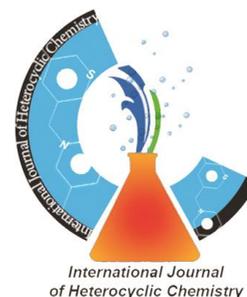

Research article

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Highly selective and sensitive sensor based on 4,13-didecyl-1,7,10,16-tetraoxa-4,13-diazacyclooctadecane as a heterocyclic ionophore

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Abstract

A new polyvinyl chloride (PVC) membrane sensor for cerium (III) was prepared based on 4,13-didecyl-1,7,10,16-tetraoxa-4,13-diazacyclooctadecane (kryptofix22DD) as an ionophore. The sensor exhibits a linear concentration range of 1.0×10^{-6} to 1.0×10^{-1} M, with a Nernstian slope of 18.0 ± 1.0 mV/decade, and a detection limit of 9.7×10^{-7} M. It has a fast response time (5 s) and can be used for two months without any considerable divergence in its potential. The proposed sensor revealed high selectivity toward Ce^{3+} ion with respect to some alkali, alkaline earth and transition metal cations. It could be used in a wide pH range of 2.0-11.0. The sensor was successfully used as an indicator electrode in potentiometric titration of Ce^{3+} ion with ethylenediaminetetraacetic acid (EDTA) and sodium iodide (NaI) solutions, and in determination of Ce (III) concentration in real samples.

Keywords: PVC membrane, Cerium (III) selective sensor, Kryptofix22DD, Potentiometry

Introduction

Cerium is a member of the lanthanum group of elements and the most abundant of them. It is found in monazite, ceric bastnaesite, and silicate rocks and is widely used in production of

ductile iron, cast steel and some stainless steels [1]. Thus, the determination of Ce (III) in different samples is of special interest.

The quick determination of trace quantities of ionic species, by simple methods, is of urgent need in analytical chemistry. Ion selective electrodes (ISEs) based on solvent polymeric membranes with incorporation of ion carriers are shown to be very useful tools for chemical, clinical and environmental analyses as well as in process monitoring [2,3]. They have been the subject of interest for analytical chemists as they provide accurate, rapid and low cost method for analysis. This technique is also nondestructive and adaptable to very small sample volume; moreover, online monitoring is also possible by these devices. Some commercialized sensors for alkali and alkaline earth metals, halides, etc. are available [4-7]; however, more efforts are required to develop ion selective electrodes of commercial standard for heavy metal ions, which are toxic beyond a certain concentration level [8-10].

Fabrication of a new, ion-specific ISE with high selectivity and sensitivity, wide linear concentration range, long lifetime, good reproducibility and low cost, is always in need. Crown ethers have been demonstrated as highly selective complexing agents for many metal ions. They can be applied in separation and determination of metal ions through molecular recognition [11]. Generally, a crown ether forms a complex with a metal ion that fits well in its cavity. Solvent polymeric membrane-based ISEs together with the incorporation of new ion carriers have shown to be a very useful tool for chemical, clinical, and environmental analyses as for process monitoring [12-14].

This research describes the use of 4,13-didecyl-1,7,10,16-tetraoxa-4,13-diazacyclooctadecane (kryptofix22DD) (Fig. 1) as a macrocyclic neutral carrier in construction of a cerium (III) PVC membrane electrode.

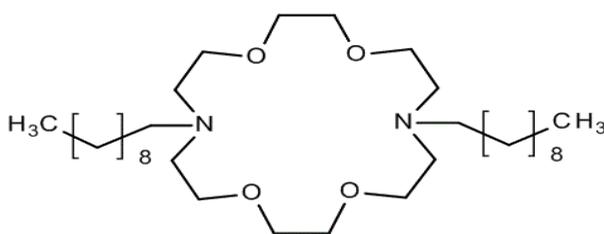


Fig. 1. Structure of 4,13-didecyl-1,7,10,16-tetraoxa-4,13-diazacyclooctadecane (kryptofix22DD).

Experimental

Reagents

Analytical reagent grade chemicals and doubly distilled water were used for preparing all aqueous solutions. 4,13-didecyl-1,7,10,16-tetraoxa-4,13-diazacyclooctadecane (kryptofix22DD),

tetrahydrofuran (THF), nitrobenzene (NB), dioctyl phthalate (DOP), dibutyl phthalate (DBP), dioctyl sebacate (DOS), sodium tetraphenylborate (NaTPB), ethylenediaminetetraacetic acid disodium salt, sodium iodide, nitric acid, sodium hydroxide and all metal salts were obtained from Merck. High molecular weight polyvinyl chloride (PVC) powder was purchased from Fluka. All reagents were of the highest purity available and used without any further purification.

Electrodes fabrication

The electrodes were prepared from a graphite bars (3 mm diameter and 50 mm long). The graphite bars were polished and put in a concentrated HNO_3 solution overnight to clean the surface of the graphite bars. Then, the bars were rinsed with THF and once again polished and washed with distilled water and allowed to dry. A mixture of ionophore (kryptofix22DD), PVC, plasticizer and membrane additive (NaTPB) to give a total mass 100 mg was dissolved in about 2 ml of THF and the solution was mixed well. The graphite bar was coated by dipping it into the membrane solution for a few seconds and allowed to dry overnight. The electrode was conditioned in 0.001 M cerium nitrate for 24 h, and stored in mild concentration solutions of cerium nitrate, when not in use. The coating solution was stable for several days and could be used for construction of new membranes. Thus, several membranes of varying compositions were prepared and investigated.

Apparatus and potential measurements

The response characteristics of the prepared coated graphite electrodes were determined by recording potential across the membrane as a function of Ce^{3+} concentration at a constant temperature of 25.0 ± 0.1 °C. All potential measurements were carried out with a digital pH/mV meter model PTR-79 (Zag Chimi, Iran) having ± 0.01 mV accuracy with an Ag/AgCl reference electrode. The potential build up across the electrode was measured using the galvanic cell of the following type:

$\text{Ag/AgCl; KCl(satd.)} \parallel \text{Ce}^{3+} \text{ sample solution} \mid \text{ion selective membrane} \mid \text{graphite bar}$

The performance of each electrode was investigated by measuring the potential of Ce^{3+} solutions with concentrations ranging from 1.0×10^{-8} to 1.0×10^{-1} M by serial dilution of the 0.1 M stock solution at constant pH. The solutions were stirred and potential readings recorded when they reached steady state values. The observed potential versus the logarithm of the Ce^{3+} ion concentration was plotted. The pH of the solutions was measured by a conventional glass pH electrode.

Results and discussion

The membrane composition influence

It should be noted that the sensitivity and selectivity of a given ionophore depend significantly on the membrane ingredients, the nature of the solvent mediator and the

used additive [15,16]. Thus, different aspects of composition of membranes based on the kryptofix22DD for Ce^{3+} ions were optimized and the results are given in Table 1.

Since the nature of the plasticizer influences both the dielectric constant of the membrane phase and the mobility of the ionophore molecules, it was expected to play a key role in the sensitivity and selectivity of ion selective sensors. As it is seen from Table 1, several plasticizers including DBP, DOP, DOS and NB, were evaluated. Among these four different plasticizers examined, NB results in the best sensitivity and linear concentration range.

The perm-selectivity optimization of membrane sensors is known to be highly dependent on the incorporation of additional membrane components. In fact, it has been demonstrated that the presence of lipophilic negatively charged additives improves the sensitivity of certain cation-selective electrodes by reducing the ohmic resistance and improving the response behavior and selectivity and in some cases by catalyzing the exchange kinetics at the sample-membrane interface [17,18]. The data given in Table 1 reveals that, in the absence of a proper additive, the sensitivity of the cerium (III) sensor based on kryptofix22DD reduces from the Nernstian slope (membrane no. 1 with a slope of 15.0 ± 1.2 mV/decade).

Table 1. Optimization of the membrane ingredients.

Membrane no.	Membrane mass composition (%)			Slope (mV/decade)	Linear range (M)	
	PVC	Ionophore (Kryptofix22DD)	Additive (NaTPB)			Plasticizer
1	30	10.0	—	60.0 (NB)	15.0 ± 1.2	$10^{-4} - 10^{-2}$
2	30	—	10.0	60.0 (NB)	10.2 ± 0.3	$10^{-3} - 10^{-1}$
3	30	6.0	4.0	60.0 (DOP)	26.8 ± 0.5	$10^{-5} - 10^{-1}$
4	30	5.0	4.0	61.0 (DOP)	17.3 ± 3.1	$10^{-8} - 10^{-6}$
5	30	5.8	4.2	60.0 (NB)	18.0 ± 1.0	$10^{-6} - 10^{-1}$
6	30	4.0	4.0	62.0 (DOP)	28.4 ± 0.6	$10^{-4} - 10^{-1}$
7	30	4.3	3.5	62.2 (DBP)	16.2 ± 0.2	$10^{-6} - 10^{-2}$
8	30	4.0	4.0	61.0 (DBP)	16.8 ± 1.2	$10^{-4} - 10^{-1}$
9	30	3.5	2.5	64.0 (DBP)	17.6 ± 0.5	$10^{-4} - 10^{-2}$
10	30	5.0	2.1	62.9 (DBP)	17.5 ± 1.6	$10^{-5} - 10^{-2}$
11	30	5.0	4.0	61.0 (DOS)	16.0 ± 1.5	$10^{-4} - 10^{-1}$

As a result, membrane composition of 30% PVC, 5.8% kryptofix22DD, 4.2% NaTPB and 60% NB (membrane no. 5) exhibits the best Nernstian slope (18.0 mV/decade) and linear concentration range (from 1.0×10^{-6} to 1.0×10^{-1} M). The calibration curve for this sensor is shown in Fig. 2. The detection limit of this sensor, as determined from the intersection of the two extrapolated segments of the calibration graph is 9.7×10^{-7} M. The standard deviation of 3 replicate measurements is ± 1.0 mV/decade. The proposed sensor was very stable and could be used for 2 month without observing any change in its response characteristics.

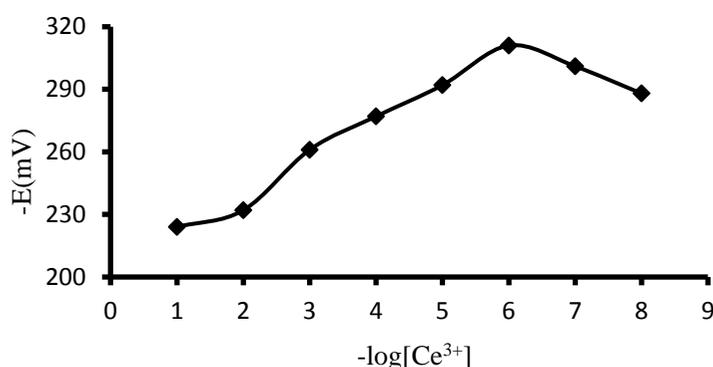


Fig. 2. Calibration curve of the Ce^{3+} selective sensor based on kryptofix22DD.

Static and dynamic response time

For analytical purposes, response time is one of the most important factors that are taken into account. Therefore, the static response time of the proposed sensor (membrane no. 5) was studied by plotting the potential response vs. time, at 1.0×10^{-4} M and 1.0×10^{-3} M of Ce^{3+} ion solutions (Fig. 3). As is evident in this figure, in the whole concentration range, the sensor reaches its equilibrium response in a short time (~ 5 s) and no change is observed in 100 second.

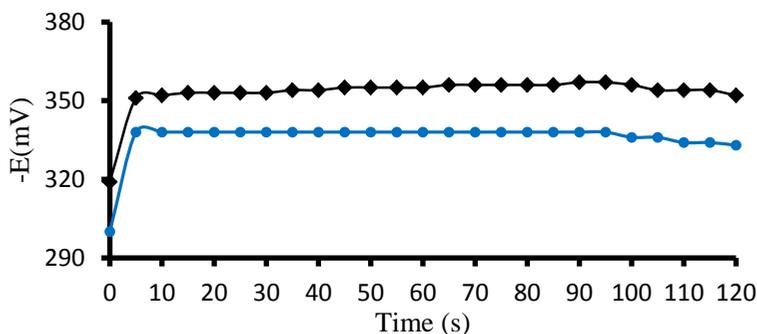


Fig. 3. Static response time curves of the Ce^{3+} selective sensor (\bullet 1.0×10^{-3} M, \blacklozenge 1.0×10^{-4} M).

For any ion selective sensor, dynamic response time is an important factor. In this study, the practical response time of the proposed sensor was recorded by changing the Ce^{3+}

concentration in solution in a concentration range of 1.0×10^{-6} to 1.0×10^{-1} M and the results are shown in Fig. 4. From this figure, it can be derived that the electrode reaches its equilibrium response rapidly (5 s), in the whole concentration range. This is most probably due to the fast exchange kinetics of the complexation-decomplexation of Ce^{3+} ions with the ionophore at the test solution-membrane interface.

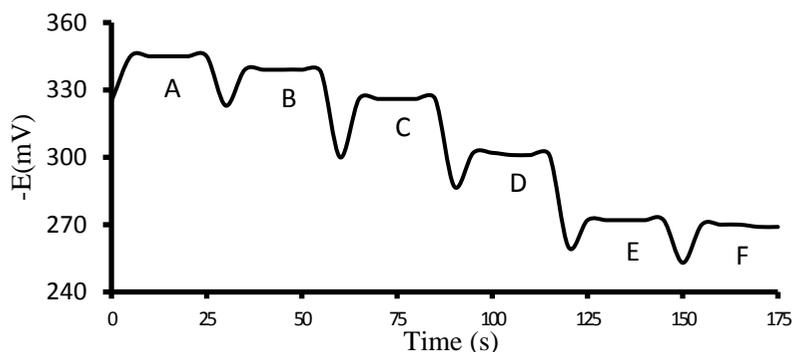


Fig. 4. Dynamic response time of the Ce^{3+} selective sensor for step changes in the concentration of Ce^{3+} : (A) 1.0×10^{-6} M, (B) 1.0×10^{-5} M, (C) 1.0×10^{-4} M, (D) 1.0×10^{-3} M, (E) 1.0×10^{-2} M, (F) 1.0×10^{-1} M.

Effect of pH

The relationship between the pH and the potentials of the proposed ion selective electrode was investigated by measuring the potential at a pH range of 1.0-12.0. Experimentally, the pH was adjusted with dilute solutions of HNO_3 and $NaOH$. The effect of the pH on the proposed ion selective electrode is shown in Fig. 5. As shown in the figure, the potential remained constant over a pH range of 2.0-11.0. Therefore, the working pH range of the proposed electrode is 2.0-11.0. A significant change in the potential response was observed at pHs greater than 11.0, which may be due to the formation of hydroxyl complexes of Ce (III) cations, which reduce the free cation concentration in solution. The observed drift in the electrode potentials at pHs less than 2.0 may be due to the protonation of the ion carrier in solution.

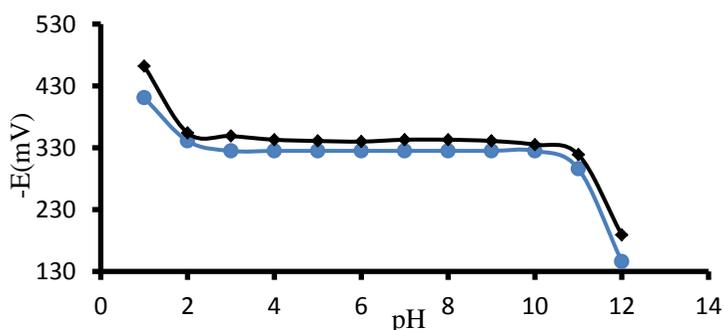


Fig. 5. Effect of the pH of test solutions on potential response of the Ce^{3+} selective sensor (● 1.0×10^{-3} M, ◆ 1.0×10^{-4} M).

Selectivity

The most important characteristic of a sensor is the selectivity, as it reflects its utility for target sample. There are a few methods to measure the potentiometric selectivity coefficients. In this study, the potentiometric selectivity coefficients of the proposed sensor were determined by the Separate Solution Method (SSM) [19,20]. The $K_{Ce,j}^{Pot}$ of mono-, di- and trivalent cations were measured and the results are summarized in Table 2. It is obvious from the selectivity coefficient data that most of the selectivity coefficients of interfering ions are low and these metal ions give no significant interference in the process of the sensor.

Table 2. Selectivity coefficients ($K_{Ce,j}^{Pot}$) of various interfering ions for cerium (III) selective sensor using Separate Solution Method (SSM).

Interfering ions	Selectivity coefficients ($K_{Ce,j}^{Pot}$)
K ⁺	2.5×10^{-3}
Ag ⁺	$< 10^{-6}$
Zn ²⁺	4.4×10^{-4}
Sr ²⁺	2.5×10^{-5}
Cu ²⁺	$< 10^{-6}$
Fe ³⁺	$< 10^{-6}$
Pb ²⁺	1.7×10^{-6}

Analytical applications

The practical utility of the proposed sensor was tested by using it as an indicator electrode for the titration of 25 ml 1.0×10^{-3} M of Ce³⁺ ions with 1.0×10^{-2} M of EDTA in Fig. 6. As can be seen, the amount of cerium (III) ions in solution can be accurately determined with the sensor. Very good inflection points, showing a perfect stoichiometry and efficiency of the sensor in the potentiometric determination of Ce³⁺ cation in solutions.

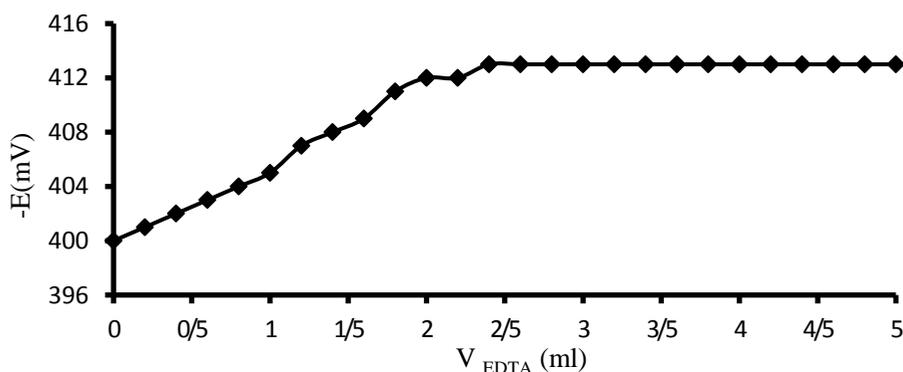


Fig. 6. Potentiometric titration curve for 25 ml 1.0×10^{-3} M of Ce³⁺ solution with 1.0×10^{-2} M of EDTA.

Determination of Ce³⁺ ion in real samples

The proposed sensor was also successfully applied to the direct determination of cerium (III) in real water samples using standard addition method and the results are shown in Table 3. As can be seen, the recoveries of cerium from different water samples are in the range of 90.0-96.6%. Results indicate that the composition of the real samples do not interfere significantly on the detection of Ce³⁺ ions. In fact, the accuracy of cerium recovery in different solution samples is almost quantitative.

Table 3. Determination of Ce³⁺ ion in real water samples using the cerium (III) selective sensor.

Real water samples	Added Ce ³⁺ concentration (mol/l)	Found Ce ³⁺ concentration (mol/l)	Recovery (%)
Tap water (Ahvaz city, Iran)	3.0×10 ⁻⁴	2.9×10 ⁻⁴	96.6
River water (Karooon river, Iran)	3.0×10 ⁻⁴	2.7×10 ⁻⁴	90.0
River water (Karkheh river, Iran)	3.0×10 ⁻⁴	2.8×10 ⁻⁴	93.3

Conclusion

In summary, 4,13-didecyl-1,7,10,16-tetraoxa-4,13-diazacyclooctadecane (kryptofix22DD) is successfully exploited to used as a neutral carrier in PVC membrane, and it is revealed Nernstian response over a wide concentration range for cerium (III) ions. The electrode is very easy to prepare and use. Its detection limit for cerium (III) is very low (9.7×10⁻⁷ M). Meanwhile, it also has some other advantages such as wide linear concentration range, high sensitivity, long lifetime, fast response time, wide pH range and fine selectivity. The sensor was successfully used as an indicator electrode in potentiometric titrations and in direct potentiometry for determination of cerium (III) in real water samples. These characters make us believe that this sensor will be used widely.

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