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Study and Comparison Between Two Gold Electrodes Functionalized with Two Calix [8] Arenes for the Detection of Cadmium in Water

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Abstract: In our work, we compared the performance of two calix [8] arenes, p-tert-butyl-calix [8] arene-tétracétone and p-tert-butyl-calix [8] arene-tetraester for cadmium detection in an aqueous medium. Both sensors were characterized by two electrochemically methods, impedance spectroscopy to evaluate the behavior of the sensitive membrane relative to the cation to be detected and cyclic voltammetry to understand the phenomena occurring at the solid-liquid interfaces. We completed our study by two physico-chemical methods. Fourier Transform Infrared spectroscopy (FTIR) and UV-Visible spectroscopy to understand the process of complexation between ionophores and the cations detected. The results of analyzes by UV-Visible and FTIR spectroscopy showed the formation of a complex between the ligand and cadmium ions. The impedance measurements showed an increase in sensor response proportionally with the increase of the concentration of the metal cation indicating sensitivity of the devices with a detection limit of 10^{-8}M. P-tert-butyl-calix [8] arene-ligand tetraester is most advantageous from the point of view sensitivity to cadmium ions. *Copyright © 2014 IFSA Publishing, S. L.*

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1. Introduction

Many investigations on dielectric, electronic and spectroscopic characterizations have been achieved on molecular materials [1-3] for their eventual applications as sensors [4] or electronic devices [5]. Supramolecular systems experiencing significant growth thanks to their remarkable recognition properties that find applications in areas as diverse, including the development of sensors for chemical species. In this context, a family of macrocycles called calixarenes knows a great interest.

Calixarenes are macrocyclic oligomers of phenol–formaldehyde condensates, capable (in their cone conformation) of forming inclusion compounds. Therefore, the variation of cavity size according to the requirements of different guests is possible, and they are easily amenable to chemical modifications. The macrocycles are characterized by the phenolic unit numbers (4, 6, 8 . . .). Calixarenes have received a great deal of attention in recent years in many fields of research because of their ease of synthesis and possessing ionic and molecular-binding properties [6]. Derivatives containing a wide range of functional groups have been synthesized and shown to exhibit different degrees of receptor ionophoric activity. Indeed calixarene derivatives containing pendant ether, amide, ketonic, ester and crown ether groups have been used recently into ion-selective electrodes sensitive to sodium ions [7–14], potassium ions [15, 16] and cesium ions [17–20], as ionophores for potentiometric ion-selective electrodes [21, 22] and field effect transistors [23, 24]. However, few papers reported that calixarene based on ion-selective electrodes sensitive to transition metal ions such as silver ions [25, 26] and lead ions [27].

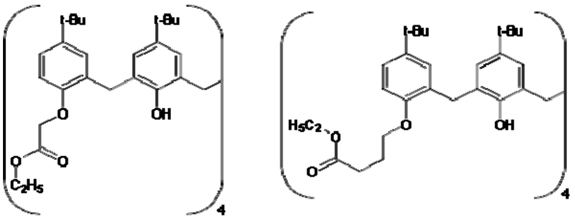
This paper reports a comparison of tow tetra-ester derivatives of p-tert-butyl-calix[8]arene used as thin films (calix 1, calix 2) in order to study the length of the carbon chain effect on the sensitivity toward the cadmium cation. These thin films were deposited on the active gold surface by spin-coating process. In order to check the effectiveness of the cleaning by piranha process cyclic voltammetry has be carried out. We have studied thin films sensitivity towards the Cd^{2+} cation by impedance spectroscopy. Nyquist diagrams were modeled by appropriate equivalent circuit.

2. Experimental

2.1. Materials

The sensing molecules used in this work, tetra-ester derivatives of p-tert-butyl-calix[8]arene, have been synthesized by analytical chemistry laboratory (laboratoire de chimie analytique) at ‘‘Claude Bernard University, Lyon’’. This calix[8]arene derivative has been characerised by the presence of an ester group at the lower rim.

The solubility of these molecules in chloroform enables their deposition on gold electrode substrate using spin-coating method.



Calix 1 Calix 2

Fig. 1. Structure of ligands.

2.2. Gold Electrode Elaboration

The gold electrodes are cleaned in two stages. In a first step, the electrodes are dipped in acetone for 10 minutes and then they are dried under nitrogen flow. Secondarily, an attack by the piranha solution is performed for one minute. The electrodes were rinsed with ultrapure water and then with ethanol and dried under nitrogen flow. After this treatment, sensing layer based on calix[8]arene derivatives ionophore is obtained from a drop (10 µL) of calixarene solution (10^{-3} mol/L) deposited on the gold electrode at 2000 rpm. The surface is then dried in air for 15 hours.

2.3. Electrochemical Measurements

The electrochemical impedance measurements were performed using Voltalab 40, model PGZ 301 instrument (Radiometer Analytical) controlled with VoltaMaster 4.0. The instrument was used in a three-electrode cell configuration. A gold electrode (0.19 cm^2) modified with calix[8]arene was used as a working electrode, while a saturated calomel electrode (SCE) purchased from Radiometer Analytical was used as a reference electrode. The auxiliary electrode was made of a platinum plate with an active surface of 0.385 cm^2. The impedance spectroscopy measurements were carried out in the frequency range from 100 kHz to 100 MHz using a modulation voltage of -400 mV. Measurements were performed in a PBS buffer solution at pH 7.

The measured impedance spectra were analyzed in terms of electrical equivalent circuits using the analysis program ZView software (Scribner Associate Inc, Southern Pines, USA). Cyclic voltammetry measurements were performed with the same equipment. The potential was cycled from −700 and 700 mV (vs. the reference electrode) with a scan speed of about 25 mV/s in PBS buffer containing 2 mM of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$.

All electrochemical measurements were carried in a Faraday cage.

3. Results and Discussions

The cyclic voltammograms of the gold electrode and the electrode functionalized by the (calix 1) and (calix 2) are presented in Fig. 2.

Before membranes deposition, clear redox peaks with a reversible voltammogram were observed indicating the effectiveness of the cleaning step of the gold electrode. After deposition, both peaks are missing which is attributed to the fact that the calix[8]arene membrane form a blocking layer to charge transfer.

Fig. 3 shows impedance spectra respectively of (calix1) and (calis2) functionalized gold electrodes after additions of different concentrations of the cadmium ion.

As it can be seen from these figures, the semicircle domains (diameters) of the respective Nyquist plots are considerably dependant on ion concentration. We also note that the charge transfer resistance decreases for calix1 and increases for the calix 2 according to the same concentrations of cadmium. So we can prove that the presence of a longer carbon chain at the lower rim change the recognition mechanism. Another possibility is then possible. We have a possible adsorption in the cavities of calix and not complexation with the functional group.

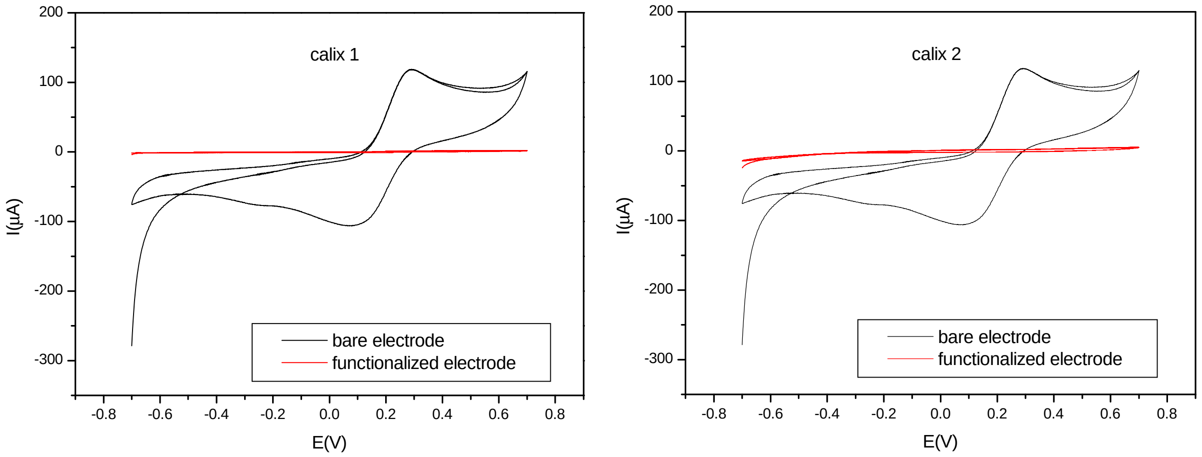


Fig. 2. The cyclic voltammograms of a bare gold electrode and a functionalized electrode by (calix1) and (calix2).

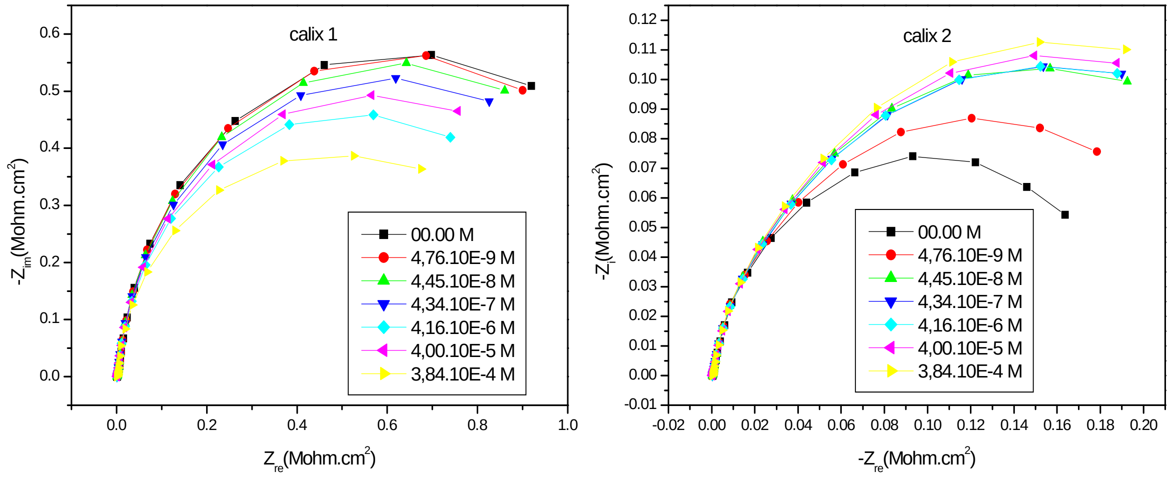


Fig. 3. Nyquist diagrams for different Cd^{2+} concentrations for calix1 and calix2 thin films.

Equivalent electrical circuits were determined by fitting the experimental impedance data using the Zview software (Scribner Associates, Inc.) by successive iterations starting from a model circuit. The best fit with a correlation coefficient $\chi \approx 10^{-3}$ was done using an equivalent electrical circuit shown in Fig. 4, in which a resistance R_s (electrolyte resistance) is in series with the association in parallel of the charge transfer resistance R_{tc}, and a constant phase element CPE. A constant phase element (CPE) is a non-ideal capacitance that takes into account the interfacial irregularities (porosity, roughness, and geometry).

From these measurements, we have plotted the variation of (Rct–Rct_0) versus the logarithm of the cadmium concentration (Fig. 5).

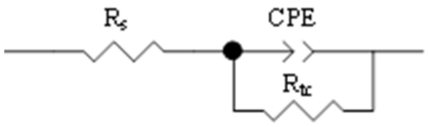


Fig. 4. Equivalent circuit used for fitting of the impedance.

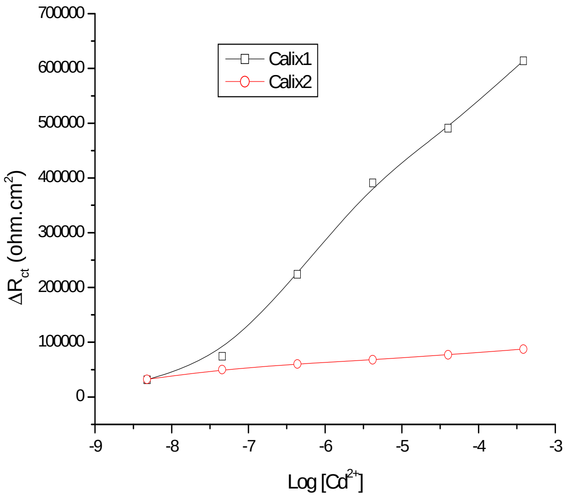


Fig. 5. Calibration curves describing the variation of charge transfer resistance ΔR_{ct} versus logarithm of the cadmium concentration.

These plots exhibit a linear relationship between the calixarene film resistance (Rct–Rct_0) versus the logarithm of the cadmium concentration, bat there is a clear difference between (calix1) and (calix2) thin films sensitivity. Thus, we can deduce that the best sensitivity determined on the calix1 thin film case, indicates that the absence of carbon chain improves the complexation efficiency.

4. Conclusion

We have investigated the ion sensitivity of gold electrodes based on tow tetra-ester derivatives of p-tert-butyl-calix[8]arene thin films. The impedance measurements showed an increase in sensor response proportionally with the increase of the concentration of the metal cation indicating sensitivity of the devices with a detection limit of 10^{-8} M. The sensitivity study has also revealed that the carbon chain doesn't favor the complex stability.

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