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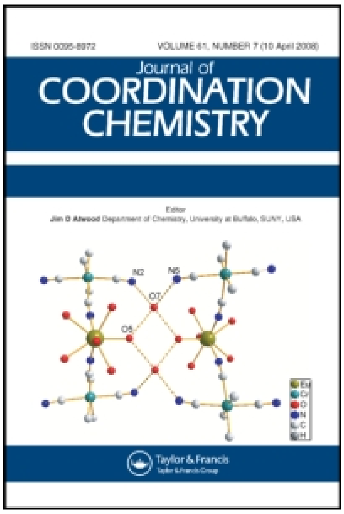

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Electrochemical reduction of SO_2 on poly-Co-3-tetraaminophenylporphyrin glassy carbon modified electrode

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Electrochemical reduction of SO_2 on poly-Co-3-tetraaminophenylporphyrin glassy carbon modified electrode¶

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This article describes the electrochemical reduction of sulfite in water–ethanol mixtures under acidic conditions on a glassy carbon electrode modified with a conducting film formed by Co(II) tetra-3-aminophenyl porphyrin. Rotating disc electrode experiments show a kinetic limitation related with the formation of an adduct between the reduced porphyrin and the sulfur compound. UV–Visible spectroelectrochemical data suggest that Co(I) is not stabilized; thus the adduct should involve a radical species of the porphyrin. However, the resulting modified electrode is stable and shows a linear relationship between current and concentration of the sulfur species at pH 1. The detection range of sulfite by the modified electrode goes from 12 to 150 $mg\,L^{-1}$. The detection limit is 4.15 $mg\,L^{-1}$.

Keywords: Reduction of sulfur compounds; Co(II) porphyrin; Modified electrodes; Electrochemical sensor; Electrocatalysts

1. Introduction

Sulfite is commonly used as a preservative and an antiseptic agent in a large variety of foods and beverages [1], but at high levels it may produce adverse reactions in asthma patients [2]. Sulfite concentration in wines must be carefully controlled, because excess can change the color, taste, and smell [3, 4].

Several analytical techniques in use for determination of sulfite are based on redox or acid–base volumetric titrations involving a series of steps. The analyses are time consuming, and the results present precision and accuracy problems [5, 6]. For this reason it is essential to develop a method to quantify this analyte in an efficient way [5, 6].

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¶This article is dedicated to Professor A. Mederos.

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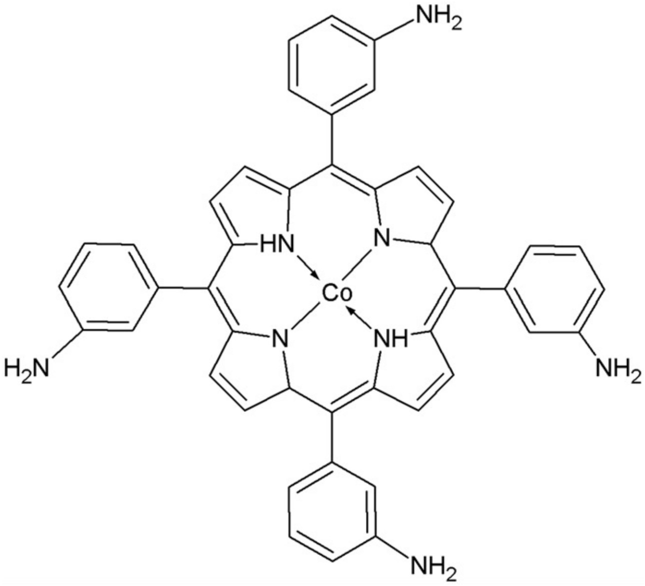

Figure 1. Molecular structure of Co(II)tetra-3-amino-phenyl-porphyrin [Co(II)TAPP].

Use of electroanalytic sensors is a feasible alternative for the development of new quantifying techniques. In electroanalysis, modified electrodes can be used as sensors [7, 8]. The methods of preparation include adsorbed monolayers, layer-by-layer adsorption, and electropolymerization, among others [9–11]. Electrodes modified with electroactive polymers are well documented in the literature, with porphyrins showing remarkable properties [12].

Porphyrins form stable complexes with a large variety of metals. Depending on the central metal [Mn(II), Co(II), Fe(II) or Ni(II)], they can have high catalytic efficiency due to the rich redox chemistry provided by the system [12].

Recent studies [13, 14] have shown that Co(II) tetra-3-aminophenyl porphyrin [Co(II)TAPP] (figure 1) polymerizes on glassy carbon electrodes forming a conductive film. This polymeric film has been studied as a catalyst for oxidation and reduction of NO_2^- and CO_2, among others. In spite of the high electrocatalytic activity of Co porphyrins, electroreductions of sulfite and other related S(IV) oxoanions mediated by this modified electrode are not known.

Red wines contain hundreds of organic compounds such as anthocyanines, polysaccharides, tannins, catechins, flavonoids, and phenolic acids, some with important antioxidant activity; indeed, they present low oxidation potentials and mask the oxidation wave of sulfite when it is measured by direct electrochemical methods [15]. For this reason it is desirable to find an electrocatalyst capable of reducing sulfite because the reduction takes place at negative potential, where the antioxidant compounds do not interfere.

In the present work, the electrochemical reduction of sulfite on a glassy carbon electrode modified with a conductive polymer of Co(II)TAPP in a water–ethanol mixture resembling a wine sample was studied at pH 1.0. The study was carried out by electrochemical techniques such as Cyclic Voltammetry (CV) and Rotating Disc

Electrode (RDE), along with UV–Vis spectroelectrochemistry in order to recognize the aspects that govern this reaction. This input will be further incorporated in the design of a sensor for this reagent.

2. Experimental

2.1. *Materials and reagents*

All reagents were of analytical grade: Co(II) tetra-3-aminophenyl porphyrin (Midcentury Co., Posen, IL), sodium perchlorate monohydrate (Fluka), sodium sulfite (Riedel-deHaën), tartaric acid (Riedel-deHaën), sodium hydroxide and perchloric acid (Sigma-Aldrich), absolute ethanol (Riedel-deHaën), *N*,*N*-dimethylformamide (DMF) (J.T. Baker), tetrabutylammonium perchlorate (TBAP) (Alfa-Aesar). The last two reagents were dried before use following the procedures reported in the literature [16]. Electrochemical experiments were carried out in a three-compartment Pyrex glass cell; the working electrodes, glassy carbon discs, were purchased from CH Instruments ($r = 1.5\,\text{mm}$) and Radiometer Analytical ($r = 3\,\text{mm}$); the reference electrode, saturated Ag/AgCl from CH Instruments; and the counter electrode, a Platinum coil ($14\,\text{cm}^2$) from Aldrich. UV–Vis spectroelectrochemical experiments were performed in a one-compartment quartz cuvette containing similar, but smaller, auxiliary and reference electrodes. In this case, ITO from Delta Technologies was used as the working electrode.

2.2. *Procedures*

2.2.1. Modified working electrode. Polymer films were grown by repetitive scanning of the potential of glassy carbon electrodes and ITO electrode in a 1 mM solutions of Co(II) tetra-3-aminophenyl porphyrin, 0.1 M (TBAP) in DMF between −1.1 V and +1.1 V *versus* Ag/AgCl during 50 cycles at $0.1\,\text{V}\,\text{s}^{-1}$. After polymerization, the modified electrodes were rinsed with ethanol and then with bidistilled water.

2.2.2. Measurements. Cyclic voltammetry was carried out in a CH Instruments model 620B potentiostat, using a 12% v/v ethanol–water solution, $5 \times 10^{-2}\,\text{M}$ tartaric acid, 0.1 M $NaClO_4$, containing variable sulfite concentration ranging from 12.6 to $150\,\text{mg}\,\text{L}^{-1}$ at pH 1. Tartaric acid was added to the solution to model a wine matrix because tartaric acid is the main acid component of red wines [1]. The pH was adjusted by adding drops of 1 M NaOH or $HClO_4$. The measurements were carried out between −0.8 and 0.2 V at $0.1\,\text{V}\,\text{s}^{-1}$. RDE experiments were carried out between −0.8 and −0.35 V at $0.005\,\text{V}\,\text{s}^{-1}$ in the same solution described above, with a fixed $12.6\,\text{mg}\,\text{L}^{-1}$ sulfite concentration. The UV–Vis spectroelectrochemical measurements were made on a Shimadzu Multispec 1501 spectrophotometer along with a CH Instruments 720B bi-potentiostat, between −0.1 and −0.7 V at $0.01\,\text{V}\,\text{s}^{-1}$. All experiments were performed under N_2 in an open system. In spite of the volatile behavior of S(IV) species in acid media, the results were reproducible because all the measurements were made under a positive nitrogen pressure.

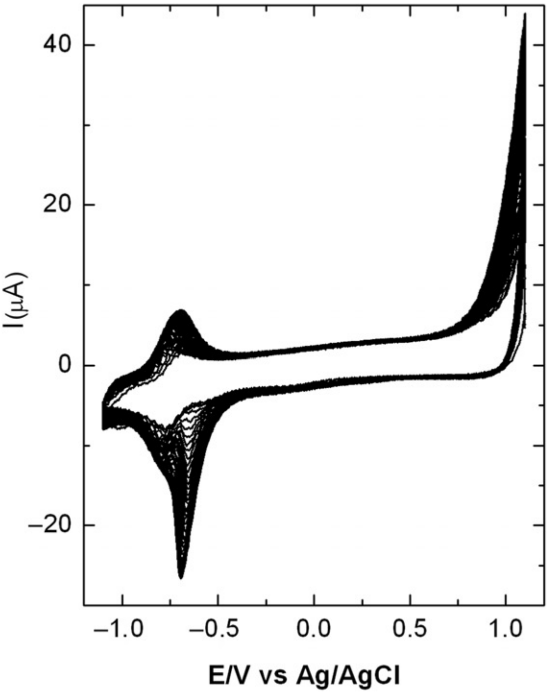

Figure 2. CV corresponding to the electropolymerization of Co(II)TAPP on a glassy carbon electrode (50 potentiodynamic cycles) in a N_2/DMF/0.1M TBAP solution with 1×10^{-3} M of the complex. Scan rate: $100\,mV\,s^{-1}$.

3. Results and discussion

Figure 1 displays the structure of Co(II) tetra-3-aminophenyl-porphyrin, Co(II)TAPP. When the molecule forms a polymeric film, the phenyl groups, which are normally almost perpendicular to the plane of the core, undergo torsion that leads to delocalization of the π cloud along the entire chain, generating conducting polymer [17]. Figure 2 shows the cyclic voltammogram for electropolymerization of Co(II)TAPP on glassy carbon using DMF as solvent. The anodic irreversible peak that appears at ca. 1.09 V *versus* Ag/AgCl corresponds to oxidation of the amino groups, generating radical cations that promote the polymerization [12]. There is one quasi-reversible couple at $Ep_{1/2} = -0.74$ V attributed to the Co(II)/Co(I) process. The cathodic part of this sharp process centered at −0.75 V is composed of the cathodic part of the metal couple and the reduction of some oligomers containing oxidized amino groups [17–19]. This assignment is made because, if the positive potential limit is scanned to only 0.5 V, polymerization does not take place, the sharp feature of the cathodic peak is not seen, and the charge under of cathodic and anodic signals becomes equivalent. Figure 3 shows the voltammetric response of the polymer (poly-Co(II)-TAPP/GC) after 50 continuous potential cycles, compared to the bare glassy carbon in a 0.1 M $NaClO_4$ aqueous solution. The capacitive current is not very different compared to the blank, indicating formation of a thin, compact polymer [20]. On the other hand, the Co(II)/Co(I) redox couple presents quasi-reversible behavior as observed from the Ep_c and Ep_a values of −0.96 and −0.71 V, respectively.

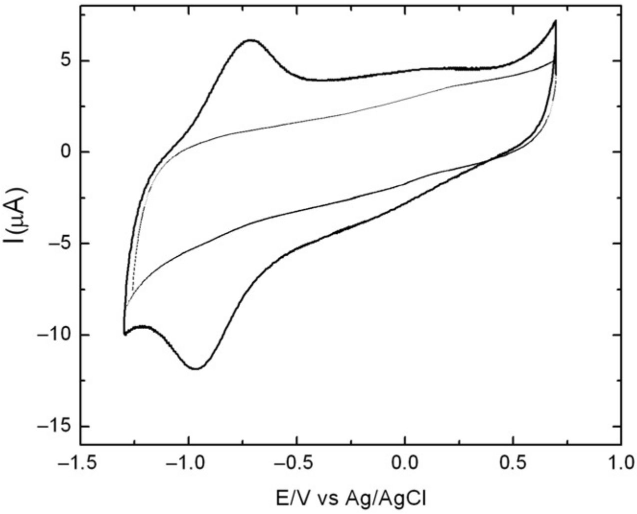

Figure 3. Cyclic voltammograms of glassy carbon electrode and poly-Co(II)TAPP glassy carbon modified in a 0.1 M $NaClO_4$ solution. Scan rate: 100 $mV\,s^{-1}$.

Figure 4 depicts the voltammetric response of the modified electrode toward electroreduction of the S(IV) compound at pH 1. At basic pH values (ethanol–water solution), the modified electrode does not have reproducible electrocatalytic behavior. At pH higher than 1, the Ip_c signal was lower than the bare glassy carbon electrode and not reproducible. Then, the modified electrode is electroactive only at pH 1. Figure 4 shows a cathodic wave centered at −0.42 V that corresponds to the reduction of the S(IV) species. At pH 1 the main sulfur species is sulfur dioxide [21, 22]. On the other hand, the Co(II)/Co(I) redox couple does not appear at acid pH. However, the current difference (ca. six times higher) for the modified electrode compared to the bare glassy carbon, as well as the shift of the potential (ca. 200 mV) to positive values for the modified electrode, confirm the catalytic behavior of the modified electrode. The inset in figure 4 shows the linear relationship between current and concentration for reduction of SO_2.

The open circuit potentials in the presence of S(IV) species are −0.13 V and 0.39 V for the bare glassy carbon and poly-Co(II)TAPP/GC, respectively. This drastic change could indicate a preferential interaction for the modified electrode. Several reports have shown a strong adsorption of SO_2 on metal cathodes such as bismuth and gold [23, 24], agreeing with the result presented here.

In terms of applicability, the modified electrode shows good behavior with no volatilization problems in the time scale of the experiments. Also, the electrode is very stable when exposed to air. It shows reproducible behavior for at least 1 week, appropriate for a voltammetric sensor for sulfite in wines.

The *I–E* polarization curves measured for electroreduction of sulfur dioxide mediated by poly-Co(II)TAPP/GC modified electrode by the RDE technique are shown in figure 5. In all cases a plateau is reached at potentials close to −0.5 V, indicating no poisoning of the electrode. From the *I–E* polarization curves it is possible to produce Levich plots that correlate I_L *versus* $\omega^{1/2}$, where I_L, the limiting

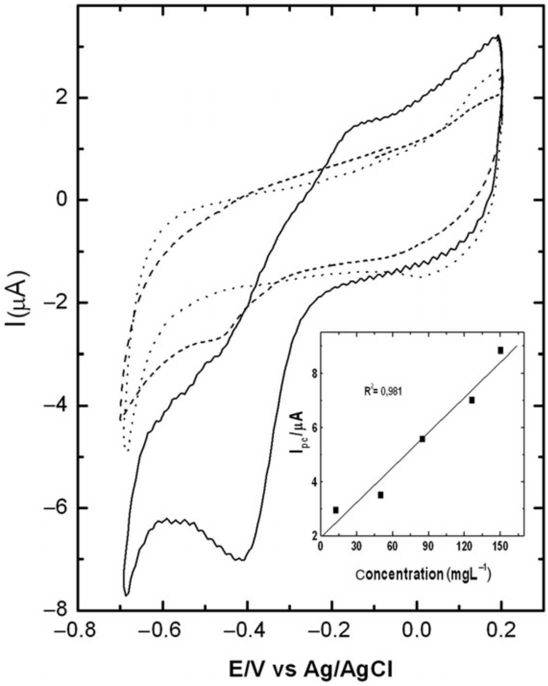

Figure 4. Cyclic voltammograms of glassy carbon electrode in a 0.1 M $NaClO_4$ 0.05 M Tartaric acid, ethanol:H_2O 12% v/v solution (dashed line) containing 126 mg/l Na_2SO_3. Poly-Co(II)TAPP glassy carbon modified electrode in a 0.1 M $NaClO_4$ Poly-Co(II)TAPP glassy carbon modified electrode in a 0.1 M $NaClO_4$ 0.05 M Tartaric acid, ethanol:H_2O 12% v/v solution (dotted line). All the solutions at pH = 1. The inset corresponds to the Ipc poly-Co(II)-TAPP/glassy carbon modified electrode vs Na_2SO_3 concentration relationship. Scan rate: 100 mVs^{-1}.

current, represents the current of the plateau and ω is the electrode rotation rate (equation 1),

$$I_L = 0.62nFD^{2/3}\nu^{1/6}c^{\infty}\omega^{1/2} \tag{1}$$

where F is Faraday's constant, D is the diffusion coefficient, ν is the kinematic viscosity of the solution and C is the bulk concentration [25–27].

A straight line plot of I_L *versus* $\omega^{1/2}$ that does not intercept the origin suggests that kinetic limitation is involved in the electron-transfer reaction [25, 26]. If generation of products requires more energy than that necessary to reduce the active site, a kinetic limitation will be seen. In other words, the Levich equation will describe the rotation rate dependence of the cathodic limiting current, except when a chemical reaction limits the current density [25, 26]. Figure 6 depicts the Levich plot of the system at pH 1.

The straight line does not intercept the origin, indicating a kinetic limitation for the electrochemical reduction, evidence of formation of a stable intermediate formed by the active site of poly-Co(II)TAPP and S(IV) species.

Also, from I–E polarization curve data it is possible to plot the Koutecky–Levich relationship (equation 2),

$$\frac{1}{I} = \frac{1}{I_k} + \frac{1}{I_L} \tag{2}$$

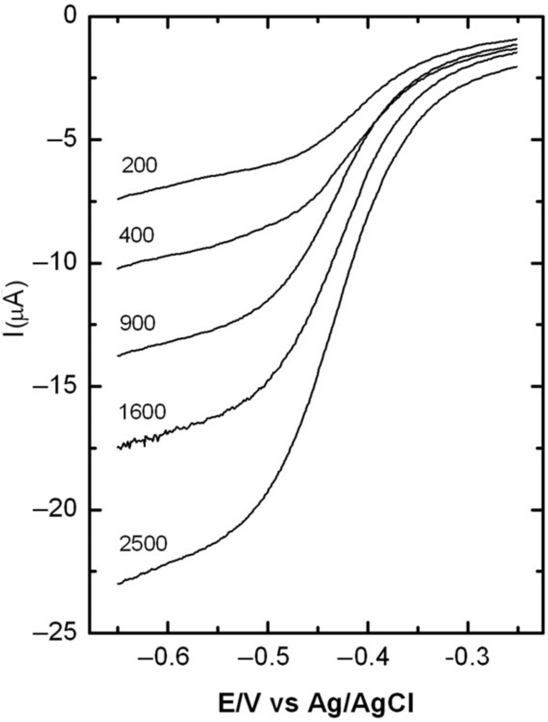

Figure 5. Linear voltammograms of a 0.1 M $NaClO_4$ 0.05 M Tartaric acid, ethanol:H_2O 12% v/v solution containing 126 mg L^{-1} Na_2SO_3, at pH = 1, on a poly-Co(II)-TAPP/glassy carbon rotating disc modified electrode (200–2500 rpm) with a scan rate of 5 mV s^{-1}.

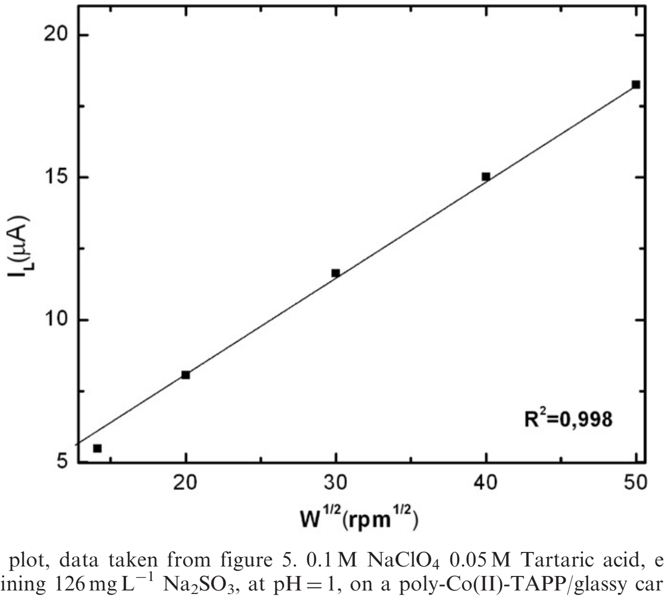

Figure 6. Levich plot, data taken from figure 5. 0.1 M $NaClO_4$ 0.05 M Tartaric acid, ethanol:H_2O 12% v/v solution containing 126 mg L^{-1} Na_2SO_3, at pH = 1, on a poly-Co(II)-TAPP/glassy carbon rotating disc modified electrode.

where $I_k = nFk_fC_0^\infty$ and $I_L = nFC_0^\infty D^{2/3}\omega^{1/2}$ for a completely irreversible reaction, I_k represents the current in the absence of any mass transfer effects, i.e. the current that would flow under the kinetic limitation if the mass transfer is efficient enough to keep the concentration on the surface constant at any applied potential. The I_L value is dependent on the electrode rotation rate. A plot of I^{-1} *versus* $\omega^{-1/2}$ should be linear and can be extrapolated to $\omega^{-1/2} = 0$ to yield I_k. Determination of I_k allows the determination of k_f, the heterogeneous rate constant of the reaction [25, 26].

For the electrochemical reaction of SO_2 at pH 1, linear Koutecky–Levich plots were obtained and the calculated k_f value is $1.45 \times 10^{-6}\,\mathrm{cm\,s^{-1}}$. This magnitude is an indication of a slow electrochemical process [25, 26].

From the polarization curves it is possible to determine the amount of energy (potential) required to increase the current by one order of magnitude [28]. This value, known as Tafel's slope, is obtained from the corrected current (equation 3).

$$I_{\mathrm{corr}} = I_L \times \frac{1}{I_L - i} \tag{3}$$

From data of the polarization curve, at pH 1, the Tafel plot is 122 mV per decade. This value is very close to 120 mV per decade, corresponding to a first electron-transfer reaction depending on the potential as the rate-determining step [28]. The results establish a possible mechanism where S represents the SO_2 species:

$$\text{poly-Co(II)TAPP} + \text{S} \rightarrow (\text{poly-Co(II)TAPP} \cdots \text{S})$$
$$(\text{poly-Co(II)TAPP} \cdots \text{S}) + \text{e} \xrightarrow{\text{rds}} (\text{poly-Co(II)TAPP} \cdots \text{S})^{1-}$$
$$(\text{poly-Co(II)TAPP} \cdots \text{S})^{1-} \rightarrow \text{products}$$

For determination of the reaction products, a 5-h electrolysis at a fixed potential of −0.65 V was carried out. The resulting solution was measured by colorimetric qualitative analysis [29], with thiosulfate as product. The solution was tested for other different possible products (sulfur and dithionite), but they were not detected. Thiosulfate was then the single product obtained from the electrolysis.

In this mechanism, an intermediate or adduct should be formed between the poly-Co(II)TAPP/GC and the S(IV) species at open circuit potential; reduction of the intermediate is rate determining. This assumption is in agreement with the change in the open circuit potential mentioned above. Normally when a kinetic limitation is seen, Tafel plots are higher than 120 mV per decade [30]. However, if the adduct is formed at open circuit potentials, a Tafel plot of 120 mV per decade indicates that the slow step of the reaction is the reduction of the previously formed adduct [31, 32]. In our case, this result is in agreement with the kinetic limitations observed from the Koutecky–Levich plots.

In order to confirm the formation of the adduct, spectroelectrochemical studies were made. Figure 7 shows the UV–Vis spectra of the poly-Co(II)TAPP/ITO modified electrode at different potentials without [figure 7(a)] and with [figure 7(b)] SO_2 in the solution at pH 1. The typical UV–Vis spectra of porphyrins consist of an intense broad absorption band at *ca.* 430 nm (Soret Band) and 1–4 less intense Q bands depending on whether the porphyrin is metalled or not [33]. Figure 7(a) shows that when a negative potential is applied the entire spectrum decays without shift of any band. This behavior indicates that when reduced the LUMO is populated, decreasing the intensity of

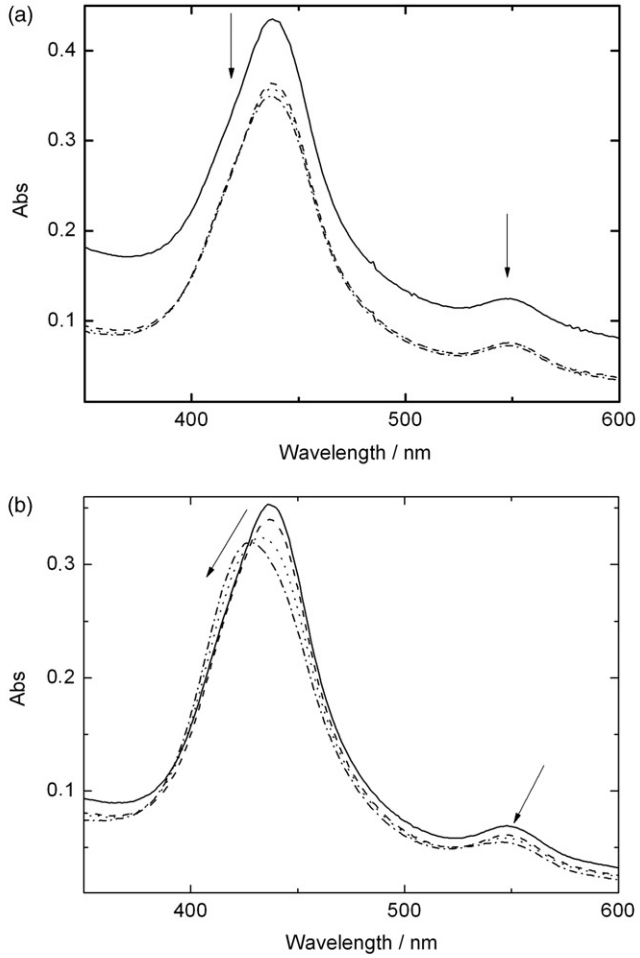

Figure 7. (a) Spectroelectrochemical reduction of poly-Co(II)TAPP/ITO modified electrode in a 0.1 M $NaClO_4$ 0.05 M Tartaric acid, ethanol:H_2O 12% v/v solution. At pH = 1, open circuit potential (solid line), −0.7 V (dashed-dotted line). (b) Spectroelectrochemical reduction of poly-Co(II)TAPP/ITO modified electrode in 0.1 M $NaClO_4$ 0.05 M Tartaric acid, ethanol: H_2O 12% v/v solution containing 126 mg L^{-1} Na_2SO_3. At pH = 1, open circuit potential (solid line), −0.7 V (dashed-dotted line).

the bands. On the other hand, if SO_2 is present in the solution, the same behavior is observed, but a blue shift of the Soret band occurs maximum when negative potentials are applied. From these results it is clear that the completely reduced system is different when SO_2 is present in the solution, confirming formation of an adduct between the active site of poly-Co(II)TAPP and S(IV) species. The nature of the interaction is not evident from these spectra [figure 7(b)]. It is known that Co porphyrins do not stabilize the Co(I) oxidation state in acid aqueous media [34–36]. It has been shown that when these macrocycles are exposed to reductants or negative potentials in acid media, an increase in the absorption of the Q band is not seen. A decrease and blue shift of the Soret band is the relevant feature, indicating that the Co(I) oxidation state reacts rapidly to form a radical anion species, localizing the electronic density on the ring of the macrocycle [34–36]. The spectrum recorded at −0.7 V [figure 7(b)] in the presence of

SO_2 follows that pattern, and therefore a plausible explanation of the interaction of the poly-Co(II)TAPP/ITO-modified electrode and SO_2 could be stabilization of a "radical anion porphyrin" without transforming into the Co(II) species [open circuit spectrum, figure 7(a)], confirming the slow electrochemical process established in the RDE experiments.

4. Conclusions

This study shows the electrochemical behavior of poly-Co(II)TAPP/GC modified electrodes in the reduction of S(IV) species. The Co(II)TAPP modified electrode promotes reduction of SO_2 under very acidic conditions in a water–ethanol mixture. The electrodes are stable when the porphyrin is previously electropolymerized, and show a linear relationship between current and concentration in the range at which sulfite is present in red wines. RDE and spectroelectrochemical experiments indicate the formation of an intermediate between the porphyrin and the S(IV) species. Reduction of the intermediate is the rate-determining step of the reaction, and it is stable enough to be detected at $-0.7\,V$ by UV–Vis spectrophotometry.

Acknowledgments

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References

[1] E. Bordeu, J. Scarpa. *Análisis Químico del Vino*, 2nd Edn, Ediciones Universidad Católica de Chile, Santiago, Chile (2000).
[2] H.J. Schwartz. *J. Allergy Clin. Immunol.*, **71**, 487 (1983).
[3] M.C.B.S.M. Montenegro, A.N. Araújo, C.M.C.M. Couto, J.L.F.C. Lima. *J. Agric. Food Chem.*, **46**, 168 (1998).
[4] L. Angnes, C.M.N. Azevedo, K. Araki, H.E. Toma. *Anal. Chim. Acta*, **387**, 175 (1999).
[5] B.W. Zoecklein, K.R. Fugelsang, B.H. Gump, F.S. Nury. *Análisis y producción de vino*, Acribia S.A., Zaragoza, España (2001).
[6] I. Hornsey. *The Chemistry and Biology of Winemaking*, RSC Publishing, Cambridge, UK (2007).
[7] J. Wang. *Analytical Electrochemistry*, Wiley–VCH, New York, USA (2001).
[8] N. Alonso-Vante (Ed.). *Electroquímica and Electrocatalisis. Materiales : Aspectos Fundamentales and Aplicaciones*, Vol. Ia, 1st Edn, Ediciones e-libro.net, Buenos Aires, Argentina (2003).
[9] J. Zagal. *Coord. Chem. Rev.*, **119**, 13 (1992).
[10] F.N. Crespilho, M. Ghica, M. Florescu, F. Nart, O. Oliveira Jr, C. Brett. *Electrochem. Comm.*, **8**, 1665 (2006).
[11] M.J. Aguirre, E. Trollund, P. Ardiles, S.R. Biaggio, R.C. Rocha-Filho. *Polyhedron*, **19**, 2303 (2000).
[12] R.W. Murray, A. Bettelheim, B.A. White, S.A. Raybuck. *Inorg. Chem.*, **26**, 1009 (1987).
[13] M. Isaacs, C. San Martín, P. Dreyse, C. García, K. Calfumán, D. Villagra. *J. Chil. Chem. Soc.*, **52**, 1126 (2007).
[14] P. Dreyse, G. Ramírez, A. Riquelme, M. Isaacs. *J. Chil. Chem. Soc.*, **51**, 923 (2006).
[15] P.A. Kilmartin, H. Zou, A.L. Waterhouse. *J. Agric. Food Chem.*, **49**, 1957 (2001).

[16] D.T. Sawyer, J.T. Roberts. *Experimental Electrochemistry for Chemists*, Wiley Interscience, New York, USA (1974).
[17] F. Armijo, M. Goya, Y. Gimeno, M. Arévalo, M. Aguirre, A. Creus. *Electrochem. Comm.*, **8**, 779 (2006).
[18] M.J. Aguirre, M. Lucero, G. Ramirez, A. Riquelme, I. Azocar, M. Isaacs, F. Armijo, J.E. Forster, E. Trollund, D. Lexa. *J. Mol. Catal. A: Chem.*, **71**, 221 (2004).
[19] M.J. Aguirre, M.A. Riquelme, M. Isaacs, M. Lucero, E. Trollund. *J. Chil. Chem. Soc.*, **48**, 89 (2003).
[20] M.J. Aguirre, M. Isaacs, F. Armijo, G. Ramirez, E. Trollund, S.R. Biaggio, J. Costamagna. *J. Mol. Cat. A: Chem.*, **165**, 169 (2005).
[21] R.G. Compton, I. Streeter, A.J. Wain, J. Davis. *J. Phys. Chem. B*, **109**, 18500 (2005).
[22] I. Kolthoff, C. Miller. *J. Am. Chem. Soc.*, **63**, 2818 (1941).
[23] Y. Tolmachev, D. Sherson. *J. Phys. Chem. A*, **103**, 1572 (1999).
[24] C. Quijada, E. Morallon, J. Vasquez, L. Berlouis. *Electrochim. Acta*, **46**, 651 (2001).
[25] A.J. Bard, L.R. Faulkner. *Electrochemical Methods: Fundamentals and Application*, 2nd Edn, John Wiley & Sons, Inc., New York, USA (2001).
[26] R. Greef, R. Peat, L.M. Peter, D. Pletcher, J. Robinson. *Instrumental Methods in Electrochemistry*, Ellis Horwood Limited, Chichester, England (1985).
[27] T. Hemmingsen, E. Skavas. *Electrochim. Acta*, **52**, 3510 (2007).
[28] J. O'Mara Bockris, A.K.N. Reddy. *Modern Electrochemistry: Vol. 2*, Plenum Press, New York (1970).
[29] F.P. Treadwell, W.T. Hall. *Química Analítica, Tomo I Análisis Cualitativo*, 9th Edn, UTEHA., DF, México (1948).
[30] J.M. Zen, A.S. Kumar, M.R. Chang. *Electrochim. Acta*, **45**, 1691 (2000).
[31] M.J. Aguirre, M. Isaacs, F. Armijo, N. Bocchi, J.H. Zagal. *Electroanalysis*, **10**, 571 (1998).
[32] M.J. Aguirre, M. Isaacs, F. Armijo, L. Basáez, J.H. Zagal. *Electroanalysis*, **14**, 356 (2002).
[33] B.M. Berezin. *Coordination Compounds of Porphyrins and Phthalocyanines*. Chap. 7, 2000, UMI Books on Demand, Bell and Howell Co., Michigan, USA (Reprinted from John Wiley and Sons 1981, Bath, Avon, UK).
[34] P. Neta, D. Behar, T. Dhanasekaran, C.M. Hosten, D. Ejeh, P. Hambright, E. Fujita. *J. Phys. Chem. A*, **102**, 2870 (1998).
[35] K.M. Kadish, P. Taglatiesta, T. Boschi, M. Franzen, E. Van Caemelbecke, A. Villard, F. D'Souza. *Inorg. Chem.*, **32**, 4042 (1993).
[36] K.M. Kadish, X.Q. Lin, B. Boisselier-Cocolios. *Inorg. Chem.*, **25**, 3242 (1986).