



## Potentiometric selectivity coefficients of a created Tm<sup>3+</sup> PVC membrane sensor

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### ABSTRACT

A Tm(III) ion-selective membrane sensor was fabricated from polyvinyl chloride (PVC) matrix membrane containing *N,N'*-bis(pyridine-2-carboxamido)-2-aminobenzylamine (BPCA) as a neutral carrier, sodium tetraphenyl borate (NaTPB) as anionic excluder, and nitrobenzene (NB) as a plasticizing solvent mediator. One of the most important characteristics of any membrane sensor is its relative response for the primary ion over other ions present in solution, usually expressed in terms of potentiometric selectivity coefficient. In this work, the so-called matched potential method was used for determination of selectivity coefficients of the sensor. The sensor possesses the advantages of very good selectivity over a large number of cations, especially, for lanthanide ions (Dy<sup>3+</sup>, Tb<sup>3+</sup>, Gd<sup>3+</sup>, Er<sup>3+</sup>, Lu<sup>3+</sup>, Eu<sup>3+</sup>, Ho<sup>3+</sup>, Nd<sup>3+</sup>, Pr<sup>3+</sup>, La<sup>3+</sup>, Yb<sup>3+</sup>, Ce<sup>3+</sup>, and Sm<sup>3+</sup>). To assess its analytical applicability the proposed Tm(III) sensor was successfully applied as an indicator electrode in the titration of Tm(III) ion solutions with EDTA.

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

### INTRODUCTION

During the last decades, many intensive studies have been reported on the design and synthesis of highly selective carriers as sensory molecules for ion-selective electrodes (ISEs). High purity individual lanthanides are used increasingly as major components in laser, phosphors, magnetic bubble memory films, refractive index lenses, fiber optics and superconductors. Thulium and other lanthanides are widely distributed in low concentrations throughout the earth's crust. Due to the increasing industrial use of Tm(III) compounds as well as their enhanced discharge, monitoring of Tm(III) has been of a recent increasing concern. The main methods for the low-

level determination of Lu(III) ions are ICP-MS, ICP-AES, spectrophotometry. Isotope dilution mass spectrometry, neutron activation analysis, and X-ray fluorescence spectrometry are also used in some laboratories. These methods are either time consuming, involving multiple sample manipulations, or 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 through judicious choice of the membrane active materials, wide linear dynamic range, and low cost. Recently, we reported a number of highly selective and sensitive membrane sensors for alkaline earth and transition metal ions [1–26].

### EXPERIMENTAL SECTION

Reagent grade dibutyl phthalate (DBP), nitrobenzene (NB), acetophenone (AP), benzyl acetate (BA), high relative molecular weight polyvinyl chloride (PVC), sodium tetraphenyl borate (NaTPB) and tetrahydrofuran (THF) were purchased from Merck and used as received. The ionophore *N,N'*-bis(pyridine-2-carboxamido)-2-aminobenzylamine (BPCA) was prepared as formerly described [27–30]. The chloride and nitrate salts of the cations used (from Merck and Aldrich) were all of the highest purity available, and used without any further purification except for vacuum drying over P<sub>2</sub>O<sub>5</sub>. Triply distilled deionized water was used throughout.

Membrane solutions were prepared by thoroughly dissolving 2 mg of BPCA, 66 mg of NB, 30 mg of PVC and 2 mg of NaTPB in 3 mL of fresh THF. The resulting solution was evaporated slowly until an oily mixture was obtained. A Pyrex tube (5 mm o.d) was dipped into the mixture for about 10 s so that a transparent membrane of 0.3 mm thickness was formed [31–36]. The tube was then pulled out from the mixture, and kept at room temperature for 12 h. The tube was then filled with an internal solution (1.0×10<sup>-3</sup> M TmCl<sub>3</sub>). The electrode was finally conditioned for about 36 h by soaking in a 1.0×10<sup>-3</sup> M TmCl<sub>3</sub> solution. A silver/silver-chloride electrode was used as the internal reference electrode.

All emf measurements were carried out with the following assembly:

Ag–AgCl | 1.0 × 10<sup>-3</sup> M TmCl<sub>3</sub> | PVC membrane: test solution | Hg–Hg<sub>2</sub>Cl<sub>2</sub>, 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.

### RESULTS AND DISCUSSION

With the obtained composition of the membrane (30 % PVC, 2 % BPCA, 2 % NaTPB and 66 % NB), BPCA as an ionophore was used to prepare a PVC-membrane ion-selective electrode. The potentiometric selectivity coefficients, which reflect the relative response of the membrane sensor towards the primary ion over other ions present in solution, is perhaps the most important characteristic of an ion-selective electrode. In this research, the potential responses of the recommended Tm<sup>3+</sup> membrane sensor to a wide variety of cations were investigated through the matched potential method (MPM) [37–40]. The results are listed in Table 1. According to this method, a specified activity (concentration) of primary ions (A: 1×10<sup>-2</sup> and 1×10<sup>-3</sup> M) is added to a reference solution (1×10<sup>-6</sup> M) and the potential is measured. In a separate experiment,

interfering ions (B:  $1 \times 10^{-2}$  and  $1 \times 10^{-3}$  M) are successively added to an identical reference solution, until the measured potential matches the one obtained before adding primary ions. The matched potential method selectivity coefficient,  $K^{\text{MPM}}$ , is then given by the resulting primary ion to interfering ion activity (concentration) ratio,  $K^{\text{MPM}} = \Delta a_A / a_B$ . As it can be seen from Table 1, for the all mono and bivalent metal ions and trivalent lanthanide ions tested, the selectivity coefficients are about or less than  $4.3 \times 10^{-3}$ , which seems to indicate negligible interferences in the performance of the electrode assembly. Table 2 compares the selectivity coefficients, the slope, the detection limit and the linearity concentration ranges of the best previously reported iron ion-selective electrodes based on different ion-carriers with those obtained for the proposed Tm(III) membrane sensor based on BPCA [38, 41, 42]. In all cases, as is immediately obvious from Table 2, the proposed Tm(III) sensor is superior to those reported for other Tm(III) ion selective electrodes. It supersedes not only in terms of selectivity coefficients and detection limit but also in terms of working concentration range.

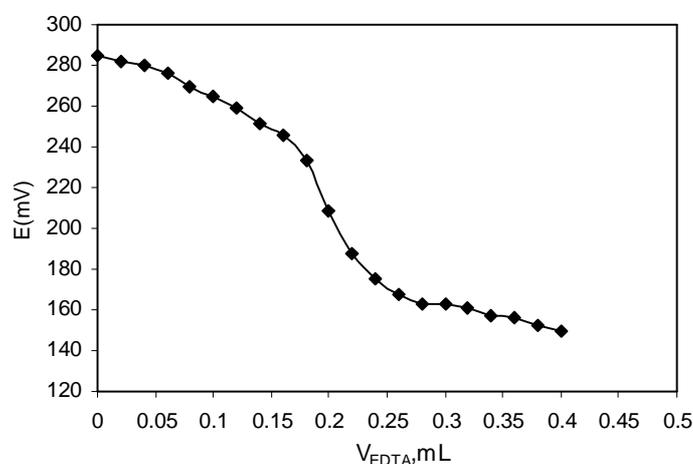
The constructed Tm(III) sensor was found to work well under laboratory conditions. It was used as an indicator electrode in the titration of  $1.0 \times 10^{-4}$  M Tm(III) ions solution with a standard  $1.0 \times 10^{-2}$  M EDTA and the resulting titration curve is shown in Figure 1. As can be seen, the amount of  $\text{Tm}^{3+}$  ions in solution can be determined with the electrode.

**Table 1: Selectivity coefficients of various interfering ions**

Interfering ion (B)	Selectivity coefficient ( $K_{\text{Tm, B}}$ )
$\text{Dy}^{3+}$	$8.7 \times 10^{-4}$
$\text{Tb}^{3+}$	$8.4 \times 10^{-4}$
$\text{Gd}^{3+}$	$3.1 \times 10^{-3}$
$\text{Er}^{3+}$	$2.6 \times 10^{-3}$
$\text{Lu}^{3+}$	$7.8 \times 10^{-4}$
$\text{Eu}^{3+}$	$3.9 \times 10^{-3}$
$\text{Ho}^{3+}$	$3.3 \times 10^{-3}$
$\text{Nd}^{3+}$	$7.6 \times 10^{-4}$
$\text{Pr}^{3+}$	$2.4 \times 10^{-3}$
$\text{La}^{3+}$	$3.5 \times 10^{-3}$
$\text{Yb}^{3+}$	$1.0 \times 10^{-3}$
$\text{Ce}^{3+}$	$6.4 \times 10^{-4}$
$\text{Sm}^{3+}$	$7.1 \times 10^{-4}$
$\text{Cr}^{3+}$	$4.3 \times 10^{-3}$
$\text{Fe}^{3+}$	$3.9 \times 10^{-3}$
$\text{Na}^+$	$6.7 \times 10^{-4}$
$\text{K}^+$	$8.5 \times 10^{-4}$
$\text{Mg}^{2+}$	$6.2 \times 10^{-4}$
$\text{Ca}^{2+}$	$7.7 \times 10^{-4}$
$\text{Ni}^{2+}$	$7.5 \times 10^{-4}$
$\text{Co}^{2+}$	$8.8 \times 10^{-4}$
$\text{Pb}^{2+}$	$2.2 \times 10^{-3}$

**Table 2: Characteristics Comparison of proposed Tm(III) sensor and the previously reported Tm(III) ion-selective electrodes**

Major interfering ions ( $K_{MPM} > 5.0 \times 10^{-3}$ )	Linear range / M	Slope / $\text{mVdecade}^{-1}$	Detection limit / M	References
$\text{Pr}^{3+}$ , $\text{Pb}^{2+}$	$1.0 \times 10^{-6}$ - $1.0 \times 10^{-2}$	19.5	$4.0 \times 10^{-7}$	[41]
$\text{Gd}^{3+}$ , $\text{Nd}^{3+}$ , $\text{Pr}^{3+}$ , $\text{Pb}^{2+}$	$1.0 \times 10^{-5}$ - $1.0 \times 10^{-2}$	19.5	$8.0 \times 10^{-6}$	[42]
$\text{Gd}^{3+}$ , $\text{Cr}^{3+}$ , $\text{Fe}^{3+}$	$1.0 \times 10^{-6}$ - $1.0 \times 10^{-2}$	19.5	$8.7 \times 10^{-7}$	[38]
-	$1.0 \times 10^{-6}$ - $1.0 \times 10^{-2}$	20.4	$6.3 \times 10^{-7}$	This work

**Figure 1. Potential titration curve of 20.0 mL from a  $1.0 \times 10^{-4}$  M  $\text{Eu}^{3+}$  solution with  $1.0 \times 10^{-2}$  M of EDTA**

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