



J. Chem. Pharm. Res., 2011, 3(4): 630-635

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

Application of N,N'-bis(pyridine-2-carboxamido)-2-aminobenzylamine in construction of a new Tm³⁺ polymeric membrane ion-selective sensor

Hassan Ali Zamani,^{a,*} Somayeh Harimi,^a Mohammad Reza Abedi,^a Soraia Meghdadi,^b

^aDepartment of Applied Chemistry, Quchan branch, Islamic Azad University, Quchan, Iran

^bDepartment of Chemistry, Isfahan University of Technology, Isfahan, Iran

ABSTRACT

A PVC membrane containing N,N'-bis(pyridine-2-carboxamido)-2-aminobenzylamine (BPCA) as a suitable ionophore, sodium tetraphenyl borate (NaTPB) as an anionic additive, nitrobenzene (NB) as solvent mediator, exhibits a Nernstian response (slope of 20.4 ± 0.3 decade of activity) for Tm(III) ions over a wide concentration range up to 1.0×10^{-6} and 1.0×10^{-2} M, with a detection limit of 6.3×10^{-7} M in the pH range 2.8–8.3. It has a fast response time (~5 s).

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

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 [1,2]. The vapors or dusts of these elements are very toxic when inhaled. Thus, determination of these ions can be important in industrial life. In general, ICP-MS and ICP-AES, spectrophotometry, and spectrofluorimetry, are the available methods for the low-level monitoring of thulium ions in solutions. Isotope dilution mass spectrometry, neutron activation analysis, and X-ray fluorescence spectrometry are also used in some laboratories. However, these techniques are either time consuming, involving multiple sample manipulations, or too expensive for most analytical laboratories. Potentiometric sensors can offer an inexpensive and convenient analysis method of lanthanide ions in solution, provided that the acceptable sensitivity and selectivity are achieved [1-3]. We have developed some ISEs for the potentiometric determination of some metal ions [4-20]. In this study, another ion selective sensor has been introduced for the potentiometric Tm(III) determination, based on N,N'-bis(pyridine-2-carboxamido)-2-aminobenzylamine (BPCA), demonstrating fast response time, relatively low detection limit and also high selectivity (Figure 1).

EXPERIMENTAL SECTION

The nitrate and chloride salts of all cations and the reagent grades of dibutyl phthalate (DBP), benzylacetate (BA), nitrobenzene (NB), acetophenone (AP), sodium tetraphenyl borate (NaTPB), tetrahydrofuran (THF) and high relative molecular weight PVC were obtained from Merck Chemical and the Aldrich Co. All reagents were used without any purification. The ionophore *N,N'*-bis(pyridine-2-carboxamido)-2-aminobenzylamine (BPCA) was prepared as formerly described [21-24]. As far as the nitrate and chloride salts of all employed cations are concerned, they were of the highest available purity and were P₂O₅-vacuum dried. During the experiments, triply distilled deionized water was used.

All emf measurements were carried out with the following assembly:

Ag–AgCl | 1.0 × 10⁻³ M TmCl₃ | 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.

30 mg of the powdered PVC and 66 mg of the NB plasticizer were completely blended in 5 mL of THF. Then, 2 mg of NaTPB and 2 mg of the BPCA ionophore were added to this mixture. The solution, after being mixed well, was transferred into a glass dish of 2 cm in diameter. The THF content of the mixture was evaporated slowly, until an oily concentrated mixture was obtained. A Pyrex tube (3–5 mm o.d.) was dipped into the mixture for about 10 s, in order to achieve a transparent membrane formation of about 0.3 mm in thickness [25–33]. In the end, the tube was removed from the solution, kept at room temperature for 12 h and filled with an internal filling solution (1.0 × 10⁻³ M TmCl₃). The electrode was conditioned for 36 h by soaking in a 1.0 × 10⁻³ M TmCl₃ solution. As an internal reference electrode, a silver/silver chloride coated wire was used.

RESULTS AND DISCUSSION

The existence of six donating atoms (four nitrogen and two oxygen) in the structure of BPCA was expected to increase both the stability and selectivity of its complexes with transition and heavy-metal ions, rather than alkali and alkaline-earth metal ions. Thus, at first, BPCA as an ion carrier for different metal ions, was used to prepare PVC-membrane ion-selective electrodes for a wide variety of cations, including alkali, alkaline-earth, lanthanide, transition, and heavy-metal ions. Among the different cations tested, Tm³⁺ with the most sensitive response seems to be suitably determined with the PVC membrane based on BPCA. This is most probably due to both, the selective behavior of the ionophore against thulium ion in comparison to other metal ions, and the rapid exchange kinetics of the resulting BPCA-Tm³⁺ complex.

Since the sensitivity and selectivity of a given ionophore depend significantly on the membrane ingredients, the nature of the solvent mediator and the used additive [34–38], the influence of the membrane composition, the potential responses of the Tm(III) sensor was investigated. The results are summarized in Table 1. It can be seen that the ionophore amount increase up to a 2 % value in the presence of 2 % of NaTPB and 66 % of polar solvent (NB) results in the best sensitivity. Generally speaking, the presence of lipophilic anions in a cation-selective membrane based on a neutral carrier not only diminishes the ohmic resistance and enhances the response behavior and selectivity but also, in cases where the extraction capability is poor, it increases the

membrane electrode sensitivity [39-43]. All the same, the membranes with a composition of 30 % PVC, 2 % BPCA, 2 % NaTPB and 66 % NB exhibit a Nernstian potential response.

The potential response of the Tm(III) PVC-based membrane sensor at various concentrations of Tm^{3+} ions (Fig. 2) indicates a linear working concentration range of 1.0×10^{-6} - 1.0×10^{-2} M. The slope of the calibration graph was 20.4 ± 0.3 mV per decade of Tm^{3+} ion concentration. The detection limit of the electrode determined from the intersection of the two extrapolated segments of the calibration graph was 6.3×10^{-7} M.

Table 1: Optimization of the membrane ingredients

No.	Composition (wt %)				Linear range (mol L ⁻¹)	Slope (mV/decade)
	PVC	Plasticizer	BPCA	NaTPB		
1	30	NB, 68	2	0	1.0×10^{-5} - 5.0×10^{-2}	11.3 ± 0.2
2	30	NB, 67	2	1	1.0×10^{-5} - 5.0×10^{-2}	16.7 ± 0.3
3	30	NB, 66	2	2	1.0×10^{-6} - 1.0×10^{-2}	20.4 ± 0.3
4	30	NB, 65	2	3	1.0×10^{-6} - 1.0×10^{-2}	17.2 ± 0.2
5	30	NB, 67	1	2	1.0×10^{-6} - 1.0×10^{-2}	17.5 ± 0.5
6	30	NB, 65	3	2	1.0×10^{-6} - 1.0×10^{-2}	18.8 ± 0.6
7	30	BA, 66	2	2	1.0×10^{-5} - 5.0×10^{-2}	15.7 ± 0.4
8	30	AP, 66	2	2	1.0×10^{-5} - 5.0×10^{-2}	16.9 ± 0.7
9	30	DBP, 66	2	2	1.0×10^{-5} - 5.0×10^{-2}	14.3 ± 0.3

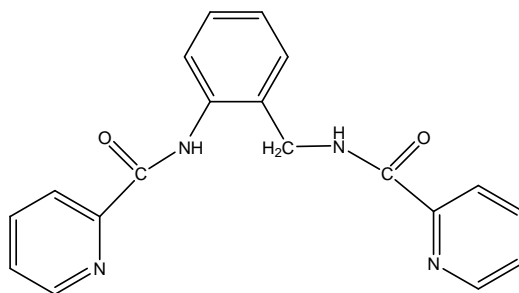


Figure 1. The BPCA chemical structure.

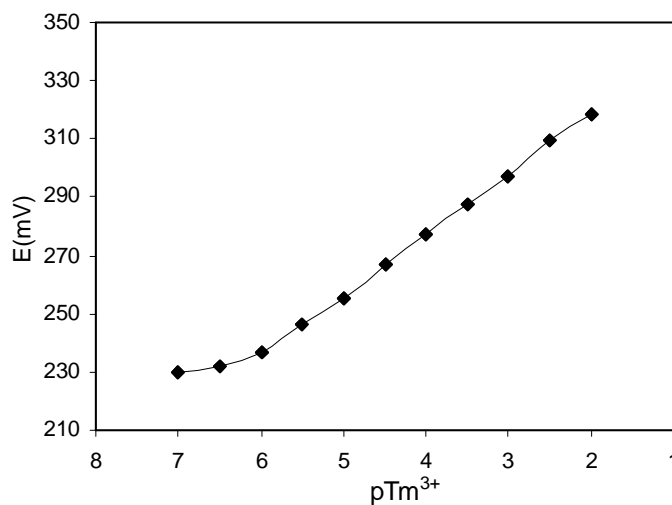


Figure 2. Calibration curve of Tm^{3+} sensor based on BPCA.

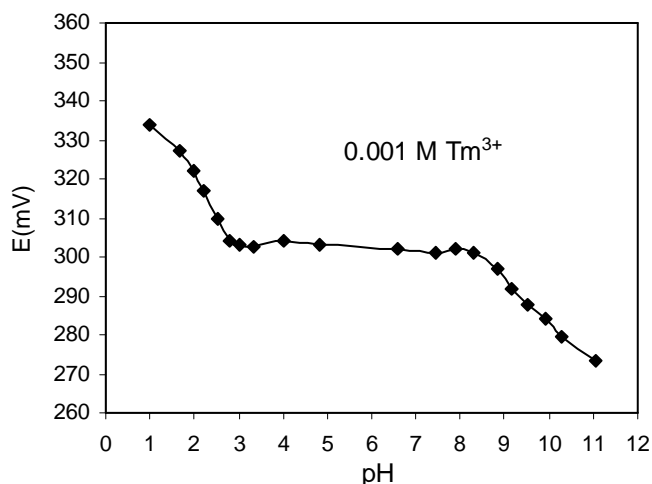


Figure 3. pH effect of the test solution (1.0×10^{-3} M of Tm^{3+}) on the potential response.

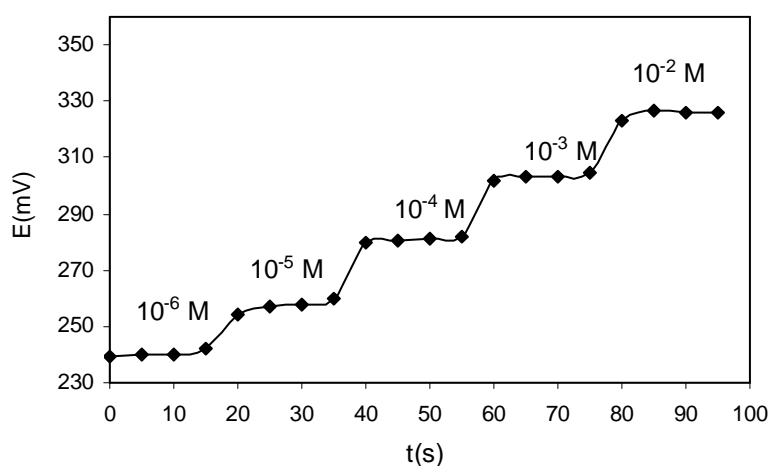


Figure 4. Dynamic response time of the Tm^{3+} sensor for step changes in the Tm^{3+} concentration: A) 1.0×10^{-6} M, B) 1.0×10^{-5} M, C) 1.0×10^{-4} M, D) 1.0×10^{-3} M, E) 1.0×10^{-2} M.

The pH response profile for the electrode was tested by use of a 1.0×10^{-3} M terbium solution over the pH range 1.0-11.0. The pH was adjusted by introducing small drops of hydrochloric acid (0.1 M) or sodium hydroxide (0.1 M) into the test solution. The influence of the pH response on the PVC membrane electrode is shown in Figure 3. As it is seen, the potential remained constant from pH 2.8 to 8.3, beyond which some drifts in the potentials were observed. For analytical applications, the dynamic response time is very important for any sensor. The dynamic response time of the membrane was measured at various concentrations (1.0×10^{-6} – 1.0×10^{-2} M) of the test solutions and the results are shown in Fig. 4. As can be seen, across the whole concentration range, the electrode reaches its equilibrium response very fast (~5 s).

Acknowledgements

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

REFERENCES

- [1] C.A. Hampel, R. Book, *The Encyclopedia of the Chemical Elements*, Corporation, Reinhold Book Corp, New York, 1968.

- [2] FX Zang; ZR Hong; WL Li; MT Li; XY Sun. *Appl. Phys. Lett.* **2004**, 84, 2679.
- [3] HA Zamani; M Nekoei; M Mohammadhosseini; MR Ganjali. *Mater. Sci. Eng. C* **2010**, 30, 480.
- [4] HA Zamani; H Ghahremani; H Behmadi. *J. Chem. Pharm. Res.* **2010**, 2, 328.
- [5] HA Zamani; A Imani; A Arvinfar; F Rahimi; MR Ganjali; F Faridbod; S Meghdadi. *Mater. Sci. Eng. C* **2011**, 31, 588.
- [7] HA Zamani; M Mohammadhosseini; M Nekoei; MR Ganjali. *Sensor Lett.*, **2010**, 8, 303.
- [8] HA Zamani; A Arvinfar; F Rahimi; A Imani; MR Ganjali; S Meghdadi. *Mater. Sci. Eng. C* **2011**, 31, 307.
- [9] HA Zamani; G Rajabzadeh; MR Ganjali; *Sensor Lett.*, **2009**, 7, 114.
- [10] HA Zamani; MS Zabihi; M Rohani; A Zangeneh-Asadabadi; MR Ganjali; F Faridbod; S Meghdadi. *Mater. Sci. Eng. C* **2011**, 31, 409.
- [11] HA Zamani; MT Hamed-Mosavian; E Aminzadeh; MR Ganjali; M Ghaemy; H Behmadi; F Faridbod. *Desalination* **2010**, 250, 56.
- [12] HA Zamani; M Rohani; A Zangeneh-Asadabadi; MS Zabihi; MR Ganjali; M Salavati-Niasari. *Mater. Sci. Eng. C* **2010**, 30, 917.
- [13] HA Zamani; M Masrournia; M Rostame-Faroge; MR Ganjali; H Behmadi. *Sensor Lett.*, **2008**, 6, 759.
- [14] HA Zamani; MR Ganjali; P Norouzi; M Adib; M Aceedy. *Anal. Sci.*, **2006**, 22, 943.
- [15] H Behmadi; HA Zamani; MR Ganjali; P Norouzi. *Electrochim. Acta* **2007**, 53, 1870.
- [16] HA Zamani; MR Ganjali; P Norouzi; A Tadjarodi; E Shahsavani. *Mater. Sci. Eng. C* **2008**, 28, 1489.
- [17] HA Zamani; MT Hamed-Mosavian; E Hamidfar; MR Ganjali; P Norouzi. *Mater. Sci. Eng. C* **2008**, 28, 1551.
- [18] HA Zamani; MR Ganjali; P Norouzi; A Tadjarodi; E Shahsavani. *Mater. Sci. Eng. C* **2009**, 28, 1489.
- [19] HA Zamani; MR Ganjali; P Norouzi; M Adib. *Sensor Lett.*, **2007**, 5, 522.
- [20] HA Zamani; M Mohaddeszadeh. *Anal. Lett.*, **2008**, 41, 2710.
- [21] S Meghdadi; M Amirnasr; MH Habibi; A Amiri; V Ghodsi; A Rohani; RW Harrington, W Clegg. *Polyhedron* **2008**, 27, 2771.
- [22] CK Patel; CS Rami; B Panigrahi; CN Patel. *J. Chem. Pharm. Res.* **2010**, 2, 73.
- [23] S Chandra; BN Ghogare; LK Gupta; CP Shinde. *J. Chem. Pharm. Res.* **2010**, 2, 240.
- [24] SK Srivastava; S Verma; SD Srivastava. *J. Chem. Pharm. Res.* **2010**, 2, 270.
- [25] MR Ganjali; A Ghesmi; M Hosseini; MR Pourjavid; M Rezapour; M Shamsipur; M Salavati-Niasari. *Sens. Actuators B* **2005**, 105, 334.
- [26] MR Ganjali; P Norouzi; A Atrian; F Faridbod; S Meghdadi; M. Giahi. *Mater. Sci. Eng. C* **2009**, 29, 205.
- [27] HA Zamani. *Anal. Lett.*, **2009**, 42, 615.
- [28] M Masrournia; HA Zamani; HA Mirrashid; MR Ganjali; F Faridbod. *Mater. Sci. Eng. C* **2011**, 31, 574.
- [29] HA Zamani; G Rajabzadeh; M Masrournia; A Dejbord; MR Ganjali; N Seifi. *Desalination* **2009**, 249, 560.
- [30] VK Gupta, RN Goyal; RA Sharma. *Anal. Chim. Acta* **2009**, 647, 66.
- [31] HA Zamani; G Rajabzadeh; MR Ganjali. *Talanta* **2007**, 72, 1093.
- [32] MR Abedi; HA Zamani; MR Ganjali; P Norouzi. *Sensor Lett.*, **2007**, 5, 516.
- [33] HA Zamani; MR Ganjali; P Norouzi; M Adib. *Mater. Sci. Eng. C* **2008**, 28, 157.
- [34] T Rostazin; E Bakker; K Suzuki; W Simon. *Anal. Chim. Acta* **1993**, 280, 197.
- [35] S Chandra; DR Singh; *Mater. Sci. Eng. A* **2009**, 502, 107.
- [36] HA Zamani; M Masrournia; S Sahebhasagh; MR Ganjali. *Anal. Lett.*, **2009**, 42, 555.
- [37] E Naddaf; HA Zamani. *Anal. Lett.*, **2009**, 42, 2838.

- [38] E Ammann; E Pretsch; W Simon; E Lindner; A Bezegh; E Pungor. *Anal. Chim. Acta* **1985**, *171*, 119.
- [39] E Bakker; P Bühlmann; E Pretsch. *Electroanalysis* **1999**, *11*, 915.
- [40] MR Abedi; HA Zamani. *Anal. Lett.*, **2008**, *41*, 2251.
- [41] E Bakker; P Bühlmann; E Pretsch. *Chem. Rev.*, **1997**, *97*, 3083.
- [42] HA Zamani, MR Ganjali, M Salavati-Niasari. *Transition. Met. Chem.*, **2008**, *33*, 995.
- [43] J Koryta. *Anal. Chim. Acta* **1990**, *233*, 1.