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A Novel Europium(III) Sensor Based on 4E-4-(2-phenylviazenyl)-2-((E)-(2-aminoethylimino)methyl)phenol

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Solution studies revealed that 4E-4-(2-phenylviazenyl)-2-((E)-(2-aminoethylimino)methyl)phenol (PMP) has a special interaction with europium ion respect with other lanthanide metal ions. PMP was evaluated as a neutral ion carrier in construction of a europium PVC-based membrane sensor. The proposed sensor exhibits a near-Nernstian response of 18.8±0.2 mV per decade of europium activity in the range of 4.0×10^{-7}-1.0×10^{-2} M with a detection limit of 1.5×10^{-7} M. The membrane with a composition containing 4% PMP as ion carrier, 3% potassium tetrakis (4-chlorophenyl) borate (KTpClPB) as an anionic excluder, 60% *o*-nitrophenyloctylether (NPOE) as solvent mediator and 33% poly(vinyl chloride) (PVC) showed the best potential response. Selectivity of the proposed europium sensor was evaluated in the presence of a number of common and lanthanide ions and the obtained results showed that the selectivity coefficients are in the range of 7.5×10^{-6}-2.4×10^{-4}. The potential response of the europium sensor is independent to pH in the range of 3.5-8.0.

Keywords: Eu(III) Sensor; Potentiometry; Ion-selective electrode; 4E-4-(2-phenylviazenyl)-2-((E)-(2-aminoethylimino)methyl)phenol

1. INTRODUCTION

The use of rare-earth oxides is numerous. For instance, they are used in optical glasses making, preparation of glass fibers, for optical purposes, gasoline-cracking catalysts, polishing compounds, carbon arcs, and iron and steel industries to remove sulfur, carbon and other electronegative elements from iron and steel [1]. Nowadays, determination of rare-earth compounds is considered necessary because of the increasing interest in bioinorganic and inorganic chemistry, increased industrial use, and also their enhanced discharge, toxic properties, and other adverse effects. Their determination is nowadays considered necessary. The available methods for low-level determination of rare-earth ions in solution include spectroscopy, mass spectrometry (MS), inductively coupled plasma atomic emission spectrometry (ICP-AES), and inductively coupled plasma mass spectrometry (ICP-MS), isotope dilution mass spectrometry, neutron activation analysis, and X-ray fluorescence spectrometry [2-8]. These methods are either time-consuming, involving multiple sample manipulations, or too expensive for most analytical laboratories. On the contrary, neutral carrier-based ion-selective electrodes (ISEs) can offer an inexpensive and convenient analysis method of rare-earth ions in solution, provided that the acceptable sensitivity and selectivity are achieved. Literature survey revealed that only four reports on europium membrane sensors based on different ion carriers. In this work, we reports a novel Eu(III) membrane sensor based on a new PMP as an excellent neutral ion carrier.

2. EXPERIMENTAL PART

2.1. Reagents

Potassium tetrakis(4-chlorophenyl) borate (KTpClPB), PVC of high relative molecular weight, *o*-nitrophenyloctyl ether (NPOE), dibutyl phthalate (DBP), tetrahydrofuran (THF), chloride and nitrate salts of cations were of the highest purity available (from Merck and Aldrich), and were used without further purification. All aqueous solutions were prepared with deionized distilled water. The pH of all solutions, were adjusted with dilute nitric acid and sodium hydroxide. The ion carrier PMP (Fig. 1) was synthesized as described in literature [9].

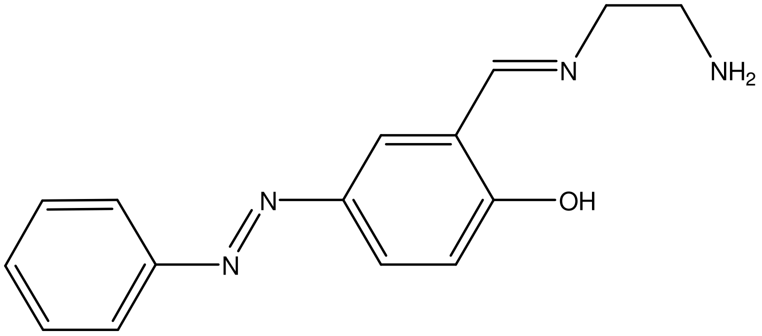

Figure 1. The chemical structure of the used ionophore (PMP)

2.2. Electrode preparation

To prepare the PVC membrane, dipping method was used [10-14], after thoroughly mixing 33 mg of powdered PVC, 59 mg of NPOE, 4 mg of additive KTpClPB, and 4 mg of PMP and 5 ml of fresh THF, the resulting mixture was transferred into a glass dish with a 2 cm diameter. The solvent was slowly evaporated until a relative oily concentrated was obtained. A Pyrex tube (5 mm o.d.) was dipped into the mixture for about 5 s so that a nontransparent membrane of about 0.3mmthickness is formed [15-17]. The tube was then pulled out from the mixture and kept at room temperature for about 12 h. Afterwards, the tube was then filled with an internal filling solution (1.0×10^{-3} M $EuCl_3$). The electrode was finally conditioned for 24 h by soaking in 1.0×10^{-2} M Eu(III) ions. A silver/silver chloride electrode was used as an internal reference electrode. The electrode was finally conditioned for 24 h by soaking in a 1.0×10^{-3} M of $EuCl_3$.

2.3. Apparatus

Potentials were measured with a Corning ion analyzer Model 250-pH/mV meter. The pH of the sample solutions was monitored simultaneously with a conventional glass pH electrode.

2.4. EMF-Measurement

All emf measurements were carried out with the following assembly:
Ag–AgCl | internal solution 1.0×10^{-3} M $EuCl_3$| PVC membrane| test solution| $Hg–Hg_2Cl_2$, KCl (satd).

3. RESULTS AND DISCUSSION

In primary experiment, PMP complexation with a number of metal ions including Li(I), Na(I), K(I), Mg(II), Ca(II), Ce(III), La(III), Yb(III), Dy(III), Gd(III), Er(III), Pr(III), Tb(III), Sm(III), Eu(III), Dy(III), Ho(III), Lu(III), and Tm(III) was investigated conductometrically in acetonitrile solutions (1.0×10^{-4} M of cation solution and 1.0×10^{-2} M of ligand solution) at 25±0.1 ℃ [18-20]. 25 ml of each ion solution was titrated with 0.01 M of PMP solution in order to obtain a clue about the stability and selectivity of the resulting complexes. The conductance of the solution was measured after each addition. Addition of the ligand was continued until the desired ligand-to-cation mole ratio was achieved. The 1:1 binding of the protonated amines with macrocyclic ligands can be expressed by the following equilibrium:

$$M^{n+} + L \xrightarrow{Kf} ML^{n+} \tag{1}$$

The corresponding equilibrium constant, K_f, is given by:

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

Where $[ML^{n+}]$, $[M^{n+}]$, [L] and f represent the equilibrium molar concentration of complexes, free cation, free ligand, and the activity coefficient of the species indicated, respectively.

Under the dilute condition we used, the activity coefficient of the unchanged ligand, $f_{(L)}$ can be reasonably assumed as unity. The use of Deby-Hückel limiting law of 1:1 electrolytes lead to the conclusion that $f_{(M^{n+})} \approx f_{(ML^{n+})}$, so the activity coefficient in equation (2) is canceled out. Thus, the complex formation constant in term of the 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

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

Here, Λ_M is the molar conductance of the cation before addition of ligand, Λ_{ML} the molar conductance of the complex, Λ_{obs} the molar conductance of the solution during titration, C_L the analytical concentration of PMP 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 equations (3) and (4) to the molar conductance-mole ratio data, using a nonlinear least-squares program KINFIT [21]. The logarithm of the formation constants (log K_f) of the resulting 1:1 complexes for mono, di and trivalent cations are given in Table 1. As seen, stability of the Eu-PMP complex is higher than other cations tested. Thus, PMP with the most stable complex with Eu(III) ion is expected to act as a suitable ion-carrier for the fabrication of a Eu(III) sensor.

Table 1. The formation constants of PMP – M^{n+} complexes

M^{n+}	Log k_f
Li^+	<2.0
Na^+	<2.0
K^+	<2.0
Mg^{2+}	2.07±0.09
Ca^{2+}	2.07±0.05
La^{3+}	2.33±0.06
Ce^{3+}	2.25±0.02
Pr^{3+}	2.11±0.04
Nd^{3+}	2.09±0.04
Sm^{3+}	2.07±0.06
Eu^{3+}	5.94±0.09
Dy^{3+}	2.61±0.06
Gd^{3+}	2.52±0.03
Tb^{3+}	2.73±0.03
Ho^{3+}	2.14±0.08
Er^{3+}	2.40±0.03
Tm^{3+}	2.15±0.07
Yb^{3+}	2.17±0.08
Lu^{3+}	2.07±0.07

Next experiments were carried out using PMP as a neutral carrier during the construction of PVC-based sensors for a variety of metal ions including sodium, potassium, magnesium, calcium, and all fourteen lanthanide members. Among these ions, the potential responses of the all metal ion used, except Eu(III) ions are much less than expected values for the mono, di and trivalent cations. Among the tested cations, Eu(III) clearly demonstrates the most sensitive response and seems to be properly determined by the PMP-based PVC membrane. This fact can be explained firstly by the selective behavior of the ionophore towards the europium ion in comparison with other metal ions and, secondly, by the rapid exchange kinetics of the resulting PMP-Eu(III) complex [22-27].

3.1. Membrane composition effect on the potential response of the PMP based Eu(III) sensor

Taking into consideration that the sensitivity and selectivity of a given ionophore depends radically on the membrane ingredients as well as the nature of the solvent mediator and the nature of the used additives [28-32], the membrane composition influences on the potential responses of the Eu(III) sensor were checked. The results are summarized in Table 2. It can be observed that the ionophore amount increase up to a value of 4%, in the presence of 3% KTpClPB and 60% of polar solvent (NPOE), results in the best sensitivity (membrane no. 9). It is well known that the presence of lipophilic anions in a cation-selective membrane, based on neutral carrier, presents the following noticeable benefits; i) ohmic resistance reduction, ii) enhancement of the response behavior and selectivity and iii) membrane electrode sensitivity increasement (when the extraction capability is poor) [33-37]. However, the membranes with the composition of 33% PVC, 4%PMP, 3% KTpClPB, and 60% NPOE, illustrate a near-Nernstian potential response (18.8±0.2 mV per decade).

Table 2. Optimization of the PVC membrane ingredients

Membrane	PVC (%wt.)	Plasticizer (%wt.)	Ionophore (%wt.)	Additive (%wt.)	Slop (mV/decade)
1	33	DBP, 65	2	-	10.3±0.2
2	33	DBP, 64	3	-	11.5±0.3
3	33	DBP, 63	4	-	12.1±0.1
4	33	DBP, 62	5	-	12.0±0.2
5	33	DBP, 62	4	1	15.3±0.4
6	33	DBP, 61	4	2	17.3±0.3
7	33	DBP, 60	4	3	18.5±0.3
8	33	NPOE, 59	4	4	18.6±0.3
9	33	NPOE, 60	4	3	18.8±0.2
10	33	NPOE, 64	-	3	2.1±0.2

3.2. Calibration graph

The critical response characteristics of the Eu(III) PVC-based sensors were assessed according to the IUPAC recommendations [38]. The emf response of the membrane at varying eu(III) activities

(Fig. 2) indicates a rectilinear range from 1.5×10^{-7} to 1.0×10^{-2} M. Furthermore, the slope of the calibration curve was 18.8±0.2 mV per decade of Eu(III) concentration, the standard deviation of nine replicate measurements was ±0.4 mV, while the detection limit of the sensor was 1.5×10^{-7} M, as calculated from the intersection of the two extrapolated segments of the calibration graph.

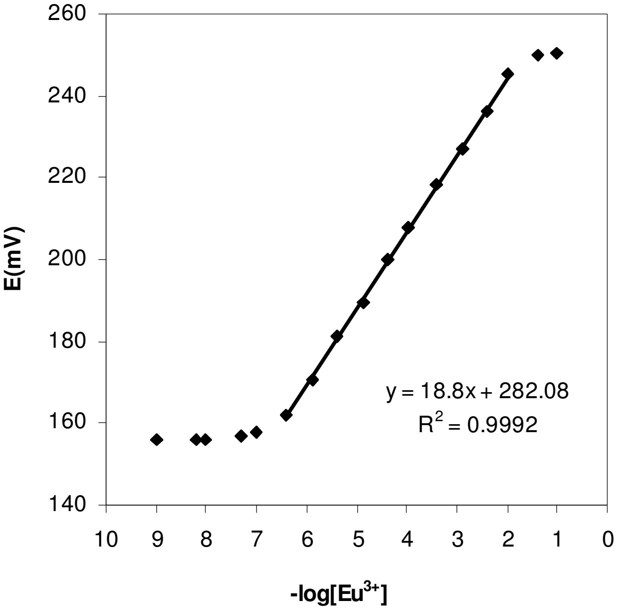

Figure 2. The calibration curve of the Eu(III) membrane sensor based on PMP

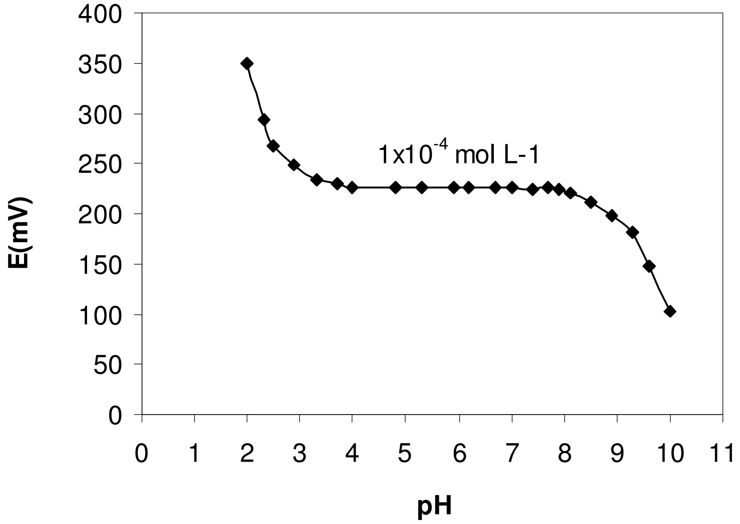

Figure 3. pH effect of the test solution on the potential response of the Eu(III) sensor

3.3. pH effect

The pH response profile for the electrode was tested with the help, by means of a 1.0×10^{-3} M Eu(III) solution over the pH range of 2.0–10.0. The pH was adjusted by introducing small drops of hydrochloric acid (0.1 M) or sodium hydroxide (0.1 M) into the test solution. The influence of the pH response on the PVC-based sensor is shown in Fig. 3. Evidently, the potential remained constant from the pH value of 3.5 up to 8.0, beyond which some potential drifts took place. The observed drift at higher pH values could be attributed to the formation of some Eu(III) hydroxyl complexes in the solution. At lower pH values, the potentials increased, indicating that the membrane sensor responded to H_3O^+ ions, as a result of the extent protonation of the ionophore nitrogen atoms. On the other hand, at lower pH values, the H_3O^+ ions started to contribute to the charge transport process of the membrane; thereby causing interference.

3.3. Dynamic response time

Dynamic response time is an important factor for the evaluation of any sensor. In this study, the practical response time of the introduced sensor was recorded by changing Eu(III) concentration in a series of solutions (1.0×10^{-6}- 1.0×10^{-1} M). The results showed that the electrode reaches its equilibrium response rapidly, about 25 s, in the whole concentration ranges.

3.4. Life time

The lifetime of the proposed Eu(III) sensor, which is a measure of sensor durability, was also considered in a 12 weeks period. During this period the sensor was used for at least 1 hour a day, and 5 days a week. After each usage it was washed completely and dried. The results are given in Table 3. As can be seen from Table 3 after eight weeks only a relatively slight changes in the sensor's slope and detection limit from 18.8 ± 0.2 and 1.5×10^{-7} M to 17.1±0.3 mV per decade and 5.5×10^{-7} M of Eu(III) activity.

Table 3. Life time of the Eu(III) sensor

Week	**Slope (mV/decade)**	**Detection limit (M)**
1	18.8±0.2	1.5×10^{-7}
2	18.8±0.3	1.6×10^{-7}
3	18.6±0.3	1.6×10^{-7}
4	18.3±0.2	1.6×10^{-7}
5	18.2±0.4	1.8×10^{-7}
6	18.0±0.3	2.1×10^{-7}
7	18.0±0.4	2.4×10^{-7}
8	17.1±0.2	5.5×10^{-7}
9	16.3±0.3	7.2×10^{-7}
10	15.1±0.5	9.5×10^{-7}

3.5. Selectivity of Eu(III)sensor

The potentiometric selectivity coefficients, describing the preference of the PMP-based membrane sensor for an interfering ion, B, relative to terbium ions, A, were determined by the matched potential method (MPM) [39-42]. In agreement with this method, the specified activity (concentration) of the primary ion (A=1×10^{-6}-1×10^{-4} M) was added to a reference solution (1.0×10^{-6} M of Eu ion) and the potential was measured. In a separate experiment, interfering ions (B=1×10^{-5} to 1.0×10^{-1} M) were successively added to an identical reference solution, until the measured potential matched that obtained before the addition of the primary ions. The matched potential method selectivity coefficients were then given by the resulting primary ion to the interfering ion activity (concentration) ratio. The selectivity coefficient, $K_{A,B}^{Pot}$, is determined as;

$$K_{A,B}^{Pot} = \Delta a_A / a_B \qquad (5)$$

Where $\Delta a = a'_A - a_A$, a_A is the initial primary ion activity and a'_A is the activity of A in the presence of the interfering ion, a_B.

Table 4. Selectivity coefficients of various interfering metal ions for Eu(III) sensor

Interfering ion	Selectivity coefficients
Li^+	4.5×10^{-6}
Na^+	6.1×10^{-6}
K^+	7.3×10^{-6}
Mg^{2+}	2.1×10^{-5}
Ca^{2+}	4.3×10^{-5}
La^{3+}	6.6×10^{-5}
Ce^{3+}	5.4×10^{-5}
Pr^{3+}	3.1×10^{-5}
Nd^{3+}	3.0×10^{-5}
Sm^{3+}	2.8×10^{-5}
Gd^{3+}	6.7×10^{-5}
Dy^{3+}	7.9×10^{-5}
Tb^{3+}	7.8×10^{-5}
Ho^{3+}	3.4×10^{-5}
Er^{3+}	6.8×10^{-5}
Tm^{3+}	2.9×10^{-5}
Yb^{3+}	2.8×10^{-5}
Lu^{3+}	2.7×10^{-5}

The resulting selectivity coefficients are given in Table 4. As can be seen from Table 3, the proposed Eu(III) sensor is very selective with respect to the most of cations. In the case of all lanthanide ions the selectivity coefficients are in the range of 2.7×10^{-5} -7.9×10^{-5}, which seems to indicate that the Eu(III) ions can be determined in the presence of other lanthanide ions with higher concentrations than Eu(III) concentration. The selectivity coefficients for other mono and divalent cations tested are also in the range of 4.5×10^{-6}-2.1×10^{-5}, and they can not disturb the functioning of the Eu(III) sensor. Such high selectivity of the Eu(III) sensor over other metal ions, and specially lanthanide ions reflects the high affinity of the PMP toward Eu(III) ions.

4. CONCLUSIONS

This research demonstrated an ISE, based on PMP, with low interference from common alkali, alkaline earth, transition and heavy metal ions. The membrane with a composition containing 4% PMP as ion carrier, 3% potassium tetrakis(4-chlorophenyl) borate (KTpClPB) as an anionic excluder, 60% *o*-nitrophenyloctylether (NPOE) as solvent mediator and 33% poly(vinyl chloride) (PVC) showed the best potential response. The recommended sensor displayed a response time (25 s) and its potential responses were pH independent across the range of 3.5–8.0.

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