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New Potentiometric Poly(vinyl chloride) Membrane Sensor for Selective Monitoring of Lutetium(III) Based on Di(N-succinimidyl)oxalate

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A new poly(vinyl chloride) membrane chemical sensor has been fabricated for the determination of lutetium(III) in aqueous solutions using Di(N-succinimidyl)oxalate (DSO) as a sensing ionophore. The Lu^{3+} sensing system was constructed by incorporating Di(N-succinimidyl)oxalate (DSO) as a neutral sensing ionophore, in the plasticized PVC membrane containing sodium tetraphenyl borate as a liphophilic anionic additive. The electrode composition of 30 wt% PVC powder, 8 wt% ionophore (DSO), 60 wt% NB, and 2 wt% NaTPB showed the stable potential response to Lu^{3+} ions with the Nernstian slope of 20.5±0.3 mVdecade^{-1} with a detection limit of 7.5×10^{-8} mol L^{-1}. In the pH range of 2.8–9.1, the sensor exhibits a wide concentration range of 1.0×10^{-7} to 1.0×10^{-2} mol L^{-1}, with a relatively fast response time (~5 second). In term of selectivity, Lu^{3+} sensor has a good selectivity over all lanthanide members and common alkali, alkaline earth, transition, and heavy metal ions. The constructed sensor was successfully used as an indicator in the potentiometric titration of Lu(III) ions with EDTA. It was also applied to the determination of lutetium(III) content in various mixtures of different ions.

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

1. INTRODUCTION

Rare-earth oxides have numerous applications. For instance, they are used in equipment such as color televisions, fluorescent and energy-saving lamps, and production of optical glasses and in the preparation of gasoline-cracking catalysts. They are also used in iron and steel industries to remove sulfur, carbon and other electronegative elements from iron and steel [1, 2]. Lutetium is a rare earth metal and perhaps the most expensive of all rare elements. It is found in small amounts with all rare earth metals, and is very difficult to separate from other rare elements. Lutetium is very expensive to obtain on useful quantities and therefore it has very few commercial uses. Lutetium is mildly toxic by ingestion, but its insoluble salts are non-toxic. Like other rare-earth metals lutetium is regarded as having a low toxicity rating but it and its compounds should be handled with care [3]. Lutetium usually occurs in association with the element yttrium and is sometimes used in metal alloys and as a catalyst in various chemical reactions [4].

The main methods for the low-level determination of Lu(III) ions 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. These methods are either time consuming, involving multiple sample manipulations, or too expensive for most analytical laboratories. Finding a method for lanthanides monitoring without destruction of sample which has enough sensitivity and reliability is of great importance. Potentiometric determination by ion-selective electrodes (ISEs) offers a simple, low cost and fast analysis procedure without any special equipment. Moreover, this method is nondestructive, without any sample pretreatment requirement. Literature survey revealed that only a number of lutetium(III) sensors based on different ionophores have been reported [5-7]. In recent year, highly selective and sensitive PVC-membrane ion-selective electrodes were reported for some ions [8–35]. In this article, we introduce a new Lu(III) PVC-based membrane sensor based on Di(N-succinimidyl)oxalate (DSO) (Figure 1) as an excellent neutral ion carrier.

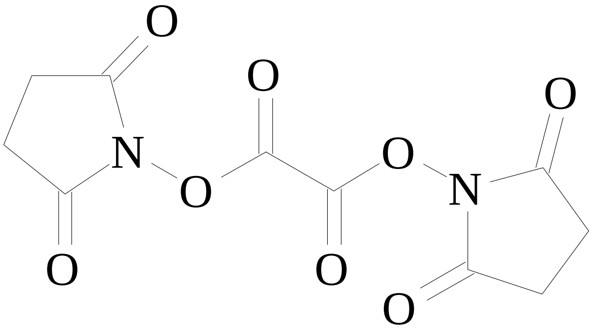


Figure 1. Structure of the ligand DSO.

2. EXPERIMENTAL

2.1. Electromotive force (EMF) measurements

All electromotive force was carried out with the membrane sensor using the following cell assembly:

Ag–AgCl| internal solution 1.0×10^{-3} mol L^{-1} $LuCl_3$ | PVC membrane: sample| Hg–Hg_2Cl_2, KCl (satd).

A Corning ion analyser 250 pH/mV meter was used for the potential measurements at 25.0 °C. Activities were calculated according to the Debye–Huckel procedure [36].

2.2. Chemicals and reagents

Reagent-grade Di(N-succinimidyl)oxalate, dibutyl phthalate (DBP), benzyl acetate (BA), acetophenon (AP), nitrobenzene (NB), sodium tetraphenyl borate (NaTPB), tetrahydrofuran (THF) and high relative molecular weight PVC were purchased from the Merck and the Aldrich Chemical Companies. The nitrate and chloride salts of all cations used (all from Merck) were of the highest purity available and used without any further purification except for vacuum drying. Doubly distilled and deionized water was used throughout.

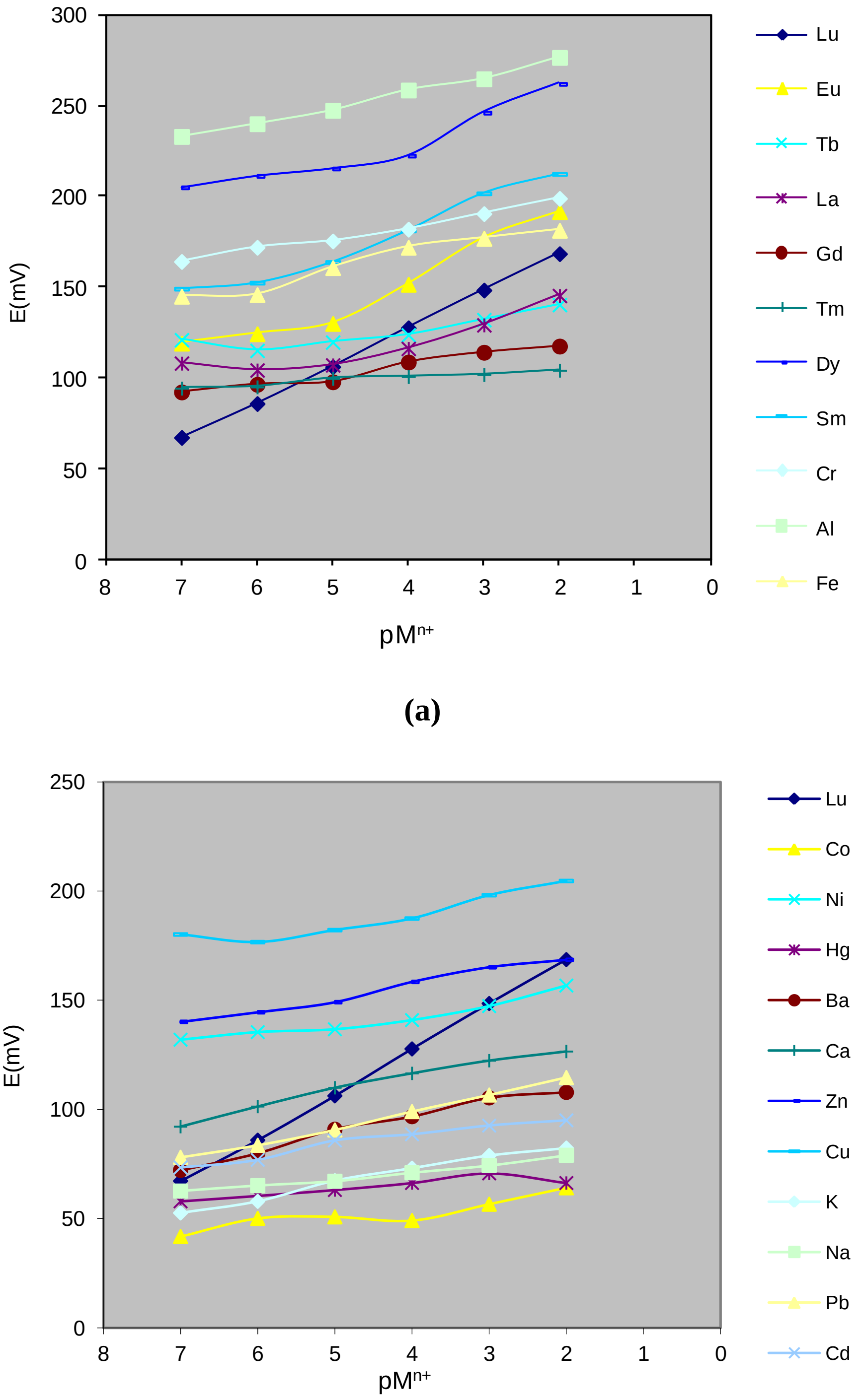
2.3. Preparation of the membrane electrode

The PVC membranes were prepared according to a general procedure. The required ingredients for the membrane construction (30 mg PVC, 60 mg NB, 2 mg NaTPB and 8 mg DSO) were mixed and dissolved in 3 mL of dry THF. The resulting mixture was transferred into a glass dish (2 cm in diameter) and the solvent was evaporated slowly until an oily concentrated mixture could be obtained. A Pyrex tube (3–5 mm in top) was dipped into the oily mixture for about 5 s, so that a transparent film of about 0.3 mm thickness was formed. After the tube removal from this mixture, the tube was kept at room temperature for about 24 h and it was filled with the internal filling solution (1.0×10^{-3} mol L^{-1} $LuCl_3$). In the end, the electrode was conditioned by soaking in a 1.0×10^{-3} mol L^{-1} $LuCl_3$ solution for 24 h [37–57]. A silver/silver chloride wire was used as an internal reference electrode.

3. RESULTS AND DISCISSION

3.1. Potential respone of the Lu^{3+} sensor based on DSO

It was found that the plasticized PVC-based membrane containing DSO (with eight donating oxygen atoms, as well as two nitrogen-group in its structure) as a neutral ionophore, generated stable potentials in solutions containing the lutetium ion, after proper conditioning in a 1.0×10^{-3} mol L^{-1} solution of $LuCl_3$. The membranes showed remarkable selectivity for Lu^{3+} compared with the most common metal ions. In order to control this requirement, , in preliminary experiments, DSO was used to prepare PVC membrane ion-selective electrodes for a wide variety of cations, including sodium, potassium, barium, calcium, zinc, nickel, cobalt, cadmium, copper, lead, mercury, iron, chromium, lanthanum, gadolinium, samarium, lutetium, dysprosium, neodymium, erbium, thulium and terbium ions. The potential responses of the most sensitive ion-selective membrane electrodes, based on DSO, are shown in Figure 2(a-b). Among the different tested cations, Lu^{3+} demonstrates the most sensitive response and seems to be suitably determined by the DSO-PVC membrane in the concentration range of 1.0×10^{-7}-1.0×10^{-2} mol L^{-1}. This is due to the selective behavior of the PVC membrane system against Lu(III) in comparison with other metal ions. Therefore, this ionophore was selected as a suitable sensor material for Lu^{3+}-selective sensor.



(a)

(b)

Figure 2. Potential responses of various PVC membrane sensors based on DSO.

3.2. Membrane composition effect

Previous studies have revealed that some important features of the PVC membranes such as the properties of the plasticizer, the plasticizer/PVC ratio, the nature and amount of ionophore and, especially, the nature and amount of the additives used, significantly influence the sensitivity and selectivity of the PVC membrane sensors [58-63]. Since the nature of the plasticizer influences the dielectric constant of the membrane phase, the mobility of the ion carrier molecules and the state of ionophore [63-73], it was expected to play a key role in determining the ion selective characteristics. Hence, the influence of plasticizer on the response characteristics of the Lu^{3+} sensor was studied by using four plasticizers of different polarities including DBP, NB, AP and BA. In general, the lipophilic anion presence in the cation-selective membrane electrodes diminishes the ohmic resistance, enhances the response behavior and selectivity, and increases the membrane electrode sensitivity [73-79]. The composition of membranes with different proportional ingredients and the performance and characteristics of the electrodes are summarized in Table 1. Obviously, among the three solvent mediators used, NB with higher polarity than DBP and BA, was used. Consequently, the use of NB increases Lu(III) ions extraction with high charge density from the solution to the membrane. It also derives from the same table that the DSO amount increase up to (6-8) % resulted in the membranes (Nos. 6-8), illustrating greater slopes. A maximum slope of 20.5±0.3 mVdecade^{-1} of Lu^{3+} concentration was observed for the membrane No. 8 with 8 % of DSO. Obviously, from Table 1, the addition of 2% NaTPB will increase the sensitivity of the electrode response considerably, so that the membrane electrode demonstrates a Nernstian behavior (membrane no. 8). The solvent mediator/PVC ratio in membrane sensors is usually about 2, because polymeric films with such a plasticizer/PVC ratio will result in optimum physical properties and high mobilities of their constituents. In this study, the same plasticizer/PVC ratio (about 2) was found to be the most suitable, for the construction of the membrane sensors. In agreement with Table 1, membrane no. 8 with PVC:NB:DSO:NaTPB percent ratio of 30:60:8:2 resulted in Nernstian behavior of the membrane electrode over a wide concentration range.

Table 1. Optimization of the membrane ingredients.

Sensor No.	Composition of the membrane (wt, %)				Slope / mVdecade^{-1}	Dynamic Linear range / molL^{-1}
	PVC	Plasticizer	DSO	NaTPB		
1	30	NB, 60	1	9	6.1 ± 0.2	1.0×10^{-5}-1.0×10^{-2}
2	30	NB, 60	2	8	8.6 ± 0.4	1.0×10^{-5}-1.0×10^{-2}
3	30	NB, 60	3	7	9.7 ± 0.2	1.0×10^{-5}-1.0×10^{-2}
4	30	NB, 60	4	6	10.3 ± 0.3	1.0×10^{-5}-1.0×10^{-2}
5	30	NB, 60	5	5	11.5 ± 0.5	1.0×10^{-6}-1.0×10^{-2}
6	30	NB, 60	6	4	14.8 ± 0.6	1.0×10^{-6}-1.0×10^{-2}
7	30	NB, 60	7	3	18.7 ± 0.4	1.0×10^{-6}-1.0×10^{-2}
8	30	NB, 60	8	2	20.5 ± 0.3	1.0×10^{-7}-1.0×10^{-2}
9	30	NB, 60	9	1	17.6 ± 0.6	1.0×10^{-6}-1.0×10^{-2}
10	30	DBP, 60	8	2	9.6 ± 0.5	1.0×10^{-6}-1.0×10^{-3}
11	30	BA, 60	8	2	12.6 ± 0.4	1.0×10^{-6}-1.0×10^{-3}
12	30	AP, 60	8	2	11.0 ± 0.3	1.0×10^{-6}-1.0×10^{-3}

3.3. Calibration graph and statistical data

The emf vs. pLu^{3+} plot (Figure 3) for optimal membrane ingredients at varying concentrations of Lu^{3+} ion solution indicates that it has a Nernstian behavior of 20.5±0.3 $mVdecade^{-1}$ over a broad concentration range from 1.0×10^{-7} to 1.0×10^{-2} mol L^{-1} of Lu^{3+} ions. The detection limit of the electrode was determined from the intersection of the two extrapolated segments of the calibration graph was 7.5×10^{-8} mol L^{-1}. The standard deviation for eight replicate measurements was ±0.4 mV. Daily, the sensor was used for one hour, washed and dried. Its usage was found to last for at least 2 months.

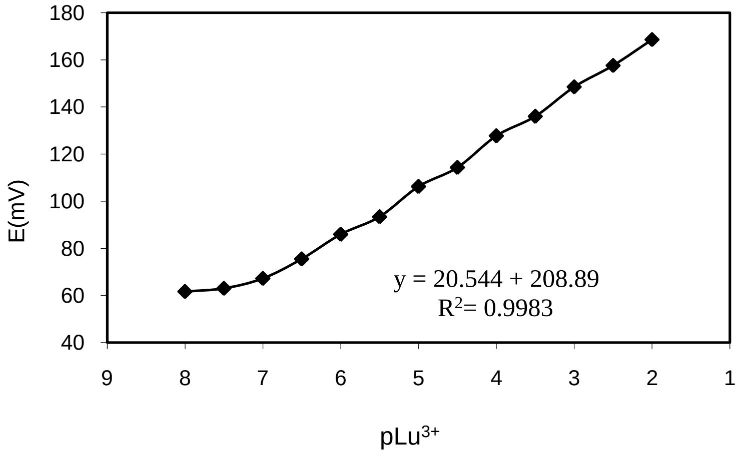


Figure 3. Calibration curve of the Lu^{3+} sensor in the range of 1.0×10^{-7} to 1.0×10^{-2} mol L^{-1} Lu^{3+} ions.

3.4. pH influence

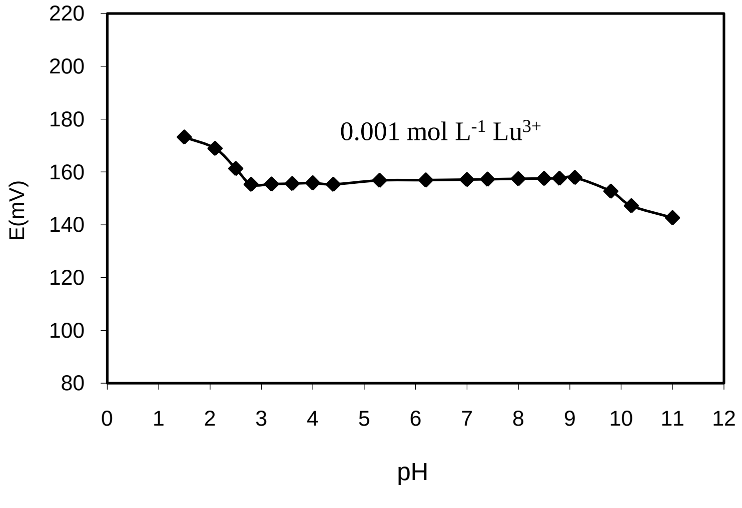


Figure 4. Effect of the pH of test solution (1.0×10^{-3} $molL^{-1}$ of Lu^{3+}) on the potential response of the Lu^{3+} sensor based on DSO.

The pH dependence of the membrane sensor was tested for the pH values in a range of 1.0–11.0 by monitoring the sensor behavior in a 1.0×10^{-3} mol L^{-1} of Lu^{3+} solution (test solution). The concentrated NaOH or HCl was used for the pH adjustment. The results are depicted in Figure 4. As it is seen, the pH effect of the test solution on the potential response of the Lu^{3+} sensor was found to remain constant in the pH range of 2.8–9.1. Beyond this range, a gradual change in potential was detected. The potential decrease at higher pH values (>9.1), is due to the formation of insoluble $Lu(OH)_3$. The increase in the potential response at lower pH values of <2.8, is most probably due to the responds of the sensor to the hydronium ions (the protonation of the nitrogen atoms of ion carrier in acidic media).

3.5. Dynamic response time of the Lu^{3+} sensor based on DSO

For the evaluation of any sensor, dynamic response time is an important factor for its analytical applications. In this study, this parameter was recorded for the best sensor composition by immediately changing the Lu(III) ion concentration from 1.0×10^{-7} to 1.0×10^{-2} mol L^{-1} and the results are illustrated in Figure 5. As it can be seen, the response time of the sensor is about 5s in the whole concentration range.

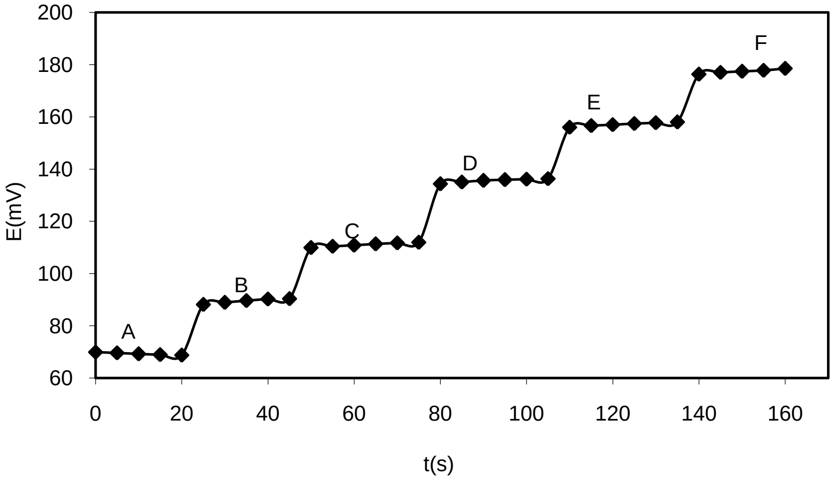


Figure 5. Dynamic response time of the Lu^{3+} sensor for step changes in the Lu^{3+} concentration: A) 1.0×10^{-7} $molL^{-1}$, B) 1.0×10^{-6} $molL^{-1}$, C) 1.0×10^{-5} $molL^{-1}$, D) 1.0×10^{-4} $molL^{-1}$, E) 1.0×10^{-3} $molL^{-1}$, F) 1.0×10^{-2} $molL^{-1}$.

3.6. Selectivity of the sensor studies

The potentiometric selectivity coefficients, describing the preference of the suggested electrode for an interfering ion, B, with reference to the lutetium ion were determined by the matched potential method (MPM) [79–84]. In line with MPM, a specified activity of the primary ion (A) is added to a reference solution, and the potential is measured. In a separate experiment, interfering ions (B) are successively added to an identical reference (containing primary ion) solution until the measured potential matched to that obtained before the addition of the primary ions. The matched potential method selectivity coefficient, K^{MPM}, is then given by the resulting primary ion to interfering ion activity (concentration) ratio, $K^{MPM}=\Delta a_A/a_B$. The resulting values are listed in Table 2. According to this Table, the selectivity coefficients for the tested monovalent cations (Na^+, K^+) are smaller than 7.5×10^{-4} and for the tried divalent cations (Ni^{2+}, Cd^{2+}, Co^{2+}, Zn^{2+}, Hg^{2+}, Pb^{2+}, and Ca^{2+}) are also less than 8.2×10^{-4}. As to the trivalent cations tested (Dy^{3+}, Yb^{3+}, Tb^{3+}, Tm^{3+}, Pr^{3+}, La^{3+}, Ho^{3+}, Sm^{3+}, Gd^{3+}, Er^{3+}, Eu^{3+}, Cr^{3+}, and Fe^{3+}), the selectivity coefficients are relatively small (from 3.6×10^{-4} to 8.2×10^{-4}). The resultant selectivity coefficients indicate that the disturbance produced by such cations, in case they occur in a test medium,,is negligible.

Table 2. Selectivity coefficients of various interfering cations.

Interfering ions (B)	This work
Method	MPM
Dy^{3+}	5.4×10^{-4}
Yb^{3+}	4.5×10^{-4}
Tb^{3+}	5.7×10^{-4}
Tm^{3+}	4.8×10^{-4}
Pr^{3+}	6.3×10^{-4}
La^{3+}	3.6×10^{-4}
Ho^{3+}	8.2×10^{-4}
Sm^{3+}	6.8×10^{-4}
Gd^{3+}	5.9×10^{-4}
Er^{3+}	5.0×10^{-4}
Eu^{3+}	6.8×10^{-4}
Cr^{3+}	8.2×10^{-4}
Fe^{3+}	7.6×10^{-4}
Na^{+}	7.1×10^{-4}
K^{+}	7.5×10^{-4}
Ca^{2+}	5.3×10^{-4}
Ni^{2+}	6.5×10^{-4}
Cd^{2+}	7.2×10^{-4}
Co^{2+}	7.4×10^{-4}
Zn^{2+}	8.2×10^{-4}
Hg^{2+}	6.8×10^{-4}
Pb^{2+}	7.8×10^{-4}
Response time (s)	~5
Linearity range (mol L^{-1})	1.0×10^{-7}-1.0×10^{-2}
Limit of detection (mol L^{-1})	7.5×10^{-8}

The formerly reported lutetium potentiometric electrodes [5-7] in terms of selectivity, dynamic linearity range, detection limit, response time, and pH range were compared in Table 3. As it can be seen from this table, the proposed sensor is superior to the previously reported Lu^{3+} sensors in terms of selectivity, detection limit and dynamic concentration range.

Table 3. 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. 5	Ref. 6	Ref. 7	This work
Detection limit (mol L^{-1})	8.0×10^{-7}	7.2×10^{-7}	6.0×10^{-7}	7.5×10^{-8}
Linear range (mol L^{-1})	1.0×10^{-6}-1.0×10^{-2}	1.0×10^{-6}-1.0×10^{-2}	1.0×10^{-6}-1.0×10^{-1}	1.0×10^{-7}-1.0×10^{-2}
Response time (s)	<10	<10	~5	~5
Interfering ion (B) K_{sel} More than 5.0×10^{-3}	Nd, Gd, Dy	Nd, Ho, Tm, Dy	Ce, Ho, Dy, NH_4^+	-
pH range	4.5-8.0	2.7-10.6	4.0-9.0	2.8-9.1

3.7. Analytical application

The developed Lu^{3+} sensor was successfully used as an indicator electrode in potentiometric titration of a 1.0×10^{-4} mol L^{-1} Lu^{3+} ion solution with a 1.0×10^{-2} mol L^{-1} EDTA. The resulting titration curve is given in Figure 6. As can be seen, the amount of Lu^{3+} ions in the solution can be effectively determined with the used of this sensor.

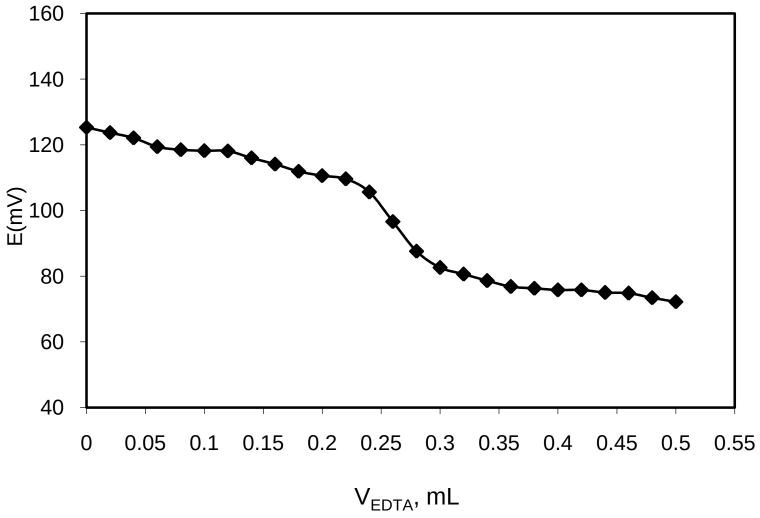


Figure 6. Potential titration curve of 25.0 mL from a 1.0×10^{-4} $molL^{-1}$ Lu^{3+} solution with 1.0×10^{-2} $molL^{-1}$ of EDTA.

To test its practical applicability of the proposed sensor, it was additionally applied to the determination of the Lu^{3+} ions in various mixtures of different cations. The resulting data of Table 4 indicate that the accuracy of the Lu^{3+} ions detection in different solutions of different metal ions is almost quantitative.

Table 4. Determination of Lu^{3+} ions in mixtures of different ions.

Serial no.	Composition	Observed content (mol L^{-1})
1	0.000010 mol L^{-1} $Lu(NO_3)_3$ + 0.0001 mol L^{-1} $Dy(NO_3)_3$ + 0.0001 mol L^{-1} $Yb(NO_3)_3$	0.0000096
2	0.000010 mol L^{-1} $Lu(NO_3)_3$ + 0.0001 mol L^{-1} $Ho(NO_3)_3$ + 0.0001 mol L^{-1} $Eu(NO_3)_3$	0.0000098
3	0.000010 mol L^{-1} $Lu(NO_3)_3$ + 0.0001 mol L^{-1} $Tm(NO_3)_3$ + 0.0001 mol L^{-1} $Tb(NO_3)_3$	0.0000102
4	0.000010 mol L^{-1} $Lu(NO_3)_3$ + 0.0001 mol L^{-1} $La(NO_3)_3$ + 0.0001 mol L^{-1} $Nd(NO_3)_3$	0.0000097
5	0.000010 mol L^{-1} $Lu(NO_3)_3$ + 0.0001 mol L^{-1} $Pr(NO_3)_3$ + 0.0001 mol L^{-1} $Gd(NO_3)_3$	0.0000103
6	0.000010 mol L^{-1} $Lu(NO_3)_3$ + 0.0001 mol L^{-1} $Al(NO_3)_3$+ 0.0001 mol L^{-1} $Cu(NO_3)_2$ + 0.0001 mol L^{-1} $Co(NO_3)_2$	0.0000098
7	0.000010 mol L^{-1} $Lu(NO_3)_3$ + 0.0001 mol L^{-1} $Ni(NO_3)_2$+ 0.0001 mol L^{-1} $Cr(NO_3)_3$ + 0.0001 mol L^{-1} KNO_3	0.0000096
8	0.000010 mol L^{-1} $Lu(NO_3)_3$ + 0.0001 mol L^{-1} $Fe(NO_3)_3$+ 0.0001 mol L^{-1} $Ca(NO_3)_2$ + 0.0001 mol L^{-1} $Zn(NO_3)_2$	0.0000102
9	0.000010 mol L^{-1} $Lu(NO_3)_3$ + 0.0001 mol L^{-1} $Pb(NO_3)_2$+ 0.0001 mol L^{-1} $Ba(NO_3)_2$ + 0.0001 mol L^{-1} $NaNO_3$	0.0000097

4. CONCLUSION

The use of Di(N-succinimidyl)oxalate (DSO) as an ionophore and nitrobenzene, being the solvent mediator, resulted in the best response characteristics with a Nernstian slope of 20.5±0.3 mVdecade^{-1} with a detection limit of 7.5×10^{-8} mol L^{-1} over a wide concentration range of 1.0×10^{-7} to 1.0×10^{-2} mol L^{-1} Lu^{3+} ions. The proposed lutetium sensor in the terms of selectivity coefficients, linear range and detection limit is superior to all previously reported lutetium sensors. Further, the developed electrode can also be used for the monitoring of Lu^{3+} ions in various mixtures of interfering ions.

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