ELECTROOXIDATION AND DETERMINATION OF SULFITE IN ETHANOL–WATER SOLUTIONS USING POLY-Cu(II)-TETRAKIS(x-AMINOPHENYL)PORPHYRIN/ GLASSY CARBON MODIFIED ELECTRODES

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Received August 13, 2008
Accepted December 17, 2008

A comparison is made of the behavior of three Cu(II)-porphyrins (with the amino substituents in different positions on the periphery of the ligand) electropolymerized on glassy carbon electrodes in HCl as solvent. The electropolymerized films show a certain degree of demetallation but the Cu amount of porphyrin in each case is sufficient to catalyze the oxidation of sulfite and hydrogensulfite in ethanol–water solutions. The ligands of the porphyrins are almost inactive in the electrocatalysis of the sulfite. The oxidation processes are favored at low scan rates. The foot of the oxidation waves depends on the positions. The most active porphyrin bears the substituents with the amino groups in para position, the oxidation occurring at low positive potentials. All the modified electrodes can be used as amperometric sensors for sulfite; they show linear relationships between the current and sulfite concentration in the range in which sulfites are present in red wines. The modified electrodes are stable and all of them promote the oxidation of sulfite to sulfate.

Keywords: Electrooxidation; Modified electrodes; Electrocatalysis; Amperometric sensors; Electrochemistry; Copper; Porphyrins.

Collect. Czech. Chem. Commun. 2009, Vol. 74, No. 4, pp. 545–557

doi:10.1135/cccc2008173

Over the last decades the oxidation and treatment of sulfur-containing species has drawn the attention of scientists in chemical and biological areas[1,2]. The term sulfite in general indicates any chemical species derived from the equilibria of SO_2 in water[3] depending on pH. It is commonly used as an antioxidant and antiseptic agent in food and pharmaceutical industries. However, the sulfite content in foods and beverages should be strictly limited due to its potential toxicity; products containing more than the established limit value must be adequately labeled. In particular, the use of sulfiting agents in the vinification process is essential[4–6] and their potentially adverse effects have been described[7,8]. The study of sulfur species has been carried out by various methods such as spectrofluorometry[9], chemiluminiscence[10], spectrophotometry[11–13], flow injection analysis[14], and acid-base titration[15]. On the other hand, electrochemical techniques have been explored for the detection of sulfite[16–18]. The present research is focused on the development of new materials capable of attachment to electrode surfaces in order to obtain an electrochemical sulfite sensor with better analytical properties. In this sense the studies of electrodes modified with different transition metal complexes by S. M. Chen are very interesting[19]. Porphyrins and other related macrocycles have been used as catalysts in many reactions of environmental and analytical significance[20–25]. These complexes show catalytic activity either in homogenous phase or immobilized onto electrode surfaces. One of the most widely used methods of obtaining electrodes modified with these macrocycles is electrochemical polymerization if the complex contains, in the ring, functional groups capable of forming new intermolecular bonds. The usual method is to carry out this polymerization in organic solvents such as dimethylformamide, dimethyl sulfoxide, and acetonitrile, because the solubility of the macrocycles in water is very poor. The preparation of electrodes modified with conducting polymers made from the macrocycles in more environmentally friendly solvents seems to be very attractive, but there are comparatively few reports in the literature on this subject[26–28].

On the other hand, Cu(II)-porphyrins are commonly studied as models of the active site of heme proteins[29,30] and in the activation of oxygen in several catalytic reactions. As electrocatalysts, Cu(II)-porphyrins were reported to show activity in several reactions such as the electroreduction of NO_2^- and NO_3^- (refs[31,32]) and glucose oxidation[33].

The purpose of this work is to evaluate the electrocatalytic activity of glassy carbon electrodes modified with a series of electropolymerized Cu(II)-tetrakis(x-aminophenyl)porphyrins in sulfite oxidation in aqueous-ethanolic solutions. The electropolymerization conditions presented in this paper are critical because they allow the production of modified electrodes, avoiding the use of environmentally harmful organic solvents.

EXPERIMENTAL

Reagents

Hydrochloric acid (Riedel–deHaën, p.a.), Cu-tetrakis(aminophenyl)porphyrin (Mid-Century), nitrogen (99.99% Indura), ethanol (Baker, p.a.), sodium chloride (Riedel–de Haën, p.a.), sodium sulfite (Merck, p.a), and sodium hydroxide (Merck, p.a.) were used without further purification. Water was deionized and double-distilled. All the used solutions were fresh.

Electrodes

Glassy carbon, GC (CHI 104) (exposed area 12.6 mm^2), was polished with 0.3-μm alumina, washed thoroughly with water, and then sonicated for 5 min. An Ag|AgCl (CHI 111) electrode was used as reference and Pt wire as counter electrode.

Modification of the Working Electrode Surface

The electrode surface was subjected to potential cycling in 0.1 M HCl solution containing 0.1 M NaCl and saturated with Cu-tetrakis(x-aminophenyl)porphyrin (Cu-x-TAPP) in nitrogen atmosphere. The potential was swept from –0.6 to 1.2 V at 0.1 V s^{-1} in 100 cycles. After polymerization the electrode was rinsed with double distilled water. Then the polymer film was overoxidized in order to inhibit the response of remaining amino groups by exposing it to a fixed potential of 1.6 V (vs Ag|AgCl) in 1 M NaOH solution in nitrogen atmosphere for 180 s. The remaining amino groups were oxidized to form nitro groups that have not redox pairs in the interval studied. After the overoxidation the electrode was washed with water.

Sulfite Solutions

The solutions were prepared from Na_2SO_3 in a deaerated 12% ethanol–water (v/v) solution containing 0.1 M NaCl. The pH 9 was adjusted by adding a NaOH solution.

Electrochemical Measurements

The voltammetric responses were obtained in deaerated solutions (by bubbling N_2 before the measurement and keeping the N_2 atmosphere during the experiment) using a conventional three compartment Pyrex glass cell. A 640C CHI electrochemical analyzer potentiostat was used for all electrochemical measurements and a HI8424 Hanna pH-meter was used for pH measurements. The working electrode was glassy carbon modified with the porphyrins, the counter electrode was a Pt wire and the reference electrode, Ag|AgCl.

Product detections were carried out by using a HPLC Chromatograph Waters 1515 isocratic HPLC pump coupled with a Waters 432 conductivity detector and 428 refractive index detector.

RESULTS AND DISCUSSION

Figure 1 shows the structure of one of the porphyrins used in this study, Cu(II)-5,10,15,20-tetrakis(2-aminophenyl)porphyrin, Cu-2-TAPP. In this work we also used Cu(II)-5,10,15,20-tetrakis(3-aminophenyl)porphyrin, Cu-3-TAPP and Cu(II)-5,10,15,20-tetrakis(4-aminophenyl)porphyrin, Cu-4-TAPP. This complex has a core with D_4h symmetry[34] and the π-cloud of the aromatic ring interacts with the glassy carbon surface allowing the formation of a conducting film if is adsorbed.

When it polymerizes by anodic oxidation, an amino radical cation is formed, which can attack a carbon of another phenyl substituent. When this takes place, torsion of the phenyl substituents, which are initially practically perpendicular to the core, occurs and the entire polymer conducts electricity, showing delocalization of the π-cloud[35,36]. Of course, the degree of torsion depends on the position of the amino substituent, and the electron density of the central metal atoms of the polymer depends on the torsion[35,36]. Figure 2 shows *I*/*E* curves of porphyrins dissolved in HCl. Figure 2a depicts the first scan of Cu-2-TAPP. At ca. –0.2 V, a high oxidation wave appears that is not observed during the second and subsequent scans. The same behavior is observed with the other porphyrins (not shown).

We assume that this sharp peak corresponds to the redissolving[37] of Cu^0, indicating that a certain degree of demetallation takes place at –0.5 V (i.e,

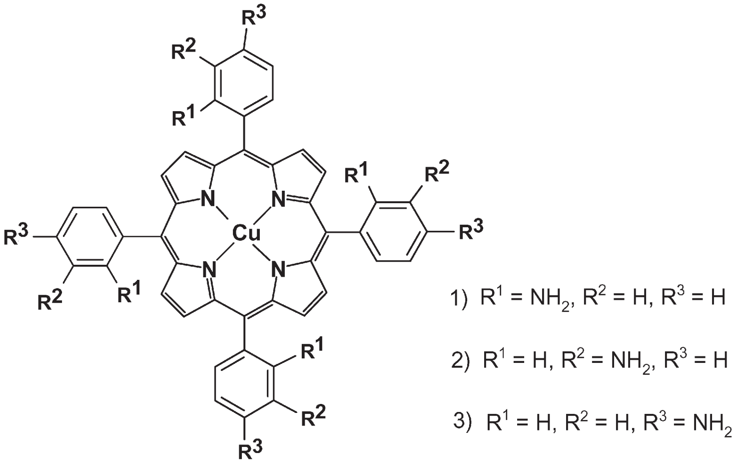

FIG. 1
Structure of Cu(II)-5,10,15,20-tetrakis(x-aminophenyl)porphyrin, Cu-x-TAPP. 1. Cu-2-TAPP, 2. Cu-3-TAPP, 3. Cu-4-TAPP

Cu(II) ions are reduced at this potential). On the other hand, the oxidation wave at ca. 0.4 V corresponding to the ligand process is observed and the irreversible process at the positive limits of potential corresponds to the oxidation of amino groups. It is not yet understood why during the first scan the oxidation wave appearing at 0.4 V is irreversible whereas in the second and subsequent scans it becomes quasi-reversible. On the other hand, for the free porphyrin ligands, only two redox processes take place. One, centered at ca. 0.4 V, quasi-reversible and the other, the irreversible oxidation of the amino groups (not shown). The second and subsequent cycles for that porphyrin are shown in Fig. 2b. The behavior is similar for the other complexes (not shown) but the potentials of the peaks are not the same (Table I). In all the cases, there are two quasi-reversible oxidation waves which, to our knowledge, have not been reported[32,38].

TABLE I
Peak potentials (in mV vs Ag|AgCl) for the Cu-x-TAPP porphyrins dissolved in HCl

Cu-2-TAPP	Cu-3-TAPP	Cu-4-TAPP	Peak (see Fig. 2)
321 ± 5	348 ± 5	311 ± 5	I
236 ± 5	310 ± 5	240 ± 5	I′
526 ± 5	527 ± 5	540 ± 5	II
426 ± 5	314 ± 5	426 ± 5	II′
	–64 ± 5		shoulder (not assigned)

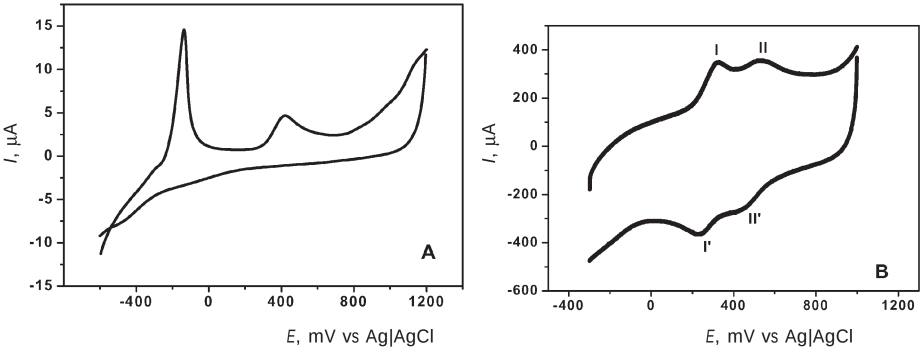

FIG. 2
A Voltammetric response of Cu-2-TAPP (first scan), B Cu-2-TAPP (stable scan); 0.1 M HCl. Working electrode: bare glassy carbon. Scan rate: 100 mV s^{-1}

We attribute these signals in all the cases to a unique redox process of the ligand L^{2-}/L^{1-}, but taking place in two kinds of porphyrins; a fraction containing the central metal and the fraction demetallated in the course of the first scan. According to our measurements, demetallation process takes place in the solvent immediately after the application of a negative potential and, during the scan to positive potentials, the Cu^0 formed on the surface of the electrode becomes Cu^{2+} and diffuses into the bulk. In spite of the demetallation, a high amount of metal porphyrin remains. The only possibility of avoiding the demetallation is the absence of water solvent. But considering the growing interest in green chemistry[39], it is preferable to use HCl as solvent instead of, i.e., dimethyl sulfoxide or dimethylformamide. Moreover, in all the cases the voltammetric response does not change (potential and current remain constant) during more than 100 cycles, indicating the stability of the complex. In fact, after the first scan, the response of all the porphyrins remains stable. Figure 3 shows the electropolymerization of Cu-2-TAPP on the glassy carbon surface.

The voltammetric response corresponds to 100 potentiodynamic cycles, but the curve is recorded only every ten cycles. Initially, a high oxidation wave of the amino groups at positive potentials is observed. In all cases the behavior is practically the same. In the beginning, a high oxidation wave appears at the positive limit, but the wave decreases during the first ten

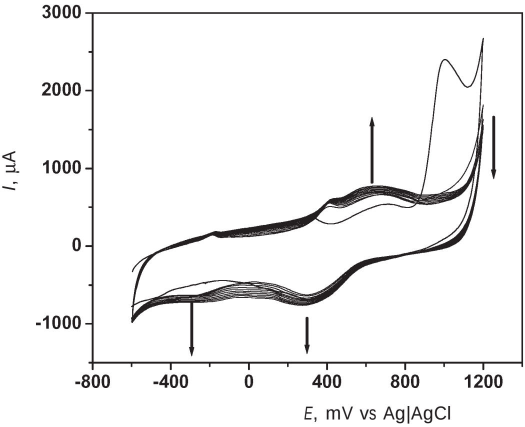

FIG. 3
Cyclic voltammetry corresponding to the electropolymerization of Cu-2-TAPP in 0.1 M HCl on glassy carbon. The profile corresponds to 100 cycles (every ten cycles). The arrows indicate the current increase or decrease. Scan rate: 100 mV s^{-1}

cycles. The growing signals (marked with arrow) at ca. 0.6 V (anodic) and ca. –0.3 and +0.3 V (cathodic) are redox processes of the ligand because they also appear for the free ligand[32]. In spite of the decrease in the amine oxidation current in first cycles, the polymer film is formed in all the potentiodynamic cycles becoming a stable film on the electrode surface. The same behavior is found for Cu-3-TAPP and Cu-4-TAPP (not shown). It is worth noting that each polymer is composed of units of metallated Cu-TAPP and non-metallated macrocycles H_2-TAPP. However, this is not a drawback because the whole polymer is a conductor and only the metal-containing units are catalytic as mentioned below. After electropolymerization, the electrode is immersed in 0.1 M NaOH (without porphyrin) at a fixed potential (1.6 V vs Ag|AgCl) for 3 min. This process is necessary to oxidize all the remaining amino groups that can mask the response of the sulfite oxidation[16]. When the polymer is obtained and electrooxidized, no peaks can be observed in the potential region studied (Fig. 4).

A comparison of bare glassy carbon and the modified polymeric electrode shows that, after the electropolymerization and overoxidation processes, the current increases indicating the formation of a thick film[24,40]. In all the cases a similar current enhancement is obtained. The modified electrode is stable when exposed to air; it can be used for a week (in ethanol–water so-

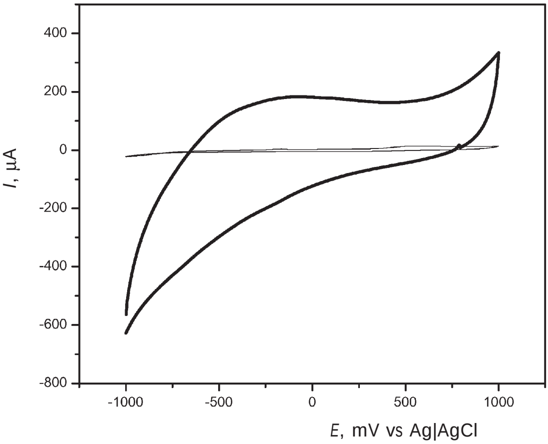

FIG. 4
Cyclic voltammogram of electropolymerized and overoxidized Cu-2-TAPP on glassy carbon (thick line), bare glassy carbon (fine line). Electrolyte: 0.1 M NaCl, 12% ethanol–water (v/v) solution. Scan rate: 100 mV s^{-1}

lutions) without losing activity. It is not poisoned by the oxidation products and/or by sulfite or hydrogensulfite, and it is also easily reproducible. The electrocatalytic studies were carried out for three polymeric systems and also for three electropolymerized ligand-modified electrodes in the whole pH range. The unique active systems are the poly-Cu-TAPP modified electrodes. However, they catalyze the oxidation of sulfite only in alkaline solutions. The best performance (in terms of the potential shifts) is obtained between pH 8.5 and 9.5. Figure 5 shows the electrocatalytic effect of the glassy carbon electrode modified with different Cu-porphyrins toward the oxidation of sulfite or hydrogensulfite at pH 9.

On the other hand, the pK_{a2} of the reaction $HSO_3^- \leftrightarrow SO_3^{2-} + H^+$ is 8.8 (by potentiometric titration in ethanol–water solution), and at pH 9 a mixture of the two species, sulfite and hydrogensulfite, at practically the same concentrations is obtained. It is noticeable that foots of the oxidation waves are very different depending on the porphyrin. In fact, for Cu-4-TAPP, the oxidation wave starts at ca. 0.15 V whereas for Cu-2-TAPP and Cu-3-TAPP at ca. 0.4 V. On the other hand, all the porphyrins show two redox processes: they are catalyzing the oxidation of sulfite (the wave appearing at more negative potentials) and hydrogensulfite (the wave appearing at more positive potentials). A change with pH of the solution was confirmed at pH higher than 9, the intensity of the formers increases whereas that of the lasts, decreases (not shown).

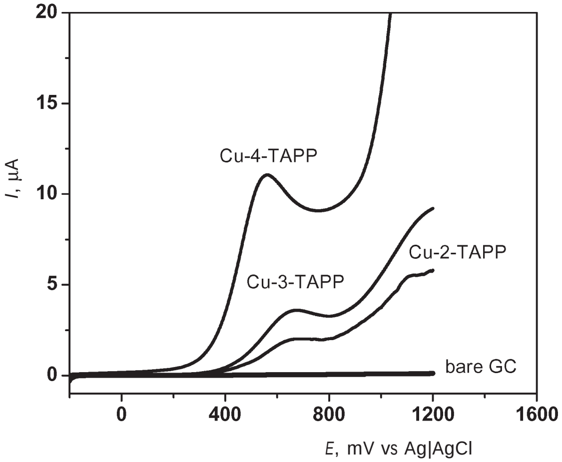

FIG. 5
Comparison of the modified electrodes in the oxidation of sulfite in ethanol–water solution at pH 9. Scan rate: 10 mV s^{-1}

The cyclic voltammetry of sulfite with the modified electrodes at different scan rates shows a linear dependence of the current peak (corresponding to the oxidation of sulfite) on the square root of the scan rate for low scan rates indicating that the electrocatalytic oxidation of sulfite is diffusion-controlled. For scan rates higher than 0.12 V s^{-1}, the current peak loses its linearity increasing the scan rate. However, the slight deviations from linearity are probably due to the involvement of kinetic effects. All the films are electroactive in the oxidation of SO_3^{2-} where the current of the anodic peaks, I_{pa}, increases with the sulfite concentration. In the case of poly-Cu-4-TAPP, the catalytic current evolves from the ligand redox pair (porphyrin ring). The mechanism proposed for the electrocatalytic oxidation of sulfite mediated by poly-Cu-4-TAPP is represented in the following equations [41]:

$$2\ \mathrm{M(II)Pc} \rightarrow 2[\mathrm{M(II)Pc}]^+ + 2e \qquad (1)$$

$$2\ [\mathrm{M(II)Pc}]^+ + SO_3^{2-} + H_2O \rightarrow 2\ \mathrm{M(II)Pc} + SO_4^{2-} + 2\ H^+. \qquad (2)$$

The mechanism avails due to the correspondence between the redox pairs of the ligand and the current of the electrooxidation of sulfite and the formation of sulfate as unique product[41]. For the other systems the current for the oxidation appears at potentials more positive than that of the foot of the wave corresponding to the ligand process.

In all the cases no poisoning occurs of any electrode and all of them maintain their response during 100 tested cycles without changes. For the three cases, after electrolysis (1 h) of a solution containing sulfite, sulfate is produced (detected by ionic chromatography); dithionate was not detected. It is interesting to point out that this behavior is observed only at low scan rates. The oxidation processes are slow and at higher scan rates (0.15 V s^{-1}), only one redox process occurs of the three modified electrodes without defined peaks (Fig. 6).

Finally, we note that the three modified electrodes can be used as amperometric sensors of sulfite in the concentration range studied, which corresponds to its concentration in red wines (ppm of SO_2; Fig. 7). The data shown in Fig. 7 were taken from polarization curves of the poly-Cu-2-TAPP-modified electrode at different sulfite concentrations in ethanol–water solutions at pH 9 at a fixed potential. In the case of poly-Cu-3-TAPP and poly-Cu-4-TAPP, linear relationships are also obtained with slopes of 21 and 19, and $R = 0.98$ and 0.99, respectively.

Finally, we proved the behavior of the modified electrodes as amperometric sensors. The same solutions were measured by electrochemical methods (polarization curves of the modified electrodes) and by titration according to the modified method of Burrough–Spark[42] (B–S), the most ac-

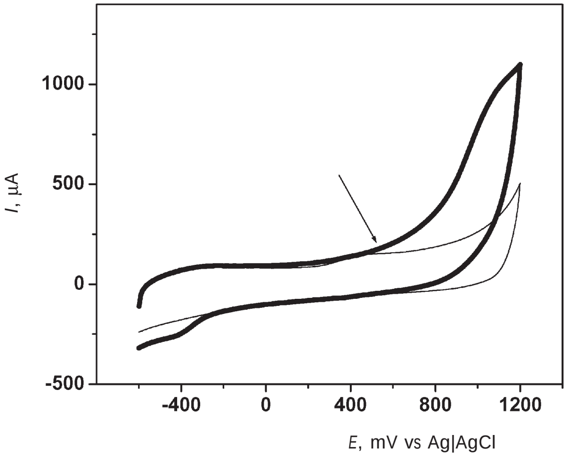

FIG. 6
Cyclic voltammogram of poly-Cu-3-TAPP/GC modified electrode corresponding to the oxidation of sulfite (150 ppm SO_2) in an ethanol–water solution at pH 9. The arrow indicates the foot of the oxidation wave. Scan rate: 100 mV s^{-1}

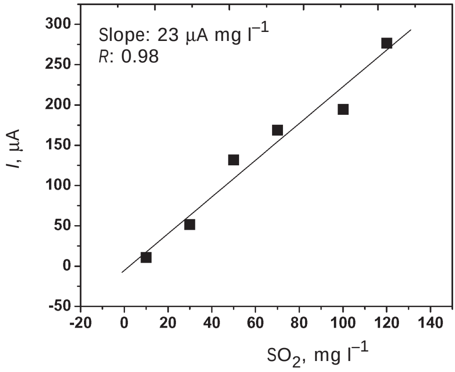

FIG. 7
Linear relationship between current and concentration of sulfite for Cu-4-TAPP-modified electrode. Data taken from polarization curves at different concentrations of sulfite and fixed potential 0.45 V vs Ag|AgCl

curate method used in wineries. The B–S method consisted in the acidification of the sulfite anion to form SO_2(g) and subsequent oxidation of SO_2 to sulfuric acid, which is determined by titration. First, we obtained a calibration curve for the current/concentration data using the B–S method. Then, we examined different test solutions containing sulfite by the electrochemical method and by the B–S method. Comparing both methods we obtain two straight lines with very good regression parameters (R = 0.9999 for the B–S method and R = 0.9992 for the electrochemical one) demonstrating that the proposed electrochemical method shows a good correlation with the B–S method (Fig. 8). This is an indirect way of validating the electrochemical method in the concentration range studied.

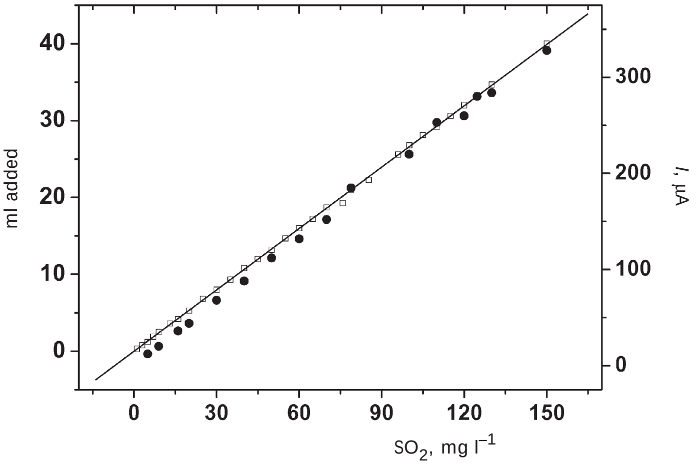

FIG. 8
Comparison of the electrochemical (●) and Burrough–Spark (☐) method. Calibration curve done using the B–S method

From the regression line (R^2 = 0.99818), the intercept is 1.22554 and the standard deviation of the intercept is 2.03019. The slope is 2.20399 and the standard deviation of the slope is 0.02427. The limit of detection is 0.033 mg l^{-1}.

CONCLUSIONS

Cu(II)-tetrakis(x-aminophenyl)porphyrins, when electropolymerized in HCl as solvent and further overoxidized on a glassy carbon surface, are capable of electrocatalyzing the oxidation of sulfite and hydrogensulfite present in a 12% ethanol–water (v/v) solution. The poly-Cu-tetrakis(x-aminophenyl)-porphyrins are catalytic only in alkaline solutions and the best performance is observed at pH close to 9. All of them catalyze sulfite and hydrogensulfite at low scan rates. The best catalytic system in terms of potentials and currents is poly-Cu-tetrakis(4-aminophenyl)porphyrin. Although the oxidation wave foot position depends on the position of the amino groups, all the modified electrodes can be used as amperometric sensors of sulfite and hydrogensulfite in the concentration range found in red wines. The sensors reproduce the linearity observed in the Burrough–Spark method normally used in wineries.

This research was supported by the World Bank/Conicyt PBCT 24 project, Fondecyt project 11075048, A/012666/07 project and financial support from PCI-Spain.

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