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Study of interfering ions on a constructed Eu(III) ion selective electrochemical sensor

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ABSTRACT

A Eu(III) ion-selective polyvinyl chloride (PVC) membrane sensor based on 1,4-bis[o-(thiophene-2-carboxamidophenyl)]-1,4-dithiobutane as a new nitrogen-, oxygen- and sulfur-containing sensing material was constructed. The sensor has a Nernstian slope of 19.5 ± 0.6 mV per decade across a wide concentration range between 1.0×10^{-6} and 1.0×10^{-2} M and a detection limit of 6.7×10^{-7} M. In this work, selectivity coefficients were determined by the matched potential method (MPM). The advantage of the sensor is its excellent Eu(III)-selectivity with regard to most common metal ions, and especially, all lanthanide ions. It was used as an indicator electrode in potentiometric titration of 25 mL of a 1.0×10^{-4} M Eu(III) solution with a 1.0×10^{-2} M EDTA solution.

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

INTRODUCTION

Europium is one of the members of lanthanide series that can be found in houses and equipments such as color televisions, fluorescent lamps, energy-saving lamps and glasses. Available methods for low level determination of rare earth ions in a solution includes: spectrophotometry, mass spectrometry (MS), inductively couple plasma atomic emission spectrometry (ICP-AES) and inductively couple plasma mass spectrometry (ICP-MS). Isotope dilution mass spectrometry, X-ray fluorescence spectrometry, etc. are also used in some laboratories. These methods are either time consuming, involving multiple sample manipulations, or too expensive for most analytical laboratories. Potentiometer membrane sensors as a detection method are used for monitoring more than seventy cations and anions, demonstrating distinct advantages such as preparation speed, ease and process, relatively short response times, reasonable selectivity, wide linear dynamic ranges and low cost [1-25]. Literature survey shows that there is a few reported sensor for Eu(III) ions [26-29]. In this work we report a Eu(III) membrane sensor based on 1,4-bis[o-(thiophene-2-carboxamidophenyl)]-1,4-dithiobutane to determine Eu(III) ions with a nice Nernstian response over a relatively wide working range.

EXPERIMENTAL SECTION

Reagent grade dibutyl phthalate (DBP), nitrobenzene (NB), acetophenon (AP), benzyl acetate (BA), high relative molecular weight polyvinyl chloride (PVC), sodium tetraphenyl borate (NaTPB) and tetrahydrofurane (THF) were purchased from Merck and used as received. The ionophore 1,4-bis[o-(thiophene-2-carboxamidophenyl)]-1,4-dithiobutane was synthesized as described elsewhere [30-33]. The chloride and nitrate salts of the cations used (from Merck and Aldrich) were all of the highest purity available, and used without any further purification except for vacuum drying over P_2O_5. Triply distilled deionized water was used throughout.

The PVC membrane preparation involved the complete blending of the following compounds; 30 mg of powdered PVC, 66 mg of NB and 2 mg of an additive (NaTPB) in 3 mL THF. To this solution, 2 mg of ionophore were added and mixed well. Then, the resulting mixture was transferred into a glass dish of 2 cm in diameter. A Pyrex tube (5 mm o.d.) was dipped into the mixture for about 5 s, leading to the formation of a transparent membrane (about 0.3 mm in thickness) [10–20]. Afterwards, the tube was removed from the mixture, kept at room temperature for at least 12 h and filled with an internal filling solution (1.0×10^{-3} M $EuCl_3$). At last, the electrodewas conditioned for 24 h by soaking in a 1.0×10^{-2} M $EuCl_3$. 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 $EuCl_3$ | PVC membrane: test solution| $Hg–Hg_2Cl_2$, 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

In the initial experiment, the ionophore applied as a neutral carrier in the construction of PVC membrane sensors for metal ions, including alkali, alkaline earth, transition and heavy metal ions, in the same conditions. Then, their potential responses were measured. A typical calibration curves for tri, di, and mono valent cations M^{3+}, M^{2+}, M^{+} and anions A^{3-}, A^{2-}, A^{-} show a slope of 59 mV per decade, 28 mV per decade, and 19 mV per decade respectively. The sign of the slopes is positive for cations and negative for anions. The results show that the membrane displays a Nernstian response with slope of 19.5±0.6 mV per decade to the concentration of Eu(III) ions in a concentration range of 1.0×10^{-6} M–1.0×10^{-2} M. The limit of detection of the Eu(III) sensor, was 6.7×10^{-7} M. The proposed sensor with composition of 30% PVC; 66% NB; 2% NaTPB, and 2% 1,4-bis[o-(thiophene-2-carboxamidophenyl)]-1,4-dithiobutane displays the best performance.
The influence of interfering ions on the response behavior of the ion-selective membrane electrodes is usually described in terms of selectivity coefficients. For the selectivity coefficients

measurement, the matched potential method [34-38] was used. According to the MPM, the selectivity coefficient is defined as the activity (concentration) ratio of the primary ion and the interfering ion, which gives the same potential change in a reference solution. Subsequently, the potential change should be measured upon changing the primary ion activity. Then, the interfering ion would be added to an identical reference solution until the same potential change would be obtained. The MPM selectivity coefficient, K^{MPM}, is then given by the resulting primary ion to the interfering ion activity (concentration) ratio, $K^{MPM} = a_A/a_B$. The resulting potentiometric selectivity coefficients values are summarized in Table 1. Clearly, the selectivity coefficients for mono and divalent metal ions (Na^+, K^+, Ca^{2+}, Ni^{2+}, Cu^{2+} and Pb^{2+}) are in the range of $7.3 \times 10^{-4} – 6.8 \times 10^{-4}$ and $7.5 \times 10^{-4} – 3.5 \times 10^{-3}$, respectively. For the trivalent ions (Tm^{3+}, Tb^{3+}, Er^{3+}, Lu^{3+}, Ho^{3+}, Yb^{3+}, Sm^{3+}, Nd^{3+}, Dy^{3+}, La^{3+}, Gd^{3+}, Al^{3+} and Fe^{3+}), the selectivity coefficients are in the range of 6.4×10^{-3} or smaller, indicating they would not radically disturb the function of the developed Eu^{3+} membrane sensor. Therefore, the electrode could be used for the Eu^{3+} ions detection in the presence of certain interfering ions.

Furthermore, Table 2 compares the linearity range, detection limit, pH range, response time and selectivity coefficients of the Eu(III) sensor with the only reported Eu(III) electrodes in the literature [26-29]. From the reported data in Table 2, it is clear that not only the concentration range, the response time, the detection limit and pH range of the proposed electrode but also its selectivity coefficients of the sensor are superior to previously reported one.

The developed Eu(III) ion-selective electrode was found to work well under laboratory conditions. It was used as an indicator electrode in the titration of 1.0×10^{-4} M Eu(III) ions solution with a standard 1.0×10^{-2} M EDTA. The resulting titration curve is shown in Figure 1, where it can be noticed that the amount of Eu(III) ions in solution can be determined with the sensor.

Table 1: Selectivity coefficients of various interfering ions

Interfering ion (B)	Selectivity coefficient ($K_{Eu, B}$)
Tm^{3+}	8.9×10^{-4}
Tb^{3+}	8.2×10^{-4}
Er^{3+}	4.1×10^{-3}
Lu^{3+}	2.7×10^{-3}
Ho^{3+}	7.7×10^{-4}
Yb^{3+}	3.5×10^{-4}
Sm^{3+}	6.4×10^{-3}
Nd^{3+}	5.6×10^{-3}
Dy^{3+}	3.8×10^{-3}
La^{3+}	2.5×10^{-3}
Gd^{3+}	4.2×10^{-3}
Fe^{3+}	2.2×10^{-3}
Al^{3+}	4.3×10^{-3}
Pb^{2+}	8.4×10^{-4}
Na^{+}	8.6×10^{-4}
K^{+}	7.3×10^{-4}
Ca^{2+}	7.5×10^{-4}
Cu^{2+}	3.5×10^{-3}
Ni^{2+}	2.7×10^{-3}

Table 2: Comparison of selectivity coefficients, detection limit, pH range, response time and linearity range of the developed Eu^{3+} sensor and the formerly mentioned Eu^{3+} ion-selective electrodes

Parameters	Ref. 26	Ref. 27	Ref. 28	Ref. 29	This work
Detection limit (M)	5.0×10^{-5}	5.0×10^{-6}	1.5×10^{-7}	7.8×10^{-7}	6.7×10^{-7}
Linear range (M)	7.0×10^{-5}-1.0×10^{-1}	1.0×10^{-5}-1.0×10^{-2}	4.0×10^{-7}-1.0×10^{-2}	1.0×10^{-6}-1.0×10^{-2}	1.0×10^{-6}-1.0×10^{-2}
Response time	<20 s	<5 s	25 s	<15 s	~5 s
Interfering ion (B) K_{sel} More than 10^{-2}	Gd, Tb, Ce, Co, Cu,Sm, La, Pr, Zn, Ca, Yb	Hg, La, Ce, Gd, Fe, Tb, Sm	-	-	-
pH range	3.0-7.0	3.0-8.5	3.5-8.0	3.5-7.8	2.7-8.8

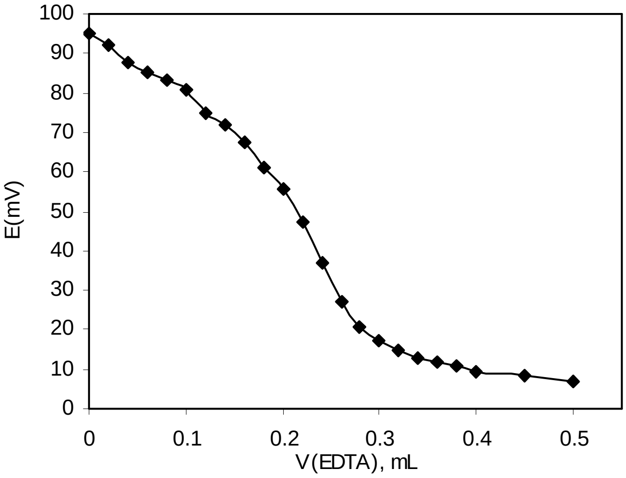

Figure 1. Potential titration curve of 25.0 mL from a 1.0×10^{-4} M Eu^{3+} solution with 1.0×10^{-2} M of EDTA.

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