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Effect of metal ions on efficiency of a fabricated Tb(III) PVC membrane electrode

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ABSTRACT

A new selective and sensitive Tb³⁺-PVC membrane sensor was developed using an ion carrier named 1,4-bis[o-(furan-2-carboxamidophenyl)]-1,4-dithiobutane (FCT). The sensor has a linear dynamic range between 1.0×10^{-7} - 1.0×10^{-2} M, with a near Nernstian slope of 20.7 ± 0.2 mV per decade, a detection limit of 7.5×10^{-8} M with a membrane composition of 30% poly(vinyl chloride), 66% dibutyl phthalate (DBP), 2% sodium tetraphenyl borate and 2% FCT. The potentiometric response of the proposed electrode is pH independent in the range of 2.5–7.8. The response time was relatively quick in the whole concentration range (~ 5 s). To investigate the membrane sensor selectivity, its potential response was determined in the presence of various interfering foreign cations using the matched potential method. This sensor demonstrated good selectivity and sensitivity towards the terbium ion for a broad variety of cations, including alkali, alkaline earth, transition and heavy metal ions. The developed sensor was successfully applied as an indicator electrode in the Tb(III) ion potentiometric titration with EDTA.

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

INTRODUCTION

Terbium is a member of the rare-earth family and is known to constitute a strong magnetic material that can be used in the production of permanent magnets. Potentiometric sensors have shown to be very effective tools for analysis of a wide variety of cations, anions, and molecules. They are very simple, inexpensive, and capable of producing reliable responses in a wide concentration range. There have been many studies on ion-selective electrodes for transition and heavy metal ions. Among these metal ions, limited attention has been paid to the development of

lanthanide electrodes [1-12]. There are only some reports in the literature concerning the design of highly selective ionophores for terbium [13-15].

EXPERIMENTAL SECTION

The Merck Co. was the provider for the reagent grades of acetophenone (AP), benzyl acetate (BA), dibutyl phthalate (DBP), nitrobenzene (NB), tetrahydrofuran (THF), sodium tetrphenyl borate (NaTPB), and high relative molecular weight PVC. The ionophore 1,4-bis[o-(furan-2-carboxamidophenyl)]-1,4-dithiobutane was prepared as formerly described [16-19]. However, all of them were used as received. The nitrate and the chloride salts of all cations (all from Merck and Aldrich) were of the highest available purity and used without any further purification, except for vacuum drying over P₂O₅. Triply distilled de-ionized water was used for the experiments.

The PVC membranes were prepared according to the following general procedure. The required ingredients for the membrane construction (30 mg PVC, 66 mg DBP, 2 mg NaTPB and 2 mg ionophore) were mixed and dissolved in 3 mL of dry THF. The resulting mixture was transferred into a glass dish of 2 cm in diameter. The solvent was then evaporated slowly, until an oily concentrated mixture was obtained. A Pyrex tube (5 mm i.d.) was dipped into the oily mixture for about 5 s, so that a transparent film of about 0.3 mm thickness was formed [20–34]. Afterwards, the tube was removed from the mixture, kept at the room temperature for about 12 h and filled with the internal filling solution (1.0×10^{-3} M TbCl₃). The electrode was, finally, conditioned for 24 h by soaking in a (1.0×10^{-3} M) solution of TbCl₃. A silver–silver chloride electrode was used as an internal reference electrode.

All emf measurements were carried out with the following assembly:

Ag–AgCl | 1.0×10^{-3} M TbCl₃ | PVC membrane: test solution | Hg–Hg₂Cl₂, KCl (satd).

A Corning ion analyser 250 pH/mV meter was used for the potential measurements at 25.0 °C. The activities were calculated according to the Debye–Huckel procedure.

RESULTS AND DISCUSSION

The existence of eleven donating atoms (two nitrogen, two sulfur and four donating oxygen) in the FCT structure 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, in order to check the FCT suitability as an ion carrier for different metal ions, it was used to prepare PVC membrane ion selective electrodes in preliminary experiments for a wide variety of cations, including alkali, alkaline earth, transition, and heavy metal ions. In comparison with the other tested cations, only the Tb(III) ion displays a strong response (with a slope of 20.7 ± 0.2 mV per decade) to the FCT-based membrane sensors. Since the plasticizer nature influences the dielectric constant of the membrane phase, the mobility of the ionophore molecules and the state of ligands, it was expected to play a key role in the determination of the selectivity, working concentration range and response time of the membrane electrode. It is well established that the presence of lipophilic anions in cation-selective membrane electrodes diminishes the ohmic resistance, enhances the response behavior and selectivity and increases the sensitivity of the

membrane electrodes [35-37]. The fabricated sensor with composition of 30% PVC; 66% DBP; 2% NaTPB, and 2% ion carrier shows the best performance.

The potentiometric selectivity coefficients, which reflect the relative response of the membrane sensor for the primary ion over other ions that are present in solution, are perhaps the most important characteristics of an ion-selective electrode. For the measurement of the selectivity coefficients, the potential response of the proposed Tb³⁺ ion-selective sensors compared with most common metal ions was investigated by the match potential method (MPM). In accordance with the MPM, the selectivity coefficient is defined as the activity ratio of the primary ion (A) and the interfering ion (B), which gives some potential change in a reference solution.

The potentiometric selectivity coefficients of the sensor towards different ions (Na⁺, Ca²⁺, Ni²⁺, Zn²⁺, Cd²⁺, Co²⁺, Pb²⁺, Pr³⁺, Tm³⁺, Lu³⁺, Ho³⁺, Yb³⁺, Sm³⁺, Gd³⁺ and Fe³⁺) was determined and the results are summarized in Table 1. As can be seen, for all cations used, the selectivity coefficients are in the order of 3.6×10^{-3} or smaller, indicating they would not significantly disturb the functioning of the Tb³⁺ sensor. In Table 2, the major interfering ions, dynamic linear range, the detection limit, pH range, the slope and response time of the proposed electrode are compared with the best data of the previously reported Tb³⁺ selective membrane electrode. It is immediately obvious that the proposed Tb³⁺ sensor in terms of selectivity coefficients, dynamic linear range, detection limit and response time is superior to the previously Tb³⁺ ion-selective electrode.

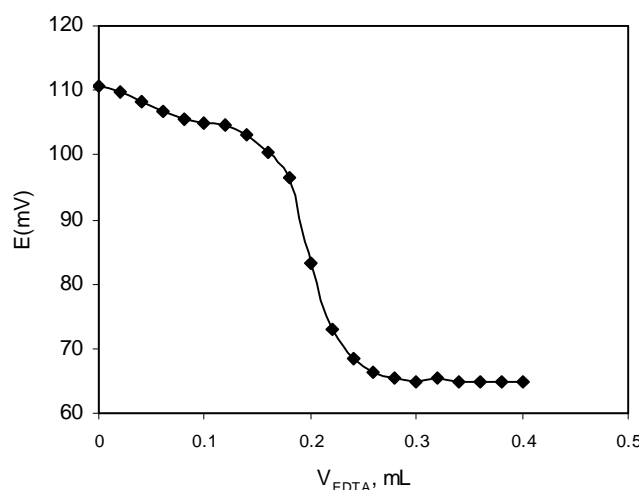
The proposed sensor works well under laboratory conditions and can be successfully employed as an indicator electrode in the potentiometric titrations of Tb³⁺ (1.0×10^{-4} M) with a standard EDTA solution (1.0×10^{-2} M). The respective titration curve is shown in Figure 1. Obviously, the amount of Tb³⁺ ions in solution can be determined with the electrode.

Table 1: Selectivity coefficients of various interfering ions

Interfering ion (B)	Selectivity coefficient ($K_{Tb,B}$)
Pr ³⁺	2.6×10^{-3}
Tm ³⁺	7.9×10^{-4}
Lu ³⁺	2.5×10^{-3}
Ho ³⁺	3.5×10^{-3}
Yb ³⁺	7.3×10^{-4}
Sm ³⁺	2.1×10^{-3}
Gd ³⁺	8.1×10^{-4}
Fe ³⁺	8.7×10^{-4}
Na ⁺	6.2×10^{-4}
Ca ²⁺	7.5×10^{-4}
Ni ²⁺	7.2×10^{-4}
Zn ²⁺	3.6×10^{-3}
Cd ²⁺	6.8×10^{-4}
Co ²⁺	5.7×10^{-4}
Pb ²⁺	2.4×10^{-3}

Table 2: Comparison of different Tb(III) electrodes

Parameter	Ref. 13	Ref. 14	Ref. 15	This work
LR (M)	1.0×10^{-6} - 1.0×10^{-1}	1.0×10^{-6} - 1.0×10^{-1}	1.0×10^{-5} - 1.0×10^{-1}	1.0×10^{-7} - 1.0×10^{-2}
DL (M)	8.0×10^{-7}	8.6×10^{-7}	7.0×10^{-6}	7.5×10^{-8}
Response time (s)	~10	15	<20	~5
pH range	3.5-8.0	3.8-8.2	3.5-7.7	2.5-7.8
Slope (mV/decade)	19.7	19.4	19.8	20.7
Log $K_{sel} > -2$	Gd	Gd	Ce, La, Dy, Yb, Sm	-

Figure 1. Potential titration curve of 20.0 mL from a 1.0×10^{-4} M Tb^{3+} solution with 1.0×10^{-2} M of EDTA

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REFERENCES

- [1] HA Zamani; H Ghahremani; H Behmadi. *J. Chem. Pharm. Res.* **2010**, 2, 328.
- [2] HA Zamani; M Mohammadhosseini; M Nekoei; MR Ganjali. *Sensor Lett.*, **2010**, 8, 303.
- [3] H Behmadi; HA Zamani; MR Ganjali; P Norouzi. *Electrochim. Acta* **2007**, 53, 1870.
- [4] HA Zamani; M Nekoei; M Mohammadhosseini; MR Ganjali. *Mater. Sci. Eng. C* **2010**, 30, 480.
- [5] HA Zamani; MS Zabihi; M Rohani; A Zangeneh-Asadabadi; MR Ganjali; F Faridbod; S Meghdadi. *Mater. Sci. Eng. C* **2011**, 31, 409.
- [6] HA Zamani; MR Ganjali; P Norouzi; M Adib; M Aceedy. *Anal. Sci.*, **2006**, 22, 943.
- [7] HA Zamani; A Arvinfar; F Rahimi; A Imani; MR Ganjali; S Meghdadi. *Mater. Sci. Eng. C* **2011**, 31, 307.
- [8] HA Zamani; G Rajabzadeh; MR Ganjali. *Talanta* **2007**, 72, 1093.
- [9] HA Zamani; A Imani; A Arvinfar; F Rahimi; MR Ganjali; F Faridbod; S Meghdadi. *Mater. Sci. Eng. C* **2011**, 31, 588.
- [10] HA Zamani; G Rajabzadeh; MR Ganjali; P Norouzi. *Anal. Chim. Acta* **2007**, 598, 51.

- [11] HA Zamani; G Rajabzadeh; MR Ganjali. *Bull. Chem. Soc. Japan* **2007**, *80*, 172.
- [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; MR Ganjali; P Norouzi; A Tadjarodi; E Shahsavani. *Mater. Sci. Eng. C* **2008**, *28*, 1489.
- [14] HA Zamani; G Rajabzadeh; MR Ganjali. *J. Braz. Chem. Soc.* **2006**, *17*, 1297.
- [15] MR Ganjali; A Ghesmi; M Hosseini; MR Pourjavid; M Rezapour; M Shamsipur; M Salavati-Niasari. *Sens. Actuators B* **2005**, *105*, 334.
- [16] S Meghdadi, V Mirkhani, PC Ford. *Synth. Commun.* **2010**, In press.
- [17] CK Patel; CS Rami; B Panigrahi; CN Patel. *J. Chem. Pharm. Res.* **2010**, *2*, 73.
- [18] S Chandra; BN Ghogare; LK Gupta; CP Shinde. *J. Chem. Pharm. Res.* **2010**, *2*, 240.
- [19] SK Srivastava; S Verma; SD Srivastava. *J. Chem. Pharm. Res.* **2010**, *2*, 270.
- [20] HA Zamani; G Rajabzadeh; MR Ganjali; *Sensor Lett.*, **2009**, *7*, 114.
- [21] MR Abedi; HA Zamani; MR Ganjali; P Norouzi. *Sensor Lett.*, **2007**, *5*, 516.
- [22] MR Ganjali; F Faridbod; P Norouzi; M Adib. *Sens. Actuators B* **2006**, *120*, 119.
- [23] MR Ganjali; P Norouzi; A Atrian; F Faridbod; S Meghdadi; M. Giahi. *Mater. Sci. Eng. C* **2009**, *29*, 205.
- [24] HA Zamani; MR Ganjali; P Norouzi; M Adib. *Sensor Lett.*, **2007**, *5*, 522.
- [25] HA Zamani. *Anal. Lett.*, **2009**, *42*, 615.
- [26] MR Abedi; HA Zamani. *Anal. Lett.*, **2008**, *41*, 2251
- [27] MR Ganjali; P Norouzi; A Atrian; F Faridbod; S Meghdadi; M. Giahi. *Mater. Sci. Eng. C* **2009**, *29*, 205.
- [28] HA Zamani; MR Ganjali; M Salavati-Niasari. *Transition. Met. Chem.*, **2008**, *33*, 995.
- [29] HA Zamani; MT Hamed-Mosavian; E Hamidfar; MR Ganjali; P Norouzi. *Mater. Sci. Eng. C* **2008**, *28*, 1551.
- [30] HA Zamani; G Rajabzadeh; M Masrornia; A Dejbord; MR Ganjali; N Seifi. *Desalination* **2009**, *249*, 560.
- [31] VK Gupta, RN Goyal; RA Sharma. *Anal. Chim. Acta* **2009**, *647*, 66.
- [32] MR Ganjali; N Davarkhah; H Ganjali; B Larijani; P Norouzi; M Hosseini. *Int. J. Electrochem. Sci.* **2009**, *4*, 762.
- [33] MR Ganjali; P Norouzi; T Alizadeh; A Tajarodi; Y Hanifehpour. *Sens. Actuators B* **2007**, *120*, 487.
- [34] HA Zamani; MT Hamed-Mosavian; E Aminzadeh; MR Ganjali; M Ghaemy; H Behmadi; F Faridbod. *Desalination* **2010**, *250*, 56.
- [35] P Bühlmann; E Pretsch; E Backer. *Chem. Rev.* **1998**, *98*, 1593.
- [36] MR Ganjali; M Rahimi; B Maddah; A Moghimi; S Borhany. *Anal. Sci.* **2004**, *20*, 1427.
- [37] HA Zamani; MR Ganjali; P Norouzi; M Adib. *Mater. Sci. Eng. C* **2008**, *28*, 157.
- [38] Y Umezawa; K Umezawa; H Sato. *Pure Appl. Chem.*, **1995**, *67*, 507.
- [39] MR Ganjali; P Norouzi; A Daftari; F Faridbod; M Salavati-Niasari. *Sens Actuators B* **2007**, *120*, 673.