The Redox Switching of Electroactive Polymers

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The present work is concerned with a thermodynamics model that describes the redox switching of electroactive polymers. It is well-known that, during the redox switching of these polymers, the following phenomena occurs: (i) conformational changes, (ii) income/outcome of solvent molecules with the subsequent changes in the state of swelling, (iii) injection/ejection of ions that specifically bind to the polymer, and (iv) injection/ejection of ions to maintain the electroneutrality inside the polymer. All these facts can be taken into account by considering that both the oxidized and reduced forms of the polymer are polyelectrolytes and that the reduced and oxidized forms of the polymers are of different chemical natures. For the different forms, the different contributions to the free energy can be determined and related to the apparent formal potential. This allows the influence of each one of the aforementioned contributions to the apparent formal potential to be calculated. The model is applied to the redox switching of a well-known electroactive polymer such as poly-(aniline) (Pani). From the knowledge of the changes in volume of Pani, the change in the number of water molecules, ion binding, and ion content inside the polymer can be computed.

I. Introduction

Electroactive polymers have aroused much interest, because of their properties and the variety of potential and actual applications.[1] These polymers are characterized by the possibility of being oxidized and reduced in a reversible way. They are usually divided into redox and conductive polymers.[2] Polymers in the first category possess, either as a part of the monomer unit or as a coordination compound, chemical groups that are participating in the redox reaction. As examples of this type of polymer, we may mention poly-*o*-aminophenol (POAP) and Os(II) bypyridyl−polyvinylpyridine (OsBPVP). In the first one, the redox centers are the amine groups that are oxidized to imine groups. In the second, it is the coordinated Os(II), which is oxidized to Os(III). Polymers in the second category (conductive polymers) are characterized by becoming conductors when they are oxidized (positively doped) to a certain degree. Examples of this class of polymers are polyaniline (Pani), polypyrrole (PPy), and polythiophene (PT).[1b] Of course, there are a wide variety of such polymers that can be obtained through procedures such as changing the coordination metal or substituents or by copolymerization with other molecules.[1b]

The applications of these polymers range from electrocatalyzers[3] to battery electrodes,[4] including displays, electrochromic devices, membranes, sensors, and mechanical actuators,[1b] just to mention a few.

The physical chemistry associated with the redox switching of these polymers has also attracted the attention of many workers. In these polymers, charge transport occurs by electron hopping from redox center to redox center in a diffusion-like way.[2,5] However, charge transport is usually controlled by the ingress/egress of ions to maintain the electroneutrality inside the polymer.[6] This transport mechanism is the one that results

in the possibility of these polymers to act as redox mediators.[7] That is, although some of these polymers are not actually electronic conductors, they can mediate the oxidation−reduction of a redox couple in the external solution. It is believed that this type of mechanism is the one operating during the oxidative phosphorilation of adenosine triphosphate (ATP) at the mitochondria.[8]

As it happens with polyelectrolytes,[9] these polymers bind ions that attach specifically to some ionized groups of the polymer. Also, they show another characteristic of polyelectrolytes: they change its conformation, according to the conditions of the external medium and its oxidation state. Thus, for instance, they show the well-known "memory effect" or "relaxation effect"; as a consequence of this process, some of these polymers change its electrochemical response, and many other properties, when submitted to a suitable oxidation state.[10]

Electroactive polymers are, in fact, polyelectrolytes.[2a] However, when modeling their electrochemical response, this property has not been properly recognized yet. Below, we will show that the recognition of their polyelectrolytic nature allows the dependence of the voltammetric response on the external media,[10] the volume increase,[11] the egress of protons,[12] and the ingress of ions[13] during the oxidation of these polymers to be explained naturally. Here we present a model that, based on the knowledge of the physical chemistry of polyelectrolytes, takes into account all of these facts. Furthermore, the present model is based on another work that has already been published.[14] For this reason, some of the thermodynamic deductions given there will be omitted here. We would like to stress that the intent of the present model is to explain the observed facts qualitatively.

II. The Model

II.1. Description of the Thermodynamic State of a Polymer. We will consider the polymer as a separate phase. On one side, it is in contact with an external solution. On the

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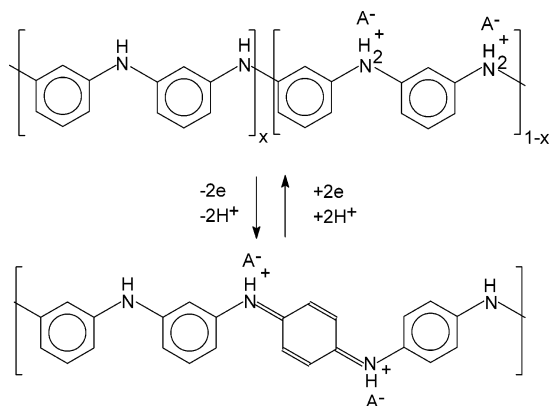
Figure 1. Schematic representation of the oxidation reaction of polyaniline (Pani) involving four monomer units.

other, it is in contact with a metallic conductor that is capable of providing holes or electrons for the polymer to be oxidized or reduced. We will consider an electrochemical process by which a reduced electroactive polymer is converted to an oxidized one. The polymer contains N_{ox} and N_{red} redox centers, the total number of them, $N_t = N_{ox} + N_{red}$, is constant. The conversion of reduced (Red) polymers to oxidized (Ox) polymers occurs through reaction 1:

$$\text{Red} \leftrightarrow \text{Ox}^+ + \text{e} \tag{1}$$

As an example, we will consider the redox switching of Pani. It is widely accepted that the overall reaction for the half oxidation of Pani-type polymers can be written as shown in Figure 1.[15] There, $x \approx 0.5$, $-\text{NH}-$ represents nonprotonated amine groups, and $-\text{N}=$ represents nonprotonated imine groups. Depending on the pH of the external solution, the amine and the imine groups are protonated to a certain extent. Later, we will consider these matters further.

We will also consider that the polymer in its reduced state consists of $N_{2,r}$ chains, each one containing, on average, $M_{2,r}$ monomer units. The total number of monomer units is given as $M_r = N_{2,r}M_{2,r}$. Similarly, for the oxidized form of the polymer, we define $N_{2,o}$, $M_{2,o}$, and M_o, respectively. Furthermore, in any state of oxidation, the polymer forms a network of entangled or cross-linked chains. This network is in contact with an external solution and is in electrochemical equilibrium with the solvent molecules and the different ionic species present there.

The polymer interacts with solvent molecules through an osmotic equilibrium. We will denote the number of solvent molecules inside the polymer as $N_{1,r}$ and $N_{1,o}$, corresponding to the reduced and oxidized polymer, respectively. For simplicity, we will consider that the molar volume of each monomer unit is of the order of magnitude of the molar volume of the solvent, v_0. The volume fractions of the polymer (ϕ_2) of each type of polymer then are $\phi_{2,r} = M_r/(M_r + N_{1,r})$ and $\phi_{2,o} = M_o/(M_o + N_{1,o})$. The volume fractions of the solvent are defined in a similar way. Obviously, $\phi_{2,o} + \phi_{1,o} = 1$ and $\phi_{2,r} + \phi_{1,r} = 1$.

In addition, each monomer unit may contain a functional chemical group capable of binding an ionic species. In the case of Pani, mentioned previously, these would be the amine groups $(-\text{NH}-)$ and imine groups $(-\text{N}=)$ that bind protons. Depending on the proton activity of the external medium, these groups would be protonated to a certain extent, resulting in charges along the polymer chains $(-\text{NH}_2^+-)$ for the amine groups and $(-\text{NH}^+ =)$ for the imine groups. We will consider that this protonation reaction is at equilibrium, and we will refer to the

free energy change of this process as the binding free energy (ΔA_b). In turn, the charges generated by protonation also cause some ions, which are present in the external electrolyte, to enter into the polymer, to maintain the electroneutrality in the region occupied by the polymer chains. We will refer to this process as the charging of the polymer and the corresponding free energy change will be called the electrical contribution (ΔA_{el}).

As the polymer is progressively oxidized, some M_r units become M_o units. It is considered that, during this process, the number of chains in the polymer that remain unchanged (that is, $N_{2,r} + N_{2,o}$) stays constant. After some number of units has been oxidized, the polymer will partially become another chemical entity. Thus, for instance, in the case of Pani, after two of four units have been oxidized, the reduced polymer (the leucoemeraldine form) becomes a half-oxidized polymer (the emeraldine form) (see Figure 1). However, we will assume that, during oxidation, each form retains its chemical entity and then the volume fraction of each form remains constant during the oxidation.

On the other hand, the free energy change involved in bringing the polymer into contact with the external solution can be considered to be composed of the following contributions (temporarily, we will omit the subindex that specifies which polymer form, reduced or oxidized, we are considering, with the understanding that the following expressions are applicable to both of them):

(1) The free energy of mixing the polymer with the solvent (ΔA_m). Following Flory,[9a] this might be written as

$$\Delta A_m = kT(N_1 \ln \phi_1 + N_2 \ln \phi_2) + \chi M_t \phi_1 \phi_2 \tag{2}$$

where ϕ_1 is the volume fraction of the solvent ($\phi_1 = 1 - \phi_2$), $M_t = N_1 + N_2 M$, and χ is the interaction parameter. This interaction parameter is defined as $\chi = -cw/(2kT)$, with c being the coordination number of the lattice and $w = w_{11} + w_{22} - 2w_{12}$ (see, for instance, Flory[9a] and Hill[9b]), where w_{11} is the interaction energy between solvent molecules, w_{22} the interaction energy between the monomers in a statistical chain, and w_{12} the interaction energy between a monomer in a statistical chain and the solvent. Good solvents have a value of $\chi < 0.0$, and bad solvents have a value of $\chi > 0.5$.[9a,9b] The phase behavior of the polymer is governed by χ. In the case of polyelectrolytes, one should consider the effective interaction parameter χ_{eff} (see below). If χ is bigger that a critical interaction parameter χ_{crit}, the system will show two phases; if $\chi < \chi_{crit}$, only one phase will be shown.[9a,9b]

The assumptions made here do not preclude the formation of separate domains of oxidized and reduced forms of the polymer. In the case of Pani, there is experimental evidence that, during the redox switching, there are coexisting domains of leucoemeraldine and emeraldine.[16]

(2) The polymer undergoes a swelling equilibrium with the solvent. As a consequence of it, the polymer network swells until the developed deformation of the network equals the osmotic pressure of the solvent. This corresponds to the case of free swelling.[9a,9b] The corresponding free energy change, ΔA_d, is purely entropic in nature. According to Flory,[9a] it can be written as

$$\Delta A_d = -T\Delta S_d = \nu M kT[\ln \phi_2 + 3(\phi_2^{-2/9} - 1)] \tag{3}$$

where νM is the number of monomer units, reduced or oxidized, that are participating in the deformation process.

(3) The change in binding free energy. This contribution can be written in terms of a Langmuir isotherm,[17] as

$$\Delta A_b = kT B\left\{\ln(1-f) + f\ln\left[\frac{f}{q(1-f)}\right]\right\} \quad (4)$$

where B is the total number of binding sites, f is the fraction of bound sites ($f = N_{ad}/B$, where N_{ad} is the total number of occupied sites), and q is the partition function of an occupied site. In our example of Pani, we can consider $B \propto M$, because the number of binding sites must be related to the number of monomer units. This matter will be further discussed below for the case of Pani. The Langmuir binding equilibrium is governed by

$$\frac{f}{1-f} = K_{ad}a_{ad} \quad (5)$$

where a_{ad} is the activity of the adsorbate in the external medium and K_{ad} is a constant that contains the partition function of the bound adsorbate and the standard chemical potential of the adsorbate in solution (see, for instance, chapter 7 in ref 9b). For simplicity, we will consider concentrations instead of activities. If, as it is the case of Pani, the reduced polymer is initially neutral, then, at a certain degree of protonation, the total number of charges on the polymer, n, will be

$$n = z_{ad}Bf \quad (6)$$

where z_{ad} is the charge of the adsorbate. In the case of Pani, the bound species are protons so that $z_{ad} = 1$. Below, we will show that, for Pani in the reduced state, the pK value is 2.5, and, for the oxidized state, p$K = 2.5$ for the amino groups and p$K = 5.5$ for the imino groups. It then should be expected that Pani in the reduced state should be almost completely charged for pH <0.5 and almost uncharged for pH >4.5. Similarly, the emeraldine form should be completely charged for pH <0.5 and uncharged for pH >7.5.

(4) As a consequence of having charged sites, counterions that come from the external solution must enter into the polymer to maintain the electrical neutrality. Much has been written about this contribution to ΔA_{el} (see, for instance, refs 9c and 9d). To keep the calculations as simple as possible, we will follow the very simple approach of Hill.[9b] According to him, the free energy change that is due to this contribution can be written as

$$\Delta A_{el} = \frac{z_{ad}^2 M f^2 \phi^2}{2v_0 I} \quad (7)$$

where $I = \Sigma c z_i^2$ is twice the ionic strength; c_i and z_i are the concentration and charge of ion i in the external solution, respectively.

The total free energy change of the polymer (ΔA_{pol}) results by adding eqs 3, 4, 5, and 7:

$$\Delta A_{pol} = \Delta A_m + \Delta A_d + \Delta A_b + \Delta A_{el} \quad (8)$$

In the following discussion, we will consider the polymer to be a network,[9a,9b] and, therefore, $N_2 = 1$. Moreover, we will consider $B = gM$, where g is the fraction of monomer units that are capable of binding protons.

The change in the chemical potentials corresponding to the different free energy contributions of the polymer can be found from the corresponding derivative, with respect to M. The chemical potentials should also have the subindex 2, indicating the polymer; however, for the sake of simplicity in the notation,

we will omit this subindex. Thus,[18]

$$\mu_m = \left(\frac{\partial \Delta A_m}{\partial M}\right)_{\phi 2} = kT\left\{\left(\frac{N_1}{M}\right)\ln\phi_1 + \chi\left[1 + \left(\frac{N_1}{M}\right)\right]\phi_1\phi_2\right\} \quad (9)$$

$$\mu_m = \left[\left(\frac{1-\phi_2}{\phi_2}\right)\right]\ln(1-\phi_2) + \chi(1-\phi_2) \quad (10)$$

$$\mu_d = \left(\frac{\partial \Delta A_d}{\partial M}\right)_{\phi 2} = \nu kT[\ln\phi_2 + 3(\phi_2^{-2/9} - 1)] \quad (11)$$

$$\mu_b = \left(\frac{\partial \Delta A_b}{\partial M}\right)_{\phi 2} = gkT\left\{\ln(1-f) + f\ln\left[\frac{f}{q}(1-f)\right]\right\} \quad (12)$$

$$\mu_{el} = \left(\frac{\partial \Delta A_{el}}{\partial M}\right)_{\phi 2,f} = kT\left(\frac{z_{ad}^2 \phi_2^2 g^2 f^2}{2v_0 I}\right) \quad (13)$$

Note that all these chemical potentials are independent of M; they are dependent only on ϕ_2. This is logical, because it has been assumed that the chemical nature of the polymers does not change.

The sum of all these contributions forms what we will call the chemical potential of each type of polymer (i.e., chemical potential of the reduced polymer ($\mu_{pol,r}$) or chemical potential of the oxidized polymer ($\mu_{pol,o}$)):

$$\mu_{pol} = \mu_m + \mu_d + \mu_b + \mu_{el} \quad (14)$$

We must keep in mind that, when both types of polymers are present, a further conformational contribution should be considered, because of the different possible distributions between N_{ox} and N_{red} among the N possible sites. As we proved previously,[14] this results in a free energy contribution, ΔA_{conf}, of the following type:

$$\Delta A_{conf} = -kT\ln\left(\frac{N!}{N_{ox}! \, N_{red}!}\right) \quad (15)$$

Also, in this case, an interaction energy will exist between the monomers in a statistical chain of the different forms of the polymer. Because we are assuming complete independence of the two types of polymers here, we will not take these terms into account.

II.2. Osmotic Equilibrium of the Polymer with the Solvent. The osmotic equilibrium of the polymer with the solvent of the external solution is determined by the equality of the chemical potentials of the solvent in the two phases (i.e., polymer and solution). The latter is determined by deriving the change in the total free energy, ΔA_{pol}, with respect to N_1, keeping the parameters T, ϕ_2, and N_2 constant.

$$\mu_1(pol) - \mu_1(sol) = \left[\frac{\partial(\Delta A_{pol})}{\partial N_1}\right]_{T,\phi_2,N_2} = 0 \quad (16)$$

$$\ln(1-\phi_2) + \phi_2 + \chi_{eff}\phi_2^2 + \nu\phi_2\left(1 - \frac{2\phi_2^{-2/9}}{3}\right) = 0 \quad (17)$$

where

$$\chi_{eff} = \chi - \frac{z_{ad}^2 n^2}{2v_0 I} \quad (18)$$

Two important parameters in the theory are the interaction parameter (χ) and the number of cross-linked chains (ν). Equation 17 can be used to obtain either χ or ν, if the volume

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fractions are known. According to eq 18, for polyelectrolytes, one must use χ_{eff} instead χ; χ_{eff} is dependent on the ionic strength. At high electrolyte concentrations, the charge in the polymer is effectively screened and χ_{eff} approaches χ. At low ionic strengths, the effect of the polymer charges should cause χ to become negative and the polymer will unfold. However, as I decreases, the pH also decreases and, as discussed previously, the charge in the polymer decreases. Therefore, at very low ionic concentration, also χ_{eff} approaches χ.

II.3. Electrode Potential. To determine the electrode potential, we proceed as done previously,[14] by writing the expression of the differential of the free energy of the system and dividing it by the differential of the number of electrons, dN_{elec}.

$$dA = \mu_{ox}^* \, dN_{ox} + \mu_{red}^* \, dN_{red} + \mu_{elec}^* \, dN_{elec} + \mu_{pol,ox} \, dM_{pol,o} + \mu_{pol,red} \, dM_{pol,r} \quad (19)$$

where μ_{ox}^*, μ_{red}^*, and μ_{elec}^* are the *electrochemical* potentials of the redox centers and of the electrons. We have previously shown that the electrode potential E (with the difference of a constant that is dependent on the reference electrode) can be written as

$$FE = \left(\frac{\partial A}{\partial N_{elec}} \right)_{N,N_{ox},T} \quad (20)$$

Taking into account that the degree of advancement of reaction 1 ($d\xi$) is related to N_{ox}, N_{red}, and N_{elec} through the relation

$$d\xi = dN_{ox} = -dN_{red} = dN_{elec} \quad (21)$$

and that the number of redox centers can be related to the number of units ($M_o = \alpha N_{ox}$ and $M_r = \alpha N_{red}$),[14] we can write all the differentials in terms of N_{elec}. Thus, eq 20 becomes

$$FE = \mu_{ox} - \mu_{red} + \mu_{elec} + \alpha(\mu_{pol,ox} - \mu_{pol,red}) \quad (22)$$

where μ_{ox}, μ_{red}, and μ_{elec} are the *chemical* potentials of the redox centers and the electrons. Note that, because the chemical potentials of the polymer (μ_{pol}) are independent of M, their contributions due to binding, electrical, mixing, and deformation forces will only enter in the apparent formal redox potential. However, it will change with the change of one or several of these contributions. Thus, for instance, if we change the pH of the external solution, the binding contribution to the reduced and oxidized states will be different and, consequently, the apparent formal potential also will be different.

Also, for the sake of simplicity, we will assume that the redox centers behave ideally, that is, their activity factors are unity. Defining the fraction of oxidized centers as $\theta = N_{ox}/N_t$, the chemical potentials of the redox centers can be written as

$$\mu_{ox} = \mu_{ox}^0 + kT \ln \theta \quad (23)$$

and

$$\mu_{red} = \mu_{red}^0 + kT \ln(1 - \theta) \quad (24)$$

The chemical potentials of the oxidized and reduced redox centers in eqs 23 and 24 correspond to the case of no interactions between them. The presence of interactions in this context has been treated as done previously.[11]

III. Calculations

III.1. Characteristic Parameters of the Oxidized and Reduced Forms of the Polymer from the Volume Changes

TABLE 1: Calculated Effective Interaction Parameters and the Fraction of Polymer Units Participating in a Polymer Chain[a]

concentration, C (M)	Effective Interaction Parameter, χ_{eff}		Fraction of Polymer Units, ν	
	for reduced polymer, $\chi_{eff,r}$	for oxidized polymer, $\chi_{eff,o}$	for reduced polymer, ν_r	for oxidized polymer, ν_o
4×10^{-4}	0.31	-4.5×10^{-2}	6.1×10^{-3}	5.7×10^{-3}
1×10^{-3}	0.39	-4.5×10^{-3}	6.1×10^{-3}	5.7×10^{-3}
1×10^{-2}	0.39	-4.5×10^{-4}	6.1×10^{-3}	5.7×10^{-3}
1×10^{-1}	0.40	-4.5×10^{-5}	6.1×10^{-3}	5.7×10^{-3}
1×10^{0}	0.40	-4.5×10^{-6}	6.1×10^{-3}	5.7×10^{-3}

a $\chi_r = 0.4$, $\chi_o = 0.0$, $f_r = 0.7$, and $f_o = 0.3$.

during the Redox Switching of the Polymer. In the following discussion, we will show some calculations that apply the model. As in the case of electroactive polymers, we lack information about χ and ν, so we will try to make reasonable guesses. As an example, we will consider the case of Pani. For this polymer, the titration curves and the pK values of both the oxidized and reduced forms[19] have been determined. Also, as we mentioned previously, the stoichiometry of the oxidation reaction is well-known (see Figure 1). In addition, the volume changes during the redox switching have been measured in 1 M H_2SO_4 solutions.[11b] In these experiments, the volume of the reduced polymer was $V_r = 7.22 \times 10^{-4}$ cm^3, and that of the oxidized one was $V_o = 7.62 \times 10^{-4}$ cm^3. The number of redox centers can be estimated from the total charge required to oxidize the polymer (Q). In the present case, $Q = 0.84$ C/cm^2 and the electrode area is $A = 1.96 \times 10^{-3}$ cm^2. Considering that the number of exchanged electrons per four monomer units is two, these figures lead to $N_t = 1.71 \times 10^{-8}$ mol. The oxidation charge, as a function of the potential $Q(E)$, can be calculated from integration of the current−potential response. It is then possible to calculate the fraction of oxidized polymer, as $\theta = Q(E)/Q$. There is general agreement among different workers that, when this polymer is oxidized from leucoemeraldine to the emeraldine form, two out of four polymer monomers are actually oxidized (see Figure 1). Therefore, we make $M = 2N_t = 3.42 \times 10^{-8}$ mol. With the total volume and the value of M, calculation of the volume fractions $\phi_{2,r}$ and $\phi_{2,o}$ becomes possible, resulting in $\phi_{2,r} = 9.78 \times 10^{-3}$ and $\phi_{2,o} = 9.20 \times 10^{-3}$.

The number of water molecules associated with the reduced and oxidized forms of the polymer then are given as $N_{1,r} = (M/\phi_{2,r}) - M$ and $N_{1,o} = (M/\phi_{2,o}) - M$. One of the main problems with the present calculations is the lack of values for the parameters, χ and ν. There is no experimental information about these parameters for the case of Pani in water. Equation 17 allows one of them to be obtained if the other is known. Therefore, we will assume a range of values for the parameter χ from values taken from the literature[9] and calculate ν using eq 17.

Calculated values of ν, assuming $\chi_r = 0.4$ and $\chi_o = 0$, for the reduced and oxidized polymer, are shown in Table 1. The values of ν suggest that the number of chains that participate in the deformation process is much smaller than the number of units; that is, one chain would be formed by a great number of units.

III.2. Solvent Injection/Ejection during the Redox Switching of the Polymer. Because we know the volume change as a function of the fraction of oxidized polymer, and assuming that $\phi_{2,r}$ and $\phi_{2,o}$ do not change during the oxidation, it is possible to obtain the number of solvent molecules associated with each polymer form, as a function of θ and E.
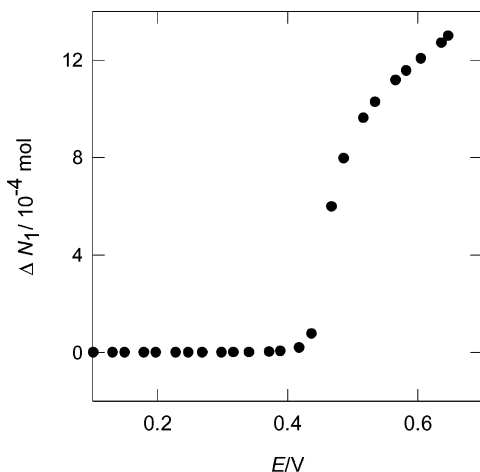
Figure 2. Calculated change in the number of solvent molecules (ΔN_1), as a function of the applied potential.

As the oxidation of the polymer progresses, the reduced polymer is converted to the oxidized polymer, and the number of polymer units changes, according to

$$M_r = M(1 - \theta) \qquad (25)$$

$$M_o = M\theta \qquad (26)$$

where θ has been previously defined. The number of water molecules associated with each form of the polymer at a particular state of oxidation is $N_{1,o} = (M_o/\phi_{2,o}) - M_o$, and a similar relation exists for $N_{1,r}$. The total number of water molecules associated with the polymer at a particular state of oxidation is $N_{tot} = N_{1,o} + N_{1,r}$. The change in the number of water molecules then is $\Delta N_1 = N_{tot} - N_{1,i}$, where $N_{1,i}$ is the initial content of water molecules of the reduced polymer. Because the volume fractions of each form of the polymer are fixed during the oxidation, it is possible to obtain the change of the number of solvent molecules, ΔN_1, as a function of the fraction θ or E. Experimental results of $\Delta V/V$, as a function of Q or E, are available for Pani.[16] Thus, ΔN_1 can be obtained as a function of E. Such a plot is shown in Figure 2. Both M_r and M_o are linear functions of θ (see eqs 25 and 26); therefore, ΔN_1 will also be a linear function of θ, with slope $M[(1/\phi_{2,o}) - (1/\phi_{2,r})]$.

III.3. Proton Binding of Pani and the Binding Contribution. Menardo et al.[19] titrated Pani in its reduced and oxidized forms. Both forms have two pK values: p$K_1 = 2.5$ and p$K_2 = 5.5$. For the reduced form, the total number of protonated sites is 0.25 equivalents per mole of monomers at p$K = 2.5$ and is practically zero at p$K = 5.5$. That is, in the reduced form, there is one protonated site for every four monomer units. This means that the sites of p$K = 2.5$ are the amine groups and only one-fourth of them are effectively protonated. In our notation, this means $B_r = M/4$, or $f_r = 0.25$.

For the oxidized form, these authors found 0.14 equivalents per mole of monomer units at p$K = 2.5$ and 0.32 equivalents per mole of monomer at p$K = 5.5$. The sites yielding p$K = 2.5$ clearly should correspond to the protonated amine groups of the polymer and those of p$K = 5.5$ should correspond to the protonated imine groups. Because one structural unit of the half-oxidized polymer can be written as in eq 6, the average number of amine groups and the average number of imine groups are one-half of the total number of monomer units. However, only one-quarter of the amine groups are protonated; therefore, $B_o(\text{amine}) = M_o/8$. And, because two-thirds of the imine groups

are protonated, $B_o(\text{imine}) = 0.66M_o/2 = M_o/3$. Therefore, the total number of protonated groups is $B_o(\text{total}) = 0.46M_o$ and $f_o = 0.46$. Note that this means that, in the oxidized state, there are two contributions to the binding energy: one from the amine groups and other from the imine groups. Therefore, in this case, we will have two contributions to the chemical potential of binding: one for the amine groups and another for the imine groups. The contribution of the amine groups (denoted by the subindex am) is

$$\mu_{b,o,am} = \left(\frac{\partial \Delta A_b}{\partial M_o}\right)_{\phi_2} = \left(\frac{kT}{8}\right)\left\{\ln(1 - f_{am}) + f_{am}\ln\left[\frac{f_{am}}{q_{am}(1 - f_{am})}\right]\right\} \qquad (27)$$

and similarly for the imine groups (denoted by the subindex im):

$$\mu_{b,o,im} = \left(\frac{\partial \Delta A_b}{\partial M_o}\right)_{\phi_2} = \left(\frac{2kT}{6}\right)\left\{\ln(1 - f_{im}) + f_{im}\ln\left[\frac{f_{im}}{q_{im}(1 - f_{im})}\right]\right\} \qquad (28)$$

Thus, the total contribution to the proton binding to the oxidized form is

$$\mu_{b,o} = \left(\frac{kT}{8}\right)\left\{\ln(1 - f_{am}) + f_{am}\ln\left[\frac{f_{am}}{q_{am}(1 - f_{am})}\right]\right\} + \left(\frac{2kT}{6}\right)\left\{\ln(1 - f_{im}) + f_{im}\ln\left[\frac{f_{im}}{q_{im}(1 - f_{im})}\right]\right\} \qquad (29)$$

Note the coefficients $1/8$ for the amine groups and $2/6$ for the imine groups. The reduced polymer only has amine groups. Therefore, the chemical potential that is attributable to them is

$$\mu_{b,r} = \left(\frac{\partial \Delta A_b}{\partial M_o}\right)_{\phi2} = \left(\frac{kT}{4}\right)\left\{\ln(1 - f_r) + f_r\ln\left[\frac{f_r}{q_{am}(1 - f_r)}\right]\right\} \qquad (30)$$

Therefore, the change in the binding contribution during the oxidation is

$$\Delta\mu_b = \mu_{b,o} - \mu_{b,r} = \left(\frac{2kT}{6}\right)\left\{\ln(1 - f_{im}) + f_{im}\ln\left[\frac{f_{im}}{q_{im}(1 - f_{im})}\right]\right\} - \left(\frac{kT}{8}\right)\left\{\ln(1 - f_{am}) + f_{am}\ln\left[\frac{f_{am}}{q_{am}(1 - f_{am})}\right]\right\} \qquad (31)$$

Now, the partition function of the occupied site is related to the standard chemical potential of the bound species, μ_{ad}^0, through[9b]

$$kT \ln q = -\mu_{ad}^0 \qquad (32)$$

Because the binding equilibrium constant K is related to the difference between the chemical potential of the binding species in the bound state and that of the binding species in the solution, $\mu^0(H^+)$, by

$$RT \ln K = -[\mu_{ad}^0 - \mu^0(H^+)] \qquad (33)$$

and remembering that, by convention, $\mu^0(H^+)$ is set equal to zero,[20] then p$K = -\ln q$.

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TABLE 2: Calculated Values of the Contribution of the Chemical Potential of the Polymer to the Apparent Formal Potential of the Redox Centers ($\Delta E^{0\prime}$)^a

concentration, C (M)	$\Delta\mu_b/F$ (V)	$\Delta\mu_{el}/F$ (V)	$\Delta\mu_m/F$ (V)	$\Delta\mu_d/F$ (V)	$\Delta E^{0\prime}$ (V)
1×10^{-4}	0.48	-2.98×10^{1}	-4.36×10^{-4}	1.56	-0.71
1×10^{-3}	0.48	-2.98×10^{0}	-4.36×10^{-4}	1.72	-0.02
1×10^{-2}	0.48	-2.98×10^{-1}	-4.36×10^{-4}	1.73	0.049
1×10^{-1}	0.48	-2.98×10^{-2}	-4.36×10^{-4}	1.73	0.056
1×10^{0}	0.48	-2.98×10^{-3}	-4.36×10^{-4}	1.73	0.057

^{a} $q_r = 2$, $q_o = 1$, $f_r = 0.7$, and $f_o = 0.3$.
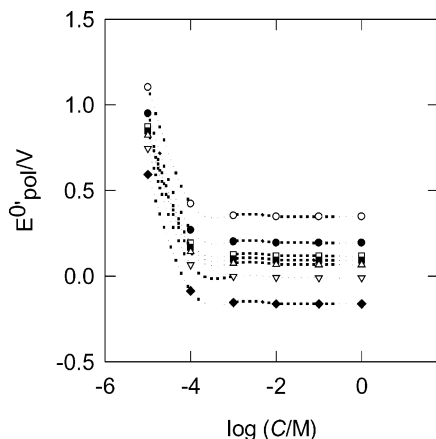
Figure 3. Correction to the formal apparent redox potential ($E_{pol}^{0\prime}$), which is due to the polymer contribution, as a function of the electrolyte concentration in the external solution for different values of the parameters $\chi_{eff,r}$ and $\chi_{eff,o}$: ($\bigcirc$) $\chi_{eff,r} = 0$ and $\chi_{eff,o} = 10$; ($\bullet$) $\chi_{eff,r} = 0$ and $\chi_{eff,o} = 4$; ($\square$) $\chi_{eff,r} = 0$ and $\chi_{eff,o} = 1$; ($\blacksquare$) $\chi_{eff,r} = 0$ and $\chi_{eff,o} = 0$; ($\triangle$) $\chi_{eff,r} = 1$ and $\chi_{eff,o} = 0$; ($\triangledown$) $\chi_{eff,r} = 4$ and $\chi_{eff,o} = 0$; and ($\blacklozenge$) $\chi_{eff,r} = 10$ and $\chi_{eff,o} = 0$.

At pH $\sim$0, practically all the amine and the imine groups are protonated. Therefore, we must consider the expressions of the chemical potentials as given by eqs 27−31 at the limit of $f \rightarrow 1$. The resulting expression for the change in the chemical potential at the binding equilibrium then is

$$\Delta\mu_b = -\left(\frac{RT}{8}\right) \ln q_{am} - \left(\frac{2RT}{6}\right) \ln q_{im} \quad (34)$$

III.4. Apparent Formal Potential of the Polymer. The contribution of the different free energy terms to the apparent formal potential of the polymer is given by the term $\mu_{pol,ox} - \mu_{pol,red}$ (the right-hand side of eq 22). The different contributions to $\mu_{pol,ox}$ and $\mu_{pol,red}$ are given by eqs 9−13. They were calculated for selected values of the partition functions for the proton binding and the interaction parameters of the reduced and oxidized forms of the polymer. The resulting values are assembled in Table 2 and its dependence on the ionic strength of the external medium is shown in Figure 3.

Figure 3 and Table 2 show that, at relatively high ionic strength, the apparent formal potential of the polymer becomes independent of the ionic strength. This is due to the effective screening of the charged sites of the polymer.

III.5. Ion Exchange during the Oxidation of the Polymer. The data mentioned at the beginning of Section III.3 can be used to estimate the net charge on the polymer, as a function of the applied potential, at a fixed proton concentration in the external medium. For the reduced polymer in a 1 M H$_2$SO$_4$ solution, the net charge per monomer unit will be, according to eq 6 and considering $z_{ad} = +1$,

$$n_o = M_o f_o \quad (35)$$
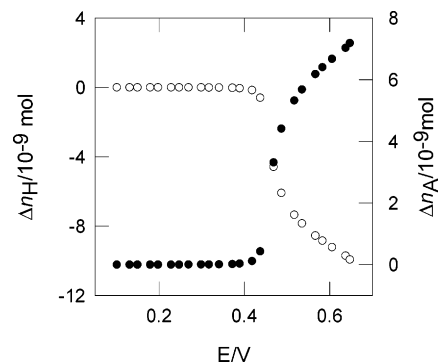
Figure 4. Calculated change in ($\bigcirc$) the number of expelled protons (Δn_H) and ($\bullet$) the number of injected anions (Δn_A) in the polymer, as a function of the applied potential.

and

$$n_r = M_r f_r \quad (36)$$

with M_r and M_o given by eqs 25 and 26, respectively. The bound charge during the oxidation (n) is simply

$$n = n_o + n_r \quad (37)$$

The polymer initially has $n_{r,i} = M f_r$ protons; therefore, the change in the charge during the oxidation is

$$\Delta n = n_o + n_r + n_{r,i} \quad (38)$$

However, as two H$^+$ ions are produced during the oxidation of four monomer units, the number of ejected protons will be this amount less the change in the total charge; therefore, the total proton change Δn_H will be

$$\Delta n_H = \Delta n - \frac{Q}{F} \quad (39)$$

The results of this calculation are shown in Figure 4. Because the change in the total number of charges is Δn, this must be equal to the number of anions (Δn_A) coming into the polymer to maintain electroneutrality. This change is also shown in Figure 4. Because both M_o and M_r are dependent linearly on θ, both Δn_H and Δn_A are also linearly dependent on θ. The slope is $M(f_o - f_r - 0.5)$ for Δn_H and $M(f_o - f_r)$ for Δn_A.

IV. Conclusions

We have shown how the polyelectrolytic nature of electroactive polymers affects its apparent formal potential and how it is dependent, through the different contributions that are considered, on the pH and salt concentration of the external electrolytic media.

Simple calculations show the relative importance of each contribution to the total apparent redox potential.

Knowledge of the volume changes during the redox switching of the polymer allows the change in the number of water molecules associated with each form of the polymer to be calculated. Moreover, if the acid−base titration curves for each form of the polymer are known, the number of ejected protons and the number of incoming counterions can be calculated.

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List of Symbols

a_{ad} = activity of the adsorbate at the external medium

c = coordination number of the polymer lattice

c_{ad} = concentration of the adsorbate in the external solution

f = fraction of bound sites

g = number of binding sites per monomer unit

k = Boltzmann constant

n = total number of charges on the polymer

Δn = change in the number of charges on the polymer during oxidation

Δn_H = change in the number of protons during the polymer oxidation

Δn_A = change in the number of anions during the polymer oxidation

q = partition function of an occupied binding site

v_0 = molar volume of the solvent

$w = w_{11} + w_{22} - 2w_{12}$

w_{11} = interaction energy between solvent molecules

w_{22} = interaction energy between the monomers in a statistical chain

w_{12} = interaction energy between a monomer in a statistical chain and the solvent

z_{ad} = ionic charge of the binding species

ΔA_b = free energy change of binding

ΔA_d = free energy change of deformation

ΔA_{el} = free energy change of electric interaction

ΔA_m = free energy change of mixing

ΔA_{pol} = total free energy change of the polymer

B = total number of binding sites on the polymer

F = Faraday constant

I = twice the ionic strength

K_{ad} = equilibrium constant of the binding process

N = total number of redox centers

N_{ox} = number of oxidized redox centers

N_{red} = number of oxidized redox centers

N_1 = number of solvent molecules in the polymer

N_2 = number of polymer chains

N_{ad} = number of bound species

M = total number of monomer units

M_o = total number of monomer units in the oxidized polymer

M_r = total number of monomer units in the reduced polymer

M_t = total number of species, monomer units, plus solvent molecules

ΔS_d = entropy change of deformation

T = absolute temperature

α = fraction of redox centers contained in a monomer unit

χ = interaction parameter between the statistical monomer units and the solvent

χ_{eff} = effective interaction parameter, including electrical and binding interactions

$\phi_{2,o}$ = volume fraction of the monomer in the oxidized polymer

$\phi_{1,o}$ = volume fraction of the solvent in the oxidized polymer

$\phi_{2,r}$ = volume fraction of monomer in the reduced polymer

$\phi_{1,r}$ = volume fraction of the solvent in the reduced polymer

ξ = degree of advancement of the redox reaction

μ_i^0 = standard chemical potential of species i

μ_i = chemical potential of species i

μ_i^* = electrochemical potential of species i

ν = fraction of monomer units participating in the deformation process

θ = fraction of oxidized redox centers

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(17) The Langmuir isotherm is the simplest way to describe the binding equilibrium. We have used it here, for simplicity. The proper binding isotherm can be determined from an analysis of the titration curve of the polyelectrolyte (see, for instance, refs 9c and 9e).

(18) The derivative of N_1, with respect to M at constant ϕ_2, might not be straightforward; it is $(\partial N_1/\partial M)_{\phi_2} = N_1/M$. Note also that $N_1/M = \phi_1/(1 - \phi_1) = (1 - \phi_2)/\phi_2$ and that $1 + (N_1/M) = 1/\phi_2$.

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