Mercury(II) ion Potentiometric Sensor Based on a Sulfur Schiff's Base 1-(2-Hydroxy-1,2-diphenylethylidene)thiosemicarbazide as Ionophore

Lan Xu, Ruo Yuan,* and Ya-Qin Chai
The College of Chemistry and Chemical Engineering, Southwest China Normal University,
Chongqing 400715, P. R. China

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A PVC membrane sensor for Hg(II) ion based on a sulfur Schiff's base 1-(2-hydroxy-1,2-diphenylethylidene)thiosemicarbazide (HDPET) as ionophore was prepared. The sensor exhibits a Nernstian response for Hg^{2+} ions over a wide concentration range 1.0×10^{-2}–2.0×10^{-6} M. It revealed very good selectivity for Hg^{2+} over a wide variety of other metal ions and could be used in a pH range of 2.0–5.0.

Much attention has been drawn on developing selective electrodes for the detection of mercury ions due to their importance for environmental monitoring. Initially, solid-state mercury(II) sulfide electrodes have been described in many papers,[1] which respond to mercury(II) ion activity in solution. Nevertheless, many factors, such as high purity of sulfides, mechanical properties, temperature, and pressure used in making pellets, strongly influence the characteristics and quality of the sensors. The use of a liquid-membrane ion-selective electrode (ISE) with ionophore trapped in an inert polymer matrix such as poly(vinyl chloride) (PVC) is the most important breakthrough in the field of ISEs.[2,3] However, there have been a few reports on the Hg^{2+}-selective membrane ISEs and few efficient commercial Hg^{2+}-selective ISEs have been produced. Metalophalocyanine complexes were used as ion-carriers in membrane ISEs for detection of thiosalicylic and applied to the potentiometric titration of Hg^{2+} ions.[4] However, this method cannot make possible direct on-line monitoring of Hg^{2+}. A novel organic and inorganic type crystalline polypyrrole/polyantimonic acid composite system is also applied as material for Hg(II) ion-selective electrode.[5] But these electrodes have not turned out to be good systems as they generally exhibit long response time, narrow working concentration range and moderate selectivity due to the cation-exchange mechanism.[1–3] Organic compounds containing sulfur atoms, which have to be laboriously synthesized, have been reported as a selective ionophore for Hg^{2+} ion used in the PVC membrane electrode.[6,7] A new liquid membrane mercury(II) ISE based on the simple and low cost ionophore 1,3-diophenylthiourea as a neutral carrier was reported.[8] It has a stable detection limit (PDL) of 10^{-6} M and high selectivity towards Hg^{2+} ions. A Schiff's base is recently reported as a Hg^{2+} ion carrier for ISE.[9] This type of Schiff's base without sulfur atoms cannot show very high selectivity for the Hg(II) ions. As reported previously, –SH or =S groups tend to show high affinity for Hg^{2+} as compared to other metals. Mercury(II), being a "soft" acid, can be expected to complex the "soft-base" such as sulfur, oxygen most strongly.[10] Keeping this in view, we prepared a new compound, sulfur Schiff's base 1-(2-hydroxy-1,2-diphenylethylidene)thiosemicarbazide (HDPET) with three different heteroatoms (N, S, O) in its structure that promote complex formation with Hg(II) ions. The sulfur Schiff's base ligand is easily obtained, simple, inexpensive and found to be a good ionophore with highly selectivity for Hg^{2+} over variously wide cations except the main interference of Ag^{+}.

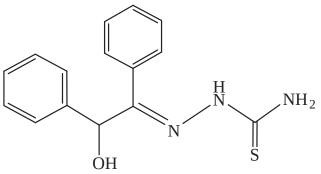

Figure 1. Structure of the ionophore 1-(2-hydroxy-1,2-diphenylethylidene)thiosemicarbazide (HDPET).

The sulfur Schiff's base HDPET (Figure 1) as the ionophore is synthesized by refluxing benzoin with semicarbazide for 2 h in ethanol. Carrier immobilized polymeric membranes were made by mixing the ionophore, the plasticizer (2-nitrophenyl octyl ether, *o*-NPOE), anionic additive (sodium tetraphenylborate, NaTPB) and PVC at composition: PVC:*o*-NPOE:HDPET:NaTPB(wt %) = 31.64:63.30:3.16:1.90. The critical response characteristics of HDPET-based electrodes were assessed according to the IUPAC recommendations.[11] The electrode cells for potential measurements were of the following cell assemblies:

Hg–$Hg_2Cl_2(s)$/KCl (satd)/salt bridge (1 M KNO_3) testing solution/PVC-ionophore membrane/0.01 M HNO_3 + 50 mM Hg $(NO_3)_2$/AgCl(s)/Ag.

The Schiff's base HDPET with donating sulfur, oxygen and nitrogen atoms in its structure, sufficient insolubility in water, low molecular weight, and flexible structure was expected to act as a suitable ion carrier in the preparation of PVC membrane ISEs for special transitional and heavy metal ions of proper size and charge. Consequently, in preliminary experiments, the compound was employed as a neutral carrier to prepare PVC membrane ISEs for a variety of transitional and heavy metal ions. The potential responses of the electrodes based on HDPET are shown in Figure 2. In the case of each cation tested, the electrode was conditioned for 48 h in a 1.0×10^{-3} M solution of the nitrate salts of corresponding cations to obtain thermodynamically meaningful potential responses and selectivity behavior. From Figure 2, it can be seen that among different tested cations, Hg^{2+} with the most sensitive response seems to be suitably determined with the PVC membrane electrode based on HDPET. The emf responses of the electrode at varing concentration of Hg^{2+} ions show linear ranges from 2.0×10^{-6} to 1.0×10^{-2} M and response slope of 30.5 ± 0.6 mV/decade. The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration graphs was 1.0×10^{-6} M. The

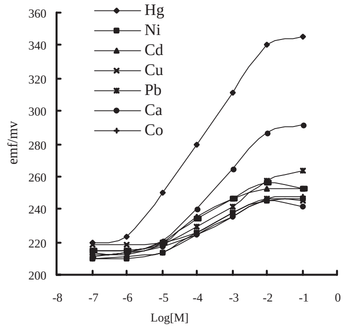

Figure 2. Potential response of various HDPET-based PVC membrane ISEs. Conditions: Membrane ingredients, 31.64% PVC, 63.30% *o*-NPOE, 3.16% HDPET and 1.90% NaTPB. Each electrode has been conditioned in 1×10^{-3} M concentration of the corresponding cation for 48 h.

emf responses obtained for all other cation-selective electrodes are much lower than that predicted by the Nernst equation.

ISE membranes without ionic additives should be avoided, since otherwise inherent ionic impurities could have a decisive influence on the response characteristics. Moreover, several sensors are known that do not induce any selectivity in membranes in the absence of anionic site additives. Lipophilic anionic components can efficiently catalyze this cation transfer. The characteristics of electrodes with different ratio (0, 20, 50, 100 mol %) of NaTPB to ionophore were investigated and the results indicated that incorporation of 50 mol % NaTPB relative to the ionophore into the membrane results a potential response with a good Nernstian slope. It is noteworthy that with the ratios of NaTPB to the ionophore increases, the slopes are super-Nernstian, which may be attributed to the formation of $Hg(TPB)^+$ ions in the membrane. Similar super-Nernstian slope for Hg(II) in addition to a large ratio of NaTPB was observed in previous research.[12]

The influence of pH of the test solution (10^{-3} M) on potential response of the electrode was tested. The pH was adjusted by introducing small drops of 0.1 M solutions of nitric acid or sodium hydroxide, and the results showed that hydrogen concentration has an effect on the electrode potential. The HDPET-based selective electrode responded only to Hg^{2+} solutions in the pH range 2.0–5.0, beyond which the potentials change considerably. The observed decreases in the measured potential at higher pH values are probably due to the hydrolysis of mercury(II) in solutions. The observed increases at low pH values indicate that the membrane sensors respond to hydrogen ions. Therefore, the experimental results were obtained for sample solutions of pH 2.0–5.0.

The selectivity behavior is obviously one of the important characteristics of ion-selective electrodes, determining whether reliable measurement in the target sample is possible. To investigate the selectivity of the potentiometric proposed electrode, its potential responses were tested in presence of a wide variety of interfering foreign metal ions using the separated solution method (SSM). According to SSM,[11] the potentials obtained using the electrode were measured in a separate solution of $Hg(NO_3)_2$ and of the interfering ion. The inference of alkali metal ions (Li^+, Na^+ and K^+), alkaline earth metal ions (Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}), transition metal ions (Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}) and other cations ((NH^+, Fe^{3+}, Al^{3+}, Cr^{3+}, La^{3+}, Ce^{3+}) were studied (see Table 1). From these values, it can be seen that the electrode is characterized by high selectivity towards Hg(II) ion with respect to most common ions, except for Ag^+. As previously reported,[8] the calculated hardness on sulfur was the lowest value among the other atoms such as C, N, O. HOMO and HOMO-1 are both localized on the sulfur atom. Therefore, the high selectivity could be explained by the special interaction between the sulfur atom of the carrier molecule as a soft acid and the anayte ion Hg^{2+} as the soft base.

Table 1. Selectivity coefficients $\log K^{pot}_{Hg^{2+},J}$ of HDPET based electrode

Ion/j	$\log K^{pot}_{Hg^{2+},J}$	Ion/j	$\log K^{pot}_{Hg^{2+},J}$
Ag^+	−0.56	Ni^{2+}	−3.41
Li^+	−4.43	Cu^{2+}	−3.58
Na^+	−3.09	Zn^{2+}	−3.61
K^+	−3.54	Cd^{2+}	−3.74
$NH_4{}^+$	−2.76	Pb^{2+}	−3.52
Mg^{2+}	−3.66	Rb^{2+}	−3.86
Ca^{2+}	−3.74	Al^{3+}	−4.60
Sr^{2+}	−3.37	Fe^{3+}	−3.46
Ba^{2+}	−3.66	Ce^{3+}	−3.80
Mn^{2+}	−2.64	Cr^{3+}	−4.10
Co^{2+}	−3.62	La^{3+}	−4.33

References

1 N. Radic, *Ion-Sel. Electrode Rev.*, **11**, 87 (1989).
2 E. Bakker, P. Bühlmann, and E. Pretsch, *Chem. Rev.*, **97**, 3083 (1997).
3 P. Bühlmann, E. Pretsch, and E. Bakker, *Chem. Rev.*, **98**, 1593 (1998).
4 S. Shahrokhian and A. Souri, *Anal. Chim. Acta*, **518**, 101 (2004).
5 A. Ali Khan and M. Mezbaul Alam, *Anal. Chim. Acta*, **504**, 253 (2004).
6 A. K. Jain, S. M. Sondhi, and V. K. Sharm, *Electroanalysis*, **12**, 301 (2000).
7 B. Marzieh, H. M. Mohammad, R. Saied, and M. Ahmad, *Electroanalysis*, **15**, 1824 (2003).
8 L. Pérez-Marín, E. Otazo-Sánchez, G. Macedo-Miranda, P. Avila-Pérez, J. Alonso Chamaro, and H. López-Valdivia, *Analyst*, **125**, 1787 (2000).
9 H. M. Mohammad and S. Iran, *Talanta*, **60**, 73 (2003).
10 R. Sahu, S. M. Sondhi, and B. Gupta, *Chem. Anal. (Warsaw)*, **41**, 293 (1996).
11 IUPAC Analytical Chemistry Division, Commission on Electroanalytical Chemistry. Recommendations for Nomenclature of Ion Selective Electrodes. *Pure Appl. Chem.*, **66**, 2527 (1994).
12 M. T. Lai and J. S. Shih, *Analyst*, **111**, 891 (1986).

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