Investigation of response behavior of a Lu^{3+} ion-selective sensor in presence of interfering ions

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ABSTRACT

A selective and sensitive polymeric membrane sensor based on the incorporation of Di-tert-butyl-1-(tert-butyl thio)-1,2-hydrazine dicarboxylate as a sensing compound in a poly(vinylchloride) (PVC) for the determination of the Lu^{3+} ions was constructed.. The membrane sensor further comprises nitrobenzene (NB) as a plasticizer, and the role of sodium tetraphenyl borate (NaTPB) as an anionic additives was also evaluated. To investigate the membrane electrode selectivity, its potential response was monitored in the presence of various interfering foreign cations using the matched potential method. The sensor's selectivity against a lot of common alkaline, alkaline earth, transition, heavy metals and specially lanthanide ions was very good. The developed sensor was successfully applied as an indicator electrode in Lu^{3+} ion potentiometric titration with EDTA. The constructed sensor accuracy was investigated by the monitoring of Lu^{3+} in mixtures of two and three different ions.

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

Solvent polymeric membrane based ISEs, together with the incorporation of new ion carriers, have shown to be a very useful tool for clinical, environmental, and chemical analyses as well as for process monitoring. In the area of membrane based ISEs, emphasis has been focused on the development of new ion-carriers. Fabrication of a new, ionspecific ISEs with high selectivity and sensitivity, wide linear concentration range, long lifetime and good reproducibility, is always in need [1, 2]. The fact that lanthanides have similar chemical and physical properties, makes their analyses an extremely time consuming and complicated procedure, especially in case other similar ions are present in the sample solution [3]. Lutetium is one of the rare elements that can

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be found in houses in equipment such as color televisions, fluorescent and energy-saving lamps, and glasses. Lutetium is hence dumped in the environment, mainly from petrol-producing industries [4]. Finding a method for its determination is hence is of desire. Such elements are inductively couple plasma mass spectrometry (ICP-MS), inductively couple plasma atomic emission spectrometry (ICP-AES), mass spectrometry (MS), Isotope dilution mass spectrometry, X-ray fluorescence spectrometry, etc. Almost all of the mentioned methods are expensive and time consuming, as compared to the application of ion selective electrodes (ISEs). ISEs are among the most popular electrochemical devices that usually show fast and selective responses in addition to their low cost and ease of preparation and use [5-21]. Regarding the fact that there have been some reports on lutetium sensors based on different ionophores [22, 23]. In this work, a ion selective electrode for Lu(III) ions based on Di-tert-butyl-1-(tert-butyl thio)-1,2-hydrazine dicarboxylate was fabricated and the effect of some metal ions as interfering ions on the response behavior of the proposed sensor was investigated.

EXPERIMENTAL SECTION

The Merck Chemical and the Aldrich Co. were the suppliers for the nitrate and chloride salts of all cations and the reagent grades of dibutyl phthalate (DBP), benzyl acetate (BA), acetophenon (AP), nitrobenzene (NB), sodium tetraphenyl borate (NaTPB), tetrahydrofuran (THF) and high relative molecular weight PVC. The ionophore Di-tert-butyl-1-(tert-butyl thio)-1,2-hydrazine dicarboxylate was purchased from Fluka. All reagents were used without any modification. As far as the nitrate and chloride salts of all employed cations are concerned, they were of the highest available purity and were P_2O_5-vacuum dried. During the experiments, doubly distilled deionized water was used.

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 10 s, leading to the formation of a transparent membrane (about 0.3 mm in thickness) [24–36]. Afterwards, the tube was removed from the mixture, kept at room temperature for at least 24 h and filled with an internal filling solution (1.0×10^{-3} M LuCl$_3$). At last, the electrodewas conditioned for 36 h by soaking in a 1.0×10^{-3} M LuCl$_3$. 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 LuCl$_3$ | PVC membrane: test solution| Hg–Hg$_2$Cl$_2$, 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 order to check the ionophore suitability as ion carrier for different metal ions, it was employed as a neutral carrier to design numerous PVC membrane ISE for a great variety of metal ions.

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From the obtained data, only the Lu^{3+} ion displayed the Nernstian behavior in comparison with that of the other tested cations.

It should be noted that the sensitivity and selectivity for each ion-selective electrodes depend significantly on the membrane ingredients, the nature and amount of the ionophore, the nature of the solvent mediator and the used additive [37-41]. Thus, the membrane composition influence on the potential responses of the Lu(III) sensor was investigated. From data, the ionophore amount increase up to a 2 % value in the presence of 2 % of NaTPB and 66 % of polar solvent (NB) results in the best sensitivity. However, the membrane sensor with a composition of 30 % PVC; 66 % NB; 2 % NaTPB and 2 % ionophore (with the slope 20.2 ± 0.4 mV per decade) exhibits the best performance. The optimum electrode response was obtained after its conditioning in a 1.0×10^{-2} M lutetium chloride for 24 h and the developed sensor exhibited a Nernstian response slope of (20.2 ± 0.4 mV/decade) across a broad concentration range of 1.0×10^{-6}-1×10^{-2} M with the detection limit of 5.8×10^{-7} M. The potential response of the electrode was considered in the pH range of 1.0-11.0 and the potential remained fairly constant in the pH range of 2.9–8.8.

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 [42-44] was used. The procedure was expected to report selectivity coefficients analytically relevant for practical applications. 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. Thus, 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 matched potential method selectivity coefficient, K^{MPM}, is then given by the resulting primary ion to the interfering ion activity (concentration) ratio, $K^{MPM} = a_A/a_B$. Table 1 presents the potentiometric selectivity coefficients of the ionophore based lutetium selective electrode. The selectivity coefficients for the all mono and divalent metal ions (Na^+, K^+, Ca^{2+}, Co^{2+}, Ni^{2+} and Pb^{2+}) and trivalent ions (Dy^{3+}, Pr^{3+}, Ho^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Tm^{3+}, La^{3+}, Fe^{3+} and Cr^{3+}) are smaller than 8.8×10^{-4} and 4.5×10^{-3} respectively, and they can not disturb the functioning of the Lu^{3+} membrane electrode.

Table 2 compared the detection limit, linearity range, response time, selectivity coefficients and the pH of the suggested sensor with the best previously reported Lu(III) sensors [45, 46]. It is evident that the newly developed sensor is superior to the formerly reported lutetium sensors in terms of selectivity, detection limit, response time and dynamic concentration range.

The suggested Lu^{3+} ion-selective membrane electrode was successfully applied as an indicator electrode in the titration of Lu^{3+} (1.0×10^{-4} M) with a standard EDTA solution (1.0×10^{-2} M). The resulting titration curve is displayed in Figure 1, where it can be observed that the Lu^{3+} amount in solution could be accurately detected by the electrode.

Because of high selectivity and low detection limit of the developed Lu^{3+} sensor (membrane no. 4), it was also applied for the determination of Lu^{3+} ions concentration in mixtures of two and

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three different ions. The corresponding results in Table 3 reveal that the recovery of Lu^{3+} ions in all mixtures is acceptable.

Table 1: Selectivity coefficients of various interfering ions

Interfering ion (B)	Selectivity coefficient ($K_{Lu, B}$)
Dy^{3+}	4.5×10^{-3}
Pr^{3+}	8.4×10^{-4}
Ho^{3+}	7.7×10^{-4}
Nd^{3+}	4.6×10^{-4}
Sm^{3+}	8.9×10^{-4}
Eu^{3+}	6.8×10^{-4}
Gd^{3+}	3.1×10^{-3}
Tm^{3+}	2.8×10^{-3}
La^{3+}	2.3×10^{-4}
Fe^{3+}	3.5×10^{-3}
Cr^{3+}	8.6×10^{-4}
Na^{+}	4.2×10^{-4}
K^{+}	1.0×10^{-4}
Ca^{2+}	6.4×10^{-4}
Co^{2+}	8.8×10^{-4}
Ni^{2+}	6.3×10^{-4}
Pb^{2+}	5.6×10^{-4}

Table 2: Comparison of selectivity coefficients, detection limit, linearity range, response time and pH range of the proposed Lu^{3+} sensor and the formerly reported Lu^{3+} sensor

Parameters	Ref. 45	Ref. 46	This work
Detection limit (M)	8.0×10^{-7}	7.2×10^{-7}	5.8×10^{-7}
Linear range (M)	1.0×10^{-6}-1.0×10^{-2}	1.0×10^{-6}-1.0×10^{-2}	1.0×10^{-6}-1.0×10^{-2}
Response time	<10	<10	~5
Interfering ion (B) K_{sel} More than 5.0×10^{-3}	Nd, Gd, Dy	Nd, Ho, Tm, Dy	-
pH range	4.5-8.0	2.7-10.6	2.9-8.8

Table 3: Determination of Lu^{3+} ions in mixtures of different ions

| Serial no.	Composition	Observed content (M)
1	0.00010 M $Lu(NO_3)_3$ + 0.001 M $Eu(NO_3)_3$ + 0.001 M $Tb(NO_3)_3$	0.000102
2	0.00010 M $Lu(NO_3)_3$ + 0.001 M $Sm(NO_3)_3$ + 0.001 M $Gd(NO_3)_3$	0.000096
3	0.00010 M $Lu(NO_3)_3$ + 0.001 M $Er(NO_3)_3$ + 0.001 M $Pr(NO_3)_3$	0.000097
4	0.00010 M $Lu(NO_3)_3$ + 0.001 M $Yb(NO_3)_3$ + 0.001 M $La(NO_3)_3$	0.000103
5	0.00010 M $Lu(NO_3)_3$ + 0.001 M $Cr(NO_3)_3$ + 0.001 M $Fe(NO_3)_3$	0.000098
6	0.00010 M $Lu(NO_3)_3$ + 0.001 M $Pb(NO_3)_2$ + 0.001 M $Co(NO_3)_2$	0.000097
7	0.00010 M $Lu(NO_3)_3$ + 0.001 M $Ni(NO_3)_2$+ 0.001 M KNO_3	0.000106
8	0.00010 M $Lu(NO_3)_3$ + 0.001 M $Dy(NO_3)_3$	0.000098
9	0.00010 M $Lu(NO_3)_3$ + 0.001 M $Nd(NO_3)_3$	0.000102
10	0.00010 M $Lu(NO_3)_3$ + 0.001 M $Tm(NO_3)_3$	0.000096

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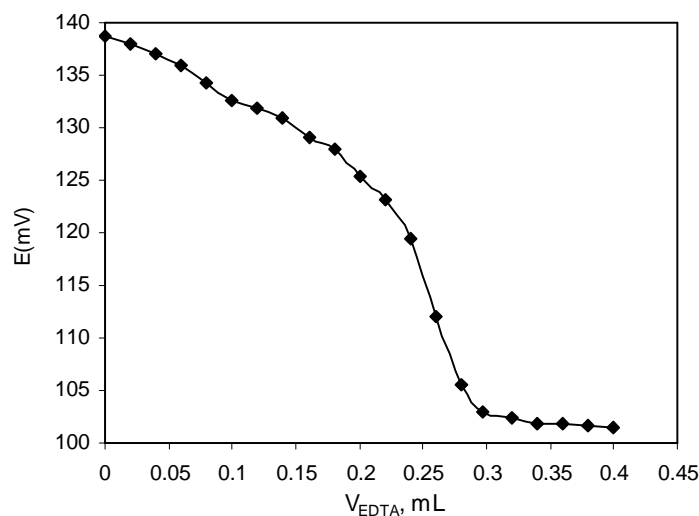
Figure 1. Potential titration curve of 25.0 mL from a 1.0×10^{-4} M Lu^{3+} solution with 1.0×10^{-2} M of EDTA.

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