Construction of Eu^{3+} Ion-Selective Electrode Based on 1,2-Diaminopropane-*N,N,N',N'*-tetraacetic acid

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Abstract: A new Eu^{3+} PVC membrane electrode based on 1,2-diaminopropane-*N,N,N',N'*-tetraacetic acid (DAPTA) as a suitable ionophore has been prepared and studied. The electrode shows a good selectivity for Eu(III) ion with respect to most common cations including alkali, alkaline earth, transition and heavy metal ions. This electrode has a wide linear dynamic range from 1.0×10^{-6} to 1.0×10^{-2} M with a Nernstian slope of 19.7 ± 0.5 mV per decade and a low detection limit of 7.2×10^{-7} M in the pH range of 2.5–9.1, while the response time was rapid (< 10 s). The practical utility of the electrodes has been demonstrated by their use as indicator electrodes in the potentiometric titration of Eu^{3+} ions with EDTA and for the determination of Eu^{3+} in some water sample solutions.

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

Introduction

Nowadays, applications of rare earth elements in agricultural, metallurgical, optical and glass industries, ceramics, and biological areas have increased. Thus, having a convenient, fast, selective and sensitive analysis methods for monitoring rare earth are required. Potentiometric ion selective electrode is one of the selective methods for the determination of rare earth elements. Although instrumental techniques such as inductively couple plasma atomic emission spectrometry (ICP-AES), neutron activation analysis, mass spectrometry (MS), x-ray fluorescence spectrometry, inductively couple plasma mass spectrometry (ICP-MS), Isotope dilution mass spectrometry, *etc.*, provide an accurate measurement in trace amount of elements. But all of these methods are expensive and need complicated equipments. In comparison, potentiometric ion selective sensors offer advantages of low cost, portability, selectivity, and simple operation. They also provide an analysis method without destruction of sample¹⁻³. We have recently reported a number of highly selective and sensitive

PVC-membrane ion-selective electrodes for alkaline earth and transition metal ions⁴⁻¹⁶. There are many studies on determination of lanthanides by this method but there is just two report on determination of europium^{17,18}. Therefore, we decide to prepare another selective sensor with a sensitive and selective component 1,2-diaminopropane-*N,N,N',N'*-tetraacetic acid (DAPTA) (Figure 1) for determination of Eu^{3+} .

Figure 1. The DAPTA structure

Experimental

The Merck Chemical and the Aldrich Co. were the suppliers for the nitrate and chloride salts of all cations and the reagent grades of dibutyl phthalate (DBP), nitrobenzene (NB) benzyl acetate (BA), acetophenone (AP), sodium tetraphenyl borate (NaTPB), tetrahydrofuran (THF) and high relative molecular weight PVC. All reagents were used without any modification. 1,2-Diaminopropane-*N,N,N',N'*-tetraacetic acid was purchased from Fluka. As far as the nitrate and chloride salts of all employed cations are concerned, they were of the highest available purity and were P_2O_5 vacuum dried. During the experiments, distilled deionized water was used.

PVC membrane electrode preparation

Membrane solutions were prepared by thoroughly dissolving 3 mg of DAPTA, 30 mg of powdered PVC, 65 mg of NB and 2.0 mg of NaTPB in 5 mL of fresh THF. The resulting clear mixture was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (3-5 mm o.d. on top) was dipped into the mixture for about 5s, so that a transparent membrane of about 0.3 mm thickness was formed¹⁹⁻²⁷. The tube was pulled out from the mixture and kept at room temperature for 12 h. The tube was then filled with an internal solution (1.0×10^{-3} M EuCl_3). The electrode was finally conditioned for 24 h by soaking in a 1.0×10^{-3} M Eu^{3+} ion solution. A silver/silver chloride electrode was used as an internal reference electrode.

The EMF measurements

The EMF measurements with the polymeric membrane were carried out with the following cell assemblies: $\text{Ag}-\text{AgCl} \mid \text{internal solution, } 1.0 \times 10^{-3} \text{ M } \text{EuCl}_3 \mid \text{PVC membrane} \mid \text{test solution} \mid \text{Hg}-\text{Hg}_2\text{Cl}_2, \text{KCl (satd.)}$

A Corning ion analyzer 250 pH/mV meter was used for the potential measurements at 25.0 °C. The emf observations were made relative to a double-junction saturated calomel electrode (SCE, Philips) with the chamber filled with an ammonium nitrate solution. The activities were calculated according to the Debye-Hückel procedure²⁸.

Results and Discussion

In order to check the suitability of DAPTA as an ion carrier for different metal ions, the DAPTA was employed as a potentially suitable neutral carrier in the construction of a number PVC membrane ion-selective electrodes under identical conditions for a large number of metal ions, including alkali, alkaline earth, transition and heavy metal ions. The results revealed that except Eu^{3+} ion with the most sensitive response, in all other cases the slopes of the corresponding emf versus pM^{n+} are much lower than the expected slopes (59, 29 and 19 mV per decade for mono, di and trivalent cations, respectively).

Membrane composition effect on the potential response of the Eu(III) DAPTA-based sensor

Since the sensitivity and selectivity for a given ionophore depend significantly on the membrane ingredients, the nature of the solvent mediator and the nature of the additive²⁹⁻³², the membrane composition influences were investigated on the potential responses of the Eu^{3+} sensor. The results are summarized in Table 1. It can be seen that the ionophore amount increase up to a value of 3%, in the presence of 2% NaTPB and 65% of polar solvent (NB), results in the best sensitivity. It is well known that the presence of lipophilic anions in cation-selective membranes based on neutral carriers not only diminishes the ohmic resistance and enhances the response behavior and selectivity but also, in cases where the extraction capability is poor, it increases the sensitivity of the membrane electrodes^{33,34}. However, the membranes with a composition of 30% PVC, 3% DAPTA, 2% NaTPB and 65% NB illustrate a Nernstian potential response.

Table 1. Composition of membrane ingredients

Membrane No.	Composition, wt %				Slope (mV/decade)	Concentration range (M)
	PVC	Plasticizer	NaTPB	DAPTA		
1	30	NB, 67	0	3	12.3 ± 0.3	1.0×10^{-5} - 1.0×10^{-3}
2	30	NB, 66	1	3	18.4 ± 0.2	1.0×10^{-6} - 1.0×10^{-3}
3	30	NB, 65	2	3	19.7 ± 0.5	1.0×10^{-6} - 1.0×10^{-2}
4	30	NB, 64	3	3	17.8 ± 0.5	1.0×10^{-6} - 1.0×10^{-2}
5	30	NB, 67	2	1	17.2 ± 0.4	1.0×10^{-6} - 1.0×10^{-2}
6	30	NB, 66	2	2	18.7 ± 0.5	1.0×10^{-6} - 1.0×10^{-2}
7	30	AP, 66	2	2	17.6 ± 0.6	1.0×10^{-6} - 1.0×10^{-2}
8	30	BA, 66	2	2	16.5 ± 0.4	1.0×10^{-6} - 1.0×10^{-2}
9	30	DBP, 66	2	2	15.2 ± 0.5	1.0×10^{-6} - 1.0×10^{-2}

Calibration curve

The emf response of the PVC membrane at varying concentrations of europium ions (Figure 2) indicates a rectilinear range from 1.0×10^{-6} to 1.0×10^{-2} M. The slope of the calibration curve was 19.7 ± 0.5 mV per decade of Eu^{3+} ions activity. The detection limit, as determined from the intersection of the two extrapolated segments of the calibration curve, was 7.2×10^{-7} M. The standard deviation of ten replicate measurements is ± 0.4 mV. The membrane electrode prepared could be used for at least 2 months without any measurable divergences in the responses.

Figure 2. Calibration curve of lutetium electrode based on DAPTA

pH effect on the electrode response

In order to study the pH effect on the performance of the sensor, the potentials were determined in the pH range of 2.0–11.0 (the pH was adjusted using concentrated NaOH or HCl) at a specific Eu^{3+} concentration (1.0×10^{-3} M). The respective results are depicted in Figure 3, where the potential remained constant from the pH value of 2.5 up to 9.1. Beyond this pH range, some potential drifts were presented. The observed potential drift at the higher pH values could be due to the formation of some hydroxyl complexes of Eu^{3+} in the solution. At the lower pH values, the potentials increased, indicating that the membrane sensor responds to hydrogen ions.

Figure 3. pH effect of the test solution (1.0×10^{-3} M of Eu^{3+}) on the potential response

Response time

For any ion-selective electrode, the dynamic response time is one of the most important factors. In this study, the practical response time of the sensor was recorded by changing the Eu^{3+} concentration in the solution across the range from 1.0×10^{-6} to 1.0×10^{-2} M. The plot of potential versus time traces is depicted in Figure 4. Obviously, the plasticized membrane electrode reaches its equilibrium responses in a very short time (<10 s) over the entire concentration range.

Figure 4. Dynamic response time of the europium electrode for step changes in the Eu^{3+} concentration: 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.

Eu(III) electrode selectivity

Selectivity coefficients, which reflects the relative response of the membrane sensor towards the primary ion over the other ions present in the solution, is perhaps the most important characteristic of an ion-selective electrode. In this research, the potential responses of the recommended Eu^{3+} membrane sensor to a wide variety of cations were investigated by matched potential method (MPM)³⁵. The resulting selectivity coefficient values are summarized in Table 2. In line with the information of this Table, the selectivity coefficients for the monovalent tested cations (Na^+ , K^+) are smaller than 7.8×10^{-4} . Additionally, the selectivity coefficients for the divalent tested cations (Ca^{2+} , Co^{2+} , Ni^{2+} and Pb^{2+}) are also small in the range of 7.2×10^{-4} – 2.7×10^{-3} . In the case of trivalent cations (Ho^{3+} , Pr^{3+} , Lu^{3+} , Yb^{3+} , Gd^{3+} , Tb^{3+} , Dy^{3+} , Sm^{3+} , Cr^{3+} and Fe^{3+}), the selectivity coefficients are relatively small (from 7.3×10^{-4} to 8.7×10^{-3}). Eventually, it can be stated that because of the good selectivity coefficients values, the disturbance produced by these cations in the function of the developed membrane sensor is negligible.

Table 2 also compares the selectivity coefficients, response times, detection limits and dynamic ranges of the Eu^{3+} sensor with those of the best previous Eu^{3+} electrodes reported in the literature by other researchers^{17,18}. From the data given in Table 3, the proposed sensor not only in terms of response time, but also in terms of selectivity is superior to the previously reported Ho^{3+} ion-selective membrane electrode.

Table 2. Comparison of selectivity coefficients, detection limit, response time and linearity range of the developed Eu^{3+} sensor and the formerly mentioned Eu^{3+} ion-selective electrodes

Interfering ion (B)	Ref. ¹⁷	Ref. ¹⁸	This work ($K_{\text{Eu}, \text{B}}$)
Pr^{3+}	2.7×10^{-2}	9.0×10^{-3}	7.3×10^{-4}
Tb^{3+}	2.7×10^{-2}	1.4×10^{-2}	5.4×10^{-3}
Ho^{3+}	-	6.3×10^{-3}	8.4×10^{-4}
Yb^{3+}	2.6×10^{-2}	9.5×10^{-3}	4.2×10^{-3}
Sm^{3+}	2.9×10^{-2}	5.7×10^{-2}	8.7×10^{-3}
Lu^{3+}	-	1.2×10^{-3}	4.8×10^{-3}
Dy^{3+}	-	-	3.4×10^{-3}
Gd^{3+}	2.8×10^{-2}	2.5×10^{-2}	5.7×10^{-3}
Cr^{3+}	-	9.5×10^{-3}	4.5×10^{-3}
Fe^{3+}	-	1.4×10^{-2}	4.8×10^{-3}
Pb^{2+}	4.3×10^{-3}	-	2.7×10^{-3}
Ni^{2+}	4.0×10^{-3}	-	2.2×10^{-3}
Co^{2+}	2.9×10^{-2}	7.1×10^{-3}	7.2×10^{-4}
Ca^{2+}	1.2×10^{-2}	5.5×10^{-4}	8.3×10^{-4}
K^+	-	9.5×10^{-4}	6.5×10^{-4}
Na^+	-	8.3×10^{-4}	7.8×10^{-4}
Detection limit	5.0×10^{-5} M	5.0×10^{-6} M	7.2×10^{-7} M
Linear range	7.0×10^{-5} - 1.0×10^{-1} M	1.0×10^{-5} - 1.0×10^{-2} M	1.0×10^{-6} - 1.0×10^{-2} M
Response time	<20 s	<5 s	<10 s

Analytical application

The proposed Eu^{3+} ion-selective membrane electrodes was successfully applied as an indicator electrode in titration of Eu^{3+} (1.0×10^{-4} M) with a standard EDTA solution (1.0×10^{-2} M with pH=10.0). The resulting titration curve showed that the amount of Eu^{3+} ions in solution can be accurately determined with the electrode.

Because of high selectivity and low detection limit of the developed Eu^{3+} sensor (membrane no. 3), it was also applied for the determination of Eu^{3+} ions concentration in water sample (tap water and river water) solutions. The corresponding results in Table 3 reveal that the recovery of Eu^{3+} ions in all mixtures is acceptable.

Figure 5. Potential titration curve of 25.0 mL from a $1.0 \times 10^{-4} \text{ mol L}^{-1} \text{Eu}^{3+}$ solution with $1.0 \times 10^{-2} \text{ mol L}^{-1}$ of EDTA

Table 3. Determination of Eu^{3+} in water samples solutions using the constructed sensor

Sample	Eu^{3+} added, mg/mL	Found, mg/mL)	Recovery, %
River water	0.25	$(0.27^a \pm 0.02)$	108
	0.5	(0.55 ± 0.03)	110
Tap water	0.25	(0.28 ± 0.03)	112
	0.5	(0.54 ± 0.05)	108

^aResults are based on three measurements

Conclusion

The results obtained from the above-mentioned study reveal that a potentiometric PVC-based membrane sensor based on DAPTA functions as an excellent Eu^{3+} selective sensor and can be used for the determination of this ion in the presence of considerable concentrations of common interfering ions. Applicable pH range, lower detection limit and potentiometric selectivity coefficients of the proposed sensor make it a superior device both compared to previously reported Eu^{3+} ion selective sensor and also to other methods used for the determinations of this ion. The authors are grateful to the Research Council of the Quchan Islamic Azad University for the financial support of this research.

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