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Electrocataltyic oxidation of hydrazine at polymeric iron-tetraaminophthalocyanine modified electrodes

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Abstract

Electrocatalytic hydrazine oxidation was studied by using a glassy carbon electrode coated with monomeric and polymeric Fe-tetraaminophthalocyanine. The polymeric complex-modified electrode is a better catalyst than the monomer-modified electrode. It presents higher activity at lower potentials and a very good reproducibility. A linear correlation between I_p and hydrazine concentration in a wide range, from 1×10^{-6} to 1×10^{-2} M at pH 13 for the polymer-modified electrode was obtained. The open circuit measurements for the polymer-modified electrode in aqueous solution in both presence and absence of hydrazine show that an electronic transfer occurs without an applied potential, from the hydrazine to the Fe (II) metal center. The kinetic electro-oxidation parameters for the polymer-modified electrode were investigated and a probable mechanism operating at pH 13 is proposed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Electrocatalytic hydrazine oxidation; Poly-Fe-tetraaminophthalocyanine; Modified electrodes; Electrocatalytic mechanism

1. Introduction

Transition-metal phthalocyanine modified electrodes have been widely studied due to their numerous applications on electrocatalysis such as O_2 [1–3] and peroxide reduction [4–7], thiols [8,9] and hydrazine oxidation [10,11]. In the last years, the possibility of electropolymerizing macrocyclic complexes on the electrode surface has also been studied, with the purpose of increasing stability and electrocatalytic activity of these systems [12–14]. In some cases, an outstanding result has been obtained such as in the oxygen electroreduction at poly-cobalt-tetraaminophthalocyanines modified electrodes, where reduction occurs via two and four electrons [14], whereas, the reduction occurs only via two electrons to give peroxide with a monomer-modified electrode [2]. The electrocatalytic behavior of poly-iron-tetraaminophthalocyanine modified-electrodes has not been extensively studied due to some electropolymerization limitations, which take place during the process, because the polymerization kinetic becomes slower as the polymer grows [15], probably due to a slow diffusion of counter ions to the inner layers of the polymer. However, this slow kinetic does not hinder the polymeric growing.

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Wang et al. [15], the first contributors in this area at our knowledge, observed the same limitation during the electropolymerization. Nevertheless, they obtain a good polymeric modified-electrode and reported their application as an amperometric sensor of organic peroxides.

In this work, we present an electrocatalytic activity study of glassy carbon electrodes modified by poly-iron-tetraaminophthalocyanine as an electrocatalyst for hydrazine oxidation reaction. These study shows an increased electrocatalytic activity for the polymer compared with the monomer modified electrode toward this reaction and presents its possible application as an amperometric sensor of hydrazine.

2. Experimental

Iron-tetraaminophthalocyanine (Midcentury Co.) was used as received. The working electrode monomer modification was performed placing a drop of monomer solution (1×10^{-3} M) in DMSO on the electrode glassy carbon surface. After 1 h the electrode was rinsed with DMSO, ethanol and deionized, bidistilled water. Polymeric films were grown by potentiodynamically cycling the glassy carbon electrode in a 1×10^{-3} M, Fe-tetraamninophthalocyanine/0.1 M TBAP/DMSO solution, between -0.6 and $+1.15$ V versus Ag/AgCl during 100 cycles. After polymerization, the modified electrode was rinsed with DMSO, ethanol and then with bidistilled water. Solvents were chromatographic grade and electrolytes were analytical grade.

Electrochemical experiments were performed in a three-compartment glass cell, one for each of the electrodes: the working electrode, glassy carbon ($A = 0.19\,\mathrm{cm}^2$), the reference electrode, saturated Ag/AgCl, to which all the potentials are quoted, and the counter electrode, a Pt coil ($A = 14\,\mathrm{cm}^2$). All measurements were carried out in aqueous solutions of 0.1 M Na_2CO_3, 0.1 M $NaHCO_3$ and 0.1 M NaOH mixed in different proportions to obtain solutions at various pH (8 to 13), deaerated with pure N_2. Hydrazine (hydrazinium sulfate, p.a. from Merck) was used without further purification. All the measurements were carried out at 23°C under nitrogen. An AFCBP1 Pine Bipotentiostat provided with PineChem 2.5 software and a Pine Analytical Rotator (AMFSRXE) were used to obtain data for the electropolymerization and hydrazine electro-oxidation.

3. Results and discussion

3.1. Characterization of electrodes modified with the monomer and the polymer

Fig. 1 shows the cyclic voltammograms corresponding to the electropolymerization of the iron-tetraaminophthalocyanine on the glassy carbon electrode from a 1×10^{-3} M solution of the monomer in DMSO/0.1 M TBAP. The increase of the peaks is due to electropolymerization growing. The irreversible oxidation wave that appears at ca. 0.9 V would correspond to the oxidation of the amino groups that give origin to the electropolymerization. The polymer is stable in DMSO solution and in aqueous solution because no appreciable change was observed in the voltammetric profile of the polymer-modified electrode at least after 100 cycles in both organic and aqueous solutions between the same potential limits used during the electropolymerization (not shown). On the other hand, the monomer-modified electrode is not stable in DMSO solutions between the same potential limits, probably because the monomer is

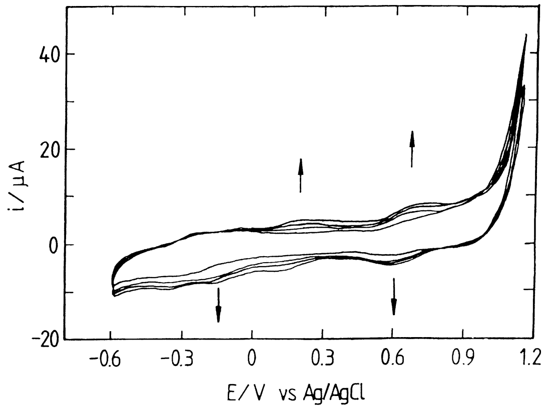

Fig. 1. Cyclic voltammetry corresponding to the electropolymerization of iron-tetraaminophthalocyanine on a glassy carbon electrode. Electrolyte: N_2/DMSO/0.1 M TBAP solution with 1 mM of the monomer. Potential limits: -0.6 and $+1.15$ V vs. Ag/AgCl. Scan rate: $200\,\mathrm{mV\,s^{-1}}$. The curves correspond to the cycles 10, 30, 60 and 100 in the sense of the arrows.

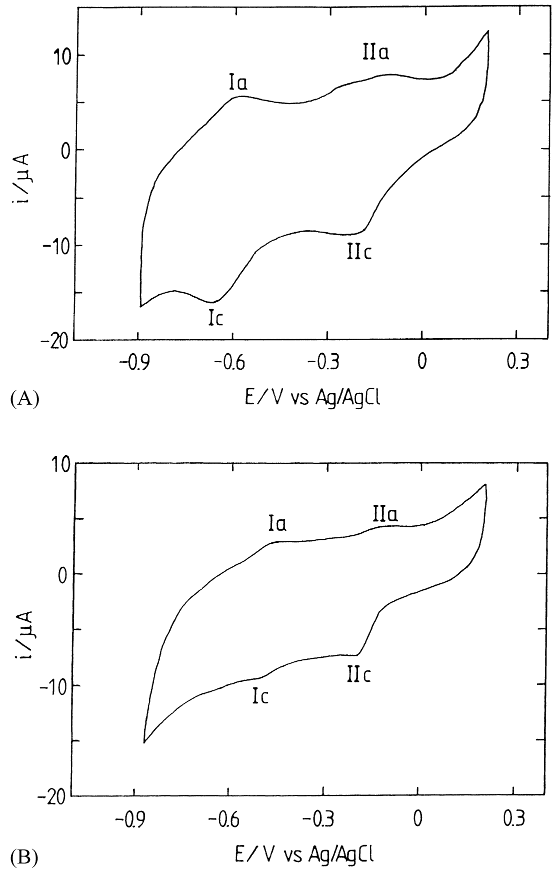

Fig. 2. (A) Voltammetric profile of the absorbed polymer on a glassy carbon electrode surface in a N_2 deaerated aqueous solution at pH 13. Scan rate: $200\,mVs^{-1}$. Potential limits: -0.9 and $+0.2$ V vs. Ag/AgCl. The Ia/Ic and IIa/IIc couples correspond to Fe (II)/Fe (I) and Fe (III)/Fe (II), respectively; (B) Voltammetric profile of the absorbed monomer on a glassy carbon electrode surface in a N_2 deaerated aqueous solution at pH 13. Scan rate: $200\,mVs^{-1}$. Potential limits: -0.9 and $+\,0.2$ V vs. Ag/AgCl. The Ia/Ic and IIa/IIc couples correspond to Fe (II)/Fe (I) and Fe (III)/Fe (II), respectively.

dissolved into the solution and/or polymerizes, but it is stable in aqueous solution (at least, 50 cycles). Fig. 2 shows the voltammetric response of both modified electrodes in aqueous solution at pH 13, where the reversible redox couples Ia/Ic and IIa/IIb would correspond to Fe(II)/Fe(I) and Fe(III)/Fe(II), respectively [16]. The potential of the couple Ia/Ic appear at lower potential for the polymer-modified electrode than for the monomer-modified electrode. It means that it is easier to oxidize Fe(I) to Fe(II) and more difficult to reduce the Fe(II) to Fe(I) in the polymer than in the monomer, probably because the electronic density in the metal center is higher in the polymer than in the monomer. A similar effect was obtained in a comparison between Co-phthalocyanine and Co-naphthalocyanine, where it was observed that the HOMO in the naphthalocyanine was higher in energy compared to the phthalocyanine because the nitrogen atoms bonded to the metal have more electronic density in the first case [11]. The extended π-system in the polymer may act as an electronic density donor to the metal center and converted it in a more reactive center to the electro-oxidation catalysis [17–19]. Similar effects have been reported for substituted phthalocyanines where the substituents, that act as electronic density donors, enhanced the electro-oxidation activity of the phthalocyanines [20]. In this case, the extended ligand, acts as a substituent that shifts the position of the redox couple Fe(II)/(I) to lower potentials. The oxidation of hydrazine begins when Fe(I) becomes Fe(II) and Fe(II) is able to form an adduct with hydrazine. That could be the reason for the higher catalytic activity of the polymer compared to the monomer modified-electrode [21].

Charges obtained from the voltammograms of Fig. 2 are quite similar for both the monomer and the polymer-modified electrodes ($Q_{\mathrm{Monomer}} = 4.2 \times 10^{-5}\,\mathrm{C}$ and $Q_{\mathrm{Polymer}} = 7.5 \times 10^{-5}\,\mathrm{C}$). This would be explained assuming that the polymer corresponds to a very thin film and the monomer form aggregates on the electrode surface [22].

3.2. Hydrazine electro-oxidation

Fig. 3 shows the voltammetric response of the monomer and polymer-modified electrodes in aqueous solution at pH 13, in presence of 5 mM hydrazine. In this figure, the hydrazine oxidation begins at a lower potential for the polymer than for the monomer-modified electrode. It means that the polymer modified-electrode is a better catalyst than the monomer-one, because for the polymer, the oxidation of hydrazine requires low energy to take place. The polymer-modified electrode shows an oxidation wave for the reverse scan where the maximum of the peak shifts to a more positive potential than for the forward scan, but this behavior takes place only for the first cycle. For the second and subsequent cycles,

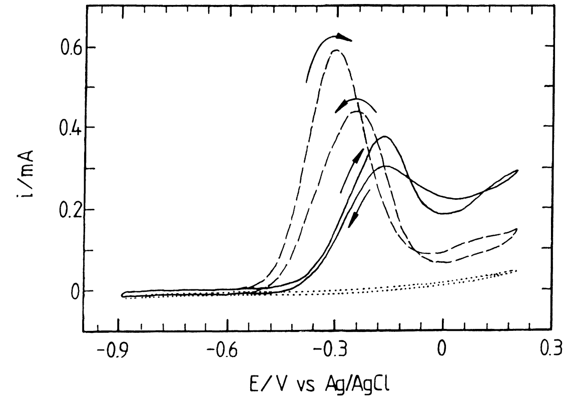

Fig. 3. Voltammetric response of the polymer (– –) and the monomer (—) modified electrodes at a pH 13, N_2 deaerated aqueous solution which contains 5 mM of hydrazine. The response of the bare electrode is also shown (· · ·). Potential limits: −0.9 and + 0.2 V vs. Ag/AgCl. Scan rate: 200 mVs^{-1}. The figure corresponds to the first cycle of both modified electrodes.

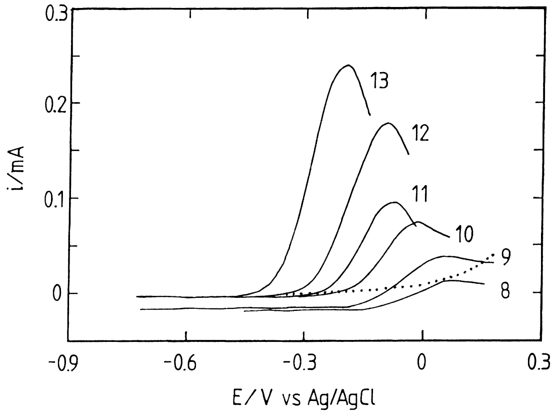

Fig. 4. Voltammetric response of the polymer-modified (—) and the bare electrode (· · ·) in the presence of 5 mM of hydrazine in N_2 deaerated aqueous solution at different pH. The conditions of the experiments are the same as in Fig. 3.

the maximum remains for the forward and reverse cycle in the same position as in the reverse scan of the first cycle. The I_p for the polymer-modified electrode, changes only for the first cycle between the forward and the reverse scan. The subsequent scans show similar waves without hysteresis (not shown). In the case of the monomer, during the first cycle the current maximum for the forward and reverse scan is practically the same. For the second and subsequent cycles, the current maximum slowly decays. These results show that the polymer-modified electrode is a better catalyst for the hydrazine oxidation than the monomer-modified electrode since the oxidation begins at a lower potential. For that reason the following results are only related to the polymer modified electrode. The behavior of the polymer-modified electrode, contrarily of the bare electrode for the hydrazine oxidation depends on pH, being the highest current and the lowest potential at pH 13, as shown in Fig. 4. In Fig. 5, it can be appreciated the Tafel slopes for the electro-oxidation of hydrazine on the polymer modified-electrode at various pH. In order to obtain a Tafel slope with a clear kinetic meaning it is necessary to utilize the portion of the current corresponding to the faradaic process. The current of the beginning of the voltammetric wave principally corresponds to faradaic current. When the voltammetric wave increases, the current has faradaic and mass-transport contributions. Near the top of the voltammetric wave, the current is predominantly diffusional and in that case, this current has not a kinetic meaning [23,24]. For that reason, it is necessary to use only the beginning of the voltammetric wave to obtain the Tafel slopes. Fig. 5 shows that the mechanism of the oxidation changes with the pH in the range pH 13–8 because the Tafel slopes are different. For pH 11–13, the Tafel slopes are 120 mV/decade that means a first electronic transfer depending on the applied poten-

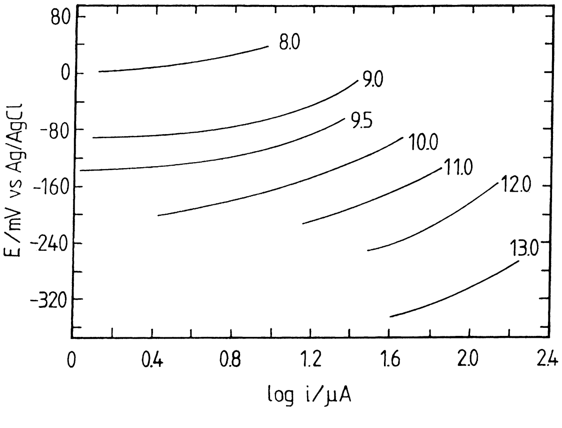

Fig. 5. Tafel slopes obtained for the hydrazine oxidation electrocatalyzed by the polymer-modified electrode in N_2 deaerated solutions at different pH. These data were obtained from polarization curves. Scan rate: 5 mVs^{-1} and at 900 rpm of rotation rate.

tial as the rate determining step [24], whereas at pH between 9 and 10, it is close to 80 mV/pH. At pH 8 the Tafel slope tends to 40 mV/decade. These results can be interpreted as follows: at pH $\geq$ 11, the rate determining step is the first electron transfer. For pH 8–10, the Tafel slopes are not very linear and it is not easy to explain what that means. A Tafel slope of Ca. 80 mV/decade could indicate the presence of two different mechanisms operating simultaneously depending on the potential [24] and/or a variation in the relationship between the number of protons related with the transfer of an electron [25]. In a similar way, a Tafel slope of 40 mV/decade corresponds to reactions involving a rapid one-electron transfer, taking place before the one-electron transfer rate-determining step [24]. Changes on the Tafel slopes of similar nature have been reported by Zagal et al. [26] for electrocatalysis promoted by transition metal phthalocyanine modified electrodes. On the other hand, the Tafel slope does not change at pH 13 for different hydrazine concentrations, and they have a unique valor equal to 120 mV/decade. This means that a unique mechanism not depending on the hydrazine concentration operates at pH 13, where the rate determining step is the first electron transfer.

To determine the OH^- order, the following relationship can be used: $(\delta E/\delta \mathrm{pH})_i = -m(\delta E/\delta \log i)_{\mathrm{pH}}$, where m is the OH^- order [26]. As the Tafel slopes for distinct pH are also different, the order in OH^- has to be calculated separately for groups, which have the same Tafel slopes. Therefore, for pH $\geq$ 11, $(\delta E/\delta \mathrm{pH})_i$ = 112 mV/pH and as the Tafel slopes are close to 120 mV/decade, the order in OH^- ions is of 1. For pH values between 9 and 10, $(\delta E/\delta \mathrm{pH})_i$ = 85 mV/pH and the Tafel slopes are close to 80 mV/decade, so, an order of 1 is also obtained for this pH range. Only at pH 8 the order in OH^- is difficult to determine. At pH 13, the Tafel slope does not change for different hydrazine concentrations and correspond to a value of 120 mV/decade. The plot (not shown), of log I_p at constant potential versus log $[N_2H_4]$ is linear and the slope is one, so the order on hydrazine is 1 at pH 13. The total number of transfer electrons for hydrazine molecule can be determined from the following equations [10,23]:

$$E_p = K + \left(\frac{0.03}{\alpha n}\right) \log v \qquad (1)$$

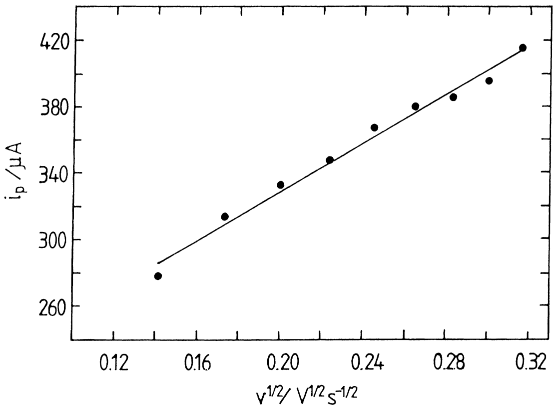

Fig. 6. Plot of I_p vs. $v^{1/2}$ (where v is the scan rate) at pH 13, in the presence of 5 mM of hydrazine, taken from voltammetric profiles. Scan rates from: 0.01 to 0.1 Vs^{-1}.

where v is the potential sweep rate and αn is an irreversibility parameter. K is a constant related to R, T, F, D_0, E^f (formal potential) and k_0 (the standard heterogeneous rate constant).

$$I_p = (2.29 \times 10^5) n (\alpha n)^{1/2} A [N_2H_4] D_0^{1/2} v^{1/2} \qquad (2)$$

where n is the total number of transfer electrons, A is the electrode area and D_0 is the diffusion coefficient. From a plot of I_p (at constant potential) versus $v^{1/2}$ (see Fig. 6) and a plot of E_p versus log v (see Fig. 7) and considering $D_0 = 1.4 \times 10^{-5}\ \mathrm{cm\,s^{-1}}$ [10], it can be estimated n = 3.7 electrons. Therefore, the net

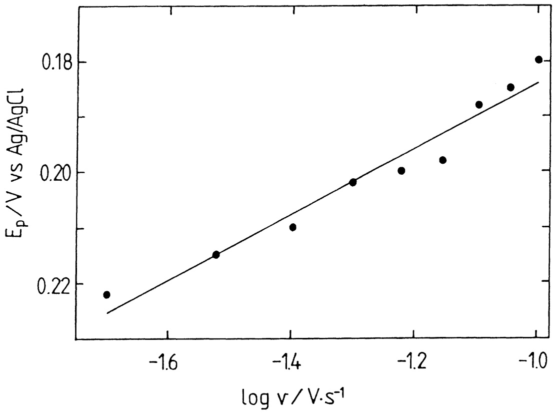

Fig. 7. Plot of E_p vs. log v (where v is the scan rate) at pH 13, in the presence of 5 mM of hydrazine, taken from voltammetric profiles. Scan rates from: 0.01 to 0.1 Vs^{-1}.

reaction at pH 13 is:

$$N_2H_4 + 4OH^- \rightarrow N_2 + 4H_2O + 4e^-$$

On the other hand, the open circuit potential for the polymer modified electrode changes from −0.179 V in the absence of hydrazine (at pH 13) to values between −0.44–0.47 V when in the solution are present variable amounts of hydrazine at the same pH. The open circuit potential obtained in absence of hydrazine would correspond to an interface where the metal is at an oxidation state of II. On presence of hydrazine, the shift of the open circuit potential could be attributed to an electron transfer from the hydrazine to the metal, which changes its oxidation state from II to I. Then, the first electron transfer depending on the applied potential would correspond to the regeneration of the metal as Fe (II), which is able to form an adduct with the hydrazine and in this way, to promote the electro-oxidation [25,27,28]. On the basis of the results shown above, we can postulate a mechanism for the first steps of this oxidation at pH 13:

$$[\mathrm{Fe(II)\text{-}Pc}] + N_2H_4 \leftrightarrow [\mathrm{Fe(I)\text{-}Pc}\cdots N_2H_4{}^+] \quad \left(\frac{k_2}{k_{-2}}\right)$$

$$[\mathrm{Fe(I)\text{-}Pc}\cdots N_2H_4{}^+] + OH^- \leftrightarrow [\mathrm{Fe(I)\text{-}Pc}\cdots N_2H_3] + H_2O \quad \left(\frac{k_1}{k_{-1}}\right)$$

$$[\mathrm{Fe(I)\text{-}Pc}\cdots + N_2H_3] \rightarrow [\mathrm{Fe(I)\text{-}Pc}\cdots N_2H_3] + e^- \quad \text{(r.d.s.)}$$

$$[\mathrm{Fe(I)\text{-}Pc}\cdots + N_2H_3]^+ \leftrightarrow [\mathrm{Fe(II)\text{-}Pc}] + N_2H_2 + H_2O + e^-$$

Finally, Fig. 8 shows a linear relationship between the I_p (current maximum) and the hydrazine concentration in the concentration range 1×10^{-6} and 1×10^{-2} M of hydrazine, at pH 13. From this figure, an order of one in hydrazine and a good and linear behavior between concentration and current for this electro-oxidation can be confirmed. In this way, it can be proposed that the polymer-modified electrode can be used as an amperometric sensor for hydrazine, because its response is high and does not change with time. Obviously, a real sensor needs to respond to the presence of the hydrazine in the same way although there were in the solution, other species. In this way, it can be interesting to form composites with

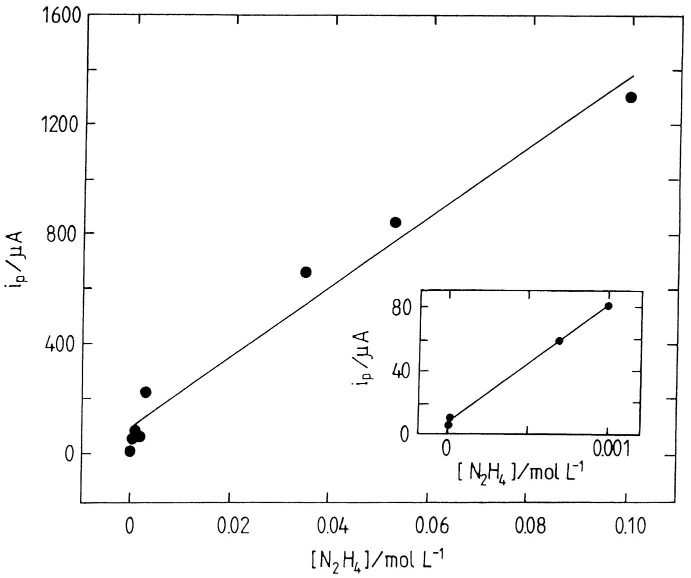

Fig. 8. Plot of I_p vs. hydrazine concentration, taken from voltammetric profiles at pH 13, at 200 mVs^{-1}. On the bottom of the figure there is the first part of it, in another scale to show the linearity at low concentration.

non-active membranes, to increment the selectivity of the polymer.

4. Conclusion

The polymer-modified electrode is a better catalyst for the oxidation of hydrazine than the monomer-modified electrode probably due to the enhanced π-system that act as an electronic density donor to the metal center Fe (II) in the polymer shifting the redox couple Fe(II)/(I) to lower potentials. The hydrazine reduces the metal center Fe (II) of the polymer in absence of applied potential. The role of the potential is the regeneration of the oxidation state (II) of the metal. It was obtained a linear correlation between I_p and hydrazine concentration in a wide range, from 1×10^{-6} to 1×10^{-2} M, at pH 13. In this sense, the polymer-modified electrode could be used as an amperometric sensor of hydrazine.

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