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A novel luminescent optical fibre probe based on immobilized tridentate bis(phosphinic amide)-phosphine oxide for europium(III) ion aqueous detection in situ

F.J. Sainz-Gonzalo [a], C. Elosua [b], J.F. Fernández-Sánchez [a,*], C. Popovici [c], I. Fernández [c], F.L. Ortiz [c], F.J. Arregui [b,*], I.R. Matias [b], A. Fernández-Gutiérrez [a]

[a] Department of Analytical Chemistry, Faculty of Sciences, University of Granada, Av. Fuentenueva s/n, 18071 Granada, Spain
[b] Public University of Navarre, Department of Electrical and Electronic Engineering, 31006 Pamplona, Spain
[c] Laboratory of Organic Chemistry, University of Almería, Ctra. Sacramento s/n, 04120 Almería, Spain

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ABSTRACT

A novel optical fibre probe based on a tridentate bis(phosphinic amide)-phosphine oxide $PhPO(C_6H_4POPhN(CH(CH_3)_2)_2)_2$ (ligand **1**) has been developed for the detection of europium(III) ions in water. The dip coating technique was used to deposit the ligand **1** encapsulated on a poly(vinyl chloride) membrane onto an optical fibre. The optimum deposition thickness of the membrane was 280 ± 40 nm. The sensing mechanism relies on the reaction between europium(III) ion and ligand **1**, which produces a strong luminescent complex of stoichiometry 1:2 Eu(III):Ligand **1** with a maximum emission peak around 612 nm. Two different configurations, aerial and aqueous, were tested for measuring the luminescence off-line and on-line, respectively. The proposed probe showed a response time of 92 s in the aqueous configuration (in situ detection of europium(III) ions in water). The luminescence of the proposed probe displayed a power-law response for the europium(III) concentration in a broad range of concentrations of at least 5 orders of magnitude, from 10 nM to 1 mM, with a correlation coefficient (R^2) of the fitted curve better than 0.99.

1. Introduction

Europium is one of the rare earth elements (REEs), which is used in anodic rays of televisions and monitor screens, fluorescent lamps, glasses, lasers, catalysts, polished glasses as well as in oil and atomic industries [1]. Diverse REE toxicity tests in animals have demonstrated that they provoke alterations in the reproduction and nervous system; and damage in liver and spleen [2–5].

Furthermore, REEs can cause lung embolisms including cancer in humans with long-term exposures of their dusts or vapours in the working environment. Therefore, the determination of europium has taken special interest in the last years due to its use in many applications in different fields and its possible toxic effects [6].

The most stable oxidation state of europium element is europium(III), which is the target ion to be detected herein. Traditional analytical methods such as spectrophotometry [7], fluorescence [8], inductively coupled plasma optical emission spectrometry (ICP-OES) [9], inductively coupled plasma mass spectrometry (ICP-MS) [10], multiple square wave voltammetry (MSWV) [11] and chelation ion chromatography (CIC) with absorbance detection [12] are used for the europium(III) determination in water samples. These methods, although accurate and with low detection limits, require expensive and sophisticated instrumentation as well as complicated and multistep sample preparation and long analysis times, so they are not very appropriate for analysis of a large number of samples. Therefore, the analysis is often limited to laboratory level only. However, the rapid and field detection of europium(III) ions is of tremendous interest in environmental applications.

The development of chemical sensors has involved a powerful alternative to the mentioned methods, because chemical sensors minimize these disadvantages and permit on-line, in situ and real time monitoring [13–16]. Therefore, the cost-effective and rapid determination of europium(III) has been achieved employing electrochemical [17–21] and optical sensors [22–23].

More specifically, sensors based on optical fibre are attracting considerable attention due to their importance in applications such as environmental monitoring, biomedical sensing and industrial process control [25–28]. Optical fibre sensors present numerous advantages such as passive nature, electromagnetic interference immunity, wide bandwidth and possibility of multiplexing [29],

* Corresponding authors. Tel.: +34 958248409; fax: +34 958243328.
E-mail addresses: jffernan@ugr.es (J.F. Fernández-Sánchez), parregui@unavarra.es (F.J. Arregui).

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among others. Furthermore, these sensors are small in size, light weight, minimally invasive and allow the remote use [30]. Different configurations can be employed for the fabrication of optical fibre devices [31–33]. The use of thin-film coatings in optical fibre sensors can enhance the sensing properties as well as adding novel functions [34]. These optical fibre chemical sensors are a kind of optical sensors, in which the immobilization of an appropriate reagent is developed in an optomembrane [35]. By choosing the proper membrane and reagent, it is possible the determination of different heavy metal ions [36–39].

In the particular case of europium(III) ion detection, the sensitized 4f-luminiscence of lanthanides [40] is a well-known technique, which is widely used for the trace determination of europium(III) ions [23]. Europium(III) ion presents a rich photophysical and coordination chemistry for the formation of luminescent complexes, which show large Stokes shift, long luminescence lifetimes and emission spectra with very narrow bands. The complex 1:2 Eu(III):Ligand **1** absorbs energy from UV–visible radiation at the characteristic wavelengths of the ligand **1** and emits electromagnetic radiation in the visible region to the characteristic emission wavelengths of europium(III) ion [23]. The observed emission peaks at 586, 612 and 690 nm tally with the europium(III) ion specific transitions [41]. The formation constant ($\log \beta_{120}$) of complex 1:2 Eu(III):Ligand **1** was 10.44 (25° C, pH 7.0, 75% EtOH (v/v) and 30 mM NaCl), and the pEu value was 6.1 [23].

Thus, the ligand **1** could be a good candidate for the development of an optical fibre sensor for europium(III) ion detection. We have recently shown the structural insights of the species established when mixing ligand **1** with yttrium [42] and europium precursors [23] (Scheme 1).

With respect to the immobilization of the reagent, polymer inclusion membranes (PIMs) could be used for entrapping the ligand **1**. PIMs are synthetic membranes in which the ligand is immobilized inside a polymeric matrix with the presence of a plasticizer. The nature of the immobilized ligand, plasticizers and ionic additives employed has significant influence on the sensitivity and selectivity of PIMs [43,44]. They offer numerous advantages as effective reagent immobilization, easy preparation, versatility and good mechanical properties, which have been used previously for the determination of europium(III) ions [18,19,23].

Ligand **1** was immobilized into a PVC membrane [23] and the resulting sensing film was sensitive to Eu(III) ion and shows a very good selectivity towards europium(III) with respect to other lanthanides(III) ions such as La, Sm, Tb and Yb [23]. This paper describes the development and optimization of a luminescent optical fibre probe for detecting europium(III) ions in situ and in water. Thus, the proposed sensor combines the advantages of optical sensors and the excellent properties of optical fibres with the sensitized luminescence of lanthanides including the great characteristics of polymer inclusion membranes. To our knowledge, this is the first time that a luminescent optical fibre probe has been developed for europium(III) ion, which has proven to have a great potential to be assembled into a portable, simple and cheap optical sensor for Eu(III) ion monitoring.

2. Experimental

2.1. Chemicals and reagents

Ligand **1** was prepared according to the synthesis procedure reported previously [23,45]. Its schematic chemical structure is shown in Fig. 1. Europium(III) chloride hexahydrate (99.9% Eu, REO) was obtained from ABCR. Poly(vinyl chloride) high molecular weight (PVC) was purchased from Fluka. Bis(2-ethylhexyl) sebacate (DOS) was obtained from Aldrich. Tetrahydrofuran (THF) was obtained from Merck. Potassium hydrogen phthalate, absolute ethanol, concentrated sulphuric acid and hydrogen peroxide were purchased from Panreac. All chemicals and reagents were of analytical grade except for DOS (reagent grade) and were used as received without further purification.

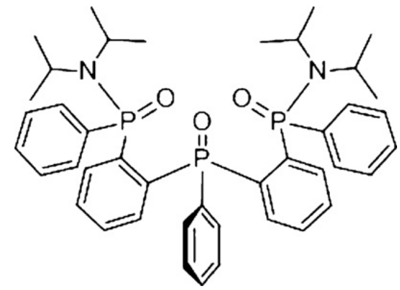

Fig. 1. Schematic chemical structure of the tridentate bis(phosphinic amide)-phosphine oxide PhPO (ligand **1**).

Aqueous solutions were prepared using doubly distilled water obtained from a Nanopure Analytical Barnstead system (Barnstead International, Dubuque, USA). A stock Eu(III) solution (1.0×10^{-2} M) was prepared by dissolving 0.0916 g of $EuCl_3 \cdot 6H_2O$ in 25 mL of deionized water. Working standard solutions of Eu(III) were prepared by appropriate dilution of the stock solution. Stock and working standard solutions of Eu(III) ions were stored in amber glass bottles at 4 °C. A stock hydrogen phthalate buffer solution (0.1 M) at pH 5.0 was prepared as follows: 4.085 g of potassium hydrogen phthalate (0.2 M) were dissolved in 100 mL of deionized water. Next, this obtained solution was adjusted with NaOH 1 M until pH was 5.0. Finally, it was diluted to a volume of 200 mL with deionized water. Working standard buffer solutions were prepared by appropriate dilution of the stock buffer solution before mentioned. Measurement solutions were prepared mixing the working standard solutions of Eu(III) ions and the stock hydrogen phthalate buffer solution in the adequate proportion, and subsequently, filling up with deionized water. The piranha solution (3:1) was prepared immediately before its use mixing 2.55 mL of sulphuric acid 98% (w/w) and 0.85 mL of hydrogen peroxide 30% (w/v), respectively.

2.2. Instrumentation and apparatus

A Leica DM2500 microscope (Leica Microsystems, Wetzlar, Germany) interfaced with a computer was used for visualizing the images of the optical fibres. The deposition thickness on optical fibres was measured by scanning electron microscopy (SEM) using a Carl Zeiss FE-SEM Ultra Plus microscope (Carl Zeiss Microscopy, USA). A Crison GLP 22 pH meter (Crison, Alella, Spain) was used to adjust the pH of the stock buffer solution.

A Nadetech ND-R rotating dip coater (Nadetech Innovations, Pamplona, Spain) was employed for the deposition of homogeneous and thin films on optical fibre by dip coating technique. It is formed by two programmable axes with vertical and rotational movements. The speed range of dipping is covered between 0.01 mm/s and 40 mm/s. It is fully controlled by an easy handling software which allows programming the parameters of each deposition (dipping speed, raising speed, initial position, final position, dipping time, drying time, etc.).

Ika MS3 digital mechanical stirrer (Ika Works, Wilmington, USA) was used to obtain the membrane cocktail solution.

2.3. Experimental set-up

A schematic diagram of the experimental set-up for probe response monitoring is depicted in Fig. 2. Two arrangements of the experimental set-up were employed for measuring