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1,1'-(1,4-butanediyl)bis(imidazole) as a Sensing Material for Fabrication of Tm^{3+}-PVC Membrane Sensor

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A novel thulium(III) membrane sensor showing a Nernstian response of 20.4±0.3 mV per decade of thulium concentration in the concentration and pH ranges of 1.0×10^{-6} to 1.0×10^{-2} mol L^{-1} and 3.4-8.6 respectively is prepared based on the incorporation of 1,1'-(1,4-butanediyl)bis(imidazole) (BYI) into a polymeric membrane sensor. The sensor had a satisfactory selectivity behavior with respect to alkaline, alkaline earth, transition and heavy metal ions and was successfully used in the determination of the fluoride ion in two mouth wash preparations.

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

1. INTRODUCTION

Thulium in metallic or oxide forms is used in portable sources of diagnostic X-ray devices and the element can also be used as a dopant in tunable fiber lasers [1].

The techniques used for the analysis of Tm(III) are either time consuming or bear costs and involve multiple sample manipulations that are difficult to perform in snail laboratories. Alternatively the successful application of ion selective electrodes in the different fields including environmental, agricultural, and medical attracted a lot of attention on the side of analytical chemists to develop novel sensing devices for other species of desire. This interest lends itself to the advantages of such devices offering inexpensive and convenient analysis methods for ions in solution phase. Our literature survey revealed that there are some reports on thulium(III) sensors [2-6] and hence based on the experience of our team in the development of several highly selective and sensitive PVC-membrane ion-selective electrodes for some ions has been reported [7-20] we decided to test the application of ,1'-(1,4-

butanediyl)bis(imidazole) (BYI) (Figure 1) as a new ionophore for the development of a new Tm(III) selective electrode.

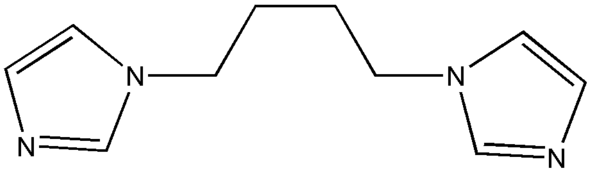

Figure 1. Chemical structure of BYI.

2. EXPERIMENTAL

2.1. Materials and reagents

The chemicals of analytical reagent grade were purchased from Merck Co. (dibutylphthalate (DBP), nitrobenzene (NB), the chloride and nitrate salts of the used cations and acetophenon (AP)), Aldrich Co. (chloride and nitrate salts of the used cations) and Fluka Co (high-molecular weight polyvinylchloride and benzyl acetate (BA)). The chloride and nitrate salts of the used cations were also purchased from Merck and Aldrich and were of the highest purity available and were used without any further treatments. All solutions were prepared using doubly distilled deionized water.

2.2. The synthesis of BYI

A mixture of imidazole (50 mmol, 3.4g) and sodium hydroxide (50mmol, 2g) in DMSO (10 mL) was stirred for 1h at 60 °C. Then 1,4-dichlorobutane (25 mmol, 3.2 g) was added to the mixture. After two hours stirring, it cooled down to room temperature and then 200 mL distilled water was added to it. After 24 h, the resulted white puffy soft solid is isolated by filtration. This compound is characterized by FT-IR, ^{1}HNMR and ^{13}CNMR and UV-Visible spectroscopic techniques. m.p.; 82-84 °C. Yield: 86%.

2.3. Preparation of the ISEs

The membranes were prepared through the general method of mixing the desired amount of powdered PVC, and the plasticizer in 5 mL of THF and then adding of the ionic additive (NaTPB) and the ionophore BYI. The resulting solution was then transferred into a glass dish of 2 cm in diameter and was let to rest so that the THF content of the mixture was evaporated and an oily concentrated mixture was obtained. Finally a Pyrex tube, meant to support the membrane, (3–5 mm o.d.) was then insterted into the oily mixture so that a transparent membrane was formed on its tip [21-28] and was then removed from the solution and stored at room temperature for about 12 hours before the tube was filled with an internal solution (1.0×10^{-3} mol L^{-1} $TmCl_3$) and the polymeric membrane was conditioned for 24 h by soaking in a 1.0×10^{-3} mol L^{-1} $TmCl_3$ solution. A silver/silver chloride coated wire was used as the internal reference electrode and the emf readings were carried out with the following cell assembly:

Ag–AgCl | internal solution, 1.0×10^{-3} mol L^{-1} $TmCl_3$ | PVC membrane | test solution | Hg–Hg_2Cl_2, KC1 (satd.)

Using a Corning ion analyzer 250 pH/mV meter at 25.0 ^{0}C.

The activities of the ions tested were calculated according to the Debye–Huckel procedure [29].

3. RESULTS AND DISCUSSION

The capability of BYI to be used as an ionophore was initially assessed by preparing PVC membrane sensors for a group of alkali, alkaline earth, transition and heavy metal ions as shown in Table 1. The results revealed that the membrane all of which contained 1mg of BYI, 67 mg of NB, 2 mg of NaTPB and 30 mg of PVC to have a rather sensitive response of 17.4±0.5 mV/decade of Tm^{3+} concentration for Tm(III) ions while they did not have any sensitivity for the other ions tested. This could roughly show that BYI could be used as an ionophore for the construction of ISEs for Tm(III) ions.

Table 1. Optimization of the membrane ingredients.

No.	Composition (wt %)					Slope (mV/decade)
	PVC	Plasticizer	BYI	NaTPB	Linear range (mol L^{-1})	
1	30	NB, 67	2	0	1.0×10^{-2}-1.0×10^{-4}	13.8±0.4
2	30	NB, 66	2	1	1.0×10^{-2}-1.0×10^{-5}	17.7±0.4
3	30	NB, 65	2	2	1.0×10^{-2}-1.0×10^{-6}	20.4±0.3
4	30	NB, 64	2	3	1.0×10^{-2}-1.0×10^{-5}	18.5±0.2
5	30	NB, 65	1	2	1.0×10^{-2}-1.0×10^{-5}	17.4±0.5
6	30	NB, 65	3	2	1.0×10^{-2}-1.0×10^{-6}	18.6±0.2
7	30	AP, 65	2	2	1.0×10^{-2}-1.0×10^{-6}	18.2±0.5
8	30	DBP, 66	2	2	1.0×10^{-2}-1.0×10^{-6}	17.3±0.2
9	30	BA, 67	2	2	1.0×10^{-2}-1.0×10^{-6}	15.6±0.4

Given that the sensitivity and selectivity behavior of polymeric membrane sensors are greatly influence by the membrane composition [30-34], different membrane compositions, as summarized in Table 1 were prepared and their characteristics were evaluated. The results showed that membranes with a composition of 30% PVC, 2% BYI, 2% NaTPB and 66 % NB (no. 3) had an optimum response.

The results also proved that among the four solvent mediators NB, AP, BA and DBP, NB which further tested NB was the best plasticizer.

Also studies on the modifying effect of the ionic additiv [34-39] showed that NaTPB had the best effect in amounts of 2% wt and led to the best responses.

3.1. Evaluation of the sensor

The response behavior of the BYI-based with the optimum composition was evaluated, after conditioning the ISEs for different time periods in a 0.01 mol L^{-1} thulium chloride solution. A Nernstian slope of 20.4±0.3 mV per decade of T(III) concentration (Figure 2) was observed in a thulium concentration range of 1.0×10^{-6} to 1.0×10^{-2} mol L^{-1} and the detection limit sensor was found to be as low as 6.4×10^{-7} mol L^{-1}.

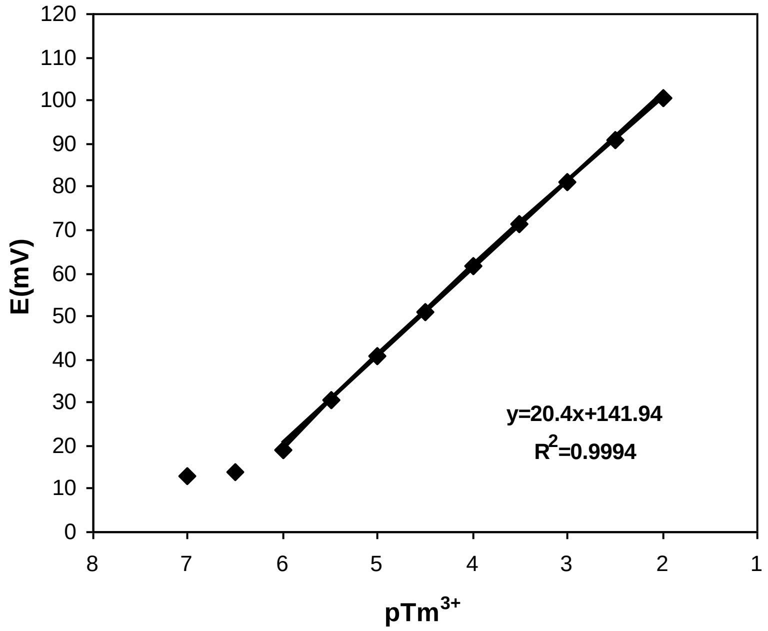

Figure 2. Calibration curves of the BYI-based Tm^{3+} electrode.

The lifetime of the electrode was also studied through a series of daily measurements for some 10 weeks, using one of the electrodes. During this period the electrode was used for 1 h each day and washed and dried. The lifetime was found to be about 2 months, during which the electrode slope displayed only slightly changed from 20.4 to 18.3 mV per decade.

The effect of the pH of the test-solution on the potential response of the ISEs was also studied through monitoring the potential response of the electrode in a Tm^{3+} solution (1.0×10^{-3} mol L^{-1}) up varying the pH in the range of 2.0 to 10.0 (Figure 3). The response of the electrode was constant in the range of 3.4 to 8.6. This could be attributed to the formation of insoluble $Tm(OH)_3$ higher and the sensor response protonium ions at lower pH values.

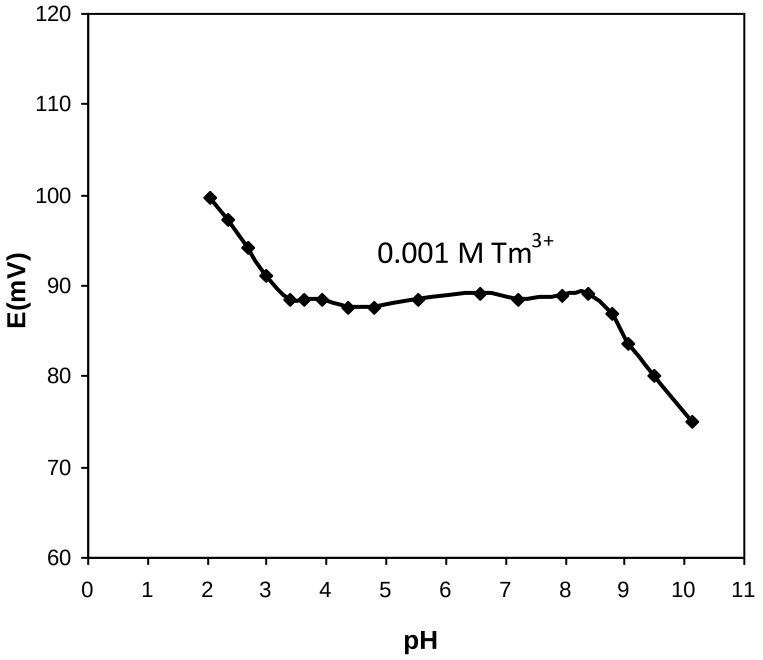

Figure 3. pH effect of the test solution (1.0×10^{-3} mol L^{-1} of Tm^{3+}) on the potential response of the thulium ion-selective electrode.

The dynamic response time of the sensor was also studied by varying the concentrations of the test solutions of 1.0×10^{-6} to 1.0×10^{-2} mol L^{-1}. The results (Figure 4) showed that the average response time did not exceed 10 s.

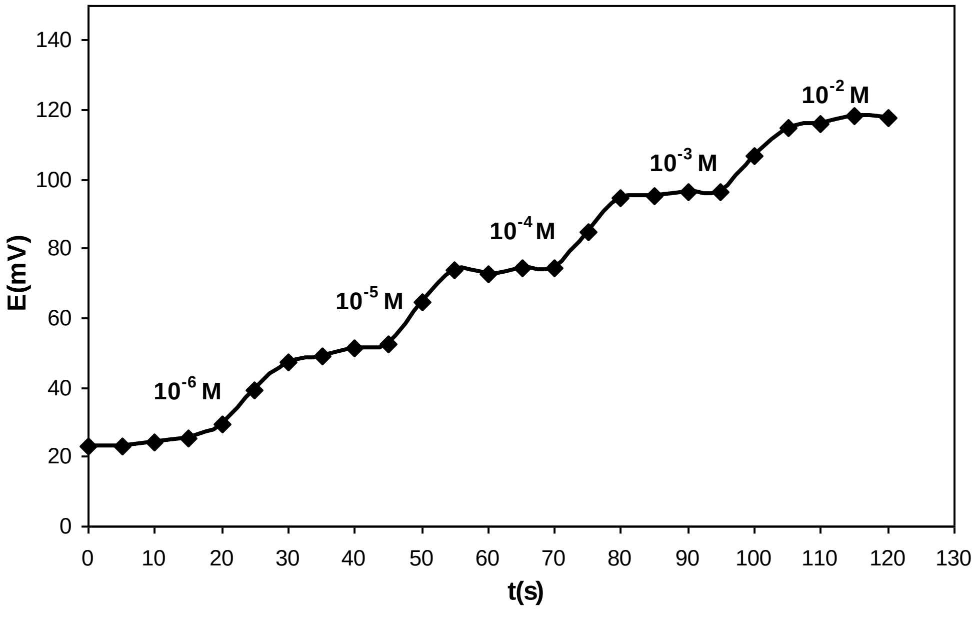

Figure 4. Dynamic response time of the thulium electrode for step changes in the Tm^{3+} concentration.

3.2. Selectivity behavior

Being the most important property of potentiometric sensors, the selectivity of the sensor were evaluated through the matched potential method (MPM) [40-42] and the results are given in Table 2. One can simply conclude that the Tm^{3+} sensor is highly selective with respect to most tested cations. In the case of trivalent ions the selectivity coefficients do not exceed 4.3×10^{-3} indicating that lanthanide ions cannot considerably disturb the measurement of Tm(III) ions. The selectivity coefficients for all mono and divalent metal ions (Na^{+}, K^{+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Zn^{2+} and Pb^{2+}) were also found to be smaller than 4.5×10^{-4}. The selectivity of the ISE most probably originates from the strong tendency of 1,1'-(1,4-butanediyl)bis(imidazole) (BYI) to complex with Tm(III) ions.

Table 2. Selectivity coefficients ($K^{MPM}_{Tm^{3+},B}$) of proposed Tm^{3+} sensor.

Ion	K_{MPM}
Eu^{3+}	8.2×10^{-4}
Pr^{3+}	8.9×10^{-4}
Tb^{3+}	3.2×10^{-3}
Sm^{3+}	3.5×10^{-3}
Ho^{3+}	4.3×10^{-3}
Ca^{2+}	2.8×10^{-3}
Na^{+}	7.4×10^{-4}
K^{+}	7.8×10^{-4}
Pb^{2+}	3.6×10^{-3}
Zn^{2+}	1.0×10^{-3}
Co^{2+}	2.4×10^{-3}
Cd^{2+}	4.5×10^{-3}

Table 3. Comparison of previously reported Tm^{3+} sensor with the proposed sensor.

Ion	Ref. 2	Ref. 3	Ref. 4	Ref.5	Ref. 6	This work
Linearity rang ($molL^{-1}$)	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^{-6}-1.0×10^{-2}	1.0×10^{-6}-1.0×10^{-2}	1.0×10^{-6}-1.0×10^{-2}
Detection limit ($molL^{-1}$)	4.0×10^{-7}	8.0×10^{-6}	8.7×10^{-7}	6.8×10^{-7}	7.2×10^{-7}	6.4×10^{-7}
Response time (s)	15	7	~10	<10	<10	<10
Slope (mV $decade^{-1}$)	19.5	19.5	19.5	19.6	19.6	20.4
$K^{MPM}>10^{-2}$	Er, Lu, Yb, Pb	Er, Nd, Ho, Mg	Lu,Yb	-	-	-

Table 3 offers a comparison between the parameters of previously reported thulium ion selective sensor [2-6] with those of the proposed one, proving the it has improved properties in terms of selectivity coefficient and detection limit.

3.3.Analytical application

To prove that the sensor can be used in real-time applications potentiometric titrations were performed by using sensor with the optimum compositions as an indicator electrode for the titration of 25 mL of 10^{-4} mol L^{-1} Tm^{3+} ions 10^{-2} mol L^{-1} EDTA. As it is seen in the titration curve is shown in Figure 5 the sensor can monitor the amount of thulium ions.

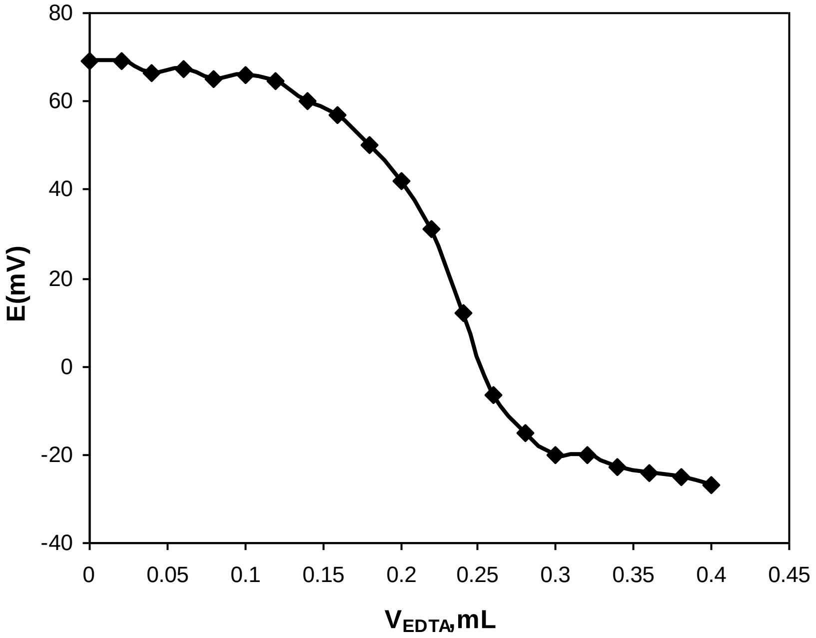

Figure 5. Potential titration curves of 25.0 mL 1.0×10^{-4} mol L^{-1} Tm^{3+} solution with 1.0×10^{-2} mol L^{-1} of EDTA.

Table 4. Determination of fluoride ions in mouth wash solutions

Sample	Labeled (mg L^{-1})	Found ISE[a] (mg L^{-1})
Sodium fluoride mouth wash solution (Aquafresh, Brentford, U.K.)	1350	(1383[b]±21)
Sodium fluoride mouth wash solution (Eurodont, DuroDont GmbH)	1450	(1477[b]±22)

a. Proposed Tm^{3+} sensor

b. Results are based on three measurements

The optimized membrane sensor (membrane no. 3) was also used for the determination of fluoride ion in two mouth wash samples. According to the method 1.0 g of each sample was taken and diluted with distilled water in a 100 mL flask and then titrated with a Tm(III) solution. The results of triplicate measurements are summarized in Table 4. Due to the formation of the complex between fluoride ion and thulium ion, the fluoride content of samples can be measured indirectly by using the proposed electrode.

4. CONCLUSION

The ion-selective sensor constructed based on 1,1'-(1,4-butanediyl)bis(imidazole) (BYI) showed good characteristics in terms of its linear concentration range of 1.0×10^{-6} to 1.0×10^{-2} mol L^{-1}, with good detection limit, and selectivity coefficients. The sensor had a short response time of <10 s, a lower detection limit of 6.4×10^{-7} mol L^{-1} and its response was pH independent across the range of 3.4–8.6. Its response towards the Tm(III) concentration was found not to be seriously influenced by the presence of the common alkali, alkaline earth, or transition and heavy metal ions.

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