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Fabrication of a PVC-Membrane Electrochemical Sensor Based on 4-(3-Nitrophenyl)-2,6-di-2-thienylpyridine as a Sensing Material for Determination of Thulium(III) Ions

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A new poly(vinyl chloride) (PVC)-based membrane sensor for thulium ions was prepared by employing on 4-(3-Nitrophenyl)-2,6-di-2-thienylpyridine (PTP) as an ionophore, sodium tetraphenyl borate (NaTPB) as an anion excluder, and nitrobenzene (NB) as plasticizing solvent mediator and investigated as a selective membrane sensor. The sensor responds to Tm^{3+} activity in a linear dynamic range of 1.0×10^{-7} to 1.0×10^{-2} mol L^{-1} with a Nernstian slope of 20.8±0.4 mV per decade and a detection limit of 8.0×10^{-8} mol L^{-1} at a pH range of 2.4–9.4. The electrode displays a fast response time (<10 s), and can be used for at least 2 months without any considerable divergences in the potentials. The Tm^{3+} membrane sensor revealed comparatively good selectivity with respect to common alkaline, alkaline earth, transition and heavy metal ions, and especially lanthanide ions. It was used as an indicator electrode in the potentiometric titration of Tm^{3+} ions with EDTA. The constructed sensor accuracy was investigated by the monitoring of Tm^{3+} ions in the mixtures of two and three different metal ions.

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

1. INTRODUCTION

Thulium, one of the lanthanide members, has found many applications such as using as a portable source of diagnostic X-radiation, as dopant in tunable fiber lasers, and as emitting materials in electroluminescence devices. This element can also be used as a dopant in tunable fiber lasers [1,2]. The element is never found in the nature in pure form but it is found in small quantities in minerals with other rare earths [3]. 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 thulium ions in solutions [4-6]. These available methods are either time consuming, involving multiple sample manipulations, or too expensive for most analytical laboratories and also the analyte is destroyed during the analysis.

Ion selective electrodes are used widely in analysis of a wide variety of ions [7-24] because of some advantages such as portability, simplicity, fast, inexpensive, and reliable response in a wide concentration range in comparison with new electrochemical methods [25]. On the other hand, potentiometric sensors offer inexpensive and convenient method for the analysis of lanthanide ions as well as a number of cations and anions, with acceptable sensitivity and selectivity. Also, they can measurement the analyte without destroying it. Lately, our team and other researchers have recently introduced a number of PVC-membrane ion-selective membrane sensors for some ions based on different noncyclical and macro cyclic ionophores [26–36]. In spite of successful progress in the design of highly selective ionophores for various metal ions, there are only a limited number of reports on the development of selective ionophores for thulium [37–41]. The aim of this research is the fabrication of a greatly selective and sensitive Tm^{3+} membrane sensor, based on 4-(3-Nitrophenyl)-2,6-di-2-thienylpyridine (PTP) (Fig. 1) as a suitable ionophore for the potentiometric measurement of the Tm^{3+} ion amounts for a certain concentration range.

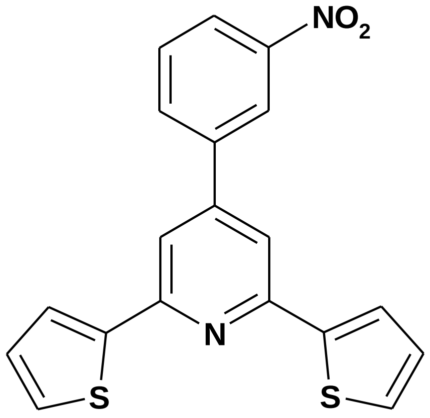

Figure 1. The PTP chemical structure.

2. EXPERIMENTAL

2.1. Reagents

The Merck and the Aldrich Chemical Co. were the providers of the following reagent. grades: benzyl acetate (BA), nitrobenzene (NB), dibutyl phthalate (DBP), acetophenone (AP), oleic acid (OA), high relative molecular weight PVC, sodium tetraphenyl borate (NaTPB) and tetrahydrofurane (THF). Chloride and nitrate salts of the cations used (from Merck and Aldrich) were of the highest purity available and used without any further purification except for vacuum drying over P_2O_5. The ligand 4-(3-Nitrophenyl)-2,6-di-2-thienylpyridine (PTP) (Fig. 1) was synthesized as described elsewhere [42]. Doubly distilled de-ionized water was used throughout.

2.2. The preparation of membrane

The PVC membranes was prepared by mixing 4 mg PTP ionophore, 2 mg NaTPB, 59 mg NB and 30 mg PVC and dissolving in 3 mL THF. The resulting homogeneous mixture was transferred into a glass dish of 2 cm diameter. A Pyrex tube (5 mm o.d.) was dipped into the mixture for about 5 s, so that a transparent membrane of about 0.3 mm thickness was formed [43-52]. The tube was then pulled out from the mixture and kept at room temperature for at least 12 h. The tube was then filled with internal filling solution (1.0×10^{-3} mol L^{-1} $TmCl_3$). The electrode was finally conditioned for 72 h by soaking in a 1.0×10^{-3} mol L^{-1} $TmCl_3$ solution. A silver/silver chloride electrode was used as an internal reference electrode.

2.3. The emf measurements

All electromotive force (emf) measurements were carried out with the following cell assembly:

Ag–AgCl | internal solution, 1.0×10^{-3} M $TmCl_3$ | 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 [53].

3. RESULTS AND DISCISSION

In order to evaluate PTP as an ionophore it was initially used to prepare PVC membrane sensors for a wide variety of alkali, alkaline earth, transition and heavy metal ions (Table 1) and the results showed that the membrane, which contained 4 mg of PTP, 64 mg of NB, 2 mg of NaTPB and 30 mg of PVC had a rather sensitive response of 20.8±0.3 mV/decade of Tm^{3+} concentration while no sensitive response for the other ions tested.

3.1. The membrane composition influence

The sensitivity and selectivity of an ion-selective electrode resulted from membrane ingredients, nature of solvent mediators and the additives used [54-57]. The influences of the membrane composition, the nature and amount of plasticizer, the plasticizer/PVC ratio, and the amount of NaTPB as lipophilic additives on the potential response of the proposed Tm(III) sensor were therefore investigated, and the results are given in Table 1. The data in Table 1, revealed that the membrane prepared with a plasticizer/PVC ratio about 2.2 was suitable, and shows the best performance. From Table 1, it is evident that the increase of the PTP amount in the membranes (No.9 and 14) up to 4% resulted in greater slopes. A maximum slope of 20.8±0.3 mVdecade^{-1} of Tm(III) concentration was observed for the membrane No.14 with 4% of PTP. As can be see from Table 1, the optimum amount of ionophore (PTP) was 4% (No.14). Table 1 also shows that among the four different plasticizers used (BA, NB, AP, and DBP), NB with a higher polarity than BA, AP and DBP is a suitable solvent mediator in preparing the Tm^{3+} ion-selective electrode and revealed the best selectivity. This is most probably due to the facilitated extraction of Tm^{3+} with high charge density from aqueous solution to the membrane phase by using polar solvent mediator.

Lipophilic anions in the composition of cationic-selective membrane sensors not only diminishes the ohmic resistance and enhances the potential behavior and selectivity, but also in poor extraction capacities, increases the sensitivity of the membrane electrodes [58–63]. In line with Table 1, the presence of additives would improve the Tm(III) sensor sensitivity considerably (no. 14 with a slope of 20.8 mVdecade^{-1}). However, in this study addition of 4% PTP (membranes no. 14) will increase the sensitivity of the electrode response to a great extent. As it can be seen from Table 1, the membrane with the composition of 30% PVC, 4% PTP, 2% NaTPB and 64% NB (no. 14) was selected as the optimum one in the development of this sensor.

Table 1. Optimization of the membrane ingredients.

Sensor No.	Composition (wt %)					
	PVC	Plasticizer	Additive	PTP	Slope (mV decade^{-1})	Concentration range (molL^{-1})
1	30	NB, 66	NaTPB,2;OA,0	2	1.0×10^{-6}-1.0×10^{-3}	20.9 ± 0.4
2	30	AP, 66	NaTPB,2;OA,0	2	1.0×10^{-6}-1.0×10^{-3}	20.3 ± 0.3
3	30	DBP, 66	NaTPB,2;OA,0	2	1.0×10^{-6}-1.0×10^{-3}	17.4 ± 0.2
4	30	BA, 66	NaTPB,2;OA,0	2	1.0×10^{-6}-1.0×10^{-3}	19.0 ± 0.3
5	30	NB, 61	NaTPB,2;OA,5	2	1.0×10^{-6}-1.0×10^{-3}	20.1 ± 0.4
6	30	NB, 56	NaTPB,2;OA,10	2	1.0×10^{-6}-1.0×10^{-3}	24.2 ± 0.5
7	30	NB, 51	NaTPB,2;OA,15	2	1.0×10^{-6}-1.0×10^{-3}	21.4 ± 0.3
8	30	NB, 65	NaTPB,0;OA,0	5	1.0×10^{-6}-1.0×10^{-2}	23.2 ± 0.8
9	30	NB, 65	NaTPB,1;OA,0	4	1.0×10^{-6}-1.0×10^{-2}	22.9 ± 0.2
10	30	NB, 65	NaTPB,2;OA,0	3	1.0×10^{-6}-1.0×10^{-3}	21.0 ± 0.2
11	30	NB, 65	NaTPB,3;OA,0	2	1.0×10^{-6}-1.0×10^{-3}	20.1 ± 0.5
12	30	NB, 65	NaTPB,4;OA,0	1	1.0×10^{-7}-1.0×10^{-3}	24.8 ± 0.2
13	30	NB, 65	NaTPB,5;OA,0	0	1.0×10^{-6}-1.0×10^{-3}	15.5 ± 0.6
14	30	NB, 64	NaTPB,2;OA,0	4	1.0×10^{-7}-1.0×10^{-2}	20.8 ± 0.3

3.2. The calibration curve of Tm^{3+} sensor

The electrode showed a linear response to the activity of Tm^{3+} ions in the range of 1.0×10^{-7} to 1.0×10^{-2} mol L^{-1} (Fig. 2). The slope of the calibration graph was 20.8±0.3 mVdecade^{-1}. The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration graph, was 8.0×10^{-8} mol L^{-1}. The membrane electrode could be used at least for 2 months without any measurable divergence.

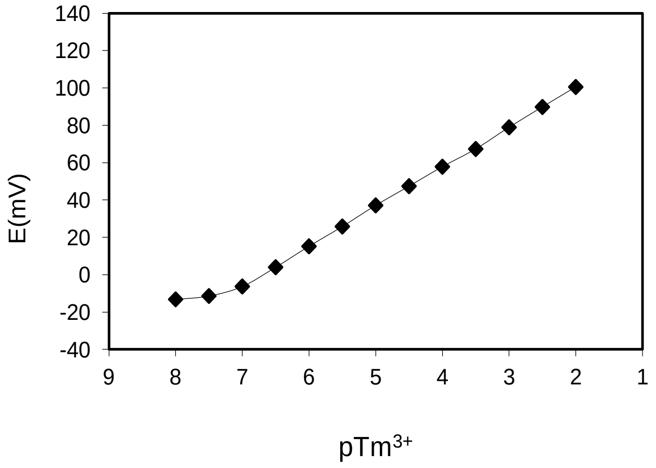

Figure 2. Calibration curves of the PTP-based Tm^{3+} sensor.

3.3. The pH effect

The influence of pH of the test solution on the potential response of the membrane sensor was tested in the pH range of 1.0–12.0 using concentrated NaOH or HCl and the results are shown in Fig. 3. As can be seen, the potential remained constant in a pH range of 2.4–9.4, beyond which the potential changed considerably. The observed drift at higher pH values could be due to the formation of some hydroxyl complexes of Tm^{3+} ions in solution. The observed potential increase at lower pH values less than 2.4 (1.0-2.4) the sensor responds to H_3O^+ ions with sub-Nerstian slope .

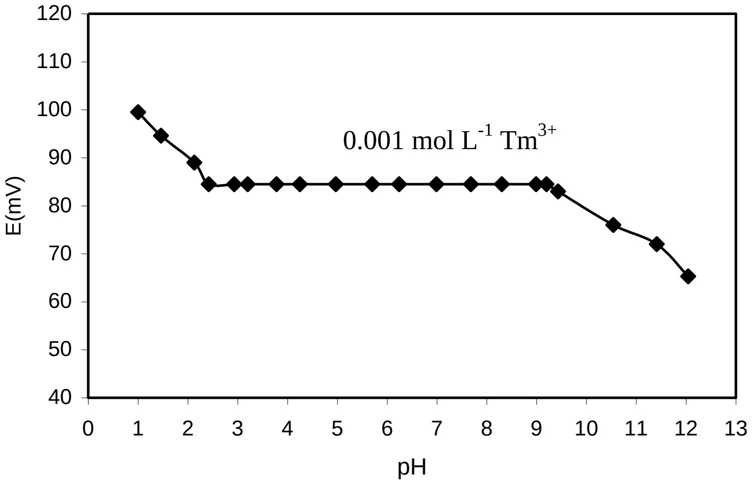

Figure 3. pH effect of the test solution $(1.0\times10^{-3}$ mol L^{-1} of $Tm^{3+})$ of the Tm^{3+}sensor based on PTP.

3.4. Dynamic response time

The average time required for the Tm^{3+} sensor to reach a potential within ~1mV of the final equilibrium value after successive immersion of a series of Tm^{3+} ion solutions, each having a 10-fold difference in concentration $(1.0\times10^{-7}$ to 1.0×10^{-2} mol $L^{-1})$, was measured. The response time of the membrane electrode thus obtained was <10 s over the entire concentration range (Fig. 4).

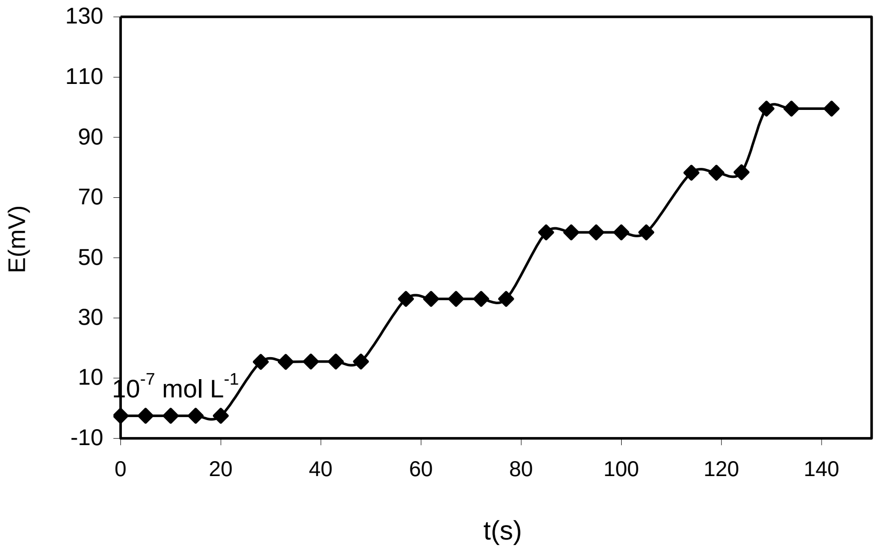

Figure 4. Dynamic response time of Tm^{3+} sensor based on PTP.

3.5. Selectivity coefficient

For the selectivity coefficient measurements, the matched potential method was used. According to the MPM [64-66], 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.

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

Interfering ions	$K^{MPM}_{Tm,B}$	Interfering ions	$K^{MPM}_{Tm,B}$
Lu^{3+}	2.5×10^{-3}	Ca^{2+}	8.0×10^{-4}
Pr^{3+}	8.3×10^{-4}	Mg^{2+}	5.5×10^{-4}
Nd^{3+}	6.3×10^{-4}	Na^{+}	4.8×10^{-4}
Eu^{3+}	6.7×10^{-4}	K^{+}	5.6×10^{-4}
Gd^{3+}	8.3×10^{-4}	Ni^{2+}	4.2×10^{-3}
La^{3+}	6.0×10^{-4}	Cd^{2+}	7.2×10^{-4}
Ho^{3+}	5.8×10^{-4}	Co^{2+}	2.2×10^{-3}
Cr^{3+}	6.5×10^{-4}	Pb^{2+}	2.8×10^{-3}
Fe^{3+}	8.5×10^{-4}		

Thus, 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 matched potential method selectivity coefficient, K^{MPM}, is then given by the resulting primary ion to the interfering ion activity (concentration) ratio, $K^{\mathrm{MPM}}=a_A/a_B$. 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 Tm(III) ion detection in the presence of certain interfering ions.

Table 3 summarizes and compares the linearity range, slope, response time, detection limit and selectivity coefficient values of the presented sensor with those of the best previously Tm^{3+} electrodes, reported in the literature by other researchers [37–41]. It becomes apparent that the newly developed sensor is superior to the formerly reported Tm^{3+} sensors in terms of selectivity, response time, detection limit and dynamic concentration range.

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

Ion	Ref. 37	Ref. 38	Ref. 39	Ref.40	Ref. 41	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^{-7}-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}	8.0×10^{-8}
Response time (s)	15	7	~10	<10	<10	<10
Slope (mV decade^{-1})	19.5	19.5	19.5	19.6	19.6	20.8
$K^{MPM}>10^{-2}$	Er, Lu, Yb, Pb	Er, Nd, Ho, Mg	Lu,Yb	-	-	-

3.6. Analytical application

The selective Tm(III) membrane sensor was used as an indicator electrode in the titration of 1.0×10^{-4} mol L^{-1} thulium ion solution with a standard 1.0×10^{-2} mol L^{-1} EDTA. EDTA is used as a good chelating agent due to its ability to complex with metal ions mostly with trivalent ions. The resulting titration curve is shown in Fig. 5. According to this figure, the sensor is capable to monitor the amount of thulium ions in the solutions.

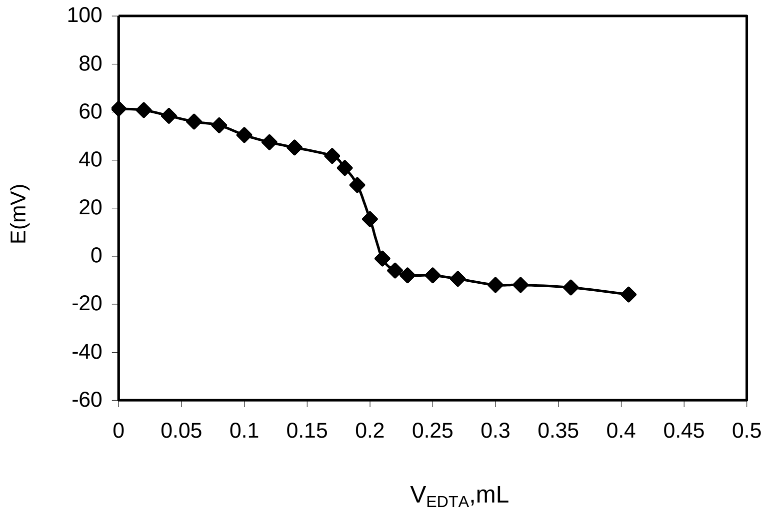

Figure 5. Potential titration curves of 20.0 mL 1.0 × 10^{-4} mol L^{-1} Tm^{3+} solution with 1.0 × 10^{-2} mol L^{-1} of EDTA.

Because of the selectivity and low detection limit of the developed Tm^{3+} sensor, it was also used to the direct determination of thulium concentration in mixtures of two and three different ions. The corresponding results in Table 4 reveal that the Tm^{3+} ions recovery in all mixtures is satisfactory.

Table 4. Determination of Tm^{3+} ion in presence of metal ions mixture.

Tm^{3+} (mol L^{-1})	Added cations (mol L^{-1})	Found[a] (mol L^{-1})	Recovery (%)
5.0×10^{-5}	Gd&Pr, 5.0×10^{-3}	$(4.69 \pm 0.04) \times 10^{-5}$	93.7
5.0×10^{-5}	Eu&Er, 5.0×10^{-3}	$(5.07 \pm 0.05) \times 10^{-5}$	101.4
5.0×10^{-5}	La&Ce, 5.0×10^{-3}	$(4.88 \pm 0.03) \times 10^{-5}$	97.6
5.0×10^{-5}	Dy&Yb, 5.0×10^{-3}	$(5.06 \pm 0.04) \times 10^{-5}$	101.2
5.0×10^{-5}	Lu&Nd, 5.0×10^{-3}	$(5.08 \pm 0.06) \times 10^{-5}$	101.6
5.0×10^{-5}	Cr&Fe, 5.0×10^{-3}	$(4.85 \pm 0.03) \times 10^{-5}$	97.0
5.0×10^{-5}	Na&Ca, 5.0×10^{-3}	$(4.74 \pm 0.05) \times 10^{-5}$	94.8
5.0×10^{-5}	Pb&Ni, 5.0×10^{-3}	$(4.79 \pm 0.06) \times 10^{-5}$	95.8
5.0×10^{-5}	K&Mg, 5.0×10^{-3}	$(5.08 \pm 0.05) \times 10^{-5}$	101.6
5.0×10^{-5}	Co&Cd, 5.0×10^{-3}	$(4.77 \pm 0.03) \times 10^{-5}$	95.4
5.0×10^{-5}	Pb&Ca&K, 5.0×10^{-3}	$(4.92 \pm 0.04) \times 10^{-5}$	98.4
5.0×10^{-5}	Fe&Na&Ca, 5.0×10^{-3}	$(4.95 \pm 0.04) \times 10^{-5}$	99.0

a. Results are based on three measurements

4. CONCLUSION

This research demonstrated that ISEs, constructed on 4-(3-Nitrophenyl)-2,6-di-2-thienylpyridine (PTP), exhibited thulium selectivity with low interference from common alkali, alkaline earth, transition and heavy metal ions. The sensor showed a Nernstian response (slope of 20.8±0.3 mVdecade^{-1}), low limit of detection (8.0×10^{-8} mol L^{-1}), applicable pH range of 2.4–9.4, fast response time (< 10 s) and wide linear range (1.0×10^{-7}–1.0×10^{-2} mol L^{-1}). This electrode was also successfully applied to the direct determination of thulium in the mixtures of different metal ions.

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