Application of *N*-Quinoline-2-carboxamido-8-aminoquinoline in Fabrication of a Ho(III)-PVC Membrane Sensor

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Abstract: The *N*-quinoline-2-carboxamido-8-aminoquinoline (QCA) was used as a suitable ion carrier in the construction of a Ho(III) PVC-based membrane sensor. This sensor demonstrated good selectivity and sensitivity towards the holmium ion for a broad variety of cations, including alkali, alkaline earth, transition and heavy metal ions. The proposed electrode exhibits a linear dynamic range between 1.0×10^{-6} and 1.0×10^{-2} M, with a near Nernstian slope of 20.4 ± 0.3 mV per decade and a detection limit of 4.2×10^{-7} M. The best performance was obtained with a membrane composition of 30% poly(vinyl chloride), 56% nitrobenzene, 2% sodium tetraphenyl borate, 10% oleic acid and 2% QCA. The potentiometric response of the constructed electrode is pH independent in the range of 2.4-7.4. The sensor possesses the advantages of short conditioning time, fast response time (~ 5 s) and especially, good selectivity towards transition and heavy metal and some mono, di and trivalent cations. The Ho^{3+} sensor was successfully applied as an indicator electrode in the potentiometric titration of Ho(III) ions with EDTA. The electrode was also used for the determination of Ho^{3+} ions in mixtures of different ions and the determination of the fluoride ion in mouth wash solutions.

Keywords: Ion-selective electrode, Potentiometry, Sensor, PVC membrane

Introduction

Nowadays, applications of rare earth elements in agricultural, metallurgical, optical and glass industries, ceramics and biological areas have increased. Thus, having a convenient, fast, selective and sensitive analysis methods for monitoring rare earth are required. One of these rare earths is holmium, whose compounds are used in ceramic and glass¹ industrials as well as phosphor lamps. Holmium compounds are rarely encountered by most people. All

holmium compounds should be regarded as highly toxic, although initial information suggests that the danger is limited. Several methods have been used for the Ho^{3+} determination like spectrometry, inductively coupled plasma-atomic emission spectrometry (ICP-AES), electrochemistry, ICP-MS, neutron activation analysis (NAA), spectrophotometry and x-ray fluorescence spectrometry. Despite the fact that these methods are precise and sensitive, they are also expensive and time-consuming. Another method for the determination of this element is the ion selective electrode (ISE) for Ho(III) potentiometric titration. The ISEs work fast and they are easily prepared without any special or expensive equipment. Potentiometric ion selective sensors offer advantages of low cost, portability, selectivity and simple operator²⁻¹⁵. Lately, highly selective and sensitive PVC-membrane ion-selective electrodes were reported for some ions¹⁶⁻²⁷. There are some reports on the literature for selective determination of holmium ion by potentiometric electrodes²⁸⁻³¹. The aim of this research is the fabrication of a greatly selective and sensitive Ho^{3+} membrane sensor, based on *N*-quinoline-2-carboxamido-8-aminoquinoline (QCA) (Figure 1) as a suitable ionophore for the potentiometric measurement of the Ho^{3+} ion amounts for a certain concentration range.

Figure 1. The QCA structure

Experimental

The Merck Co. was the provider for the reagent grades of dibutyl phthalate (DBP), nitrobenzene (NB), acetophenon (AP), tetrahydrofuran (THF), oleic acid (OA), sodium tetraphenyl borate (NaTPB) and high relative molecular weight PVC. The nitrate and the chloride salts of all cations (all from Merck, Aldrich and Fluka) were of the highest available purity and used without any further purification, except for vacuum drying over P_2O_5 . *N*-quinoline-2-carboxamido-8-aminoquinoline (QCA) was synthesized as described elsewhere³². Triply distilled de-ionized water was used throughout.

Preparation of the sensor

The PVC membranes were prepared according to the following general procedure. The required ingredients for the membrane construction (30 mg PVC, 56 mg NB, 2 mg NaTPB , 10 mg OA and 2 mg QCA) were mixed and dissolved in 3 mL of dry THF. The resulting mixture was transferred into a glass dish of 2 cm in diameter. The solvent was then evaporated slowly, until an oily concentrated mixture was obtained. A Pyrex tube (3-5 mm in top) was dipped into the oily mixture for about 5 s, so that a transparent film of about 0.3 mm thickness was formed³³⁻⁴³. Afterwards, the tube was removed from the mixture, kept at the room temperature for about 12 h and filled with the internal filling solution (1.0×10^{-3} M of HoCl_3). The electrode was, finally, conditioned for 24 h by soaking in a (1.0×10^{-2} M) solution of holmium chloride. A silver-silver chloride electrode was used as an internal reference electrode.

The emf measurements

All electromotive force (emf) measurements were carried out with the following cell assembly; $\text{Ag/AgCl} \mid \text{internal solution, } (1.0 \times 10^{-3} \text{ mol L}^{-1} \text{ HoCl}_3) \mid \text{PVC membrane} \mid \text{test solution} \mid \text{Hg}_2\text{Cl}_2, \text{KCl (saturated)}$. A corning ion analyzer 250 pH/mV meter was used for

the potential measurements at 25.0 ± 0.1 °C. The activities were calculated according to the Debye–Huckel procedure⁴⁴.

Results and Discussion

Potential responses of the electrode

In order to check the QCA suitability as an ion carrier for different metal ions, it was used to prepare PVC membrane ion-selective electrodes in preliminary experiments for a wide variety of cations, including alkali, alkaline earth, transition and heavy metal ions. In comparison with the other tested cations, only the Ho(III) ion displays a strong response (with a slope of 20.4 ± 0.3 mV per decade) to the QCA-based membrane sensors. This is likely due to the high ionophore selectivity for holmium ions over other metal ions, together with the quick exchange kinetics of the resulting Ho^{3+} -QCA complex. Therefore, the ionophore (QCA) was selected as a suitable sensing material for Ho^{3+} ions in PVC matrix.

Membrane composition effect

The influences of the membrane composition, the nature and the plasticizer amount along with the NaTPB amount and OA (as a suitable lipophilic additives) were investigated on the potential response of the Ho^{3+} sensor. Table 1 exhibits the data obtained with membranes having various ratios of different constituents. It is well-known that the sensitivity and selectivity of the ion-selective sensors not only depend on the nature of the employed QCA but also on the membrane composition and the used additives. It is noteworthy that the plasticizer nature affects the dielectric constant of the polymeric membranes, the ionophore mobility and its complex⁴⁵⁻⁴⁸.

Table 1. Composition of membrane ingredients

Membrane No.	Composition, wt. %				Slope, mV/decade	Concentration range, M
	PVC	Plasticizer	Additive	QCA		
1	30	NB, 66	NaTPB,2	2	14.7 ± 0.2	1.0×10^{-5} - 1.0×10^{-2}
2	30	AP, 66	NaTPB,2	2	13.7 ± 0.7	1.0×10^{-5} - 1.0×10^{-2}
3	30	BA, 66	NaTPB,2	2	25.3 ± 0.4	1.0×10^{-5} - 1.0×10^{-2}
4	30	DBP, 66	NaTPB,2	2	30.8 ± 0.3	1.0×10^{-5} - 1.0×10^{-2}
5	30	NB, 61	NaTPB,2; OA,5	2	16.4 ± 0.6	1.0×10^{-6} - 1.0×10^{-2}
6	30	NB, 56	NaTPB,2; OA,10	2	20.4 ± 0.3	1.0×10^{-6} - 1.0×10^{-2}
7	30	NB, 51	NaTPB,2; OA,15	2	17.8 ± 0.5	1.0×10^{-6} - 1.0×10^{-2}
8	30	NB, 57	NaTPB,1; OA,10	2	18.6 ± 0.2	1.0×10^{-6} - 1.0×10^{-2}
9	30	NB, 55	NaTPB,3; OA,10	2	17.4 ± 0.3	1.0×10^{-6} - 1.0×10^{-2}
10	30	NB, 57	NaTPB,2; OA,10	1	18.4 ± 0.2	1.0×10^{-6} - 1.0×10^{-2}
11	30	NB, 55	NaTPB,2; OA,10	3	17.3 ± 0.5	1.0×10^{-6} - 1.0×10^{-2}

From Table 1, it is evident that with the exception of the NB membrane, the resulting membranes of the other three plasticizers disclosed no stable potential response. This can be attributed to the NB polarity that facilitates the extraction of holmium ions with high charge density from the aqueous solution to the organic membrane phase. It is well established that the presence of lipophilic anions in cation-selective membrane electrodes diminishes the ohmic resistance, enhances the response behavior and selectivity and increases the sensitivity of the membrane electrodes⁴⁹⁻⁵¹. Obviously from Table 1, the addition of 2% NaTPB and 10% OA will increase the sensitivity of the electrode response considerably,

so that the membrane electrode demonstrates a Nernstian behavior (membrane no. 6). However, the membrane sensor with a composition of 30% PVC; 56% NB; 2% NaTPB, 10% OA and 2% QCA exhibits the best performance.

Calibration curve

The potential response of the Ho(III) PVC-based membrane sensor at varying concentrations of HoCl_3 (Figure 2) indicates a linear working concentration range from 1.0×10^{-6} to 1×10^{-2} M. The slope of the calibration graph was 20.4 ± 0.3 mV per decade of holmium ions concentration. The detection limit of the electrode that determined from the intersection of the two extrapolated segments of the calibration graph was 4.2×10^{-7} M. The standard deviation for ten replicate measurements was ± 0.5 mV.

pH Effect

The potential electrode response was considered in the pH range of 1.0–11.0 (the pH adjustment was performed with the help of concentrated NaOH or HCl) at a certain holmium ion concentration (1.0×10^{-3} M) and the associated results is depicted in Figure 3 where it is evident that the potential sensor response remains constant in the pH range of 2.4–7.4. At lower pH, a potential increase was observed, owing to the membrane response to hydronium ion (protonation of nitrogen atoms in acidic media). On the contrary, at pH values higher, a potential decrease was observed, due to the formation of the insoluble holmium hydroxide.

Figure 2. Calibration curve of holmium electrode based on QCA

Figure 3. pH effect of the test solution (1.0×10^{-3} M of Ho^{3+}) on the potential response of the Ho^{3+} ion-selective electrode

Dynamic response time

For analytical applications, the dynamic response time consists of an essential parameter in the sensor field⁵². Furthermore, the average time was measured, which was required for the Ho(III) sensor to reach a ± 1 mV potential of the final equilibrium value, after successive immersions into a series of Ho(III) ion solutions, each having a 10-fold concentration difference. The potential versus time traces plot is shown in Figure 4, where it is clear that over the entire concentration range the plasticized membrane electrode reaches its equilibrium responses in a short time (~ 5 s).

Figure 4. Dynamic response time of the holmium electrode for step changes in the Ho^{3+} concentration: A) 1.0×10^{-6} M, B) 1.0×10^{-5} M, C) 1.0×10^{-4} M, D) 1.0×10^{-3} M, E) 1.0×10^{-2} M

The selectivity of the sensor

One of the most important characteristics of a cation-selective membrane electrode is its relative response towards the primary ion over other ions present in the solution, which is usually expressed in terms of potentiometric selectivity coefficients. In this work, the matched potential method was used for the evaluation of the selectivity of the sensor^{53,54}. According to the MPM method, a specified activity (concentration) of primary ions (A) is added to a reference solution and the potential is measured. In a separate experiment, interfering ions (B) are successively added to an identical reference solution until the measured potential matches that obtained before the primary ion addition. The matched potential method selectivity coefficient, K^{MPM} , is then given by the resulting primary ion to interfering ion activity (concentration) ratio, $K^{\text{MPM}} = a_A/a_B$. The resulted potentiometric selectivity coefficients values are summarized in Table 2. From the data given in Table 2, it is immediately obvious that the proposed Ho(III) sensor is highly selective with respect to most of cations. In the case of other lanthanide ions (*i.e.* Pr^{3+} , Lu^{3+} , Yb^{3+} , Tm^{3+} , Gd^{3+} , Tb^{3+} and Er^{3+}), the selectivity coefficients are equal or smaller than 4.4×10^{-3} , which seems to indicate that the Ho(III) ions can be determined in the presence of other lanthanides.

Table 2. Selectivity coefficients of various interfering ions (B)

Interfering ions (B)	Selectivity coefficient ($K_{\text{Ho, B}}$)	Interfering ions (B)	Selectivity coefficient ($K_{\text{Ho, B}}$)
Na^+	2.8×10^{-3}	Zn^{2+}	6.2×10^{-4}
K^+	7.1×10^{-4}	Pr^{3+}	4.8×10^{-4}
Ca^{2+}	7.6×10^{-4}	Lu^{3+}	8.5×10^{-4}
Mg^{2+}	8.9×10^{-4}	Yb^{3+}	1.0×10^{-3}
Co^{2+}	6.2×10^{-4}	Tm^{3+}	4.4×10^{-3}
Ni^{2+}	5.8×10^{-4}	Gd^{3+}	3.4×10^{-3}
Cd^{2+}	6.8×10^{-4}	Tb^{3+}	6.7×10^{-4}
Pb^{2+}	2.7×10^{-3}	Er^{3+}	3.6×10^{-4}
Hg^{2+}	3.4×10^{-3}	Fe^{3+}	2.5×10^{-3}

As can be seen from Table 2, the selectivity coefficients for other metal ions tested (Fe^{3+} , Zn^{2+} , Hg^{2+} , Pb^{2+} , Cd^{2+} , Ni^{2+} , Co^{2+} , Mg^{2+} , Ca^{2+} , K^{+} and Na^{+}) are equal or smaller than 3.4×10^{-3} , indicating they would not significantly disturb the functioning of the proposed Ho(III) membrane sensor. The surprisingly high selectivity of the membrane electrode for Ho^{3+} ions over other cations used, most probably arises from the strong tendency of the carrier molecules for Ho^{3+} ions.

Analytical application

The suggested holmium(III) ion-selective electrode was found to work well under the laboratory conditions. The selective holmium membrane sensor was used as an indicator electrode in the titration of a 1.0×10^{-4} M holmium ion solution with a standard 1.0×10^{-2} M EDTA. The resulting titration curve is shown in Figure 5. According to this Figure, the sensor is capable of monitoring the amount of holmium ions.

Figure 5. Potential titration curve of 25.0 mL from a 1.0×10^{-4} M Ho^{3+} solution with 1.0×10^{-2} M of EDTA

The electrode was also used in the potentiometric determination of fluoride ions in two mouth wash samples and the direct determination of Ho^{3+} ions in mixtures of different ions. The results were derived from triplicate measurements and they are listed in Table 3 and Table 4. From Table 3, there is a satisfactory agreement between the declared fluoride content and the determined values. Also, the corresponding results in Table 4 reveal that the Ho^{3+} ions recovery is quantitative and they support the fact that the holmium membrane sensor can be used for the direct Ho^{3+} monitoring in solutions.

Table 3. Determination of Ho^{3+} ions in mixtures of different ions

S No.	Composition	Observed content, M
1	0.00010 M $\text{Ho}(\text{NO}_3)_3$ + 0.001 M $\text{Tb}(\text{NO}_3)_3$ + 0.001 M $\text{Eu}(\text{NO}_3)_3$	0.000101
2	0.00010 M $\text{Ho}(\text{NO}_3)_3$ + 0.001 M $\text{Dy}(\text{NO}_3)_3$ + 0.001 M $\text{Nd}(\text{NO}_3)_3$	0.000103
3	0.00010 M $\text{Ho}(\text{NO}_3)_3$ + 0.001 M $\text{Sm}(\text{NO}_3)_3$ + 0.001 M $\text{Gd}(\text{NO}_3)_3$	0.000098
4	0.00010 M $\text{Ho}(\text{NO}_3)_3$ + 0.001 M $\text{Er}(\text{NO}_3)_3$ + 0.001 M $\text{Pr}(\text{NO}_3)_3$	0.000105
5	0.00010 M $\text{Ho}(\text{NO}_3)_3$ + 0.001 M $\text{La}(\text{NO}_3)_3$ + 0.001 M $\text{Yb}(\text{NO}_3)_3$	0.000097
6	0.00010 M $\text{Ho}(\text{NO}_3)_3$ + 0.001 M $\text{Tm}(\text{NO}_3)_3$ + 0.001 M $\text{Lu}(\text{NO}_3)_3$	0.000102
7	0.00010 M $\text{Ho}(\text{NO}_3)_3$ + 0.001 M $\text{Cr}(\text{NO}_3)_3$ + 0.001 M $\text{Fe}(\text{NO}_3)_3$	0.000098
8	0.00010 M $\text{Ho}(\text{NO}_3)_3$ + 0.001 M $\text{Ni}(\text{NO}_3)_2$ + 0.001 M KNO_3	0.000101
9	0.00010 M $\text{Ho}(\text{NO}_3)_3$ + 0.001 M $\text{Cd}(\text{NO}_3)_2$ + 0.001 M $\text{Zn}(\text{NO}_3)_2$	0.000104
10	0.00010 M $\text{Ho}(\text{NO}_3)_3$ + 0.001 M $\text{Ca}(\text{NO}_3)_2$ + 0.001 M $\text{Mg}(\text{NO}_3)_2$	0.000098
11	0.00010 M $\text{Ho}(\text{NO}_3)_3$ + 0.001 M $\text{Hg}(\text{NO}_3)_2$ + 0.001 M NaNO_3	0.000097

Table 4. Fluoride ions determination in mouth wash solutions

Sample	Labeled, ppm	Found ISE ^a , ppm
Sodium fluoride mouth wash solution (Aquafresh, Brentford, U.K.)	1350	(1384±22)
Sodium fluoride mouth wash solution (Eurodont, DuroDont GmbH)	1450	(1478±23)

a. Suggested Ho³⁺ sensor, b. Results are based on three measurements

Conclusion

This research demonstrated that ISEs, fabricated on *N*-quinoline-2-carboxamido-8-aminoquinoline (QCA), exhibited holmium selectivity with low interference from common alkali, alkaline earth, transition and heavy metal ions. The constructed electrode showed a Nernstian response (slope of 20.4±0.3 mV/decade), low limit of detection (4.2×10^{-7} M). The proposed sensor displayed a quick response time (~ 5 s). The sensor works well in a pH range of 2.4-7.4 and it can be successfully employed for the Ho³⁺ estimation in real samples.

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