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ORIGINAL PAPER

Fabrication of a novel holmium(III) PVC membrane sensor based on 4-chloro-1,2-bis(2-pyridinecarboxamido)benzene as a neutral ionophore

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Abstract This paper introduces the development of an original PVC membrane electrode, based on 4-chloro-1,2-bis(2-pyridinecarboxamido)benzene (CBPB) as a suitable carrier for the Ho^{3+} ion. The electrode presents a Nernstian slope of 19.7 ± 0.3 mV per decade for the Ho^{3+} ions across a broad working concentration range from 1.0×10^{-6} to 1.0×10^{-2} M. The lower detection limit was 8.5×10^{-7} M in the pH range 2.7–9.8, while the response time was rapid (<15 s). Therefore, this potentiometric sensor displayed good selectivity for a number of cations such as alkali, alkaline earth, transition and heavy metal ions. The practical applicability of the electrode was demonstrated by its use as an indicator electrode in the potentiometric titration of Ho^{3+} ions with EDTA and in the determination of F^- in mouth wash samples.

Keywords PVC membrane · Holmium(III) ion-selective electrode · Potentiometry · 4-Chloro-1,2-bis(2-pyridinecarboxamido)benzene

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1 Introduction

With the increase in rare earth applications in agricultural, metallurgical and functional material areas, etc., convenient, fast and sensitive analysis methods are urgently required. One of these rare earths is holmium, whose compounds are used in ceramics and glasses as well as phosphor lamps. It is also capable of absorbing fission-bred neutrons; therefore, it is used in nuclear reactors to control atomic chain reactions. All holmium compounds should be regarded as highly toxic, although initial information suggests that the danger is limited. The metal dust presents fire and explosion hazards.

The low-level determination of rare-earth ions in solution, for the first time, was carried out by Houk et al. [1] in 1980 by using inductively coupled argon plasma as anion-source for mass-spectrometeric determination. In 1991, Al-Merey et al. [2] determined rare-earth elements in phosphate rocks using both inductively coupled plasma atomic emission spectrometry and instrumental neutron activation analysis. In 1996, determination of dysprosium, holmium and erbium in high purity rare earth oxides by second order derivative spectrophotometry [3] and neodymium, erbium and holmium in rare earth mixtures with 2-phenyltrifluoroacetone and octylphenol poly(ethyleneglycol) ether by third-derivative spectrophotometry [4] were reported. Wang et al. [5] has also developed spectrochemical methods and Li et al. [6] have reported an electrochemical method, adsorption voltammetry, at a carbon paste electrode. These methods are either time consuming, involving multiple sample manipulations, or are too expensive for most analytical laboratories.

Potentiometric detection based on ion-selective electrodes (ISEs) offer the advantages of speed and ease of preparation and procedures, relatively fast response, reasonable selectivity thorough judicious choice of the membrane active materials, wide linear dynamic range, and low cost. These characteristics have inevitably led to the preparation of numerous sensors for several ionic species, and the list of available electrodes has grown substantially over the past years.

It is important to have a high selectivity method for lanthanides because as a group they display similar physical and chemical properties. Only one paper describes holmium determination using an ion selective electrode with a narrow dynamic range (from 1.0×10^{-5} to 1.0×10^{-2} M) [7].

Several highly selective and sensitive membrane sensors for alkaline earth and transition metal ions have been reported [8–17]. However, this study describes the development of a new ion selective sensor for the Ho(III) determination and, in particular, the use of 4-chloro-1,2-bis(2-pyridinecarboxamido)benzene (CBPB) as an ionophore for the preparation of a highly Ho(III) ion-selective electrode (Fig. 1).

2 Experimental

2.1 Reagents

The Merck Chemical and the Aldrich Co. were the suppliers for the nitrate and chloride salts of all cations, the reagent grades of dibutyl phthalate (DBP), benzyl acetate (BA), 2-nitrophenyl octyl ether (NPOE), sodium tetraphenyl borate (NaTPB), tetrahydrofuran (THF) and relatively high molecular weight PVC. All reagents were used without any modification. As far as the nitrate and chloride salts of all employed cations were concerned, they were of the highest available purity and were P_2O_5-vacuum dried. During the experiments, triply distilled deionized water was used. 4-Chloro-1,2-bis(2-pyridinecarboxamido)benzene (CBPB) was synthesized by a literature method [18].

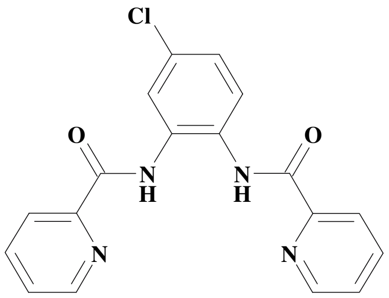

Fig. 1 Structure of the ionophre 4-chloro-1,2-bis(2-pyridinecarboxamido)benzene (CBPB)

2.2 Electrode preparation

The PVC membrane preparation involved the blending of the following compounds; 32 mg of powdered PVC, 60 mg of the NPOE plasticizer, 2.5 mg of the NaTPB additive and 5.5 mg of the CBPB ionophore in 5 ml of fresh THF. The resulting mixture was transferred into a glass dish (2 cm in diameter) and the solvent was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (3–5 mm i.d.) was dipped into the mixture for about 10 s, so that a transparent membrane of about 0.3 mm in thickness was formed. The tube was, then, removed from the mixture, kept at room temperature for about 24 h and filled with an internal filling solution (1.0×10^{-3} M of $HoCl_3$). Finally, the electrode was conditioned by soaking in a 1.0×10^{-2} M $HoCl_3$ solution for 36 h [19–28]. As an internal reference electrode, a silver-silver chloride wire was used.

2.3 The emf measurements

All electromotive force (emf) measurements were carried out with the following cell assembly; Ag/AgCl | internal solution, ($1{\times}10^{-3}$ M $HoCl_3$) | PVC membrane | test solution | Hg_2Cl_2, 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 procedure [29].

3 Results and discussion

3.1 Potential responses

The ionophore CBPB was used as a neutral carrier to prepare the PVC ion-selective membrane electrodes. The potential sensor responses of various ions are shown in Fig. 2(a) and (b). For all these ions, except for the Ho(III) ion, the slope of the corresponding potential pM plots was much lower than the expected Nernstian slopes of 59, 29.5 and 20 mV decade^{-1}, for the uni, di and trivalent cations, respectively. This was likely due to the high ionophore selectivity towards Ho(III) ion over the other metal ions as well as the rapid exchange kinetics of the resulting Ho(III)–Ho(III) complex.

3.2 Membrane composition effect on the potential response

It is well known that the membrane composition and, especially in some cases, the nature of the additive have a significant influence on the sensitivity and selectivity for a certain ionophore [30]. The performance characteristics of

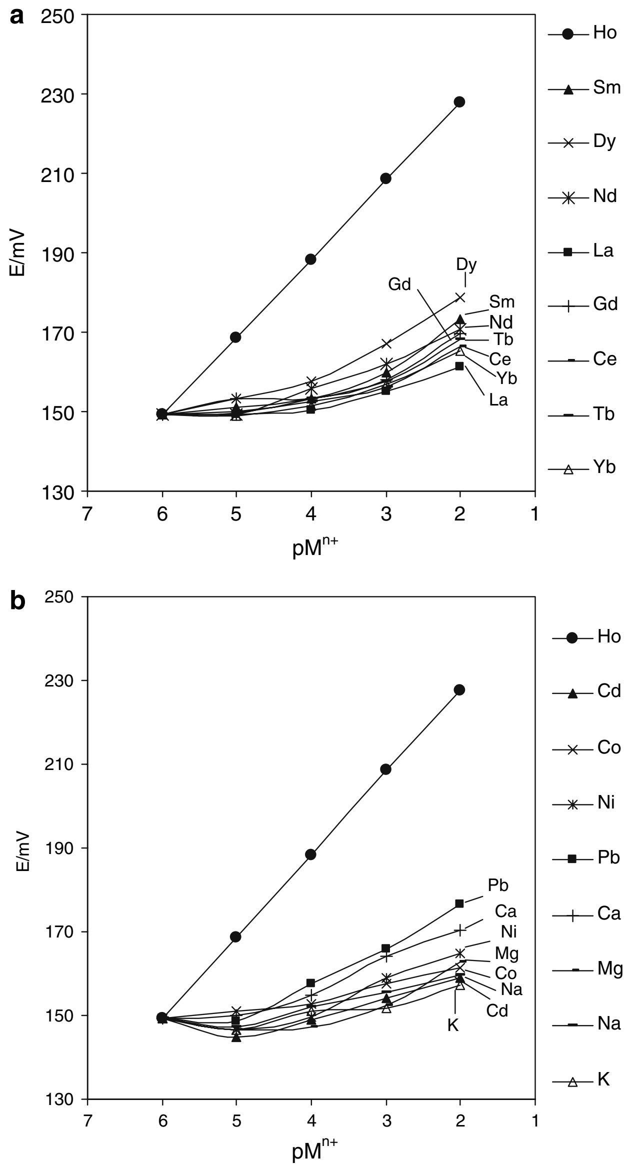

Fig. 2 Potential responses of different ion-selective electrodes based on CBPB with the membrane no. 10 composition

several membranes, having ingredients of different proportions, are listed in Table 1. It is seen that the membrane number 10 with the PVC:NPOE:CBPB:NaTPB ratio of 32:60:5.5:2.5 exhibits a Nernstian slope over a broad Ho(III) ion concentration range.

Moreover, it is interesting to note that the presence of lipophilic and immobilized ionic additives [31] could influence the membrane resistance and, sometimes, the selectivity pattern of the ion-selective PVC membrane, resulting in a good working performance. In line with Table 1, the PVC membrane sensitivity was low, when an appropriate additive was absent (nos. 1–6 with slopes of 8.7–15.7 mV decade^{-1}). Nonetheless, the presence of additives would improve the Ho(III) sensor sensitivity considerably (no. 10 with a slope of 19.7 mV decade^{-1}). Furthermore, Table 1 summarizes the results from the potential sensor response in the absence of the ionophore (nos. 14–16). The corresponding response was found to be weak.

3.3 Calibration curve and statistical data

The detection limit, defined as the obtained Ho(III) concentration when extrapolating the linear region of the sensor calibration curve with the optimum concentration (Fig. 3) to the baseline potential, was 8.5×10^{-7} M. The optimum electrode response was tested after conditioning for different time periods in 1.0×10^{-2} M Ho(III) chloride. The slope deriving from a 24 h conditioning was closer to the theoretical slope, expected on the basis of the Nernstian equation. Longer conditioning time showed no further improvements in response. The optimum conditioning solution was determined to have a concentration of about 1.0×10^{-2} M. In addition, the standard deviation of eight replicate measurements was ±0.5 mV. The electrode lifetime, which is a measure of the electrode durability, was also studied over a period of 12 weeks. The membrane sensor lifetime was at least 10 weeks. During this period; the electrode was used for 1 h per day and 5 days per week. After each usage, it was washed thoroughly. After 10 weeks, only relatively slight changes were observed in the electrode slope and the detection limit from 19.7 ± 0.3 and 8.5×10^{-7} M to 17.2 ± 0.2 mV decade^{-1} and 7.0×10^{-5} M of Ho(III) activity, respectively. These results are shown in Table 2.

3.4 pH effect and response time

In order to study the pH effect on the sensor performance, the potentials were determined at pH values from 1.5 to 12.0 (concentrated NaOH or HCl was used for pH adjustment) at a specific Ho^{3+} concentration (1.0×10^{-3} M). The corresponding results are depicted in Fig. 4. The potential remained constant from pH 2.7 to 9.8, beyond which some drift in potential was observed. The observed drift at higher pH may be attributed to the formation of some Ho^{3+} hydroxyl complexes in the solution. At lower pH, the potentials increased, indicating that the membrane sensor responded to protonium ions, as a result of some extent nitrogen atom protonation of the ionophore.

In analytical applications the dynamic response time is an essential parameter [32]. In this study the average time required for the Ho(III) sensor to reach a ±1 mV potential of the final equilibrium value was measured, after successive immersions into a series of Ho(III) ion solutions, each having a 10-fold concentration difference. The potential

Table 1 Optimization of the membrane ingredients

Electrode No.	Composition/wt%, PVC 32%					Slope/mV decade^{-1}	Conc. Range/M
	CBPB	NaTPB	NPOE	DBP	BA		
1	2	0	66.0	0	0	8.7 ± 0.3	1.0×10^{-4}–5.0×10^{-2}
2	3	0	65.0	0	0	11.2 ± 0.4	1.0×10^{-4}–1.0×10^{-2}
3	4	0	64.0	0	0	15.6 ± 0.6	1.0×10^{-4}–1.0×10^{-2}
4	5	0	63.0	0	0	14.9 ± 0.4	1.0×10^{-4}–1.0×10^{-2}
5	6	0	62.0	0	0	14.7 ± 0.3	1.0×10^{-4}–1.0×10^{-2}
6	5.5	0	62.5	0	0	15.7 ± 0.1	1.0×10^{-5}–1.0×10^{-2}
7	5.5	1.0	61.5	0	0	18.0 ± 0.7	1.0×10^{-6}–1.0×10^{-2}
8	5.5	1.5	61.0	0	0	18.2 ± 0.4	1.0×10^{-6}–1.0×10^{-2}
9	5.5	2.0	60.5	0	0	18.5 ± 0.5	1.0×10^{-6}–1.0×10^{-2}
10	5.5	2.5	60.0	0	0	19.7 ± 0.3	1.0×10^{-6}–1.0×10^{-2}
11	5.5	3.0	59.5	0	0	17.4 ± 0.4	1.0×10^{-5}–1.0×10^{-2}
12	5.5	2.5	0	60	0	16.6 ± 0.5	1.0×10^{-6}–1.0×10^{-2}
13	5.5	2.5	0	0	60	18.2 ± 0.7	1.0×10^{-6}–1.0×10^{-2}
14	0	2.5	65.5	0	0	4.3 ± 0.3	1.0×10^{-4}–1.0×10^{-3}
15	0	2.5	0	65.5	0	3.8 ± 0.5	1.0×10^{-4}–1.0×10^{-3}
16	0	2.5	0	0	65.5	4.1 ± 0.3	1.0×10^{-4}–1.0×10^{-3}

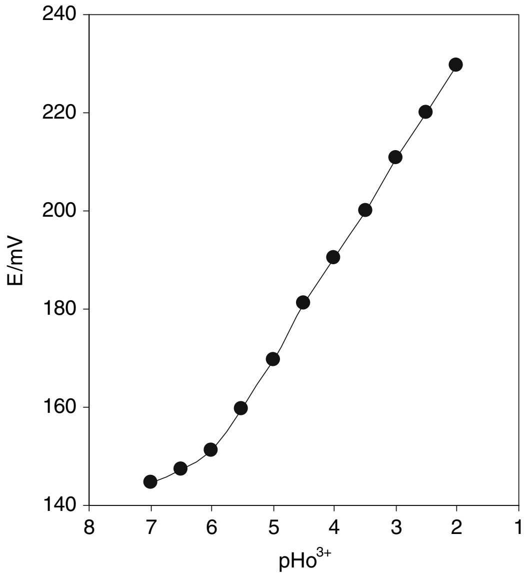

Fig. 3 Calibration curve of holmium electrode based on CBPB with the membrane no. 10 composition. The results are based on eight measurments (R^2:0.998)

versus time plot is shown in Fig. 5, where it is clear that over the entire concentration range the plasticized membrane electrode reached equilibrium responses in a short time (<15 s).

3.5 Ho(III) electrode selectivity

For the selectivity coefficient measurements, the matched potential method was used. According to the MPM [33], 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 MPM selectivity coefficient is then given by the resulting primary ion to the interfering ion activity (concentration) ratio, $K^{\mathrm{MPM}} = a_{\mathrm{A}}/a_{\mathrm{B}}$. The experimental conditions and the resulting values are listed in Table 3. For all the tested ions, the selectivity coefficients were of the order 8.2×10^{-3} or smaller, indicating that they would not radically disturb the function of the sensor. Therefore, the electrode may be used for Ho(III) ion detection in the presence of certain interfering ions.

The characteristics of the sensor were compared with those of the best holmium electrodes reported in the literature [7] (Table 4). It can be concluded that this sensor in terms of selectivity, detection limit, and dynamic concentration range, was superior to all previously described holmium sensors.

3.6 Analytical application

3.6.1 *Titration with EDTA*

The Ho(III) membrane electrode was found to work well under laboratory conditions. It was successfully applied to the titration of a Ho(III) solution with EDTA. The resulting titration curve is displayed in Fig. 6, where it can be observed that the Ho(III) amount in solution can be accurately detected.

Table 2 The lifetime of the Ho^{3+} microelectrode sensor

Week	Slope/mV decade^{-1}	D.L
First	19.7 ± 0.3	8.5×10^{-7} M
Second	19.7 ± 0.5	8.7×10^{-7} M
Third	19.6 ± 0.4	9.0×10^{-7} M
Fourth	19.5 ± 0.2	9.2×10^{-7} M
Fifth	19.4 ± 0.3	9.5×10^{-7} M
Sixth	19.2 ± 0.2	9.6×10^{-7} M
Seventh	19.1 ± 0.2	9.9×10^{-7} M
Eighth	18.9 ± 0.4	1.0×10^{-6} M
Ninth	18.8 ± 0.3	1.5×10^{-6} M
Tenth	18.6 ± 0.2	3.0×10^{-6} M
Eleventh	18.0 ± 0.4	8.0×10^{-6} M
Twelve	17.2 ± 0.2	7.0×10^{-5} M

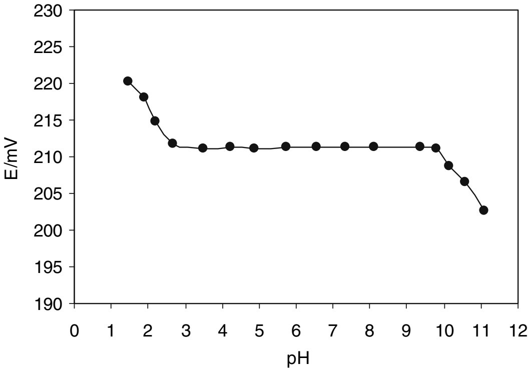

Fig. 4 pH effect of the test solution (1.0×10^{-3} M of Ho^{3+}) on the potential response of the Ho^{3+} ion-selective electrode with the membrane no. 10 composition

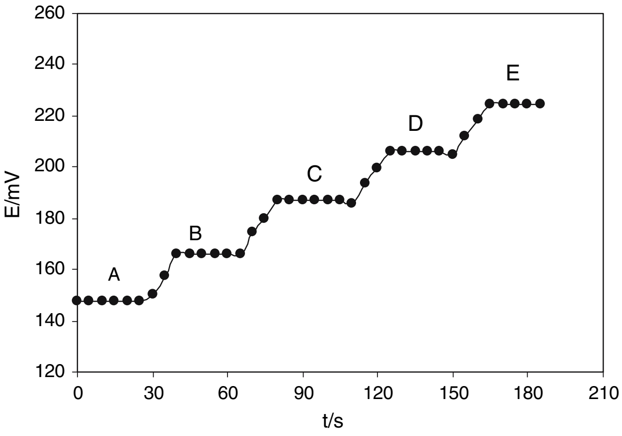

Fig. 5 Dynamic response time of the Ho^{3+} ion-selective electrode for step changes in the Ho^{3+} concentration: (**A**) 1.0×10^{-6} M, (**B**) 1.0×10^{-5} M, (**C**) 1.0×10^{-4} M, (**D**) 1.0×10^{-3} M, (**E**) 1.0×10^{-2} M, (**F**) 1.0×10^{-1} M

Table 3 Selectivity coefficients of various interfering ions (B)

Interfering ion	$K^{MPM}_{Ho^{3+},B}$	Interfering ion	$K^{MPM}_{Ho^{3+},B}$
Na^+	5.9×10^{-4}	Sm^{3+}	5.3×10^{-3}
K^+	6.7×10^{-4}	Nd^{3+}	5.0×10^{-3}
Mg^{2+}	1.9×10^{-3}	Dy^{3+}	8.2×10^{-3}
Ca^{2+}	3.3×10^{-3}	La^{3+}	8.7×10^{-4}
Pb^{2+}	7.4×10^{-3}	Yb^{3+}	4.2×10^{-3}
Ni^{2+}	8.5×10^{-4}	Gd^{3+}	6.4×10^{-3}
Co^{2+}	7.5×10^{-4}	Tb^{3+}	7.5×10^{-3}
Cd^{2+}	6.4×10^{-4}	Ce^{3+}	1.2×10^{-3}

3.6.2 Fluoride ion determination

This sensor was also successfully applied to the determination of F^- ions in two mouth wash samples. 1.0 g of each sample was taken and diluted with distilled water in a 100 ml flask and titrated with a Ho^{3+} solution (1.0×10^{-3} M). The results, after triplicate measurements, are summarized in Table 5. The measurement principle for the determination of fluoride ions was based on the monitoring of the Ho^{3+} ion concentration. At the beginning of the titration, the Ho^{3+} concentration was zero. With Ho^{3+}

Table 4 Comparison of selectivity coefficients, detection limit, response time and linearity range of the developed Ho(III) sensor and the formerly mentioned Ho(III) ion-selective electrodes

	Ref. [7]	This work
Linearity range/M	1.0×10^{-5}–1.0×10^{-2}	1.0×10^{-6}–1.0×10^{-2}
Detection limit/M	7.0×10^{-6}	8.5×10^{-7}
Response time/s	<15	<15
Selectivity coefficients	MPM	MPM
Na^+	4.0×10^{-2}	5.9×10^{-4}
K^+	7.0×10^{-3}	6.7×10^{-4}
Mg^{2+}	3.0×10^{-2}	1.9×10^{-3}
Ca^{2+}	8.5×10^{-3}	3.3×10^{-3}
Pb^{2+}	4.5×10^{-2}	7.4×10^{-3}
Ni^{2+}	–	8.5×10^{-4}
Co^{2+}	–	7.5×10^{-4}
Cd^{2+}	–	6.4×10^{-4}
Sm^{3+}	3.0×10^{-2}	5.3×10^{-3}
Nd^{3+}	8.5×10^{-3}	5.0×10^{-3}
Dy^{3+}	7.0×10^{-2}	8.2×10^{-3}
La^{3+}	1.0×10^{-2}	8.7×10^{-4}
Yb^{3+}	–	4.2×10^{-3}
Gd^{3+}	4.0×10^{-2}	6.4×10^{-3}
Tb^{3+}	–	7.5×10^{-3}
Ce^{3+}	–	1.2×10^{-3}

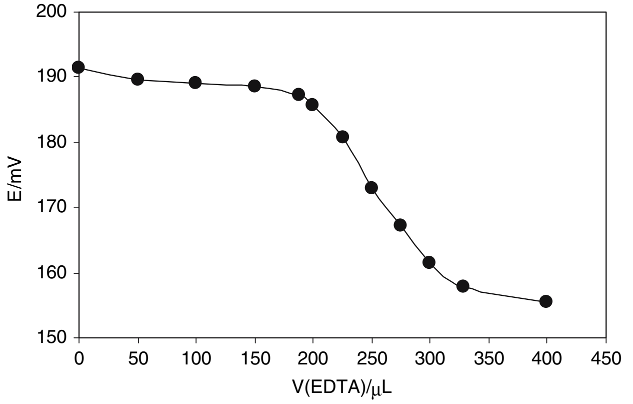

Fig. 6 Potential titration curves of 25.0 ml 1.0×10^{-4} M Ho(III) solution with 1.0×10^{-2} M of EDTA (pH = 10)

Table 5 Fluoride ions determination in mouth wash solutions

Sample	Labeled/ ppm	Found ISE[a]/ ppm	Commercial flouride ISE[b]/ppm
Sodium fluoride mouth wash solution (Aquafresh, Brentford, U.K.)	1,350	(1,384 ± 16)	(1,343 ± 15)
Sodium fluoride mouth wash solution (Eurodont, DuroDont GmbH)	1,450	(1,478 ± 22)	(1,446 ± 18)

[a] Suggested Ho^{3+} sensor

[b] Results are based on three measurements

addition to the solution containing F^- ions, insoluble HoF_3 was formed and the potential during the titration remained almost constant. This is due to the formation of insoluble HoF_3 and the potential changes caused by the K_{sp} of HoF_3. After total F^- ion conversion to HoF_3 by addition of Ho^{3+} ions, the solution potential changed sharply. The beginning of the sharp change was the end point of the titration. There was a satisfactory agreement among the declared fluoride contents, the values determined by the sensor and the commercial solid fluoride sensor (ELIT 101).

4 Conclusion

A potentiometric CBPB-PVC-based membrane sensor functioned as an excellent Ho^{3+} selective membrane sensor and could be used for Ho^{3+} detection in the presence of considerable concentrations of common interfering ions. The characteristics making the device suitable for the determinations of this ion were the applicable pH range, the lower detection limit and the potentiometric selectivity coefficients, determined after use of the sensor. The sensor was successfully applied to the determination of fluoride ions in mouth wash preparations. It was also used as an indicator electrode in the potentiometric titration of Ho(III) ions with EDTA.

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