Potentiostatic Oxidation of Polyaniline under Conformational Relaxation Control: Experimental and Theoretical Study

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Electrogenerated films of polyaniline were studied by potential steps in acetonitrile solutions to check for the presence of compaction, relaxation, and diffusion processes giving like-nucleation chronoamperograms such as those described by the electrochemically stimulated conformational relaxation (ESCR) model. This solvent was used to avoid both proton discharge during cathodic compaction of the film at high cathodic potentials and proton exchange during redox processes. Chronoamperograms obtained from different cathodic potentials to different anodic potentials under different concentrations of electrolyte or at different temperatures indicate the presence of compaction, relaxation, nucleation, and diffusion processes under electrochemical stimulation. The ESCR model, developed to describe the electrochemical behavior of polypyrrole films by the quantification of these processes, was used to determine if it can be applied to simulate the chronoamperometric responses of the polyaniline and the influence of the different variables on the experimental chronoamperograms. Constants required to simulate the chronoamperograms were obtained from experimental results: the same model indicates the required experimental conditions. Good agreement was obtained between simulated and experimental results.

1. Introduction

Some of the applications of conducting polymers, as artificial muscles,[1] show evidence of swelling and shrinking processes during reverse electrochemical oxidation and reduction. Theoretical models and, moreover, electrochemical models trying to explain the electrochemistry of conducting polymers should include structural aspects to explain those changes.

When a film of polypyrrole is in a reduced state, it presents a compact amorphous structure due to the strong polymer—polymer interactions. The ESCR (electrochemically stimulated conformational relaxation) model[2,3] explains changes in the film composition during oxidation in the way that positive charges[4] (polarons or bipolarons) generated along the polypyrrole chains promote Coulombic repulsions: conformational changes along chains are stimulated, generating free volume, opening channels, and allowing the penetration of counterions (and solvent)[5−7] to keep electroneutrality in the solid. Thus, the oxidized polymer is a soft, amorphous, and complex material including polypyrrole, counterions, and solvent.

Reverse transitions between compact, or neutral, films (Scheme 1a) and open, or oxidized, films (Scheme 1b) are controlled by electrochemical oxidation or reduction[8] of the polymer. The complete reduction and compaction of the polymer (Scheme 1a) can be attained only by polarization at high cathodic potentials. Conformational changes required to relax and open a compact and reduced structure are the kinetic controlling processes[2] at the beginning of the polymeric oxidation. This electrochemically stimulated relaxation does not occur in a uniform way at the polymer/solution interface; it takes place on specific points that can be visualized on electrochromic films (nuclei)[3]. Once the molecular structure of the film is

opened, the oxidation is completed under diffusion control. Both relaxation—nucleation and diffusion processes are influenced by the usual electrochemical variables: temperature, counterion concentration in solution, compaction potential (cathodic potential), and oxidation level (anodic potential). The model provided a self-consistent chronoamperometric equation, including, in a quantitative way, all of those variables that allowed for a good simulation of the experimental chronoamperograms obtained from polypyrrole films[3]. In this way, the presence of a maximum on the chronoamperograms and the maximum shift for different values of a variable[3,9] or the effects described in the literature as anomalous[10−12] or "break-in"[13−15] effects can be explained and described by the ESCR model. The model also allows us to describe similar effects on voltammetric[16] and chronocoulometric[17] responses of polypyrrole, which comprise the asymmetry of those processes.

Our aim now is to determine if the ESCR treatment can be extended to different conducting polymers. Polyaniline was selected in this work because of its ability to interchange both anions and protons during oxidation and reduction processes in a solution containing proton acceptors.

Polyaniline exists in different oxidation states and is conductive only as an emeraldine salt. The basic form of the polymer[18] is
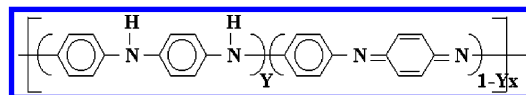
When $0 < y < 1$, they are poly(paraphenileneamineimines). The fully reduced form ("leucoemeraldine") corresponds to a value of $y = 1$. The fully oxidized form ("pernigraniline") corresponds to a value of $y = 0$, and the 50% oxidized form ("emeraldine") corresponds to a value of $y = 0.5$. The terms leucoemeraldine, emeraldine, and pernigraniline refer to different

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SCHEME 1: Acetonitrile Solution//Compact and Reduced Polymer//Metal (a) and Oxidized and Expanded Polymer (Oxidized Chains + Counterions + Solvent)//Metal (b)[a]
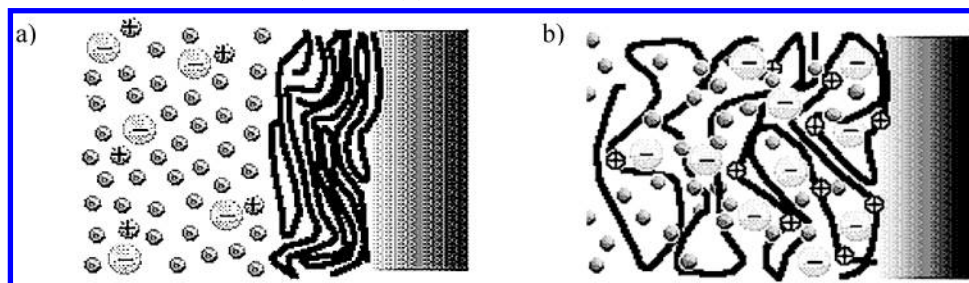
[a] Electrochemical oxidation and reduction promote reverse structural transitions between the situations represented in parts a and b.
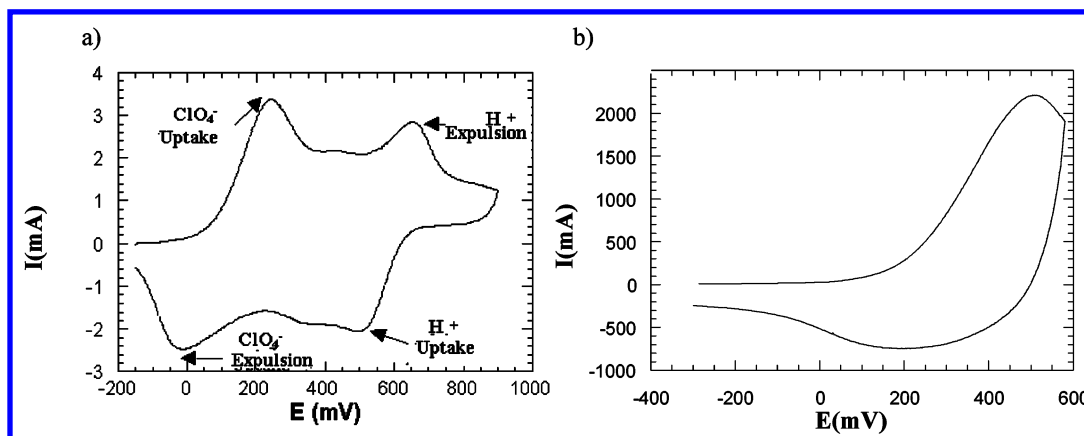

Figure 1. (a) Cyclic voltamperometry of Pany in 0.2 M H_2SO_4 aqueous solutions showing the preponderant ion interchanged along every maximum. (b) Cyclic voltamperometry of Pany in aprotic media (0.2 M $LiClO_4$ acetonotrile solution). Sweep rate: 50 mV/s in both media. Temperature: 25 °C.

oxidation states of polyaniline. Electrochemical or chemical[19] oxidation and reduction allow an interchange between every one of these states, thereby enabling selective color change and switching from the conductive to the nonconductive form:
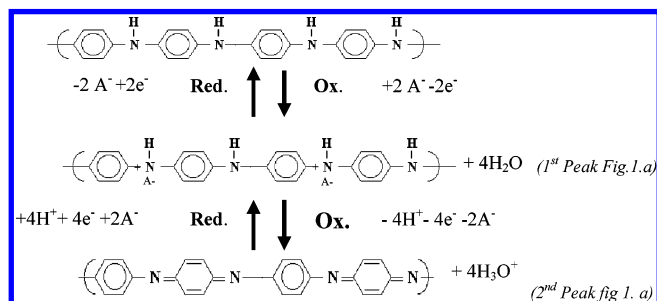
The ESCR model was described when anions are the main interchanged ion, pushing us to try to avoid the interchange of protons. Anomalous effects were described in the literature for the electrochemical responses of polyaniline[20−23] in aprotic media. The goal of this work is to obtain experimental chronoamperograms measured under conformational relaxation control from electrogenerated polyaniline films. If that is possible, we will try to determine the applicability of the ESCR model in describing and simulating the chronoamperometric behavior of this polymer.

2. Experimental Methodology

Polyaniline films were electropolymerized and checked in a one-compartment electrochemical cell connected to a PAR M273 potentiostat−galvanostat and controlled from a PC by Research Electrochemistry software, version 4.23. Two platinum sheets having 1 and 4 cm^2 of surface area were used as the

working electrode and the counterelectrode, respectively. A saturated calomel electrode (SCE) from Crison Instruments was used as the reference electrode. Aniline (Merck p.a.) was distilled under vacuum before use and stored under N_2 at −10 °C. Acetonitrile (Lab Scan, HPLC grade), anhydrous lithium perchlorate (Aldrich), and sulfuric acid (Merck, 95−97% pure) were used as received. All of the solutions were deaerated by bubbling N_2 for 10 min before the electrochemical experiment was started. A Huber Ministat thermostat allowed us to keep a constant temperature.

3. Experimental Results

Polyaniline films were grown on the working electrode by potential cycling at 50 mV s^{-1} between −100 and 900 mV in a 0.2 M aniline + 0.1 M H_2SO_4 aqueous solution until a final consumed polymerization charge (anodic charge − cathodic charge) of 100 mC was obtained. A polyaniline film having a thickness of 0.22 μm (observed by SEM) was obtained, showing reverse electrochromic changes along the potential cycles.

A voltammogram of this film in aqueous solution is presented in Figure 1a. It shows two different maxima related to perchlorate and proton exchange between the polymer and the aqueous solution.[24,25] Using an aprotic organic solvent, we observed only one maximum in the studied potential range (Figure 1b) associated with the interchange of anions. In this solvent, the discharge of protons does not occur because none of the species present in solution can incorporate protons released from the polymer.

Therefore, all of the chronoamperograms described in this work were performed in acetonitrile solutions because the ESCR model establishes that a good reduction of the polymer is possible only if the film can be polarized at high cathodic overpotentials (up to −3 V related to the reference electrode)
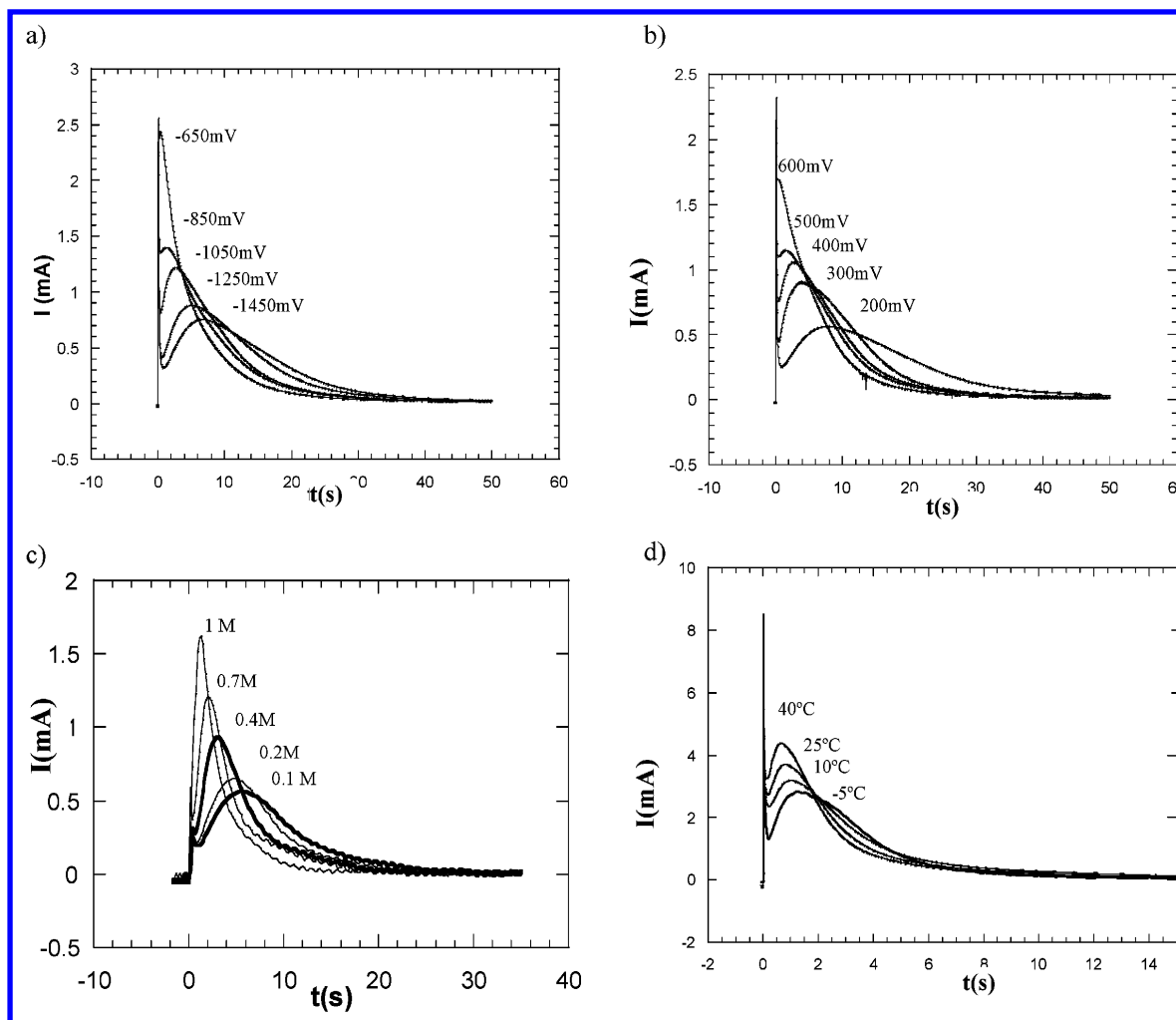
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Figure 2. Experimental chronoamperograms obtained in 0.1 M LiClO$_4$ acetonitrile solutions by potential steps (a) from different cathodic potentials (closure potential) maintained for 60 s to the oxidation potential of 400 mV, (b) from −900 mV maintained for 60 s to different oxidation potentials, (c) from different concentrations of the electrolyte, and (d) at different temperatures. The potentiostatic standards conditions were −900 mV for 60 s and a step to 400 mV. Electrode: 1-cm^2 platinum foil coated with a 0.22-μm-thick polyaniline film; temperature: 25 °C.

in the absence of any release of hydrogen. Along the reduction process in Figure 1a, the polymer shrinks by expelling counterions toward the solution under diffusion control. The polymeric structures become more and more compact, and up to 10% of the counterions are entrapped before the reduction is completed. Those remaining counterions can be expelled only if a way is opened throughout the polymer with the generation of free volume by conformational movements of the polymeric chains. Long polarization times or high energy (high overpotentials) is required to complete the reduction (and counterion expulsion) process under relaxation control of the polymeric chains. To complete the reduction process, stable electrolytes (solvent and salts) and high cathodic overpotentials are required. Once compacted, the subsequent oxidation of the film by an anodic potential step starts on those points of the polymer/solution interface showing a greater mobility of the chains: it starts from different nuclei that expand on the reduced polymer under relaxation control. The result is a like-nucleation chronoamperogram showing a maximum or an anodic shift at the beginning of the oxidation process in voltammograms. Once the structure was open, the oxidation was completed under diffusion control. Our initial aim was to verify the presence of relaxation−compaction and nucleation processes in polyaniline under electrochemical stimulation.

After the electrogeneration of a film, the platinum-coated electrode was rinsed with acetonitrile and transferred to the control solution (acetonitrile + 0.2 M lithium perchlorate). There, the polymer was reduced and compacted by polarization for 1 min to an initial potential (E_c). Then, the potential was stepped to a potential (E) that was more anodic than the starting oxidation potential of the polymer (E_0). The oxidation potential E was maintained for a time that was long enough to allow the oxidation of the film to occur. Most of the chronoamperograms obtained under these conditions show a maximum that is similar to those obtained from the electrodeposition of metals involving nucleation processes.[21] The polymeric compaction and the subsequent time of the maxima on the anodic chronoamperograms are influenced by the cathodic polarization potential, the polarization time, the oxidation potential, the temperature of the electrolyte, and the electrolyte concentration. Subsequently, the shapes of the anodic chronoamperograms also are influenced by those variables.

Several experimental series were performed, changing one of the magnitudes every time in order to follow its influence on the described like-nucleation chronoamperograms. As a standard procedure, the film was compacted by polarization at −0.9 mV versus SCE for 60 s. Then, the potential was stepped to 400 mV in a 0.1 M LiClO$_4$ acetonitrile solution at 25 °C. The experimental results obtained by changing the above-mentioned variables one-by-one can be observed in Figure 2.

The maxima observed on the chronoamperograms show a shift toward longer times and lower current densities when (a) the potential of compaction becomes more negative (the compaction overpotential increases), (b) the oxidation potential becomes less positive (the oxidation overpotential decreases), (c) the temperature decreases, or (d) the concentration of counterions in solution decreases. Shifts toward increasing time mean an increase in the compaction of the film (increasing overpotentials of compaction) or a decrease in the electrochemical stimulation rate of the relaxation−oxidation (decreasing oxidation overpotentials, decreasing temperatures, or decreasing concentrations of counterions). Therefore, we can conclude that the polyaniline films can be compacted, relaxed, and oxidized under conformational relaxation control in a way similar to that previously described in the literature for polypyrrole films.

Our aim now is to determine if the theoretical equation supplied by the ERCS model for the simulation of chrono-amperometric responses from polypyrrole films also gives a good description of chronoamperometric responses using polyaniline films. The model includes several constants, which are specific for every studied polymer, that must be obtained from the results of experiments performed under conditions indicated by the model. Those constants are

(a) the charge required to close and compact 1 mol of polymeric segments (z_c) by cathodic polarization;

(b) the charge required to relax and open 1 mol of compacted polymeric segments (z_r) by anodic polarization;

(c) the starting oxidation potential for a noncompacted film (E_0);

(d) the cathodic potential where the compaction starts (closing potential) (E_s);

(e) the conformational energy consumed per mole of polymeric segments to be opened in the absence of any electric field (ΔH^*); and

(f) a diffusion constant *(b)*.

3.1 Theoretical Background

The energy required to complete 1 mol of conformational changes is ΔH, which in any other relaxation model is related to the relaxation time (τ). It is given by the general expression $\tau = \tau_0 \exp(\Delta H/RT)$. To describe the electrochemistry of a conducting polymer, this enthalpy includes three components[2,3,16−17]: a polymeric component (ΔH^*), in the absence of any polarization, and two electrochemical components— compaction by cathodic polarization $z_c\eta_c$ [mC mV] and swelling by anodic polarization $z_r\eta$ [mC mV]:

$$\Delta H = \Delta H^* + z_c\eta_c - z_r\eta \quad (1)$$

Any of these three components is a molar conformational energy. ΔH^* contains all of the increments on the energetic terms of the system (conformational, polymer−polymer, polymer−solvent, polymer−ions) between two stationary states in the absence of any applied potential change. (Both overpotentials are zero, and $\Delta H = \Delta H^*$.) The second one represents the increment in conformational energy that arises from the closure of the polymeric structure by cathodic polarization and electrochemical reduction. Here, z_c is a constant related to the charge required to close and compact 1 mol of polymeric segments at a cathodic overpotential ($\eta_c = E_s - E_c$). The third term includes the energy required to relax and swell a compacted structure, allowing, under anodic polarization ($\eta = E - E_0$), the penetration of counterions. z_r is the coefficient of electrochemical
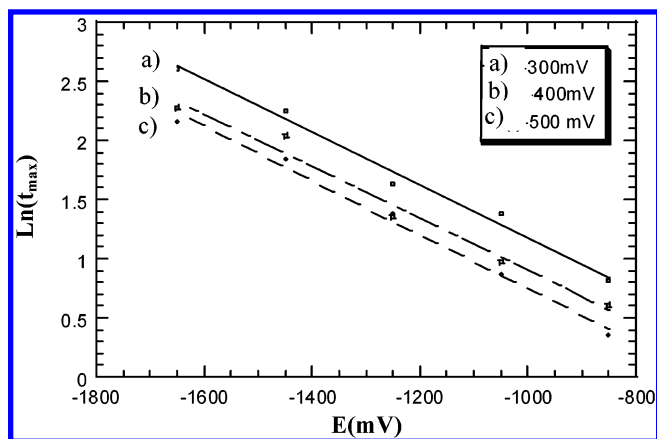

Figure 3. Semilogarithmic plot of t_{max} (attained from three experimental series such as that shown in Figure 2a) vs the cathodic potential of polarization for 60 s. Three series were performed by stepping the potential from every cathodic potential to three different anodic potentials (300, 400, and 500 mV vs SCE) in 0.1 M LiClO$_4$−acetonitrile solutions at 25 °C.

relaxation (charge consumed to relax 1 mol of polymeric segments), and E_0 is the starting oxidation potential of a relaxed polymer.

The model relates the maxima of the chronoamperograms to the three energetic components[3]:

$$\ln t_{max} = C_1 + \frac{\Delta H}{RT} = C_1 + \frac{\Delta H^*}{RT} + \frac{z_c}{RT}\eta_c - \frac{z_r}{RT}\eta \quad (2)$$

R is the gas constant, and T is the temperature (K). From this equation, different experimental strategies can be established to obtain z_c, z_r, or ΔH^* by changing one of the experimental magnitudes every time.

3.2 Obtaining z_c

By maintaining a constant cathodic polarization time, temperature, electrolyte concentration, and oxidation overpotential, eq 1 becomes

$$\ln t_{max} = C' - z_c\frac{\eta_c}{RT} \quad (3)$$

The model predicts that times for the maxima shift in a semilogarithmic way with the cathodic overpotential of compaction ($\eta_c = E_c - E_s$). Following these indications, a polyaniline film was submitted to potential steps from different initial potentials of compaction (−1650, −1450, −1250, −1050, and −850 mV versus SCE, maintained for 1 min) to a final oxidation potential. Three experimental series were performed from these compaction potentials until three different anodic potentials were obtained (300, 400 (Figure 2a), and 500 mV) to determine if the anodic potential affects the obtained z_c value. Three semilogarithmic evolutions were obtained for the times of the maxima as a function of the closing potential, as can be seen in Figure 3:

In good agreement with theoretical predictions, parallel variations (correlation coefficient 0.99) were obtained. The same cathodic compaction coefficient, z_c, was obtained from the slopes, being independent of the anodic potential used to open and oxidize the polymeric film:

$$z_c = 5541 \text{ C mol}^{-1}$$

3.3 Molar Coefficient of Electrochemical Relaxation, z_r

Following a similar procedure to that above, we can use eq 2 to get the relaxation coefficient z_r. When all of the potential

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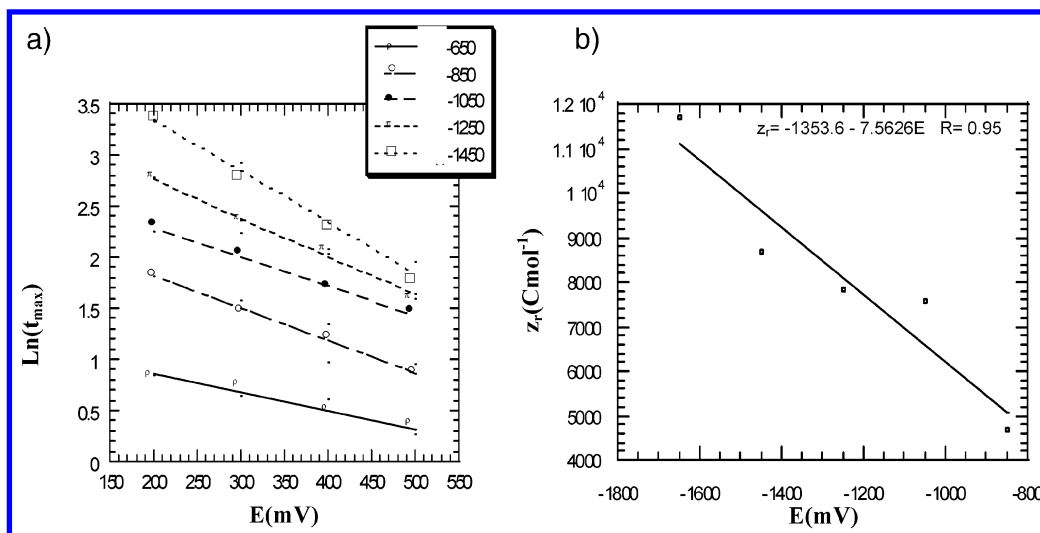
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Figure 4. (a) Semilogarithmic plot of t_{max} vs the anodic potential of oxidation (200, 300, 400, and 500 mV) for potential steps performed until those potentials from each of the different (five series) cathodic potentials (-1450, -1250, -1050, -850, and -650 mV vs SCE) of polarization and compaction for 60 s were reached. Relaxation coefficients were obtained from slopes. (b) Evolution of those coefficients (z_r) with the cathodic potential of compaction.
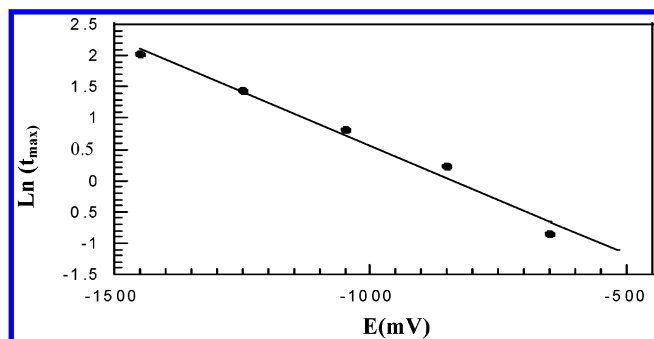

Figure 5. $\ln(t_{max})$ vs the cathodic potential of prepolarization (-650, -850, -1050V, -1250, and -1450 mV vs SCE) for 60 s, followed by a potential step to 400 mV (Figure 2a).

steps were performed from the same cathodic potential, which was maintained for 1 min, to different anodic potentials (E_r), considering that $\eta = E_r - E_0$ and keeping both electrolyte concentration and temperature constant, eq 2 becomes

$$\ln t_{max} = C'' - z_r \frac{\eta}{RT} \qquad (4)$$

Experimental results similar to those shown by Figure 2b were obtained. To determine if the cathodic potential affects the obtained z_r value, five different experimental series were performed. The potential was stepped from five different cathodic potentials of compaction, and held for 1 min every time (-1450, -1250, -1050, -850, and -650 mV vs SCE), to four anodic potentials: 200, 300, 400, and 500 mV versus SCE. Semilogarithmic evolutions between t_{max} and the oxidation potential were obtained (Figure 4), as predicted by eq 4. The coefficient of electrochemical relaxation z_r was obtained from the slopes. This empirical coefficient shows a linear dependence on the potential of compaction, as depicted by Figure 5 , where z_r increases for increasing compaction overpotentials. More cathodic initial potentials promote a deeper reduction and more compact polymeric entanglements; therefore, more charge will be consumed to open 1 mol of segments during the subsequent anodic oxidation. The empirical relaxation coefficient ranges from 3562 C mol^{-1}, when the polymer was compacted at -650 mV, to 9612 C mol^{-1}, when the compaction was performed at -1450 mV.
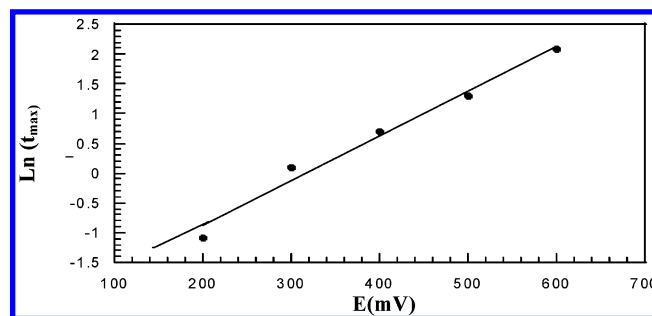

Figure 6. $\ln(t_{max})$ vs the anodic potential of polarization. Experimental data were taken from Figure 2b.

3.4 Closing (E_s) and Oxidation (E_0) Potentials

When the polymeric film is reduced, under constant temperature (25 ° C) and constant electrolyte concentration (0.1 M Li ClO$_4$), at a potential ranging from E_s to E_0 , the polymeric structure was not closed; then the potential was stepped to a potential more anodic than E_0, where the polymer is oxidized, the experimental chronoamperogram shows a pure diffusion exponential drop, and the kinetics of the thin-film oxidation is under diffusion control. To obtain E_0, the following experimental procedure was established. By taking eq 2 into account, E_s can be obtained by extrapolation at short times (a time for the maxima that is short enough that it cannot be measured under our experimental conditions, i.e., 0.1 s) of the semilogarithmic evolution of the maxima obtained under conformational relaxation control from different closing potentials, maintained for the same time, to the same oxidation potential. The obtained closing or compacting potential E_s was -550 mV. (See Figure 5.)

The polymer never oxidizes if the anodic potential limit is lower than (E_0). More anodic potentials control the oxidation level, increasing the rate of the relaxation−nucleation−oxidation process. The experimental E_0 was obtained from eq 2 by extrapolation at 0.1 s of the semilogarithmic evolution of the maxima obtained under conformational relaxation control from the same closing potentials, maintained for the same time, to different oxidation potential. The obtained E_0 was 180 mV (Figure 6).

Potentials E_0 and E_s can be better observed in Figure 7. There, the dotted-line voltammogram represents the voltammetric
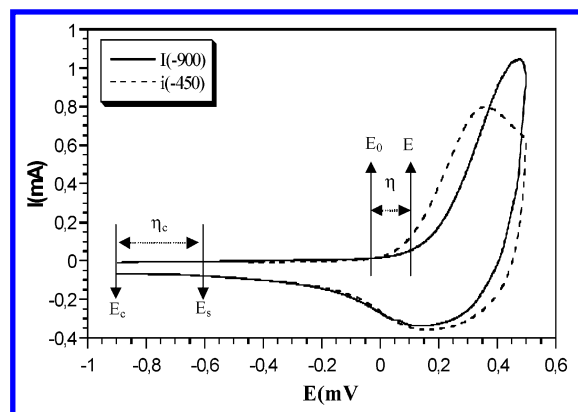
Figure 7. Voltammograms performed from −900 mV, for 60 s, and 500 mV at 50 mV/s in 0.1 M LiClO₄−acetonitrile solution, applied to a film of polyaniline (−), and from −500 and 500 mV (− −). E_s is the closing potential; E_c is the potential of polarization; η_c is the closing overpotential; and E_0 is the starting oxidation potential for a noncompacted film. Any polarization at an anodic potential more anodic than E originates an oxidation overpotential η.

behavior of a noncompacted film, performed between −500 mV (between E_s and E_0) and 500 mV at 50 mV/s. The solid line was obtained by prepolarization at −900 mV for 60 s (film compaction) and then cycling between this potential and 500 mV. The relaxation of the compact structure is observed here as an overpotential (extra energy) required to open and oxidize the compact polymer. The polymer compacts by polarization at E_c, a more cathodic potential than the closing potential E_s. In our chronoamperometric results, the polyaniline is oxidized only by a potential step from E_c if the potential is stepped to a potential E, which is more anodic than the beginning of the oxidation process of a noncompacted polymer E_0.

3.5 Relaxation Molar Enthalpy ΔH^*

Once again, the increment of conformational enthalpy per mole of polymeric segments between two stationary oxidation states of the polymer (ΔH) can be obtained from eq 2. All of the experiments were performed from the same cathodic overpotential (η_c) to the same anodic overpotential (η), changing the temperature of the electrochemical bath (−5, 10, 25, 40 °C) for every experiment. Therefore, using eq 2,

$$\ln t_{max} = C_1 - \frac{\Delta H}{RT} \tag{5}$$

The experimental t_{max} values were measured from the chronoamperograms depicted in Figure 2d. By plotting these values versus the concomitant reverse experimental temperatures, a linear variation was obtained (Figure 8), allowing us to obtain ΔH (eq 2) as 14.5 kJ/mol.

Considering the above obtained values of constants z_c and z_r, the experimental overpotentials, and eq 1, the enthalpic increment per mole of polymeric segments between the two stationary states of the polymer in the absence of any electric field (ΔH^*) can be easily calculated from ΔH:

$$\Delta H^* = 14 \text{ kJ mol}^{-1}$$

3.6 Constant b

The diffusion constant b can be obtained from eq 8. All of the relaxation processes were avoided when the experimental chronoamperograms were performed from a more anodic potential that the closing potential (−600 mV): the oxidation takes place under diffusion control. All of the charge is
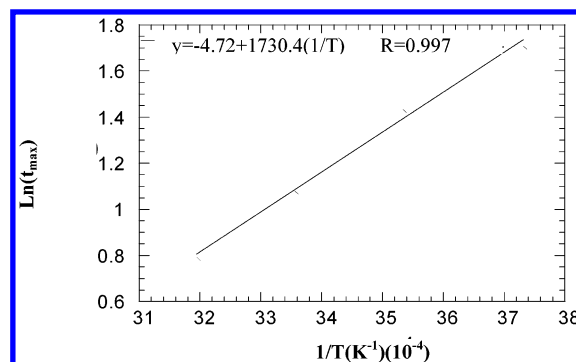

Figure 8. Semilogarithmic representation of t_{max} vs $1/T$; the experimental values are taken from Figure 2d. The conformational energy consumed per mole of polymeric segments in the absence of any electric field (ΔH^*) can be obtained from the slope, following eq 5.

compensated by counterions arriving by diffusion without any kinetic interference of the relaxation processes. Electric currents and charges consumed under those conditions were described as[3]

$$I_d(t) = bQ_d e^{-bt} \tag{6}$$

$$Q_d(t) = Q_d \lfloor 1 - e^{-bt} \rfloor \tag{7}$$

The constant b is related to the diffusion coefficient of the counterions into the polymer. Under those conditions, by applying the natural logarithm we obtain

$$\ln\left[1 - \frac{Q_d(t)}{Q_d}\right] = -bt \tag{8}$$

A semilogarithmic plot of $\{(1 - Q_d(t))/Q_d\}$ versus the polarization time at −550 mV (at which the polymer structure remains open) allows us to get b from the slope. When the procedure is repeated by stepping the potential to different oxidation potentials, the variation of b as a function of the oxidation potential is obtained, as can be seen in Figure 9: b (including the diffusion constant) changes as a function of the oxidation potential:

$$b = 0.07398 + 0.0000265E$$

4. Simulation

Equation 9 describes the theoretical chronoamperograms predicted by the ERCS model. The first term describes the evolution of the charge consumed by the relaxation (relaxation−oxidation−nucleation) processes after a potential step. The second term describes the evolution of the diffusion charge.

$$I(t) = 2aQ_r t e^{(-at^2)} + 2abQ_d e^{(-bt)} \int_0^t t' e^{(bt' - at'^2)} \, dt' \tag{9}$$

where a and b are

$$a = \frac{\pi N_0 \lambda^2 k_0^2}{A}[C_{LiClO_4}]^{0.25} e^{[-(2\Delta H)/(RT)]} \tag{10}$$

$$b = \frac{2D}{h^2} \tag{11}$$

Considering that ΔH includes η and η_c, all of the experimental variables (compaction potential, oxidation potential, temperature, and electrolyte concentration) are present in this theoretical
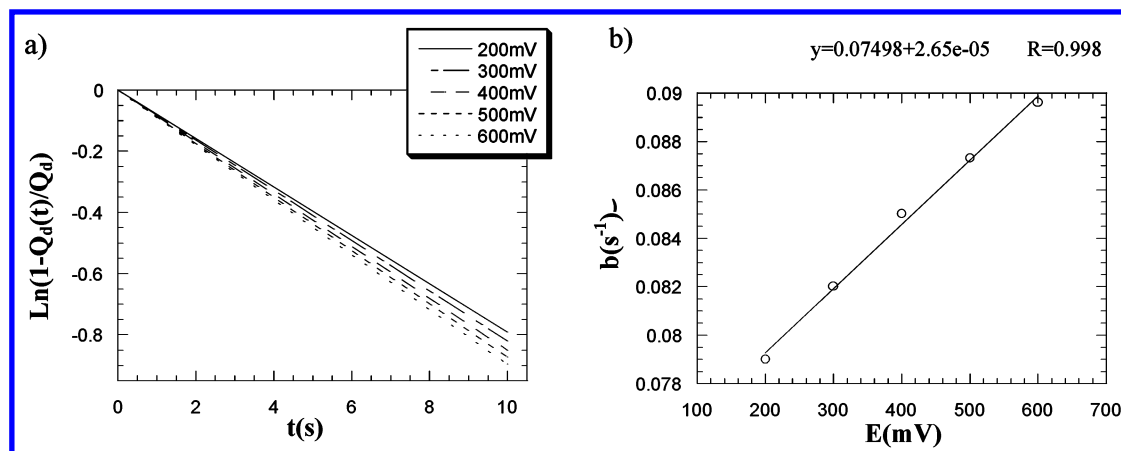
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Figure 9. (a) Semilogarithmic plot of $\{(1 - Q(t))/Q\}$ vs oxidation time obtained from chronoamperograms attained by potential steps from -550 mV to different indicated oxidation potentials. (b) Plot of the diffusion constant b obtained from the slopes of the lines in part a as a function of the oxidation potential.
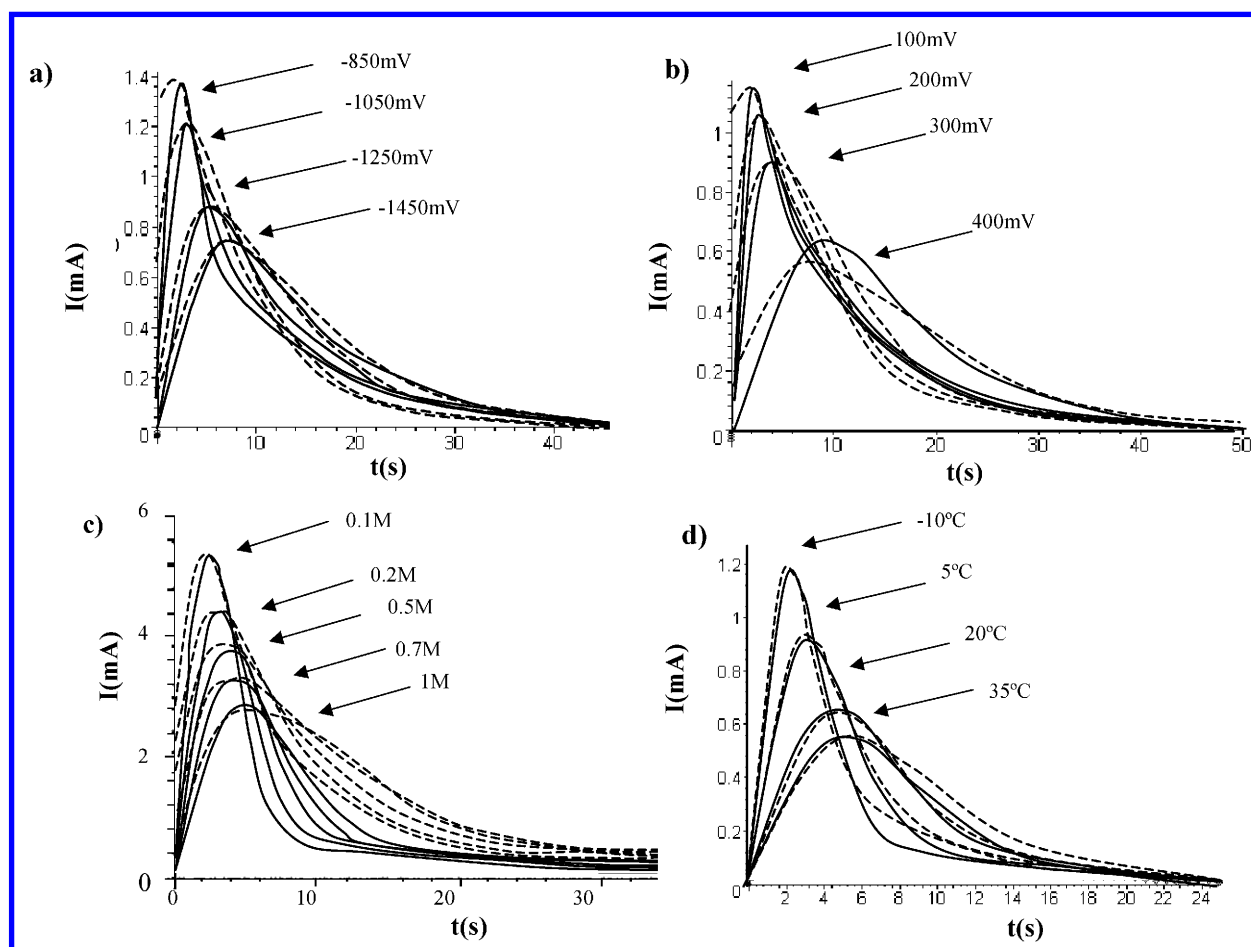

Figure 10. Overlapping of theoretical ($-$) and experimental ($--$) chronoamperograms obtained (Figure 2) or simulated under different experimental conditions: (a) different compaction potentials; (b) different oxidation potentials; (c) different electrolyte (or counterion) concentrations, and (d) different temperatures.

equation. In this way, this is a self-consistent model without any adjustable parameters. Considering that the different constants had being obtained above, we can determine if this equation is able to simulate the experimental chronoamperograms shown by Figure 3 and obtained under the influence of different variables.

An electrochromic film of polyaniline synthesized on a mirror-polished platinum electrode having a thickness of 0.22 μm (obtained from the polymer weight, the density of the polymer, and the electrode surface) was used. The number of nucleation cylinders (blue circles initiated on a green reduced

electrochromic film) formed per square centimeter (N_0) of our film was 7. The area of the working electrode (A) was 1 cm^2. The above obtained values of b, z_r, z_c, and ΔH^* were used. Finally, a value for the quotient λ/τ_0 of 1×10^{-5} cm s^{-1} was obtained from the chronoamperogram obtained when the coated electrode was submitted to a potential step from -900 to 400 mV. Using times included in the experimental range, eq 9 allows us to obtain the theoretical chronoamperograms. The good agreement attained between the theoretical (dotted lines) and experimental (continuous lines) values for the different studied variables is depicted by Figure 10.

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To realize the good agreement between experimental and theoretical curves, it is necessary to emphasize that no adjustable parameters were used. Only the constant λ/τ_0 has to be obtained from one of the experimental results.

5. Conclusions

The electrochemically stimulated conformational relaxation model was applied to the chronoamperometric behavior of polyaniline in acetonitrile, which is an aprotic media where a preponderant interchange of anions takes place during oxidation and reduction processes. The experimental results proved that, under these conditions, each chronoamperogram performed after polarization at a high cathodic potential has a similar nucleation shape with a maximum, as predicted by the ESCR model. Times of the maxima increase when, at constant polarization times, the chronoamperograms were obtained by potential steps from increasing cathodic potentials of polarization to the same oxidation potential. Keeping both the cathodic potential and cathodic polarization time constant, the chronoamperometric maxima show increasing times when they were obtained by steps to decreasing oxidation overpotentials. By subjecting the polymeric film to the same potential step after the same polarization times at the cathodic potential, slower relaxation processes (increasing times for the maxima) were obtained from decreasing concentrations of the electrolyte or at decreasing temperatures.

According to the ESCR model, the polyaniline film is reduced and compacted by cathodic polarization at more cathodic potentials that the closing potential. High cathodic overpotentials and long polarization times are required to complete the reduction processes: extra energy is required to expel counterions from a material showing rising compaction during reduction. The oxidation of a compacted film goes through two consecutive kinetic controlling processes: relaxation–nucleation and diffusion.

To apply the theoretical equation described for the modelization of polypyrrole films, specific constants for the polyaniline films (E_s, E_0, z_r, z_c, b, and ΔH^*) were obtained from the experimental conditions indicated by the model. Using those constants, we simulated the experimental chronoamperograms for the studied experimental variables. Good agreement was obtained between experimental and simulated chronoamperograms, and we conclude that the ESCR model gives a good description of the chronoampeometric behavior of polyaniline.

Taking into account the applicability of the ESCR model to a polymer whose redox processes differ from that of the polypyrrole, which was initially used to develop the model, we will now try to perform a comparative study of different conducting polymers by the ESCR model.

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