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Effect of the potential on the electrochemically induced ageing of polyaniline films

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ABSTRACT

The electrochemically induced ageing of polyaniline films, as a function of the ageing potential, was investigated employing films of different thicknesses in 3.7 M H_2SO_4 solutions. The ageing process was monitored by the change of the voltammetric response in a subsequent positive going potential scan after the ageing. It is observed that the ageing process, at more positive potentials, involves increasing amounts of non-reduced polymer. Also, it is observed that the rate of ageing decreases as the ageing potential increases. The changes in the voltammetric response after ageing is interpreted through a model for the voltammetric response, previously developed, that includes capacitive currents and interactions between the redox centers. The analysis shows that neither the capacitive parameters nor the total faradaic charge change during the ageing. On the other hand, only the interaction energy between the reduced centers change during the ageing. This fact leads to a narrowing of the formal redox potential distribution that can be characterized by the apparent number of exchanged electrons. The decrease of the interaction energy between reduced centers is consistent with the reduction of the free energy of the polymer during the ageing. The kinetics of ageing is analyzed through an Elovich type of equation from which k_0, the *pseudo* zero order rate constant and β, a parameter that indicates how fast the activation free energy changes with the extent of the process, can be obtained.

1. Introduction

The term *physical ageing* is employed to describe a process in which amorphous materials irreversibly go through slow structural modifications after being cooled below the glass transition temperature [1]. During the physical ageing, the variation of several properties of the material (such as specific volume, enthalpy and entropy) is linear with the logarithm of the ageing time [2], thus suggesting that only structural changes occurs during the process. Of course, heating the material again erases all memory of the ageing process. When certain electrochemically active polymers, i.e. polymers that can reversible oxidized and reduced, mostly conducting polymers (CPs), are submitted to a suitable reductive potential, undergo a process that have many similarities with the phenomenon of physical ageing. Thus, after ageing the subsequent electrochemical oxidation shows changes in the current peak and the peak potential, a decrease in the specific volume, changes in the ESR and UV–Vis response, etc. The most striking similarity between physical and "electrochemical" ageing is that the mentioned changes are linearly related to the logarithm of the ageing time. This particular kinetic feature indicates that both phenomena (physical and electrochemical) are self-inhibiting. Here again, the polymer oxidation erases all traces of the ageing process. Although this electrochemical ageing has received many names such as "slow relaxation", "memory effect", and "first cycle effect", we proposed [3] the term "Electrochemically Induced Ageing" (*EIA*) to refer to this phenomenon in order to enforce the idea that the condition at which the polymer ages is achieved by an electrochemical perturbation and that is a physical ageing process.

Many workers have studied the *EIA* [3–45]. Several explanations and models have been proposed to explain this behavior [24–34]. Besides voltammetry [3–23], electrochemical ageing have been studied by numerous "in situ" techniques: ERS [9], injection/ejection of protons [35], volume changes [36,37], UV–Vis spectra [38–40], XPS [41], EIS [42] and other studies such as the effect of the pH [43], the temperature[44], and the effect of substituents on the ageing rate [45].

As it was said above, the *EIA* of CPs has been often studied measuring the changes in the voltammetric peak parameters j_p and E_p during the first voltammetric potential scan in the positive direction (the *first cycle*) after the ageing. This electrochemical response gives a typical kinetic behavior in which the property being monitored (i.e. j_p or E_p) changes linearly with the logarithm of the ageing time. This behavior indicates that the modifications of the peak parameters are related to the changes that happen during the *EIA*.

However, the relationship between the changes in the voltammetric response and the ageing process is complex because the electrochemical response of CPs contains an indeterminate amount

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of capacitive contribution, and even the faradaic contribution cannot be considered as an ideal Nernstian process [46,47]. Previously, it was published a model that takes into account not only the capacitive contribution, but also the presence of interactions between redox centers to formally represent the voltammetric response [3,47]. In the present work this model is employed to interpret the changes in the voltammetric parameters during the ageing process, focussing on the effect of the ageing potential on the *EIA*.

2. Experimental

A conventional three-electrode glass cell was employed for the electropolimerization procedure and the electrochemical measurements. The working electrode was a 0.05 cm diameter Au wire of 0.154 cm^2. The auxiliary electrode was a cylindrical Pt foil. The reference electrode was a Saturated Calomel Electrode (SCE). All potentials in the text, *E*, are referred to this electrode. Conventional voltammetry was performed using a Teq_02 potentiostat.

The polymer films were synthesized by electropolymerization from 0.5 M aniline (Fluka-Garantie, puriss. p.a. previously distilled under reduced pressure) solutions in 3.7 M H_2SO_4 (Backer, p.a.).

The deposition procedure was performed by cycling the potential at $v = 0.100$ V s^{-1}, between −0.200 V vs. SCE, and the potential corresponding to that of the beginning of the oxidation of the monomer, around 0.800 V vs. SCE, as described before [16]. The film characterization was performed by voltammetry in 3.7 M H_2SO_4 solutions by cycling the potential at $v = 0.100$ V s^{-1} between −0.200 V and 0.450 V.

In a typical ageing experiment, the potential was cycled until a steady voltammogram was reached. Then, during the cathodic scan the sweep was stopped and held at the ageing potential (E_a) during a variable time ($0\ s < t_a < 1000\ s$), being t_a the ageing time. After each ageing time, the scan was restarted in the positive direction, recording the *first cycle*. E_a was comprised between −0.200 V and 0.000 V.

The voltammetric charge of the films employed in this work, $Q_T(0.45)$, was determined from the integration of the anodic *j*/*E* profiles of the voltammetric response in the potential range comprised between −0.200 and 0.450 V vs. SCE at $v = 0.1$ V s^{-1}. The voltammetric charges employed in this work are in the range comprised between $20.0\ mC\ cm^{-2} < Q_T(0.45) < 95.0\ mC\ cm^{-2}$. The voltammetric charge will be employed as a measure of the film thickness. This can be estimated from data previously obtained for Pani and other substituted arylamine polymers, by ellipsometry [48–50]. Employing the relation thickness/charge reported by Zerbino et al., for a related polymer such as poly methylaniline [50], these film thicknesses would correspond to 1200–5700 nm.

3. Results

Fig. 1 shows the steady voltammetric anodic response of a Pani film for different negative potential limits. It is seen that the peak current decreases as this limit increases. However, all the voltammetric traces end at the same current value. This means that at the upper potential limit, the amount of oxidized polymer, which is proportional to Q^0 (see below), is the same irrespective of the negative potential limit. In turn, this means that as the negative potential limit increases the amount of reduced polymer, during the cathodic scan, is slightly smaller and therefore the oxidation charge becomes also smaller.

Fig. 2 shows the voltammetric response of the first cycle after waiting for increasing ageing times, t_a, at three different ageing potentials, E_a, for a Pani film $Q_T(0.45) = 92.9\ mC\ cm^{-2}$, in 3.7 M H_2SO_4 solution. As it can be observed, the qualitative behavior is

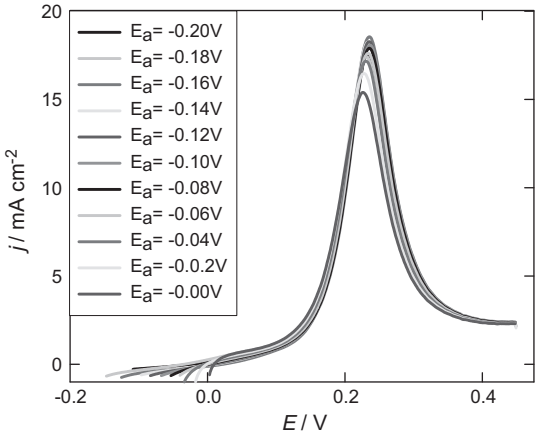

Fig. 1. Stationary anodic *j*/*E* response of a Pani film for different negative potential limits (E_a) (see the box) in 3.7 M H_2SO_4. $Q_T(0.45) = 21.5\ mC\ cm^{-2}$, $v = 0.100$ V s^{-1}.

the same at the three potentials: the anodic peak current increases with the ageing time and the corresponding peak potential moves in the positive direction. Note that it does not no matter what the E_a value is, the current at the positive potential limit is the same for the different ageing times; what it means that the amount of oxidized polymer at this potential does not change after ageing. Fig. 3 shows the evolution of those peak parameters as a function of the logarithm of the ageing time for a Pani film aged at different potentials.

EIA is characterized by showing a nearly linear dependence of j_p and E_p on the logarithm of the ageing time, t_a [47 and references therein]. As it was mentioned at the introduction, this kinetic behavior is also characteristic of the physical ageing of amorphous solids. In the literature of physical ageing, the rate of ageing is defined as the slope of these semi-logarithmic plots [1,2]. So, it is possible to define a rate of *EIA* in terms of the anodic peak current in the same way as it is defined for the specific volume or fluorescence emission for the physical ageing [1,2,51–53].

$$r_a^j = \frac{1}{j_{p,0}} \frac{\partial j_p}{\partial \ln(t_a)} \tag{1}$$

where $j_{p,0}$ is the peak current for the steady voltammogram. Although it is not a true rate in a kinetic sense, it results to be a useful parameter that allows characterizing and comparing the temporal evolution of the *EIA*. In Fig. 4 are shown the values of this rate, for different films at different ageing potentials. The ageing rate defined by Eq. (1) decreases as the ageing potential is increased. To interpret the changes observed in the voltammetric response, in the frame of the physicochemical processes involved, a suitable model is needed. The analysis of these experimental data within the model previously presented is the subject of the next section [47].

4. Discussion

4.1. A Model for the voltammetric response and the EIA

The voltammetric response of CPs is complex because the total current contains a capacitive current contribution that cannot be separated from the faradaic current just employing the voltammetric information.

In the model previously presented [47], the voltammetric total charge is considered to be composed by a capacitive charge as well as a faradaic charge. The capacitance is considered to be propor-

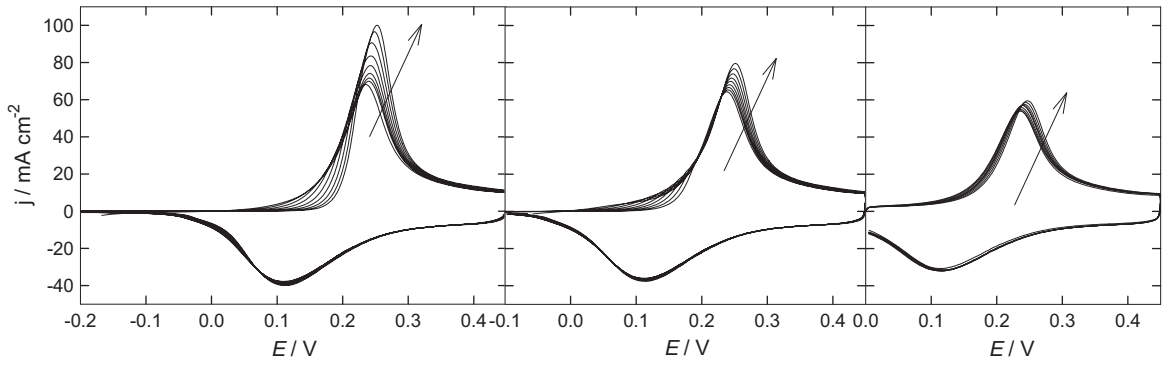

Fig. 2. Current–potential response after different ageing times, t_a/s = 0, 6, 12, 24, 48, 96, 192, 384, 768 at E_a = −0.200 V (left); −0.100 V (center); and 0.000 V (right). $Q_T(0.45)$ = 92.9 mC cm^{-2}. Arrows indicate increasing ageing times.

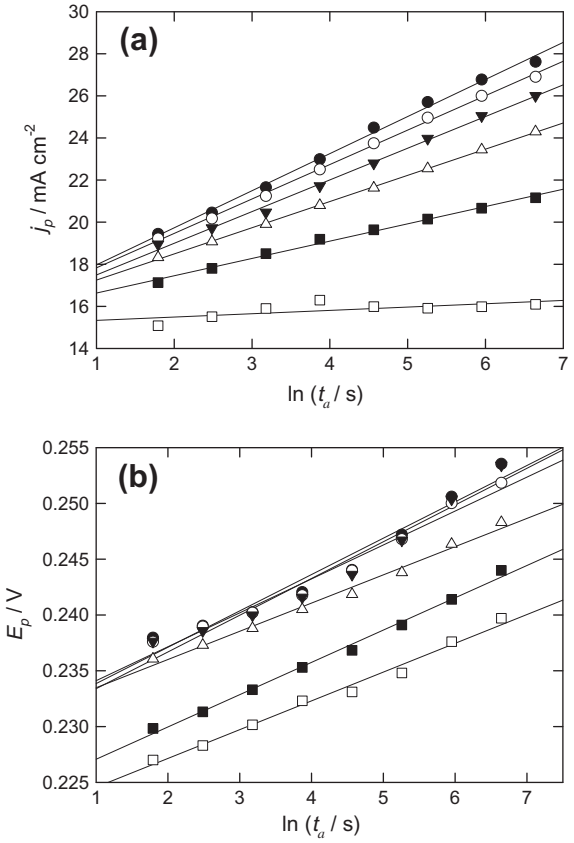

Fig. 3. Anodic peak current density (a) and anodic peak potential (b) as a function of the logarithm of the ageing time for different ageing potentials, E_a/V, (●)−0.200 V; (O) −0.160; (▼) −0.120; (Δ) −0.080; (■)−0.040; (□) 0.000. $Q_T(0.45)$ = 21.5 mC cm^{-2}.

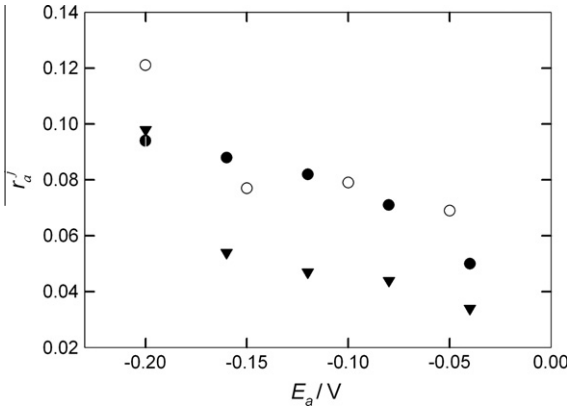

Fig. 4. Ageing rate in terms of the peak current, as a function of the ageing potential for different Pani films. $Q_T(0.45)$/mC cm^{-2}: (●) 21.5; (O) 33.3; (▼) 92.9.

tional to the fraction of oxidized material and independent on the applied potential [46].

Under these conditions, the voltammetric current obtained for a linear potential scan results to be [46,47].

$$\frac{j_T(E)}{\nu C_d} = (E+\sigma)\frac{j_f(E)}{\nu Q^0} + \frac{Q_f(E)}{Q^0} \qquad (2)$$

where ν is the scan rate, j_f and Q_f are the faradaic current and charge respectively; and Q^0 is the faradaic charge involved in the complete oxidation of the film. Then, the ratio $Q_f/Q^0 = x$ is the fraction the redox centers in the oxidized state. Finally, C_d and σ are parameters related to the capacitive response [46]. The first one is the capacitance when the whole polymer film is oxidized. That being so, C_d is proportional to the amount of the redox centers in the film, $C_d = aQ^0$, and the height of the capacitive plateau after the voltammetric peak is νC_d. As it was mentioned in reference to Figs. 1 and 2, it means that if the current at the plateau remains constant, independent of E_a and t_a, also C_d has the same value. And, as it is very unlikely that the proportionality constant, a, and the charge, Q^0, exactly compensates to each other, it must be concluded that both of them, Q^0 and a, remain constant after ageing. This reasoning also applies to the experiments in which the cathodic potential limit is changed (see Fig. 1). On the other side, within this formalism $\sigma = a^{-1} - E_Z$; where E_Z is the extrapolated potential at which the charge capacitance of the polymer film should be zero.

Although a complete separation of faradaic and capacitive contributions is not possible from the voltammetric response, both capacitive parameters, C_d and σ, are experimentally accessible and they can be evaluated from the knowledge of the integrated voltammetric charge as a function of potential [3,47].

Figs. 5 and 6 show the temporal variation of these two capacitive parameters during the ageing of three different Pani films at different ageing potentials. As C_d is proportional to Q^0, it is also proportional to the voltammetric charge Q_T. However, C_d does not sensibly change either with the potential at which the scan is started or with the ageing time. As it can be seen, σ slightly diminishes as the film thickness increases and during the ageing, but it does not depend much on the ageing potential.

Although the capacitive contribution does affect the height and position of the voltammetric peak, its effect is not very important. Moreover, as the capacitive parameters change very little during

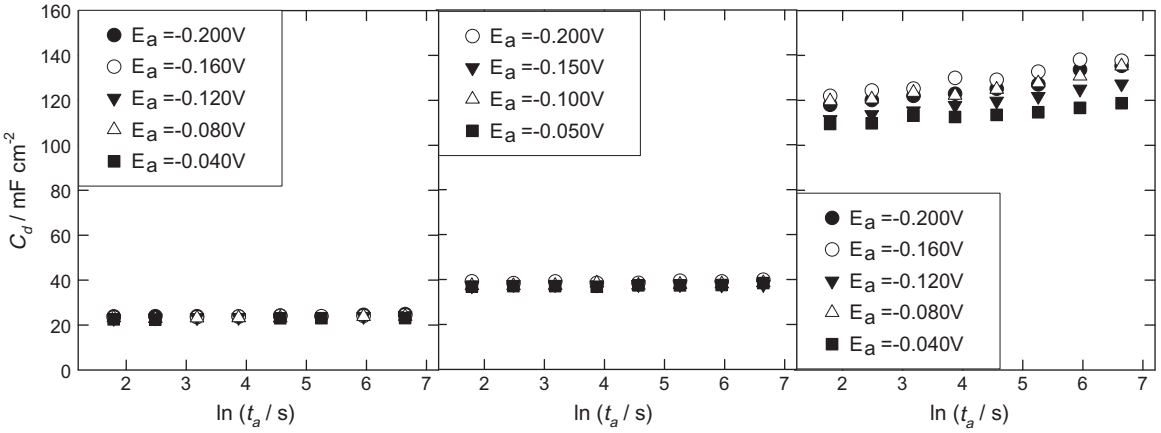

Fig. 5. The capacitive parameter C_d as a function of the logarithm of the ageing time, for Pani films of different thicknesses, aged at different potentials indicated in each graphic. Q_T(0.45): 21.5 mC cm^{-2} (left); 33.3 mC cm^{-2} (center); 92.9 mC cm^{-2} (right).

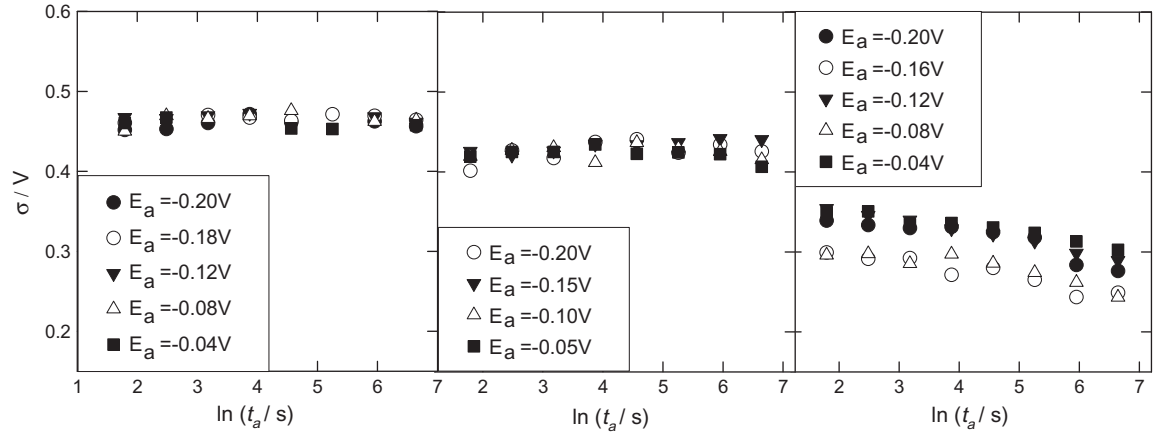

Fig. 6. The capacitive parameter σ as a function of the logarithm of the ageing time, for c Pani films different thicknesses, aged at different potentials indicated in each graphic. Q_T(0.45): 21.5 mC cm^{-2} (left); 33.3 mC cm^{-2} (center); 92.9 mC cm^{-2} (right).

the *EIA*, the modifications of the voltammetric peak features must be due to the variations of the faradaic process during the first positive potential scan after ageing.

In order to analyze the faradaic contribution during the *EIA*, a suitable model for the electrochemical transformation of the redox centers must be considered. An expression for the total voltammetric current as a function of the fraction of the redox centers, x, can be derived, assuming that the redox process is electrochemically reversible during the potential scan and taking into account the existence of interactions between the redox centers within the *mean field approximation* [47].

$$\frac{j_T}{vC_d} = \frac{nF}{RT}\frac{(E+\sigma)(1-x)x}{[1-(\xi_{Ox}+\xi_R)(1-x)x]} + x \tag{3}$$

In Eq. (3) the dependence of the potential on x is implicit because from the model the dependence of E on x results:

$$E = E^{o\prime} - \frac{RT}{nF}[(\xi_{Ox}+\xi_R)x - \xi_R] - \frac{RT}{nF}\ln\left(\frac{1-x}{x}\right), \tag{4}$$

where $E^{0\prime}$ is the formal redox potential and ξ_{Ox} and ξ_R are dimensionless interaction parameters. ξ_{Ox} is proportional to the difference of mean interaction energy between the pairs of neighbor redox centers, *Ox–R* (ε_{OR}) and *Ox–Ox* (ε_{OO}) and, correspondingly, ξ_R is proportional to the difference in the mean interaction energy between *Ox–R* and *R–R* pairs (ε_{RR}) [3,47]

$$\xi_R = -\frac{cN_{Av}(\varepsilon_{RR}-\varepsilon_{OR})}{RT} \tag{5}$$

and

$$\xi_{Ox} = -\frac{cN_{Av}(\varepsilon_{OO}-\varepsilon_{OR})}{RT} \tag{6}$$

where c is the mean number of redox neighbor centers.

The peak potential is found from the condition that the derivative of the right-hand side of Eq. (3) with respect to the potential is equal to zero, and then Eq. (3) gives the peak current [47]. Then, the expression for the oxidized fraction at the peak potential, x_p, results:

$$x_p = \frac{1}{2} + \frac{RT}{nF}\frac{[1-(\xi_{Ox}+\xi_R)(1-x_p)x_p]^2}{(E_p+\sigma)} \tag{7}$$

Here the subscript "p" indicates peak values. Having previously determined σ and C_d, the interaction parameters can be evaluated from the values of j_p and E_p by employing an iterative procedure in which $x = x_p$ is considered in Eqs. (3) and (4) [47].

Following this procedure, the interaction parameters for different Pani films after different ageing times were determined. Previously, it was calculated that the variations of the ξ_{Ox} parameter are not noticeable and the changes in the faradaic contribution can be almost exclusively assigned to ξ_R [3]. Fig. 7 shows the time varia-

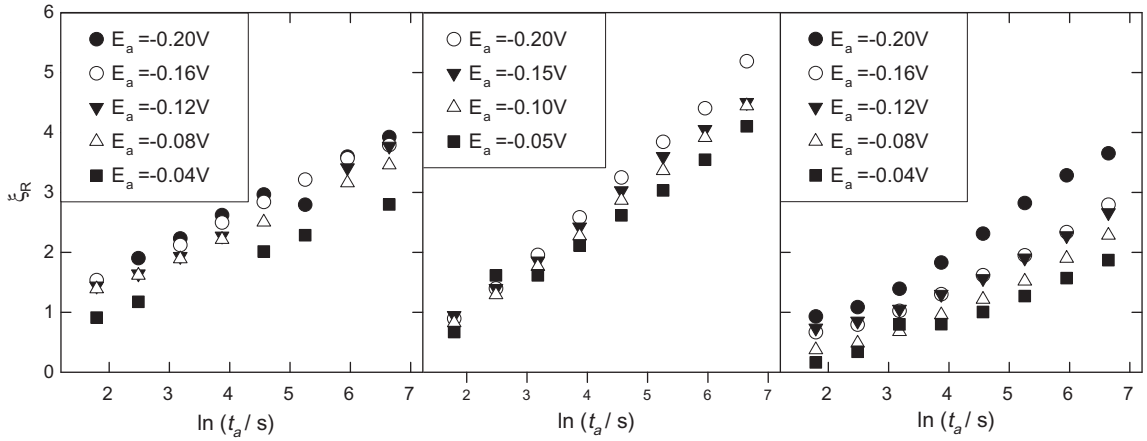

Fig. 7. Time variation of the interaction parameter ξ_R for three Pani films aged at different potentials indicated in each graphic. Q_T(0.45): 21.5 mC cm^{-2} (left); 33.3 mC cm^{-2} (center); and 92.9 mC cm^{-2} (right).

tion of this parameter for different Pani films aged at different potentials.

It is observed that the ξ_R values are smaller for the more positive ageing potentials. Also, it is observed that its values increase linearly with the logarithm of the ageing time, and that they do not depend markedly on the film thickness. Then, being ξ_{Ox} nearly constant [3], and taking into account the definition of ξ_R, its increase as the *EIA* progresses means that the interaction energy between reduced centers, ε_{RR}, decreases and it is the responsible for the change in the voltammetric response after the ageing. The decrease of the interaction energy between reduced centers is consistent with the reduction of the free energy of the polymer in the reduced state during the ageing. As this form becomes more stable, its subsequent oxidation is more difficult and happens at higher applied potentials.

Eq. (4) shows that this system does not correspond to an ideal Nernstian one; the activity coefficients for both reduced and oxidized centers depend exponentially on the degree of oxidation. In the present model, that point is a consequence of the introduction of interactions between redox centers and it results in a formal redox potential distribution. In this particular case, the formal redox potential varies linearly with the degree of oxidation [47].

The apparent number of exchanged electrons, n_{ap}, is a useful parameter that describes the width of the formal redox potential distribution and it is defined from the slope of the plot of the derivative of the potential respect to $\ln[x/(1-x)]$. For an ideal Nernstian system, this slope is $-RT/nF$, while for many systems the slope is constant at least in a range around $x = 0.5$ but its value is different to $-RT/nF$. In this particular case the slope of the plot E vs. $\ln[x/(1-x)]$ its constant in the range $0.25 < x < 0.75$, but is value is smaller than $-RT/nF$ [54,55]. In general the slope may be written as:

$$\frac{\partial E}{\partial \ln((1-x)/x)} = -\frac{RT}{n_{ap}F} \tag{8}$$

By series expansion of E with respect to $\ln[x/(1-x)]$ around the point $x = 0.5$ in Eq. (4), and equating the result to $-RT/nF$, according to Eq. (8), the following relation results:

$$n_{ap} = \frac{4}{4-(\xi_R+\xi_{Ox})}n \tag{9}$$

As expected, when the interaction parameters are null, the system becomes an ideal Nernstian one and $n = n_{ap}$. By considering that in the voltammetric peak, the degree of oxidation is approximately 0.5, the peak current results,

$$j_p = \nu C_d\left(\frac{n_{ap}F(E^O+\sigma)}{4RT}+\frac{1}{2}\right) \tag{10}$$

where $E^O = E^{o'} - (RT/2nF)(\xi_{Ox} - \xi_R)$. This indicates that the peak current is approximately proportional to the apparent number of electrons. In Fig. 8, the time dependence of n_{ap} (calculated by Eq. (9)) is shown for the same Pani films presented in the former figures. In the present case, $n = 2$ and n_{ap} is always smaller than n (see Fig. 8). This means that the formal redox potential distribution is wider than in the absence of interactions. However, n_{ap} increases as the waiting time increases indicating that, as a consequence of the *EIA*, the formal redox potential distribution becomes narrower during the ageing process. This effect is directly monitored by the increase in the current peak.

It is interesting to note that n_{ap} also increases linearly with the logarithm of the ageing time. An ageing rate in terms of n_{ap} could be then defined in the same way it was done for the peak current,

$$r(n_{ap}) = \frac{\partial n_{ap}}{\partial \ln t_a} \tag{11}$$

The correlation between the ageing rates defined in terms of both the peak current and the apparent number of electrons is shown in Fig. 9. As it can be seen, they are well correlated in a linear way indicating the peak current changes can be attributed to the changes in the apparent number of electrons, whose temporal variation means that the formal redox potential distribution becomes narrower as a consequence of the *EIA*.

Additionally, it deserves to point out that the analysis of the current peak behavior allows to determine that the major variations in n_{ap} are achieved at more negative values of the ageing potential. That is, the ageing rate increases as the potential becomes more negative.

4.2. The kinetics of the EIA

The *EIA* is characterized by a particular time behavior which is also found in the physical ageing of amorphous solids. The extent of the process, expressed as the relative change of some particular property (specific volume, fluorescence emission, etc.), depends linearly on the logarithm of the ageing time. This time dependence was also found by Elovich when studying heterogeneous chemical reactions. Therefore, an Elovich type of kinetics can be also used to describe the time evolution of the *EIA* [45]. This kinetic can be represented by the following rate law [56]:

$$\nu = \mathrm{d}q/\mathrm{d}t = k_0\exp[-(\Delta G_0^* + \beta q)/RT] \tag{12}$$

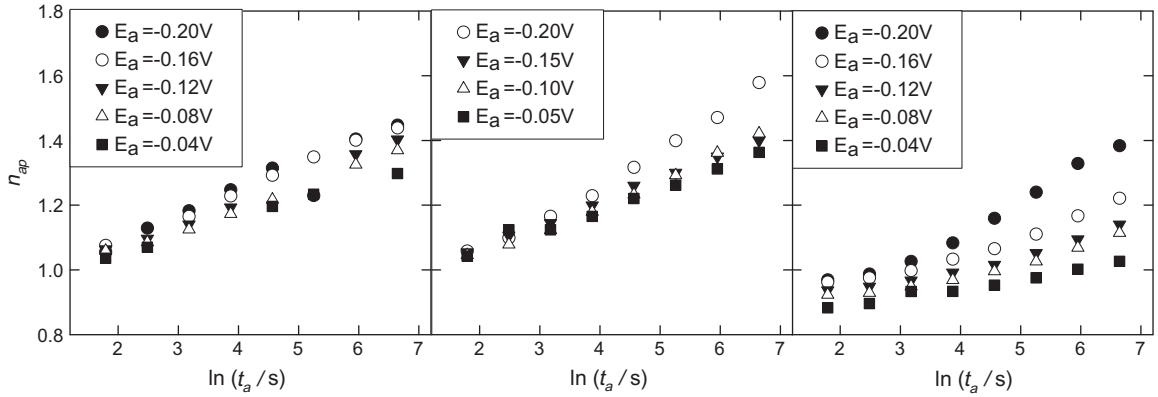

Fig. 8. Time variation of the apparent number of electrons for the same three Pani films shown in Fig 7.

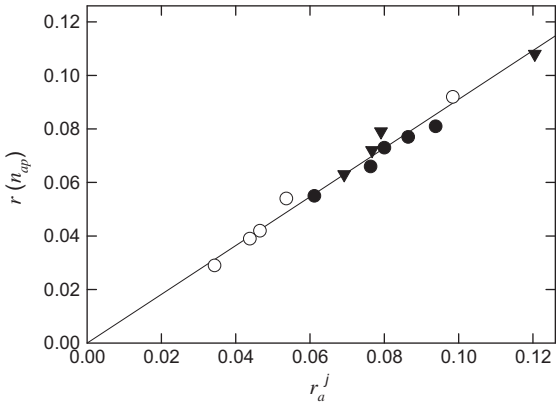

Fig. 9. Correlation between the ageing rate defined in terms of: the apparent number of electrons and the peak current, for the films presented in previous figures. (●) $Q_T(0.45)$ = 21.5 mC cm^{-2}; (O) 33.3 mC cm^{-2}; (▼) 92.9 mC cm^{-2}.

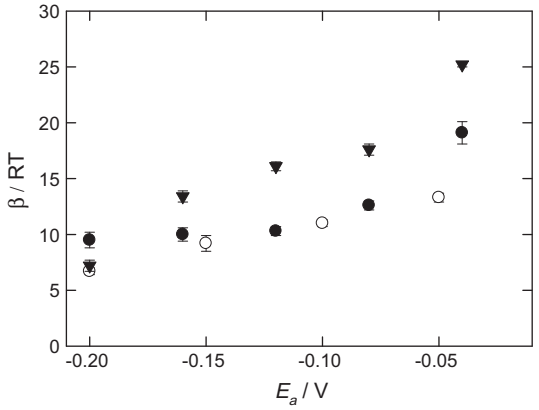

Fig. 10. Parameter β/RT as a function of the ageing potential for different Pani films. $Q_T(0.45)$/mC cm^{-2}: (●) 21.5; (O) 33.3; (▼) 92.9. The bars are the standard errors of the fit.

where q is the extent of the process, k_0 is a *pseudo* zero order rate constant, ΔG_0^* is the activation free energy at zero extent and β is a parameter that indicates how fast the activation free energy changes with the extent of the process. For large values of β, the rate of the process quickly diminishes, so this parameter is a measure of the self-inhibition. By integration of Eq. (12), the time dependence of the extent of the process results,

$$q = (RT/\beta)[\ln(t_a + t_0) - \ln(t_0)] \tag{13}$$

where, $t_0 = RT/\beta k$ and $k = k_0 \exp -(\Delta G_0^*/RT)$.

As the variations of the peak current are related to the change in the interaction parameters, it could be chosen for measuring the extent of the ageing. By defining the extent as the relative change of the peak current, q can be expressed as:

$$q = (j_p - j_{p,0})/j_{p,0} \tag{14}$$

So, the experimental peak current evolution can be adjusted to Eq. (13).

Figs. 10 and 11 show the values of the parameters β/RT and t_0, respectively, for the *EIA* of different films as a function of the ageing potential. These parameters were obtained by fitting the experimental values of q to Eq. (13) employing a non-linear fitting routine. When the ageing potential becomes more positive, the β parameter increases. It means that the self-inhibition is more important as the *EIA* occurs at higher potentials. On the other hand, the t_0 values decrease in the same direction.

At the beginning of the *EIA*, the rate is $v_0 = k_0 \exp[-\Delta G_0^*/RT]$. When $t = t_0$, according to Eq. (13), $q = (RT/\beta)\ln(2)$, and $v = 0.5\ v_0$.

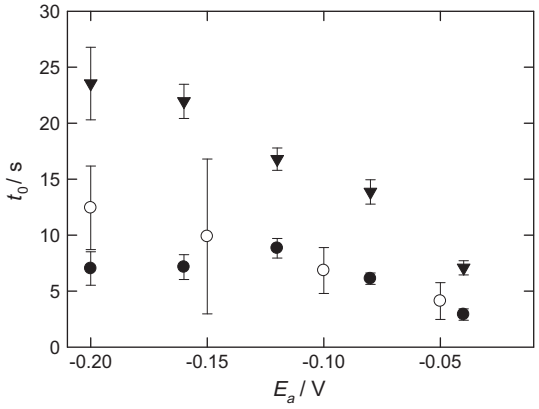

Fig. 11. Parameter t_0 as a function of the ageing potential for different Pani films. $Q_T(0.45)$/mC cm^{-2}: (●) 21.5; (O) 33.3; (▼) 92.9. The bars are the standard errors of the fit.

So, t_0 is the time required for the rate to get a half of its initial value. Obviously, when the self-inhibition is bigger, the ageing process is rapidly slowed down and this time results shorter.

For $t >> t_0$, Eq. (13) predicts a linear relationship between q and the logarithm of the time. This explains the experimental results. In this conditions, $q \approx (RT/\beta)\ \ln(t_a)$, which allows finding the approximate relation $r_a^j \approx (RT/\beta)$. Fig. 12 shows the correlation between these two parameters for the ageing of different Pani films

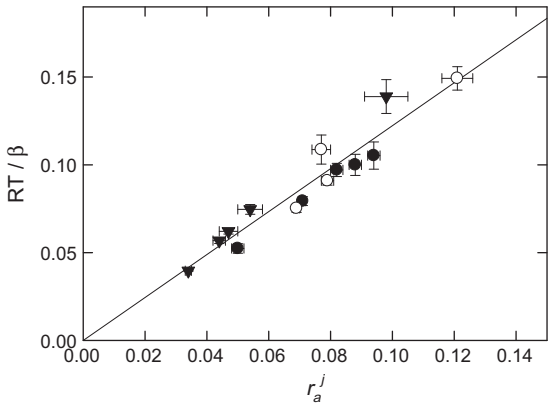

Fig. 12. Correlation between RT/β and the ageing rate defined in terms of the peak current for the films presented in previous figures. (●) 21.5 mC cm^{-2}; (O) 33.3 mC cm^{-2}; (▼) 92.9 mC cm^{-2}. The bars are the standard errors of each fit.

at several ageing potentials. As it can be seen, they are roughly linearly related.

It is known that during the ageing of Pani an important reduction of the volume of the polymer is observed [37]. This leads to the idea that during the ageing process folding of the polymer occurs. This process may happen with the reduced form of Pani because the amine units has the possibility to rotate one relative to the other. Contrary to the reduced form, the oxidized one does not age at room temperature. This is most probably due to the fact that the double bonds of the imine groups strongly hinder the rotation of the monomer units. On the other hand, the extent of ageing seems to be dependent on the free volume available in the polymer [45].

It was pointed out that as the negative potential limit is increased, the amount of oxidized polymer at that potential increases and the polymer should consist of a dispersion of the oxidized polymer domains in large domains of reduced polymer. The presence of the oxidized domains would make more difficult the chain movements in the reduced polymer and therefore the rate of ageing would decrease as the ageing potential increases.

5. Conclusions

Experimental results for the *EIA* of Pani films in 3.7 M H_2SO_4 were reported and analyzed in different ways. The ageing rate was measured in terms of the current peak of the first cycle voltammogram. Independently on the film thickness, as the ageing potentials is more negative the rate of the *EIA* is higher.

Changes in current peak were shown to be mainly related to variations in the interaction energy between reduced redox centers as a consequence of the ageing. This also leads to a narrowing of the formal redox potential distribution that can be characterized by the apparent number of exchanged electrons. The time behavior of the peak current is linked to the temporal variations of this parameter, which reinforces the use of this voltammetric parameter for monitoring the *EIA*.

As it is related to changes in energy parameters, the peak current was chosen for defining the extent of the ageing process. A suitable kinetic model was proposed and its parameters were fitted. The self-inhibition is more important at more positive potentials, resulting in smaller ageing rates.

The analysis in terms of the empirical ageing rate based on the works on physical ageing of amorphous solids results to be equivalent to that obtained on the basis of the self-inhibition parameter of the Elovich kinetics. However, this last kinetic model is more adequate as it describes not only the linear portions of the semi-logarithmic plots but also the initial stages. Within this model, a characteristic time of the *EIA* can be also determined.

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