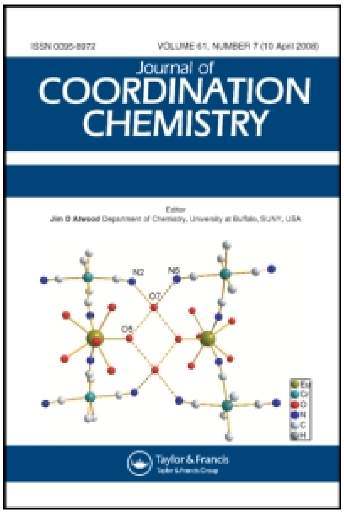

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Nitrite electro-oxidation mediated by Co(II)-[tetra(4-aminophenyl)porphyrin]-modified electrodes: behavior as an amperometric sensor

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Nitrite electro-oxidation mediated by Co(II)-[tetra(4-aminophenyl)porphyrin]-modified electrodes: behavior as an amperometric sensor

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Electro-oxidation of nitrite mediated by Co(II)-[tetra(4-aminophenyl)porphyrin]-modified electrodes (4-CoTAPP) is presented in this article. Catalytic activity of electrodes modified with porphyrin polymeric films (poly-4-CoTAPP) and with multilayer of monomers (m-4-CoTAPP) for the oxidation of nitrite was compared. The number of cycles for the electrosynthesis of poly-4-CoTAPP determines the activity of the electrode toward nitrite oxidation because the system loses its catalytic activity as the number of polymerization cycles increases above 15. The effect of pH on activity is also reported. The response for the nitrite oxidation of electrodes modified with 4-CoTAPP and with metal-free ligand, that is, tetra(4-aminophenyl)porphyrin, either as multilayer of monomers or as polymer (m-4-H_2TAPP and poly-4-H_2TAPP, respectively), was compared. An increase of activity in the presence of the metal was found. Furthermore, when the device was tested as an amperometric sensor for different nitrite concentrations under the optimum working conditions, only poly-4-CoTAPP exhibited a linear response throughout the concentration range studied with a reasonably low limit of detection, while m-4-CoTAPP and poly-H_2TAPP systems have no linear response throughout the range of concentration. Finally, the number of electrons involved and the Tafel slope for the reaction were estimated.

Keywords: Nitrite electro-oxidation; Modified electrodes; Amperometric sensor; Porphyrins; Electrocatalysis

1. Introduction

Nitrite is important for environmental and biological processes and is one of the active intermediates in the nitrogen cycle. Nitrites are often used as fertilizer, which has an environmental impact through the pollution of water sources, and are also added to food as preservative. Concern about the role of nitrite as precursor in the formation of *N*-nitrosamines, many of which are carcinogenic compounds found in nature [1–3], has increased interest in its research. A variety of techniques have been reported for the determination of nitrite, for example, chromatography [4, 5], spectrophotometry [6, 7], and electrochemistry [8–10]. Electrochemical techniques offer advantages over other

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analytical approaches, for example, faster, cheaper, and safer. The electrochemical determination of nitrite can be performed either by reduction or oxidation. Nitrite oxidation has the advantage of being interference-free from nitrate and molecular oxygen, which are usually the main constraints in cathodic determination [11, 12]. The determination of this ion is difficult at conventional electrodes because nitrite oxidation requires high potentials [13] and, due to the poisoning of the electrode by the species produced during the electrochemical process [14]. In addition, the electrochemical determination of nitrite is prone to interference from other easily oxidizable substances. Therefore, the modification of electrode surfaces with suitable catalysts has the possibility of performing nitrite oxidation at low potentials. Sometimes it is possible to enhance the sensitivity and selectivity of the electrode by immobilizing materials which form 3-D networks containing suitable electro-catalytically active sites. In this way, improvement of the electrode activity is possible [15]. Nitrite oxidation at modified electrodes has been extensively described, including carbon paste electrodes chemically modified with *N*,*N*′-bis(salicylaldehyde)-4-methyl-1,2-phenylenediimino oxovanadium (IV) [16], glassy carbon electrodes modified with phthalocyanines [17, 18], alternating layers of iron(III) tetra-(*N*-methyl-4-pyridyl)-porphyrin and cobalt(II) tetrasulfonated phthalocyanine [19], carbon paste electrodes modified with cobalt(II) porphyrins adsorbed on SiO_2/SnO_2/phosphate [20], and polymers based on iron(III) porphyrin [15, 21]. Porphyrin- and metalloporphyrin-coated electrodes have shown interesting features as analytical sensors because they can electrocatalyze the charge transfer process, thus increasing the sensitivity and selectivity of the electrode [22–28]. An attractive method reported in the literature for the modification of electrodes with porphyrin films consists of electropolymerization of metalloporphyrins bearing suitable peripheral groups [29]. In particular, amino-substituted porphyrins can be electropolymerized to afford surface-modified electrodes aimed at preparing amperometric or potentiometric sensors [15, 30–32]. In this article, the development of an electrode modified with cobalt tetra(4-aminophenyl)porphyrin (4-CoTAPP) is reported. Oxidation of nitrite at electrodes modified with multilayer of monomers (m-4-CoTAPP) and by electropolymerization (poly-4-CoTAPP) was studied. The effect of pH, metal, and electropolymerization conditions on nitrite oxidation was also investigated. Nitrite oxidation is pH, number of electro-polymerizing cycles, and metal (poly-4-CoTAPP) dependent. Under the optimum working conditions the modified electrode obtained by electropolymerization (poly-4-CoTAPP) displayed amperometric response as a sensor for nitrite. In addition, a reaction mechanism based on electrochemical calculations has been suggested.

2. Experimental

2.1. *Materials*

Co(II)-tetra(4-aminophenyl)porphyrin (4-CoTAPP) was purchased from Organix. Tetrabutylammonium perchlorate (TBAP), monobasic and dibasic potassium phosphate (Sigma Aldrich), citric acid monohydrate, sodium nitrite, dimethylformamide (DMF), NaOH, and HCl (Merck) were analytical grade reagents. Deionized water was obtained from a Millipore-Q-system. Nitrogen (99.99% pure) gas was purchased from AGA-Chile.

2.2. *Equipment*

Cyclic voltammetry studies were performed on a Voltalab PST050 potentiostat-galvanostat. The conventional three electrode system consisted of a glassy carbon working electrode, Ag/AgCl (3 M KCl) reference electrode, and a platinum wire counter electrode.

2.3. *Preparation of modified electrode*

The glassy carbon electrode was polished to a mirror finish on a felt pad using alumina slurries (3 µm). The monomer-modified electrode was obtained by dispensing a drop of 1 mM Co-4-TAPP/DMF on the glassy carbon electrode surface (dry-drop method). Electropolymerization was conducted by consecutive potential cycling (50, 25, and 15 cycles) in a 0.1 mM Co-4-TAPP +0.1 M TBAP (supporting electrolyte)/DMF solution at 0.1 $V s^{-1}$. The modified electrodes were carefully rinsed with DMF to remove excess electrolyte and finally with Milli-Q water. The modified electrode was stabilized in phosphate buffer by cycling the potential within the potential window at which nitrite oxidation is performed.

3. Results and discussion

3.1. *Nitrite electro-oxidation at 4-CoTAPP modified electrodes*

Figure 1 shows the structure of the porphyrin used in this study (4-CoTAPP) with amino groups in the ring periphery, enabling its electropolymerization [15, 29–32]. Figure 2 depicts the voltammetric profile of CoTAPP (poly-4-CoTAPP) electropolymerization, obtained in 0.1 M TBPA/(DMF), last cycle (figure 2a), and its response for the nitrite oxidation of a 2 mM solution at pH 7.1 (figure 2b). Figure 2(a) shows that as the cycling proceeds, the polymer film becomes less conductive (the current decreases). This has been ascribed to the blockage of active sites as the number of cycles increases. Therefore, a polymer less active toward nitrite (in terms of peak current, I_p) was generated (figure 2b). When poly-4-CoTAPP was obtained from 15 cycles, maximum activity is achieved with peak currents of *ca* 220 µA. When the polymer was obtained by 25 cycles, the activity toward nitrite significantly decreased and I_p dropped to about 100 µA. If polymerization is performed by 50 cycles, a polymer with similar or less activity than that of an unmodified glassy carbon (GC) substrate was obtained (figure 2b). In fact, when more than 15 cycles are employed, the polymer starts losing activity toward nitrite and the current decrease indicates that polymer growth is blocking active sites, deactivating the electrode as the number of cycles increases. A likely explanation for this phenomenon is that an increase in the number of cycles provokes a change from an initial 2-D nucleation mechanism to a 3-D polymeric growth, deactivating the polymer [33]. Thus, the best condition for

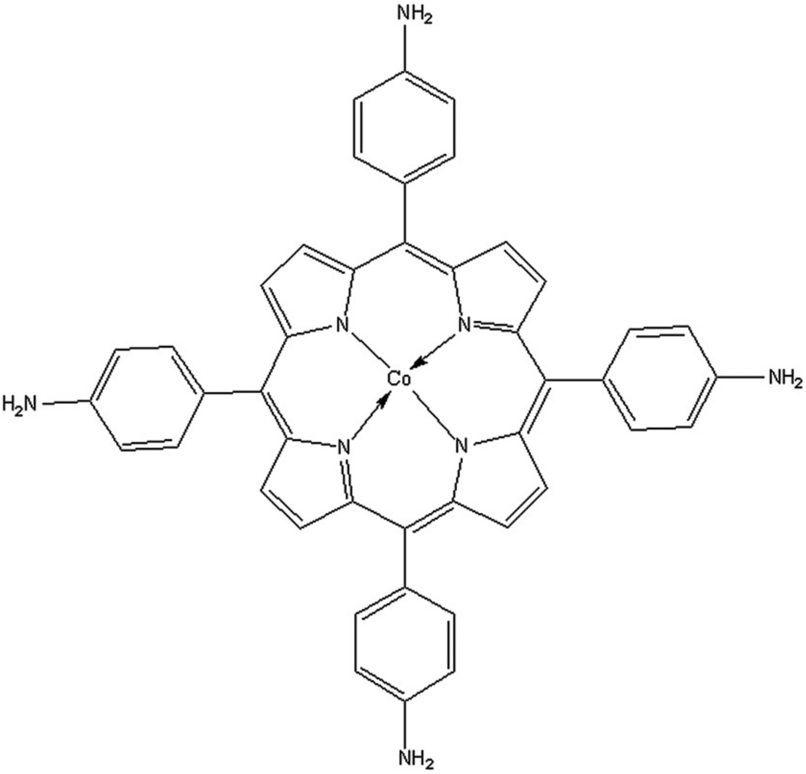

Figure 1. Structure of Co(II)-[tetra(4-aminophenyl)porphyrin] (4-Co-TAPP).

poly-4-CoTAPP-modified electrode formation is to utilize 15 polymerization cycles, which is the approach used here. Comparison between poly-4-CoTAPP, the multilayer modified electrode with physically adsorbed monomers (m-4-CoTAPP), and unmodified GC electrode is illustrated in figure 3. The poly-4-CoTAPP electrode (heavy solid line) is much more active than the m-4-CoTAPP (thin solid line) with a slight potential shift and a higher peak current. This behavior is expected for this type of system, where polymer films are generally more active and stable than the multilayer of physically adsorbed monomers. This might be explained considering the generation of a more uniform film with an extensively conjugated π system, with directional conductivity strongest along the axis of the chain due to the formation of covalent bonds between nitrogen and carbon of a phenyl substituent of another porphyrin. This feature confers superior characteristics for electrocatalytic reactions [33–37]. Indeed, the interaction among porphyrin units can strongly modify the activity, as in the case of supramolecular or polymeric films [38]. Although the m-4-CoTAPP electrode proved to be slightly more active than bare GC, it was unstable and loses its activity completely for a second sweep in the presence of nitrite.

Figure 4 shows a comparison between electrodes modified by 4-CoTAPP and free ligand, 4-H_2TAPP. Figure 4(a) shows a comparison between the polymeric systems (poly-4-CoTAPP and poly-4-H_2TAPP) and figure 4(b) the comparison between multilayer physically adsorbed systems (m-4-CoTAPP and m-4-H_2TAPP). Clearly, for

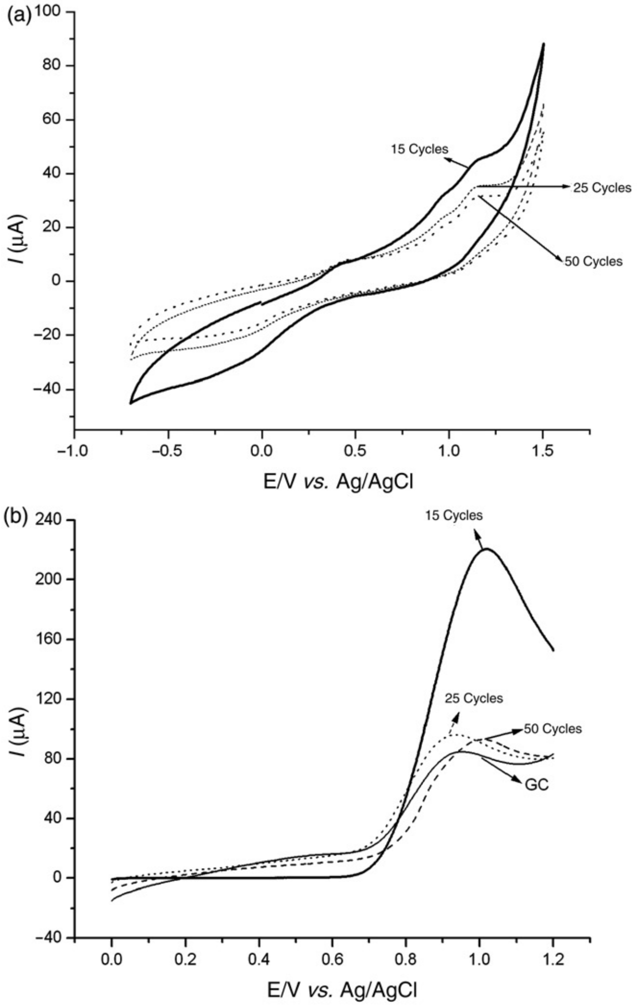

Figure 2. Voltammetric profile of (a) poly-4-CoTAPP electropolymerization in DMF/TBPA 0.1 M, 0.1 V s^{-1} (scan rate), (last cycle) and (b) poly-4-CoTAPP (obtained at 15, 25, and 50 cycles), toward nitrite electro-oxidation (2 mM nitrite in pH 7.1 phosphate buffer solution), 0.1 V s^{-1} (scan rate), N_2 atmosphere.

(poly-4-CoTAPP) polymeric systems, Co plays a fundamental role in the nitrite oxidation mechanism. On the other hand, the central metal of the porphyrin ring has no effect on the electrocatalysis when modification is carried out with the multilayer of monomers, indicating that the mechanism of poly-4-CoTAPP-mediated nitrite oxidation is different from that occurring at the m-4-CoTAPP electrode, where the central metal would not participate (figure 4b). It is noteworthy that m-4-CoTAPP and m-4-H_2TAPP systems displayed higher activity than bare GC (figure 4b), suggesting that the electrode indeed has been modified and that the response is no longer that of an unmodified GC. In the case of electrodes modified with monomers, identical response of Co-containing porphyrin and demetalated porphyrin would suggest that the ligand is the actual active site. For polymers, the potential shift observed for poly-4-CoTAPP compared with poly-4-H_2TAPP indicates that cobalt is the preferred active site.

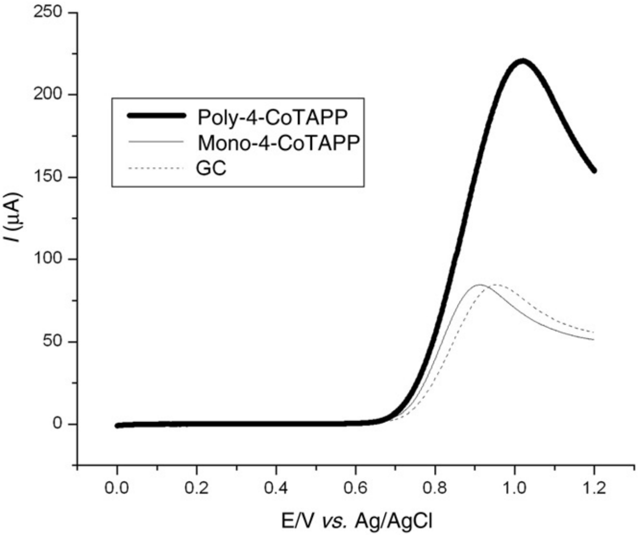

Figure 3. Voltammetric profile of poly-4-CoTAPP (thick solid line), m-4-CoTAPP (thin solid line) and bare GC (dashed line) toward nitrite oxidation (2 mM nitrite in pH 7.1 phosphate buffer solution), $0.1\,\mathrm{V\,s^{-1}}$ (scan rate), N_2 atmosphere.

3.2. *Effect of pH on nitrite electro-oxidation*

Figure 5 depicts the influence of pH on the electro-oxidation of a 2 mM nitrite solution on a poly-4-CoTAPP modified electrode at pH 2, 4.5, 7.1, and 7.8. Figure 5(a) shows that the peak current, I_p, reaches a maximum at pH 7.1, followed by pH 7.8. At a more acidic pH the current decreases and the reaction becomes less favored. Nonetheless, E_p remains practically independent of pH (figure 5b). Similar behavior has been observed in other studies [11, 39] and suggests that in the kinetics of nitrite oxidation the rate-limiting step is proton-independent over the studied pH range [39].

3.3. *Assessment of the systems as amperometric sensor for nitrite*

Figure 6 illustrates the behavior of a poly-4-CoTAPP-modified electrode as amperometric sensor for nitrite. As seen, the electrode response is linear over the entire range of nitrite concentration studied (0.1 mM–10 mM), $R = 0.99936$, being potentially useful for the detection and quantification of nitrite in a wide range of concentration. This behavior was observed only for the poly-4-CoTAPP system, because m-4-CoTAPP exhibited nonlinear response (figure 7a) and poly-4-H_2TAPP presented nonlinear response throughout the range of concentration and could not be applied to the concentrations below 2 mM (figure 7b).

For other analytes, such as sulfite or hydrogen sulfite, that can be measured by similar methods, the observed limit of detection for sulfite or hydrogen sulfite utilizing other modified porphyrin electrodes was 0.1 mM [40] and 0.02 mM when the detection limit was determined at glassy carbon modified with a poly[copper(II) tetra-aza-annulene] film [41]. For practical purposes, the system studied in this work showed a reasonably low detection limit over a reasonable wide range.

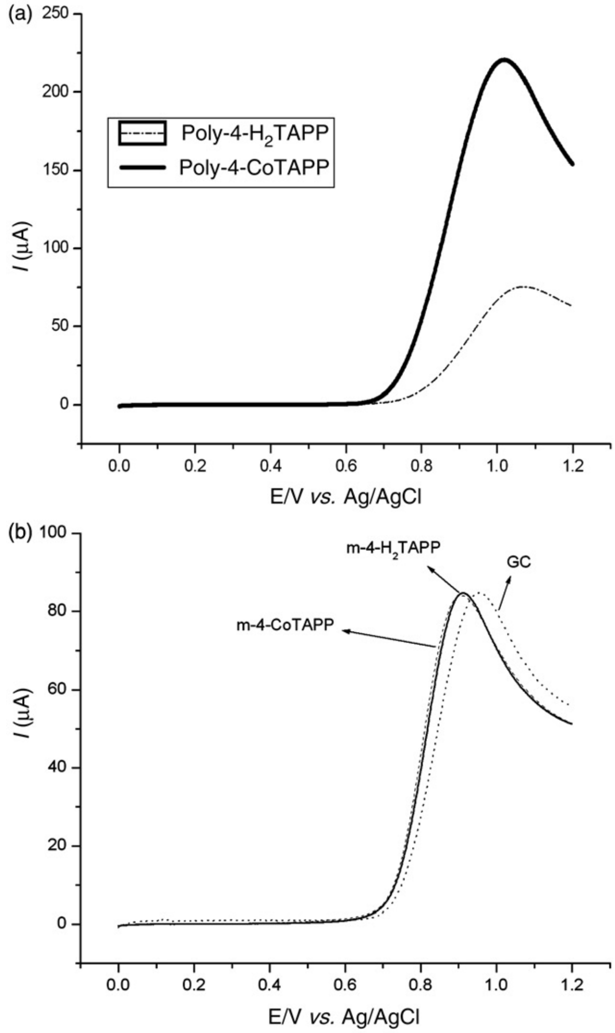

Figure 4. Voltammetric profile of (a) poly-4-CoTAPP (solid line) and poly-4-H2TAPP (dashed line) and (b) m4-CoTAPP (thick dashed line), m-4-H2TAPP (solid line) and GC (thin dashed line), toward nitrite electro-oxidation, (2mM nitrite in pH 7.1 phosphate buffer solution), 0.1 V s^{-1} (scan rate), N_2 atmosphere.

3.4. *Electrochemical studies on nitrite oxidation*

Figure 8 presents a plot of I_p *versus* the square root of scan rate for nitrite oxidation. A good linear relationship was obtained, pointing to a diffusion-controlled process consistent with a high rate-constant catalytic system [42, 43]. The total number of electrons, n, involved in the reaction can be worked out from the I_p *versus* $\nu^{1/2}$ plot using equation (1), valid for a totally irreversible diffusion controlled process [42, 43],

$$I_p = (2.99 \times 10^5) n[(1-\alpha)n_a]^{1/2} C_o A D_o^{1/2} \nu^{1/2} \tag{1}$$

where α is the electron transfer coefficient, n_a the number of electrons involved in the rate-determining step of the reaction, D_o (cm^2 s^{-1}) the diffusion coefficient of the

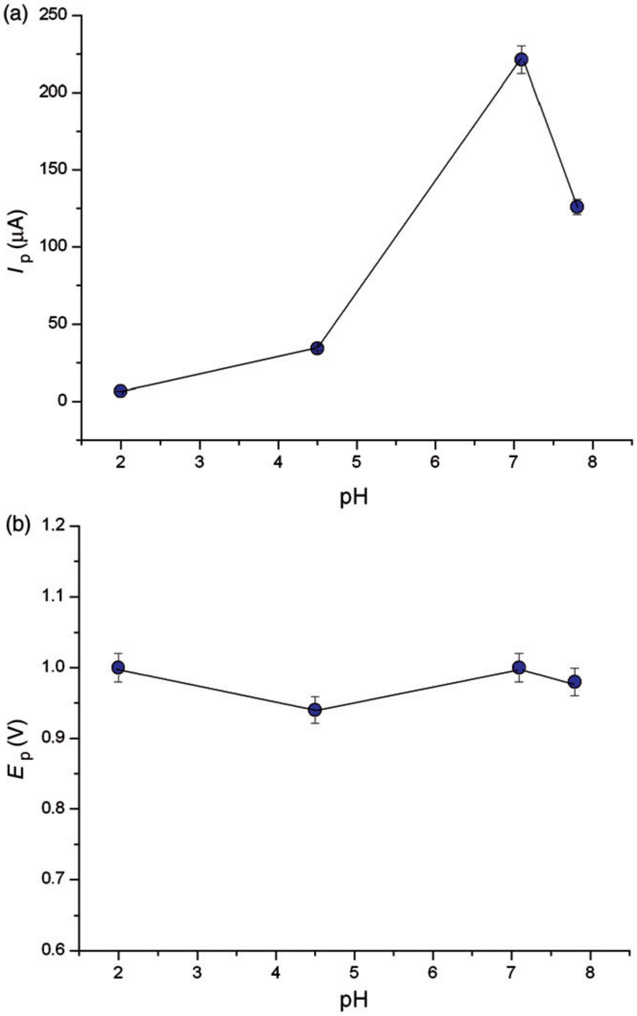

Figure 5. Influence of pH in (a) the peak current, I_p, and (b) the peak potential, E_p, in the nitrite (2 mM) electro-oxidation. Scan rate $0.1\,\mathrm{V\,s^{-1}}$.

electroactive species, A the electrode area (cm^2), and C_o (mM) the concentration of electroactive species. In the present work, C_o 2 mM and D_o $3.7 \times 10^{-5}\,\mathrm{cm^2\,s^{-1}}$ [44] were used.

Also considering that $(1-\alpha)\,n_a$ must be known, an approximation based upon its dependence on the difference between the peak potential E_p and the mean peak potential $E_{p/2}$, given by equation (2), was employed [42, 43].

$$(1-\alpha)n_a = 47.7\mathrm{mV}/(E_p - E_{p/2}) \tag{2}$$

where $(1-\alpha)n_a$ was 0.34. Inserting this value in equation (1) and with the value of the slope $270\,\mu\mathrm{A}/(\mathrm{V\,s^{-1}})^{1/2}$, obtained from figure 8, yields $n = 1.8$, indicating that the

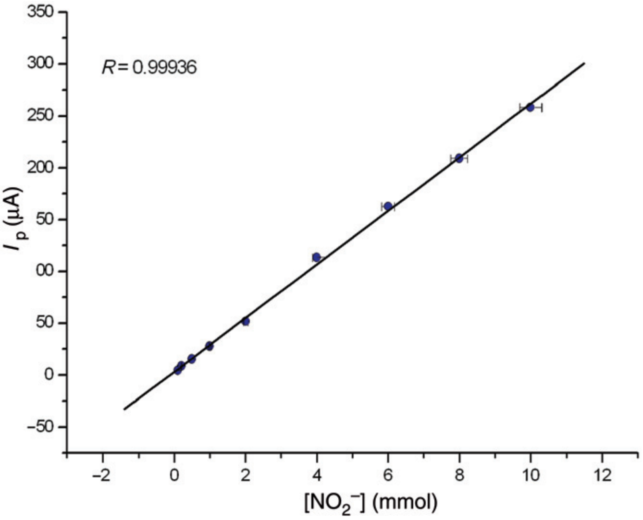

Figure 6. Plot of I_p *vs.* nitrite concentration (between 0.1 and 10 mM) for poly-4-CoTAPP at pH 7.1, scan rate 0.1 V s^{-1}; N_2 atmosphere.

number of transferred electrons is two, which agrees with other studies for nitrite oxidation [17, 19]. It is evident from the $(1-\alpha)n_a$ values obtained from this approach that nitrite oxidation involves two electrons, agreeing well with the literature, wherein NO_3^- would be the main reaction product [8, 17, 19, 45].

In order to obtain information concerning the rate-determining step involved in the electro-oxidation of nitrite, the Tafel slope for this reaction was calculated as depicted in figure 9. The value was 123 mV per decade, indicating that the limiting step corresponds to the transfer of the first electron.

Consequently, it is possible to put forward a mechanism for the oxidation of nitrite, consistent with the above findings, where the limiting stage corresponds to step 1 of the following mechanism:

(1) $Co(II)TAPP \rightarrow [Co(III)TAPP]^+ + e^-$ (slow step)
(2) $[Co(III)TAPP]^+ + NO_2^- \rightarrow [Co(III)TAPP^+ — NO_2^-]$
(3) $[Co(III)TAPP^+ — NO_2^-] \rightarrow Co(II)TAPP + NO_2$

Finally, the formation of NO_2 is followed by a fast disproportionation step

(4) $2NO_2 + H_2O \rightarrow NO_2^- + NO_3^- + 2H^+$

Step 1 has to occur twice in order to obtain nitrite and nitrate ions as final products, involving two electrons [11].

4. Conclusions

Co-4-TAPP-modified electrodes catalyze the nitrite oxidation. However, this behavior strongly depends on the type of modification. To behave as a good catalyst

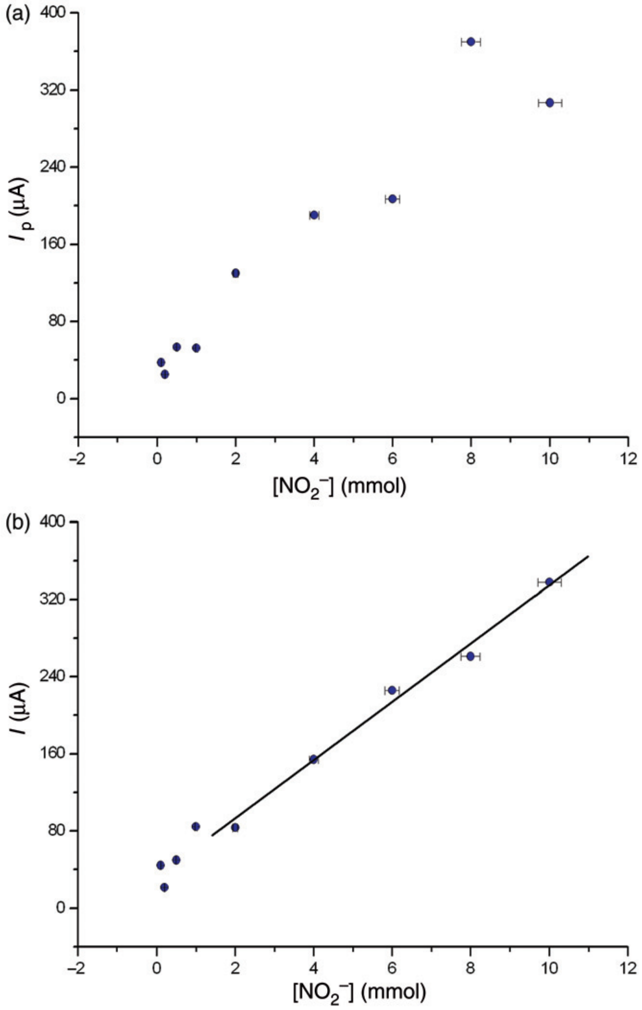

Figure 7. Plot of I_p *vs.* nitrite concentration (between 0.1 and 10 mM) for (a) m-4-CoTAPP and (b) poly-4-H2TAPP, at pH 7.1, scan rate $0.1\,V\,s^{-1}$, N_2 atmosphere.

and amperometric sensor, the porphyrin must be previously electro-polymerized. The results accomplished in this work demonstrate that the electrocatalytic mechanism was modified when the porphyrin was electropolymerized. Moreover, dependence between the rate of reaction (current) and pH exists: at pH 7.1 the modified electrode displayed maximum activity. Nevertheless, the potential is not pH-dependent, meaning that when the metal is oxidized and becomes a redox mediator, it need not previously lose a proton nor gain a hydroxide. Electrodes modified with the free ligand also show slight catalytic activity, indicating that cobalt in the polymer is a preferred active site but not unique. A mechanism where the limiting-reaction step, according to Tafel slope value, is the first electron transfer has been proposed. Finally, the poly-4-CoTAPP-modified electrode behaves as a stable amperometric sensor in the concentration range

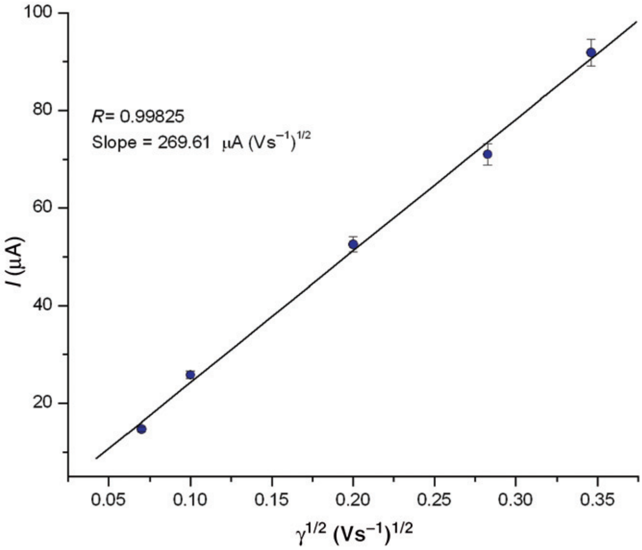

Figure 8. Plot of I_p *vs.* $\nu^{1/2}$, for poly-4-CoTAPP, in pH 7.1 phosphate buffer, containing 2 mM of nitrite. Scan rate: 0.005–0.120 V s^{-1}.

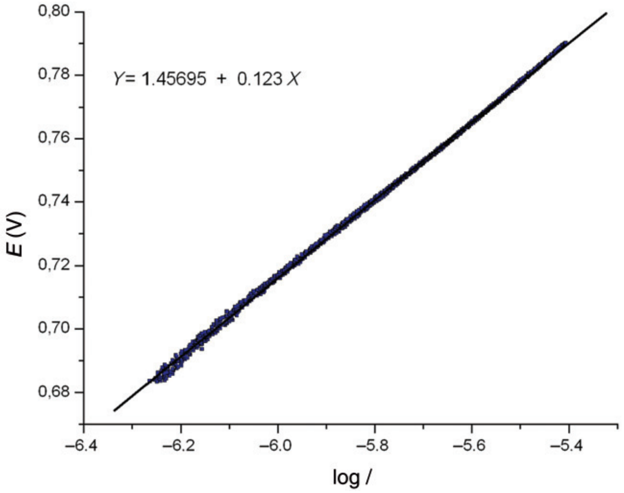

Figure 9. Plot of E_p *vs.* log I (Tafel plot), for poly-4-CoTAPP, in pH 7.1 phosphate buffer, containing 2 mM of nitrite. Scan rate: 0.005 V s^{-1}.

of 0.1−10 mM. In addition, the device showed a satisfactory low detection limit as compared with other modified electrodes.

Acknowledgments

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