Materials Science and Engineering C 33 (2013) 870–874

Contents lists available at SciVerse ScienceDirect

Materials Science and Engineering C

journal homepage: www.elsevier.com/locate/msec

Fabrication of a PVC membrane samarium(III) sensor based on N,N′,N″-tris(4-pyridyl)trimesic amide as a selectophore

Hassan Ali Zamani [a,*], Fatemeh Naghavi-Reyabbi [b], Farnoush Faridbod [c], Majid Mohammadhosseini [d], Mohammad Reza Ganjali [c], Azadeh Tadjarodi [e], Maryam Rad [e]

[a] Department of Applied Chemistry, Mashhad Branch, Islamic Azad University, Mashhad, Iran
[b] Resident of General Surgery, Endoscopic and Minimaly Invasive Surgery Research Center, Ghaem Hospital, Faculty of Medicine, Mashhad University of Medical Sciences, Mashhad, Iran
[c] Center of Excellence in Electrochemistry, Faculty of Chemistry, University of Tehran, Tehran, Iran
[d] Department of Chemistry, Faculty of Basic Sciences, Shahrood Branch, Islamic Azad University, Shahrood, Iran
[e] Department of Chemistry, Iran University of Science and Technology, Tehran, Iran

ARTICLE INFO

Article history:
Received 5 January 2012
Received in revised form 28 July 2012
Accepted 4 November 2012
Available online 16 November 2012

Keywords:
Sensor
Ion-selective electrode
Potentiometry
PVC membrane

ABSTRACT

A new ion-selective electrode for Sm^{3+} ion is described based on the incorporation of N,N′,N″-tris(4-pyridyl) trimesic amide (TPTA) in a poly(vinylchloride) (PVC) matrix. The membrane sensor comprises nitrobenzene (NB) as a plasticizer, and oleic acid (OA) as an anionic additive. The sensor with the optimized composition shows a Nernstian potential response of 19.8 ± 0.5 mV decade^{-1} over a wide concentration range of 1.0×10^{-2} and 1×10^{-6} mol L^{-1}, with a lower detection limit of 4.7×10^{-7} mol L^{-1} and satisfactor applicable pH range of 3.6–9.2. Having a short response time of less than 10 s and a very good selectivity towards the Sm^{3+} over a wide variety of interfering cations (e.g. alkali, alkaline earth, transition and heavy metal ions) the sensor seemed to be a promising analytical tool for determination of the Sm^{3+}. Hence, it was used as an indicator electrode in the potentiometric titration of samarium ion with EDTA. It was also applied to the direct samarium recovery in binary mixtures.

1. Introduction

Application of the rare-earth elements in industry is growing and the average increase over the past years has been 5–15%. High purity individual lanthanides are used increasingly as major components in laser, phosphors, magnetic bubble memory films, refractive index lenses, fiber optics and superconductors [1]. On the other hand, these elements are only slightly toxic based on the Hodge-Sterner classification system and hence it can be handled safely, but when rare-earth vapors or dust enter the respiratory system, they tend to be somewhat more toxic and remain in the slowly being absorb into the body [2]. Samarium, a bright silver rare-earth element, is an important member of the lanthanide series and is known to constitute strong magnetic material and thus has found particular use in production of permanent magnets. Samarium can be very dangerous if present in the working environment, since its dusts can be inhaled with air leading to lung embolisms, especially caused by long-term exposures thereto. It can also be a threat to the liver in high concentration, because it can remain in the body and get adsorbed slowly [3,4].

Regarding the importance of determination of the element, many techniques have been used to this end, most of which belong to the spectroscopic family such as ICP-MS, electron spin resonance, high resolution γ-spectroscopy atomic emission spectroscopy, spectrophotofluorimetric, laser-based multi step resonance ionization and some neutron activation methods. These methods are either time intensive or they constitute multiple sample manipulations which is expensive.

The application of ion selective sensors has however proved to be a simple method offering advantages like speed and ease of sample preparation, short response times, reasonable selectivity, wide linear dynamic ranges, and low cost. A survey on the literature proves that there exist only a limited number of reports on selective determination of Sm^{3+} ions in the presence of other rare earth elements by electrochemical method [3–7]. Numerous reports on the selective and sensitive PVC-membrane ISEs have recently been published [8–26] which made us believe another ion selective sensor could be introduced for the potentiometric determination of Sm^{3+} ion based on N,N′,N″-tris(4-pyridyl)trimesic amide (TPTA) (Fig. 1). The initial solution study on the complexation of TPTA and cation ions showed a selective behavior between TPTA and samarium ions.

2. Experimental

2.1. Reagents

Merck Chemical and Aldrich Co. were the suppliers for the nitrate and chloride salts of all cations (Europium nitrate pentahydrate, Gadolinium(III) nitrate hexahydrate, Erbium(III) chloride hexahydrate,

* Corresponding author.
E-mail address: haszamani@yahoo.com (H.A. Zamani).

0928-4931/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.msec.2012.11.014

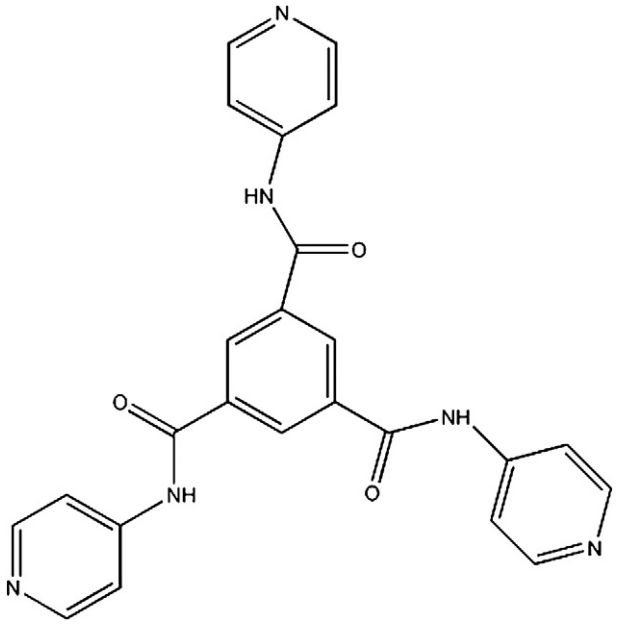

Fig. 1. The TPTA structure.

Neodymium(III) nitrate hexahydrate, Praseodymium(III) nitrate hexahydrate, Thulium(III) nitrate pentahydrate, Ytterbium(III) nitrate pentahydrate, Chromium(III) chloride hexahydrate, Lead(II) nitrate, Nickel(II) chloride hexahydrate, Cobalt(II) nitrate hexahydrate, Cadmium chloride hydrate, Copper(II) nitrate hydrate, Calcium chloride, Magnesium nitrate hexahydrate, Sodium chloride, and Pottasium Nitrate) and the reagent grades of benzyl acetate (BA), acetophenone (AP), nitrobenzene (NB), 2-dibutyl phthalate (DBP), sodium tetraphenyl borate (NaTPB), oleic acid (OA), tetrahydrofuran (THF), and high relative molecular weight PVC (average molecular weight ~100000). The chemicals were used without further purification. During the experiments, doubly distilled deionized water was used.

2.2. Synthesis of TPTA

The ionophore N,N′,N″-tris(4-Pyridyl)trimesic amide (TPTA) was prepared as formerly described [27]. A solution of 4-aminopyridine (3.4 g, 36.0 mmol) and distilled triethylamine (5.4 mL, 38.8 mmol) in distilled THF (40 mL) was added dropwise to a solution of 1,3,5-benzene tricarboxytrichloride (3.22 g, 12.0 mmol) in THF (12 mL) at 0 °C. As triethylamine (1.8 mL, 5.78 mmol) was added, the reaction mixture was stirred for 7 h. The temperature was then allowed to step up to room temperature. The gummy product was collected by filtration and washed with THF. The product was recrystallized from DMSO (140 mL) and H_2O (300 mL) by stirring for 1 h. The product was washed with acetone (200 mL) by stirring for 1 day. The pale yellowish white powder was collected by filtration, washed with acetone, and dried under vacuum for 35 h at room temperature (0.0957 g).

2.3. Electrode preparation

The membrane solution preparation involved the dissolution of proper amounts the ionophore, powdered PVC, NaTPB or OA as ionic additives and NB plasticizer in 3 mL of THF. The THF content of the resulting mixture was then gradually evaporated so as to get an oily concentrated mixture. Then A Pyrex tube (5-mm o.d.) was dipped into the oily mixture for ~10 s, to achieve a transparent membrane of 0.3 mm in thickness at the tip [28–41]. The tube were then kept at room temperature for 24 h and filled with an internal solution (1.0×10^{-3} mol L^{-1} $SmCl_3$), and finally conditioned for 36 h by soaking in a 1.0×10^{-2} mol L^{-1} $SmCl_3$ solution. A silver/silver chloride electrode was used as the internal reference electrode.

2.4. The emf measurements

The potentiometric cell used for the emf (electromotive force) measurements had the configuration of

$$\mathrm{Ag\text{–}AgCl}\left|\text{internal solution, } 1.0\times10^{-3}\ \text{mol}\ L^{-1}\mathrm{SmCl_3}\right.$$
$$\left|\text{PVC membrane}\right|\text{sample solution}\left|\mathrm{Hg\text{–}Hg_2Cl_2},\ \mathrm{KC1}\ (\text{satd.})\right.$$

And a Corning ion analyzer with a 250 pH/mV meter for the potential measurements at 25.0 ± 0.1 °C.

All activities were calculated according to the Debye–Hückel procedure [42].

3. Result and discussion

The complexation study in acetonitrile solution [35–38,40] was initially carried out to find the selectivity behavior of TPTA in complexation. The study showed that a selective complexation between Sm(III) and TPTA in comparison with other alkali, alkaline earth, transition metals and other lanthanide cations.

3.1. The potential response of the TPTA-based sensor

To assess TPTA as a potential ion carrier for different metal ions a series of experiments was performed using the species to prepare the PVC membrane ion-selective electrodes for a wide variety of cations, including alkali, alkaline earth, transition and heavy metal ions. The

Table 1
Optimization of the membrane ingredients.

No.	Composition (w/w, %)				Slope (mV decade^{-1})	Dynamic linear range (mol L^{-1})
	TPTA	Plasticizer	Additive	PVC		
1	2	NB, 68	NaTPB,2	30	17.5 ± 0.3	1.0×10^{-2}–1.0×10^{-5}
2	2	AP, 68	NaTPB,2	30	16.2 ± 0.5	1.0×10^{-2}–1.0×10^{-5}
3	2	BA, 68	NaTPB,2	30	15.7 ± 0.4	1.0×10^{-2}–1.0×10^{-4}
4	2	DBP, 68	NaTPB,2	30	15.3 ± 0.6	1.0×10^{-2}–1.0×10^{-4}
5	2	NB, 61	NaTPB,2; OA5	30	17.2 ± 0.4	1.0×10^{-2}–5.0×10^{-6}
6	2	NB, 56	NaTPB,2; OA10	30	18.6 ± 0.5	1.0×10^{-2}–1.0×10^{-6}
7	2	NB, 51	NaTPB,2; OA15	30	17.4 ± 0.3	1.0×10^{-2}–1.0×10^{-6}
8	2	NB, 58	NaTPB,0; OA10	30	13.6 ± 0.6	1.0×10^{-2}–1.0×10^{-5}
9	2	NB, 57	NaTPB,1; OA10	30	17.5 ± 0.3	1.0×10^{-2}–1.0×10^{-5}
10	2	NB, 55	NaTPB,3; OA10	30	17.8 ± 0.4	1.0×10^{-2}–1.0×10^{-6}
11	1	NB, 57	NaTPB,2; OA10	30	17.9 ± 0.6	1.0×10^{-2}–1.0×10^{-6}
12	3	NB, 55	NaTPB,2; OA10	30	19.8 ± 0.5	1.0×10^{-2}–1.0×10^{-6}