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Construction of a Highly Selective and Sensitive Ytterbium(III) Membrane Sensor Based on 4-Methoxybenzyl Carbazate as a New Neutral Ionophore

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In this research, 4-Methoxybenzyl carbazate (MBC) was used as an excellent sensing ion carrier in the construction of a poly vinyl chloride membrane sensor for Yb^{3+} ions. The electrode shows a good selectivity for the Yb^{3+} ion with respect to most common cations including alkali, alkaline earth, transition, and heavy metal ions, and especially lanthanide ions. The sensor exhibits Nernstian response to Yb^{3+} ions in the concentration range of 1.0×10^{-7} to 1.0×10^{-2} mol L^{-1} with a detection limit of the proposed sensor is 8.3×10^{-8} mol L^{-1}. It displays a Nernstian slope of 19.8±0.4 mV $decade^{-1}$ in the pH range of 2.2–9.7. The proposed sensor also exhibits a fast response time of ~5 s and can be used over a period of 10 weeks without significant changes in its response. To test the analytical applicability of the designed device, it was used as an indicator electrode in the potentiometric titration of Yb^{3+} ions with EDTA and the determination of concentration of Yb^{3+} ions in water samples and in various mixtures of interfering ions.

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

1. INTRODUCTION

Ytterbium is not found free in nature but is found in a number of minerals: mainly monazite, yttria, gadolinite euxenite and xenotime. It is used in metallurgical and chemical experiments [1]. Ytterbium is a rare earth element, and it is readily attacked and dissolved by the strong mineral acids. It reacts slowly with cold water and it oxidizes slowly in air [2]. Ytterbium can also be used as a dopant to help improve the grain refinement, strength, and other mechanical properties of stainless steel. Ytterbium and other lanthanides are used for gasoline cracking catalysts, carbon arcs, and movie projectors [3]. Ytterbium has no biological role, but it has been noted that its salts stimulate metabolism. Ytterbium is a skin and eye irritant and it is also a suspected teratogen. All compounds should be stored in closed containers, protected from air and moisture and treated as highly toxic [2].

Inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) and spectrofluorimetry are among the available methods used for low-level monitoring of Yb^{3+} ions in solutions. neutron activation analysis, X-ray fluorescence spectrometry, etc., are also used in some laboratories. All these methods are time consuming, involving multiple sample manipulations, or too expensive for most analytical laboratories.

Potentiometric detection based on ISEs, as a simple method, offers several advantages such as speed and ease of preparation and procedures, simple instrumentation, relatively fast response, wide dynamic range, reasonable selectivity, and low cost. A literature survey shows that there are a limited number of reports on ytterbium selective sensors [4–10] three of which have been reported by our research group. Several highly selective and sensitive membrane sensors for alkaline earth and transition metal ions have been reported by our research team and other researchers[11–40]. In this work, we report the preparation of a highly selective and sensitive Yb^{3+} sensor by using 4-methoxybenzyl carbazate (MBC) as an suitable ionophore in the construction of a PVC-based Yb^{3+}-selective membrane electrode (Fig. 1).

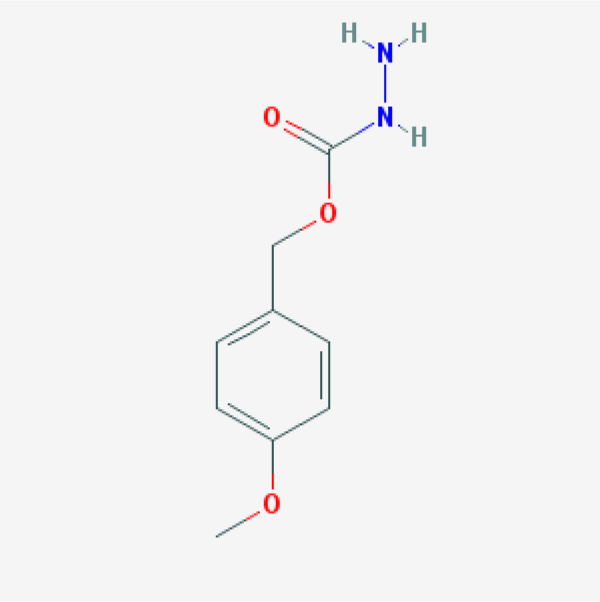

Figure 1. Structure of the ligand MBC.

2. EXPERIMENTAL

2.1. Electromotive force (EMF) measurements

All electromotive force was carried out with the membrane sensor using the following cell assembly:

Ag–AgCl| internal solution 1.0×10^{-3} mol L^{-1} $YbCl_3$ | PVC membrane: sample| $Hg–Hg_2Cl_2$, KCl (satd).

A Corning ion analyser 250 pH/mV meter was used for the potential measurements at 25.0 °C. Activities were calculated according to the Debye–Huckel procedure [41].

2.2. Chemicals and reagents

Reagent-grade 4-Methoxybenzyl carbazate (MBC), dibutyl phthalate (DBP), benzyl acetate (BA), acetophenon (AP), nitrobenzene (NB), sodium tetraphenyl borate (NaTPB), tetrahydrofuran (THF) and high relative molecular weight PVC were purchased from the Merck and the Aldrich Chemical Companies. The nitrate and chloride salts of all cations used (all from Merck) were of the highest purity available and used without any further purification except for vacuum drying. Doubly distilled and deionized water was used throughout.

2.3. Membrane sensor construction based on MBC

PVC-based ion-selective membranes were prepared according to a general procedure. The required ingredients were formulated by dissolving appropriate amounts of ionophore (5 mg), anionic additive NaTPB (2 mg), plasticizer NB (63 mg), and PVC (30 mg) in 3 mL 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 could be obtained. A Pyrex tube (3–5 mm in top) was dipped into the oily mixture for about 10 s, so that a transparent film of about 0.3 mm thickness was formed. After the tube removal from this mixture, the tube was kept at room temperature for about 24 h and it was filled with the internal filling solution (1.0×10^{-3} mol L^{-1} $YbCl_3$). In the end, the electrode was conditioned by soaking in a 1.0×10^{-3} mol L^{-1} $YbCl_3$ solution for 24 h [42–60]. A silver/silver chloride wire was used as an internal reference electrode.

3. RESULTS AND DISCISSION

3.1. Potential respone of the Yb^{3+} sensor

To investigate the suitability of the ionophor MBC as a selective ionophore toward lanthanide cations, in preliminary experiments, it was used in construction of the plasticized PVC-membrane sensors for a number of metal ions. The potential responses of the most sensitive electrodes, prepared under the same experimental conditions (except for 24 h conditioning in a 1.0×10^{-3} mol L^{-1} of the corresponding cations), are shown in Figure 2. As is obvious, with the exception of Yb^{3+} ion, the slope of the emf responses obtained for all other cation selective sensors are much lower than that predicted by the Nernst equation. This observation was attributed both to the selective behavior of the ionophore against the Yb^{3+} ions with respect to the other metal ions and the rapid exchange kinetics of the resulting $MBC–Yb^{3+}$ complex.

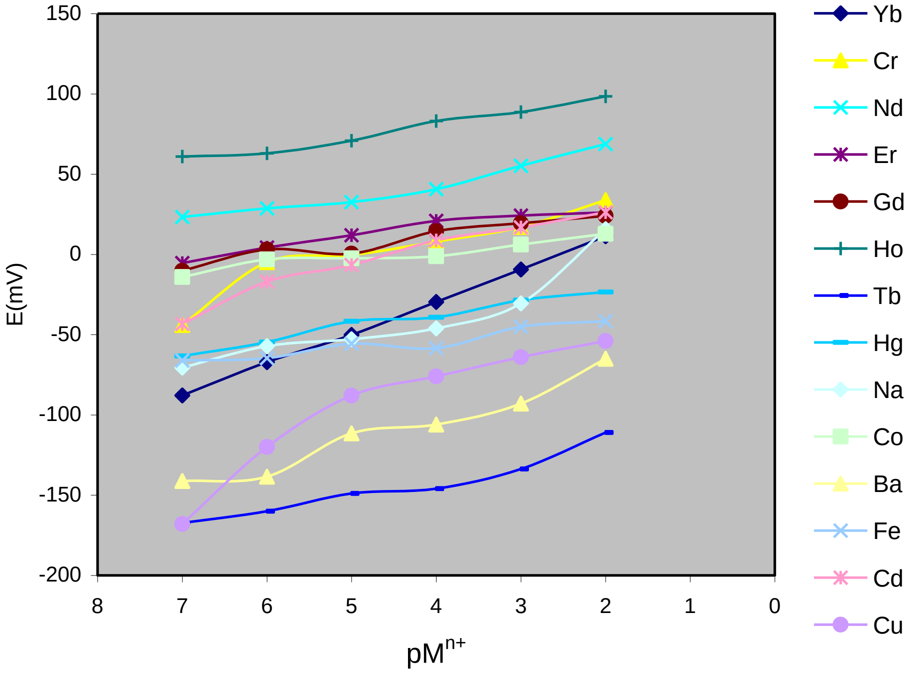

Figure 2. Potential responses of various PVC membrane sensors based on MBC.

3.2. Effect of membrane composition on the potential response

Some important features of the PVC membranes, such as properties of plasticizer, plasticizer/PVC ratio, nature and amount of ionophore and, especially, the nature and the amount of the used additives, are reported to significantly influence ISEs sensitivity and selectivity [61-70]. To investigate these effects on the sensor response, several tests were performed and the results are summarized in Table 1. The membrane plasticizer plays a key role in determining the selectivity, working concentration range and response time of the membrane electrode [70-76]. The influence of the plasticizer was investigated on the potential response of the Yb^{3+} sensor. From Table 1, among four different solvent mediators tested, NB is superior with respect to dibutyl phthalate, benzyl acetate and acetophenone. All the used plasticizers have a nearly low donocity number (DN) but different dielectric constants (DC). NB is used as a plasticizer because of having a higher dielectric constant than the others. The higher DC of NB helps the better extraction of the polar Yb^{3+} ion, which is a cation with high charge density from the aqueous layer to the organic layer of the membrane and causes a better and faster response. The data in Table 1 revealed that the membrane manufactured with the plasticizer/PVC ratio of 2.2 was suitable, displaying the best performance. From the same Table, it is evident that the increase of the MBC amount in the membranes (no. 2) up to 2% resulted in greater slopes. The maximum slope of 19.8±0.4 mVdecade^{-1} of Yb^{3+} concentration was observed for the membrane no. 2 with 2% of MBC. As can be seen from Table 1, the optimum amount of ionophore (MBC) was 2% (no. 2).

In general, the presence of lipophilic anions in cation selective membranes based on a neutral carrier not only diminishes the ohmic resistance and enhances the response behavior and selectivity, but also, in cases where the extraction capability is poor, increases the sensitivity of the membrane electrodes [76–82]. Obviously, from Table 1, the sensor slope in the absence of sodium tetraphenyl borate (NaTPB) is lower than the expected Nernstian value (membrane no. 9). Nevertheless, the addition of 2% NaTPB will increase the sensitivity of the electrode response considerably, so that the membrane electrode demonstrates a Nernstian behavior (membrane no. 2). However, the membranes with the composition of 30% PVC, 2% MBC, 2% NaTPB and 66% nitrobenzene (NB) exhibit a Nernstian potential response.

Table 1. Optimization of membrane ingredients**.**

Electrode No.	Composition (wt%)				Slope (mV decade^{-1})	Linear range (mol L^{-1})
	MBC	NaTPB	Plasticizer	PVC		
1	2	2	AP, 66	30	14.7 ± 0.3	1.0×10^{-6}-1.0×10^{-2}
2	2	2	NB, 66	30	19.8 ± 0.4	1.0×10^{-7}-1.0×10^{-2}
3	2	2	BA, 66	30	14.5 ± 0.6	1.0×10^{-6}-1.0×10^{-2}
4	2	2	DBP, 66	30	13.2 ± 0.5	1.0×10^{-6}-1.0×10^{-3}
5	1	2	NB, 67	30	14.4 ± 0.3	1.0×10^{-6}-1.0×10^{-2}
6	1.5	2	NB, 66.5	30	17.3 ± 0.2	1.0×10^{-7}-1.0×10^{-2}
7	2.5	2	NB, 65.5	30	18.2 ± 0.5	1.0×10^{-7}-1.0×10^{-2}
8	3	2	NB, 65	30	18.9 ± 0.2	1.0×10^{-7}-1.0×10^{-2}
9	2	0	NB , 68	30	13.1 ± 0.5	1.0×10^{-5}-1.0×10^{-2}
10	2	1	NB, 67	30	17.5 ± 0.3	1.0×10^{-6}-1.0×10^{-2}
11	2	3	NB, 65	30	18.2 ± 0.6	1.0×10^{-7}-1.0×10^{-2}

3.3. Calibration graph and lifetime

The critical response characteristics of the Yb^{3+} ion-selective electrode were assessed according to IUPAC recommendations [83]. The Emf response of the membrane at varying Yb^{3+} concentrations (Figure 3) depicts a rectilinear range from 1.0×10^{-7} to 1.0×10^{-2} mol L^{-1} with a Nernstian slope of 19.8±0.4 mV decade^{-1}. The detection limit, defined as the obtained Yb^{3+} concentration when extrapolating the linear region of the sensor calibration curve with the optimum concentration to the baseline potential, was 8.3×10^{-8} mol L^{-1}. The standard deviation of ten replicate measurements is ±0.5 mV. The electrode lifetime, which is a measure of the electrode durability, was also studied. over a period of 12 weeks. For this propose, two similar membrane sensors were selected and their slopes were recorded over a period of 12 weeks. The membrane sensor lifetime was obtained at least 10 weeks without significant change in its slope. During this period; the electrodes were used for 1 h per day and 5 days per week. After each usage, they were washed thoroughly. After this time a slight decrease in the slope (19.8–17.9 mV decade^{-1}) was observed.

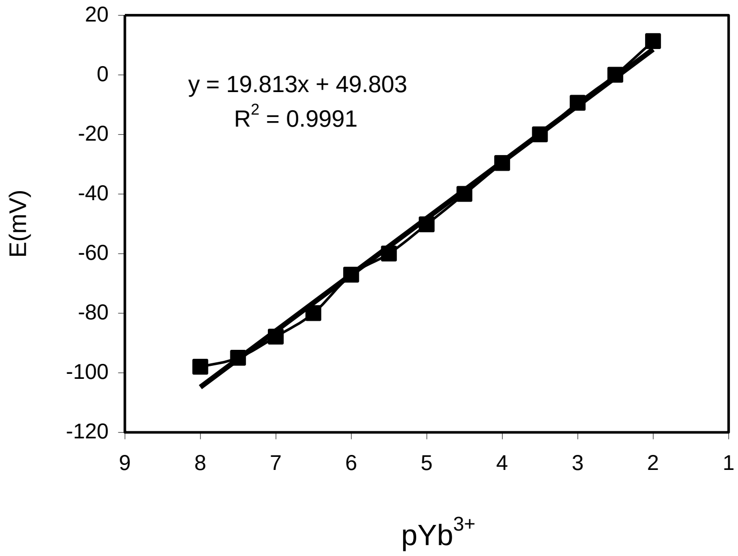

Figure 3. Calibration curve of the Yb^{3+} sensor based on MBC in the range of 1.0×10^{-7} to 1.0×10^{-2} mol L^{-1} Yb^{3+} ions.

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 1.0 to 12.0 (concentrated NaOH or HCl was used for pH adjustment) at a specific Yb^{3+} concentration (1.0×10^{-3} mol L^{-1}). The corresponding results are depicted in Figure 4. The potential remained constant from pH 2.2 to 9.7, beyond which some drift in potential was observed. The observed drift at higher pH may be attributed to the formation of some Yb^{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.

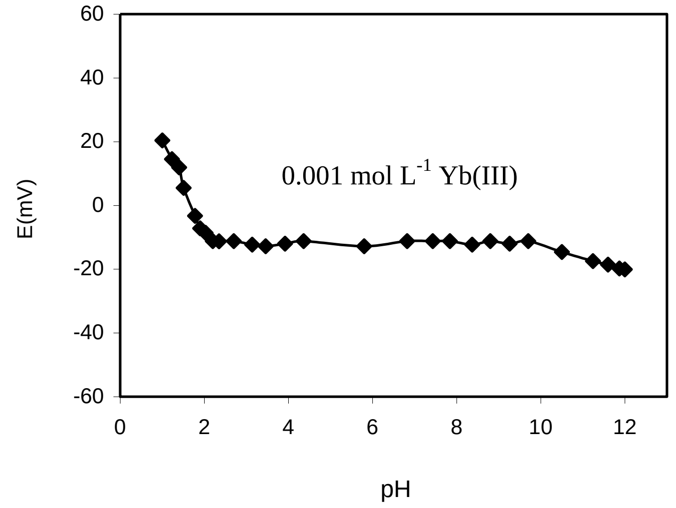

Figure 4. Effect of the pH of test solution (1.0×10^{-3} molL^{-1} of Yb^{3+}) on the potential response of the Yb^{3+} sensor based on MBC.

The response time of the proposed sensor was recorded by changing the Yb^{3+} concentration in a series of solutions (1.0×10^{-7} to 1.0×10^{-2} mol L^{-1}). The potential versus time plot is shown in Figure 5, where it is clear that over the entire concentration range the plasticized membrane electrode reached equilibrium responses in a short time (~5 s).

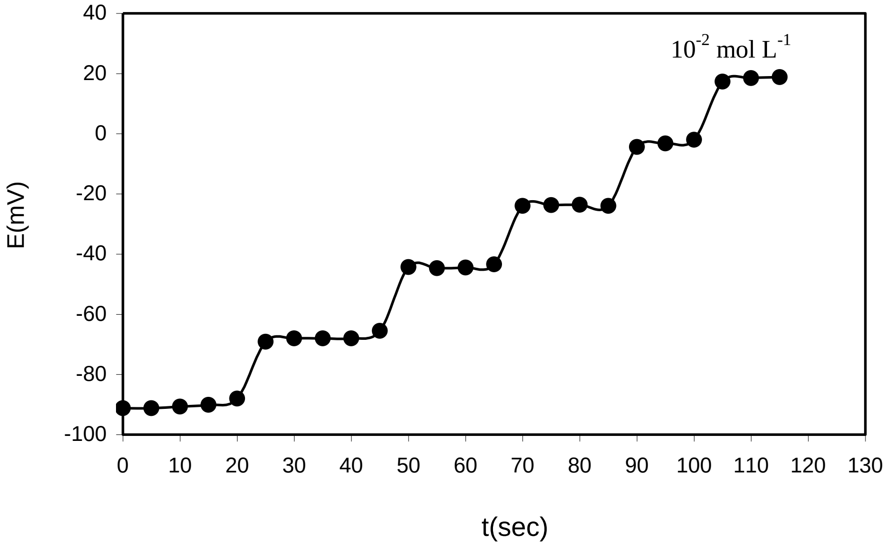

Figure 5. Dynamic response time of the Yb^{3+} sensor for step changes in the Yb^{3+} concentration.

3.5. Yb^{3+} *sensor selectivity*

Table 2. Selectivity coefficients of the Yb^{3+} electrode.

M^{n+}	$K^{MPM}_{Yb^{3+},B}$	M^{n+}	$K^{MPM}_{Yb^{3+},B}$
Sm^{3+}	5.4×10^{-4}	Tb^{3+}	4.2×10^{-3}
La^{3+}	2.6×10^{-3}	Cr^{3+}	3.7×10^{-3}
Pr^{3+}	4.8×10^{-4}	Fe^{3+}	1.0×10^{-3}
Dy^{3+}	4.2×10^{-4}	Ca^{2+}	4.6×10^{-4}
Er^{3+}	1.0×10^{-4}	Pb^{2+}	7.5×10^{-4}
Eu^{3+}	3.2×10^{-3}	Ni^{2+}	6.3×10^{-4}
Tm^{3+}	3.7×10^{-3}	Co^{2+}	8.7×10^{-4}
Ho^{3+}	5.6×10^{-4}	Na^{+}	3.8×10^{-4}
Lu^{3+}	6.7×10^{-4}	K^{+}	2.2×10^{-4}

For the selectivity coefficient measurements, the matched potential method was used [84-88]. According to the MPM, a specified activity of the primary ion (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 (containing primary ion) solution until the measured potential matched to that obtained before the addition of the primary ions. The matched potential method selectivity coefficient, K^{MPM}, is then given by the resulting primary ion to interfering ion activity (concentration) ratio, $K^{MPM}=\Delta a_A/a_B$. The experimental conditions and the resulting values are listed in Table 2. For all the tested ions, the selectivity coefficients were of the order 4.2×10^{-3} or smaller, indicating that they would not radically disturb the function of the sensor. Therefore, the electrode may be used for Yb^{3+} ion detection in the presence of certain interfering ions.

The characteristics (selectivity, dynamic linearity range, detection limit, response time, and pH range) of the sensor were compared with those of the best ytterbium sensors reported in the literature [4-6] (Table 3). It can be concluded that this sensor in terms of selectivity, detection limit, pH range, response time and dynamic concentration range, was superior to all previously described ytterbium sensors.

Table 3. Comparison of selectivity coefficients, detection limit, linearity range, response time and pH range of the proposed Yb^{3+} sensor and the formerly reported Yb^{3+} sensor.

Parameters	Ref. 4	Ref. 5	Ref. 6	This work
Detection limit (mol L^{-1})	7.0×10^{-7}	5.0×10^{-7}	4.2×10^{-7}	8.3×10^{-8}
Linear range (mol L^{-1})	1.0×10^{-6}-1.0×10^{-2}	1.0×10^{-6}-1.0×10^{-2}	1.0×10^{-6}-1.0×10^{-1}	1.0×10^{-7}-1.0×10^{-2}
Response time (s)	~15	8-10	<10	~5
Interfering ion (B) K_{sel} More than 5.0×10^{-3}	Cu	Dy	Pr, Dy, Fe, K, Ni	-
pH range	3.0-8.0	3.5-9.0	3.2-8.3	2.2-9.7

3.6. Analytical application

The proposed Yb^{3+} membrane sensor was used for the determination of ytterbium ion concentrations in different water samples (tap water and river water samples). The 10.0 mL of each water samples was taken and diluted with distilled water in a 25.0 mL volumetric flask. The potential of this solution was measured by the proposed sensors. The results are shown in Table 4. It is seen that quantitative recovery of Yb^{3+} ions from the sample solution was achieved.

Table 4. Recovery of Yb^{3+} spiked in tap and river water samples by use of the proposed electrode.

Sample	Yb^{3+} added (mg mL^{-1})	Found (mg mL^{-1})	Recovery (%)
River water	0.25 0.5	$(0.28^{a} \pm 0.04)$ (0.54 ± 0.03)	112 108
Tap water	0.25 0.5	(0.27 ± 0.04) (0.53 ± 0.02)	108 106

It should be noted that the developed Yb^{3+} membrane sensor can not only be used for the direct monitoring of the Yb^{3+} ions but also as an indicator electrode in the potentiometirc titration of Lu^{3+} ions with EDTA. Figure 6 shows the titration of 25 mL Yb^{3+} solution (1.0×10^{-4} mol L^{-1}) with a standard solution of EDTA (1.0×10^{-2} mol L^{-1}). As can be, the end point of the titration curve is sharp.

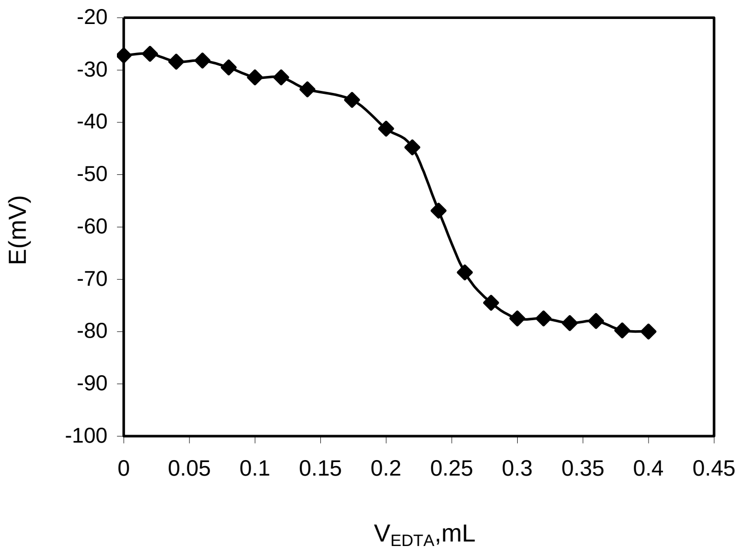

Figure 6. Potential titration curve of 25.0 mL from a 1.0 × 10^{-4} $molL^{-1}$ Yb^{3+} solution with 1.0×10^{-2} $molL^{-1}$ of EDTA.

Table 5. Determination of Yb^{3+} ions in mixtures of different ions.

Serial no.	Composition	Observed content (mol L^{-1})
1	0.00010 mol L^{-1} $Yb(NO_3)_3$ + 0.001 mol L^{-1} $Tm(NO_3)_3$ + 0.001 mol L^{-1} $Er(NO_3)_3$ + 0.001 mol L^{-1} $Eu(NO_3)_3$	0.000102
2	0.00010 mol L^{-1} $Yb(NO_3)_3$ + 0.001 mol L^{-1} $Nd(NO_3)_3$ + 0.001 mol L^{-1} $La(NO_3)_3$ + 0.001 mol L^{-1} $Dy(NO_3)_3$	0.000098
3	0.00010 mol L^{-1} $Yb(NO_3)_3$ + 0.001 mol L^{-1} $Gd(NO_3)_3$ + 0.001 mol L^{-1} $Ce(NO_3)_3$ + 0.001 mol L^{-1} $Sm(NO_3)_3$	0.000104
4	0.00010 mol L^{-1} $Yb(NO_3)_3$ + 0.001 mol L^{-1} $Tb(NO_3)_3$ + 0.001 mol L^{-1} $Lu(NO_3)_3$ + 0.001 mol L^{-1} $Pr(NO_3)_3$	0.000101
5	0.00010 mol L^{-1} $Yb(NO_3)_3$ + 0.001 mol L^{-1} $Ho(NO_3)_3$ + 0.001 mol L^{-1} $Er(NO_3)_3$+ 0.001 mol L^{-1} $Pr(NO_3)_3$	0.000096
6	0.00010 mol L^{-1} $Yb(NO_3)_3$ + 0.001 mol L^{-1} $Fe(NO_3)_3$ + 0.001 mol L^{-1} $Cr(NO_3)_3$+ 0.001 mol L^{-1} $Cu(NO_3)_2$	0.000098
7	0.00010 mol L^{-1} $Yb(NO_3)_3$ + 0.001 mol L^{-1} $Pb(NO_3)_2$+ 0.001 mol L^{-1} $Ni(NO_3)_2$ + 0.001 mol L^{-1} $Co(NO_3)_2$	0.000103
8	0.00010 mol L^{-1} $Yb(NO_3)_3$ + 0.001 mol L^{-1} $Hg(NO_3)_2$+ 0.001 mol L^{-1} $Cd(NO_3)_2$+ 0.001 mol L^{-1} KNO_3	0.000096
9	0.00010 mol L^{-1} $Yb(NO_3)_3$ + 0.001 mol L^{-1} $Hg(NO_3)_2$+ 0.001 mol L^{-1} $Ca(NO_3)_2$+ 0.001 mol L^{-1} $NaNO_3$	0.000098

The proposed electrode was also applied to the determination of Yb^{3+} ion in various mixtures of different cations and the results are summarized in Table 5. The recovery of Yb^{3+} ions is very good (96–104%). This is due to the relatively good selectivity of the Yb^{3+} electrode.

4. CONCLUSION

A potentiometric Yb^{3+}-selective membrane based on MBC functions as a good Yb^{3+} selective sensor and can be used for the determination of this ion in the presence of considerable concentrations of common interfering ions. The fabricated Yb^{3+} sensor is superior to the existing electrodes with regard to the working concentration range, lower detection limit, applicable pH range, response time and selectivity over a number of cations. The proposed electrode was successfully applied to determining Yb^{3+} ions in water samples and in various mixtures of cations.

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