



*J. Chem. Pharm. Res.*, 2011, 3(4): 820-824

ISSN No: 0975-7384  
CODEN(USA): JCPRC5

**Potentiometric  $Tb^{3+}$ -Selective Sensor Based on 1, 3-Diaminopropane-  
N,N,N',N'-tetraacetic acid as an Ionophore**

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**ABSTRACT**

A poly(vinyl chloride) (PVC)-based membrane sensor for  $Tb^{3+}$  ions was prepared by employing 1, 3-Diaminopropane-N,N,N',N'-tetraacetic acid (APTAA) as an ionophore, sodium tetraphenyl borate (NaTPB) as an anion excluder, and dibutylphthalate (DBP), benzylacetate (BA), acetophenon (AP) and nitrobenzene (NB) as plasticizing solvent mediators and investigated as a selective membrane sensor. The sensor displays a linear dynamic range between  $1.0 \times 10^{-8}$  and  $1.0 \times 10^{-2}$  M, with a nice Nernstian slope of  $19.8 \pm 0.4$  mV per decade and a detection limit of  $8.4 \times 10^{-9}$  M. The proposed sensor displays a fast response time ( $\sim 5$  s). The potentiometric response is independent of pH in the range of 2.1–9.5.

**Keywords:** PVC Membrane, Potentiometry, Sensor, Ion-Selective Electrode.

**INTRODUCTION**

Terbium is an important member of the rare earth family and is used in cathode ray tubes, magnets optical computer memories and magnetostrictive alloys. Spectrophotometry, spectrofluorimetry, ICP-MS and ICP-AES are the main methods for the low-level monitoring of terbium ions in solutions. Isotope dilution mass spectrometry, neutron activation analysis, X-ray fluorescence spectrometry, etc. are also used in some laboratories. These methods are either time consuming, involving multiple sample manipulations, or too expensive for most analytical laboratories. Potentiometric monitoring of metal ions based on ionselective electrodes (ISEs) [1-25] offer the advantages of speed and ease of preparation and procedures, relatively fast responses, reasonable selectivity thorough judicious choice of the membrane active materials, wide linear dynamic range, and very low cost. We have been recently involved in the preparation of new ion-selective electrodes for some metal ions [20-30]. In this work, we wish to introduce a highly selective and sensitive  $Tb^{3+}$  ion-selective membrane electrode by incorporation of APTAA as an ionophore in a PVC-based on membrane sensor.

## EXPERIMENTAL SECTION

Reagent grade sodium tetrphenylborate (NaTPB), dibutyl phthalate (DBP), acetophenone (AP), benzyl acetate (BA), nitrobenzene (NB), tetrahydrofuran (THF) and high relative molecular weight poly(vinyl chloride) (PVC) were purchased from Merck and used as received. The 1, 3-Diaminopropane-N,N,N',N'-tetraacetic acid, terbium chloride and the nitrate salts of other cations used (all from Merck and Aldrich) were of the highest purity available and used without any further purification except for vacuum drying over P<sub>2</sub>O<sub>5</sub>. Doubly distilled de-ionized water was used throughout.

The general procedure to prepare the PVC-membrane was to mix thoroughly 30 mg of powdered PVC, 65 mg of plasticizer NB and 2 mg of additive NaTPB in 5 mL of THF. To this solution was added 3 mg of ionophore APTTA, and its mixture was obtained. A Pyrex tube (3–5 mm in diameter on top) was dipped into the oily mixture for about 5 s so that a non-transparent film of about 0.3 mm thickness was formed [15–20]. The tube was then pulled out from the mixture and kept at the room temperature for about 12 h. The tube was then filled with an internal filling solution ( $1.0 \times 10^{-3}$  M TbCl<sub>3</sub>). The electrode was finally conditioned for 24 h by soaking in a  $1.0 \times 10^{-3}$  M solution of terbium chloride. A silver–silver chloride electrode was used as an internal reference electrode.

The emf measurement with the polymeric membrane electrode was carried out with the following cell assembly:

Ag–AgCl | internal solution,  $1.0 \times 10^{-3}$  M TbCl<sub>3</sub> | PVC membrane | sample solution | Hg–Hg<sub>2</sub>Cl<sub>2</sub>, KCl (satd.).

A Corning ion analyzer with a 250 pH/mV meter for the potential measurements at  $25.0 \pm 0.1$  °C. The activities were calculated according to the Debye–Hückel procedure.

## RESULTS AND DISCUSSION

The APTTA was used as a neutral carrier in construction of PVC-membrane electrodes for a number of metal ions, including alkali, alkaline earth, transition, and heavy metal ions. In each, the electrode was conditioned for 24 h by soaking in a  $1.0 \times 10^{-3}$  M solution of the chloride or nitrate salts of the corresponding cation, to obtain thermodynamically meaningful potential responses and selectivity behaviors. It is noted that the resulting Tb<sup>3+</sup> potential response showed a Nernstian behavior, while the slopes of the linear parts of the emf responses to other cations were much lower than those expected by the Nernst equation. Thus, APTTA may be used as a suitable selective ionophore in construction of a Tb<sup>3+</sup> ion-selective membrane electrode.

Sensitivity and selectivity of any given membrane sensor are significantly related to the composition of the ion-selective membrane, and the nature of the solvent mediators and additives used [31–35], and therefore we decided to study such effects on the behavior of the proposed sensor. The effects of the nature and amount of plasticizer and additive on the potential response of the proposed Ho(III) sensor are summarized in Table 1. These data revealed that the four different plasticizers used (AP, BA, NB, and DBP), NB is very polar and was chosen as a suitable solvent mediator. It has long been known that the presence of 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 [36–38]. In addition, one can understand

from Table 1, that increasing the amount of the ion carrier up to 3%, addition of 2% NaTPB (membrane no. 3) increased the sensitivity of the electrode response to a great extent. The best response was exhibited by the (no. 3) membrane incorporating APTTA, PVC, NB and NaTPB in the ratio of 3:30:65:2 (wt%), respectively.

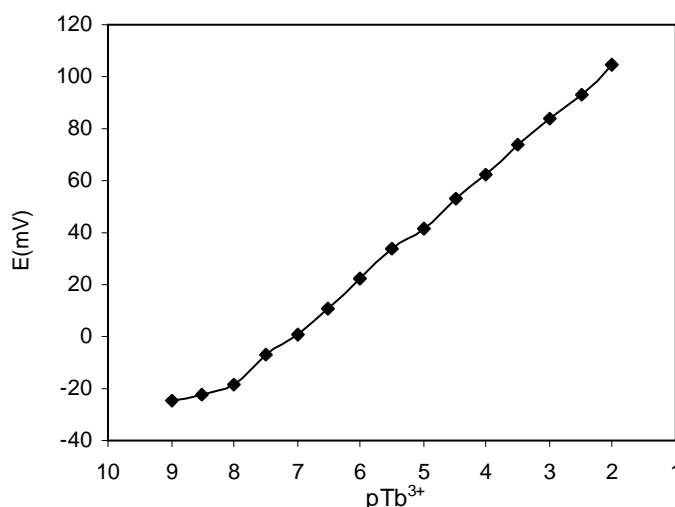
The potential response of the electrode at varying concentration of Tb(III) ions displays a linear response to the concentration of  $Tb^{3+}$  ions in the range of  $1.0 \times 10^{-8}$  to  $1.0 \times 10^{-2}$  M (Fig. 1). The slope of calibration graph was  $19.8 \pm 0.4$  mV per decade of the activity of  $Tb^{3+}$  ions. The detection limit of the sensor, as determined from the intersection of the two extrapolated segments of the calibration graph was  $8.4 \times 10^{-9}$  M.

The influence of pH of the test solution on the potential response of the membrane sensor was tested in the pH range of 1.5–11.0 and the results are shown in Figure 2. As can be seen, the potential remained constant in a pH range of 2.1–9.5.

The average time required for the  $Tb^{3+}$  sensor to reach a potential within  $\sim 1$  mV of the final equilibrium value after successive immersion of a series of Tb(III) ion solutions, each having a 10-fold difference in concentration, was measured (Fig. 3). The static response time of the membrane electrode thus obtained was  $\sim 8$  s over the entire concentration range.

**Table 1: Composition of membrane ingredients**

Membrane No.	Composition (wt %)				Slope (mV/decade)	Concentration range (M)
	PVC	Plasticizer	NaTPB	APTAA		
1	30	NB, 67	0	3	$11.8 \pm 0.5$	$1.0 \times 10^{-6}$ - $1.0 \times 10^{-3}$
2	30	NB, 66	1	3	$15.8 \pm 0.6$	$1.0 \times 10^{-7}$ - $1.0 \times 10^{-2}$
3	30	NB, 65	2	3	$19.8 \pm 0.4$	$1.0 \times 10^{-8}$ - $1.0 \times 10^{-2}$
4	30	NB, 64	3	3	$18.1 \pm 0.3$	$1.0 \times 10^{-7}$ - $1.0 \times 10^{-2}$
5	30	NB, 67	2	1	$13.5 \pm 0.4$	$1.0 \times 10^{-6}$ - $1.0 \times 10^{-2}$
6	30	NB, 66	2	2	$17.4 \pm 0.3$	$1.0 \times 10^{-7}$ - $1.0 \times 10^{-2}$
7	30	AP, 66	2	2	$15.8 \pm 0.2$	$1.0 \times 10^{-6}$ - $1.0 \times 10^{-2}$
8	30	BA, 66	2	2	$14.3 \pm 0.5$	$1.0 \times 10^{-6}$ - $1.0 \times 10^{-2}$
9	30	DBP, 66	2	2	$13.6 \pm 0.2$	$1.0 \times 10^{-6}$ - $1.0 \times 10^{-2}$



**Figure 1. Calibration curve of  $Tb^{3+}$  sensor based on APTAA.**

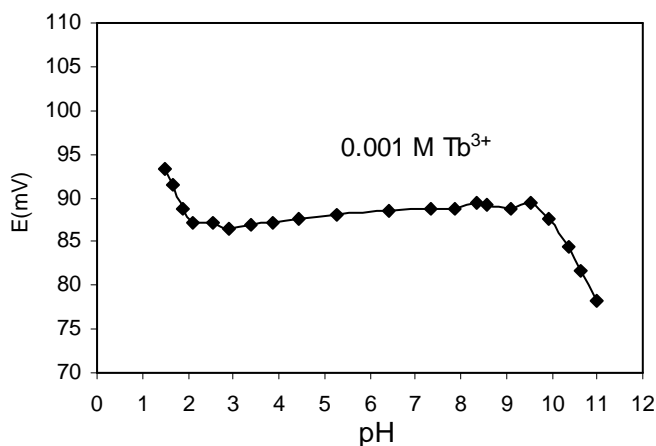


Figure 2. pH effect of the test solution ( $1.0 \times 10^{-3}$  M of  $Tb^{3+}$ ) on the potential response.

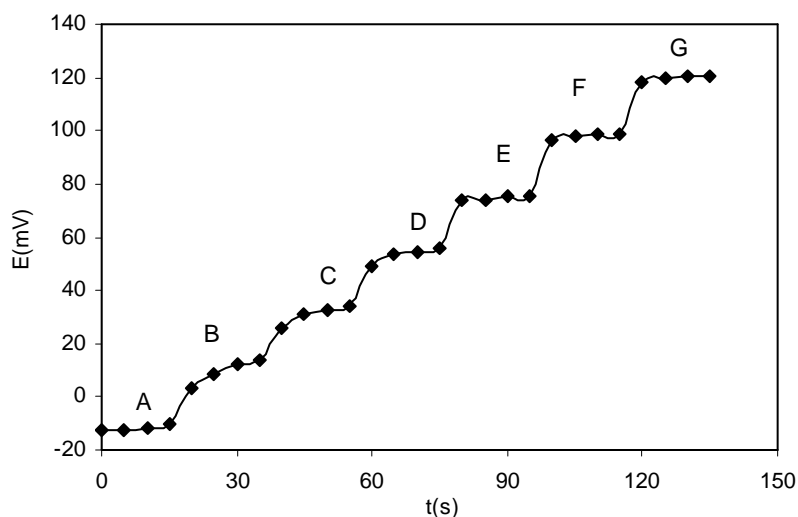


Figure 3. Dynamic response time of the terbium electrode for step changes in the  $Tb^{3+}$  concentration: A)  $1.0 \times 10^{-8}$  M, B)  $1.0 \times 10^{-7}$  M, C)  $1.0 \times 10^{-6}$  M, D)  $1.0 \times 10^{-5}$  M, E)  $1.0 \times 10^{-4}$  M, F)  $1.0 \times 10^{-3}$  M, G)  $1.0 \times 10^{-2}$  M.

### Acknowledgements

The authors acknowledge the financial support kindly offered by the Research Council of Quchan Branch Islamic Azad University for the preparation of this study.

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