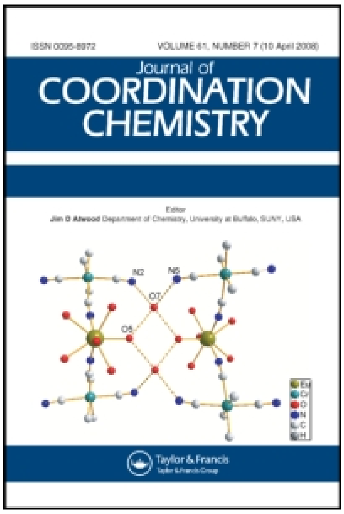

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Iron porphyrin-modified electrodes: influence of the method of modification on the stability and electroactivity in oxidation of sulfite or hydrogensulfite in ethanol-water solutions

G. Ramírez[a]; M. C. Goya[b]; L. Mendoza[c]; B. Matsuhiro[c]; M. Isaacs[d]; YO-Ying Chen[c]; M. C. Arévalo[b]; J. Henríquez[e]; W. Cheuquepán[c]; M. J. Aguirre[c]
[a] Facultad de Ecología y Recursos Naturales, Departamento de Ciencias Químicas, Universidad Andres Bello, Santiago, Chile [b] Facultad de Química, Departamento de Química Física, Universidad de La Laguna, 38071-La Laguna, S/C de Tenerife, Spain [c] Facultad de Química y Biología, Universidad de Santiago de Chile, Santiago, Chile [d] Facultad de Ciencias, Departamento de Química, Universidad de Chile, Santiago, Chile [e] Instituto de Química y Recursos Naturales, Universidad de Talca, Talca, Santiago, Chile

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Iron porphyrin-modified electrodes: influence of the method of modification on the stability and electroactivity in oxidation of sulfite or hydrogensulfite in ethanol–water solutions

G. RAMÍREZ†, M.C. GOYA‡, L. MENDOZA§, B. MATSUHIRO§, M. ISAACS¶, YO-YING CHEN§, M.C. ARÉVALO‡, J. HENRÍQUEZ‖, W. CHEUQUEPÁN§ and M.J. AGUIRRE*§

†Facultad de Ecología y Recursos Naturales, Departamento de Ciencias Químicas, Universidad Andres Bello, República 275, Santiago, Chile
‡Facultad de Química, Departamento de Química Física, Universidad de La Laguna, 38071-La Laguna, S/C de Tenerife, Spain
§Facultad de Química y Biología, Universidad de Santiago de Chile, Casilla 40, correo 33, Santiago, Chile
¶Facultad de Ciencias, Departamento de Química, Universidad de Chile, Las Palmeras 3425, Casilla 653, Santiago, Chile
‖Instituto de Química y Recursos Naturales, Universidad de Talca, 2 Norte 685, Casilla 721, Talca, Santiago, Chile

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The aim of this work is to study four types of modification of a glassy carbon electrode by Fe(III)-tetrakis(p-tetraaminophenyl)porphyrin and determine the influence of the method of immobilization of the complex on glassy carbon in electrocatalytic properties for the sulfite and hydrogensulfite oxidation in ethanol–water. The first modification was deposition of a drop of solution containing the porphyrin on a glassy carbon electrode and evaporation of the solvent (dry-drop method). The second method was immersion of the electrode at 54°C in a solution of dimethylformamide containing the porphyrin for 2 h. The third method consisted of the same heating treatment but after formation of a chemical bond of 4-aminopyridine on the glassy carbon surface, which acts as an axial ligand for the first layer of porphyrin. The fourth method involves electropolymerization of the porphyrin on the electrode surface. Important differences in stability, the potential where the oxidation wave begins and selectivity of the electrode to sulfite or hydrogensulfite were observed. The behavior of the polymer-modified electrode is different in water compared to ethanol–water.

Keywords: Modified electrodes; Iron porphyrins; Oxidation of sulfite; Supramolecular electrode; Electrocatalysis

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*Corresponding author. Email: maria.aguirre@usach.cl

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1. Introduction

Sulfite is an antioxidant in foods and beverages [1] and a pollutant that produces acid rain. Electrochemical oxidation of hydrogensulfite and sulfite ions has been studied on different electrode surfaces in several media [2–10]. Electrochemical oxidation of sulfite depends on the type of carbon electrode [4], and on the modification of electrode surfaces by electrochemical treatment [5, 6, 10] or by molecules coated on them [11–16]. In general, metallomacrocycles exhibit good electrocatalytic properties towards the oxidation and reduction of a wide range of chemical substances like oxygen, sulfur-containing compounds, some neurotransmitters, and nitrite [14, 17–21]. Amino-substituted porphyrins and derivatives can be electropolymerized [22–27] to obtain modified electrodes with high electroactivity. Reduction of CO_2 mediated by a supramolecular electrode formed by packed Co(II)-tetrabenzoporphyrin anchored on a glassy carbon surface show that the system is active and the monolayer deposited on the same surface is not [28]. The properties and the electrocatalytic activity of a modified electrode depend on the kind of film (monomer, polymer, aggregates) deposited on the electrode, which strongly depends on the method of deposition. For example, electro-oxidation of nitric oxide mediated by metallophthalocyanine-modified glassy carbon electrode (Co and Ni) show the effect of film formation conditions on electroactivity [28].

In this article, we report the electrochemical activity in the oxidation of sulfite and hydrogensulfite of four glassy carbon electrodes modified with Fe(III)-tetrakis (p-tetraaminophenyl)porphyrin at pH 9 in ethanol–water (12% v/v). This mixture of solvents was chosen for possible application in wine samples. The methods of modifying the electrode surface are: drop-dry method (*ddm-electrode*); physisorption at 54°C from a solution containing the porphyrin (*phy-electrode*); preparing a supramolecular-like system where the method is not reflux but heating the glassy carbon previously chemically modified with 4-aminopyridine anchored by a covalent bond to the surface at 54°C with a solution containing the porphyrin (*supra-electrode*); and polymerization of the complex (*polym-electrode*). The purpose is to study the influence of the method of modifying a glassy carbon electrode with the same complex in the oxidation of sulfite and hydrogensulfite.

2. Experimental

Reactants: Fe(III)-tetrakis(p-tetraaminophenyl)porphyrin chloride (Organix), ethanol (Soviquim, p.a.), sodium sulfite (Merck, p.a.), tetrabutylammonium perchlorate (TBAP) (Alfa Aesar, p.a.), dimethylformamide (DMF) (Fischer, p.a.), 4-aminopyridine (Aldrich), sodium chloride (Riedel de Haen, p.a.), and sodium hydroxide (Merck, p.a.) were used without purification. Water was deionized and doubly distilled. *Electrodes*: Glassy carbon, GC, (CHI 104) (geometrical exposed area: 12.6 mm^2) was polished with 0.3 µm alumina and washed thoroughly with water, then sonicated for 5 min. The reference electrode was Ag/AgCl (CHI 111). The counter electrode was a platinum wire. *Modification of electrodes*: (a) *ddm-electrode*: a drop of DMF solution containing 0.2 mM of the iron porphyrin was deposited on the GC electrode surface, exposed to air, and after evaporation of the solvent, the surface was thoroughly washed with water.

(b) *phy-electrode*: the GC electrode was submerged into a solution (DMF/0.2 mM iron porphyrin) that was heated at 54°C for 2 h. After this treatment, the surface was thoroughly washed with water. (c) *supra-electrode*: the first step involves covalent linkage of 4-aminopyridine according to the method reported in [28]. Then the amino-modified electrode is modified by the same procedure described in (b). (d) *polym-electrode*: the glassy carbon was submerged in a solution of DMF/TBAP 0.1 M containing 0.2 mM of the porphyrin under nitrogen and cycled between -0.6 and $+1.2$ V *versus* Ag/AgCl during 100 cycles at 100 mVs^{-1}. After electropolymerization, the electrode was dried with warm air and then thoroughly washed with water. It was necessary to overoxidize the polymeric film in order to inhibit the response of the remaining amino groups. It was exposed at a fixed potential of 1.6 V *versus* Ag/AgCl in a 1 M NaOH solution (under nitrogen atmosphere) for 180 s. After overoxidation, it was washed with water. The voltammetric profile of the modified electrode does not present any visible couple in ethanol–water solution.

Sulfite solutions were prepared by weight (and dilution) of Na_2SO_3 dissolved in deaerated ethanol–water (12% v/v) containing 0.1 M NaCl. The pH was adjusted adding NaOH or HCl to the solution. *Electrochemical measurements*: The voltammetric responses were obtained in deaerated solutions (by bubbling N_2 before measurement and keeping N_2 during the experiment) using a conventional three compartment Pyrex glass cell. The potential limits were -0.2 to 1.3 V *versus* Ag/AgCl. The electrolyte was 0.1 M NaCl solutions of ethanol–water (12% v/v) containing 1 mM of Na_2SO_3. *Equipment*: A 640C CHI Electrochemical Analyzer Potentiostat and a 900B CHI Scanning Electrochemical Microscope Bipotentiostat were used for all electrochemical measurements. Product detections were carried out using a HPLC Chromatograph Waters 1515 isocratic HPLC pump coupled with a Waters 432 conductivity detector and 428 refractive index detector in solutions electrolyzed for 1 h at 1 V.

3. Results and discussion

Figure 1 shows the porphyrin used in this study. It is cationic because Fe is Fe(III). The counterion, chloride, is not shown. The phenyl groups are practically perpendicular to the core of the molecule; when polymerization occurs, torsion takes place and the phenyl groups tend to planarity permitting delocalization of π electrons along the chain [29]. Figure 2(a) shows the voltammetric response of iron porphyrin adsorbed on glassy carbon in ethanol–water at pH 9.5. A shoulder that begins at *ca* 0.7 V corresponds to the Fe(IV)/Fe(III) redox pair completely irreversible as in water at the same pH (see figure 2b) [14]. At potentials more positive than this redox pair an irreversible wave corresponding to oxidation of the amino substituents appears. The profile is very similar in ethanol–water and in aqueous solutions. The currents are different because both experiments were realized in different area substrates and at different scan rates. Very similar profiles are obtained for the other modified electrodes in both solvents (not shown).

Figure 3 shows the voltammetric response (at low scan rates) of the four modified electrodes in the oxidation of sulfite and hydrogensulfite at pH 9.5. GC does not show appreciable current for these oxidations in the range of potential from 0 to 800 mV compared to the modified electrodes. Depending on the systems, one or two oxidation waves appear corresponding to sulfite and hydrogensulfite. The more negative peak

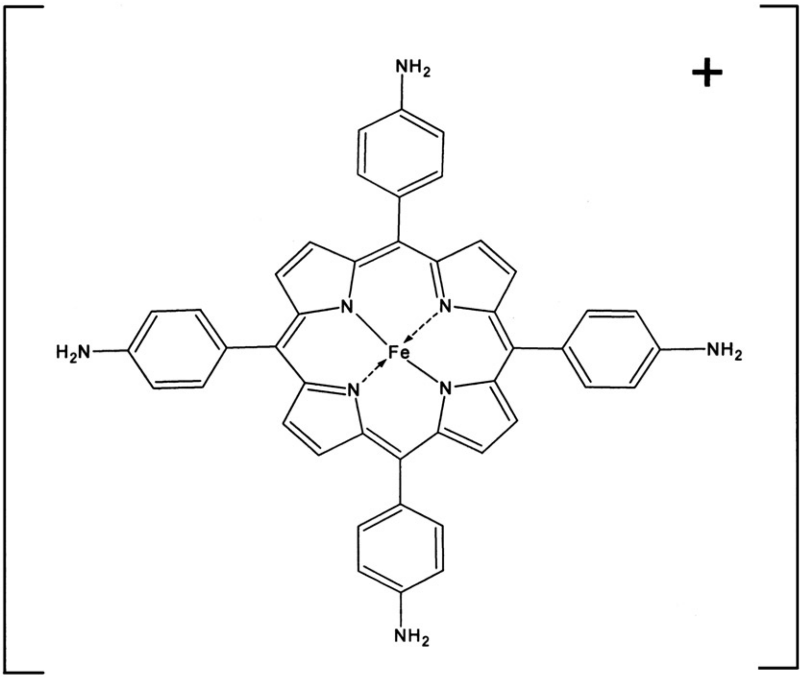

Figure 1. Structure of Fe(III)-tetrakis (p-tetraaminophenyl)porphyrin.

corresponds to sulfite and the more positive, to hydrogensulfite. It was proved by changing the pH of the solution and observing the increase or decrease of the current of each peak. The peak that appears at lower potential (more negative) corresponds to oxidation of sulfite and the second one (at potentials more positive) to hydrogensulfite. The first peak is not attributable to the metal center because it begins at potentials more negative than the potential of Fe(IV)/Fe(III) redox pair. The second peak is possibly related to the metal center's mediator role. According to the potentials where the oxidation peaks appear, two mechanisms can be proposed (based on detection of sulfate as the unique electrolysis product obtained by the stable systems):

Mechanism 1

$$[\mathrm{Fe(III)Pc}]^+ + \mathrm{SO}_3^{-2} \rightarrow \left[\mathrm{Fe(III)Pc}^+ \cdots \mathrm{SO}_3^{-2}\right]^- \qquad (1)$$

$$[\mathrm{Fe(III)Pc}^+ \cdots \mathrm{SO}_3^{-2}]^- \rightarrow [\mathrm{Fe(III)Pc} \cdots \mathrm{SO}_3]^+ + 2e \qquad (2)$$

$$[\mathrm{Fe(III)Pc} \ldots \mathrm{SO}_3]^+ + \mathrm{H_2O} \rightarrow [\mathrm{Fe(III)Pc}]^+ + \mathrm{SO}_4^{-2} + 2\mathrm{H}^+ \qquad (3)$$

Peak I is attributed to the first mechanism (equations (1) and (2)). The oxidation of sulfite probably occurs after formation of an open-circuit adduct that oxidizes at the potentials where peak I appears. Equation (3) proposes a chemical step where sulfate is generated and the porphyrin returns to its original oxidation state.

Mechanism 2

$$2[\mathrm{Fe(III)Pc}]^+ \rightarrow 2[\mathrm{Fe(IV)Pc}]^{2+} + 2\mathrm{e} \qquad (4)$$

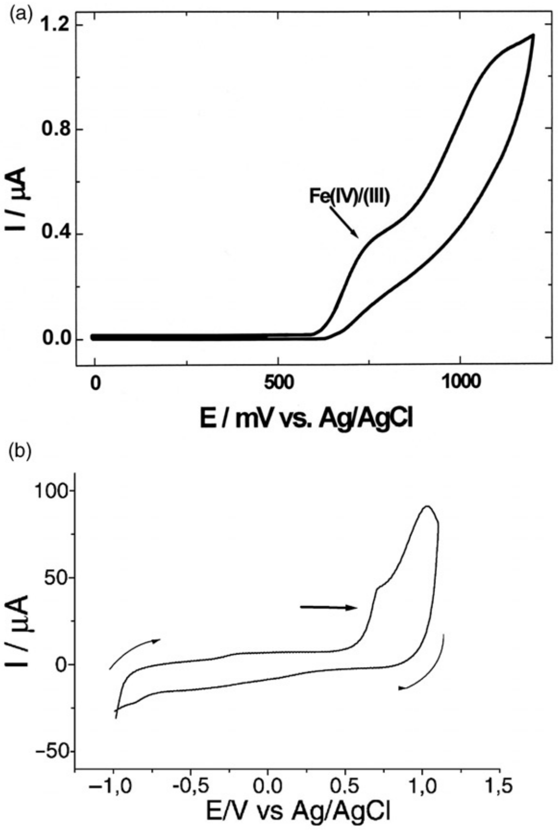

Figure 2. Voltammetric response of Fe(III)-tetrakis (p-tetraaminophenyl)porphyrin adsorbed on glassy carbon. (a) in ethanol–water solution at pH 9.5. Scan rate: $10\,\mathrm{mV\,s^{-1}}$; (b) in aqueous solution at pH 9.5. Scan rate: $100\,\mathrm{mV\,s^{-1}}$. (Figure 2(b) is reprinted from Ref. [14], p. 74. Copyright (2004), with permission from Elsevier).

$$2[\mathrm{Fe(IV)Pc}]^{2+} + \mathrm{HSO_3^-} + \mathrm{H_2O} \rightarrow 2[\mathrm{Fe(III)Pc}]^{+} + \mathrm{SO_4^{2-}} + 3\mathrm{H^+} \qquad (5)$$

Peak II is attributed to the second mechanism (equations (3) and (4)). In this case, oxidation of hydrogensulfite occurs, promoted by the previous oxidation of the metal center.

For the modified electrodes, figure 3 clearly reflects the dramatic differences among the four electrodes. In terms of catalysis compared to the blank, all modified electrodes are electrocatalysts in oxidation of SO_2 ethanol–water species. However, each system shows very different behavior. For example, supra-electrode has two peaks, i.e. catalyzes the oxidation of sulfite and hydrogensulfite, whereas ddm-electrode and phy-electrode only catalyze the oxidation of hydrogensulfite. Polym-electrode catalyzes both oxidations. In a previous paper [14] we reported for the same complex polymerized in glassy carbon, oxidation of SO_2 aqueous species at pH 9.5 gives only one peak. The difference of polym-electrode in aqueous [14] or in ethanol–water in the electrocatalysis of the same compound is remarkable.

We also proved the GC electrode chemically modified with 4-aminopyridine without porphyrin in the oxidation process, and the response is identical to that

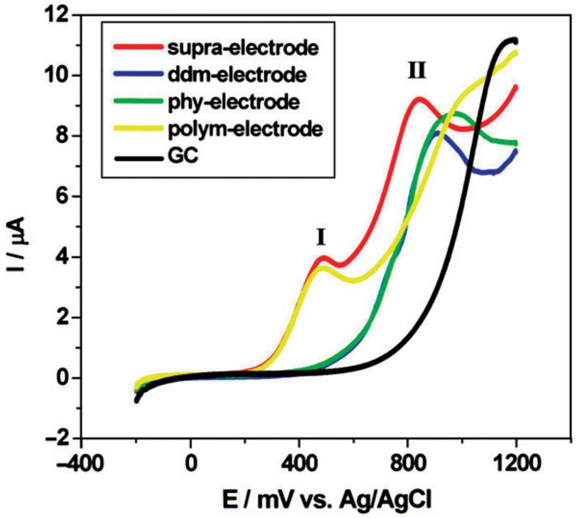

Figure 3. Cyclic voltammetry of glassy carbon and modified electrodes in the presence of sulfite (1 mM Na_2SO_3). Scan rate: $5\,mV\,s^{-1}$, in ethanol–water 12% v/v, 0.1 M NaCl, pH 9.5.

obtained with the bare glassy carbon (not shown). It is clear from these results that there is a great difference among the active sites of the different electrodes. Supra-electrode is capable of coordinating sulfite and hydrogensulfite and its profile resembles the polym-electrode. The ddm-electrode and phy-electrode profiles are very similar, indicating that the electronic density and the place where the analyte is coordinated are very similar and only one mechanism is operating (mechanism 2). Considering that in the polymer the main difference to monomeric electrodes (ddm-electrode and phy-electrode) is the enhancement in conductivity through the chain, it is possible that the supra-electrode resembles the polym-electrode due to the enhancement in the conductivity through a packing of columns of porphyrin [28]. We assume that the main difference of supra-electrode compared to ddm-electrode and phy-electrode is that the supramolecular system enhances the conductivity and changes the electronic density of the active sites and that it is not necessary to reflux the chemically-modified electrode in a solution containing the porphyrin [28], but only to submerge the 4-aminopyridine-modified electrode in a solution heated during 2 h to obtain the supramolecular structure. This is important because during reflux, the solvent also polymerizes and if the method to obtain the supramolecular system involves reflux, it is possible to have a mixture of polymerized DMF and a supramolecular system. Finally, it is important to mention that the unique systems as electrocatalysts toward oxidation of sulfite and hydrogensulfite are supra-electrode and polym-electrode. Indeed, the most catalytic system is supra-electrode toward the oxidation of sulfite and hydrogensulfite (this comparison is related to potentials and not current because the real area of each system is not known). Why polym-electrode shows two peaks in ethanol–water and only one in water has not been elucidated yet. The pKa of SO_2 equilibria are very similar in both solutions [30]. The effect is then not due to a change in the relative concentrations of sulfite and hydrogensulfite, but to a change in the characteristics of the polymer when stabilized in ethanol–water

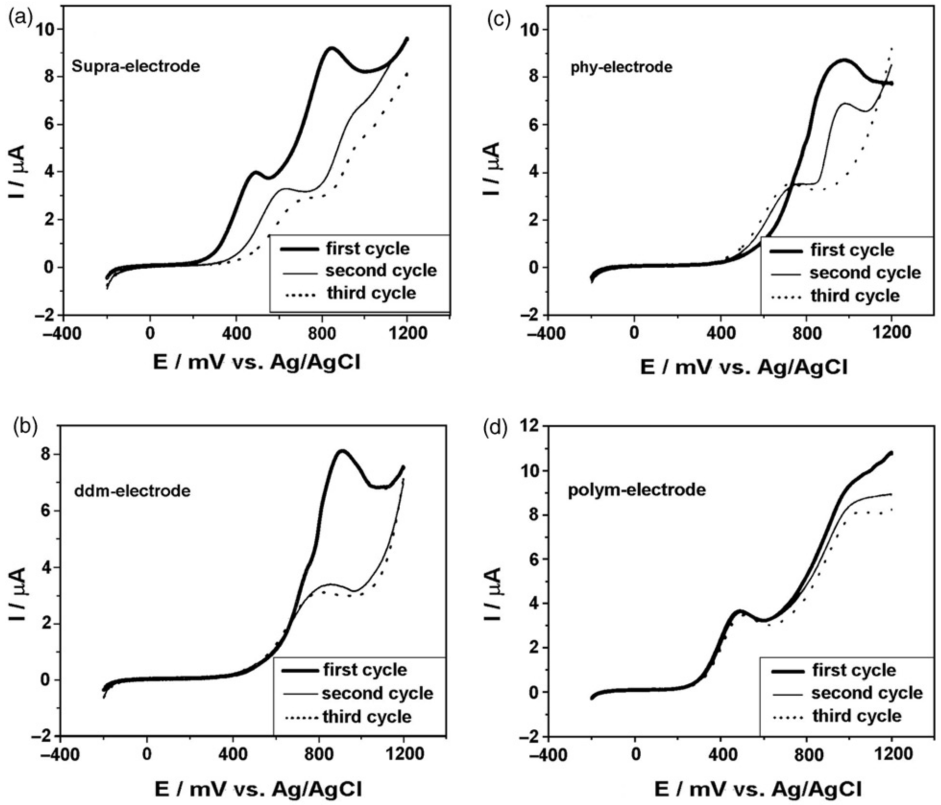

Figure 4. Stability of modified electrodes, three cycles (pH 9.5) (1 mM Na_2SO_3, ethanol-water solution). Scan rate: $5\,mV\,s^{-1}$. After each cycle the solution was stirred. (a) supra-electrode; (b) ddm-electrode; (c) phy-electrode; (d) polym-electrode.

compared to the polymer stabilized in water as a solvent. Studies in this area are currently being carried out in our laboratory.

Variation among the three cycles in each system stands out (see figure 4). In the case of supra-electrode (figure 4a), the profile diminishes its intensity and shifts to more positive potentials along the cycles but the behavior is maintained, indicating that after oxidation reorganization takes place modifying the electronic density of the active sites. The shift to more positive potentials indicates that the electronic density of the active sites decreases. This can be attributed to sulfite, hydrogensulfite, or intermediates blocking the surface (forming an adduct) that modifies the electronic density of the "free-active sites". In the case of ddm-electrode (figure 4b) oxidation of hydrogensulfite (main peak) shows a rapid decrease in intensity for the second cycle and then maintains its behavior. In this case, during the first cycle a shoulder appears that corresponds to oxidation of sulfite. This shoulder becomes in a real peak during the second cycle because the system does not oxidize hydrogensulfite after the first cycle. For the second and third cycle the potential of the peak shifts more negative of the potential of the main peak (not the shoulder) appearing during the first scan, indicating that only oxidation of sulfite is occurring. The second oxidation at potentials close to 1000 mV corresponds to oxidation mediated by glassy carbon.

A dramatic change also occurs for phy-electrode (figure 4c). In the first cycle only one peak is observed corresponding to oxidation of hydrogensulfite. In the second cycle oxidation of sulfite and hydrogensulfite are catalyzed. In the third cycle only oxidation of sulfite takes place (see the shift of the potential in the oxidation wave to more negative values). The oxidation wave that appears at potentials close to 1000 mV is due to the response of the bare glassy carbon. These features indicate a total reorganization of the complexes on the surface. Both systems (ddm-electrode and phy-electrode) are very unstable and the active sites in each case are different. Phy-electrode does not show the shoulder but probably a similar situation is taking place. The main difference between these systems is that phy-electrode maintains its ability to catalyze hydrogensulfite during the second cycle. During the third cycle both systems only catalyze the oxidation of sulfite. In order to determine if a reorganization of the complexes in the surface is taking place, we compared the voltammetric responses before and after the oxidation of the species (after the third cycle). In both cases the voltammogram after the oxidation process shows a response that resembles the unmodified electrode. Only the polym-electrode maintains its profile during the three cycles (figure 4d). It is, therefore, the most stable system. Polym-electrode shows a response where the profile practically does not change for peak I and a diminishing in the current is obtained for peak II. This behavior is not easy to explain because if the polymer is blocked, both peaks must be affected. The potential of peak II maintains its value indicating that the surface is catalytic to hydrogensulfite, but the quantity of active sites for this species diminishes.

The catalytic activity depends on the method of modifying the electrode with monomer. For supra-electrode this difference is reasonable due to the presence of the 4-aminopyridine that can act as a fifth ligand of the porphyrin changing the electronic density of the metal. A difference is also to be expected for polym-electrode. Both electrodes are good electrocatalysts for oxidation of sulfite and hydrogensulfite. The supra-electrode is better than polym-electrode in terms of catalysis, but is not as stable. Finally, electrolysis of ethanol–water solutions containing 1 mM Na_2SO_3 at pH 9.5 for 1 h electrocatalyzed by the supra-electrode and polym-electrode only generate sulfate as product. The ddm-electrode and phy-electrode lose activity at *ca* 5 min of electrolysis and the product is under the detection limit of the equipment.

4. Conclusions

Catalytic activity is drastically changed depending on the modification of an electrode surface with the same active molecule. The following order of activity is obtained:

supra-electrode > polym-electrode > phy-electrode > ddm-electrode

The chemical nature of the active sites also depends on the modification. Supra-electrode and polym-electrode catalyze the oxidation of sulfite and hydrogensulfite, and ddm-electrode and phy-electrode only catalyze the oxidation of sulfite. We attribute the similarities between supra-electrode and polym-electrode to enhancement of the conductivity, due to the electropolymerization, in the case of polym-electrode, or formation of a supramolecular assembly, in the case of the supra-electrode.

For supra-electrode we exposed the chemically-modified surface to a solution maintained at 54°C for 2 h. This mild treatment has the advantage of avoiding the polymerization of the solvent (DMF) that takes place simultaneously with the formation of the supramolecular assembly during the reflux.

In the case of the ddm-electrode and phy-electrode a reorganization of the adsorbed layers takes place in the presence of sulfite, probably after the first voltammetric cycle and the catalytic behavior drastically changes. The phy-electrode resembles supra-electrode during the second cycle, indicating that probably the inner layers of the first are ordered.

In terms of stability, the best electrode is polym-electrode. However, supra-electrode maintains its profile, but a shift to higher potentials of both peaks is observed. In the case of polym-electrode the catalytic activity does not vary for the peak corresponding to sulfite, but the activity diminishes (in terms of current) for hydrogensulfite. The ddm-electrode and phy-electrode are completely unstable.

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