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A Highly Selective and sensitive Lu³⁺ PVC-Membrane Sensor based on Di-tert-butyl-1-(tert-butyl thio)-1,2-hydrazine dicarboxylate

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ABSTRACT

Di-tert-butyl-1-(tert-butyl thio)-1,2-hydrazine dicarboxylate (DBHC) was used as a sensing material which plays the role of a suitable ionophore in the creation of a Lu(III) PVC membrane sensor. It shows a Nernstian behavior (with slope of 20.2 ± 0.4 mV per decade) over a wide concentration range (1.0×10^{-6} - 1.0×10^{-2} M) with the detection limit of 5.8×10^{-7} M. The sensor has a very short response time, in the whole concentration range (~ 5 s), and can be used in the pH range of 2.9-8.8.

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

INTRODUCTION

In recent decades, many intensive studies on the design and synthesis of highly selective ionophores as sensory molecules for ion-selective electrodes (ISEs) have been reported [1]. Lutetium is a very rare element commonly used as a fluorescent and magnetic material, the uses of which are growing, due to its applicability in the production of catalysts used in oil and gas technologies and glass polish. The main methods for the low-level determination of Lu(III) ions are ICP-MS, ICP-AES, spectrophotometry. Isotope dilution mass spectrometry, neutron activation analysis, and X-ray fluorescence spectrometry are also used in some laboratories. Nevertheless, almost all of these methods are expensive and time consuming, with the exception of one; the ion selective electrode (ISE) method. It is one of the most popular electrochemical methods and it can be employed as a sensor for the determination of ions. These sensors are fast, selective, low cost, inexpensive and can be prepared easily [2-25]. Recently, we have reported a number of selective and sensitive membrane sensors for the some metal ions [26-31]. In this paper we wish to introduce a new Lu(III) PVC-based membrane sensor base on a new ionophore Di-tert-butyl-1-(tert-butyl thio)-1,2-hydrazine dicarboxylate (DBHC) as an excellent neutral ion carrier.

EXPERIMENTAL SECTION

The ionophore Di-*tert*-butyl-1-(*tert*-butyl thio)-1,2-hydrazine dicarboxylate was purchased from Fluka. Nitrate and chloride salts of all cations, as well as reagent grade, dibutyl phthalate (DBP), benzyl acetate (BA), acetophenon (AP), nitrobenzene (NB), sodium tetraphenyl borate (NaTPB), tetrahydrofuran (THF) and high relative molecular weight PVC of the highest purity available were procured from Merck and Aldrich, and used without any further treatments, except for the vacuum drying of the salts over P₂O₅. Doubly distilled deionized water was used in all experiments.

The membrane solutions were prepared by thoroughly dissolving 30 mg PVC, 66 mg of NB, 2 mg NaTPB and 2 mg of ionophore in 5 mL of fresh THF. The mixture was completely dissolved in 3 mL of THF. The resulting clear mixture was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (3–5 mm i.d.) was dipped into the mixture for about 10 s so that a transparent membrane of about 0.3 mm thickness is formed [25-31]. The tube was then pulled out from the mixture and kept at room temperature for about 24 h. The tube was then filled with internal filling solution (1.0×10⁻³ M of LuCl₃). The electrode was finally conditioned for 36 h by soaking in a 1.0×10⁻³ M lutetium chloride. 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| 1.0 × 10⁻³ M LuCl₃ | PVC membrane: test solution| Hg–Hg₂Cl₂, KCl (satd).

The potential measurements were made using a Corning ion analyser 250 pH/mV meter. The measurements were performed at room temperature (25.0 °C) and the activities of the species were calculated according to the Debye–Huckel procedure.

RESULTS AND DISCUSSION

The ionophore was used as a potential neutral ion carrier in the fabrication of the PVC membrane sensors for a number of alkali, alkaline earth, transition and heavy metal ions. The potential responses of all the membrane sensors were studied in a wide range of concentrations. Among different tested metal ions, only the Lu³⁺ ion displays a stronger and the most sensitive response (with a slope of 20.2 ± 0.4 mV per decade) and seems to be suitably determined by the DBHC-PVC membrane.

The effect of membrane ingredients on the properties of the membrane electrodes, including the effect of the plasticizer, the plasticizer/PVC ratio, the nature and amount of ionophore, and especially, the nature and amount of the additives used, have been reported to significantly influence the behavior of ion-selective electrodes. The presence of lipophilic anions in cation-selective membranes based on neutral carriers is known not only to decrease the ohmic resistance and enhances the response behavior and selectivity of the electrodes but also, in cases where the extraction capability of the membrane is low, it increases the sensitivity of the membrane electrodes [32-36]. The results are summarized in Table 1. As it is seen from Table 1, it is revealed that the four different plasticizers used, DBP, AP, NB and BA have almost the same results if the optimum composition is used. Also from Table 1 (membrane no.4), NB is a more effective solvent mediator than DBP, AP and BA in preparing the Lu³⁺ ion-selective electrode. It is noteworthy that the plasticizer nature influences both the dielectric constant of the polymeric

membranes and the mobility of the ionophore and its complex [37]. From Table 1, it is evident that the increase of the DBHC amount in the membranes (No. 4, 8 and 9) up to 2% resulted in greater slopes. A maximum slope of 20.2 ± 0.4 mV per decade of lutetium concentration was observed for the membrane No. 4 with 2% of DBHC. However, the membrane sensor with a composition of 30 % PVC; 66 % NB; 2 % NaTPB and 2 % DBHC exhibits the best performance. The developed sensor (composition no. 4) demonstrated a linear response in the range of 1.0×10^{-6} – 1.0×10^{-2} M at varying lutetium ions concentrations (Fig. 1). The slope of the calibration curve was 20.2 ± 0.4 mV per decade of Lu^{3+} ions activity. The detection limit, defined as the Lu(III) concentration obtained after the extrapolation of the linear region of the standard plot to the baseline potential, was 5.8×10^{-7} M.

Table 1: Composition of membrane ingredients

Sensor No.	Composition (wt %)				Slope (mV/decade)	Concentration range (M)
	PVC	Plasticizer	NaTPB	DBHC		
1	30	DBP, 66	2	2	15.2 ± 0.6	1.0×10^{-5} – 1.0×10^{-2}
2	30	BA, 66	2	2	16.3 ± 0.5	1.0×10^{-5} – 1.0×10^{-2}
3	30	AP, 66	2	2	17.4 ± 0.2	1.0×10^{-5} – 1.0×10^{-2}
4	30	NB, 66	2	2	20.2 ± 0.4	1.0×10^{-6} – 1.0×10^{-2}
5	30	NB, 68	0	2	13.4 ± 0.5	1.0×10^{-5} – 1.0×10^{-2}
6	30	NB, 67	1	2	18.3 ± 0.4	1.0×10^{-6} – 1.0×10^{-2}
7	30	NB, 65	3	2	18.2 ± 0.3	1.0×10^{-6} – 1.0×10^{-2}
8	30	NB, 67	2	1	15.8 ± 0.6	1.0×10^{-6} – 1.0×10^{-2}
9	30	NB, 65	2	3	18.5 ± 0.3	1.0×10^{-6} – 1.0×10^{-2}

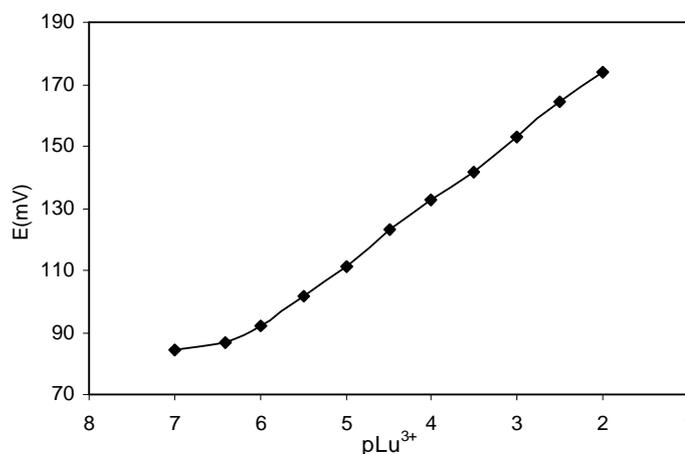


Figure 1. Calibration curve of Lu(III) electrode based on DBHC.

The effect of pH on the potential response behavior of the sensor was studied across a pH range of 1.0–11.0 and using a Lu^{3+} solution of a fixed concentration of 1.0×10^{-3} M throughout the experiment. The results are shown as Fig. 2. As it can be seen, the potential remains fairly constant in the pH range of 2.9–8.8 (the pH adjustment of the solutions was performed either by HNO_3 or NaOH).

In analytical applications, the dynamic response time consists of an essential parameter in the sensor field. In this study, the practical response time was recorded by changing the concentration of the Lu^{3+} solution from 1.0×10^{-6} to 1.0×10^{-2} M. The corresponding results are illustrated in Figure 3, where it can be evidently observed that within 5 s reasonably fast and stable potentials were achieved.

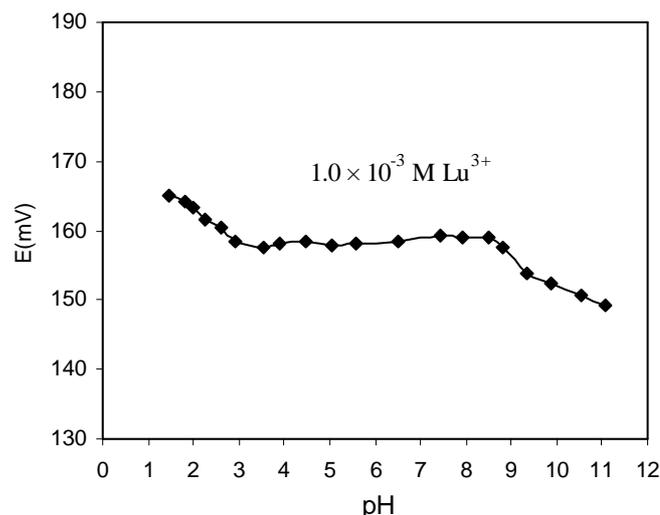


Figure 2. pH effect of the test solution (1.0×10^{-3} M of Lu^{3+}) on the potential response.

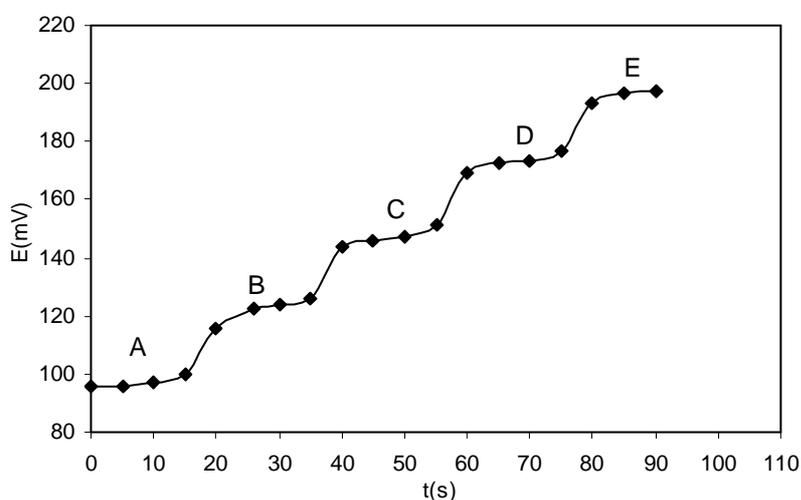


Figure 3. Dynamic response time of the lutetium electrode for step changes in the Lu^{3+} concentration: A) 1.0×10^{-6} M, B) 1.0×10^{-5} M, C) 1.0×10^{-4} M, D) 1.0×10^{-3} M, E) 1.0×10^{-2} M.

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