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Response mechanism of a neutral carrier Hg(II) polymeric membrane ion-selective electrode. SEM and EDAX study

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Scanning electron microscopy (SEM) and energy dispersive atomic X-ray spectrometry (EDAX) were used to study the response mechanism of a previously reported new Hg membrane ion-selective electrode (ISE) based on 1,3-diphenylthiourea. These techniques allowed the study of the membrane surface characteristics, such as the morphological homogeneity and chemical composition. A 'twice Nernstian' response at $\text{pH} \geq 7$ was explained by the detection of the $Hg(OH)^+$ cation. A normal Nernstian response was found at acidic pH values. Using these techniques, both coordination compounds, [Ligand–Hg–OH] at pH 7 and [Ligand–Hg–Ligand] at pH 4.5, were confirmed on the electrode membrane surface activated with $Hg(NO_3)_2$ solution at both pH values. These methods provide results which are independent of the potential measurement data and in agreement with them. A successful response model has explained both independent and unbiased sets of results. These conclusions confirm the proposed response mechanisms for this new Hg membrane sensor.

Introduction

In a recent paper,[1] we reported a new liquid membrane mercury(II) ion-selective electrode (ISE) based on the simple and low cost ionophore 1,3-diphenylthiourea (DFT) as a neutral carrier. The membrane ISEs were prepared with poly(vinyl chloride) (PVC) and tris(2-ethylhexyl)phosphate (TEHP) as plasticizers. This ISE presents advantages in selectivity compared with other electrodes previously reported. It has a stable detection reproducibility during 6 weeks, with a practical detection limit (PDL) of 10^{-6} mol dm^{-3} and a high selectivity towards most ions. Ag^+ was the only interference found. This ISE exhibited two linear response slope values at different pH values: the expected Nernstian value for a divalent ion (Hg^{2+}) of 30.8 mV decade^{-1} at pH 4.5 and an unexpected slope, typical of a monovalent ion (so-called 'twice Nernstian' slope[2]), of 58.6 ± 0.8 mV decade^{-1} at pH 7. The latter was explained by the presence of the $Hg(OH)^+$ ion in solution at neutral and alkaline pH.

Some authors[2,3] have reported an apparent 'twice Nernstian' response in regular divalent selective electrodes, *i.e.* Ba^{2+} and Ca^{2+} ISEs. They explain this phenomenon in the light of a continuous interchange of H^+ and M^{2+}. This explanation is feasible because all of the ionophores were acidic molecules. A similar hypothesis was evaluated in this case, but was rejected because the ionophore DFT has no active acidic proton, and the plasticizer used is also neutral. Moreover, no ionic sites were present. Lindner *et al.*[4] also found a 'twice Nernstian' response for Pb^{2+} ISEs, and reported Pb^{2+} ions associated with anions A^- present in the sample solution as OH^-, *i.e.* $Pb(OH)^+$. The Bakker mathematical model[5] explains Lindner's results.

Similar to Lindner's results, we proposed[1] the detection of $Hg(OH)^+$ due to the chemical equilibrium:[6] $Hg^{2+} + OH^- \leftrightarrow Hg(OH)^+ + OH^- \leftrightarrow Hg(OH)_2Hg^{2+}$ is the predominant cation at more acidic pH values. However, when the pH is nearly neutral, the most abundant cation is $Hg(OH)^+$ and is coordinated with the ligand in the membrane.

The earlier model proposed by Stefanac and Simon[7,8] is that most generally accepted to explain the response mechanism of ISEs. The phenomenon of ion detection is due to the selective formation of complexes between the ionophore and certain cations. Since a successful response model must explain the results at the two pH values, we have studied the surface and composition of the membranes in order to demonstrate the existence of such complexes in the membranes of ISEs conditioned in both pH media. Scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDAX) were used to study the ISE membranes. In principle, these physical methods provide results which are independent of potential determinations. No studies are available on the use of this approach to study membrane ISEs.

Experimental

Equipment

Potentiometric measurements were performed using a Cole Parmer (Vernon Hills, IL, USA) digital potentiometer (Model 59003-00, ±0.1 mV sensitivity). The reference electrode was an

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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 Labnet Company, Woodbridge, NJ, USA) Model V-20, 2–20 μl and BRAND (Rudolf Brand GmbH-Co, Wetheim, Germany) 20–100 μl micropipettes and a Sybron Thermoline (Dubuque, IA, USA) Model sp-A1025B magnetic stirrer were used. Additionally, a scanning electron microscope (Philips, Eindhoven, The Netherlands) Model XL30 (1997) with X-ray analysis (EDAX) (Mahwah, NJ, USA) was used to assess the morphology and elemental composition of the membrane.

Reagents and solutions

Standard solutions containing pure water (0.1 μS cm^{-1}) and the appropriate analytical reagent grade salts were prepared according to the literature.[9–16] Buffer solution, 0.001 M at pH 7, was prepared with NaH_2PO_4–Na_2HPO_4. TEHP was used as solvent mediator. High molecular weight PVC and tetrahydrofuran (THF) were purchased from Aldrich Chemical Company Inc. (Milwaukee, WI, USA). The ionophore DFT (Merck, for synthesis) was purified by double recrystallization from ethanol and dried over $CaCl_2$ for several days. The graphite-epoxy transducer was prepared with powdered graphite (1–2 μm), purchased from Aldrich, Araldite M4 and hardener (HR) HY5162 from Ciba-Geigy (Basel, Switzerland).

Electrode preparation

The ISEs were constructed as typical all-solid-state PVC matrix membranes, as described previously.[13–15] The conductive polymer composite (graphite-loaded epoxy resin), used as internal contact and transducer, was prepared by mixing 0.15 g (32 wt.%) of Araldite M, 0.06 g (13 wt.%) of hardener HR and 0.26 g (55 wt.%) of powdered graphite. The mixture was dried at 40 °C for 48 h.

The sensor membrane was prepared as described previously[1] with the following composition: DFT, 5 wt.% (10 mg); TEHP, 61 wt.% (0.137 ml); and PVC, 34 wt.% (66.67 mg). The components were dissolved in 5 ml THF and dropped onto the solid conductive support by successive applications. The membrane was dried at room temperature for 2 d. TEHP was used as plasticizer because it gave the best electrode parameters.[1]

Before calibration of the electrodes, they were conditioned by soaking in a 10^{-3} mol dm^{-3} solution of $Hg(NO_3)_2$ for 48 h.

Calibration of the electrodes (potentiometric method)

The addition method[9–16] was used as a standard technique for evaluating the electrode response characteristics. The solution was stirred in order to guarantee equilibrium. Aliquots (5, 10, 25 or 50 μl) of the tested ion solution were added to 25 ml of water. Emf 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.[17]

Table 1 shows the electrochemical characteristics of the ISE: *S* (slope), LLLR (lower limit of linear range), LLD (lower limit of detection). The statistical evaluation of these data has been described previously.[1]

Physical characterization of the electrode membrane surfaces

Preparation of the electrodes: membrane conditioning for SEM and EDAX studies Electrodes, 3 cm in length, were specially designed for this purpose. The ISE membranes were analysed in the electrode without destroying them.

SEM study of membranes before activation Two series of electrodes (A and B), each one of three units, were prepared. These were observed and studied before calibration conditioning.

SEM study of active membranes in working ISE Series A was conditioned by soaking in a 10^{-3} mol dm^{-3} solution of $Hg(NO_3)_2$ for 48 h at buffered pH 7. Series B was equally conditioned without buffer at pH 4.5. In all cases, the pH was checked with a pH meter. Both series were then calibrated in order to confirm the Nernstian response and reproducible slope values at both pH values. Series A showed 58.6 ± 0.8 mV decade^{-1} and series B gave 30.8 mV decade^{-1}, as previously reported.[1] This procedure was repeated three times, leading to a total of nine electrodes in each series. All were studied.

SEM and EDAX measurement conditions To obtain the SEM images, we set the beam energy at an acceleration potential of 20 kV. The beam current was 60 μA. The Philips software for Model XLFS was the 5.28 version corresponding to 1999.

An EDAX CDU LEAP X-ray detector was used for the elemental chemical analysis in restricted zones. The recollection time was 150 s, constant time 40s and dead time 30% at 3000 counts s^{-1}. The automatic retrieval software from the EDAX editor was the EDAM 2.91 version. The standardless quantification method was applied for the matrix (ZAF).

Statistical considerations

The elemental composition of each membrane was determined by EDAX at 20 points. In unconditioned membranes, points were selected using a square pattern of four horizontal and five vertical points. In conditioned membrane ISEs, these points were randomly selected cumulus and no pattern was followed. Larger (about 8 μm) and smaller (about 3 μm) particles were measured. EDAX was calibrated with aluminium and copper. The program EDAM is included in the equipment software for the output results. An error of ±1.29% was calculated considering the 100% minus sum of each component per cent calculated from EDAX experimental data of non-conditioned membranes. Images were taken and EDAX analysis was performed for 20 different spherical cumulus in each membrane. The percentages of atoms obtained were reproducible and independent of the size of the cumulus.

Results and discussion

Representative SEM images of the studied membranes are shown in Figs. 1(a) and 2(a), at the same magnification of

Table 1 Electrochemical characteristics of the ISE

pH	Slope (*S*)/ mV decade^{-1}	LLLR/ mol dm^{-3}	LLD/ mol dm^{-3}	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.

5000×. Some unconditioned membranes were flat and homogeneous. Others presented spherical shapes at the surface. Both kinds contained no solid particles and exhibited the same macroscopic behavior as sensors. Apparently, the calibration parameters and Nernstian response are not strongly affected by these differences. Nevertheless, SEM is a strong and reliable tool for studying in detail the influence of the morphology of the membranes and the reproducibility of the preparation conditions.

Fig. 1(a) shows a typical homogeneous unconditioned membrane. Observe the absence of cumulus or particles. The EDAX spectrum is shown in Fig. 1(b) and gives the elemental composition at the surface. Table 2 shows the EDAX surface elemental composition data of a homogeneous membrane and data corresponding to the bulk elemental composition calculated from the weight of each constituent in the membrane preparation. EDAX data of the selected elements (S, P, Cl) were used for the calculation of the surface elemental composition and exclusively represent each membrane component (ionophore, plasticizer and PVC, respectively). In addition, these heavier third row elements have a better readability and fitness in EDAX than second row elements.

It is interesting that the surface composition does not agree with the bulk composition. Note that the sum of the surface data percentages gives 101.3%. The ionophore and mediator contents are higher at the surface than in the bulk.

Figs. 2(a) shows typical conditioned membranes of good working sensors of series A and B, respectively. Both present spherical white cumulus particles, with diameters of 8–9 μm and 3–4 μm, respectively. These were presumed to be complexes formed between the ionophore and the specific Hg species. This is the first time that this observation has been made at the surface of an Hg liquid membrane electrode, to the authors' knowledge. In order to determine the actual ion detected in both conditions, and consequently to demonstrate the response mechanism of this new sensor at both pH conditions, elemental analysis was performed for these cumulus. The EDAX spectra of both particles are shown in Figs. 2(b) and 3. Note the new characteristic lines of Hg (compare with Fig. 1). The calculated elemental analyses of the particles are shown in Table 3.

In series A, the atomic ratio S:Hg = 1:1. In series B, the atomic ratio S:Hg = 2:1. This means that, in the complex formed at pH 7, there is only one DFT ligand (L), as expected from the proposed $Hg(OH)^+$ species in the mechanism of the

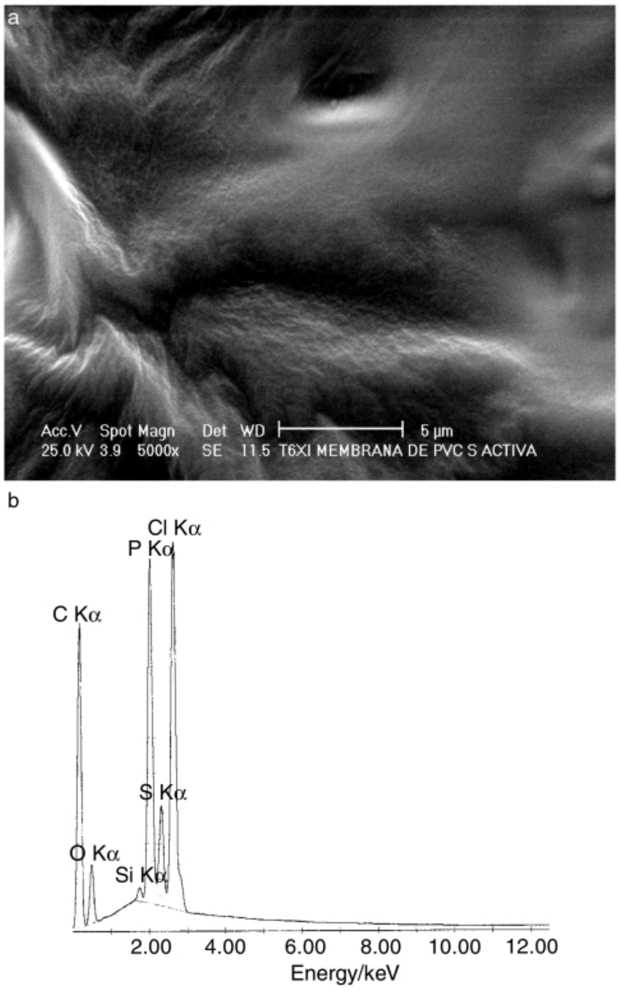

Fig. 1 (a) Membrane recently prepared before activation. (b) Chemical spectrum of membrane before activation.

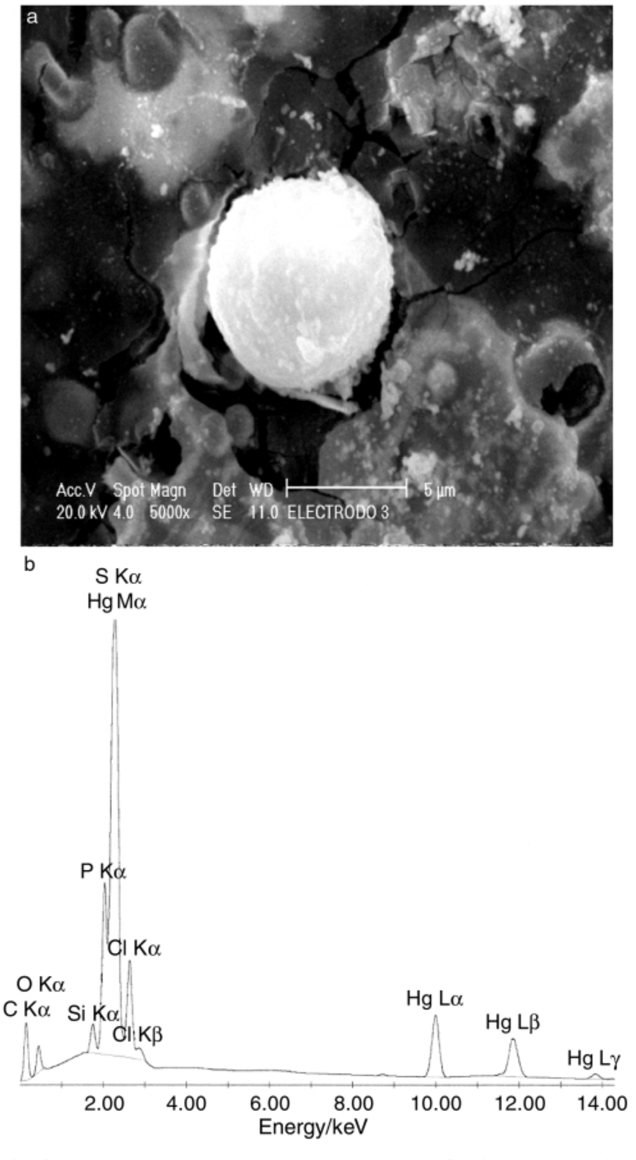

Fig. 2 (a) Single particle shown at 5000× magnification. (b) Chemical spectrum of this particle (pH 7).

Table 2 Bulk and surface elemental composition of an unconditioned homogeneous membrane

Component	Representative element	Elemental wt.%	Wt.% (surface EDAX)	Wt.% (bulk membrane preparation)
Ionophore	S	1.66	11.8	5
Plasticizer	P	5.51	77.3	61
PVC	Cl	6.91	12.2	34

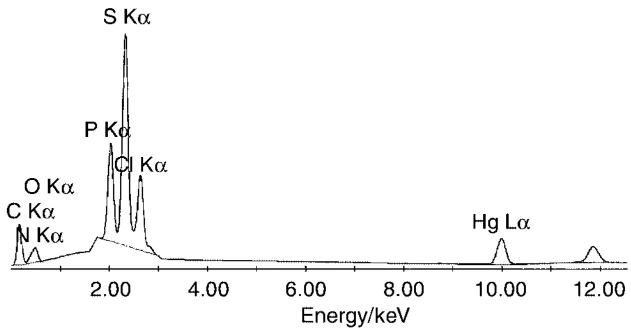

Fig. 3 Spectrum of particles activated at pH 4.

Table 3 Chemical composition of particles seen in series A electrode surfaces (working at pH 7) and those seen in series B electrode surfaces (working at pH 4.5)

	Particles at pH 7		Particles at pH 4.5	
Element	Wt.%	Atom%	Wt.%	Atom%
S	6.18	5.01	10.15	6.65
P	5.67	4.76	4.74	3.21
Cl	5.27	3.87	5.70	3.38
Hg	43.76	5.67	29.26	3.06

'twice Nernstian' response of this sensor in neutral to basic pH.[1] The elemental analysis agrees with the complex L–Hg-OH. At pH 4.5, the elemental analysis agrees with the complex L–Hg–L, as expected from the species Hg^{2+}.

These results provide confirmation of the formation of both pH-dependent complexes in the membranes. We have used physical methods to characterize the complexes formed at the electrode surface. These methods provide results which are independent of potential measurement data and are in agreement with them. A successful response model has explained both independent and unbiased sets of results. These conclusions confirm the proposed response mechanisms for this new Hg membrane sensor.

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