH $>$ 5, but the presence of sulfur atoms in crown ethers improves the selectivity towards heavy metal ions. Other ISEs based on sulfur ionophores, without high selectivity, have also been reported.[1,4]

In recent years, we have studied some thiourea derivatives as neutral carriers in PVC electrode membranes for heavy metal ions. A Pb(II) ISE based on 1-furoyl-3-phenylthiourea[17] and a Cd(II) ISE based on 1-furoyl-3-benzyl–3-phenylthiourea[18] have been reported. Fig. 1 shows the structure of the best Pb(II) and Cd(II) ionophores found in this family. These molecules contain three different heteroatoms (N, S, O) that promote complex formation with transition and heavy metal ions.

The optimized structure of 1-furoyl-3-phenylthiourea and the energies of HOMO, HOMO-1 and LUMO, recently reported,[19] have also been calculated using DFT methods and the Dgauss program. The calculated hardness (η†) on sulfur was the lowest value among the other atoms present. HOMO and HOMO-1 are both localized on the sulfur atom. Therefore, the interaction of this molecule with soft cations could be carried out preferably through the sulfur atom. That explains its high reactivity

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† Where η according to the Koopmans theorem is defined by $\eta = ([-E(\mathrm{HOMO})] - [-E(\mathrm{LUMO})]/2$, in which E(HOMO) and E(LUMO) are the energies of the HOMO and LUMO, respectively.

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towards Hg^{2+} and Ag^+, which strongly interfere with the Pb(II) ISE. Other furoylthiourea derivatives have been reported as ISE ionophores for ions.[20,21]

This paper reports the behavior of a Hg(II) ISE based on the simple and inexpensive ionophore 1,3-diphenylthiourea. This electrode can detect Hg^{2+} at low pH and $Hg(OH)^+$ at near neutral pH with selectivity advantages over other previously reported electrodes.

Experimental

Equipment

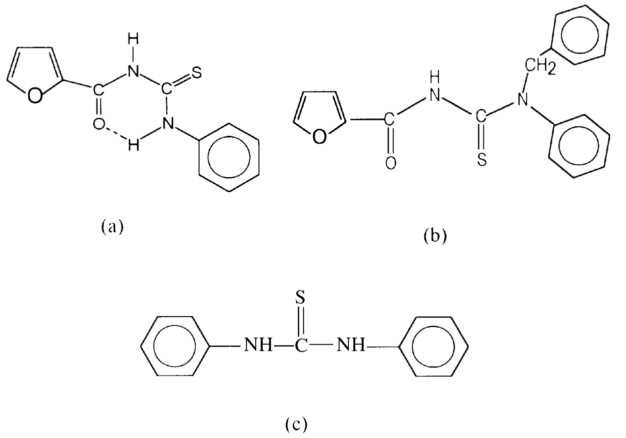
Potentiometric measurements were performed with a Cole Parmer (Vernon Hills, IL, USA) digital potentiometer (Model 59003-00, ±0.1 mV sensitivity). The reference electrode was an Orion, (Cambridge, MA, USA) Model 90-00-01 double-junction Ag/AgCl electrode. pH values were determined with a Cole Parmer Model 05772-20 simple junction glass electrode. Labnet (National Labmet Co., Woodbridge, NJ, USA) V-20 (2–20 μl) and Brand 20–100 μl (Rudolf Brand GMBH-Co, Wetheim, Germany) micropipettes and a Sybron Thermoline (Dubque, IA, USA), Model SP-A1025B magnetic stirrer were used. Additionally, scanning electron microscopy (Phillips Eindhoven, The Netherlands; XL30) with X-ray analysis (EDAX, Mahwah, NJ, USA) was used to assess the morphology and elemental composition of this membrane.

Reagents and solutions

Standard solutions made with high-purity water (0.1 μS cm^{-1}) and the appropriate analytical reagent-grade salts were prepared according to the literature.[22,23] Tris(2-ethylhexyl) phosphate (TEHP), bis(2-ethylhexyl) sebacate (BEHS), dioctyl phthalate (DOP), *o*-nitrophenyl octyl ether (oNPOE), 3-nitro-1,2-xylene (NOX) and dibutyl phthalate (DBP) were tested as solvent mediators. High molecular weight poly(vinyl chloride) (PVC) and tetrahydrofuran (THF) were purchased from Aldrich (Milwaukee, WI, USA). The ionophore was purified by double recrystallization from ethanol and dried over $CaCl_2$ for several days. A graphite–epoxy transductor was prepared with powdered graphite (1–2 μm) purchased from Aldrich and Araldite hardener from Ciba-Geigy (Basle, Switzerland).

Solubility tests

The best mediator and its concentration at which the total solubility of ionophore is achieved was obtained in the following manner: 4 mg of ionophore were placed in six containers to study six different mediators, 18 μl of the mediator were added to the particular container in steps of 2 μl and after each step the solubility properties of the ionophore were observed. The results of the qualitative and quantitative solubility tests for each mediator are given in Table 1.



(a) (b) (c)

Fig. 1 Structures of previously studied ionophores, (a) for Pb(II), (b) for Cd(II), and (c) ionophore used in this work.

Electrode preparation

The ISEs were constructed as typical all-solid-state PVC matrix membranes as described previously.[8,24–26]

The conductive polymer composite (graphite-loaded epoxy resin) used as internal contact and transducer was prepared by mixing 0.15 g (32% w/w) of Araldite M, 0.06 g (13% w/w) of Hardener HR and 0.26 g (55% w/w) of powdered graphite and drying the mixture at 40 °C for 48 h.

The sensor membrane was prepared as described previously[8,24–26] with the following composition: 1,3-diphenylthiourea, 5% w/w, 10 mg; TEHP, 61% w/w, 0.137 ml as plasticizer; and PVC, 34% w/w, 66.67 mg. The components were dissolved in THF (5 ml) and the solution was dropped on the solid conductive support in portions. The membrane was dried at room temperature for 2 d. Before using the electrodes, they were conditioned by soaking them in a 10^{-3} mol l^{-1} solution of $Hg(NO_3)_2$ and in 0.01 M KCl for 48 h according to the Bakker method.[27–29]

Calibration of the electrode

Standard techniques for the evaluation of the electrode response characteristics were used. The measurements were performed by the additions method.[26,30–32] The solution was stirred to ensure equilibrium, aliquots (5, 10, 25 and 50 μl) of the tested ion solution were added to 25 ml of water and e.m.f. values were recorded when stable readings were obtained after each addition (usually after 30 s) in an open cell at room temperature (20 ± 1.5 °C). The electrodes were washed prior to use and ion activities were calculated according to the Debye–Hückel procedure.[33]

Table 2 gives the electrochemical characteristics of the ISE: *S* (slope), LLLR (lower limit of linear range) and LLD (lower limit of detection)

Table 1 Solubility tests on the ionophore 1,3-diphenylthiourea with six mediators[a]

Addition/ μl	Mediator					
	TEHP	3-NOX	BEHS	DOP	DBP	2-NPOE
2	*	*	*	*	*	*
4	*	++	+++	*	++	++
6	*	+++	+++	++	+++	++
8	+++	+++	+++	++	+++	+++
10	+++	+++	+++	+++	+++	+++
12	+++	+++	+++	+++	+++	+++
14	◆	+++	++++	++++	++++	++++
16		+++	++++	++++	++++	++++
18		+++	++++	++++	++++	++++

[a] *, Insoluble; +, hardly soluble; ++, slowly soluble; +++, crystal not soluble; ++++, almost soluble; ◆, totally soluble.

Table 2 Electrochemical characteristics of the ISE

pH	Slope (*S*)/ mV per decade	LLLR/ mol l^{-1}	LLD/ mol l^{-1}	Response time/s
6–7[a]	58.6 ± 0.8	2.0×10^{-6}	2×10^{-6}	20
4	30.8	6×10^{-6}	4×10^{-6}	20

[a] Relative deviation = 1%; linear correlation coefficient r = 0.970.

Selectivity

K^{pot} values were determined by the three approved IUPAC[34,35] methods: the fixed interference method (FIM), the separate solution method (SSM) and the matched potential method (MPM); additionally, K^{pot} was determined using Bakker's method.[27–29] In all cases the resulting K^{pot} values were very similar (Table 3). The initial concentration for the interfering ions in the fixed interference method[34] was 10^{-2} mol l^{-1}.

Statistical evaluation data

Five series of three electrode units were prepared. Potential measurements were performed daily in the first week, on alternating days during the next 2 weeks and twice a week subsequently. Linear correlation coefficients, slope values and statistical data were obtained.

Results and discussion

1,3-Diphenylthiourea was completely soluble in the TEHP employed as a plasticizer. It was necessary to prepare the membrane at controlled humidity and temperature, because high relative humidity and low temperature (< 16 °C) affect its quality.

Calibration curves obtained for a selected electrode at different pH values are shown in Fig. 2 and 3. At pH 6.0–7.0, the average response characteristic of the ISEs showed a twice Nernstian response in the concentration range 2.0×10^{-6}–2.0×10^{-4} mol l^{-1} with a slope of 58.6 ± 0.8 mV per decade. This is a typical value for monovalent cations, and it is assumed that the $[Hg(OH)]^+$ ion is present in this near neutral medium, because it is well known[35] that, in pure water, Hg(II) can be found in two different ions forms, Hg^{2+} and $[Hg(OH)]^+$, as a function of the pH.

At pH 4.0 the response characteristic of the ISEs showed a Nernstian response in the concentration range 6.0×10^{-6}–5.0×10^{-4} mol l^{-1} with a slope of 30.8 mV per decade. This is a typical slope value for a divalent cation and in this case the electrode can therefore be used for the determination of Hg^{2+} species.

The ion selectivity test for this liquid membrane was performed using four methods. The K^{pot} values obtained were very similar with all four methods employed; the unbiased method (Bakker) gave slightly better results than the IUPAC methods. The highest significant difference was observed for Ag^+ ions, impossible to measure using the FIM method; the SSM and MPM methods gave K^{pot} values of 10^{-1} and for the unbiased method 10^{-2} was obtained. These experimental K^{pot} values demonstrate the selectivity of these ionophores towards all the interferent cations studied.

Table 4 shows the different slopes for some interfering ions; in general, all the response curves, are not exactly Nernstian but have a potential *vs.* log *a* dependence, except for Ag^+, which does not respond if the electrode is activated by a principal cation. However, when the SSM, MPM and Bakker methods were applied their response was the correct one.

Table 3 Ion selective electrode based on 1,3-diphenylthiourea: selectivity coefficients (K^{pot}) measured at pH 6 for various interfering ions by four methods

Ion	FSM	SSM	MPM	Bakker
Mn^{2+}	7.10×10^{-4}	3.90×10^{-5}	-4.47×10^{-4}	5.64×10^{-5}
Sr^{2+}	2.00×10^{-5}	1.85×10^{-5}	-9.97×10^{-4}	8.36×10^{-5}
NH_4^+	4.30×10^{-4}	3.08×10^{-3}	-5.12×10^{-4}	5.26×10^{-3}
Ca^{2+}	1.40×10^{-3}	1.35×10^{-5}	-6.88×10^{-4}	4.12×10^{-5}
Co^{2+}	2.70×10^{-5}	1.15×10^{-5}	-2.96×10^{-3}	3.21×10^{-5}
Cu^{2+}	8.00×10^{-5}	1.43×10^{-5}	7.29×10^{-4}	5.02×10^{-5}
Pb^{2+}	5.30×10^{-5}	1.99×10^{-5}	-1.47×10^{-3}	6.84×10^{-5}
Ag^+	Absent	5.77×10^{-1}	6.43×10^{-1}	5.35×10^{-2}
Zn^{2+}	2.70×10^{-5}	6.19×10^{-5}	8.93×10^{-4}	5.39×10^{-5}
Cd^{2+}	1.30×10^{-5}	4.16×10^{-5}	1.03×10^{-3}	3.99×10^{-5}
Mg^{2+}	7.10×10^{-4}	2.89×10^{-5}	7.60×10^{-4}	8.10×10^{-5}

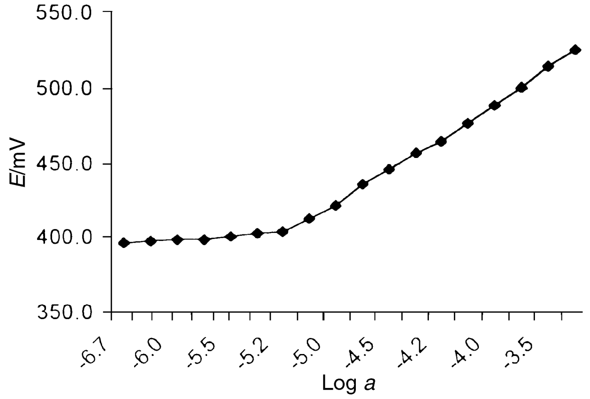


Fig. 2 Calibration curve for $Hg(OH)^+$ with a linear response at pH 7.0. Slope of 58.6 mV per decade typical of M^+ ions.

Response mechanisms

Some workers[36,37] have reported apparently twice Nernstian responses with regular divalent selective electrodes, namely Ba^{2+} and Ca^{2+} ISEs, and explained this phenomenon by a continuous interchange of H^+ and M^{2+} ions. This explanation is believable because all of the ionophores were acidic molecules. A similar hypothesis was evaluated in this work but it was rejected because the ionophore 1,3-diphenylthiourea does not have such an active acidic proton, and the plasticizer used is neutral. Also, no ionic sites were present. Lindner *et al.*[38] also

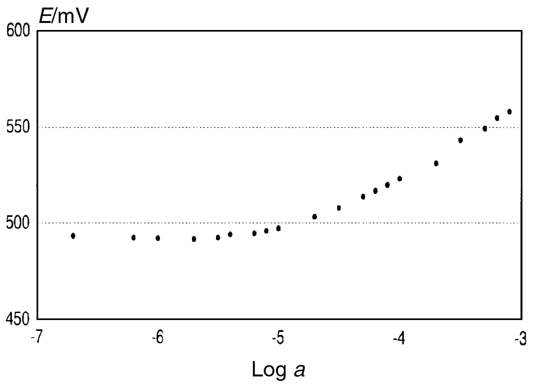


Fig. 3 Calibration curve for Hg^{2+} with a linear response at pH of 4.0. Slope of 30.8 mV per decade typical of M^{2+} ions.

Table 4 Slope of the calibration lines for the different cations

Cation	Slope/mV per decade
Cu^{2+}	24.53 ± 0.3
Zn^{2+}	62.45 ± 0.3
Pb^{2+}	49.18 ± 0.3
Ca^{2+}	35.81 ± 0.3
Mg^+	51.94 ± 0.3
Ag^+	1.73 ± 0.5

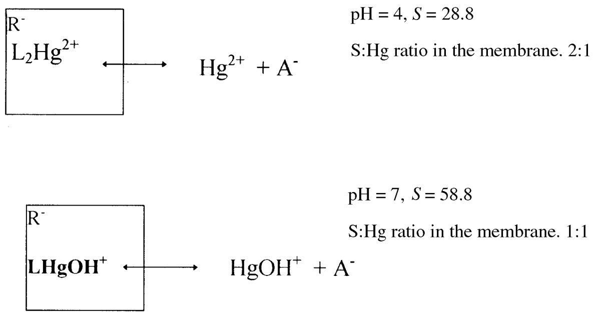


Fig. 4 Schematic diagram of the composition of the membrane with the complexes of the primary ion with the ligand at two different pH values.

found a twice Nernstian response for Pb^{2+} ISEs, and reported a Pb^{2+} ion associated with A^- anions present in the sample solution for OH^- and $Pb(OH)^+$.

For Hg^{2+} chemical equilibrium[38,39]

$$Hg^{2+} + OH^- \rightleftharpoons HgOH^+ + OH^- \rightleftharpoons Hg(OH)_2$$

under more acidic conditions the predominant cation is Hg^{2+}, but when the pH is nearly neutral the fundamental cation is $HgOH^+$ and this is the cation to react with the ligand. The above observation is in agreement with Lindner *et al.* but in this case for Hg ions.

In order to test this idea, several samples of activated electrodes at different pH were observed under an electron microscope to study the process in the membrane, where it was possible to observe particles of the ligand–metal complex, and a quantitative chemical analysis was carried out using X-ray analysis coupled with SEM. For the ISE operated at pH 4 the observed S : Hg was 2 : 1, so the complex must be ligand–Hg–ligand, typical of Hg^{2+} coordination. At pH 6 the S : Hg ratio is 1 : 1, so the complex must be ligand–Hg–X, and X must be OH^- owing to the pH dependence.

Fig. 4 shows a schematic diagram of the membrane composition with the complexes of the primary ion with the ligand at two different pHs, in which the complexes L_2Hg^{2+} and $LHgOH^+$ are in agreement with the S : Hg ratio.

The ISE could be used for at least 6 weeks and the response time was 20 s.

The electrochemical performance characteristics of the electrode were systematically evaluated according to IUPAC recommendations[23] and the results are given in Table 1. Linear correlation coefficients and statistical data are also reported. The reported data for the ISE operated at pH 6.0–7.0 is the average value from 64 reproducible calibration measurements for each electrode (15 units). The parameter values decrease after 6 weeks.

The pH dependence of the membrane electrode was tested over the pH range 2–10 at 3.0×10^{-5} mol l^{-1} Hg^{2+} concentration. The ISE has a working pH range of 4–7, but the recommended working pH range is 6–7. The drastic drift of the potential values at pH > 7 are attributed to the formation of mercury(II) hydroxide.

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