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Original scientific paper

A lutetium PVC membrane sensor based on (2-oxo-1,2-diphenylethylidene)-*N*-phenylhydrazinecarbothioamide

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Abstract: Based on the former experience on the design and construction of metal ions sensors, especially those of high sensitivity for lanthanides, (2-oxo-1,2-diphenylethylidene)-*N*-phenylhydrazinecarbothioamide (PHCT) was used to construct a Lu^{3+} PVC sensor exhibiting a Nernstian slope of 19.8±0.3 mV dec^{-1}. The sensor was found to function well over a concentration range of 1.0×10^{-2} and 1.0×10^{-6} mol L^{-1} of the target ion with a detection limit of 6.8×10^{-7} mol L^{-1}. The sensor selectivity against many common alkaline, alkaline earth, transition, heavy metals and specially lanthanide ions was very good and it functioned well in the pH range 2.5–8.7. Having a lifetime of at least 2 months and a short response time of ≈ 5 s, the sensor was successfully used as an indicator electrode in the potentiometric titration of Lu^{3+}.

Keywords: potentiometry; sensor; PVC membrane; ion-selective electrode.

INTRODUCTION

The fact that lanthanides have similar chemical and physical properties, makes their analyses an extremely time consuming and complicated procedure, especially in case when other similar ions are present in the sample solution.[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 element is hence dumped in the environment, mainly from petrol-producing industries.[2] Thus, finding a method for its determination would be useful.

Such methods are inductively couple plasma mass spectrometry (ICP–MS), inductively couple plasma atomic emission spectrometry (ICP–AES), mass spec-

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trometry (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

Since there are some reports on lutetium sensors based on different ionophores[3–6] and also recent experience on the development of highly selective and sensitive PVC-membrane ISEs,[7–20] it was decided to assess the possibility of constructing a novel Lu^{3+} sensor by testing (2-oxo-1,2-diphenylethylidene)-*N*-phenylhydrazinecarbothioamide (PHCT) (Fig. 1) as a neutral ion carrier.

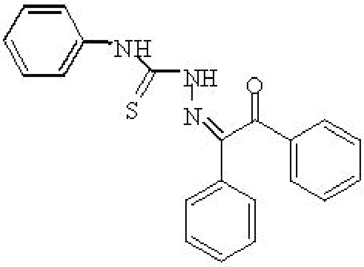

Fig. 1. Chemical structure of PHCT.

EXPERIMENTAL

Reagents

Nitrate and chloride salts of all cations, as well as reagent grade dibutyl phthalate (DBP), benzyl acetate (BA), acetophenone (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 P_2O_5. Doubly distilled water was used in all experiments.

Synthesis of PHCT

To prepare (2-oxo-1,2-diphenylethylidene)-*N*-phenylhydrazinecarbothioamide, 1 mmol (0.21 g) of benzil was dissolved in hot ethanol, and then 1 mmol (0.167 g) of *N*-phenyl hydrazinecarbothioamide and a catalytic amount of acetic acid were added to the benzyl solution. The reaction mixture was next refluxed for an hour, before crystallizing the solid product from a solution of acetone and ethanol (1:1).

EMF Measurements

The cell assembly used in all experiments was as follows: Ag/AgCl | 1.0×10^{-3} mol L^{-1} $LuCl_3$ | PVC membrane: test solution| Hg/Hg_2Cl_2, KCl (satd.).

The potential measurements were made using a Corning ion analyzer 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–Hückel procedure.[21] The pH was adjusted to 4 using sodium acetate buffer.

Electrode preparation

In general, the desired amount of the components, *i.e.*, powdered PVC, the plasticizer, the ionic additive and the ionophore (PHCT), were completely dissolved in 5 mL of THF in a glass dish of 2 cm in diameter and then some of the THF was allowed to evaporate to yield a rather viscose solution that was used for forming a layer of the membrane on the tip of Pyrex tubes of 3–5 mm o.d. To do this, the tips of the tubes were dipped into the mixture for a short time.[22-34] The tube, now having a layer of the membrane on the tip were next kept at room temperature for 12 h before being filled with an internal filling solution (1.0×10^{-3} mol L^{-1} of the target ion) and conditioned for 24 h in a 1.0×10^{-2} mol L^{-1} solution of the target ion. The electrodes were furnished with an internal reference silver/silver chloride coated wire.

RESULTS AND DISCUSSION

The response behavior of the sensors

Having four medium to soft base donating nitrogen and sulfur atoms in PHCT structure, it was expected to form stable complexes with transition metal ions. Therefore, in the initial tests to check the suitability of PHCT as an ionophore for different metal ions, PHCT complexation with a number of metal ions including mono-, di- and tri-valent cations was investigated by conductometric method in acetonitrile solution (1.0×10^{-4} mol L^{-1} of cation solution and 1.0×10^{-2} mol L^{-1} of ligand solution) at 25±0.1 °C.[29–31] Then, 25 mL of each ion solution was titrated with 0.01 mol L^{-1} of PHCT solution. The conductance of the solution was measured after each addition. Ligand addition was continued until the desired ligand-to-cation mole ratio was achieved. The 1:1 binding of the cations with ligands can be expressed by the following equilibrium:

$$M^{n+} + L \xleftrightarrow{K_f} ML^{n+} \tag{1}$$

The formation constant of the equilibrium, K_f, is given by:

$$K_f = \frac{[ML^{n+}]}{[M^{n+}][L]}\frac{f_{(ML^{n+})}}{f_{(M^{n+})}f_{(L)}} \tag{2}$$

where $[ML^{n+}]$, $[M^{n+}]$, [L] and f represent the equilibrium molar concentration of complex, free cation, free ligand, and the activity coefficient of the species indicated, respectively. The activity coefficient of the unchanged ligand, $f_{(L)}$ can be assumed as unity in diluted solutions. The Debye–Hückel limiting law of 1:1 electrolytes leads to activity coefficient in Eq. (2) being canceled. Hence, the complex formation constant in term of molar conductance can be expressed as:

$$K_f = \frac{[ML^{n+}]}{[M^{n+}][L]} = \frac{(\Lambda_M - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_{ML})[L]} \tag{3}$$

where:

$$K_f = c_L - \frac{c_M(\Lambda_M - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_{ML})} \tag{4}$$

where, Λ_M is the molar conductance of the cation before the addition of ligand, Λ_{ML} is the molar conductance of the complex, Λ_{obs} the molar conductance of the solution during the titration, c_L the analytical concentration of PHCT added and c_M the analytical concentration of the cation.

The complex formation constants, K_f, and the molar conductance of complex, Λ_{ML}, were obtained by computer fitting of Eqs. (3) and (4) to the molar conductance–mole ratio data, using the non-linear least-squares program KINFIT.[29–31] The logarithm of the formation constants (log K_f) of the resulting 1:1 complex between Lu^{3+} and PHCT was calculated as 5.55±0.27. The results of this experiment showed that stability of the Lu–PHCT complex was higher than those of the other cations tested (Table I). Thus, PHCT can act as a suitable ion-carrier for making a Lu^{3+} membrane sensor.

TABLE I. Formation constant of the complex between M^{n+} and PHCT

Ion	K_f	Ion	K_f
La^{3+}	<2	Yb^{3+}	<2
Ce^{3+}	<2	Lu^{3+}	5.55±0.27
Pr^{3+}	<2	Na^+	<3
Nd^{3+}	2.5±0.22	K^+	<3
Sm^{3+}	2.3±0.34	Mg^{2+}	<2
Eu^{3+}	3.2±0.13	Ca^{2+}	2.7±0.14
Gd^{3+}	3.3±0.27	Pb^{2+}	2.9±0.22
Tb^{3+}	<2	Fe^{3+}	3.7±0.23
Dy^{3+}	3.6±0.31	Cu^{2+}	<2
Ho^{3+}	<2	Cd^{2+}	<2
Er^{3+}	<2	Ni^{2+}	2.1±0.13
Tm^{3+}	<2	Co^{2+}	<2

In next experiment, PHCT was used as a suitable ionophore in construction of PVC membrane electrode for a number of alkali, alkaline earth, transition and heavy metal ions, to confirm the selectivity of the ionophore. The prepared potential responses of all the membrane sensors were studied in a wide range of concentrations of different ions. Among the ions tested, the sensor was found to demonstrate very sensitive responses to Lu^{3+}, which could be regarded as a promising result that could be exploited for the design and construction of a suitable sensor for Lu^{3+}.

The effect of the membrane composition

It is well known that sensitivity and selectivity of a given ionophore significantly depends on the membrane components, the nature of the solvent mediator and the ionic additive.[35–37] To investigate these effects on the sensor response, several tests were performed and the results are summarized in Table II.

TABLE II. Optimization of the membrane components (dynamic linear range: 1.0×10^{-2}–-1.0×10^{-6} mol L^{-1})

Sensor No.	Composition of the membrane, mass% (PVC content: 30 mass%)			Slope mV dec^{-1}
	Plasticizer	PHCT	NaTPB	
1	NB, 66	2	2	15.8±0.3
2	AP, 66	2	2	16.1±0.5
3	BA, 66	2	2	16.5±0.2
4	DBP, 66	2	2	18.4±0.3
5	DBP, 67	1	2	14.3±0.6
6	DBP, 65	3	2	19.8±0.3
7	DBP, 67	3	0	11.7±0.4
8	DBP, 66	3	1	13.5±0.5
9	DBP, 64	3	3	18.3±0.2

The initial composition (No. 7, Table II), prepared based on previous experience gained on other sensors for similar ions,[4–20] of 66 mg of DBP, 30 mg of PVC powder and 2 mg of the ionophore (in the absence of an ionic additive) showed a selective response toward Lu^{3+}, but the slope of 11.7±0.4 mV dec^{-1} of the calibration curve showed its low sensitivity which could be caused by the high ohmic resistance of the membrane, as well as the co-extraction of the cations in the solutions together with the ions present therein. Hence, in the next experiments, 1, 2, and even 3 mg of an appropriate ionic additive (NaTPB) was added to the membrane composition (Nos. 8, 4 and 9, respectively, Table II). Changes of the slopes from 13.5±0.5 to 18.4±0.3, and finally to 18.3±0.2 mV dec^{-1} resulting from changes in the amount of ionic additive in the membrane, showed that 2 mg of the ionic additive could be regarded as the optimum amount.

To find the best plasticizer for the membrane, four common plasticizers namely NB, AP, BA, and DBP were used in an amount of 66 mg (Nos. 1–4, Table II). NB showed the lowest response of 15.8±0.3 mV dec^{-1}, while AP and BA had better and rather identical responses of 16.1±0.5 and 16.5±0.2 mV dec^{-1}, respectively. The best response was, however, observed in the case of DBP with a response of 18.4±0.3 mV dec^{-1}.

To assess the optimal amount of the ionophore for the membrane composition, two more compositions were prepared and compared with composition 4. The results (Nos. 5 and 6, Table II) showed that decreasing the amount of the ionophore in the membrane to 1 mg considerably decreased the potential slope. While increasing the amount up to a value of 3 mg increased the potential response to the optimum Nernstian value of 19.8±0.3 mV dec^{-1}. Hence, this composition was chosen as the optimum one and used for the further experiments.

Calibration and statistical data

The potential response of the electrode with the best composition at varying concentration of Lu^{3+} was found to display a linear response in the concentration range of 1.0×10^{-6} to 1.0×10^{-2} mol L^{-1} Lu^{3+} (Fig. 2). The slope of calibration graph had the optimum value of 19.8±0.3 mV dec^{-1} and the detection limit of the sensor, determined from the intersection of the two extrapolated segments of the calibration graph, was 6.8×10^{-7} mol L^{-1}. The standard deviation of 7 replicate measurements was calculated as ±0.3 mV. The membrane electrode was also found to show good results for at least 2 months without any measurable divergence.

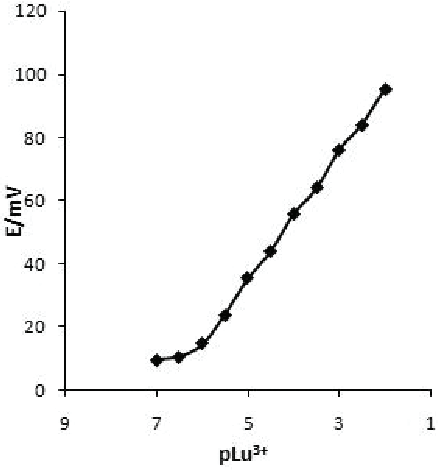

Fig. 2. Calibration curve of the PHCT-based lutetium electrode.

pH Effect, response time and selectivity

The pH dependence of the sensor response was tested using a 1.0×10^{-3} mol L^{-1} $Lu(NO_3)_3$ solution over the pH range of 1.0–12.0 (the pH was adjusted using concentrated NaOH or HCl). The results are depicted in Fig. 3, from which it is clear that the sensor response remained constant in the pH range 2.5–8.7. Outside this range, the potential drifted towards lower values at higher pH values, probably due to the formation of some hydroxyl complexes of Lu^{3+} in the solution and drifted toward negative potentials at lower pH values, indicating that the membrane sensor responded to protonium ions, as a result of the partial protonation of nitrogen atoms of the ionophore.

The practical response time of the sensor was assessed by recording the equilibrium time when changing the Lu^{3+} concentration in a series of solutions (1.0×10^{-6}–1.0×10^{-2} mol L^{-1}). The results, summarized in Fig. 4, indicate a short response time of about 5 s.

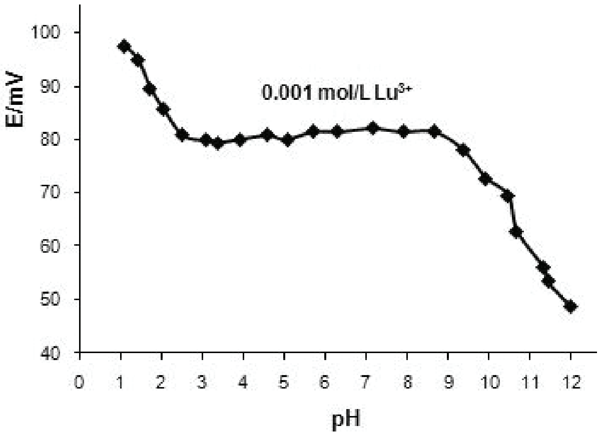

Fig. 3. Effect of the pH of the test solution (1.0×10^{-3} mol L^{-1} Lu^{3+}) on the potential response of the Lu^{3+} ion-selective electrode.

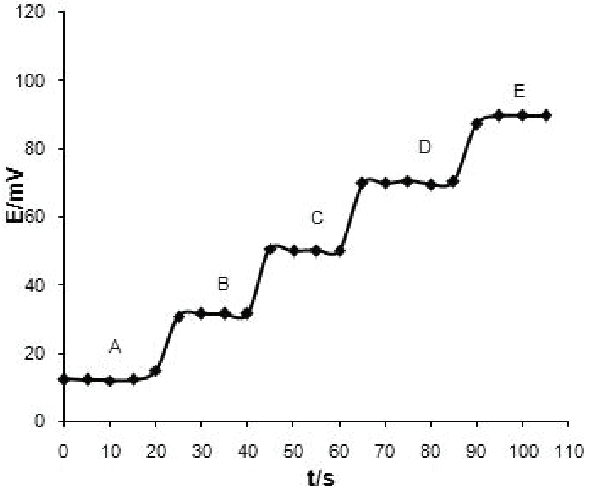

Fig. 4. Dynamic response time of the lutetium electrode for step changes in the Lu^{3+} concentration:
A) 1.0×10^{-6},
B) 1.0×10^{-5},
C) 1.0×10^{-4},
D) 1.0×10^{-3} and
E) 1.0×10^{-2} mol L^{-1}.

Finally, and most importantly, the potentiometric selectivity coefficients of the sensor, which are supposed to describe the preference of the PHCT-based membrane electrode for the target ion in the presence of an interfering ion were determined through the matched potential method.[40–42] According to this method, the primary ion (A) of a specified activity 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 matches to that obtained only with the primary ions. A comparison between the selectivity coefficients of the developed Lu^{3+} sensor with those of the best previously reported Lu^{3+} electrodes is made in Table III.[3–6] It is clear that the selectivity coefficients of the electrode for all ions were in the order of 6.2×10^{-3} or smaller. This means these ions would not significantly disturb the response of the Lu^{3+} selective membrane sensor, especially if their concentrations were low in the test solution. A comparison made of the detection range, the response time, the detection limit and the selectivity coefficients of the sensor with those existing in the literature is evidence enough for the comparative superiority of the sensor investigated in the present study.

TABLE III. Comparison of the selectivity coefficient, MPM×10^4, linearity range, detection limit and response time of the developed Lu^{3+} electrode and previously reported Lu^{3+} PVC-membrane sensors

Element	Reference				
	3	4	5	6	This work
Nd^{3+}	200	0.10	65	–	3.6
Eu^{3+}	–	3.0	21	2.0	7.2
Gd^{3+}	63	1.0	47	1.7	6.8
Dy^{3+}	80	1.0	62	80	7.7
Sm^{3+}	2.5	2.0	8.5	50	7.5
Cr^{3+}	–	–	8.6	–	57
Fe^{3+}	–	–	10	–	22
Pb^{2+}	7.9	0.20	–	1.0	62
Ni^{2+}	–	–	–	–	2.7
Co^{2+}	–	–	–	–	5.9
Ca^{2+}	1.6	1.0	–	8.0	1.8
Na^+	3.2	2.5	8.7	2.5	6.3
K^+	6.3	8.0	21	9.0	8.4
Response time, s	<10	≈5	<10	≈5	≈5
Linearity range, mol L^{-1}	1.0×1^{-6}–1.0×10^{-2}	1.0×1^{-6}–0.10	1.0×1^{-6}–1.0×1^{-2}	1.0×1^{-6}–0.10	1.0×1^{-6}–1.0×10^{-2}
Limit of detection, mol L^{-1}	8.0×10^{-7}	6.3×10^{-7}	7.2×10^{-7}	6.0×10^{-7}	6.8×10^{-7}
pH Range	4.5–8.0	3–7.5	2.7–10.6	4–9	2.5–8.7

Analytical accuracy

The electrode was found to function well under laboratory conditions and the sensor was used as an indicator electrode in the titration of a 1.0×10^{-4} mol L^{-1} lutetium ion solution with a standard 1.0×10^{-2} mol/L EDTA solution. The resulting titration curve is shown in Fig. 5, which indicates that the sensor was capable of monitoring the amounts of lutetium ions in such measurements.

The proposed sensor was also applied to Lu^{3+} determination in a certified reference material (CRM), called coal and fuel ash (FFA 1 fly ash). According to Table IV, where the CRM analysis is summarized, the Lu^{3+} concentration was 0.658 mg kg^{-1}. Employing the calibration method a Lu^{3+} concentration value of 0.669±0.5 mg kg^{-1} was obtained.

These experimental data reveal that the proposed electrode performed a trustworthy detection of Lu^{3+}, despite the presence of other rare earth elements.

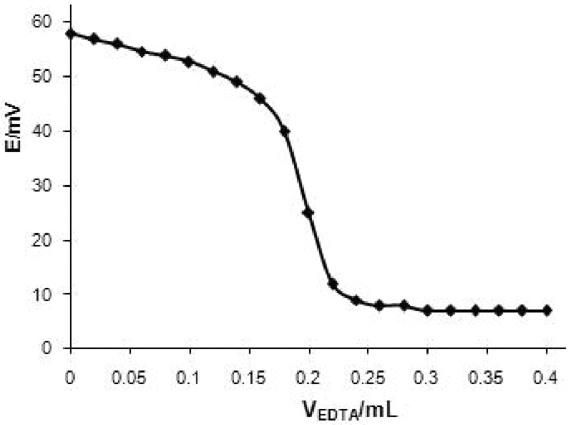

Fig. 5. Potential titration curve of 25.0 mL of a 1.0×10^{-4} mol L^{-1} Lu^{3+} solution with a 1.0×10^{-2} mol L^{-1} solution of EDTA.

TABLE IV. Results (certified values in mg kg^{-1}) from the coal and fuel ash analysis (FFA 1 fly ash)

Element	Value	Element	Value
Al	14.87	Hf	6.09
As	53.6	La	60.7
Ba	835	Li	128
Ce	120	Lu	0.658
Co	39.8	Mn	1066
Ca	156	Na	2.19
Cs	48.2	Nd	56.8
Cu	158	Ni	99.0
Dy	9.09	P	725
Er	4.52	Pb	369
Eu	2.39	Rb	185
F	198	Sb	17.6
Fe	4.89	Sc	24.2
Gd	10.0	Si	22.48
Sm	10.9	Sr	250
Ta	2.11	Tb	1.38
Th	29.4	Tm	0.705
U	15.1	V	260
W	10.5	Y	45
Yb	4.24	Zn	569

CONCLUSIONS

Based on the results obtained in this paper, (2-oxo-1,2-diphenylethylidene)-*N*-phenylhydrazinecarbothioamide (PHCT) can be used as an excellent electroactive carrier to prepare Lu^{3+} ISEs with excellent electrode characteristics, such as the wide dynamic linear concentration range of 1.0×10^{-6}–1.0×10^{-2} mol L^{-1}, a fast response time of about 5 s, a wide applicable pH range of 2.5–8.7, sensitivity and selectivity with a number of commonly occurring interfering ions. The analysis of a certified reference material showed the accuracy of the sensor for application in real samples.

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ИЗВОД

СЕНЗОР ЗА ЛУТЕЦИЈУМ НА БАЗИ (2-ОКСО-1,2-ДИФЕНИЛЕТИЛИДЕН)-*N*-ФЕНИЛХИДРАЗИНКАРБОТИОАМИДА У PVC МАТРИЦИ

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На основу ранијег искуства у дизајну и конструкцији сензора за јоне метала, посебно оних високе осетљивости за лантаноиде, направљен је сензор за Lu^{3+} на бази (2-оксо-1,2-дифенилетилиден)-*N*-фенилхидразинкарботиоамид (PHCT) у PVC матрици, који је показао Нернстов нагиб од 19,8±0,3 mV dek^{-1}. Показано је да сензор ради добро у опсегу концентрација Lu^{3+} од $1,0\times10^{-2}$ до $1,0\times10^{-6}$ mol L^{-1} и да му је граница осетљивости $6,8\times10^{-7}$ mol L^{-1}. Селективност сензора према многим уобичајеним алкалним, земноалкалним, прелазним и тешким металима, а посебно према јонима лантаноида је веома добра и може се употребљавати у опсегу pH 2,5–8,7. Са периодом употребе од најмање 2 месеца и кратким временом одзива од ≈5 s, сензор је успешно коришћен као индикатроска електрода у потенциометријској титрацији Lu^{3+}.

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