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ORIGINAL ARTICLE

Ion sensing film optodes based on chromogenic calix[4]arene: application to the detection of Hg^{2+}, Ni^{2+} and Eu^{3+} ions

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Abstract The development of sensors for the detection of transition metal ions has attracted a special attention because of the toxic impact of these elements on our environment. Due to their sensitivity, reliable, inexpensive and easy use for on site analysis, optical chemical sensors (optodes) have received an increasing attention for a rapid determination of toxic species in water. A new chromogenic calix[4]arene has been investigated on the basis of the high recognition properties of calixarenes associated to the optical response provided by their functionalization with a phenyl azo group. Thin tetrakis-(phenylazo) calix[4]arene amide derivative layers deposited on a glass suprasil substrate have been characterized by contact angle measurements showing a good surface coverage whereas a uniform morphology of the calixarene membrane in acetonitrile solvent was observed by scanning electron microscopy (SEM). The ability of the tetrakis-(phenylazo) calix[4]arene amide derivative thin film to complex Hg^{2+}, Ni^{2+} and Eu^{3+} ions have been demonstrated by the modification of the calixarenes main absorption band at 343 nm and appearance of a new absorption band at 500 nm upon addition of Eu^{3+}. The different sensors could be regenerated with hydrochloric acid. The dynamic concentration range, ion selectivity, response time, repeatability and reproducibility are discussed. These results are suitable to the development of optodes for the detection of metal pollutants.

Keywords azo-calix[4]arene · Complexation · Sensor · Optode membrane

Introduction

In recent years, a growing interest has been shown to the development of chemical sensors based on optical transduction (optodes) [1–3]. Optode have emerged during the last decades as viable alternatives to other types of sensors (electrochemical, potentiometric…) due to several advantages. The optical sensors involve simple preparation, reasonable selectivity, improved sensitivity, no need for separate reference devices and low cost [4, 5]. Chemical sensors based on optical transduction are used in the analysis of a broad spectrum of analytes including the detection of charged compounds. Several properties are important for a successful use of optical transduction. The detection is based on the optical response to specific analyte. Generally, optodes involve a sensing membrane that selectively reacts with the analyte, a light source, a wavelength selection device and a detector. Seitz [1] has

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discussed the theoretical response behavior of optical sensors for electrically neutral analytes. Morf and al. [6] have described the theoretical design of bulk optode membranes containing neutral carrier type ligands which are selective for charged species. Seiler and Simon [7] have described in detail the principles of bulk optode membranes, which are based on a reversible mass transfer of the analyte from the sample into the bulk of the sensing layer. They have discussed the theoretical performance of bulk optodes based on plasticized PVC membranes. Thus, in recent years, a number of optodes based on different optical principles have been reported for the detection of toxic species in aqueous environment using absorbance or fluorescence measurements [8]. The toxic effects of heavy metals have been well documented [9, 10]. The detection of heavy metals in the aquatic environments is of tremendous interest due to their hazardous effects on the ecosystem and the human health. Heavy metals may enter the food chain as a result of their uptake by edible plants. So, the dosage of heavy metals in environmental samples is very important in regard to their toxicity.

Optical sensing of many cations has been reported such as sodium [11, 12], potassium [13, 14], lithium [15, 16], ammonium [17], calcium [18, 19], mercury [20, 21] and lead [22, 23]. In optical sensors the concentration dependence of the signal is a direct result of the interaction of the carrier/receptor molecule (ligand, ionophore) with the metal ions to be analyzed. Chromogenic ionophores (crows ether, calixarenes…) [24, 25] and fluorophores [26] have been considered in view of their direct optical transduction. The optical absorption of these ligands in the UV/Vis region is changing upon complexation with selected ions. Calixarenes, cyclic oligomers of phenol–formaldehyde condensates, have attracted interest for the development of ion-selective and optical sensors [27]. Calixarene derivatives are good candidates for chemical sensors due to their selective ion/molecular binding properties and their relatively easy synthesis [27, 28]. Chromoionophores based on calix[4]arene showing selectivity for different metal ions have been reported [29]. Chromogenic calixarene molecules exhibiting a variation of their absorption or fluorescent spectra induced by the interactions with metal cations in solution, are available. Jens et al. [30] have used a chromogenic calix[4]arene for the development of a calcium selective optode showing a 3–10 Mm dynamic range. The development of a fluorescent optode membrane involving calix[4]arene and tetraphenylporphyrine based on a cation-exchange mechanism has been reported by Xiaohai Yang [31] for the detection of sodium cation.

In this work, an azo-calix[4]arene amide derivative membrane deposited on glass suprasil substrate has been characterized by contact angle measurements and scanning electron microscopy (SEM). Then, we have investigated the complexation properties of different metal ions by calixarene thin film using UV–Visible spectrophotometry. The complexation properties of the sensory membrane has enable the development of an ion bulk optode for the detection of Hg^{2+}, Ni^{2+} and Eu^{3+} ions. The dynamic concentration range, ion selectivity, response time, reproducibility, repeatability and regeneration of the optical sensor are discussed.

Experimental

Reagents

The choice of the supramolecular calixarene in this work, specially the chromogenic calix[4]arene, is due to their well defined molecular cavity and their ability to accommodate a variety of guest molecules. On the basis of this early work, calix[4]arenes have been used as a platform to build derivatives showing new complexing properties by grafting new functional groups at the upper or lower rim. Calixarenes involving a photochromic group are of particular interest for an easy detection of main pollutants. The tetrakis-(phenylazo) calix[4]arene amide derivative, used in this report and presented in Fig. 1, has been synthesized according to previously described methods [32, 33]. So, the choice of this material containing a conjugated chromogenic (–N=N–) is based on their optical response by changing their spectra upon the binding of metal cations. Several works developped by Bohmer [34] and Arnaud [35] have shown that the amide donor group show greater efficiency for metal ion complexation than oxo, ester and ether group. It has been grafted onto the lower rims of calix[4]arene for the complexation of alkali [36], alkaline earth metal ions [37], lanthanide ions [38] and transition metal ions [39].

Salt solutions of different cations: $NiCl_2 + 6H_2O$, $Hg(NO_3)_2 + 2H_2O$ and $Eu(ClO_4)_3$, have been used at different concentrations. The buffer solution corresponding to

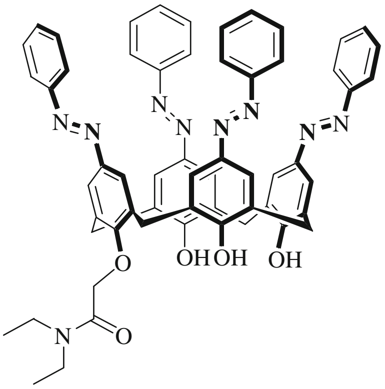

Fig. 1 5,11,17,23-tetrakis(phenylazo)-25,27,28-trihydoxy-26-mono[(*N*,*N*-diethylaminocarbonyl)methoxy]-calix[4]arene

pH = 7 and pH = 8 are commercialized from Sigma-Aldrich.

Contact angle measurements

Glass suprasil substrates have been first cleaned in acetone for about 20 min in ultrasonic bath, then in iso-propanol for about 20 min under ultrasounds too. After this treatment, they have been dried under a nitrogen flow. The tetrakis-(phenylazo) calix[4]arene amide derivative (5×10^{-3}M), prepared in acetonitrile solvent, has been deposited by spin coating on a glass suprasil substrate with the following parameters: rpm = 2500, rpm/s = 2000, $t = 30$ s.

Contact angle, θ, is a quantitative measure of the wetting of a solid by a liquid. It is defined geometrically as the angle formed by a liquid at the three phase boundary where a liquid, vapor and solid intersect (Fig. 2).

Contact angle is the most direct measure of wetting. Physicochemical properties of the interactions between the solid and a liquid such as wettability, affinity, adhesiveness and repellency can be studied. Using different reference liquids it is possible to probe the surface energy components of the solid. Several models are available to calculate these parameters from the measured contact angles. We have used the Van Oss acid–base theory to determine the surface energy components: total energy (γ_S), dispersive energy (γ^{LW}), acid–base energy (γ^{AB}), acid energy (γ^{+}) and base energy (γ^{-}) using polar and apolar test liquids [40, 41].

The first step of the measurement was to place a water of defined volume on the solid simple surface, which should be perfectly horizontal. To apply reproducible uniform volume (less than 2 µl), drops of de-ionized water, calibrated micropipettes have been used. The drop shape was recorded with a high speed framing camera; images were then processed by a computer and stored. The drop shape is then automatically evaluated in terms of contact angle as represented by the angle between the substrate surface and the tangent from the edge to the contour of the drop. The uncertainty in the measurements depends on the light–dark contrasts of the drop picture, in particular at the air–liquid–solid triple point, and on the method used for the evaluation. The measurements have been performed using the "Digidrop" instrument from the GBX society (Romans, France). The surface free energy of solids and their components have been calculated with the Windrop ++ Software. Three different liquids (Distilled water, diiodomethane and formamide) have been used. Distilled water checks the hydrophobe/hydrophile character of the surface, while the other liquids (diiodomethane and formamide) have been used for the determination of the surface free energy.

Morphological characterization

A rapid imaging and characterization of heterogeneous organic and inorganic materials on a nanometer (nm) to micrometer (µm) scale can be performed by SEM [42]. The topographic images of the calixarene membrane have been obtained using a Hitachi S800 SEM in the secondary electron mode since enabling a large depth of field. A Pd–Au alloy coating of the sample surface was done before observations to prevent charging artefacts by the electron beam.

Optical measurements

Optical absorbance spectra have been performed using a UV/VIS spectrophotometer ("Lambda 35", Perkin Elmer). A quartz cell of 1 cm optical path was used for all measurements. Glass suprasil substrates covered by the tetrakis-(phenylazo) calix[4]arene amide derivative membrane according to the procedure mentioned above were mounted vertically inside the cell containing the buffer solution at fixed pH (Fig. 3).

Results and discussion

Contact angle measurements

In order to check the effectiveness of the functionalization process, contact angle measurements, obtained with water

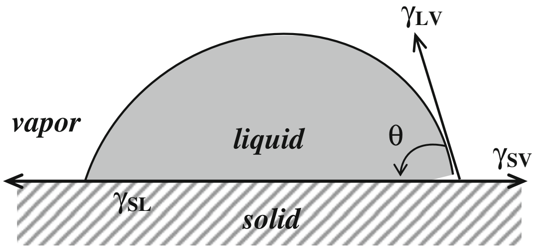

Fig. 2 Contact angle and surface energy

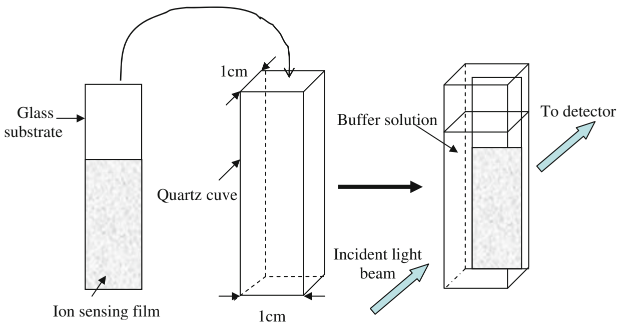

Fig. 3 Schematic view of the film optode experimental set-up

Table 1 Contact angle measurements

	$\theta°$ (water as test liquid)	γ_S	γ^{LW}	γ^{AB}	γ^+	γ^-
Bare glass substrate cleaned	47.4 ± 2	48.1	38.9	9.3	0.7	30.1
Glass substrate/Calixarene	74.3 ± 3	48.8	47.2	1.6	0.1	9.4

as test liquid, have been carried out for the tetrakis-(phenylazo) calix[4]arene amide derivative deposited on glass suprasil substrate. The wetting properties have been compared before and after glass suprasil substrate functionalization process (Table 1). We note that the contact angle increases after functionalization indicating that the azo-calix[4]arene amide derivative form a continuous film at the surface of the glass substrate. Thus, we note from Table 1 that this membrane affords a hydrophobic behaviour. For further characterization of surface wettability, calculation of surface energy components was performed using contact angle measurements for three different fluids whose surface tension components data are given in Table 1. An increase in the dispersive energy (γ^{LW}) from 38.9 to 47.2 for the suprasil substrate, when coated with a calixarene layer indicates the well dispersion of the membrane onto the substrate. A higher value of the basic energy components ($\gamma^- = 9.4$) is obtained compared to the acid energy compound ($\gamma^+= 0.1$). From these results, we can deduce that the basic character of the surface is due to the presence (OH) group and also the amide group coming from the molecule. Then, we can imagine that the molecule is in interaction with glass suprasil substrate with benzene group via aromatic π-stacking.

Scanning electron microscopy (SEM)

SEM was utilized to characterize the topography and the organization of calixarene deposited on the glass suprasil substrate in acetonitrile and THF solutions. The SEM images reported in Fig. 4 show a tremendous difference between the surface morphologies of the film with either solvent. Large islands appear at the surface of the THF-film (Fig. 4b), whereas a more uniform dispersion is observed over the substrate of the tetrakis-(phenylazo) azo-calix[4]arene amide derivative dissolved in acetonitrile (Fig. 4a). The THF and acetonitrile are classified as aprotic polar solvents having a dielectric constant of 7. 5 and 37, respectively, which makes the Van Der Waals intermolecular interaction weaker in acetonitrile solvent. That's why we have a good dispersion of the tetrakis-(phenylazo)calix[4]arene amide derivative in acetonitrile solvent compared to the THF. Then, we have considered acetonitrile solvent for the remaining work.

Characteristics of the optode

In this study, we have been interested in the development of new optodes based on azo-calix[4]arene amide derivative for the detection of Ni^{2+}, Hg^{2+} and Eu^{3+} because of their ability to form complexes shown in solution. A comparative study of the performances of these three optodes has been performed.

Spectral characteristics

The UV/Visible absorption spectra of the azo-calix[4]arene amide derivative dispersed in acetonitrile solution

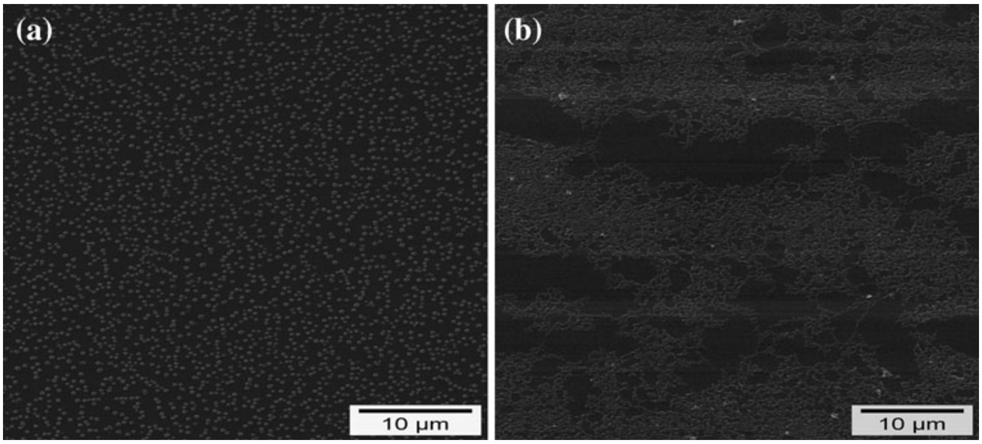

Fig. 4 SEM image of azo-calix[4]arene deposited on glass suprasil substrate **a** in acetonitrile, **b** in THF

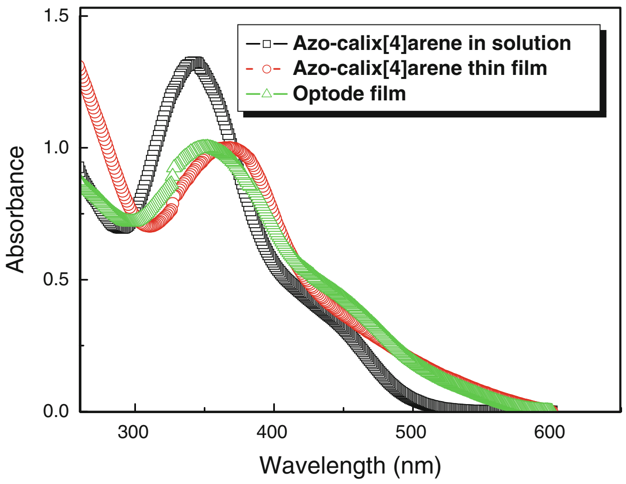

Fig. 5 UV–Vis spectra of azo-calix[4] arene derivative (*open square*) in solution, (*open circle*) as thin film and (*open triangle*) optode film (buffer at pH = 7)

(5×10^{-5}M) or as thin film deposited on a glass suprasil substrate as optode in a buffer solution at pH = 7 are shown in Fig. 5. The spectrum of calixarene in solution is characterized by a maximum absorption peak at 343 nm and a second band at 452 nm corresponding to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ photon transitions, respectively. A 24 nm bathochromic shift is observed when the membrane is deposited on a glass substrate. This bathochromic shift is reduced to 7 nm when the substrate is placed in the spectrophometer cell containing the buffer solution forming the optode. These results confirm that the azo-calix[4]arene structural conformation is more planar in the thin film membrane than for its solution analogue [43, 44].

The functionalization of the lower and upper rims of the calixarene platform favor the interaction and the complexation towards different metal ions by this derivative. The optical recognition properties of azo-calix[4]arene amide derivative towards Ni^{2+}, Hg^{2+} and Eu^{3+} have been investigated in regard to the interest of these cations in environmental and biomedical application. Modifications of the absorption spectrum of azo-calix[4]arenes are observed when adding the metallic cations to the calixarenes in acetonitrile (Fig. 6a) or after deposition of the blend of cations and calixarenes in solution on the glass suprasil substrate (Fig. 6b). A new band appearing at 500 nm shows the complexation of Eu^{3+} ions and the hypsochromic shift of all the spectra indicates the deprotonation of the ligand upon complexation with the different metal ions. The hypsochromic shift may be assigned to a photoinduced charge transfer mechanism (PCT) between the membrane thin layer and the cation [45, 46]. These recognition properties of this ligand towards Ni^{2+}, Hg^{2+} and Eu^{3+} in solution or as thin film stimulate the study of "optodes" for the detection of these metals. A comparative study of the optode performances is presented for the detection of each cation.

To begin, a test of the recognition properties of three optode membranes towards these cations has been done. Absorption spectra of the sensing membrane deposited on a glass suprasil substrate and placed into the buffer solution at the corresponding pH in the presence of different concentrations of the metals are shown in Fig. 7. The spectra indicate that the maximum absorbance at 350 nm increased in contact to Eu^{3+} (9.9×10^{-5}M) at pH = 7 and decreased in the presence of Ni^{2+} (2.9×10^{-4}M) at pH = 7 and Hg^{2+} (3×10^{-4}M) at pH = 8. Thus, this wavelength was selected to measure the absorbance of the optodes for the different cations.

Effect of the pH of the buffer solution on the response of the optode

The pH of the sample solution influences the sensor selectivity and the linear dynamic range [47]. The membrane dipped into the spectrophotometer cell for different buffer solutions was tested. 10 µl of a sample containing the desirable ion (10^{-2}M) was injected into the cell and was shaken for 10 min to obtain an homogeneous solution. The effect of the pH on the complex formation was studied

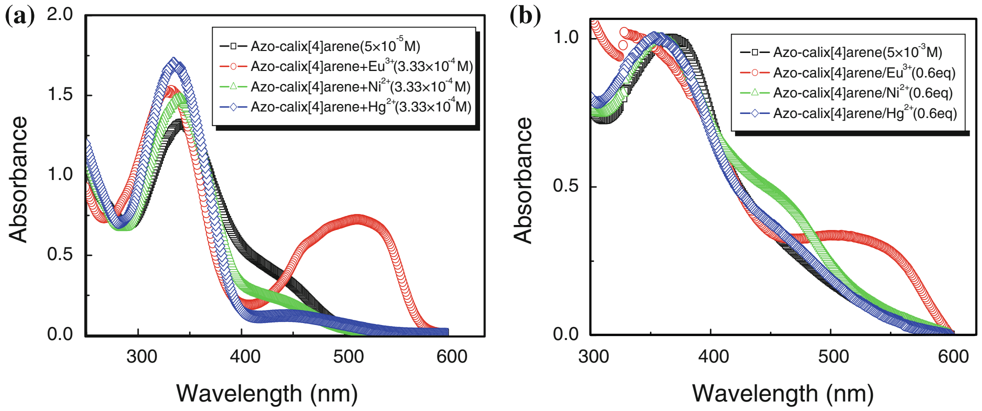

Fig. 6 Absorption spectra **a** in acetonitrile solution, **b** as thin film of azo-calix[4]arene in contact to Ni^{2+}, Hg^{2+} and Eu^{3+} in solution

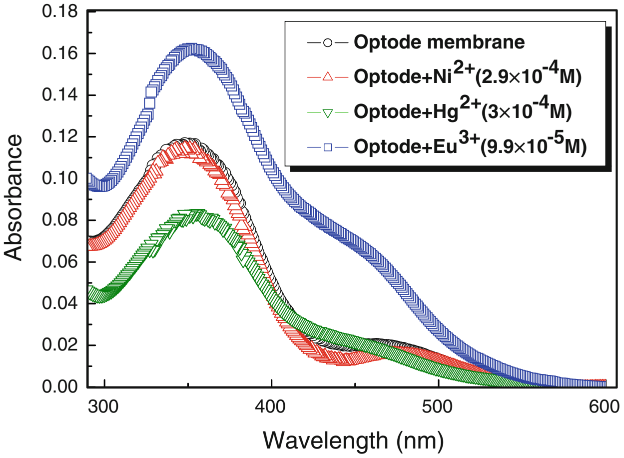

Fig. 7 Absorption spectra of different optodes in the presence of the following cation concentrations and pH: (*open triangle*) Ni^{2+} (2.9×10^{-4}M) at pH = 7, (*inverted triangle*) Hg^{2+} (3×10^{-4}M) at pH = 8, (*open square*) Eu^{3+} (9.9×10^{-5}M) at pH = 7

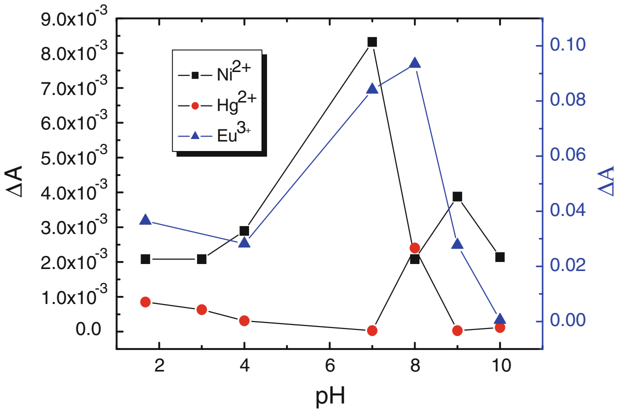

Fig. 8 Effect of the buffer pH on the optodes responses

by changing the pH of the buffer solution from 1 to 10. The absorbance dependence is expressed as the absorbance difference defined as the difference in the absorbance at 350 nm of the optode in the presence and absence of the checked ion for different pH value. We can see in Fig. 8 that the value of the difference in absorbance increases for each optode as the pH increases from 1 to 7. The response decreases when the pH value more increases above 8. This phenomenon might be due to the fact that the complexation of the different ions is weak at the lowest pH values. The maximum difference in absorbance occurs at pH = 7 for Ni^{2+} optode and at pH = 8 for Eu^{3+} and Hg^{2+} optodes. These results show that in neutral medium an azo-calix[4]arene amide derivative thin film can form complexes with these metal cations.

Response time

The response time of the optodes is an important analytical feature. The response time is controlled by the time needed for the ion to diffuse from the buffer solution into the membrane followed by its association with the ionophore. The response time of the optode film is governed by three processes: (i) diffusion in the film, (ii) the rate of complex formation between metal ion and ligand and (iii) the rate of complex dissociation [48, 49].

Figure 9 depicts the typical response time of the different optodes versus time for 1.995×10^{-5}M europium ion, 4.97×10^{-5}M nickel ion and 3.32×10^{-5}M mercury ion. These cation concentrations have been chosen since providing the larger absorbance response of the optode (see Fig. 10). The response times for the different cations are gathered in Table 2. The shorter response time of the sensing thin film towards lanthanide Eu^{3+} ion shows that the europium ion sensing optode is more efficient than the other optodes. This result may be due to the high charge density of Eu^{3+} which increases the mobility of the ion towards the ionophore immobilized on the glass suprasil substrate.

The lower charge density of the Ni^{2+} and Hg^{2+} decrease the mobility of these cations limiting the diffusion rate and complexation reaction into the membrane. These processes are at the origin of the long time responses of these cations compared to the lanthanide one.

Dynamic range

The membrane response of the different optodes may be defined as the ratio of the concentration of the

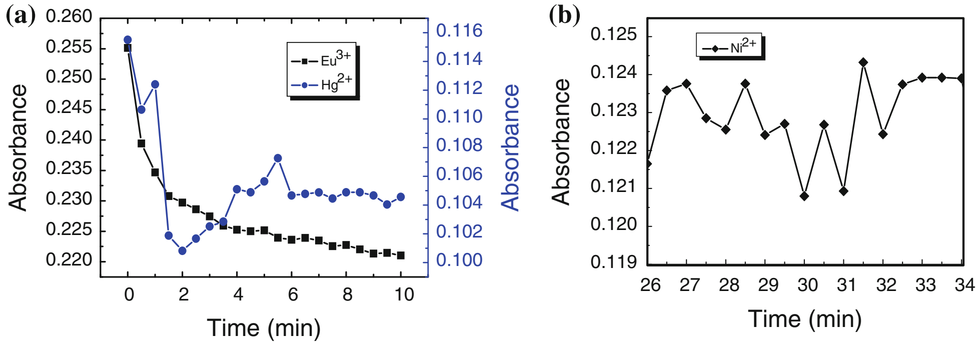

Fig. 9 Typical response curve of the optode at 350 nm as a function of time when the membrane is exposed to **a** (*filled square*) 1.995×10^{-5}M of Eu^{3+}, (*filled circle*) 3.32×10^{-5}M of Hg^{2+}, **b** (*filled diamond*) 4.97×10^{-5}M of Ni^{2+}

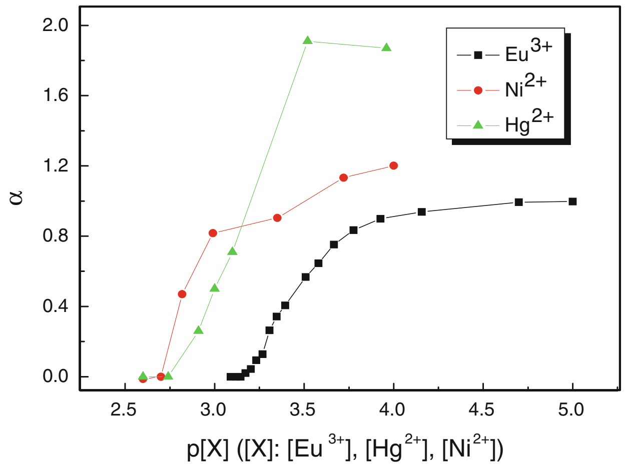

Fig. 10 Membrane response (α) at 350 nm as a function of the co-logarithm of the cation concentrations at pH = 7 and pH = 8

Table 2 Response time of the different optodes

	Eu^{3+}	Hg^{2+}	Ni^{2+}
Response time (min)	3–10 min	7–10 min	32–34 min

uncomplexed [M] to the total chromoionophore amount present in the membrane $[M]_t$;

$$\alpha = \frac{[M]}{[M]_t} \tag{1}$$

If fact, the measured absorbance A is directly related to α assuming that the optode membrane follows, Beer's law:

$$\alpha = \frac{A_1 - A}{A_1 - A_0} \tag{2}$$

The α values have been calculated by absorbance measurements at the wavelength of the complexed chromoionophore where A_1 is the absorbance of the membrane when all the ionophores have been complexed, A_0 the absorbance of free chromoionophore and A the absorbance measured at any time during the titration procedure [50]. Figure 10 shows the response of the different optodes versus the co-logarithm of the concentrations of different ions. The dynamic ranges of the different optodes are gathered in Table 3.

Repeatability and reproducibility

The repeatability and reproducibility of the different membrane optodes have been investigated. For that purpose, the responses of a single membrane sensor has been checked in successive runs. Ten determinations have been performed with the same buffer solution for each membrane in the presence of 6.95×10^{-5}M of Eu^{3+} at pH = 8, 1.96×10^{-4}M of Ni^{2+}at pH = 7 and 3×10^{-4}M of Hg^{2+} at pH = 8. The relative standard deviations of the measured absorbance values (at $\lambda_{max} = 350$ nm) for the different optodes are gathered in Table 4. The best repeatability has been obtained in the case of the Eu^{3+} optode.

Table 3 Dynamic range of the response of different optodes

	Eu^{3+}	Hg^{2+}	Ni^{2+}
Dynamic range	10^{-4}–$10^{-3.1}$M	$10^{-3.5}$–$10^{-2.7}$M	$10^{-3.7}$–$10^{-2.6}$M

Table 4 The relative standard deviation corresponding to the repeatability and the reproducibility of different optodes

	Eu^{3+} (%)	Hg^{2+} (%)	Ni^{2+} (%)
Repeatability RSD	0.48	0.68	1.46
Reproducibility RSD	4.81	7.97	8.82

The reproducibility has been evaluated by carrying out similar procedure on four different membranes for each ion optode in the presence of the same ionic concentration previously mentioned. The results obtained in Table 4 showed that the repeatability and reproducibility of the proposed optical sensors are satisfactory with a minimum relative standard deviation for the Europium ion optode.

Regeneration of the different optode

One of the main characteristics of an optical sensor is its regeneration ability which allows the use of the sensor many times. A good sensor should be regenerated in a short time. A treatment of the used membranes with a HCl (0.2 M) solution for 5 min was tested for the regeneration of the different optodes. The measurements were performed in the presence of 6.95×10^{-5}M of Eu^{3+} at pH = 8, 1.96×10^{-4}M of Ni^{2+}at pH = 7 and 3×10^{-4}M of Hg^{2+} at pH = 8 for the different ion optodes. After regeneration for times, a drift of about 1.24, 2.19 and 8.1% of the responses of Eu^{3+} optode, Ni^{2+} and Hg^{2+} ion optodes has been observed. These results show that the Eu^{3+} sensing optode can be regenerated in 5 min with a minimum drift compared to the Ni^{2+} and Hg^{2+} sensors. Prepared membranes have been stored in water between runs.

Interferences with foreign ions

The interference of the metal ions on the response at 350 nm of the sensor was investigated for each ion optode in solutions at pH = 7 and pH = 8. The tests have been performed with a fixed cation concentration (6.95×10^{-5}M) for europium ion, (1.96×10^{-4}M) for nickel ion and (3×10^{-4}M Hg^{2+}) for mercury ion and different foreign interferents. No significant interferences

Table 5 Effect of interferent ions on the absorbance response of the optode membranes

Interferents	Eu^{3+} ion optode		Ni^{2+} ion optode		Hg^{2+} ion optode	
	Absorbance change $\Delta A = A_1 - A_2$	Relative signal change $(\Delta A/A_2) \times 100$ (%)	Absorbance change $\Delta A = A_1 - A_2$	Relative signal change $(\Delta A/A_2) \times 100$ (%)	Absorbance change $\Delta A = A_1 - A_2$	Relative signal change $(\Delta A/A_2) \times 100$ (%)
Al^{3+}	0.00256	1.26	0.01363	10.5	0.0129	14.34
Ca^{2+}	0.00249	1.22	0.00602	4.64	0.02189	24.38
K^{+}	0.0006	0.29	0.00304	2.34	0.00967	10.77
Ni^{2+}	0.0031	1.53	–	–	0.00148	1.64
Hg^{2+}	0.00551	2.71	0.01249	9.62	–	–
Eu^{3+}	–	–	0.00164	12.64	0.06468	72.04

A_1 and A_2 are the absorbance of the sensing membrane in the presence of the tested ions respectively with and without interferent ions

$(\Delta A/A_2) \times 100$ is the relative signal change

are observed in a ±5% relative error limit. The test results of potential interferences are summarized in Table 5. It can be observed that ions often found in environmental water such as Al^{3+}, Ca^{2+}, and K^{+} show no interference for the detection of 6.95×10^{-5}M of Eu^{3+}. Cation such as Ni^{2+} and Hg^{2+}, which can be complexed by the sensing membrane, lead to an absorbance signal changes less than ±5% in the presence of Eu^{3+}. From this first analysis, we can conclude that azo-calix[4]arene membrane has a fairly high selectivity for Eu^{3+}. From the analysis of Ni^{2+} and Hg^{2+} ion optodes, the absorbance response change is larger than ± 5% in the presence of Eu^{3+} as in the presence of other metals ions. Therefore, we can conclude that Ni^{2+} and Hg^{2+} ions optodes are not selective for the determination of Ni^{2+} and Hg^{2+} in the presence of foreign interferents. Only the Eu^{3+} ion optode shows, in the presence of interferent ions, the suitable selectivity for application to the analysis of real samples.

Conclusion

The complexation of Eu^{3+}, Hg^{2+} and Ni^{2+} by a tetrakis-(phenylazo)calix[4]arene amide derivative thin film can be monitored by the optical absorption response of the membrane deposited on glass suprasil substrate. These results allow the development of new “optodes” for the detection of these metal cations. The principle of the response of these optodes is based on the complexation properties of Eu^{3+}, Hg^{2+} and Ni^{2+} by the ionophore thin film. These sensors can be regenerated readily with HCl (0.2 M). A comparative study of the performance of the different optodes has been performed. A minimum response time, a large dynamic range and a low relative standard deviation were obtained for the Eu^{3+} ion sensing film optode which make it applicable to the determination of this lanthanide cation in real samples.

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