

# Deactivation of Poly(o-Aminophenol) After its Interaction with Ferric Cations: Effects on the Protonation Reaction and Electron Transport

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**Abstract:** The aim of this work was to demonstrate that interaction of ferric cations with poly(o-aminophenol) (POAP) films causes their deactivation. Spectroelectrochemical measurements and rotating disk electrode voltammetry (RDEV) were employed on both freshly prepared and deactivated POAP films. It was observed a reduction (deactivation) of the redox activity of POAP after its treatment with ferric cations. A degree of deactivation of POAP was defined on the basis of the reduction of the voltammetric charge after its interaction with a ferric cation solution. With regard to spectroelectrochemical measurements, absorbance as a function of both wavelength and electrode potential, seem to demonstrate that redox sites of a deactivated POAP film are less protonated than redox sites of a freshly prepared film. RDEV measurements indicate the existence of a slower electron transport in a POAP film treated with a ferric cation solution, as compared with the electron transport in a non-deactivated film.

**Keywords:** Poly(o-aminophenol) films, ferric cations, deactivation, spectroelectrochemistry.

## 1. INTRODUCTION

Oxidation of o-aminophenol on different electrode materials (gold, platinum, carbon, indium-tin oxide, etc.) in aqueous acid medium was shown to form poly-o-aminophenol (POAP) [1, 2]. POAP exhibits its maximal electroactivity within the potential range  $-0.2 \text{ V} < E < 0.5 \text{ V}$  (vs. SCE) at  $pH$  values lower than 3 [3]. This electroactivity was explained by a redox mechanism which involves an addition/elimination of protons coupled with a reversible electron transfer [3, 4]. With regard to this electroactivity, we have shown that POAP is able to suffer deactivation when the polymer being subject to rough conditions, such as, prolonged potential cycling [5], excessive positive potential limits [6] and contact with solutions of high  $pH$  values [7]. In [8] it was also demonstrated that a POAP film can be deactivated by soaking during several hours into a 50 mM  $\text{Fe}_2(\text{SO}_4)_3$  solution. This effect was detected by the attenuation of the voltammetric response of POAP [8]. Deactivation of POAP after contact with a ferric cation solution was explained on the basis of the ability of the polymer to capture metal ions because of the simultaneous presence of hydroxyl and amino groups, whose lone pair electrons is available to coordinate with the metal ions [8, 9]. In [8] was suggested that this interaction, prevents the redox reaction of POAP because redox sites cannot accept protons. The aim of this work is demonstrate that this deactivation of POAP affects both its protonation reaction and the electron transport across the polymer. To this end two types of experiments were performed: firstly, spectroelectrochemical measurements in the only presence of the supporting electrolyte solution and then Rotating Disc Electrode Voltammetry (RDEV) in the

presence of an electroactive substance, such as *p*-hydroquinone, where POAP acts as mediator in its reduction reaction [10]. This work can be considered as complementary of those reported in [5-7], where de-activation of POAP caused by other external variables was studied.

## 2. EXPERIMENTAL

Two types of base electrodes were employed to deposit POAP films. Semi-transparent gold films were employed as base electrodes in spectroelectrochemical measurements. This base gold semi-transparent electrode (about 7 nm thick) was obtained by vacuum deposition onto an optically polished glass slide [11]. The area of the gold film electrode was  $0.56 \text{ cm}^2$ . A rotating gold disc electrode (RDE) was used as base electrode to deposit POAP films in RDEV measurements. This RDE consisted of a gold rod press-fitted with epoxy resin into a Teflon sleeve so as to leave a disc area  $0.56 \text{ cm}^2$  exposed. The gold electrode was carefully polished with emery paper of decreasing grit size followed by alumina suspensions of size 1, 0.3 and  $0.05 \mu\text{m}$ , respectively, until a mirror-like finish was obtained. Then, it was submitted to ultrasonic cleaning to remove residual abraded polishing material. In order to obtain a more specular and reproducible gold surface to deposit POAP films, a gold film of about 100 nm of thickness was deposited by vacuum evaporation ( $\sim 10^{-7}$  Torr) on the gold disc [11].

### 2.1. Freshly Prepared POAP films

POAP films were grown on both types of base electrodes by employing Cyclic Voltammetry (CV), as described in [1]. That is, by immersing the bare electrodes in a  $10^{-3} \text{ M}$  *ortho*-aminophenol + 0.4 M  $\text{NaClO}_4$  + 0.1 M  $\text{HClO}_4$  solution and cycling the potential between  $-0.25$  and  $0.8 \text{ V}$  (vs. SCE) at a scan rate  $\nu = 0.05 \text{ V s}^{-1}$ . In order to obtain a measure of the polymer thickness, these POAP coated gold film electrodes were then rinsed and transferred to the supporting electrolyte solution ( $0.4 \text{ M NaClO}_4 + 0.1 \text{ M HClO}_4$ ) free of mo-

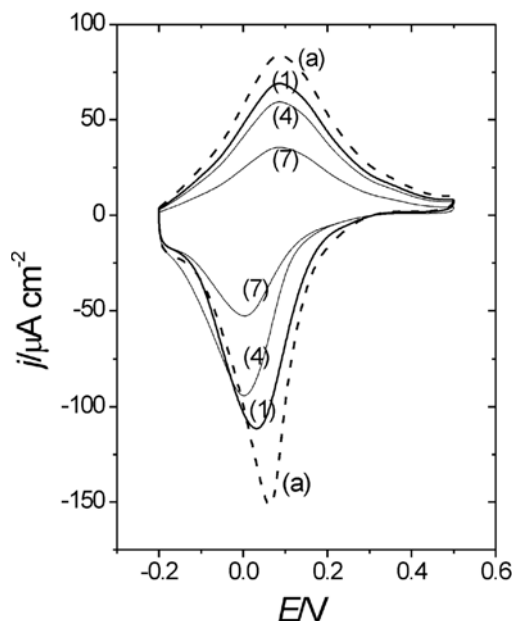
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nomer where the voltammetric reduction charge  $Q_c^0$  was obtained by integration the cathodic current of the voltammetric response. Values of  $Q_c^0 = 2.8 \text{ mC cm}^{-2}$  were employed in this work. This  $Q_c^0$  value corresponds to a POAP thickness ( $\phi_p$ ) value around  $\phi_p \sim 60 \text{ nm}$  [1,6]. These POAP films are referred to as freshly prepared ones. All electrode potentials reported in this work are referred to the SCE.

## 2.2. Deactivated POAP Films

Freshly prepared POAP films deposited on both types of base electrodes above mentioned, were deactivated by soaking in a  $0.1 \text{ M H}_2\text{SO}_4 + 0.05 \text{ M Fe}_2(\text{SO}_4)_3$  solution.

These POAP films are referred to as deactivated films. In this sense, when these films are transferred again to the supporting electrolyte solution, an attenuation of their voltammetric response was observed, as compared with the response of the film before the treatment with a ferric cation solution (Fig. 1). Thus, the voltammetric reduction charge  $Q_c$  of these films are lower than that of a freshly prepared one ( $Q_c < Q_c^0$ ) (see third column of Table 1). Ten freshly prepared POAP films were deactivated by immersion in the ferric cation solution. Each one of them was soaked in the ferric cation solution for a different time period (see second column of Table 1). Then, several  $Q_c$  values, representing different degrees of de-activation, were obtained.



**Fig. (1).** Voltammetric ( $j$ - $E$ ) responses for  $2.8 \text{ mC cm}^{-2}$  thick POAP films: (a) a freshly prepared POAP film. Number (1), (4) and (7) correspond to POAP films with different degrees of deactivation. (See Table 1). Electrolyte:  $0.1 \text{ M HClO}_4 + 0.4 \text{ M NaClO}_4$ . Scan rate  $0.01 \text{ V s}^{-1}$ .

## 2.3. Spectroelectrochemical Experiments

The spectroelectrochemical cell was a rectangular cuvette to which two glass slides (one of them containing the transparent gold electrode) were attached at opposite ends. The lid of the cell supported both, the reference electrode and the auxiliary electrode, and also it had a provision for bubbling nitrogen gas. The electrodes were arranged so as not to disturb the light beam path through the cell. POAP films were

deposited on the gold thin film electrodes and absorption spectra were recorded. Then, these films were deactivated as described above, and again absorption spectra were recorded. Two types of spectroelectrochemical experiments were carried out: (i) at fixed wavelength ( $\lambda$ ), the electrode potential ( $E$ ) was swept at scan rates comprised between  $5 \times 10^{-3}$  to  $3 \times 10^{-2} \text{ V s}^{-1}$  and (ii) at constant electrode potential, the wavelength was scanned at a rate of 256 points per second. The absorbance reading was corrected by subtracting the absorbance value of the transparent gold electrode in the same solution. The spectrophotometer was a rapid scan Hewlett-Packard Model 8452.

**Table 1.**  $Q_c$  Values for Different De-Activated POAP Films

*POAP film	<sup>b</sup> t/hs	<sup>c</sup> $Q_c/\text{mC cm}^{-2}$
1	2	2.44
2	4	2.30
3	5	2.10
4	10	2.06
5	16	1.88
6	21	1.72
7	24	1.38
8	35	1.23
9	40	1.12
10	44	1.06

<sup>a</sup>Numbers (1) to (10) in column 1 indicate different POAP films.

<sup>b</sup>Different soaking times of films indicated in column 1 in a  $0.1 \text{ M HClO}_4 + 0.4 \text{ M NaClO}_4 + 0.05 \text{ M Fe}_2(\text{SO}_4)_3$  solution.

<sup>c</sup>Voltammetric reduction charge for each one of the deactivated POAP films indicated in column 1.

## 2.4. RDEV Experiments

With freshly prepared POAP films immersed in a  $0.1 \text{ M HClO}_4 + 0.4 \text{ M NaClO}_4 + 2 \times 10^{-3} \text{ M p}$ -benzoquinone (pQ) solution, stationary current-potential ( $I$ - $E$ ) curves at different electrode rotation rates  $\Omega$  were recorded at potential values  $E < 0.0 \text{ V}$ . From these  $I$ - $E$  curves, cathodic limiting current vs. electrode rotation speed ( $I_{\text{lim,c}}$  vs.  $\Omega^{1/2}$ ) dependencies were obtained. Then, these films were extracted from the solution containing pQ and they were deactivated as indicated above. Then, these deactivated POAP films were subjected to the same RDEV experiment in the presence of the solution containing pQ, as described for freshly prepared films, and again stationary current-potential ( $I$ - $E$ ) curves at different electrode rotation rates  $\Omega$  were recorded. From these curves  $I_{\text{lim,c}}$  vs.  $\Omega^{1/2}$  dependencies were obtained.

Steady-state measurements were performed using a PAR model 173 potentiostat and a PAR Model 175 function generator, were used. A X1-X2-Y Hewlett-Packard Model 7046 B Plotter was used to record the  $I$ - $E$  responses. The electrode rotation speed  $\Omega$  was controlled with a home-made equipment that allows one to select a constant  $\Omega$  in the range  $50 \text{ rev min}^{-1} < \Omega < 8000 \text{ rev min}^{-1}$ . This was periodically controlled with a digital phototachometer (Power Instruments Inc., model 891). CV experiments were also performed with the same potentiostat and function generator.

## 2.5. Chemical and Electrolyte Solutions

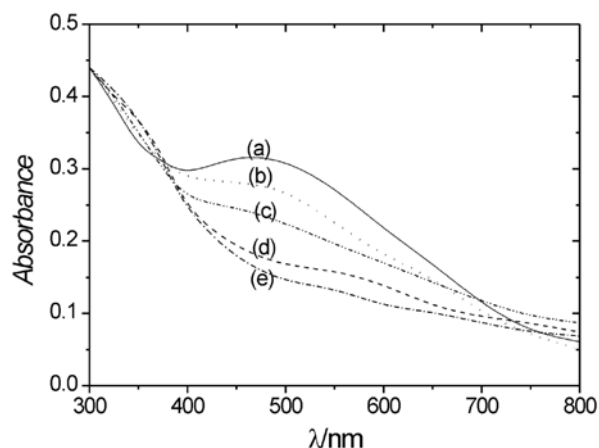
AR grade chemicals were used throughout. *o*-aminophenol (Fluka) was purified as described elsewhere [1,3]. HClO<sub>4</sub> and NaClO<sub>4</sub> Merck were used without further purification. Benzoquinone Merck were also used without purification. Ferric sulfate Mallinckrodt analytical reagent grade, was employed in preparing the corresponding solutions. The solutions were prepared with water purified using a Millipore Milli-Q system.

## 3. RESULTS AND DISCUSSION

POAP films employed in this work were synthesized under different electrochemical conditions as those reported in [8], that is, in a different electrolyte medium and by cycling the potential within a different potential region (*vs.* SCE). Then, in order to verify the cation capturing ability of our POAP films, XPS spectra were obtained and also their potential responses to iron cations in solution, were examined as in [8]. XPS spectra of our POAP films after soaking in a ferric cations solution were almost the same as that shown in [8]. Also, with our POAP films, potentiometric experiments were performed in solutions containing Fe(II) and Fe(III), respectively, as described in [7]. That is, when the potential (*E vs.* SCE) for deactivated POAP films was measured as a function of the cation concentration in these solutions, no potential response was observed to Fe(II) ions. However, when the same experiment was repeated in the presence of solutions containing different concentrations of Fe(III) ions, a Nernstian potential response to Fe(III) in solution was found. The response time of our electrodes was around 25 seconds and the slope of the linear response (*E vs.* log [Fe(III)]<sub>sol</sub>) was about 0.06 V. This linear behavior was observed up to a concentration about 10<sup>-4</sup> M of ferric cation. These results are not shown here because they are in coincidence with those reported in [8].

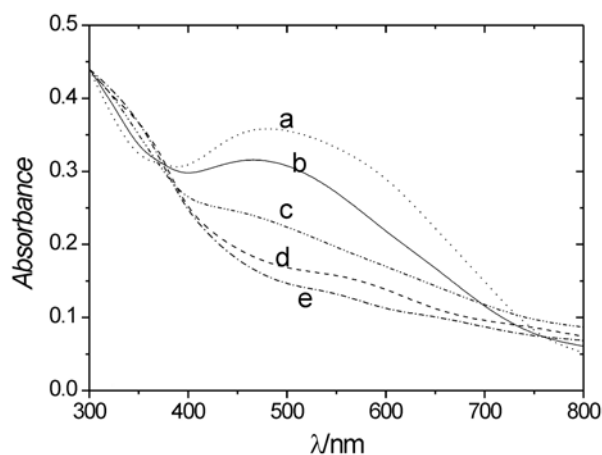
### 3.1. Spectroelectrochemical Measurements

In [4] we have reported an optical study in the UV-Vis region of POAP films contacting solutions of different *pH*. Fig. (2) shows the absorbance as a function of the wavelength when a freshly prepared POAP film at *pH* 1 goes from the reduced (*E* = -0.2 V) to the oxidized state (*E* = 0.5 V).

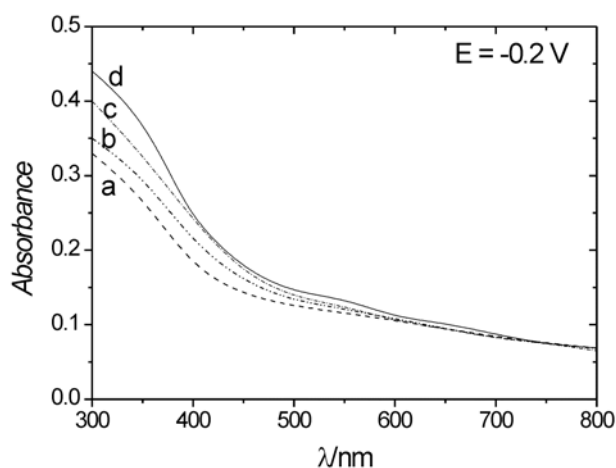


**Fig. (2).** Absorbance as a function of wavelength ( $\lambda$ ) at constant electrode potentials, *E*: (a) 0.5 V, (b) 0.2 V, (c) 0.0 V, (d) -0.1 V, (e) -0.2 V. A freshly prepared film with  $Q_c = 2.8 \text{ mC cm}^{-2}$ . Electrolyte: 0.1 M HClO<sub>4</sub> + 0.4 M NaClO<sub>4</sub>.

Fig. (3) shows the absorbance as a function of the wavelength when a deactivated POAP film ( $Q_c = 1.72 \text{ mC cm}^{-2}$ ) goes from the reduced (*E* = -0.2 V) to the oxidized state (*E* = 0.5 V). As for a freshly prepared film [4], Fig. (3) shows a broad band at about 450 nm, which increases with oxidation together with a decrease of the absorbance between the two isosbestic points placed at 310 nm and 375 nm, respectively. Even when the shape of the spectrum of a deactivated film (Fig. 3) is qualitatively similar to that of a freshly prepared one at the same *pH* (Fig. 2), absorbance values result higher than those values corresponding to a freshly prepared film. This effect can be seen in more detail when spectra at the reduced state (*E* = -0.2 V) of different deactivated POAP films whose degree of deactivation increases ( $Q_c = 2.30, 2.10$  and  $1.72 \text{ mC cm}^{-2}$ ) are compared with the spectrum of a freshly prepared film (Fig. 4). In Fig. (4) it is observed an increase of the *uv* tail with increasing the degree of deactivation. The increase of the *uv* tail can be explained by a red shift of the band due to an increase of the auxocro-



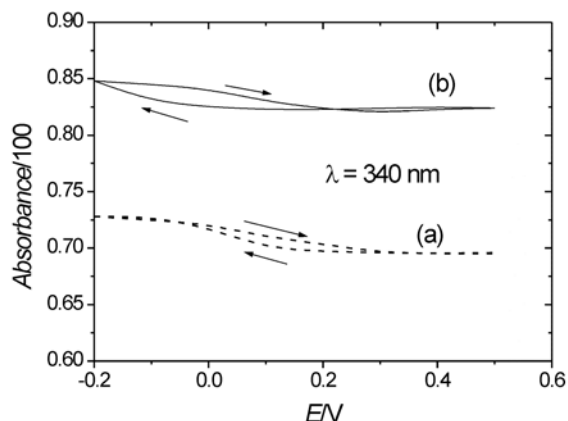
**Fig. (3).** Absorbance as a function of wavelength ( $\lambda$ ) at constant electrode potentials, *E*: (a) 0.5 V, (b) 0.2 V, (c) 0.0 V, (d) -0.1 V, (e) -0.2 V. Deactivated film with  $Q_c = 1.72 \text{ mC cm}^{-2}$ . Electrolyte: 0.1 M HClO<sub>4</sub> + 0.4 M NaClO<sub>4</sub>.



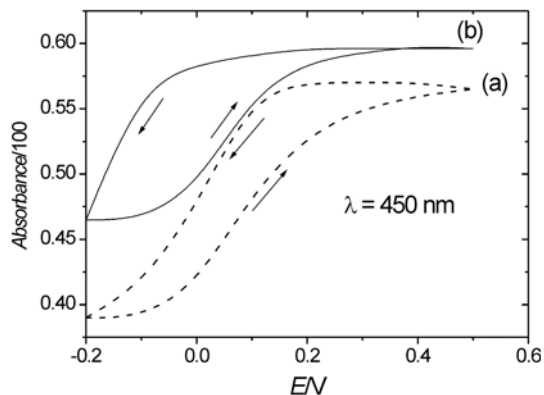
**Fig. (4).** Absorbance as a function of wavelength ( $\lambda$ ) at *E* = -0.2 V for a freshly prepared film (a) and three different deactivated films with  $Q_c$  values (b) 2.30, (c) 2.10 and (d)  $1.72 \text{ mC cm}^{-2}$ . Electrolyte: 0.1 M HClO<sub>4</sub> + 0.4 M NaClO<sub>4</sub>.

mic effect of the amino group as they become less protonated [4]. Furthermore, in de-activated films this effect is followed by a slight absorption increase in the wavelength region comprised between 400 nm and 800 nm (Fig. 4). The broad adsorption increase can be attributed to residues of the oxidized forms which are not completely reduced at -0.2 V, as the content of protons decreases [4]. Then, by comparing optical experiments performed in [4] with the present ones it can be concluded that the increase of the content of iron ions in POAP films causes similar spectra changes as the increase of the solution *pH*. That is, as the content of iron ions increases, amine groups of POAP should become less protonated.

With regard to optical measurements as a function of the electrode potential, Figs. (5 and 6) show a comparison of absorbance vs. *E* for a deactivated POAP film and a freshly prepared one at  $\lambda = 340$  nm and  $\lambda = 450$  nm, respectively. The absorbance at  $\lambda = 340$  nm decreases, as *E* increases in the positive direction, showing the disappearance of the reduced form of POAP. On the contrary, absorbance at  $\lambda = 450$  nm increases in the same potential direction, indicating the appearance of the oxidized form.

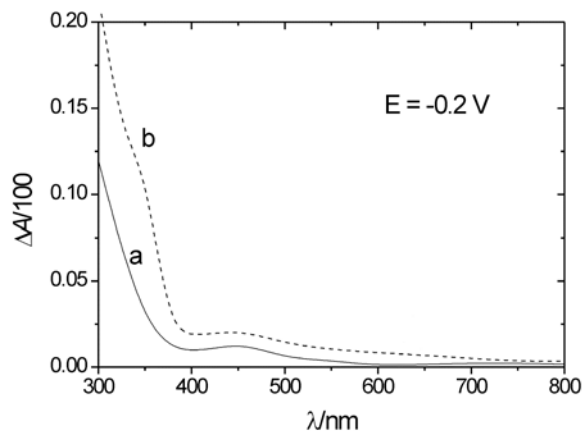


**Fig. (5).** Absorbance as a function of potential, *E*, at constant wavelength ( $\lambda = 340$  nm) for a (a) freshly prepared film and (b) deactivated film  $Q_c = 1.06$  mC cm<sup>-2</sup>. The arrows indicate the potential scan direction. Scan rate:  $\nu = 0.01$  V s<sup>-1</sup>. Electrolyte: 0.1 M HClO<sub>4</sub> + 0.4 M NaClO<sub>4</sub>.



**Fig. (6).** Absorbance as a function of potential, *E*, at constant wavelength ( $\lambda = 450$  nm) for a (a) freshly prepared film and (b) deactivated film  $Q_c = 1.06$  mC cm<sup>-2</sup>. The arrows indicate the potential scan direction. Scan rate:  $\nu = 0.01$  V s<sup>-1</sup>. Electrolyte: 0.1 M HClO<sub>4</sub> + 0.4 M NaClO<sub>4</sub>.

For freshly prepared POAP films, both absorbances, at 340 and 450 nm, present sigmoidal shapes with inflexion points at about 0.1 V during the scan in the positive potential direction. Also, both absorbances exhibit a hysteresis during the potential scan in the negative direction, in such a way, that inflexion points for the curves corresponding to the scan in the negative potential direction, are shifted to more negative potential values ( $E = 0.075$  V). In previous work [4], it was demonstrated that this hysteresis increases as the solution *pH* increases. This hysteresis was attributed to the difficulty in reducing the non-protonated imine groups of oxidised POAP [4]. Then, similar effects are observed in Figs. (5 and 6) with the content of iron ions. That is, absorbances, at the same wavelengths, for a deactivated film exhibit a more marked hysteresis, as compared with those for a freshly prepared one. At the same time, a shift of inflexion points towards more negative potential values is observed for the curves corresponding to a deactivated film as compared with those of a freshly prepared one. Again, this effect is indicative of a major difficulty to reduce nonprotonated groups in a deactivated film as compared with a freshly prepared one. On the basis of Absorbance vs. *E* dependencies at different  $\lambda$  during potentiodynamic scans, the difference of absorbances ( $\Delta A$ ) between different deactivated films ( $Q_c = 1.06$  mC cm<sup>-2</sup> and  $Q_c = 2.3$  mC cm<sup>-2</sup>) and a freshly prepared were calculated and compared for the reduced state of POAP (Fig. 7). An increase of the *uv* tail followed by a slight increase of the absorption in the region between 400 and 800 nm was observed. A similar result was reported in [4] for a freshly prepared POAP film contacting solutions of different *pH* values. Then, in the present work, the increase in the *uv* tail as the content of iron ions increases, can be explained on the basis of the presence of less protonated amine groups in a deactivated film. All these optical results confirm that interaction of POAP with iron ions indeed restricts its protonation reaction [8].

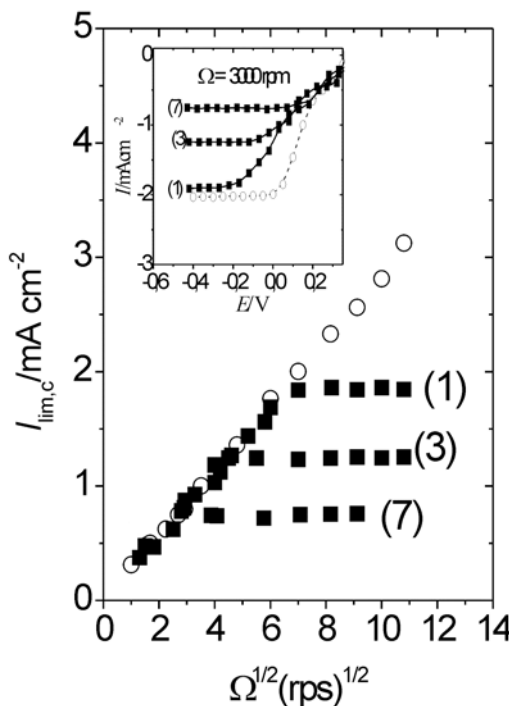


**Fig. (7).** Difference spectra,  $\Delta A$ , between the absorbances of: a deactivated film with  $Q_c = 2.30$  mC cm<sup>-2</sup> and a freshly prepared one (a) and a deactivated film with  $Q_c = 1.06$  mC cm<sup>-2</sup> and a freshly prepared one (b), as a function of  $\lambda$ .  $E = -0.2$  V. Electrolyte: 0.1 M HClO<sub>4</sub> + 0.4 M NaClO<sub>4</sub>. Scan rate:  $\nu = 0.01$  V s<sup>-1</sup>.

### 3.2. RDEV Measurements

Also, in these experiments ten POAP coated rotating gold disk electrodes were employed. The degree of de-activation ( $Q_c$ ) of each one of them is indicated in Table 1.

The discharge process of *p*-benzoquinone (pQ) at freshly prepared POAP films, was studied in a previous work [10]. Cathodic limiting currents ( $I_{\text{lim,c}}$ ) at  $E < 0.0$  V for the pQ reduction were related to a rapid electron-transfer mediation at the POAP|redox active solution interface. Then, in this work  $I_{\text{lim,c}}$  was obtained as a function of  $\Omega^{1/2}$  for different deactivated films. The inset in Fig. (8), shows that at a given electrode rotation rate value, as the more deactivated becomes the polymer film the lower is the limiting current value ( $I_{\text{lim,c}}$ ). As can be seen from Fig. (8), within a wide range of  $\Omega$  values freshly prepared film exhibit a linear  $I_{\text{lim,c}}$  vs.  $\Omega^{1/2}$  dependence (empty circles), which follows the Levich equation.

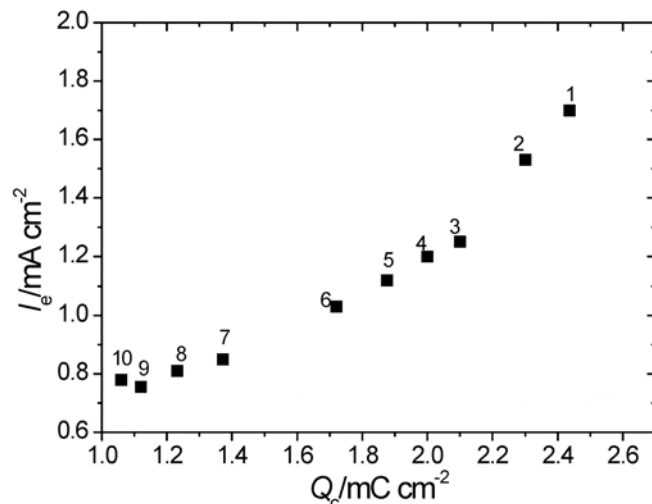


**Fig. (8).** Levich representations  $I_{\text{lim,c}}$  vs  $\Omega^{1/2}$  for POAP films contacting a 0.1 M HClO<sub>4</sub> + 0.4 M NaClO<sub>4</sub> +  $2 \times 10^{-3}$  M (pQ) solution. (O) a freshly prepared POAP film; (1), (3) and (7) correspond to same three deactivated films indicated in Table 1.  $E = -0.2$  V. Inset: steady-state ( $I$ - $E$ ) curves for potential values  $E < 0.2$  V at  $\Omega = 3000$  rpm. The same films indicated above.

However, for deactivated films after a certain  $\Omega$  value, a constant limiting current value  $I_{\text{lim,c}}$  independent of  $\Omega$ , is achieved. These constant  $I_{\text{lim,c}}$  values can be related to maximum rates for the electron transport across the polymer film. That is, as one increases the flux of pQ (increase of  $\Omega$ ) from the bulk solution, if this flux exceeds the supply of electrons from the electrode through the polymer to the electrolyte interface, the rate limiting step will shift from the limiting transport of pQ ( $I_{\text{lim,c}}$ ) to the limiting transport of the electron charge ( $I_e$ ) through the polymer. Under these conditions, when  $I_{\text{lim,c}}$  becomes independent of  $\Omega$  it can be replaced by  $I_e$  ( $I_{\text{lim,c}} = I_e$ ). Then, it is observed that as the POAP film being deactivated more, a change in the rate limiting process during the mediated electron-transfer reaction is detected at lower electrode rotation rates. These results can be interpreted on the basis of Eq. (1) [12]:

$$I_e = n F A D_e (c/\phi_p) \quad (1)$$

In Eq. (1),  $c$  is the concentration of active redox sites of the polymer and  $\phi_p$  the polymer film thickness.  $D_e$  represents a measure of the electron hopping rate and  $n$  express the numbers (fractions) of unit charges per monomer unit of the polymer.  $A$  is the electrode area and  $F$  the Faraday's constant. As can be seen from Fig. (9),  $I_e$  decreases as  $Q_c$  decreases, that is, as the film becomes deactivated more. According to Eq. (1), the decrease of  $I_e$  can be attributed to both, a slower electron transport across the polymer film (decrease of  $D_e$ ) and also to a lower  $c$  value, as the polymer becomes deactivated more. The last effect can be adjudicated to deactivation of redox sites of POAP by interaction with iron ions, which hinders the protonation reaction of redox sites, and then redox sites become inactive. This effect should reduce the number of active sites ( $c$ ). However, it also should affect  $D_e$ . In this sense, the electron diffusion coefficient,  $D_e$ , has been expressed in terms of the mean distance between adjacent active redox sites [13], according to  $D_e = (a^2 k_0)$ .  $k_0$  is the intermolecular electron-transfer rate constant and  $a$  is the mean distance between two adjacent redox sites. The hopping rate  $k_0$  exhibits an exponential dependence on  $a$ , through the energy  $[-U(x+a)]$  of a state with an electron in the position  $x$  along the current direction [13]. That is, the principal effect of the hopping distance  $a$  on  $D_e$  proceeds from the exchange rate. In this sense, the effect of increase the mutual separation  $a$  between adjacent active redox centers is to decrease the exchange rate  $k_0$ , which in turn should lead to a  $D_e$  decrease. Then, interaction of iron ions with redox sites of POAP not only reduces  $c$ , but also creates inactive gaps within the redox sites configuration of POAP, which increases the distance among even active redox sites. This should lead to a decreasing value of  $D_e$ . Thus, even when the decrease of  $I_e$  with increasing the deactivation should be related to  $c$  and  $D_e$  decrease, we are not able to separate the corresponding contributions. However, as the transition at which the cathodic limiting current becomes independent of  $\Omega$  occurs at much lower  $\Omega$  values when deactivation is increased, our interpretation of a change in the rate limiting process during mediated electron-transfer reaction seems to be correct. Thus, these RDEV experiments seem to demonstrate the existence of an effect of deactivation on the electron transport within the polymer film. Eq. (1) can be



**Fig. (9).**  $I_e$  vs.  $Q_c$  dependence for deactivated POAP films. Numbers 1 to 10 indicate the different deactivated films in Table 1.

used to estimate a maximum  $D_e$  value for our deactivated films employing  $\phi = 60$  nm, a value of  $c = 4.3$  M [3],  $n = 0.44$  [10] and values of  $I_0/A \sim 1-2$  mA cm<sup>-2</sup> (Fig. 9).  $D_e$  results of the order of  $10^{-11}$  cm<sup>2</sup> s<sup>-1</sup>. This value is near one order of magnitude lower than that obtained for films freshly prepared by employing other techniques of measure [14]. It is evident that microscopic interpretation of the diffusion coefficient will clearly be dependent on the model used to describe the charge propagation in electroactive polymers. Thus, the rate of charge transport is usually characterized by an apparent diffusion coefficient ( $D$ ) which can vary over several orders of magnitude for these materials (*i.e.*  $10^{-7}$  to  $10^{-14}$  cm<sup>2</sup> s<sup>-1</sup>) and the factors governing the magnitude of  $D$  are not well understood.

## CONCLUSION

In this work spectroelectrochemical measurements and Rotating Disk Electrode Voltammetry were employed to demonstrate that deactivation of poly-*o*-aminophenol after contact with a ferric cation solution affects both, its protonation reaction and also the electron transport rate across the film. By comparing spectroelectrochemical data obtained in this work for different deactivated films, with those obtained in a previous work [4] with freshly prepared films contacting solutions of different *pH* values, it was concluded that deactivation of poly-*o*-aminophenol yields an inhibition of its protonation reaction. Also, by comparing rotating disc electrode voltammetry results obtained in this work for deactivated poly-*o*-aminophenol films contacting a redox active solution containing p-benzoquinone, with those reported in other work [10] relative to freshly prepared films in contact with the same active solution, it was concluded that interaction of ferric cations reduces the electron transport rate of poly-*o*-aminophenol film electrodes.

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