Influence of interfering ions as a key parameter on response of a fabricated Tm^{3+} solvent polymeric membrane ion-selective electrode

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ABSTRACT

A new Tm(III) ion-selective liquid polymeric membrane sensor based on N-[(E)-1-(2-thienyl)methylidene]-N-(4-{[(Z)-1-(2-thienyl)methylidene]amino}phenyl)amine (TTPA) has been developed. When optimized, it displays a linear Nernstian response over the range of 1.0×10^{-7} - 1×10^{-2} M of Tm(III) ion, with a slope of 20.1 mV per decade and detection limit was 8.6×10^{-8} M. The effect of several parameters, such as: a) content of the ionophore in the membrane, b) kind of the plasticizer in the membrane, c) content of additive in the membrane, d) pH of the sample solution, e) response time of the sensor and f) potentiometric selectivity coefficient were investigated. The potentiometric selectivity coefficients of thulium sensor was evaluated using the matched potential method. The sensor displayed a good selectivity for thulium with respect to number of common foreign metal ions. In order to investigate the sensors analytical applicability, it was tested as an indicator electrode in potentiometric titration of thulium against EDTA and to the determination of fluoride ions in mouth wash samples.

Keywords: Sensor, PVC membrane, Ion selective electrode, Potentiometry.
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INTRODUCTION

Potentiometric ion sensors such as neutral-carrier-type ion-selective electrodes (ISEs) are very useful [1]. The ion-selectivities are generally determined by the ion-exchange equilibrium at the interface between the membrane and the aqueous sample phases, which is in turn the metal-ion extraction equilibrium between the two immiscible phases. They offer several advantages as small size, simplicity of operation and low cost per sample [2]. Electrochemical sensors have shown to be the most rapidly growing class of chemical sensors, in analytical chemistry. A chemical sensor is device that provides continuous information about some specific chemical

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properties of its environment. An ideal chemical sensor provides a certain type of response that is directly related to the quantity of a specific chemical species [3]. In the field of ion-selective electrode development, the formation of new electrodes and research into new ionophores are currently active areas. Additionally, miniaturization has been recognized for many years as an important area of research [4]. One important application of thulium, relatively independent of its high cost, is the use of a (0.1–0.2)-g pellet of the metal or oxide as a portable source of diagnostic X-radiation. ICP-MS and ICP-AES, spectrophotometry, and spectrofluorimetry, are the available methods for the low-level monitoring of thulium ions in solutions. These methods are either time consuming, involving multiple sample manipulations, or too expensive. There are only some reports in the literature concerning the design of highly selective ionophores for thulium [5-8]. Recently, we have reported a number of selective sensors based on different ion carriers containing nitrogen or sulfur, or both donating atoms, for some metal ions [9-30].

EXPERIMENTAL SECTION

Reagent grade oleic acid (OA), dibutyl phthalate (DBP), nitrobenzene (NB), *o*-nitrophenyloctyl ether (NPOE), acetophenone (AP), sodium tetraphenyl borate (NaTPB), tetrahydrofuran (THF) and high relative molecular weight poly(vinyl chloride) (PVC) were purchased from Merck chemical company and used as received. The nitrate and chloride salts of the cations used (from Merck or Aldrich) were of the highest purity available and used without any further purification except for vacuum drying over P_2O_5. Doubly distilled de-ionized water was used throughout.

The PVC membranes were prepared according to the following general procedure. The required amounts of the membrane ingredients (30 mg PVC, 55 mg NPOE, 1 mg NaTPB, 10 mg OA and 4 mg TTPA) 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 up to the point that an oily concentrated mixture was created. A Pyrex tube (3–5mmin top) was dipped into the oily mixture for about 10 s, so that a transparent film of about 0.3mm in thickness was formed [31–35]. The tube was then removed from the mixture and kept at the room temperature for about 12 h. Eventually, the tube was filled with the internal filling solution (1.0×10^{-3} M thulium chloride). The electrode was finally conditioned for 24 h by soaking in a ($1.0 \times 10{-2}$ M) solution of $TmCl_3$. A silver–silver chloride electrode was used as an internal reference electrode. The ionophore N-[(E)-1-(2-thienyl) methylidene]-N-(4-{[(Z)-1-(2-thienyl) methylidene] amino}phenyl) amine (TTPA) was synthesized in the usual manner by reaction of thiophene-2-carbaldehyde with diamine in a 2:1 molar ratio in methanol as follows. Thiophene-2-carbaldehyde (0.01 mol, 1.12 g) and diamine (0.005 mol, 0.54 g) were placed in 100 mL round-bottom flask equipped with a condenser and a magnetic bar. Methanol (50 mL) was then added to the mixture and the mixture was refluxed far 3 h while stirring, and then cooled to room temperature. The solid product was filtered, and the product was recrystallized from chloroform [36-38].

All emf measurements were carried out with the following assembly:
Ag–AgCl| 1.0×10^{-3} M $TmCl_3$ | PVC membrane: test solution| Hg–Hg2Cl2, KCl (satd).

A Corning ion analyser 250 pH/mV meter was used for the potential measurements at 298K. Activities were calculated according to the Debye–Huckel procedure.

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RESULTS AND DISCUSSION

The high Tm(III) ion extraction into the liquid membrane was a result of the elevated ionophore tendency to form a selective complex with the Tm(III) ions. Because the degree of sensitivity and selectivity for a certain ionophore is greatly related to the membrane ingredients, the membrane composition influence on the potential responses of the Tm(III) sensor was inspected [39-42]. In this study, different membrane compositions were tested. The membrane with the composition of 30% PVC, 4% TTPA, 1% NaTPB, 10% OA and 55% NPOE was the optimum one in the development of this sensor. This membrane composition was selected after many considerations. The pH dependence of the sensor potential response was tested and the potential response of the proposed sensor is pH independent in the range of 3.0–8.7.

The critical response characteristics of the recommended sensor were assessed according to the IUPAC recommendations [43]. The emf response of the polymeric membrane indicated a Nernstian slope of 20.1 ± 0.3 mV per decade across an extended thulium concentration range from 1.0×10^{-7} to 1.0×10^{-2} M. The detection limit, defined as the thulium concentration obtained when extrapolating the linear region of the calibration graph to the base line potential, was 8.6×10^{-8} M.

In this study, the practical response time was recorded by changing the Tm^{3+} concentration in solution, over a concentration range 1.0×10^{-7}-1.0×10^{-2} M. The results showed that in whole concentration range the electrode reaches its equilibrium response in a very short time (<10 s).

Table 1: Selectivity coefficients of various interfering ions

Interfering ion (B)	Selectivity coefficient ($K_{Tm, B}$)
La^{3+}	8.5×10^{-4}
Pr^{3+}	7.3×10^{-4}
Nd^{3+}	6.2×10^{-4}
Eu^{3+}	5.8×10^{-4}
Gd^{3+}	2.5×10^{-3}
Dy^{3+}	7.1×10^{-4}
Tb^{3+}	6.8×10^{-4}
Lu^{3+}	7.9×10^{-4}
Er^{3+}	3.2×10^{-3}
Sm^{3+}	8.7×10^{-4}
Yb^{3+}	7.3×10^{-4}
Ho^{3+}	3.7×10^{-3}
Cr^{3+}	4.6×10^{-4}
Fe^{3+}	3.5×10^{-4}
Na^{+}	2.1×10^{-3}
K^{+}	8.1×10^{-4}
Ca^{2+}	2.6×10^{-3}
Cd^{2+}	8.4×10^{-4}
Ni^{2+}	7.6×10^{-4}
Co^{2+}	1.0×10^{-4}
Pb^{2+}	6.5×10^{-3}

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Table 2: Comparison of selectivity coefficients ($K_{Tm^{3+},B}^{MPM}$), linearity range, detection limit, response time and slope of proposed Tm^{3+} sensor and the previously reported Tm^{3+} ion-selective electrodes.

Ion	Ref. 5	Ref. 6	Ref. 7	This work
Linearity rang (M)	1.0×10^{-6}- 1.0×10^{-2}	1.0×10^{-5}- 1.0×10^{-2}	1.0×10^{-6}- 1.0×10^{-2}	1.0×10^{-7}- 1.0×10^{-2}
Detection limit (M)	4.0×10^{-7}	8.0×10^{-6}	8.7×10^{-7}	8.6×10^{-8}
Response time (s)	15	7	~10	<10
Slope (mV/decade)	19.5	19.5	19.5	20.1
Lu^{3+}	1.2×10^{-2}	4.0×10^{-3}	7.3×10^{-3}	7.9×10^{-4}
Nd^{3+}	4.5×10^{-3}	2.0×10^{-2}	2.3×10^{-4}	6.2×10^{-4}
Eu^{3+}	-	-	5.6×10^{-3}	5.8×10^{-4}
Er^{3+}	1.4×10^{-2}	2.0×10^{-2}	4.5×10^{-3}	3.2×10^{-3}
Dy^{3+}	1.6×10^{-3}	-	4.3×10^{-3}	7.1×10^{-4}
Gd^{3+}	3.7×10^{-3}	5.2×10^{-3}	5.7×10^{-3}	2.5×10^{-3}
La^{3+}	7.6×10^{-4}	-	3.6×10^{-4}	8.5×10^{-4}
Tb^{3+}	-	-	5.8×10^{-3}	6.8×10^{-4}
Sm^{3+}	-	2.0×10^{-3}	3.2×10^{-4}	8.7×10^{-4}
Ho^{3+}	-	3.1×10^{-2}	5.5×10^{-3}	3.7×10^{-3}
Yb^{3+}	1.0×10^{-2}	3.0×10^{-3}	6.7×10^{-3}	7.3×10^{-4}
Pr^{3+}	1.0×10^{-2}	7.0×10^{-3}	4.3×10^{-3}	7.3×10^{-4}
Fe^{3+}	-	-	5.6×10^{-3}	3.5×10^{-4}
Cr^{3+}	-	-	6.7×10^{-3}	4.6×10^{-4}
Ni^{2+}	-	-	6.8×10^{-4}	7.6×10^{-4}
Cd^{2+}	1.2×10^{-3}	4.0×10^{-3}	8.1×10^{-4}	8.4×10^{-4}
Co^{2+}	7.5×10^{-4}	-	8.2×10^{-4}	1.0×10^{-4}
Pb^{2+}	1.2×10^{-2}	7.0×10^{-3}	3.4×10^{-4}	6.5×10^{-3}
Ca^{2+}	8.9×10^{-4}	2.0×10^{-2}	7.6×10^{-4}	2.6×10^{-3}
Na^{+}	3.8×10^{-4}	-	8.3×10^{-4}	2.1×10^{-3}
K^{+}	1.7×10^{-3}	2.0×10^{-3}	-	8.1×10^{-4}

The Selectivity is an important characteristic of a sensor that delineates the extent to which the device may be used in the estimation of analyte ion in the presence of other ions and extent of utility of any sensor in real sample measurement. In this work, the selectivity coefficients of the sensor toward different metal ions (B) were evaluated by using the matched potential method (MPM) [44-47]. According to the MPM, the selectivity coefficient is defined as the activity (concentration) ratio of the primary ion and the interfering ion, which gives the same potential change in a reference solution. Subsequently, the potential change should be measured upon changing the primary ion activity. Then, the interfering ion would be added to an identical reference solution until the same potential change would be obtained. The MPM selectivity coefficient, K^{MPM}, is then given by the resulting primary ion to the interfering ion activity (concentration) ratio, $K^{MPM} = a_A/a_B$. The resulting values are listed in Table 1. Clearly, the selectivity coefficients for mono and divalent metal ions (Na^{+}, K^{+}, Ca^{2+}, Co^{2+}, Cd^{2+}, Ni^{2+} and Pb^{2+}) are about or less than 6.5×10^{-3}. For the trivalent ions (La^{3+}, Pr^{3+}, Nd^{3+}, Eu^{3+}, Gd^{3+}, Dy^{3+}, Tb^{3+}, Lu^{3+}, Er^{3+}, Sm^{3+}, Yb^{3+}, Ho^{3+}, Cr^{3+} and Fe^{3+}), the selectivity coefficients are in the range of 3.7×10^{-3} or smaller, indicating they would not radically disturb the function of the developed Tm^{3+} membrane sensor. Table 2 compares the selectivity coefficient values, the linear range, the detection limit, the response time and the slope of the Tm^{3+} sensor with those of the best Tm^{3+}

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electrodes previously reported in the literature by other researchers [5-7]. Table 2 reveals that the proposed sensor is superior to the formerly published Tm^{3+} sensor.

The proposed membrane electrode was used as an indicator electrode in the potentiometric titration of a 1.0×10^{-4} M Tm^{3+} ion solution with a standard 1.0×10^{-2} M of EDTA. The resulting titration curve is shown in Figure 1. As seen, the sensor is capable of monitoring of the amount of Tm^{3+} ions.

The membrane sensor was also used for the fluoride ion determination 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 Tm^{3+} solution (1.0×10^{-3} M) and the results of triplicate measurements are summarized in Table 3. It is clear that there is a satisfactory agreement between the declared fluoride content and the values determined by the proposed electrode.

Table 3: Determination of fluoride ions in mouth wash solutions

Sample	Labeled (ppm)	Found ISE[a] (ppm)
Sodium fluoride mouth wash solution (Aquafresh, Brentford, U.K.)	1350	$(1383^{b} \pm 22)$
Sodium fluoride mouth wash solution (Eurodont, DuroDont GmbH)	1450	$(1485^{b} \pm 17)$

a. Proposed Tm^{3+} sensor
b. Results are based on three measurements
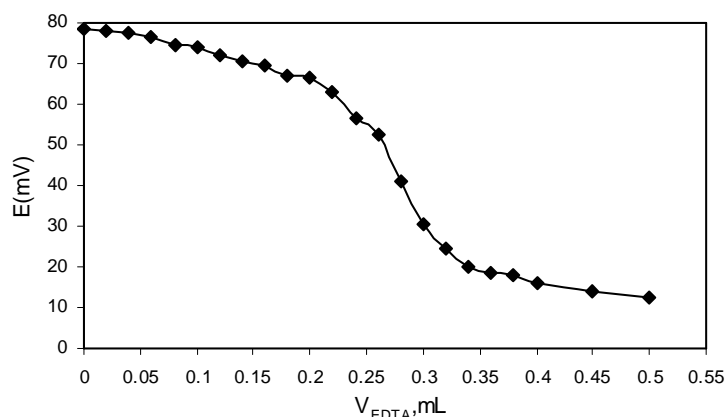
Figure 1. Potential titration curve of 25.0 mL from a 1.0×10^{-4} M Tm^{3+} solution with 1.0×10^{-2} M of EDTA.

Acknowledgements

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