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Correlation between ion-exchange properties and swelling/shrinking processes in hexasulfonated calix[6]arene doped polypyrrole films: *ac*-electrogravimetry and electrochemical atomic force microscopy investigations

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ABSTRACT

Electrogenerated polypyrrole films doped with hexasulfonated calix[6]arenes were subjected to *ac*-electrogravimetry and electrochemical atomic force microscopy (EC-AFM) studies in aqueous potassium nitrate solutions. The former technique reveals that these films are mainly cation exchangers although solvent molecules (H_2O) and anions (NO_3^-) are also exchanged, in much lower amounts, in the course of the doping/undoping process. Unexpectedly, within the potential range encompassing this process, K^+ cations were found to be exchanged for more cathodic potentials whereas H_3O^+ are exchanged for more anodic potentials. EC-AFM investigations revealed substantial shrinking and swelling during the oxidation (doping) and reduction (undoping) processes respectively. An obvious correlation can easily be built between these observations: the oxidation of the polymer films provokes an expulsion of the cations, as expected from cation exchanger polymer films, and therefore a decrease of the volume (and thickness) of these films whereas their reduction causes an insertion of cations and an increase of their volume (and thickness). This electromechanical mechanism is amplified by the simultaneous exchange of free water molecules. Suggestions based on these observations, on structural characteristics of polypyrrole films, and on complexation ability of hexasulfonated calix[6]arenes incorporated in the films are discussed to explain (i) the change of the identity of the exchanged cations as a function of the potential, (ii) the exchange of free water molecules and, (iii) the exchange of small amounts of nitrate ions.

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1. Introduction

Calixarenes are metacyclophanes produced from the condensation of phenol with formaldehyde [1,2]. As they are poorly soluble in water, the necessity of appending ionic functional groups, such as carboxylic acid (–COOH) or sulfonic acid (–SO_3H) groups at the para-position of the phenolic units has been reported in literature (see [3,4] and Chapter 24 in [1]). Sulfonated calix[n]arenes are consequently versatile water-soluble binding agents able to bind with a significant selectivity a large set of interesting species, whether these latter are molecular or mono-atomic, ionic or neutral, and organic, inorganic or biological [5]. In the case of hexasulfonated calix[6]arenes (C6S) employed in this contribution, let us cite as possible targeted analytes in a non-exhaustive list, UO_2^{2+} and some transition metal (Ni^{2+}, Zn^{2+}, Cu^{2+}, Fe^{3+}) [6,7] and lanthanide [8] cations, ferrocene and cobaltocenium derivatives [9–12], quaternary ammonium cations [13], cationic surfactants [14,15], neutral molecules [16], as well as proteins (such as Bovine Serum Albumin (BSA)), amino-acids, oligo-peptides, drugs, and other small bioactive molecules [17,18] and even iron oxide nanoparticules [19].

Among the various applications of these versatile complexation behaviours, the elaboration of calixarene based electrochemical sensors has been thoroughly investigated although it required the exploration of strategies allowing the immobilisation of sulfonated calixarenes on classical working electrode surfaces. One way to achieve this goal consists in using these ionic calixarenes as doping anions in electronically conducting polymer matrices (films or colloids) such as polypyrrole [20–22], poly-(ethylene-dioxythiophene) (PEDOT) [23] or polyaniline [24]. The elaboration of electrochemical sensors based on this strategy will succeed only on condition that the calixarene based dopants conserve the binding character and the selectivity they display in solution once they are incorporated in the polymer matrix, which was shown to be achieved for C6S doped polypyrrole films with a targeted analyte such as uranyl cations [22]. Interestingly, the success of this strategy will also rely on the ion exchange properties of the resulting C6S doped conducting polymer films, which in turn depend, for a part, on the structural characteristics of these films possibly at the nanometric or molecular scale. Let us notice here that information

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on the structural characterisation is poor in literature in the case of electrodeposited electronically conducting polymers (ECPs) films.

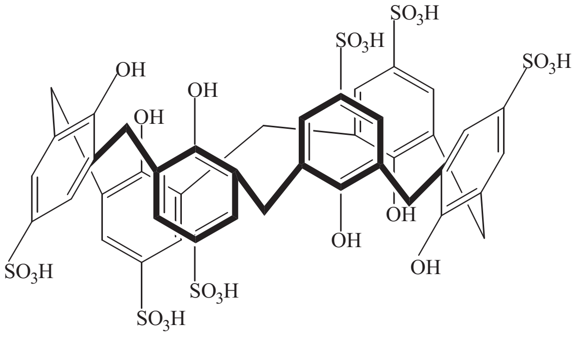
The purpose of this contribution was first to develop a deep understanding of ion (and potentially solvent) exchanges taking place in electrodeposited C6S doped polypyrrole (PPy) films during electrochemically controlled doping/undoping using *ac*-electrogravimetry experiments based on a well-established procedure.

Our second intention was to identify the electromechanical (swelling/shrinking) behaviour resulting presumably from these ions and solvent exchanges in our PPy/C6S films. A few research groups have indeed developed strategies allowing the accurate in-situ measurement of these volume (and topographical) changes under electrochemical control of the doping state of the polymer film either at locale or global scale [25–34]. In this contribution, we used electrochemical atomic force microscopy (also referred to as EC-AFM), i.e. AFM in an electrolytic solution allowing an electrochemical conditioning of the substrate (C6S doped PPy films in this contribution).

2. Experimental

2.1. Electrochemical deposition of PPy/C6S thin films

Hexasulfonated calix[6]arene doped polypyrrole (PPy/C6S) thin films were electrochemically deposited from aqueous solutions containing the pyrrole monomer (0.1 M) and hexasulfonated calix[6]arene (C6S, 1.66×10^{-3} M, see its structure on Scheme 1). Such electrolytic solution was always prepared immediately prior the electropolymerisation was launched so as to avoid the formation of insulating polypyrrole particles via an autopolymerisation mechanism reported in literature [35]. The six sulfonic acid groups all possess a same and very low pK_a value which was suggested to be below 1, as reported in [36]. On the other hand, the acidic power of the six phenolic protons (OH groups) is measured by different pK_a values revealing intramolecular hydrogen bonds resulting from the removal of one or several of these phenolic protons. As a poly-acid, C6S was shown to possess only two ionisable OH groups in the pH range 2.5–7 ($pK_{a_1} = 3.37 - 3.45$ and $pK_{a_2} = 4.76 - 5.02$) whereas the remaining four phenol groups are only weakly acidic ($pK_{a_3} > 11$) [36–38]. As a consequence, the pH of our electrolytic solutions used for the electrodeposition step is expected to be 2, which is largely above the pK_a values of the sulfonic acid groups and below that of the phenolic protons. C6S is thus expected to be hexa-anionic in this electrolytic solution. In spite of the low ionic strength of the resulting electrodeposition solution, no other background salt was added in the electrodeposition solution so as to make sure that the produced PPy films were doped with hexasulfonated calixarenes only, and display therefore ion exchange properties resulting only from the incorporation of those large anions during the electrodeposition step. The electrochemical technique used for the electrodeposition of these films was cyclic voltammetry. The potential range chosen for this electrodeposition step extends from −1 V to 0.4 V vs an aqueous K_2SO_4 saturated mercurous sulphate (SSE) reference electrode so as to avoid the electrochemical oxidation (and subsequent degradation) of the hexasulfonated calix[6]arene anions as reported in literature [39–41]. PPy films dedicated to EC-AFM investigations were electrodeposited on a working electrode made of a thin layer of platinum (thickness: ≈60 nm, RMS: ≈2.5 nm, area: 0.126 cm^2) deposited on mica through a mask using the sputtering technique. Those dedicated to *ac*-electrogravimetry (and cyclic electrogravimetry) investigations were electrogenerated on a quartz bearing a key shaped gold electrode on each of its two faces. A typical voltammogram corresponding to the electrodeposition of these films in these experimental conditions is shown on Fig. 1. SEM-FEG imaging of the profile of the obtained film reveals a thickness close to 500 nm. This is only an estimation as it was measured in vacuum conditions required by SEM-FEG imaging. As a consequence, it is definitely not the thickness of a fully water-loaded and hydrated film.



Scheme 1. Molecular structure of hexasulfonated calix[6]arene (C6S).

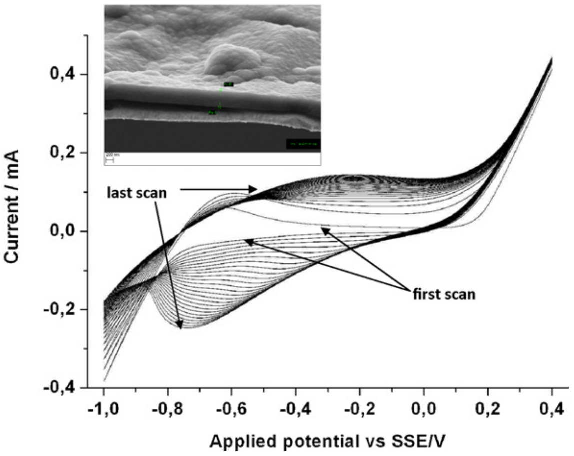


Fig. 1. (a) Typical consecutive cyclic voltammograms (25 scans) obtained during the electrodeposition of PPy/C6S from an aqueous solution containing Py (0.1 M) and C6S (1.66 mM). WE: thin Pt layer on mica (0.126 cm^2). CE: Pt. Ref: SSE. $V = 100$ mV s^{-1}. (b) SEM-FEG image of the profile of the resulting film.

2.2. Ac-electrogravimetry investigations

The experimental procedure and setup used to carry out the *ac*-electrogravimetry experiments have been reported elsewhere in previous publications of our group [42–45]. The quartz crystals used in the present investigations have a base frequency of 9 MHz.

2.3. EC-AFM measurements

EC-AFM experiments required a home made electrochemical cell in which the working electrode bearing the PPy film lies flat in the back of the cell whereas a platinum grid and a silver wire covered with an electrogenerated silver chloride film are used respectively as counter- and Ag/AgCl reference electrodes respectively. A SP300 potentiostat (Bio-Logic, Claix, France) is connected simultaneously to (i) this electrochemical cell so as to apply various potential conditionings and to read the resulting current on the working electrode and (ii) the AFM controller (Picoscan 2100, Agilent, USA) so as to allow this latter to read these two signals at the acquisition frequency of the data related to proper AFM imaging. This was also necessary so as to insure a perfect synchronization of the acquisition of height, potential and current data.

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