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Fabrication of Eu^{3+} Polymeric Membrane Ion-Selective Sensor

Hassan Ali Zamani,^{a,*} Neda Rohani,^a Mohammad Reza Abedi,^a Soraia Meghdadi,^b

^aDepartment of Applied Chemistry, Quchan branch, Islamic Azad University, Quchan, Iran

^bDepartment of Chemistry, Isfahan University of Technology, Isfahan, Iran

ABSTRACT

A new $\text{Eu}(\text{III})$ PVC membrane sensor has been constructed by using 1,4-bis[o-(thiophene-2-carboxamidophenyl)]-1,4-dithiobutane (TCD) as a suitable ion carrier. The proposed electrode based on (TCD) with nitrobenzene (NB) as a solvent mediator in a poly(vinyl chloride) membrane matrix exhibited a near-Nernstian response to Eu^{3+} in the concentration range of 1.0×10^{-6} to 1.0×10^{-2} M with a slope of 19.5 mV per decade of activity of Eu^{3+} , a relatively fast response of ~5 s in a wide pH range 2.7-8.8. The lower limit of detection was 6.7×10^{-7} M.

Keywords: PVC Membrane, Potentiometry, Ion-Selective Electrode, Sensor.

INTRODUCTION

Construction and then application of ion-selective electrode as a potentiometric sensor offers interesting advantages such as simplicity, speed, fast response, low cost, wide linearity range and procedure. These characteristics have inevitably led to sensors for ionic species. Although instrumental techniques such as inductively couple plasma atomic emission spectrometry (ICP-AES), neutron activation analysis, mass spectrometry (MS), X-ray fluorescence spectrometry, inductively couple plasma mass spectrometry (ICP-MS), Isotope dilution mass spectrometry, etc, provide an accurate measurement in trace amount of elements. But all of these methods are expensive and need complicated equipments [1,2]. In this paper we report a highly selective europium electrode using 1,4-bis[o-(thiophene-2-carboxamidophenyl)]-1,4-dithiobutane (TCD) as an active material in poly vinyl chloride matrix for the preparation of Eu^{3+} -selective electrode.

EXPERIMENTAL SECTION

Analytical reagent grade chemicals and triply-distilled water were used for preparing all aqueous solutions. The ionophore 1,4-bis[o-(thiophene-2-carboxamidophenyl)]-1,4-dithiobutane was prepared as formerly described [3-6]. The high molecular weight PVC powder, dibutyl phthalate

(DBP), sodium tetraphenyl borate (NaTPB), acetophenone (AP), nitrobenzene (NB), benzylacetate (BA) and tetrahydrofuran (THF) were obtained from Fluka. The nitrate and chloride salts of all the used cations (all from Merck) were of the highest available purity and were used without any further purification, except for vacuum drying over P_2O_5 .

The membrane solutions were prepared by thoroughly dissolving 2 mg of TCD, 30 mg of powdered PVC, 66 mg of NB and 2 mg of NaTPB in 5 mL of fresh THF. The resulting clear mixture was evaporated slowly, until the attainment of an oily concentrated mixture. A Pyrex tube (3 - 5 mm o.d. on top) was dipped into the mixture for about 5 s, so that the formation of a transparent membrane (about 0.3 mm) in thickness could be achieved [7-20]. Then, the tube was removed from the mixture, kept at room temperature for 12 h and then filled with an internal solution (1.0×10^{-3} M $EuCl_3$). The electrode was finally conditioned for 24 h by soaking in a 1.0×10^{-2} M Eu^{3+} ion solution. A silver/silver chloride electrode was used as an internal reference electrode.

The EMF measurements with the polymeric membrane were carried out with the following cell assemblies:

Ag–AgCl | internal solution, 1.0×10^{-3} M $EuCl_3$ | PVC membrane | test solution | Hg–Hg₂Cl₂, KCl (satd.)

A Corning ion analyzer 250 pH/mV meter was used for the potential measurements at 25.0 °C. The emf observations were made relative to a double-junction saturated calomel electrode (SCE, Philips) with the chamber filled with an ammonium nitrate solution. The activities were calculated according to the Debye–Hückel procedure.

RESULTS AND DISCUSSION

In order to check the TCD suitability as an ionophore for different metal ions, TCD was used as a neutral carrier to design numerous PVC membrane ISE under identical conditions for a great variety of metal ions, including alkali, alkaline earth, transition and heavy metal ions. Only the Eu^{3+} ions displayed a stronger response (with a slope of 19.5 ± 0.6 mV per decade) to the TCD-developed sensor in comparison with that of the other tested cations.

It is well-known that the sensitivity and selectivity of the ion-selective sensors not only depend on the nature of the employed TCD but also on the membrane composition and the used additives. 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 [21-40]. Consequently, the influences of the membrane composition, the plasticizer nature and amount as well as the NaTPB amount, as a suitable lipophilic additive on the potential response of the Eu^{3+} sensor, were investigated. The resulting data are summarized in Table 1, where it is revealed that the membrane no. 4 with the PVC:NB:TCD:NaTPB ratio of 30:66:2:2 exhibited a Nernstian slope over a broad Eu^{3+} ion concentration range.

The measuring range of an ion-selective electrode includes the linear part of the calibration graph (emf vs. pEu^{3+}) (Fig. 1). The slope and the linear range of the resulting calibration graph were 19.5 ± 0.6 mV per decade and 1.0×10^{-6} – 1.0×10^{-2} M, respectively. Limit of detection, defined as the Eu^{3+} ion concentration obtained when two segment of the calibration graph was intersected each other. Here, it was 6.7×10^{-7} M.

pH Effect of the test solution (1.0×10^{-3} M) on the potential response of the membrane sensor (membrane no. 4) was tested in the pH range of 1.5–11.0. These results are depicted in Fig. 2. As it can be seen from Fig. 2, the potential remains constant over a pH range of 2.7–8.8.

Table 1: Composition of membrane ingredients

Membrane No.	Composition (wt %)				Slope (mV/decade)	Concentration range (M)
	PVC	Plasticizer	NaTPB	TCD		
1	30	AP, 66	2	2	17.6 ± 0.3	1.0×10^{-6} - 1.0×10^{-2}
2	30	BA, 66	2	2	16.8 ± 0.5	1.0×10^{-6} - 1.0×10^{-2}
3	30	DBP, 66	2	2	16.3 ± 0.4	1.0×10^{-6} - 1.0×10^{-2}
4	30	NB, 66	2	2	19.5 ± 0.6	1.0×10^{-6} - 1.0×10^{-2}
5	30	NB, 68	0	2	12.2 ± 0.5	1.0×10^{-5} - 1.0×10^{-2}
6	30	NB, 67	1	2	17.3 ± 0.3	1.0×10^{-6} - 1.0×10^{-2}
7	30	NB, 65	3	2	18.4 ± 0.4	1.0×10^{-6} - 1.0×10^{-2}
8	30	NB, 67	2	1	15.5 ± 0.6	1.0×10^{-6} - 1.0×10^{-2}
9	30	NB, 65	2	3	17.8 ± 0.5	1.0×10^{-6} - 1.0×10^{-2}

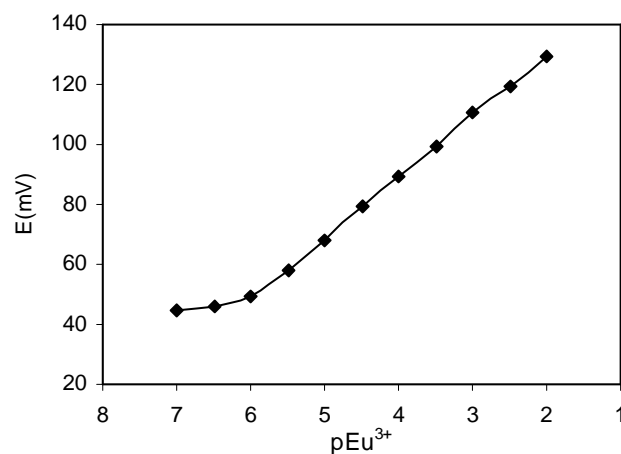


Figure 1. Calibration curve of Eu(III) electrode based on TCD.

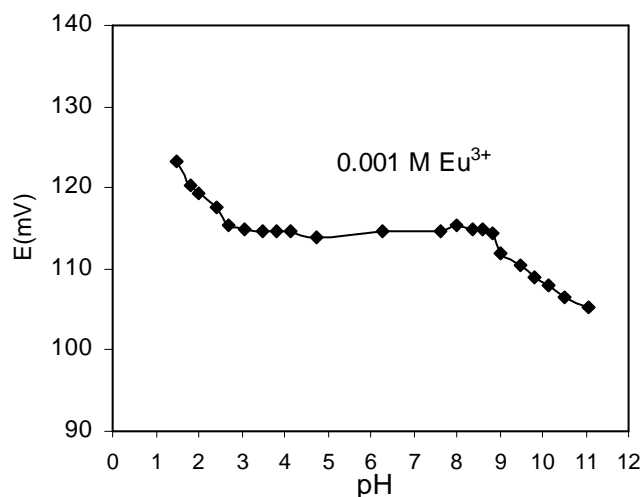


Figure 2. pH effect of the test solution (1.0×10^{-3} M of Eu^{3+}) on the potential response.

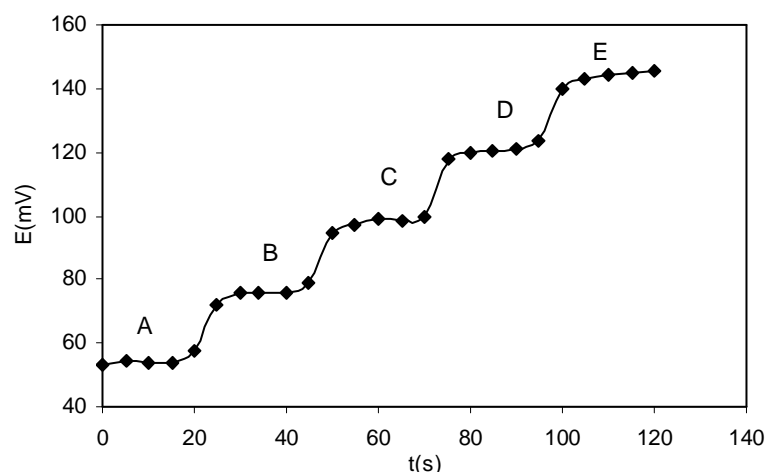


Figure 3. Dynamic response time of the europium electrode for step changes in the Eu^{3+} concentration: A) 1.0×10^{-6} M, B) 1.0×10^{-5} M, C) 1.0×10^{-4} M, D) 1.0×10^{-3} M, E) 1.0×10^{-2} M.

The average time required for the Eu^{3+} sensor to reach a potential within ± 1 mV of the final equilibrium value after successive immersion in a series of Eu^{3+} solutions, each having a 10-fold difference in concentration (from 1.0×10^{-6} M to 1.0×10^{-2} M), was measured. The dynamic response time thus obtained was about 5 s in the whole concentration ranges (Fig. 3).

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