

Quasi-Equilibrium Volume Changes of Polyaniline Films upon Redox Switching. Formal Potential Distribution and Configurational Modeling

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The quasi-equilibrium electrochemomechanical behavior of relatively thick polyaniline films in sulfuric acid is investigated through experimental measurements and theoretical modeling. The leucoemeraldine (LE)–emeraldine (EM) conversion, or redox switching, is studied. The dependence of film volume and electrochemical charge is determined as a function of applied potential. It is observed that the film volume follows the charge, showing an expansion during the second half of the LE–EM oxidation. The model postulates the existence of a stable intermediate, protoemeraldine (PE), with a formal potential distribution for the PE–EM reaction. The volume change is modeled statistically considering contributions from mixing, polymer deformation, and electrostatic charge. The model shows very good agreement with the experiments, indicating that, in the conditions studied, the deformation contribution dominates the volume changes as a result of the conformational modifications undergone by the polymer in the PE–EM oxidation.

Introduction

Polyaniline (PANI) is one of the most interesting and intensely studied conducting polymers.¹ It has outstanding properties, such as electrical conductivity or electrochromism. These properties and their changes, accompanying both redox and acid–base reactions, have spawned a number of proposed applications which include actuators,² sensors,³ corrosion protection,⁴ solid-phase microextraction,⁵ supercapacitors,⁶ and batteries,⁷ to mention only a few. However, the physicochemical processes of these polymers are not fully understood yet. The redox behavior of arylamine polymers such as PANI has been extensively investigated and is usually interpreted in terms of three redox states, reduced leucoemeraldine (LE), oxidized emeraldine (EM), and fully oxidized pernigraniline, the conversions between them involving two-electron reactions.⁸ The conversion between LE and EM (known as redox switching) is the most important because pernigraniline is unstable in aqueous solution. It involves an intermediate state, usually known as a radical cation or polaron state, which shows unpaired spins in electron paramagnetic resonance spectroscopy measurements⁹ and is often considered to be a transient one. However, one of the first studies on PANI chemistry¹⁰ described it as a distinct, stable oxidation state called protoemeraldine (PE), and recently, it was also considered a stable state, explaining the temperature dependence of the PANI magnetic susceptibility in terms of the LE–PE–EM equilibrium.^{9c}

Although these reactions have usually been described in terms of simple Nernstian steps, it should be considered the idea of a distribution of formal potentials for some of these steps. This idea is not a new one; several times it has been considered to explain the behavior of different systems. It has been applied

to electrodes modified by adsorbed layers,¹¹ covered by different electroactive polymers,¹² and particularly by PANI films.¹³ Moreover, Vorotyntsev et al. have presented theoretical models that consider the equilibrium conditions for the electronic and ionic species including the metal/polymer and the polymer/solution interfaces¹⁴ and the electron–ion interactions within the polymer phase.¹⁵ These models can explain the cyclic voltammetric response of conducting and redox polymers. On the other hand, there is considerable evidence that, during the redox switching of arylamine-ring-substituted polymers, they develop strains¹⁶ and undergo contractions and expansions.¹⁷ Actually, the redox switching of the polyvinylferrocene polymer has been interpreted along these lines and reinterpreted¹⁴ by the theoretical models mentioned above.

Among the physicochemical properties of electroactive polymers, such as PANI and substituted arylamines, one which has attracted attention in recent years is the so-called “electrochemomechanical effect”, that is, the expansion and contraction that arise upon redox switching.^{17–19} This effect has led to the proposal of PANI as a material for actuators.^{1,19b} It has been analyzed in terms of a sigmoid distribution of apparent formal potentials and a statistical thermodynamical model, including the development of strains during the redox switching,^{18a,b} and it has been presented as a thermodynamic model, considering that the reduced and oxidized forms of the polymers are polyelectrolytes and that both forms are of a different chemical nature.^{18c} Recent voltammetric volume-change studies^{17b} have shown that two stages are clearly distinguishable, each one comprising about half the charge spent in the LE–EM oxidation, thus, additionally supporting the existence of PE as a relatively stable state between LE and EM. These changes have been attributed to several factors such as polymer–backbone charging, ion and/or solvent exchange, and conformational changes upon oxidation.¹⁹ Well-known statistical treatments for these issues have been developed previously, among others, by Flory and Hill.²⁰ The study of mechanical deformations of arylamine

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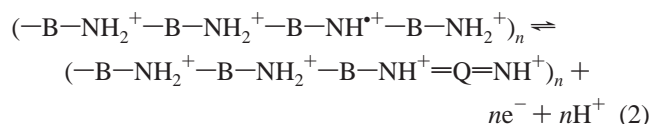
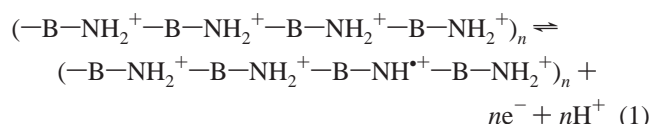
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polymers, besides its own interest related to applications such as actuators, is useful also because it should be an aid to gain insight into the electrochemical-switching process. In this work, the volume changes of PANI are analyzed under (nearly) equilibrium conditions by theoretical modeling and experimental studies under potentiostatic conditions with a simultaneous microscopic observation of thick PANI films. We present here a theoretical model based on formal potential distribution and conformational statistics that allows us to explain quantitatively the expansion and contraction mentioned above.

Theoretical Section

The polymer film is treated as a separate phase in electrochemical equilibrium with the metal electrode and the external solution. It is composed of N_1 molecules of electrolyte solution (assumed to be similar to water in its bulk properties) and N_2 polymer molecules each having on average n_m monomer units, with the film comprised of a total of $M = n_m N_2$ monomer units. From the point of view of the redox processes, the polymer film is considered to be composed of $n = M/4$ tetrameric redox units. First the electrochemical behavior and afterward the swelling process will be treated.

Electrochemical Behavior. The redox units of PANI are assumed to be in one of these redox states: fully reduced LE, intermediate PE, and (half) oxidized EM. These states are, in principle, protonated, albeit to a different degree (see below). The further oxidation to pernigraniline is not considered here. The polymer redox changes can be described by these reactions:



where $-\text{NH}_2^+$ represents protonated amine groups, $-\text{NH}^+=$ represents protonated imine groups, B represents benzenoid rings, Q represents quinoid rings, and $\text{B}-\text{NH}^{*+}-\text{B}$ represents the radical cation (polaron) protonated PE state. Considering the system to be in electrochemical equilibrium (or quasi-equilibrium), reactions 1 and 2 should have a Nernstian behavior so that it can be written

$$E = E_1^{0'} - \frac{kT}{e} \ln \frac{x_{\text{LE}}}{x_{\text{PE}}} \quad (3)$$

$$E = E_2^{0'} - \frac{kT}{e} \ln \frac{x_{\text{PE}}}{x_{\text{EM}}} \quad (4)$$

where x_{LE} , x_{PE} , and x_{EM} are the fractions of redox units in the LE, PE, and EM states, respectively, $E_1^{0'}$ and $E_2^{0'}$ are the formal potentials of reactions 1 and 2 in the medium employed, and e , k , and T have their usual meaning. It can be easily deduced that

$$x_{\text{PE}} = \frac{1}{1 + K_2 w + (1/K_1 w)} \quad (5)$$

$$x_{\text{EM}} = \frac{K_2 w}{1 + K_2 w + (1/K_1 w)} \quad (6)$$

with $x_{\text{LE}} + x_{\text{PE}} + x_{\text{EM}} = 1$, and

$$Q = Q_m \left(\frac{x_{\text{PE}}}{2} + x_{\text{EM}} \right) \quad (7)$$

where Q is the electrical charge, $K_1 = \exp(-eE_1^{0'}/kT)$, $K_2 = \exp(-eE_2^{0'}/kT)$, $w = \exp(eE/kT)$, and Q_m is the charge spent to fully oxidize the polymer from LE to EM. However, the experimental Q versus E data (see Figure 1) cannot be described satisfactorily by eqs 5–7; specifically, those points above half the maximum charge do not fit adequately. As it has been already pointed out,¹⁸ conductive polymers show an apparent distribution of redox formal potentials. Here, it will be assumed that a formal potential distribution arises for reaction 2 as a result of strong interactions between quinoidic groups, caused by the electronic delocalization of the EM salt form. Note that this is equivalent to considering activity coefficient changes. To make the problem tractable, the following (hypothetical) steps will be considered: (i) At a given electrode potential value E , the polymer, initially in the LE state, oxidizes from LE to PE, reaching the equilibrium value of x_{LE} at E ; the remaining part of the polymer, $x' = 1 - x_{\text{LE}}$, being PE. (ii) The fraction x' evolves, oxidizing until the equilibrium values of x_{PE} and x_{EM} are reached. In this last step, the redox units react according to a distribution of formal potentials $g(E_2^{0'})$; in a small polymer fraction, dx' , having a uniform formal potential, eq 4 can be written

$$E = E_2^{0'} - \frac{kT}{e} \ln \frac{dx' - dx_{\text{EM}}}{dx_{\text{EM}}} = E_2^{0'} - \frac{kT}{e} \ln \frac{1 - dx'_{\text{EM}}}{dx'_{\text{EM}}} \quad (8)$$

where $dx'_{\text{EM}} = dx_{\text{EM}}/dx'$. Equation 8 can be rearranged to a Langmuir type form:

$$dx'_{\text{EM}} = \frac{1}{1 + 1/K_2 w} \quad (9)$$

The total fraction x'_{EM} of x' in EM form can be found by integrating eq 9, taking into account the distribution function g :

$$x'_{\text{EM}} = \int_{-\infty}^{\infty} g(E_2^{0'}) \frac{1}{1 + \frac{\exp(eE_2^{0'}/kT)}{w}} dE_2^{0'} \quad (10)$$

Equation 10 is well-known, for example, in surface chemistry and catalysis²¹ and in the chemistry of natural heterogeneous substances.²² Here, as it is usual, a Langmuir (noninteraction) isotherm is employed as the local isotherm, and interactions are accounted for by the distribution g . Depending on g , it may or may not have an analytical solution. Posadas et al.^{18a,b} found a distribution that, in differential form, produces results very similar to a Gaussian one but which does not yield an analytical solution in eq 10. Sips²¹ has introduced a quasi-Gaussian distribution function that, from eq 10, yields a Langmuir–Freundlich type expression:

$$x'_{\text{EM}} = \frac{(K_{2,m} w)^m}{1 + (K_{2,m} w)^m} \quad (11)$$

where m ($0 < m \leq 1$) is related to the width of the distribution

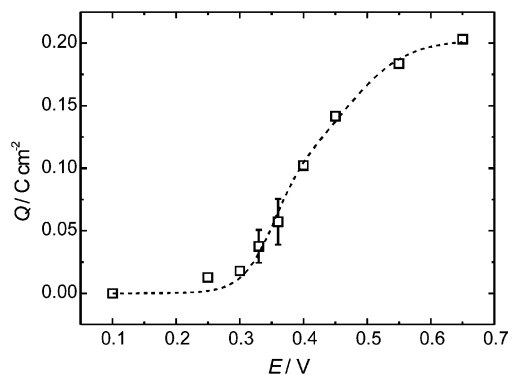


Figure 1. Stationary charge vs potential data for PANI in 1 M H₂SO₄. Squares, experimental points; dotted line, fitting to equations (7, 13, and 14).

($m = 1$ gives a Dirac's delta function) and $K_{2,m}$ is the value of K_2 corresponding to the maximum of the distribution. Rearranging eq 11

$$E = E_{2,m}^0 - \frac{kT}{me} \ln \frac{1 - x'_{EM}}{x'_{EM}} = E_{2,m}^0 - \frac{kT}{me} \ln \frac{x_{PE}}{x_{EM}} \quad (12)$$

where $E_{2,m}^0 = -(kT/e) \ln K_{2,m}$. Thus, the presence of a quasi-Gaussian distribution of formal potentials is tantamount to an effective number of electrons lower than unity. When eq 12 is used instead of eq 4, eqs 5 and 6 result in

$$x_{PE} = \frac{1}{1 + (K_{2,m}w)^m + (1/K_1w)} \quad (13)$$

$$x_{EM} = \frac{(K_{2,m}w)^m}{1 + (K_{2,m}w)^m + (1/K_1w)} \quad (14)$$

which, together with eq 7, describe satisfactorily the stationary Q versus E behavior, as shown in the Results section.

Configurational Statistics. The polymer molecules are entangled and/or cross-linked, thus, behaving as a network. The process of swelling of this network is assumed to be isotropic and composed of several contributions, namely, polymer–electrolyte mixing, polymer-network deformation, and polymer charging through hydrogen binding.²⁰ These contributions are assumed to be independent. The condition for swelling equilibrium can be written as

$$\left. \frac{\partial F}{\partial V} \right|_{T,N_2} = 0 \quad (15)$$

where F is the Helmholtz free energy and V the volume.

Proton Binding and Electrostatic Contribution. Because the polymer backbone charges through proton binding, it is relevant to consider the protonation equilibria inside the film. As previously found,^{17b} there is a considerable fraction of electrolyte inside the film with Donnan equilibrium expected between the external and the internal media, and the H⁺ concentration is expected to be lower inside the film. Thus, the protons bound to the polymer backbone should be considered in equilibrium at the internal pH. As it is well-known, the quinoidic N atoms have higher pK_a values; thus, the number of charges on the polymer chain will increase upon oxidation, with the increase being lower as the pH becomes lower. If it is assumed that the protonation of each N atom is independent of the protonation state of its neighbors, it can be written

$$\alpha_i = \frac{c_{H^+}^{\text{int}}}{c_{H^+}^{\text{int}} + K_{ai}} \quad (16)$$

where $i = \text{LE, PE, EM}$, $c_{H^+}^{\text{int}}$ is the internal proton concentration, and K_{ai} is the conditional equilibrium constant in the electrolyte employed. Considering the tetrameric units, a LE tetramer unit will have, on average, $4\alpha_{\text{LE}}$ protonated and $4(1 - \alpha_{\text{LE}})$ unprotonated benzenic N atoms; a PE unit will have α_{PE} protonated and $1 - \alpha_{\text{PE}}$ unprotonated radical cation N atoms along with $3\alpha_{\text{LE}}$ and $3(1 - \alpha_{\text{LE}})$, respectively, benzenic nitrogens; and finally, an EM unit will have $2\alpha_{\text{EM}}$ and $2(1 - \alpha_{\text{EM}})$ protonated quinoidic nitrogen atoms along with $2\alpha_{\text{LE}}$ and $2(1 - \alpha_{\text{LE}})$ benzenic ones. The total number of positive charges on the polymer backbone, Z , will be given by

$$Z = n[4x_{\text{LE}}\alpha_{\text{LE}} + x_{\text{PE}}(3\alpha_{\text{LE}} + \alpha_{\text{PE}}) + x_{\text{EM}}(2\alpha_{\text{LE}} + 2\alpha_{\text{EM}})] \quad (17)$$

The electrostatic contribution to the free energy will be treated following the procedure described by Hill.^{20a} Because the film is big enough to neglect the bending of the potential profile at the interfaces, the electrostatic potential will be assumed to be constant inside it (Donnan potential) so that the Poisson–Boltzmann equation can be written

$$0 = \rho e + \sum_i z_i e c_i (1 - \varphi_2) \exp(-z_i e \psi / kT) \quad (18)$$

where $\rho = Z/V$ is the number density of charge of the polymer backbone, z_i is the charge of ion i , c_i is its concentration (number density), and ψ is the Donnan potential. For a 1–1 electrolyte of concentration c , assuming that the standard chemical potentials and activity coefficients are equal in the internal and external solutions, eq 18 results in

$$\psi = \frac{kT}{e} \operatorname{arcsinh} \left[\frac{\rho}{2c(1 - \varphi_2)} \right] \quad (19)$$

with

$$c_{H^+}^{\text{int}} = c \exp \left(-\frac{z_i e \psi}{kT} \right) \quad (20)$$

The electrostatic contribution to the free-energy change is found to be^{20a}

$$\Delta F_{\text{el}} = ZkT \left\{ \operatorname{arcsinh} \left[\frac{\rho}{2c(1 - \varphi_2)} \right] - \sqrt{1 + 2 \left[\frac{2c(1 - \varphi_2)}{\rho} \right]} + \frac{2c(1 - \varphi_2)}{\rho} \right\} \quad (21)$$

Mixing Contribution. The free energy of mixing is given by^{20a,b}

$$\Delta F_{\text{mix}} = kT \left[\frac{N_1 v_1}{v_2} \ln \varphi_1 + \chi N_1 v_1 \varphi_2 \right] \quad (22)$$

where

$$\varphi_1 = \frac{V_1}{V} = \frac{N_1 v_1}{N_1 v_1 + M v_2} \quad (23)$$

and

$$\varphi_2 = \frac{V_2}{V} = \frac{Mv_2}{N_1v_1 + Mv_2} \quad (24)$$

are the volume fractions of the electrolyte and polymer, respectively, v_1 is the partial molecular volume of the electrolyte, and v_2 is the monomer partial molecular volume in the swollen polymer film.

χ is an interaction parameter related to the “Van Laar heat of mixing”,^{20c} ΔU_m , by

$$\Delta U_m = kT\chi(M + N_1)\varphi_1\varphi_2$$

Deformation Contribution. The deformation contribution is purely entropic and is given by^{20b}

$$\Delta F_{\text{def}} = -N_2kT \left[\frac{3}{2} \left(\frac{V}{V_0} \right)^{2/3} - \frac{3}{2} + \frac{2}{f} \ln \frac{V_0}{V} \right] \quad (25)$$

where V_0 is the unperturbed volume of the dry network corresponding to the equilibrium configurational distribution and f is the Flory functionality^{20b} related to the cross-linking of the polymer molecules. Here, V_0 will be considered as a function of the electrode potential because the quinoidic structures developed upon oxidation will have different molecular geometries and, consequently, different configurations. To estimate the dependence of V_0 with the redox state in an analytically tractable form, the configurational behavior of the polymer will be approximated with the freely rotating model.^{20d} The unperturbed volume is assumed to be proportional to the third power of the mean radius of gyration, r_G , which, as it is well-known, is related to the end-to-end polymer length r , so it can be written

$$V_0 = A(\overline{r_G^2})^{3/2} = A \left(\frac{\overline{r^2}}{6} \right)^{3/2} \quad (26)$$

where A is a geometrical constant. Now, the mean-square value of r can be deduced for the freely rotating polymer, considering it to be built up from M straight segments of length l joined by the N atoms (the internal rotational states of the aromatic rings will not be considered because they will likely have a vanishing average). The segments have all the same length, and the configuration is determined by the state of rotation around the N atoms. The relevant parameters are the bond angles θ_i (see Figure 2 for the definitions), whose values depend on the redox and protonation states of each segment.

When the case of simple chains is extended,^{20d} if the polymer network is composed of Mx_{LE} reduced units, Mx_{PE} PE units, and Mx_{EM} EM units [each one divided into $\alpha_i Mx_i$ protonated and $(1 - \alpha_i)Mx_i$ unprotonated] randomly distributed, the mean-square value of r will be given, taking into account that a PE unit contains three benzenoid atoms and one radical N atom and an EM unit contains two benzenoid and two quinoid N atoms, in the limit of large M , by

$$\begin{aligned} \overline{r^2} = Ml^2 \{ & 1 + [\cos(\theta_{\text{LB}})^{\alpha_{\text{LE}}} \cos(\theta_{\text{LS}})^{1-\alpha_{\text{LE}}}]^{x_{\text{LE}}+3x_{\text{PE}}/4+x_{\text{EM}}/2} \times \\ & [\cos(\theta_{\text{PB}})^{\alpha_{\text{PE}}} \cos(\theta_{\text{PS}})^{1-\alpha_{\text{PE}}}]^{x_{\text{PE}}/4} \times \\ & [\cos(\theta_{\text{EB}})^{\alpha_{\text{EM}}} \cos(\theta_{\text{ES}})^{1-\alpha_{\text{EM}}}]^{x_{\text{EM}}/2} \} / \{ 1 - \\ & [\cos(\theta_{\text{LB}})^{\alpha_{\text{LE}}} \cos(\theta_{\text{LS}})^{1-\alpha_{\text{LE}}}]^{x_{\text{LE}}+3x_{\text{PE}}/4+x_{\text{EM}}/2} \times \\ & [\cos(\theta_{\text{PB}})^{\alpha_{\text{PE}}} \cos(\theta_{\text{PS}})^{1-\alpha_{\text{PE}}}]^{x_{\text{PE}}/4} \times \\ & [\cos(\theta_{\text{EB}})^{\alpha_{\text{EM}}} \cos(\theta_{\text{ES}})^{1-\alpha_{\text{EM}}}]^{x_{\text{EM}}/2} \} \quad (27) \end{aligned}$$

When $\overline{r^2}$ is known, the unperturbed volume at any potential

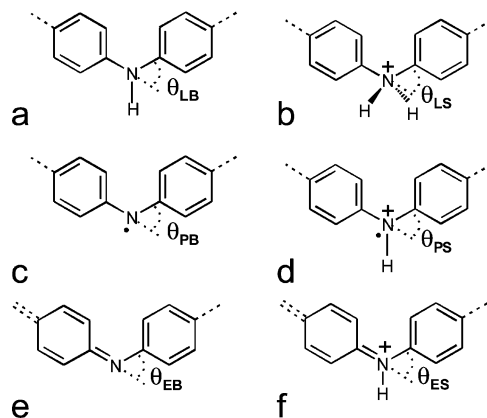


Figure 2. Definitions of bond angles around nitrogen atoms in the freely rotating model. (a) LE base, (b) LE salt, (c) PE base, (d) PE salt, (e) EM base, and (f) EM salt.

can be obtained as

$$V_0 = V_{0r} \left(\frac{\overline{r^2}}{r_r^2} \right)^{3/2} \quad (28)$$

where V_{0r} is the unperturbed volume in the fully reduced state ($x_{\text{LE}} = 1$) and r_r^2 is the corresponding mean-square distance.

Swelling Equilibrium Condition. Considering the different contributions above derived in eq 15, the following condition is obtained:

$$\begin{aligned} \frac{1}{v_2} \left[\chi \varphi_2^2 + \varphi_2 + \ln(1 - \varphi_2) + \frac{N_2 \varphi_2^{1/3} (Mv_2)^{2/3}}{MV_{0r}^{2/3} (\overline{r^2}/r_r^2)} - \frac{2N_2 \varphi_2}{Mf} \right] + \\ 2c \left[1 - \sqrt{1 + \left(\frac{\rho}{2c(1 - \varphi_2)} \right)^2} \right] = 0 \quad (29) \end{aligned}$$

From this expression, φ_2 can be obtained and, when eq 24 is used, the volume can be computed.

Numerical Calculations

The above model is examined by fitting it to experimental data. The Q versus E data is fitted using a Levenberg–Marquardt nonlinear least-squares algorithm to eqs 7, 13, and 14; from this procedure, E_1^0 , $E_{2,m}^0$, and m are found. The computations of the swelling model were as follows:

i. The bond angles θ_i were found by standard AM1 calculations over PANI segments (typically eight monomers long) and averaging. The results were (all within $\pm 1^\circ$) $\theta_{\text{LB}} = \theta_{\text{PB}} = 52^\circ$, $\theta_{\text{LS}} = \theta_{\text{PS}} = 65^\circ$, $\theta_{\text{EB}} = 56^\circ$, and $\theta_{\text{ES}} = 50^\circ$.

ii. The values of the acidity constants for LE and EM were taken from the literature²³ as $\text{p}K_{\text{aLE}} = 2.5$ and $\text{p}K_{\text{aEM}} = 5.5$, V_{0r} was estimated from measurements as described below, f was taken as 3, corresponding to linear chains partially cross-linked, and $\text{p}K_{\text{aPE}}$, χ , v_2 , and N_2 were taken as adjustable parameters to be found by fitting.

iii. For each E value, the polymer LE, PE, and EM fractions were computed using eqs 13 and 14, and eq 29 was solved for φ_2 using a secant method. Thus, a V versus E curve is computed for the given parameter values.

iv. A least-squares fitting of the V versus E experimental data is performed by adjusting the aforementioned parameters.

All the fittings were performed extensively starting from different initial values to test the uniqueness of the fit. No significant differences in the resulting fitting values were found.

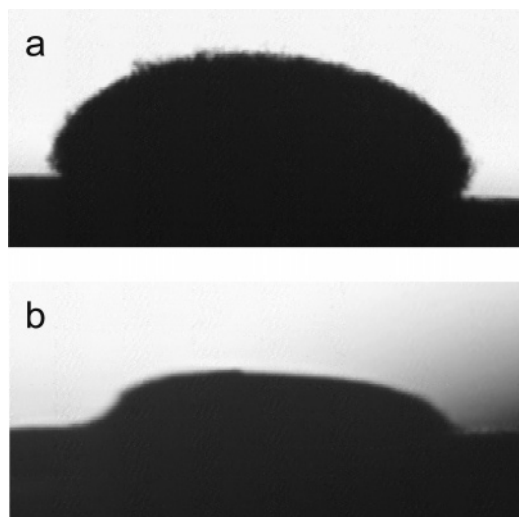


Figure 3. Video images of a PANI film fully reduced and relaxed in 1 M H_2SO_4 (a) and after treatment with NH_3 to remove the acid and drying (b). Image dimensions: $906 \times 418 \mu\text{m}$.

Experimental Methods

PANI films were synthesized electrochemically from 0.5 M aniline solutions in a 1.5 M sulfuric acid + 1.5 M perchloric acid mixture. For further details, see Lizarraga et al.^{17b} A standard three-compartment electrochemical cell with a reversible hydrogen electrode in the same solution was employed. All potentials are presented in the standard hydrogen electrode scale.

The working electrode was a platinum disk of 0.5-mm diameter that was inserted into a Teflon holder. The electrode was polished with alumina, washed in an ultrasonic bath, and rinsed carefully. The electropolymerization was performed by potential cycling at a scan rate of 0.05 V s^{-1} between 0.1 and 1.0 V. The process was monitored through the anodic charge of the first peak (between 0.3 and 0.5 V), and it was stopped when it reached a value of 0.5 C/cm^2 .

After polymerization, the working electrode was extracted from the cell, carefully rinsed with high-purity water, and transferred to a second cell suitable for microscopical observation.^{17b} This cell was filled with 1 M sulfuric acid, and voltammetric cycling was performed between 0.1 and 0.65 V at 0.012 V/s until the stationary state was obtained. Subsequently, the potential was held at the lower limit for 90 min to bring the polymer to its fully reduced and relaxed state.²⁴ After the holding time, the image of the fully reduced and relaxed polymer film was captured and its processing yielded the initial area value A_i of the film projected in the video images (see Figure 3); details of the image processing have been given previously.^{17b} Chronoamperometric measurements were performed at different potentials between 0.1 and 0.65 V, both in increasing and in decreasing steps. In each case, the potential was held until the current reached a stationary, nearly zero value (90 min, approximately). Then, video images were recorded, yielding the corresponding area values A_E . Apart from this, charge values at each potential were obtained by integrating the current transients.

From the images captured, the relative changes in the observed area, $\Delta A/A = (A_E - A_i)/A_i$, were obtained. Because the film expansion is approximately isotropic, the ratio $\Delta V/V$ and the film volume V can be calculated from $\Delta A/A$ assuming cylindrical symmetry.^{17b} In the following, results will be presented as volumes.

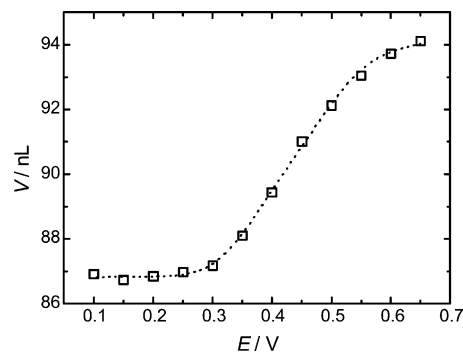


Figure 4. PANI film volume as a function of electrode potential in 1 M H_2SO_4 . Squares, experimental points; dotted line, model fitting.

To estimate the unperturbed (in the sense given by Flory)^{20d} LE volume V_{0r} , after the potentiostatic experiments, the film was again held at the lower potential limit to obtain it in the fully reduced and relaxed state. Afterward, it was removed from the cell with applied potential, treated with 1 M NH_3 solution to obtain the base form, thoroughly rinsed, and dried under vacuum at 45°C . To keep the film reduced, hydroxylamine was added both to the ammonia solution and to the rinsing water. After the drying process, an image was obtained and processed to determine the film volume as was done previously.^{17b}

Results

Figure 3 shows images of a PANI film in its fully reduced and relaxed state at $E = 0.1 \text{ V}$ in 1 M H_2SO_4 , before and after treatment with ammonia and drying. The volumes are obtained from these images as described previously.^{17b} From measurements made on the images, the reduced film in Figure 3a had a maximum thickness of $238 \mu\text{m}$, a diameter of $739 \mu\text{m}$, and a volume of 74 nL, whereas after drying, the volume was reduced to 24 nL.

Figure 1 shows the Q versus E average curve obtained from several chronoamperometric measurements.²⁵ The points shown are averages between the increasing and the decreasing potential sequences. In general, results for those sequences were coincidental except in the region of 0.33–0.36 V where a noticeable difference was observed, as indicated by the error bars. This indicates the difficulty in attaining equilibrium as a result of the essentially nonconducting character of the polymer at these potentials. It is observed that there is a change in the shape of the curve at about half the maximum charge, suggesting a different character for the two oxidation steps. The data points in Figure 1 can be satisfactorily fitted to eq 7 with $E_{10'} = 0.35 \pm 0.01 \text{ V}$, $E_{2,m} = 0.47 \pm 0.02 \text{ V}$, and $m = 0.57 \pm 0.20$ with $Q_m = 0.20 \text{ C cm}^{-2}$. The agreement is very good.

Figure 4 shows the film volume as a function of applied potential, whereas Figure 5 shows the volume–charge relationship. It is observed in Figure 4 that a shape very similar to that observed in Figure 1 results, indicating that the volume follows closely the faradic charge, as previously observed under voltammetric conditions.^{17b} The dotted line shows the fitting to the model developed here, with an excellent agreement. The parameter values found were $\chi = 3.26$, $\text{p}K_{a2} = 3.2$, $N_2 = 3 \times 10^{12}$, and $v_2 = 95 \text{ cm}^3 \text{ mol}^{-1}$. Because of the rather convoluted method used to fit the results, it was very difficult to obtain uncertainty estimates for these parameters; however, it was found that the fitting was highly sensitive to the values of χ and v_2 but much less sensitive to $\text{p}K_{a2}$ and N_2 : it was observed that changes of 2–3% in χ and v_2 led to significant differences in fitting quality, whereas changes of at least an order of magnitude higher in $\text{p}K_{a2}$ and N_2 were needed to find similar

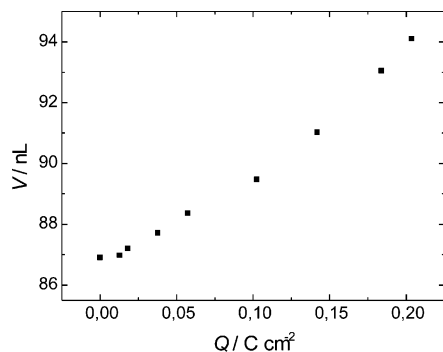


Figure 5. PANI film volume as a function of film oxidation charge in 1 M H₂SO₄.

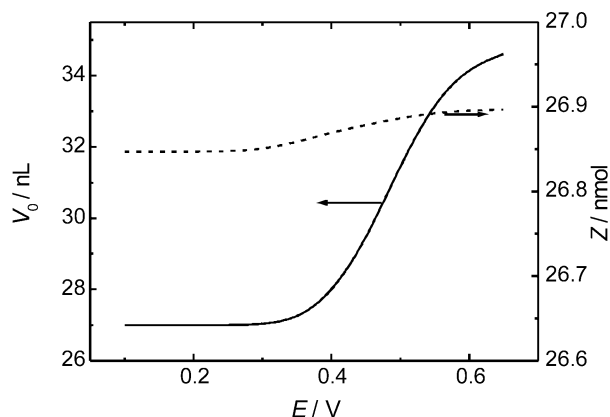


Figure 6. Model-predicted variations of the unperturbed volume V_0 and the total charge Z (in moles of bound H⁺) as a function of electrode potential.

deviations. Also, the value of f (between 2 and 4) had very little influence on the results.

From the model equations, the magnitude of the different contributions to the polymer volume change can be evaluated. Figure 6 shows the model-predicted variations of the total polymer charge Z and the unperturbed volume V_0 . As it can be seen, Z shows very little variation in the conditions studied here, so that the main effect is due to the conformational changes reflected in V_0 . This is mainly a result of the changes in the bond angles in the EM form of the polymer in eq 27.

Discussion

A (apparent) formal potential distribution for the second oxidation step of the PANI redox switching, namely, the PE–EM redox couple, is proposed here. This distribution is consistent with the experimental data presented in this work. It can explain the shape usually observed during the positive scan in the cyclic voltammetry of arylamine polymers such as PANI, where a relatively high current is observed after the first voltammetric peak; this current can be attributed to the gradual oxidation from PE to EM resulting from the distributed formal potential. Energy distributions are observed in different aspects of macromolecular and surface chemistry^{21,22} and appear to be a consequence of close interactions between identical or similar groups or sites. Recently, when temperature effects on the relaxation of arylamine polymers were analyzed,²⁶ it was found that the interaction between the reduced redox centers is attractive, whereas the interaction between oxidized ones is repulsive. This is consistent with an apparent formal potential distribution, because as the polymer oxidation progresses, the energy required increases.

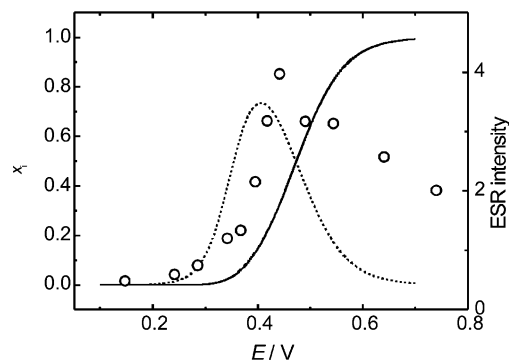


Figure 7. Comparison of the predicted distribution of redox species (in 1 M H₂SO₄ potentiostatic conditions and a thickness of 238 μ m) with ESR measurements from Glarum and Marshall^{9a} (in 0.5 M H₂SO₄, potentiostatic conditions, and a thickness of about 1 μ m) as a function of applied potential. Dotted line, x_{PE} ; continuous line, x_{EM} ; circles, ESR data.

Additional support for the electrochemical model can be gained by comparing it to electron spin resonance (ESR) measurements. The intermediate state PE, which is assumed to have unpaired electrons, should show an ESR signal. ESR response has indeed been observed in PANI by a number of authors.⁹ In Figure 7, results of Glarum and Marshall^{9a} are compared with the model predictions for the fraction of PE; the behavior is similar, considering the different experimental conditions. Petr et al.^{9c} have also explained the temperature dependence of the magnetic susceptibility for the different PANI forms in terms of a (electro) chemical equilibrium between these forms, which is in line with the model presented here.

The configurational model parameters found by fitting are physically reasonable. The value of χ (3.26, which corresponds to a mixing energy $\Delta U_m/(M + N_1)\phi_1\phi_2 = 1.34 \times 10^{-20}$ J) is greater than 0.5, indicating a mainly repulsive polymer–solvent interaction, which is in line with the fact that PANI is insoluble in water even in strongly acidic media. The monomer partial volume v_2 (95 cm³ mol⁻¹) is close to the aniline molar volume (91 cm³ mol⁻¹), the difference being also consistent with essentially repulsive polymer–solvent interactions. The pK_{a2} value, 3.2, is similar to pK_{a1} , presumably because of the structural similarity between LE and PE suggested by the semiempirical AM1 calculations. However, this value should be taken with caution because in the experimental conditions employed here the polymer is almost fully protonated and, consequently, the fitting is not very sensitive to the pK_a values. The results also show very little dependence on the N_2 and f values. These parameters appear in the cross-linking deformation entropy term in eq 29, thus, indicating that this term is not important in determining the polymer film volume. This, in turn, could be related to the fact that the polymer remains as a separate phase essentially because it is insoluble in water, irrespective of the presence of cross-links.

The statistical model for the volume changes predicts that the determining contribution comes from the conformational changes due to the formation of quinoidic moieties through the important changes in bond angles. This implies that the PE form does not have quinoidic structures in a smaller proportion than that of EM but that the radical cation units remain essentially isolated and do not migrate to form quinone imine units. This is supported by a recent investigation with PANI oligomers, which shows that the unpaired spins remain essentially confined to phenylenediamine moieties.²⁷ The electrostatic contribution shows little influence because, at the electrolyte concentration employed, almost all the N atoms are protonated with little

change occurring upon oxidation. It should be pointed out here that protonation not only affects swelling through polymer charging but also through conformational changes resulting from the significant bond angle variations. In a previous study,^{17b} it was found that in more acidic media the volume changes are smaller, which is in qualitative agreement with the present model.

Conclusions

1. The stationary charge-potential response of the first redox couple of the PANI films in acidic media can be satisfactorily described by considering two oxidation stages (from LE to PE and from PE to EM, respectively), with the second one having a quasi-Gaussian distribution of formal potentials.

2. The PE form (polaron or radical cation) is considered to be a stable one.

3. The volume-potential behavior is consistent with a model based on freely rotating chain statistics of the polymer film.

4. The model predicts that the main contribution to the volume changes in strongly acidic media is the conformational change due to bond angle variations upon the development of quinoidic structures.

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