Synthesis of a New Hexadendates Schiff's Base and Its Application in the Fabrication of a Highly Selective Mercury(II) Sensor

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A new PVC membrane potentiometric sensor that is highly selective to Hg^{2+} ions was prepared, using bis(2-hydroxybenzophenone) butane-2,3-dihydrazone (HBBD) as an excellent hexadendates neutral carrier. The sensor works satisfactorily in the concentration range of 1.0×10^{-6} to 1.0×10^{-1} mol L^{-1} (detection limit 4×10^{-7} mol L^{-1}) with a Nernstian slope of 29.7 mV per decade. This electrode showed a fast response time (~8 s) and was used for at least 12 weeks without any divergence. The sensor exhibits good Hg^{2+} selectivity for a broad range of common alkali, alkaline earth, transition and heavy metal ions (lithium, sodium, potassium, magnesium, calcium, copper, nickel, cobalt, zinc, cadmium, lead and lanthanum). The electrode response is pH independent in the range of 1.5-4.0. Furthermore, the developed sensor was successfully used as an indicator electrode in the potentiometric titration of mercury ions with potassium iodide and the direct determination of mercury in some binary and ternary mixtures.

Key Words : Mercury ion-selective electrode, PVC membrane, Potentiometry, Hexadendate, Schiff's base

Introduction

The ion-selective membrane sensor is the basis of potentiometric detection. This is a simple detection method which offers several advantages such as speed and ease of preparation and procedure, simple instrumentation, relatively fast response, wide dynamic range, reasonable selectivity and low cost. These characteristics have inevitably led to sensors for several ionic species. As a result, the list of the available electrodes has grown substantially over the last few years.

There are many examples concerning the selective affinity of Schiff's bases toward the metal ions and, hence, their application in the construction of ISEs.[1-5] Regarding this phenomenon as well as the charge density, the mercury ion size and also the soft-hard acid-base concept, it was decided to design an ionophore that contained suitable intermediate or soft donor atoms. Such an ionophore had to have a semi-cavity of proper size and be able to form wrap-around complexes with mercury ions. As it is obvious, all the above mentioned take place under the optimum free energy regime. This can be justified if the soft nature of the mercury ion is considered. In fact, it is caused by its free d-orbital, making it suitable to complex with the Schiff's base, which contains intermediate donor atoms.

Firstly, the need for monitoring the toxic heavy metal ions such as Hg^{2+} in the environmental samples and, secondly, the lack of efficient commercial mercury(II) ion-selective electrodes, have made the development of new Hg^{2+}-ion-selective electrodes a challenging problem.

A number of recent articles are dealing with the introduction of new mercury ion-selective electrodes, based on different neutral ion carriers.[6-14] Lately, some neutral carriers have been used containing sulfur and nitrogen donor atoms in the construction of a number of PVC-based membrane sensors for the selective determination of some transition and heavy metal ions.[15-22] Specifically, this article presents the use of the bis(2-hydroxybenzophenone) butane-2,3-dihydrazone (Figure 1) as an excellent neutral carrier in the construction of a greatly selective mercury(II)-PVC membrane electrode for the fast determination of Hg^{2+} ions in different samples.

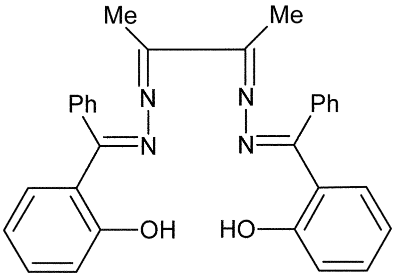

Figure 1. HBBD structure.

Experimental

Reagents. The reagent-grades of dibutyl phthalate (DBP), *o*-nitrophenyloctyl ether (NPOE), benzyl acetate (BA), potassium tetrakis (*p*-chlorophenyl) borate (KTpClPB), tetrahydrofuran (THF) and high relative molecular weight PVC were purchased from Merck and Aldrich and they were used as received. The Merck Chemical Co. was the provider of the nitrate salts of all used cations, which were of the highest available purity and were P_2O_5-vacuum dried. During the experiments, triply distilled deionized water was used.

Bis(2-hydroxybenzophenone) Butane-2,3-dihydrazone

synthesis. The ligand preparation was in line with the literature survey. In particular, 2-hydroxybenzophenone (0.02 mol, 3.96 g) were dissolved in 75 mL of ethanol and, then, a solution of 2,3-butanedihydrazone (0.01 mol, 1.14 g) was added to the former solution in 50 mL of ethanol. The consequent reaction mixture was refluxed on a water bath for 4 h. After the solution volume reduction to *ca.* 50 mL, the flask was kept at an ambient temperature for 6 h. On cooling the yellow crystalline, Schiff's Base ligand was collected by filtration, washed with ethanol and dried. Finally, the ligand was recrystallized from ethanol, giving pure crystal yield ≈57%. Anal. Calcd. For $C_{30}H_{26}N_4O_2$: C, 75.93; H, 5.52; N, 11.81. Found: C, 75.81; H, 5.43; N, 11.92. IR (KBr, cm^{-1}): 3450 ($\upsilon_{\text{O-H}}$, $\upsilon_{\text{C N}}$). ^{1}H-NMR δ(d_6-DMSO), ppm: 2.43 (2 CH_3), 6.67 (2 C_6H_4), 7.35 (2 C_6H_5), 12.85 (2 OH).

Electrode Preparation. For the PVC membrane preparation, 30 mg of powdered PVC, 5 mg of ionophore HBBD, 62 mg of plasticizer NPOE and 3 mg of additive KTpClPB were blended completely until the PVC was wet. Afterwards, the blend was dissolved in 5 mL of dry freshly distilled THF. The resulting clear mixture was transferred into a glass dish of 2 cm in diameter. The solvent was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (5 mm i.d.) was dipped into the mixture for about 10 s, so that a nontransparent membrane of about 0.3 mm in thickness was formed. The tube was, then, pulled out from the mixture, kept at room temperature for about 6 h and filled with an internal solution (1.0×10^{-3} M mercuric nitrate). In the end, the electrode was conditioned for 24 h by soaking in a 1.0×10^{-2} M $Hg(NO_3)_2$ solution. As an internal reference electrode, a silver-silver chloride electrode was used.[15-22]

EMF Measurements. All EMF (Electro Motive Force) measurements were carried out with the following assembly:

Ag-AgCl/internal solution (1.0×10^{-3} M $Hg(NO_3)_2$, and 1.0×10^{-2} M HNO_3)/PVC membrane/test solution/Hg-Hg_2Cl_2, KCl (saturated)

A Corning ion analyzer with a 250 pH/mV meter was used for the potential measurements at 25.0 ± 0.1 °C.

Results and Discussion

The existence of four donating nitrogen and two oxygen atoms in the HBBD structure was expected to increase both the stability and selectivity of HBBD-transition metal ions complexes over HBBD-alkali and alkaline earth cations.[14-23] As a consequence, in order to examine the HBBD suitability as an ion carrier for the Hg^{2-} ion, several PVC membrane ion-selective electrodes were constructed for a wide variety of cations, including alkali, alkaline earth and transition metal ions. The potential responses for the more sensitive HBBD ion-selective electrodes are depicted in Figure 2. Figure 2 shows the slopes of the potential responses, except for Hg^{2-}. In all cases, the slopes are much lower than expected for mono, di and trivalent metal ions. Actually, the Hg^{2-} sensor exhibits a Nernstian response across the range of 1.0×10^{-6} ~ 1.0×10^{-1} M.

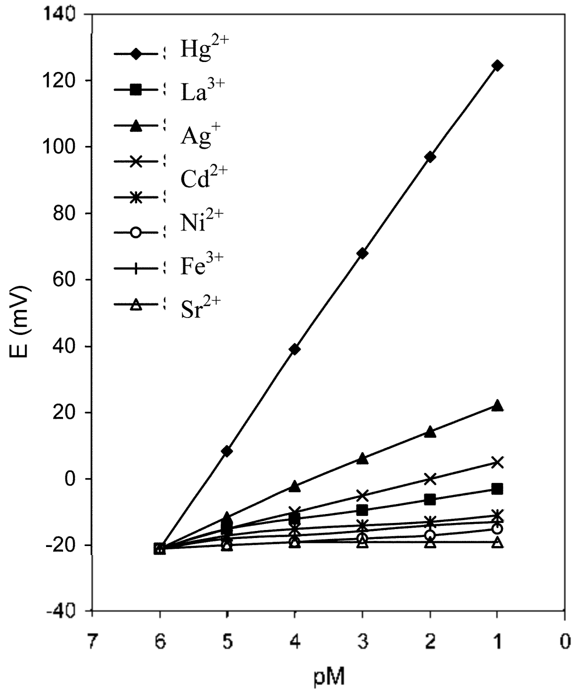

Figure 2. Potential responses of various metal ion-selective electrodes based on HBBD.

Generally, the membrane composition and, primarily in some cases, the nature of the additive may have significant influence on the obtained sensitivity and selectivity for a given ionophore.[24,25] The performance characteristics of several membranes, having ingredients of different proportions, are listed in Table 1. Table 1 illustrates that the membrane number 6 with the PVC : NPOE : HBBD : KTpClPB ratio of 30 : 62 : 5 : 3 presents a Nernstian behavior for an extensive concentration range of the Hg^{2+} ions.

In addition, Table 1 displays that among four different solvent mediators, the NPOE plasticizer demonstrated the highest polarity in comparison with the other plasticizers (DBP and BA). This is attributed to the NPOE ability as a polar solvent to extract mercury ions with relatively high charge density from the aqueous solution to the organic membrane phase.

The data of the same Table revealed that in the absence of KTpClPB in the membrane, the slope of the sensor is lower than the Nernstian response (No. 7 with a slope 20.9 mV per decade). The membrane, containing KTpClPB, presents a nice Nernstian response (No. 6 with a slope of 29.7).

Noticeably, the presence of lipophilic and immobilized ionic additives could influence the membrane resistance and, in some cases, the selectivity pattern of the ion-selective PVC membranes, resulting in a good working performance. It has been clearly illustrated that the presence of lipophilic additives in ion-selective electrodes is necessary to induce perm-selectivity, so that without these additives the electrodes do not respond properly.[26] The presence of such additives not only reduces the ohmic resistance[27] and improves the response behavior and selectivity,[27-35] but also it increases

Table 1. The optimization of the membrane ingredients

Number of Composition	PVC	Ionophore	KTpClPB	BA	NPOE	DBP	Slop
1	30	4	2	64	–	–	18.9
2	30	4	2	–	64	–	25.6
3	30	4	2	–	–	64	21.2
4	30	5	2	–	63	–	26.3
5	30	6	2	–	62	–	24.9
6	30	5	3	–	62	–	29.7
7	30	5	–	–	65	–	20.9
8	30	–	3	–	67	–	5.3

the sensitivity of the membrane electrode when the extraction capability of the ionophore is poor.[16-25]

Moreover, the developed sensor was examined at various concentrations of the inner reference solution in the range of 1.0×10^{-4}-1.0×10^{-2} M. The results illustrated that the variation of the internal solution concentration does not cause any significant difference in the corresponding potential response, except for an expected change in the intercept of the resulting Nernstian plot. A 1.0×10^{-3} M concentration of the reference solution is quite appropriate for the smooth function of the electrode membrane.

The contact time and the equilibrating solution concentration were optimized so that the electrode generates stable and reproducible potentials at comparatively short response times. The optimum equilibration time in a 1.0×10^{-2} M Hg$(NO_3)_2$ was 24 h.

The critical response characteristics of the Hg^{2-} ion-selective electrode were assessed according to the IUPAC recommendations.[36] The electrode displayed a linear response to the Hg^{2+}activity across the range of 1.0×10^{-6}-1.0×10^{-1} M (Figure 3). The slope of the calibration plot was 29.0 ± 0.5 mV per decade of activity change at 25 °C. The detection limit was 4.0×10^{-7} M, as determined from the intersection of the two extrapolated segments of the calibration plot.

Furthermore, we measured the average time required for the Hg(II) ion-selective electrode to reach a potential within ± 1 mV of the final equilibrium value, after successive immersions in a series of mercury ion solutions, each having a 10-fold difference in concentration. The static response time of the membrane electrode, which was obtained, was about 10 s for all the concentrations (Figure 4). Potentials remained constant for about 5 min and the standard deviation of 10 replicate measurements was = 0.3 mV. The performance characteristics of the electrode remained unchanged, when the potentials were recorded either from low to high concentrations or vice versa.

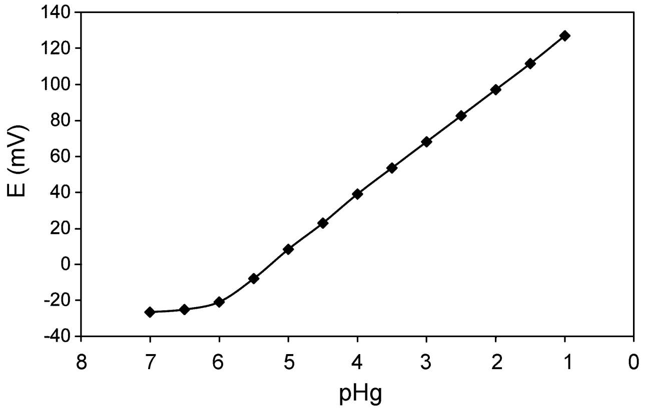

Figure 3. Calibration curve of the Hg(II) sensor at the membrane.

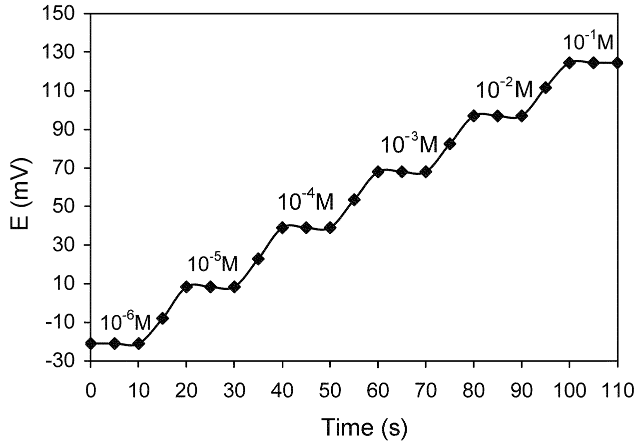

Figure 4. Response time of the electrode for step changes in the concentration of the Hg(II) solution.

The lifetime of the recommended membrane electrode lasted for at least 3 months, during which it could be used without any measurable divergence. The electrodes were kept aside after drying and for further use they should be reconditioned for 24 h by soaking in a 1.0×10^{-2} M Hg$(NO_3)_2$ solution.

The interfering ions influence on the response behavior of the ion-selective membrane electrodes is usually described in terms of selectivity coefficients. The potentiometric selectivity coefficients of the mercury-HBBD membrane sensor were evaluated by the matched potential method.[37] The resulting values of the selectivity coefficients are summariz-

Table 2. The selectivity coefficients of various interfering cations for the membrane sensor

Ion	K_{sel}	Ion	K_{sel}
La^{3+}	$5.0 \cdot 10^{-5}$	Fe^{3-}	3.0×10^{-4}
Sr^{2-}	$< 10^{-5}$	Cd^{2-}	8.0×10^{-5}
Ag^{-}	$3.1 \cdot 10^{-5}$	Ni^{2-}	1.5×10^{-5}

Table 3. Comparison of the characteristics of the proposed sensor with those of the previously reported Hg(II) sensor

No.	Linear Dynamic Range	Response Time	Slope	-Log K_{sel} Ag^+	-Log K_{sel} Fe^{3+}	-Log K_{sel}, Cd^{2+}	Ref
1	5×10^{-5} - 1×10^{-2}	–	28	1.25	0.4	–	[7]
2	5×10^{-5} - 1×10^{-2}	–	29	0.2	3.4	–	[8]
3	1×10^{-6} - 1×10^{-3}	60 s	30	3.4	1.4	3.1	[3]
4	1×10^{-5} - 1×10^{-1}	29 s	32.1	0.7	1.4	0.5	[4]
5	1×10^{-5} - 1×10^{-3}	–	41	2.6	–	3.9	[6]
6	3.2×10^{-6} - 1×10^{-3}	–	28.4	0.4	< 4	–	[9]
7	1×10^{-5} - 1×10^{-2}	–	70	3.9	> 6	> 6	[5]
8	1×10^{-6} - 1×10^{-3}	–	30	–	0.7	–	[1]
9	1×10^{-6} - 1×10^{-3}	45 s	29	2.1	3.2	3.5	[2]
10	1×10^{-6} - 1×10^{-1}	~10 s	29.7	3.5	5.8	4.1	This work

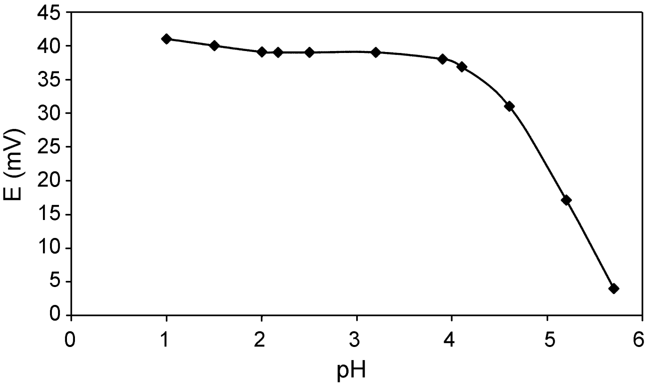

Figure 5. pH effect on the potential response of the Hg(II) ion-selective electrode.

ed in Table 2, where it is evident that the selectivity coefficients (obtained for all the other cations) were in the order of 3.0×10^{-4} or smaller, indicating that they do not disturb the function of the Hg^{2-} ion-selective electrode greatly.

A comparison of the detection limit, the dynamic range and the serious interference of the proposed sensor with those of the previously reported Hg^{2-} sensors is reported in Table 3. Obviously, the recommended sensor not only in terms of detection limit and dynamic range but also in terms of selectivity coefficients is superior to the formerly reported sensors.

The pH influence of the test solution on the potential response of the mercury sensor was tested at the 1.0×10^{-3} M Hg^{2-} concentration over the pH range of 1.0-5.8. The respective results are shown in Figure 5. It is evident that the potential remained constant from the pH value of 1.5 to 4.0, beyond which a drastic drift was observed. The observed drift at higher pH values could be due to the formation of some hydroxyl complexes of the Hg^{2-} ion in solution.

Apart from the usage of the introduced Hg^{2-}-selective membrane electrode in the direct determination of the Hg^{2+} ions, the sensor was found useful in the titration of Hg^{2+} with different chelating and precipitating agents. For example, it was applied to the titration of 15.0 mL Hg^{2-} ion solution (1.0×10^{-4} M) with potassium iodide (2×10^{-2} M). The resulting titration curve is depicted in Figure 6. Clearly, the amount of Hg^{2-} ions in solution can be accurately determined with the electrode [$(1.0\pm0.03)\times10^{-4}$ M].

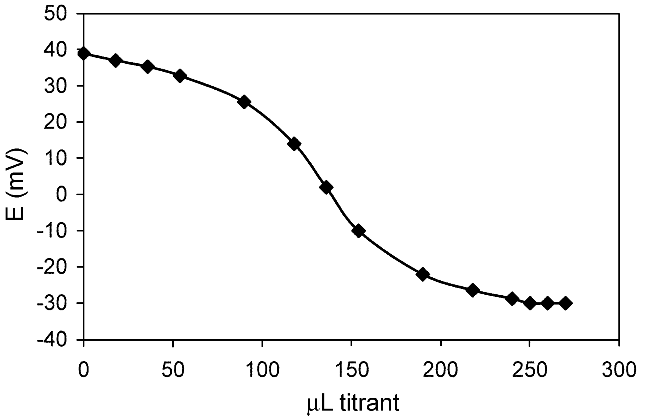

Figure 6. Potentiometric titration curve of 15.0 mL of a 1.0×10^{-4} M Hg(II) solution with a 2.0×10^{-2} M potassium iodide, using the proposed membrane sensor as an indicator electrode.

Table 4. Determination of Hg (II) ions in binary and ternary mixtures

Hg^{2-} (M)	Added cation (M)	Recovery (%)^a
1×10^{-5}	Na^+ (1×10^{-2})	100.4 ± 0.3
1×10^{-5}	K^+ (1×10^{-2})	100.6 ± 0.1
1×10^{-5}	Ca^{2+} (1×10^{-2})	100.9 ± 0.5
1×10^{-5}	Mg^{2+} (1×10^{-2})	100.3 ± 0.4
1×10^{-5}	Pb^{2+} (1×10^{-2})	101.9 ± 0.4
1×10^{-5}	Cu^{2+} (1×10^{-2})	101.8 ± 0.7
1×10^{-5}	Na^- and K^- (1×10^{-2})	101.2 ± 0.4
1×10^{-5}	Na^- and Ca^{2-} (1×10^{-2})	101.5 ± 0.5
1×10^{-5}	K^- and Mg^{2-} (1×10^{-2})	101.9 ± 0.4
1×10^{-5}	K^- and Pb^{2+} (1×10^{-2})	102.6 ± 0.6
1×10^{-5}	Na^- and Cu^{2-} (1×10^{-2})	102.3 ± 0.5
1×10^{-5}	K^- and Cu^{2-} (1×10^{-2})	102.4 ± 0.5

^{a}results are based on triplicate measurements

In the end, the suggested sensor was applied for the direct determination of the Hg^{2-} ion concentration in some binary and ternary mixtures. The corresponding results are summarized in Table 4. According to this Table, the Hg^{2-} recovery is good. This observation can be attributed to the high sensor selectivity towards the Hg^{2+} ions in comparison with the common metal ions.

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