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A New Cerium(III) Ion-Selective Electrode Based on Dicyclohexano-18-crown-6 as Ionophore[1]

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Abstract—A coated membrane electrode has been designed and constructed for measuring the cerium(III) cation activity in solution by using dicyclohexano-18-crown-6 (DCH18C6) as a membrane carrier (ionophore), dibuthyl phthalate (DBP) as plasticizer, sodium tetraphenylborate (NaTPB), poly(vinyl chloride) (PVC) as matrix, and tetrahydrofuran (THF) as solvent. A graphite rod was then coated with the membrane by the dip–dry method. The calibration curve for the constructed electrode under the optimized conditions exhibit a Nernstian response of 19.8±0.5 mV/decade for Ce^{3+}cation over a relatively wide concentration range (10^{-2} to 10^{-5} M) at 25°C and pH 4–8. The detection limit for the electrode was found to be 1.44×10^{-6} M. The response time of the cerium(III)-selective electrode was less than 25 s. The effect of interfering ions and the selectivity of the electrode were also studied. This electrode was successfully used as an indicator electrode for potentiometric titration of cerium(III) nitrate with a standard solution of NaF. The electrode could be used for at least 30 days without any appreciable change in its sensitivity.

Keywords: ion-selective electrode, cerium(III) cation, dicycleohexano-18-crown-6, potentiometric titration
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Carrier-based ion-selective electrodes (ISEs) are well established as analytical tools that are routinely used to selectively and directly measure a wide variety of different ions in complex samples. Ion-selective electrodes, especially those with neutral carrier-based polymeric membranes, have been studied in the past years, and are now routinely employed for direct potentiometric measurements of various ionic species in environmental, industrial, and clinical samples [1, 2].

Ionophores used in sensors should exhibit rapid exchange kinetics and have suitable complex formation constants in the membrane. Moreover, they should be soluble in the membrane matrix and have sufficient lipophilicity to prevent leaching from the membrane into the sample solution. In addition, the selectivity of neutral carrier-based ISEs is governed by the stability constant of the neutral carrier–ion complex and the partition constant between the membrane and sample solution [3].

Ion-selective electrodes based on matrices such as solid crystalline, glass, ceramic, and liquid membranes have been reported, the sensing layer of most ISEs today is formed from an organic polymeric membrane matrix [3]. With this scheme, each component of the sensing layer is trapped within a polymer membrane that afterward is used to construct an ion-selective electrode. The most widely employed polymer for ISE membranes is poly(vinyl chloride) (PVC) due to its relatively low cost, good mechanical properties, and amenability to plasticization [4].

Cerium is a rare earth metal which is the most abundant member of the lanthanide series. Cerium is used in metallurgy as a stabilizer in alloys and in welding electrodes, polishing agent in glass, and decolorizer, as well as to render glass opaque to near-ultraviolet radiation. It is also used in ceramics and as a catalyst. Cerium is used as a component of some diesel fuel additives, and it may be added to residual fuel oils to improve combustion. Cerium is found in portable rechargeable batteries [5–7]. Cerium(III) occurs in monazite, ceric bastnaesite, and silicate rocks and is widely used in the production of ductile iron, cast steel, and stainless steel. Therefore, determination of Ce(III) in various samples is of significant interest [8, 9].

[1] The text was submitted by the authors in English.

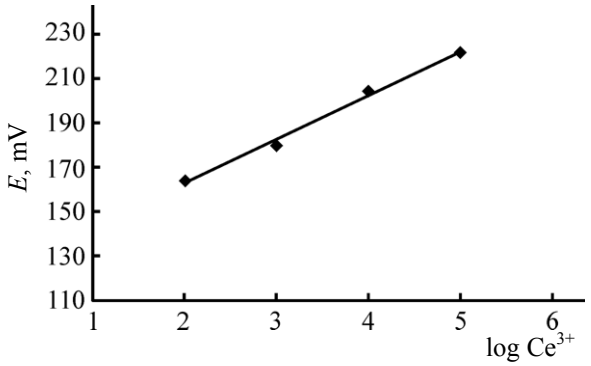

Fig. 1. Calibration curve of Ce^{3+}-selective electrode based on DCH18C6.

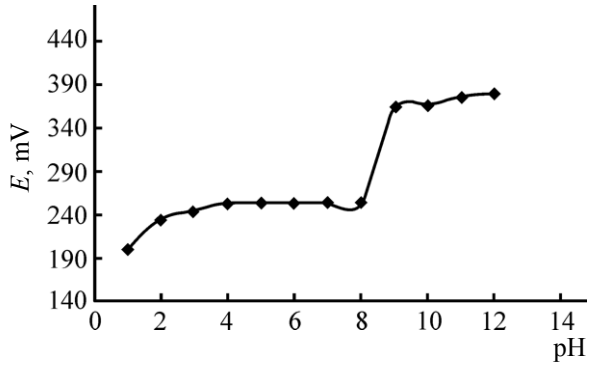

Fig. 2. Effect of pH on the potential response of the Ce^{3+}-selective membrane electrode; $c(Ce^{3+}) = 10^{-3}$ M.

Several techniques have been used for the determination of trace amounts of cerium in various samples, including inductively coupled plasma–atomic emission spectrometry (ICP-AES) [10], electrothermal atomic absorption spectrometry, spectrofluorimetry [11], ICP-AES/HPLC [12], and stripping voltammetry [13]. These methods are expensive and may be unavailable in some areas. Potentiometric electrodes

Table 1. Optimization of membrane ingredients

Membrane no.	Membrane composition, mg				Slope, mV/decade	Linear range, M
	additive	plasticizer	DCH18C6	PVC		
1	NaTPB, 1	DBP, 65	4	30	5.1	10^{-2}–10^{-5}
2	NaTPB, 2	DBP, 65	3	30	6.2	10^{-2}–10^{-5}
3	NaTPB, 3	DBP, 65	2	30	17.5	10^{-2}–10^{-5}
4	NaTPB, 4	DBP, 65	1	30	6.9	10^{-2}–10^{-5}
5	NaTPB, 3	DBP, 65	2	30	7.8	10^{-2}–10^{-5}
6	NaTPB, 1	DBP, 66	3	30	13.2	10^{-2}–10^{-5}
7	NaTPB, 2	DBP 65	3	30	7.9	10^{-2}–10^{-5}
8	NaTPB, 2	DBP 66	2	30	24.9	10^{-2}–10^{-5}
9	NaTPB, 2	NB, 66	2	30	11.2	10^{-2}–10^{-5}
10	NaTPB, 2	BA, 66	2	30	9.6	10^{-2}–10^{-5}
11	NaTPB, 2	AP, 66	2	30	6.1	10^{-2}–10^{-5}
12	NaTPB, 3	NB, 65	1	30	6.9	10^{-2}–10^{-5}
13	NaTPB, 2	DOP, 66	2	30	5.6	10^{-2}–10^{-5}
14	Oleic acid (OA), 2	DBP, 66	2	30	10	10^{-2}–10^{-5}
15	NaTPB, 1	DBP, 67	2	30	19.8	10^{-2}–10^{-5}
16	NaTPB, 1	NB, 66	3	30	9.3	10^{-2}–10^{-5}
17	NaTPB, 2	DOP, 65	3	30	17.6	10^{-2}–10^{-5}
18	NaTPB, 1	DBP, 68	1	30	0.6	10^{-2}–10^{-5}
19	NaTPB, 1	NB, 67	2	30	70.9	10^{-2}–10^{-5}
20	NaTPB, 1	BA, 67	2	30	9.5	10^{-2}–10^{-5}

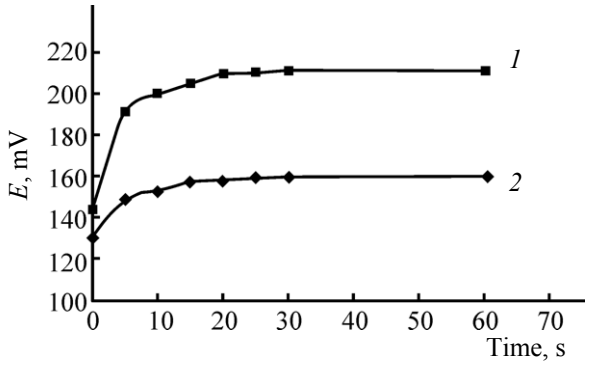

Fig. 3. Static potential vs. time plots at a Ce^{3+} concentration of (*1*) 10^{-2} and (*2*) 10^{-5} M.

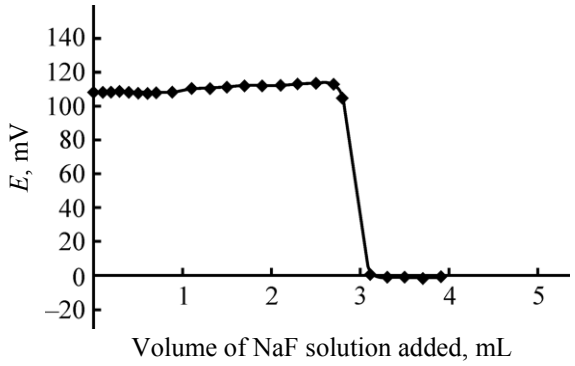

Fig. 4. Potentiometric titration curve of a 10^{-3} M solution of cerium(III) nitrate (10 mL) with a 10^{-2} M solution of sodium fluoride using the proposed electrode.

have several advantages, including direct, simple, rapid, inexpensive, and selective detection of ionic activity in solution. The selectivity of these electrochemical sensors stems from the highly selective interactions between the membrane material and the target species [14].

In this paper, we introduce a new ion-selective electrode based on the incorporation of dicyclohexano-18-crown-6 (DCH18C6) as a neutral carrier for the selective and sensitive determination of Ce^{3+} cation in solution.

The sensitivity and selectivity of the electrode response substantially depend on the chemical nature and amounts of the membrane compounds and the nature of the solvent and additive used in the electrode construction [15–17]. Thus, we investigated the effect of the membrane composition on the potential response of the proposed sensor. The dielectric constant of the membrane phase, the mobility of ionophore molecules in the membrane, and the selectivity of the electrochemical sensor, are influenced by the plasticizer nature [18, 19]. Therefore, different membranes were prepared, using several plasticizers such as dibutyl phthalate (DBP), dioctyl phthalate (DOP), benzyl acetate (BA), acetophenone (AP), and nitrobenzene (NB) with DCH18C6 as ionophore, and the obtained results are given in Table 1. It is evident the membrane no. 15 with the composition NB–PVC–sodium tetraphenyl-borate (NaTPB)–DCH18C6 at a weight ratio of 67 : 30 : 1 : 2 (mg) shows Nernstian behavior for the membrane electrode. The calibration curve for this electrode shown in Fig. 1 indicates Nernstian behavior of the constructed electrochemical sensor over a wide range of Ce^{3+} concentration (10^{-2} to 10^{-5} M. The slope of the calibration curve is 19.8 ± 0.5 mV/decade, and the detection limit (DL) is 1.44×10^{-6} M. The proposed electrode was very stable, and it can be used for four weeks without any change in its response characteristics.

The effect of pH on the performance of the constructed electrode was studied by measuring the potential at a Ce^{3+} concentration of ~10^{-3} M in the pH range from 1 to 12. The pH was adjusted by adding NaOH or HNO_3. The results are shown in Fig. 2. The potential remains approximately constant over pH values of 4.0– 8.0. At lower pH values, protonation of the crown ether occurs in the membrane, and the observed increase of the potential at higher pH values could be due to the formation of some hydroxy complexes of Ce^{3+} in solution.

The response time of an ion-selective electrode is an important factor. In the present study, the static response time of the electrode was evaluated by measuring the average time required to achieve the

Table 2. Selectivity coefficients for different ionic interferences (M^{n+}) for the Ce^{3+}-ISE

M^{n+}	K_{AB}^{pot}
Li^+	2.66×10^{-3}
Ca^{2+}	4.95×10^{-3}
Mg^{2+}	4.35×10^{-7}
Pb^{2+}	3.99×10^{-1}
Sr^{2+}	2.77×10^{-6}
Cd^{2+}	1.44×10^{-9}
Al^{3+}	7.39×10^{-3}
Fe^{3+}	1.71×10^{-1}

final steady state potential. For this purpose, the potential vs. time plots were recorded at two different Ce^{3+} concentrations (c = 10^{-1} and 10^{-2} M), and the results are shown in Fig. 3. In all cases, the electrode exhibited a constant and stable potential within 20 s.

The selectivity behavior is one of the most important characteristics of an ion-selective electrode. It is estimated as the relative electrode response to a specific ion (A) over other ions present in solution (B) in terms of the potentiometric selectivity coefficients (K_{AB}^{pot}). In this work, the separate solution method (SSM) [20] was applied for the determination of the selectivity coefficients of the proposed electrode. The selectivity coefficients are listed in Table 2. It is seen that most selectivity coefficients are very low, indicating no significant interference in the performance of the electrode.

The analytical application of the constructed ISE was investigated by using it as an indicator electrode in the potentiometric estimation of Ce^{3+} concentration by titrating 10 mL of a 10^{-3} M solution of $Ce(NO_3)_3$ with a 10^{-2} M solution of NaF. The titration curve is presented in Fig. 4. A sharp titration curve was obtained using this electrochemical sensor; therefore, the amount of Ce^{3+} cation can be accurately determined in aqueous solution.

In summary, a new ion-selective electrode for the determination of cerium(III) cation in solution has been fabricated using dicyclohexano-18-crown-6 (DCH18C6) as ionophore. The results obtained in this investigation show that DCH18C6 is a suitable ligand for the construction of a PVC-based membrane selective electrode for the direct determination of cerium(III) ion in solution. The sensor displayed a Nernstian slope of 19.8±0.5 mV/decade for Ce^{3+} cation over a relatively wide concentration range from 10^{-2} to 10^{-5} M at 25°C with a response time of ~20 s. The detection limit for the constructed electrode was found to be 1.44×10^{-6} M. The proposed electrode works well under laboratory conditions and can be successfully applied as an indicator electrode in potentiometric titration for the determination of cerium(III) cation in aqueous solution.

EXPERIMENTAL

Potentiometric measurements were carried out at 25°C with a Metrohm Model 1.691.0020 digital potentiometer equipped with a saturated calomel electrode as reference electrode. The pH of solutions was measured by a conventional glass pH electrode. The performance of each electrode was evaluated by measuring its potential in cerium(III) nitrate solutions with the concentrations ranging from 10^{-1} to 10^{-9} M, which were prepared by serial dilution of a 0.1 M stock solution. The solutions were stirred, and the potential readings were recorded when they reached steady state values.

Tetrahydrofuran (THF), dicyclohexano-18-crown-6 (DCH18C6), dibutyl phthalate (DBP), sodium tetraphenylborate (NaTPB), acetophenone (AP), nitrobenzene (NB), lead(II) nitrate, aluminum nitrate, iron(III) nitrate, sodium hydroxide, hydrochloric acid, and sodium fluoride were purchased from Merck. Poly (vinyl chloride) (PVC) powder, dioctyl phthalate (DOP), potassium nitrate, lithium carbonate, calcium nitrate, magnesium nitrate, and strontium nitrate were obtained from Fluka. All reagents were of the highest purity available and were used without any further purification. Doubly distilled deionized water was used throughout the study.

The membrane was prepared by dissolving plasticizer, poly(vinyl chloride), additive, and ionophore in 2 mL of THF. The solvent was evaporated slowly until an oily concentrated mixture was obtained. Consequently, a graphite bar was dipped into the mixture for a few seconds. The graphite bar was kept to dry at room temperature for about 24 h. The electrodes were conditioned in a 0.1 M solution of cerium(III) nitrate for 48 h before use.

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