Available on line www.jocpr.com

Journal of Chemical and Pharmaceutical Research

J. Chem. Pharm. Res., 2011, 3(4): 760-765

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

Synthesis of thio schiff-base as sensing material for fabrication of Tm^{3+}-PVC membrane sensor

Hassan Ali Zamani,[a*] Mohammad Reza Ganjali,[b] Mohammad Reza Abedi,[a] Masoud Salavati-Niasari[c]

[a]*Department of Applied Chemistry, Quchan branch, Islamic Azad University, Quchan, Iran*
[b]*Center of Excellence in Electrochemistry, Faculty of Chemistry, University of Tehran, Tehran, Iran*
[c]*Department of Chemistry, Faculty of Science, University of Kashan, Kashan, Iran*

ABSTRACT

The Thio Schiff-Base (TSB) was used as an excellent ionophore in the construction of a Tm^{3+} PVC-based membrane sensor. The constructed PVC membrane sensor containing TSB exhibits a Nernstian response of 20.1 ± 0.3 mV per decade for Tm^{3+} ions over a wide concentration range between 1.0×10^{-7} and 1×10^{-2} M, with a limit of detection of 8.6×10^{-8} M. It has a fast response time (<10 s), operates well in the pH range of 3.0–8.7. The best performance was obtained with a membrane composition of 30% poly(vinyl chloride), 55% o-nitrophenyloctyl ether (NPOE), 4% TSB, 10% oleic acid (OA) and 1% sodium tetraphenyl borate (NaTBP).

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

INTRODUCTION

Schiff's base compounds have the ability to form selective stable complexes with metal ions of compatible dimensions and can potentially be used in their separation and determination.[1,2] Thulium is the least abundant of the rare earths and it slowly tarnishes in air, but is more resistant to oxidation than most rare-earth elements [3]. Radioactive thulium is used to power portable x-ray machines, eliminating the need for electrical equipment. Today, there are some methods for the low-level detection of thulium ions and other transition metal ions in solution including inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectroscopy (ICP-AES) and spectrofluorimetry. These available methods are either time consuming, involving multiple sample manipulations, or too expensive for most analytical laboratories and also the analyte was destroyed during the analysis. On the other hand, potentiometric sensors offer inexpensive and convenient analysis methods for the analysis of lanthanide ions as well as a number of cations and anions, with acceptable sensitivity and selectivity. Recently the development of several highly selective and sensitive PVC-membrane ion-selective electrodes for some ions has been reported [4-25]. In this work, we wish to introduce a highly Tm(III)-selective sensor based on Thio Schiff-base (TSB) (Fig. 1), as a novel ionophore for the potentiometric determination of Tm(III) ion over a wide concentration range.

EXPERIMENTAL SECTION

Nitrate and chloride salts of all cations and the reagent grades of dibutyl phthalate (DBP), *o*-nitrophenyloctyl ether (NPOE), nitrobenzene (NB), oleic acid (OA), acetophenone (AP), sodium tetraphenyl borate (NaTPB), tetrahydrofuran (THF) and high relative molecular weight PVC were all purchased from Merck Chemical Co. All reagents were used without any further modification. During the experiments, deionized distilled water was used.

The general procedure to prepare the PVC membrane adding different amounts of the ionophore (TSB) along with appropriate amounts of PVC, plasticizer and additive were dissolved in tetrahydrofuran (THF). The solution was then thoroughly mixed prior to being transferred into a glass dish of 2 cm diameter, and letting the THF content slowly evaporate to yield an oily concentrated mixture. The next step included dipping a Pyrex tube (3–5 mm o.d.) into the mixture for about 10 s to form a transparent membrane of about 0.3 mm thickness on its tip. The tube was then pulled out of the mixture and kept at room temperature for about 12 h before being filled with an internal filling solution (1.0×10^{-3} M $TmCl_3$) and finally being conditioned for 24 h by soaking in a 1.0×10^{-3} M $TmCl_3$ solution [26-30]. A silver/silver chloride coated wire was inserted into the electrode to serve as the internal reference and the 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.

The Thio Schiff-base (TSB) was synthesized in the usual manner by reaction of thiophene-2-carbaldehyde with diamine in a 2:1 molar ratio in methanol as follows. Thiophene-2-carbaldehyde (0.01 mol, 1.12 g) and diamine (0.005 mol, 0.54 g) were placed in 100 mL round-bottom flask equipped with a condenser and a magnetic bar. Methanol (50 mL) was then added to the mixture and the mixture was refluxed far 3 h while stirring, and then cooled to room temperature. The solid product was filtered, and the product was recrystallized from chloroform [31-33]. Anal. calcd for $C_{16}H_{12}N_2S_2$: C, 64.84; H, 4.08; N, 9.45. Found: C, 64.66; H, 3.85; N, 9.59%; IR bands (KBr, cm^{-1}), $\upsilon_{C=N}$, 1605 cm^{-1}; Yield = 69%; M.P. = 170 ^{0}C; ^{1}H-NMR (400 MHz, $CDCl_3$, internal reference TMS): δ 7.33 (4H, dd, C_6H_4), 8.88 (2H, s, CH=N), 7.13 (2H, m, C_4H_3S), 7.40 (2H, m, C_4H_3S), 7.55 (2H, m, C_4H_3S).

RESULTS AND DISCUSSION

In order to check the TSB suitability as an ionophore for different metal ions, it was initially used to prepare a great deal of membrane electrodes for a wide variety of alkali, alkaline earth, transition and heavy metal ions. The respective potential responses of the most sensitive ion-selective TSB-based electrodes clearly exhibited that only the Tm^{3+} ion illustrated a strong response (with a slope of 20.1±0.3 mV/decade) to the TSB-based membrane sensors in comparison with the other tested cations. The presence of lipophilic anions in a cation-selective membrane electrode diminishes the ohmic resistance, enhances the response behavior and selectivity and increases the sensitivity of the membrane electrodes [34-37]. It is well-known that the sensitivity and selectivity of the ion-selective sensors not only depend on the nature of the employed TSB but also on the membrane composition and the used additives [37-42]. Thus, different aspects of the preparation of a Tm^{3+}-selective membrane based on TSB were optimized and the results are given in Table 1. It can be seen that the ionophore amount increase up to a value of 4%, in the presence of 55% of plasticizer (NPOE), results in the best sensitivity (no. 11). The maximum slope of 20.1 ± 0.3 mV per decade of Tm(III) concentration was observed for the membrane no. 11 with 4% of TSB. The membrane with the composition of 30% PVC, 4% TSB, 1% NaTPB, 10% OA and 55 % NPOE (no. 11) was found to be the optimum membrane. After evaluating four solvent mediators NPOE, NB, AP and DBP, NPOE was still found to be the best plasticizer.

The potential response of the Tm(III) PVC-based membrane sensor at varying concentrations of thulium (Fig. 2) indicates a linear working concentration range from 1.0×10^{-7} to 1.0×10^{-2} M. The results may be summarized as follows: the slope of the calibration graph was 20.1 mV per decade of thulium ions concentration; the detection limit of the sensor, as determined from the intersection of the two extrapolated segments of the calibration graph, was 8.6×10^{-8} M; the standard deviation for ten replicate measurements was ± 0.4 mV.

The pH influence on the potential response of the membrane electrode was studied in a pH range 2.0–11.0 for 1.0×10^{-3} M Tm^{3+}. The results are illustrated in Figure 3. As seen, the potential was found to stay fairly constant in the pH range 3.0–8.7 (the pH of the solutions was adjusted by either HNO_3 or NaOH solutions). In alkaline media (pH > 8.7) a gradual change in potential was observed. The observed decrease in potential at higher pH values could be due to the formation of some hydroxyl complexes of Tm^{3+} in solution. At the lower pH values than 3.0, the potentials increase, indicating that the membrane sensor responds to hydrogen ions.

The dynamic response time of the TSB-based Tm^{3+} sensor was next measured at various concentrations (1.0×10^{-7} to 1.0×10^{-2} M) of the test solutions (Fig. 4). The results show that in the whole concentration range the electrode reaches its equilibrium response very fast (<10 s).

Table 1: Optimization of the membrane ingredients

Sensor No.	Composition of the membrane (wt,%) PVC	Plasticizer	TSB	NaTPB, OA	Slope (mV decade^{-1})	Dynamic Linear range (M)
1	30	NPOE, 66	2	2, 0	16.8 ± 0.4	1.0×10^{-6}-1.0×10^{-2}
2	30	NB, 66	2	2, 0	15.4 ± 0.5	1.0×10^{-6}-1.0×10^{-2}
3	30	AP, 66	2	2, 0	14.2 ± 0.6	1.0×10^{-6}-1.0×10^{-2}
4	30	DBP, 66	2	2, 0	13.5 ± 0.3	1.0×10^{-6}-1.0×10^{-2}
5	30	NPOE, 61	2	2, 5	16.5 ± 0.7	1.0×10^{-7}-6.0×10^{-2}
6	30	NPOE, 56	2	2, 10	18.3 ± 0.4	1.0×10^{-7}-1.0×10^{-2}
7	30	NPOE, 51	2	2, 15	17.8 ± 0.2	1.0×10^{-7}-1.0×10^{-2}
8	30	NPOE, 57	1	2, 10	15.5 ± 0.5	1.0×10^{-7}-6.0×10^{-2}
9	30	NPOE, 55	3	2, 10	17.9 ± 0.2	1.0×10^{-7}-1.0×10^{-2}
10	30	NPOE, 54	4	2, 10	18.7 ± 0.4	1.0×10^{-7}-1.0×10^{-2}
11	30	NPOE , 55	4	1, 10	20.1 ± 0.3	1.0×10^{-7}-1.0×10^{-2}
12	30	NPOE , 53	4	3, 10	18.5 ± 0.5	1.0×10^{-7}-1.0×10^{-2}

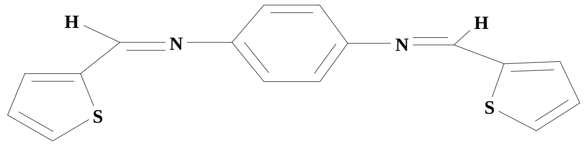

Figure 1. The TSB chemical structure

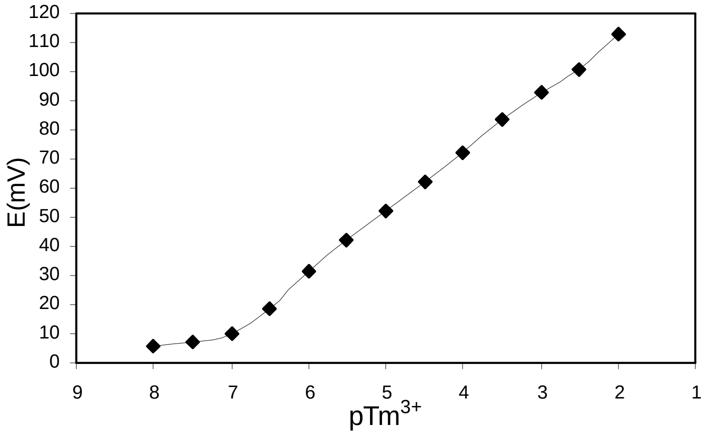

Figure 2. Calibration curve of Tm^{3+} sensor based on TSB.

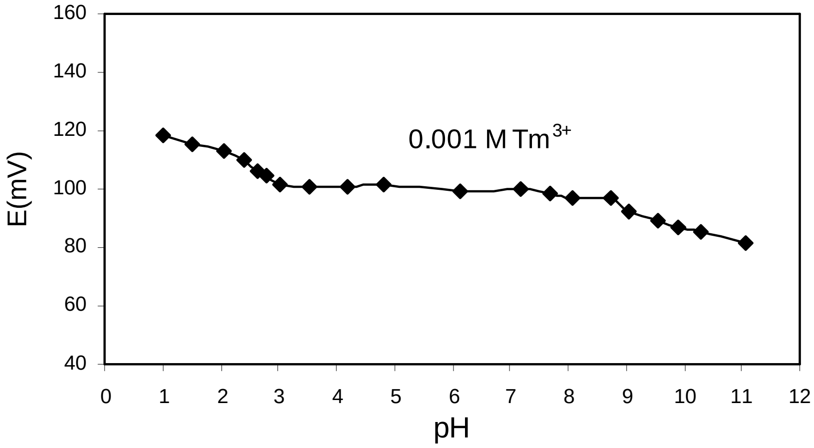

Figure 3. pH effect of the test solution (1.0×10^{-3} M of Tm^{3+}) on the potential response.

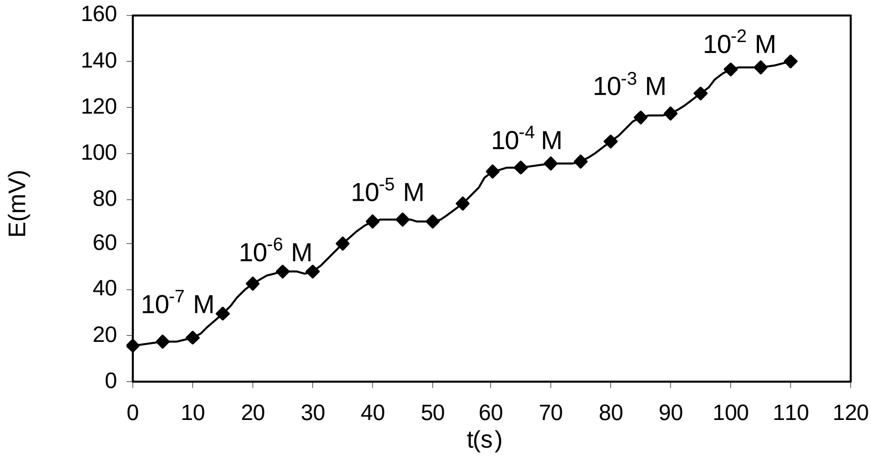

Figure 4. Dynamic response time of the Tm^{3+} sensor for step changes in the Tm^{3+} concentration.

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] John Emsley Nature's building blocks: an A-Z guide to the elements. US: Oxford University Press. **2001**, pp. 442.
[4] HA Zamani; H Ghahremani; H Behmadi. *J. Chem. Pharm. Res.* **2010**, 2, 328.
[5] HA Zamani; G Rajabzadeh; MR Ganjali; *Sensor Lett*., **2009**, 7, 114.
[6] HA Zamani; MS Zabihi; M Rohani; A Zangeneh-Asadabadi; MR Ganjali; F Faridbod; S Meghdadi. *Mater. Sci. Eng. C* **2011**, *31*, 409.
[7] HA Zamani; M Rohani; A Zangeneh-Asadabadi; MS Zabihi; MR Ganjali; M Salavati-Niasari. *Mater. Sci. Eng. C* **2010**, *30*, 917.
[8] HA Zamani; M Masrournia; M Rostame-Faroge; MR Ganjali; H Behmadi. *Sensor Lett.*, **2008**, *6*, 759.
[9] MR Ganjali; A Ghesmi; M Hosseini; MR Pourjavid; M Rezapour; M Shamsipur; M Salavati-Niasari. *Sens. Actuators B* **2005**, *105*, 334.
[10] MR Ganjali; P Norouzi; A Atrian; F Faridbod; S Meghdadi; M. Giahi. *Mater. Sci. Eng. C* **2009**, *29*, 205.
[11] HA Zamani. *Anal. Lett*., **2009**, *42*, 615.
[12] HA Zamani; M Mohammadhosseini; M Nekoei; MR Ganjali. *Sensor Lett.*, **2010**, *8*, 303.
[13] HA Zamani; A Arvinfar; F Rahimi; A Imani; MR Ganjali; S Meghdadi. *Mater. Sci. Eng. C* **2011**, *31*, 307.
[14] HA Zamani; MR Ganjali; P Norouzi; A Tadjarodi; E Shahsavani. *Mater. Sci. Eng. C* **2008**, *28*, 1489.
[15] HA Zamani; M Nekoei; M Mohammadhosseini; MR Ganjali. *Mater. Sci. Eng. C* **2010**, *30*, 480.
[16] HA Zamani; A Imani; A Arvinfar; F Rahimi; MR Ganjali; F Faridbod; S Meghdadi. *Mater. Sci. Eng. C* **2011**, *31*, 588.
[17] VK Gupta, RN Goyal; RA Sharma. *Anal. Chim. Acta* **2009**, *647*, 66.
[18] HA Zamani; G Rajabzadeh; MR Ganjali. *Talanta* **2007**, *72*, 1093.
[19] MR Abedi; HA Zamani; MR Ganjali; P Norouzi. *Sensor Lett*., **2007**, *5*, 516.
[20] HA Zamani; MT Hamed-Mosavian; E Aminzadeh; MR Ganjali; M Ghaemy; H Behmadi; F Faridbod. *Desalination* **2010**, 250, 56.
[21] HA Zamani; MR Ganjali; P Norouzi; M Adib. *Sensor Lett*., **2007**, *5*, 522.
[22] HA Zamani; M Mohaddeszadeh. *Anal. Lett.*, **2008**, *41*, 2710.
[23] HA Zamani; MR Ganjali; P Norouzi; A Tadjarodi; E Shahsavani. *Mater. Sci. Eng. C* **2009**, *28*, 1489.
[24] M Masrournia; HA Zamani; HA Mirrashid; MR Ganjali; F Faridbod. *Mater. Sci. Eng. C* **2011**, *31*, 574.
[25] HA Zamani; G Rajabzadeh; M Masrornia; A Dejbord; MR Ganjali; N Seifi. *Desalination* **2009**, *249*, 560.
[26] HA Zamani; MR Ganjali; P Norouzi; M Adib. *Mater. Sci. Eng. C* **2008**, *28*, 157.
[27] H Behmadi; HA Zamani; MR Ganjali; P Norouzi. *Electrochim. Acta* **2007**, *53*, 1870.
[28] HA Zamani; MT Hamed-Mosavian; E Hamidfar; MR Ganjali; P Norouzi. *Mater. Sci. Eng. C* **2008**, *28*, 1551.
[29] HA Zamani; MR Ganjali; P Norouzi; M Adib; M Aceedy. *Anal. Sci*., **2006**, *22*, 943.
[30] HA Zamani; M Masrournia;, S Sahebnasagh; MR Ganjali. *Anal. Lett.*, **2009**, *42*, 555.
[31] CK Patel; CS Rami; B Panigrahi; CN Patel. *J. Chem. Pharm. Res.* **2010**, 2, 73.
[32] S Chandra; BN Ghogare; LK Gupta; CP Shinde. *J. Chem. Pharm. Res.* **2010**, 2, 240.

[33] SK Srivastava; S Verma; SD Srivastava. *J. Chem. Pharm. Res.* **2010**, 2, 270.
[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] E Naddaf; HA Zamani. *Anal. Lett.,* **2009**, *42*, 2838.
[37] E Ammann; E Pretsch; W Simon; E Lindner; A Bezegh; E Pungor. *Anal. Chim. Acta* **1985**, *171*, 119.
[38] E Bakker; P Buhlmann; E Pretsch. *Electroanalysis* **1999**, *11*, 915.
[39] MR Abedi; HA Zamani. *Anal. Lett.,* **2008**, *41*, 2251.
[40] HA Zamani, MR Ganjali, M Salavati-Niasari. *Transition. Met. Chem.,* **2008**, *33*, 995.
[41] J Koryta. *Anal. Chim. Acta* **1990**, *233*, 1.
[42] E Bakker; P Bühlmann; E Pretsch. *Chem. Rev.,* **1997**, *97*, 3083.