

Electrodeposition of pyrocatechol based films is influenced differently by cationic and anionic surfactants

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ABSTRACT: Pyrocatechol (benzene-1,2-diol) is known to form conformal films on electrodes under potential cycling conditions from aqueous solutions. In analogy with monomers like pyrrole, the electrodeposition of pyrocatechol based films may be modified in the presence of surfactants. The present communication describes the influence of an anionic and a cationic surfactant, namely sodium dodecyl sulfate (SDS) and hexadecyltrimethylammonium bromide (HTMAB), on the electrodeposition of pyrocatechol on amorphous carbon electrodes. It is found that SDS favors the electrodeposition process with respect to HTMAB but the films produced in the presence of the cationic surfactant display a higher resistance to electron transfer as inferred from electrochemical impedance spectroscopy. These results are interpreted in terms of HTMAB-pyrocatechol interactions, probably via a cation- π effect.

Date of Submission: 27-10-2019

Date of acceptance: 15-11-2019

I. INTRODUCTION

The synthesis of films using electrochemical methods like cyclic voltammetry or chronoamperometry is an efficient way to coat conductive substrates with conformal films [1]. The efficiency originates from the specific oxidation-polymerization at the electrode surface, the non transformed monomers in solution being available for further chemical processes. As a direct application of such films is their possible role to protect metallic surfaces against corrosion [2, 3]. If the obtained films contain moieties able to undergo secondary functionalization, the films can be potentially used as electrochemical sensors [4]. From this perspective, electropolymerized films made from catecholamines [4, 5] and catechols [6-8] or polyphenols [9] offer interesting perspectives since the obtained coatings can be easily modified with enzymes for biosensing purposes [4]. The addition of redox inactive species in the oxidizable monomer solution may allow to produce composite electrodeposited films with modified properties, like permeability or electrical conductivity (doping effect) [10] as well as improved adhesion of the coatings to their substrates. It is the aim of this investigation to study the influence of a negatively charged, sodium dodecyl sulfate (SDS), and a positively charged, hexadecyltrimethylammoniumbromide (HTMAB) surfactant on the electropolymerization of pyrocatechol. The concentration of the surfactant in the pyrocatechol solution (fixed at $1 \text{ mg}\cdot\text{mL}^{-1}$) has also been changed above and below the critical micellar concentration of the surfactant.

II. MATERIALS AND METHODS

All solutions were freshly prepared before each electrochemical deposition experiment using distilled and demineralized water having a resistivity of $18.2 \text{ M}\Omega\cdot\text{cm}$ (Millipore Direct 8 system, Molsheim, France). Pyrocatechol (ref. C9510), sodium dodecyl sulfate (SDS, ref. 436143), hexadecyltrimethylammonium bromide (HTMAB, ref. H9151) and potassium hexacyanoferrate ($\text{K}_4\text{Fe}(\text{CN})_6$, ref. P9387) were all purchased from Sigma-Aldrich and used without further purification. The surfactants as well as pyrocatechol were solubilized in 50 mM sodium acetate buffer at $\text{pH} = 5.0$. The pH of the sodium acetate buffer was adjusted with concentrated hydrochloric acid and checked with a calibrated Hanna 221pH meter. In all electrodeposition experiments, pyrocatechol was used at a constant concentration of $1 \text{ mg}\cdot\text{mL}^{-1}$ ($9.1 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$) whereas the concentration of SDS and of HTMAB was changed ($0, 5, 10$ and $20 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$). At 25°C , the critical micellar concentration of the two surfactants are equal to $8 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ [11] and $1.0 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ [12] for SDS and HTMAB respectively.

The pyrocatechol based films were deposited on amorphous carbon electrodes (ref. CHI 104, CHInstruments, Houston, Texas) using a CHI604B potentiostat (CHInstruments, Houston, Texas) in a three electrode configuration with an Ag/AgCl reference (ref. CHI111 with saturated KCl +AgCl as the internal electrolyte) and a platinum wire (ref. CHI 115) as the counter electrode. Before each deposition experiment, the

amorphous carbon electrode was successively polished on a SiC disk, Al₂O₃ slurries with 1 and 0.1 μm in diameter (Escil, Villeurbanne, France). Each polishing step lasted over 1 min and was separated from the next one with extensive rinse with distilled water. After the last polishing step, the electrode was sonicated for 2 min in a bath of distilled water. This sonication step was repeated twice just before the beginning of the deposition experiment. First of all, the quality of the polishing-cleaning steps was checked by performing cyclic voltammetry (CV) in the presence of 1 mM potassium hexacyanoferrate in sodium acetate buffer between -0.6 and +1.0 vs Ag/AgCl at a potential sweep rate of 100 mV.s⁻¹. The polished working electrode was considered satisfactory when the oxidation and reduction peak currents of the redox probe were separated by less than 80 mV with oxidation-reduction peak currents equal within 10 %. The electrodeposition was performed for 25 CV cycles at a potential sweep rate of 20 mV.s⁻¹. Thereafter the electrodes were put in the same buffer, eventually containing the surfactant, as used for the electrodeposition to acquire the capacitive curve on the film in the same potential window and at 100 mV.s⁻¹. Finally, the electrochemical cell was rinsed with sodium acetate buffer and put in the potassium hexacyanoferrate containing buffer to assess the film permeability to the redox probe. That CV was performed in the same potential window at a potential sweep rate of 100 mV.s⁻¹ and compared to the CV performed on the polished electrode. In the case of an impermeable film, this CV should be identical to the capacitive curve obtained on the same deposit.

Electrochemical impedance spectra (EIS) were acquired on all the deposited pyrocatechol based films at the peak potential of potassium hexacyanoferrate (220 ± 10 mV vs Ag/AgCl) with a potential amplitude change of 5 mV in the frequency range between 10⁵ and 10⁻² Hz.

III. RESULTS AND DISCUSSION

The 25 CV cycles of pyrocatechol (1 mg.mL⁻¹ in sodium acetate buffer) at a potential sweep rate of 20 mV.s⁻¹ in the absence of surfactant and in the presence of 5 mM SDS or HTMAB are displayed in Figure 1.

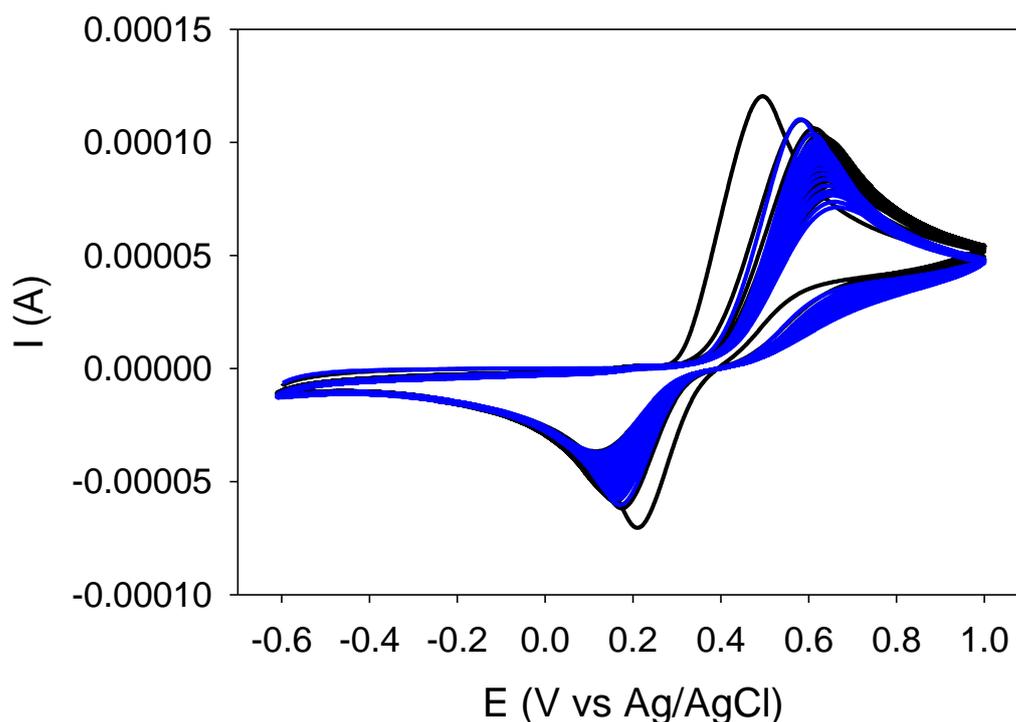


Figure 1: CV curves of pyrocatechol (1mg.mL⁻¹ in 50 mM sodium acetate buffer) performed in the absence of surfactant (black line), in the presence of 5 mM SDS (blue line) and in the presence of 5 mM HTMAB (red line) at a potential scan rate of 20 mV.s⁻¹ for 25 successive cycles.

It appears that in all cases the oxidation and reduction currents decrease from one sweep cycle to the next one but in a manner that is surfactant dependent. In all cases the oxidation peak potentials are also shifted to anodic potentials upon an increase in the cycle number. These findings indicate that the oxidation of pyrocatechol is progressively hindered requiring higher and higher energies to continue the oxidation process. In the particular case of HTMAB, the oxidation peak current is systematically lower than the oxidation current measured in the absence of surfactant or in the presence of SDS for a given pyrocatechol concentration (accurate at better than 2%). This means that in the case of HTMAB, the concentration of available pyrocatechol at the

electrode surface is lowered, most probably through interactions with the cationic surfactant. One can guess that these interactions are of the cation- π type [13]. After having performed 25 CV cycles, the cell was rinsed with the same buffer (contacting or not the same surfactant as used during the electrodeposition process) to acquire the capacitive current of the deposited material. The obtained CV curves were compared with the capacitive current acquired in the same conditions (potential sweep rate of $100 \text{ mV}\cdot\text{s}^{-1}$) on the pristine and polished electrode. It appears that the film capacitance, the area under the CV curves, is much higher after the electrodeposition process and that the curves display some oxidation and reduction peaks (Figure 2). This highlights that the deposited material is by itself electroactive in agreement with previous reports [4,5,8]. At 20 mM in added surfactant, above the critical micellar concentration of both surfactants, the capacitance of the deposited coating is much higher in the case of SDS, compared with pyrocatechol in the absence of additive and compared with HTMAB (Figure 2). This highlights that SDS (at 20 mM) favors the deposition of a pyrocatechol based films compared to the situation where the electrodeposition is performed in the absence of additive. Conversely, HTMAB (at 20 mM) hinders the film deposition as already inferred by inspection of the CV performed in the presence of pyrocatechol (Figure 1). It has also to be noted that the capacitive curve obtained after deposition of pyrocatechol in the presence of HTMAB displays a typical oxidation-reduction signature above $+0.8 \text{ V}$ vs Ag/AgCl (Figure 2, red line). The same oxidation-reduction wave is found in an HTMAB containing solution (data not shown) and strongly points to the incorporation of this cation surfactant in the pyrocatechol based film or to an incomplete surface coverage of the electrode allowing access of the detergent to the electrode surface to be oxidized-reduced there. Indeed, the capacitive curves have been measured in the presence of the same surfactant concentration as used during the electrodeposition process.

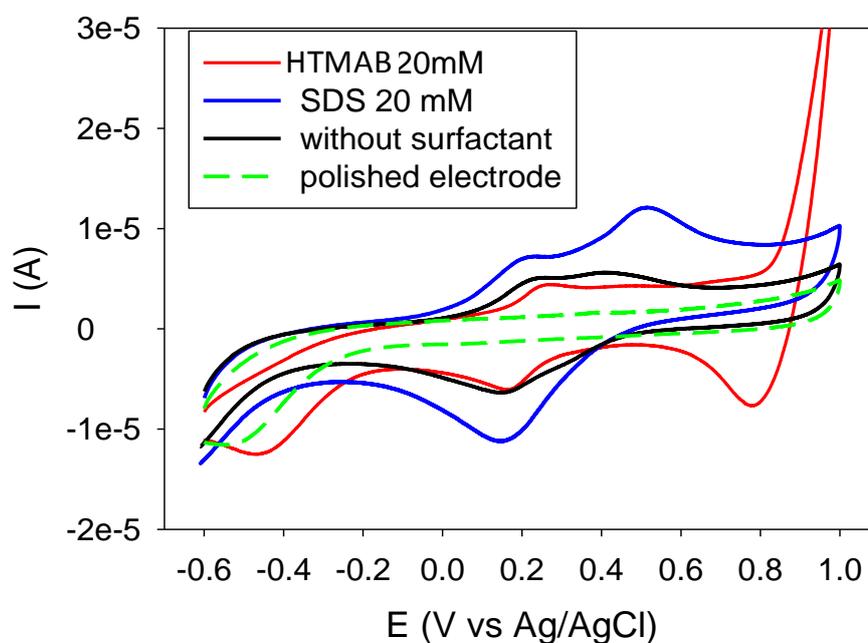


Figure 2: Typical capacitive CV curves (in the absence of redox probe in the solution) performed at a potential scan rate of $100 \text{ mV}\cdot\text{s}^{-1}$ in the presence of sodium acetate buffer and the same surfactant as used for the deposition of a pyrocatechol based deposit. The deposits were obtained as shown in Figure 1, namely by cycling the potential at $20 \text{ mV}\cdot\text{s}^{-1}$ for 25 cycles in the presence or absence of surfactants. The inset indicates in which solution conditions the capacitive curves were measured.

Playing on the SDS concentration has a major influence on the capacitive curves, with a marked increase in film capacitance and hence in film deposition with the SDS concentration (Figure 3). On the other hand, the HTMAB concentration seems to play a minor influence on the film capacitance, this quantity being always lower than the one of the film produced in the presence of $1 \text{ mg}\cdot\text{mL}^{-1}$ of pyrocatechol in the absence of surfactant (Figure 4).

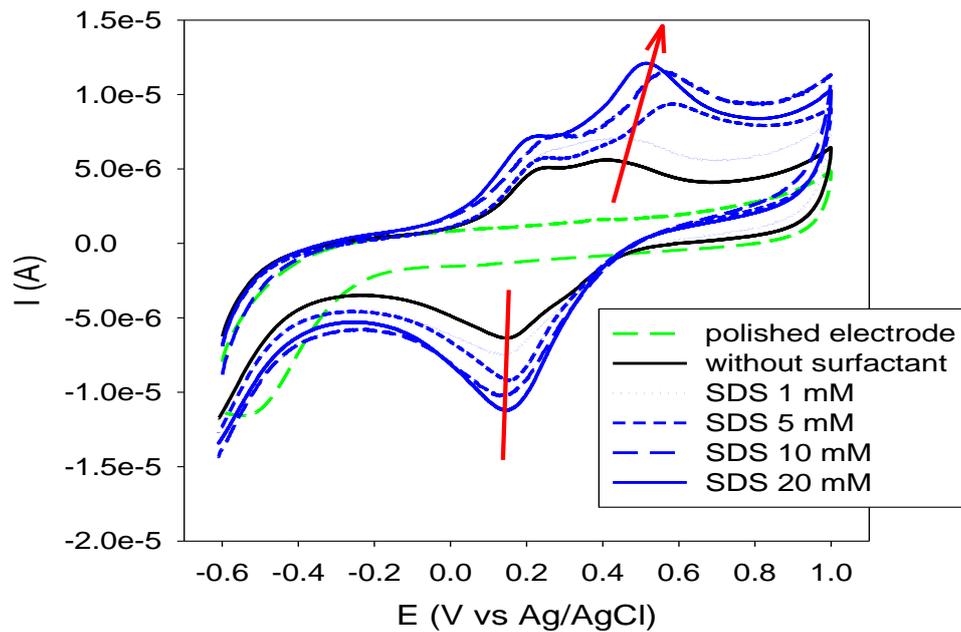


Figure 3: Influence of the SDS concentration on the capacitive CV curves (potential scan rate of 100 mV.s^{-1}) measured in the presence of the surfactant solution after having performed 25 deposition cycles (potential scan rate of 20 mV.s^{-1}) in the presence of the same surfactant concentration and with pyrocatechol at 1 mg.mL^{-1} . The used SDS concentration is indicated in the inset. The red arrows indicate the evolution of the capacitive curve with increasing SDS concentration.

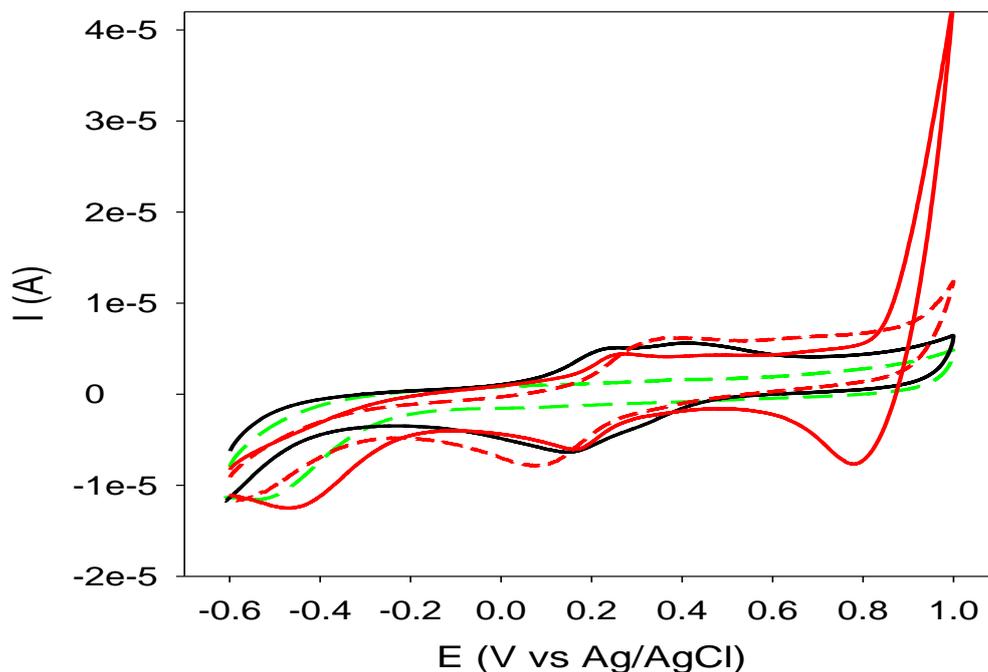


Figure 4: Influence of the HTMAB concentration on the capacitive CV curves (potential scan rate of 100 mV.s^{-1}) measured in the presence of the surfactant solution after having performed 25 deposition cycles (potential scan rate of 20 mV.s^{-1}) in the presence of the same surfactant concentration and with pyrocatechol at 1 mg.mL^{-1} . The green dashed curve corresponds to the capacitive curve measured on the polished electrode, the black full line to the capacitive curve on the film produced in the absence of surfactant, whereas the red dashed line and the full red line correspond to the capacitive curves obtained in the presence of CTAB at 5 and 20 mM respectively.

After 25 CV cycles of the electrodeposition process, the carbon electrode becomes impermeable to potassium hexacyanoferrate when the deposition is performed in the absence of surfactant or in the presence of SDS (Figure 5A). However, in the presence of HMTAB, the access of potassium hexacyanoferrate to the electrode even if strongly reduced is not totally suppressed (Figure 5B).

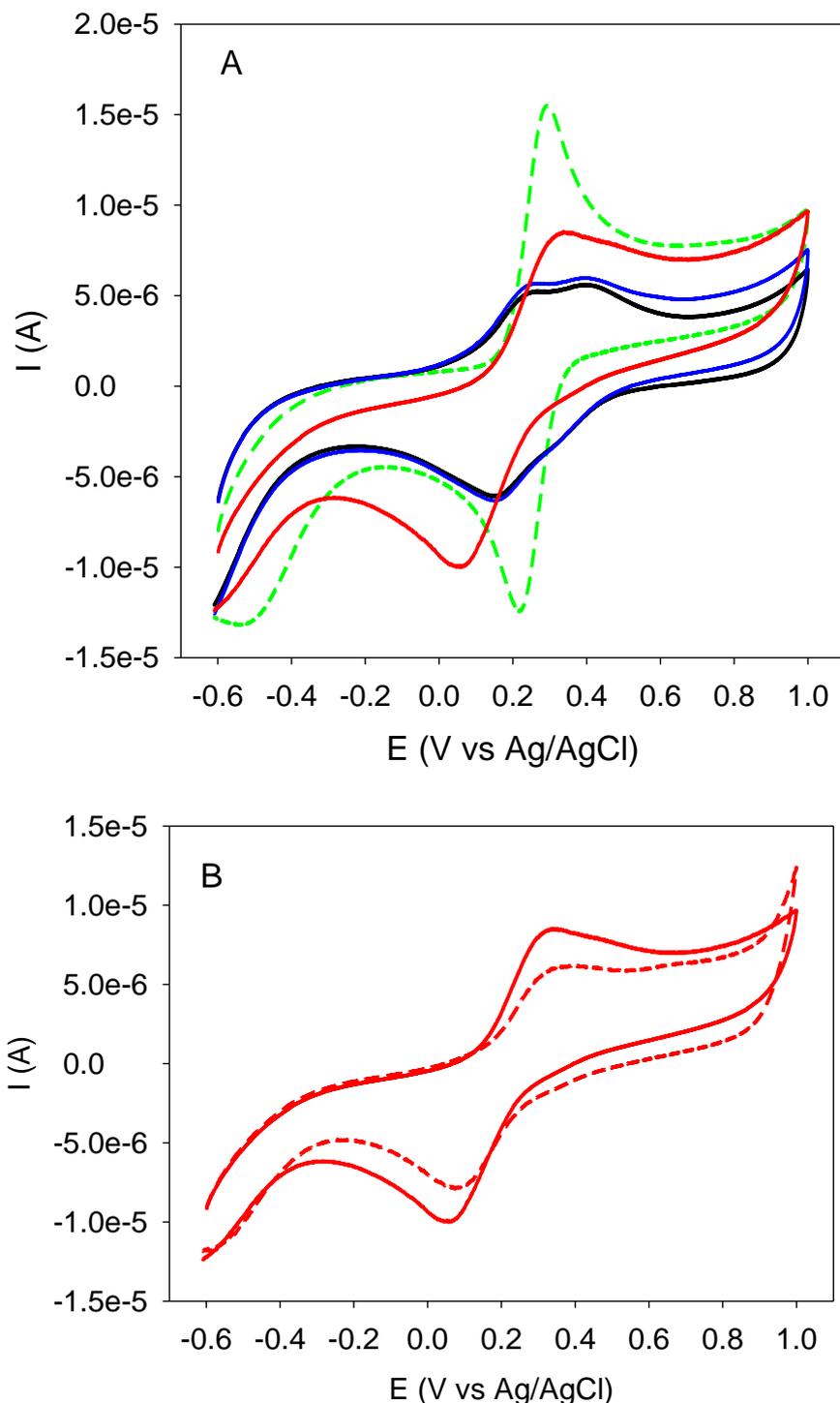


Figure 5: A: CV of a potassium ferrocyanide solution (1 mM in the presence of sodium acetate buffer, potential sweep rate : $100 \text{ mV}\cdot\text{s}^{-1}$) after having performed 25 deposition cycles (pyrocatechol at $1 \text{ mg}\cdot\text{mL}^{-1}$) in the absence of surfactant (black line), in the presence of SDS at 5 mM (blue line) and in the presence of HMTAB at 5 mM (red line). The CV of a potassium ferrocyanide solution on the polished electrode is also represented (green dashed line).

B: CV of the electrode after 25 deposition cycles (pyrocatechol at 1 mg.mL^{-1}) in the presence of the buffer with 5 mM HTMAB (red dashed line) and with the buffer containing 1 mM potassium ferrocyanide (red line).

The findings that HTMAB hinders the electrodeposition of pyrocatechol based films is also confirmed by means of electrochemical impedance spectroscopy (Figure 6). In the case of the films deposited in the presence of HTMAB, the impedance is much higher in the high frequency domain than for the films prepared without surfactant or with SDS (Figure 6B). Since the impedance is essentially of ohmic nature at high frequency [14], it has to be concluded that the pyrocatechol based films prepared in the presence of HTMAB display a higher resistance to electron transfer than their counterparts prepared either in the absence of surfactant or in the presence of SDS. This may well be due to the incorporation of HTMAB in the film, and hence to strong interactions between this cationic species and the pyrocatechol based material. Cation- π interactions are suspected to be at the origin of this effect. This assumption has to be verified in future investigations.

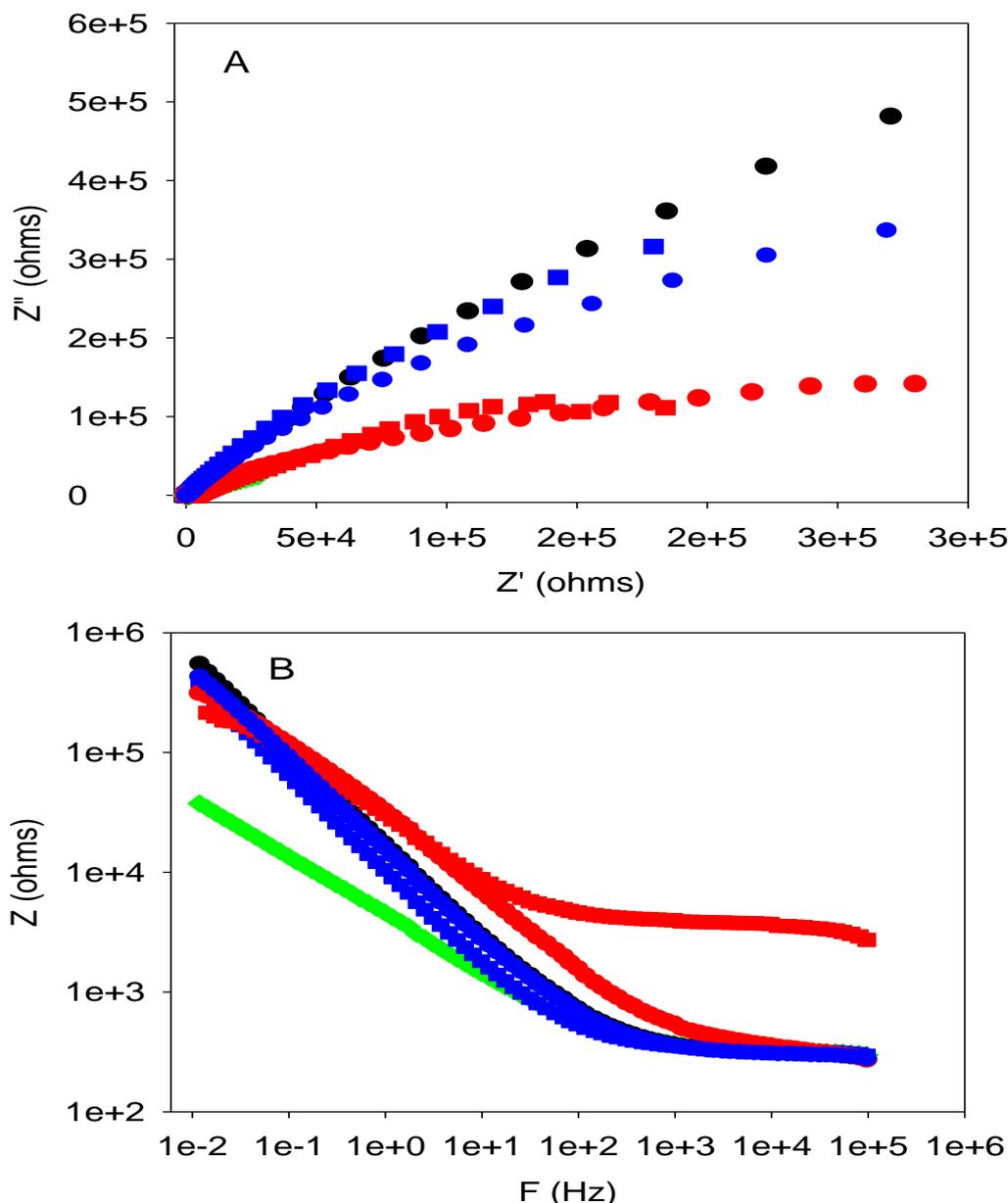


Figure 6 : Electrochemical impedance spectra of the polished electrode (green dashed line), of the films produced after 25 CV cycles in the presence of pyrocatechol alone (1 mg.mL^{-1} , black curve), in the presence of pyrocatechol at the same concentration and SDS (5 mM : blue circles, 20 mM : blue squares), in the presence of pyrocatechol at the same concentration and CTAB (5mM : red circles, 20 mM : red squares).
 A: Nyquist representation of the impedance spectra.
 B: Modulus of the impedance versus frequency representation.

IV. CONCLUSIONS

The electrodeposition of pyrocatechol leading to conformal films impermeable to potassium hexacyanoferrate is markedly affected by the presence of surfactants, in a manner similar to the electrodeposition of pyrrole [3]. This investigation also highlights the marked difference between an anionic surfactant, SDS, and a cationic surfactant, HTMAB, the former one favoring the deposition of more material (higher film capacitance) than the later. HTMAB may interact with pyrocatechol in the solution phase, reducing the concentration of available pyrocatechol at the electrode as well as in the deposited film phase (where the oxidation/reduction wave of HTMAB is measured simultaneously to the capacitive behavior of the electrodeposited film). The suspected interaction mechanism between HTMAB and pyrocatechol is via cation- π interactions. This remains to be demonstrated in forthcoming studies with structural analytical methods like X-ray photoelectron spectroscopy. The eventual anti-corrosive properties of the pyrocatechol electropolymerized films will also be investigated in the future.

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Vincent BALL " Electrodeposition of pyrocatechol based films is influenced differently by cationic and anionic surfactants" *International Journal of Research in Engineering and Science (IJRES)*, vol. 07, no. 3, 2019, pp. 62-68