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Lanthanum(III) Ion Selective Electrode Based on a New Ionophore

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Abstract

A PVC membrane electrode based on 1-[({[(butylsulfunyl)carbothioyl]disulfanyl} carbothioyl)sulfanyl] butane as a suitable ion carrier for determination of lanthanum(III) ion was prepared. This electrode revealed such a good selectivity toward La^{3+} ion over a wide variety of other metal ions. Some experimental parameter such as membrane composition, nature, and amount of plasticizer, the amount of additive, and concentration of internal solution on the potential response of La^{3+} sensor were investigated. The electrode exhibits a Nernstian slope of 20.9±1.8 mV per decade of La^{3+} over a wide concentration range 3.3×10^{-7}-1.0×10^{-2} M in the pH range 3.7-7.3. The response time is about 7s and detection limit is 2.5×10^{-7} M and it can be used for at least 1month without any considerable divergence in potential. It was used as an indicator electrode in potentiometric titration of lanthanum(III) ion with EDTA.

Keywords: Lanthanum (III), Ion Selective Electrode, PVC

Introduction

The development of chemical sensors is important with respect to several objectives. A first aim is the substitution of classical methods by sensor measurements[1-3]. A typical example here is the systematic replacement of flame photometer for determination of blood electrolyte, such as lithium, sodium, and calcium by ion selective electrodes.

A second objective results from the increasing requirements for automation of industrial processes. Measurement of chemical parameters is needed for monitoring and controlling a process. Thus in process analytical chemistry the methods for on-line analysis are based on the availability of chemical sensors. Special requirements in industry are robustness, long term stability, or temperature insensitivity of the sensors. Additional needs arise in connection with biotechnological processes where multifunctional, biocompatible sensors are required [4-5].

Monitoring chemical quantities is also important in the environment, industrial plants, in safety technique and in medicine conceivably, the pollution of water by heavy metals and organic compounds may be monitored continuously by sensors rather than by other expensive and time consuming methods. Chemical sensors will be needed not only for individual analytes but also for sum parameters.

Rare-earth compounds containing lanthanum are extensively used in carbon lighting application, especially by the motion picture industry for studio lighting and projection. Lanthanum compounds are encountered rarely

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by most people. All lanthanum compounds should be regarded as highly toxic although initial evidence would appear to suggest the danger is limited. Lanthanum salts may damage the liver. The metal dust presents a fire and explosion hazard. Lanthanum is never found in nature as the free element. Lanthanum is found in the ores monazite sand [(Ce, La, etc.)PO_4], ores containing small amounts of all the rare-earth metals. Other ores include allanite. It is difficult to separate from other rare elements [6].

In recent years, some La-selective electrodes have been reported [7, 8]. Moreover, cadmium and cobalt ion selective electrodes base on crown ethers have been reported [9,10]. It is well known that sulfur-containing ligands coordinate selectively with transition and heavy metal ions [11]. In this work, a recently synthesized sulfur containing compound is used to construct a highly sensitive La(III) selective electrode base on PVC-membrane and membrane coated graphite.

Experimental

Reagents and chemicals

O-nitrophenyl octyl ether (O-NPOE), dimethyl sebacate (DMS), diethyl sebacate (DES), dibutyl phthalate (DBP), poly(vinyl chloride) (PVC), tetrahydrofurane (THF), and sodium tetraphenylborate (STPB) all from Fluka or Merck Chemical Companies were used. 1-[({[(butylsulfunyl)carbothioyldisulfanyl} carbothioyl)sulfanyl] butane was used as a carrier in liquid membrane electrodes. This carrier (Figure 1) was synthesized and purified as described elsewhere [12].

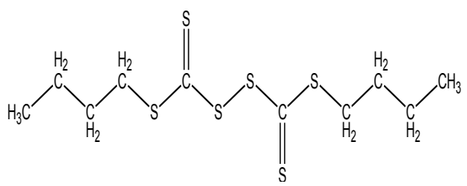


Fig.1. Structure of 1-[({[(butylsulfunyl carbothioyl] disulfanyl} carbothioyl)sulfanyl]butane

Triply distilled deionized water was used throughout the experiments. Chloride and nitrate salts of metals provided from either Merck or Fluka were used without further purification.

Membrane preparation

Membrane solution was prepared by thoroughly dissolving mg amounts of membrane ingredients under optimal conditions (i.e., 28.1mg PVC, 56.1mg NPOE, 12.0mg OA and 3.8mg **L**) in 4mL of THF. The resulting solution was evaporated slowly until an oily mixture was obtained. Pyrex tubes (5mm o.d. on top) were dipped into the mixture for about 10 s so that non-transparent membranes of about 0.3mm thickness were formed. The tube were then pulled out from the mixture and kept at room temperature for 6 h. The tubes were then filled with an internal solution (1.0×10^{-2} M $La(NO_3)_3$). The electrodes were finally conditioned for 24h in a 1.0×10^{-2} M $La(NO_3)_3$solution. A silver/silver chloride electrode was used as the internal reference. To prepare the coated graphite a spectroscopic grade graphite rod (10mm×3mm o.d.) was used, respectively. In the case of CGE, a shielded copper wire was glued to the end of the graphite rod. The electrodes were then sealed into the end of PVC tubes of about the same diameter with epoxy resin. The working surface of the electrodes were polished with fine alumina slurries on a polishing close, washed with water and dried in air. The polished electrodes were dipped into the membrane solution mentioned above, and the solvent was evaporated. A membrane was formed on the electrode surfaces, and the electrodes were then allowed to be stabilized over night. The electrodes were finally conditioned by soaking in a 1.0×10^{-2} M $La(NO_3)_3$ solution for 36 h.

Electrode system

All emf measurements were carried out with the following assembly:

Ag-AgC | xM $M(NO_3)_n$, yM KC l | sensor membrane | test solution | Hg-Hg_2Cl_2, KCl (sat'd.). A HIOKI digital hitester (Model 3256-01) was used for measuring the potential. The emf observation was made relative to a saturated calomel electrode (SCE, Philips).

Result and Discussion

In preliminary experiments, the ionophore was used as a neutral carrier to prepare PVC membrane ion selective electrode for a wide variety of metal ions, including alkali, alkaline earth, transition and heavy metal ions. The potential responses of various ISEs based on 2, 2-dithiodipyridine were obtained separately for each ion and the results are shown in Figure 2. As it is seen in this figure, the lanthanum ISE has shown the most sensitive response, which indicates that the membrane electrode based on 2,2-dithiodipyridine could be suitable for determination of La^{3+} ion.

It was found that variation of the concentration of the internal solution does not cause any significant difference in the potential response, except for an expected change in the intercept of the resulting Nernstian plots. A 1.0×10^{-3} M concentration of the reference solution is quite appropriate for smooth functioning of the electrode system. Optimum conditioning time for the membrane sensor in a 1.0×10^{-3} M La^{3+} solution was obtained to be 20 h. Then, the electrode generates stable potentials when placed in contact with La^{3+} solution. The response time of the electrode was tested by measuring the time required to achieve a 90% of the steady potential when the concentration of $La(NO_3)_3$ solution was rapidly increased by one decade from 1.0×10^{-4} to 1.0×10^{-3} M. The static response time thus obtained was less than 7 s over the entire concentration range, and potentials stayed constant for about 5 min, after which only a very slow divergence was recorded. The sensing behavior of the membrane remained unchanged when the potentials were recorded either from high to low concentrations or vice versa.

Electrode optimization

It is well known that the sensitivity, linearity and selectivity obtained for a given ionophore depends significantly on the membrane composition [13–19]. Since the nature of the plasticizer influences the dielectric constant of the membrane phase as well as the mobility of the ionophore molecule and its complexes [20], it is expected to play a fundamental role in specifying the selective electrode characteristics. So, several solvent mediators such as *o*-NPOE, DMS, DES and DBP which are often used in PVC-membrane electrodes, were evaluated and the results are summarized in the Table 1.

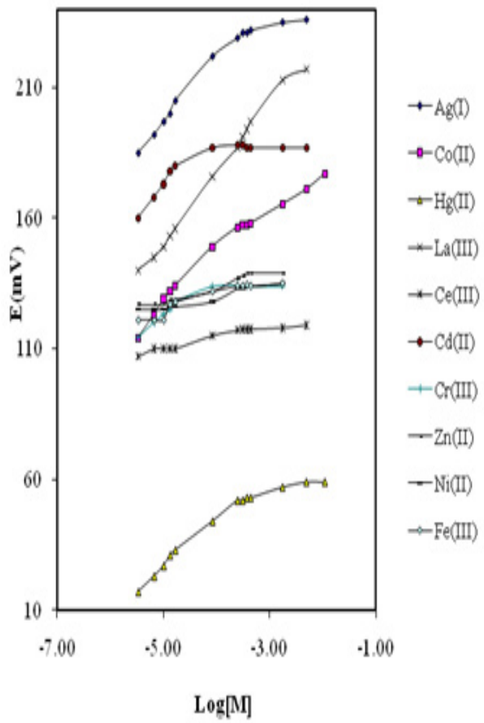


Fig. 2. Potential responses of various transitions metal electrodes based on the proposed carrier

Among these plasticizers, DES provided faster more stable and sensitive response in the concentration range of 3.1×10^{-7}-5.8×10^{-3} of La^{3+} ion (Table 1). In general hardness and thickness of membrane depends mainly on PVC content of membrane. So DES to PVC ratios 1.5, 2 and 2.5 were tested and summarized on Fig 3. As it is shown membrane with the ratio of 1.5 represents the best response characteristics, the higher plasticizer to PVC

ratio makes membrane weak and swell up in the aqueous solution, the lower ratio make it too dense so it makes transport of the cation into the membrane more difficult.

The sensing behavior of the membrane remained unchanged when the potentials were recorded either from high to low concentrations or vice versa.

Table 1. Effect of various solvent mediators on the responses of the La^{3+}- SE

Log[La^{3+}]	E(mV)				
	DES	**DMS**	**DBS**	**DOS**	**NPOE**
-5.48	159.0	139.0	125.0	75.0	193.0
-5.18	164.5	147.0	132.0	77.5	197.0
-5.00	168.5	152.0	135.0	79.0	200.0
-4.10	186.6	162.0	140.0	87.0	199.0
-3.62	194.0	172.0	145.0	89.0	199.0
-3.25	199.0	176.0	147.0	93.0	198.0
-3.05	201.2	178.0	143.0	95.0	198.0
-2.92	202.5	180.0	143.0	98.0	197.0
-2.82	205.0	180.0	142.0	98.0	-
-2.67	209.0	180.0	142.0	98.0	-
-2.43	215.0	182.0	140.0	98.0	-
-2.18	215.0	182.0	-	-	-
-2.03	215.0	182.0	-	-	-
slope	16.8	12.5	4.5	8.24	0.397
R^2	0.991	0.952	0.645	0.986	0.029

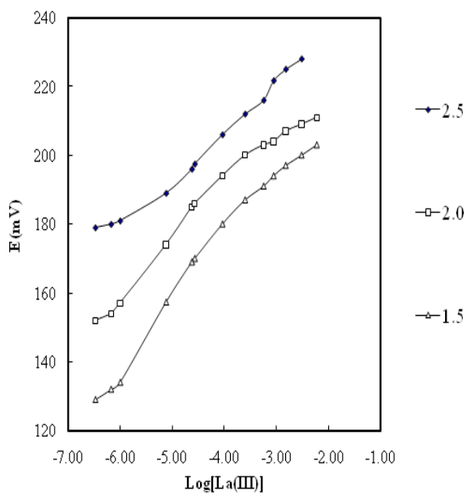


Fig. 3. Effect of different weight ratio of DES/PVC on the response of the La^{3+} ISE

The pH dependence of the electrode potential was investigated over the pH range of 2.0–10.0 in a 1.0×10^{-4} M solution of La^{3+} ion. As shown in Fig 4, the potential was independent of pH in the range of 3.7–7.3 pH unit. At higher pH values, the potential decreased due to the formation of lanthanum hydroxide in solution; and at lower pH values, the potential increased, indicating that the electrode also responds to hydrogen ion.

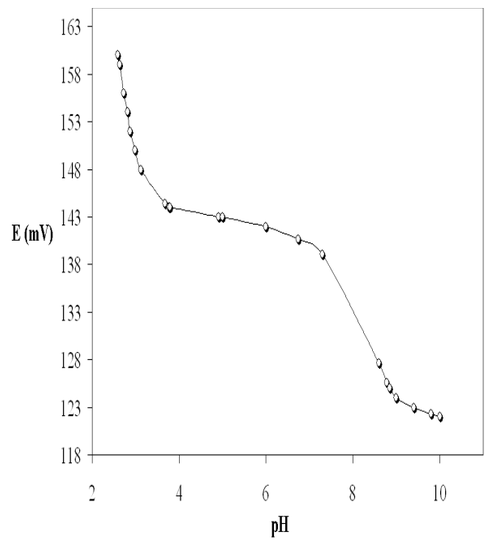
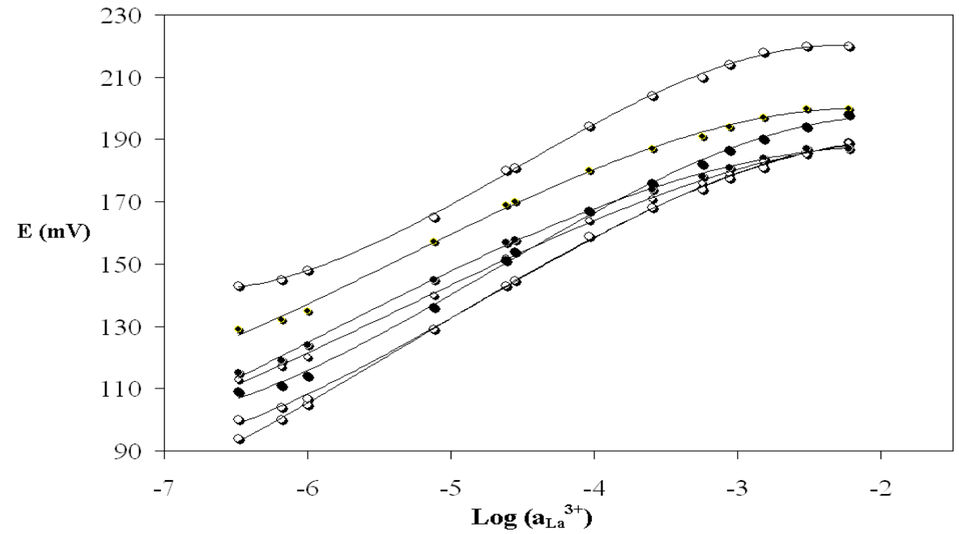


Fig. 4. Effect of pH on the La^{3+} ISE responses

The reproducibility of the electrode was examined using seven similarly constructed electrodes under the same optimum conditions. The results (not shown) confirmed that the electrode had good reproducibility (RSD= 2.5 %) (Fig. 5). The long-term stability of the electrode was also studied by periodically re-calibrating in standard solutions and calculating the response slope. The slope of the electrode response was reproducible over a period of at least 2 months. Therefore, the proposed electrode could be used for 2 months without any considerable change in its response characteristics towards La^{3+} ion.

The selectivity behavior is obviously one of the most important characteristics of a membrane sensor, determining whether a reliable measurement in the target sample is



Slope	R^2
Mean=20.9	Mean=0.988
SD = ±1.8	SD = ±0.003
RSD = 8.6	RSD = 0.3

Fig. 5. Reproducibility of the lanthanum ion selective electrode responses

possible [21,22]. In this work, the influence of several transition and heavy metal ions on the potential response of the cadmium-selective electrode was tested by determining the potentiometric selectivity coefficients of the electrodes by the separate solution method (SSM) [22,23]. In this method, the potential of a cell comprising an ion selective electrode and a reference electrode is measured with two separate solutions. One contains the ion of interest i at the activity a_i (but no j) and the other containing the interfering ion j at the same activity $a_j = a_i$ (but no i). In this method the values are the selectivity coefficient can be derived from the following equation:

$$K_{ij}^{\text{pot}} = \frac{E_2 - E_1}{2.303\, RT/Z_i F} + \left(1 - \frac{Z_i}{Z_j}\right) \log a_i$$

where E_1, E_2 and Z_i, Z_j are the respective measured potentials and charges on the ions i and j. The resulting log $K^{pot}_{La,M}$ values obtained are summarized in Table 2. It is seen that, in all cases, the selectivity coefficients are in

Table 2. Selectivity coefficients of various interfering ions for the La^{3+} ISE

M^{n+}	Selectivity coefficient
Ag^+	1.0×10^{-1}
Al^{3+}	3.3×10^{-5}
Ca^{2+}	$<1.0\times10^{-6}$
Cd^{2+}	3.0×10^{-4}
Ce^{3+}	7.5×10^{-4}
Co^{2+}	5.0×10^{-4}
Cr^{3+}	1.3×10^{-3}
Cu^{2+}	7.5×10^{-4}
Fe^{3+}	1.3×10^{-3}
Hg^{2+}	3.3×10^{-3}
Mg^{2+}	$<1.0\times10^{-6}$
Mn^{2+}	3.3×10^{-4}
Na^+	$<1.0\times10^{-6}$
NH_4^+	$<1.0\times10^{-6}$
Ni^{2+}	1.2×10^{-4}
Pb^{2+}	3.3×10^{-2}
Sr^{2+}	$<1.0\times10^{-6}$
Zn^{2+}	1.7×10^{-3}

the order of 10^{-2} and lower, except for silver ion which is about 0.1, indicating negligible interference in the performance of the membrane sensor assemblies.

Analytical application

The practical utility of the proposed membrane sensors were tested by their use as indicator electrodes for titration of 30mL of La^{3+} 1.0×10^{-3}M with a 0.01M standard solution of ethylenediamine tetraacetic acid (EDTA) solution at pH 6, and results are shown in Fig 6. As seen, the amount of cadmium ions in solution can be accurately determined with this electrode.

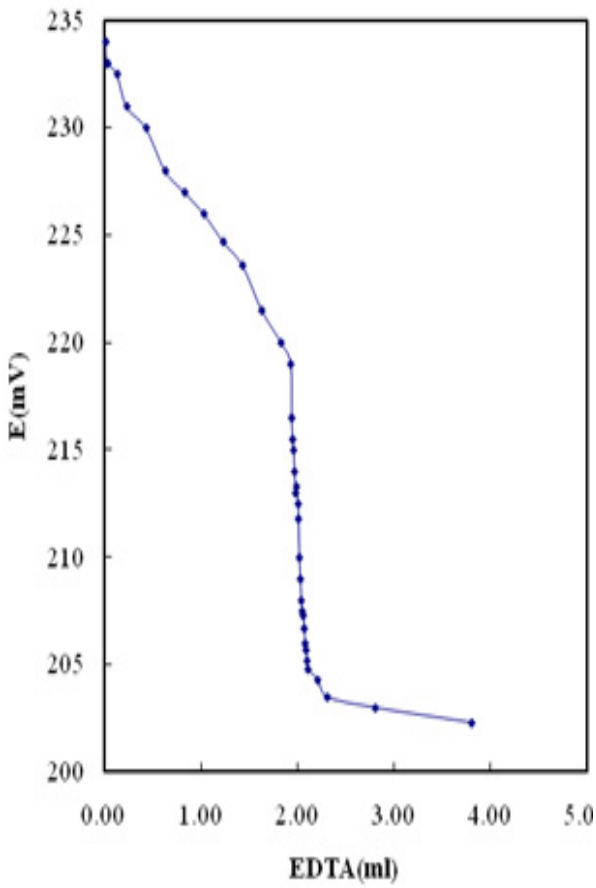


Fig. 6. Potentiometric titration curve for 30 ml of $6.6\times10^{-4}La^{3+}$ in acetate buffer pH=6.0 with 0.01M EDTA solution using the La^{3+} ISE

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