Redox Potential Distribution in the Presence of Mechanical Stress. The Case of Electroactive Polymers

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The current/potential response during the redox switching of electroactive polymers derived from substituted arylamines is analyzed in terms of a sigmoidal distribution of apparent formal potentials. This kind of polymers shows expansion and contraction during the redox switching. A thermodynamic analysis of these systems, including mechanical stresses developed during the oxidation and reduction cycles, leads to a distribution of apparent formal potentials. It is shown that the concept of electron binding can be applied to describe the redox switching of an electroactive polymer. On the basis of this concept, simple statistical thermodynamic models can be applied to describe the distribution of apparent formal potentials during the redox switching of this kind of polymers. In particular, a simple model based on the mean field approximation, including interaction between near neighbors, leads to a linear distribution of the apparent formal potential. On the other hand, a statistical thermodynamical model, including the development of strains during the redox switching, successfully describes the experimental sigmoidal distribution of apparent formal potentials.

1. Introduction

The thermodynamic quantities that characterize the chemical equilibrium between a bulk phase and an interfacial region do not have, in general, a unique value. Instead, they present a distribution of values. This distribution of values is observed in different magnitudes such as the energy of adsorption in physical adsorption[1], the equilibrium constant for the ionization/protonation reactions of colloidal oxides[2] and polymers,[3] the complexation constants of polymers[4] and complex compounds such as humic and fulvic acids,[4] and the formal potential of electrochemical reactions in which adsorbed species participate.[5] This fact, recognized long ago in different fields such as physical adsorption, electrochemistry, and ion binding to polymers, has not been properly generalized yet. The arrival of new materials makes necessary a proper thermodynamic and modelistic description of these complex systems, as many of them require taking into account distributed thermodynamic quantities.

All the processes described above can be considered as binding processes: a particle binding to a surface, a proton or metal ion binding to a basic site of a polymer or an oxide, and electrons binding to an oxidized species to form a reduced one. The basic nature of the problem can be described as follows. As the binding process or titration[6] of the material progress, some of their sites change their chemical nature and then change the interaction energy among them. This fact leads to activity factors that depend on the titration fraction and, therefore, on the apparent formal quantity on the titration factor.

For these binding processes, much theoretical work has been done to predict from statistical mechanics the different possible binding isotherms.[1,7] However, the problem is a complex one, and for analytical solutions, it is difficult to go beyond the mean field or Bragg−Williams approximation.[1a,7]

Many electroactive materials show an electrochemical behavior that can be rationalized through a distribution of apparent formal potentials. In this work, we will specialize in the apparent potential distribution in electroactive polymers.

The occurrence of an apparent formal potential distribution in electroactive polymers has been considered before.[8] Albery et al.[8a] proposed a Gaussian distribution of formal potentials to explain their results for thionine-covered electrodes. Recently, Sabatani and Anson[8b] also applied Gaussian distribution formal potentials of cationic complexes of Ru(II) confined within Nafion coatings on electrodes. The idea was also proposed by Heinze et al. to explain the voltammetric insulator/conductor transition in conducting polymers such as polyaniline (Pani).[9] Also, a dependence of the redox potential on the degree of doping has been proposed in a model for the redox switching of conducting polymers on the basis of the potential dependencies of polaron and bipolaron densities.[10a]

On the other hand, it is known that many of the electrochemically active polymers develop stresses when they are submitted to oxidation−reduction cycles,[11] and it has been shown that this change in the stress affects its apparent formal redox potential.[12] Bowden et al. developed a model to interpret such changes,[12a] and it has been applied to redox[12b,c] and to conducting polymers.[12d] Additional considerations about the expansion and contraction in electroactive polymers can be found in a recent review.[13a] Moreover, recently, the expansion/contraction during redox cycling of a conducting polymer, such as poly- *o*-toluidine (POT), has been measured quantitatively.[13b]

In the case of electroactive conducting polymers, other types of models have been proposed to interpret the redox behavior: those based on polaron−bipolarons,[10] electron−ion interactions,[14] and percolation models.[15]

In this work, we first will consider the phenomenological analysis that leads to the appearance of an apparent formal potential distribution. Then we will consider the redox reactions

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taking place in a heterogeneous material, such as an electroactive polymer, within the framework of electron binding processes. As a necessary previous step, we will formulate the thermodynamic equations that describe such systems. There, we will show that the appearance of mechanical stresses during the redox switching leads to a distribution of formal potentials. Second, we will apply some simple models, based on the Bragg−Williams approximation, in the absence of mechanical stresses, to the process of electron binding. After that, we will consider the case in which the electron binding leads to the appearance of strains in the electroactive material. By applying a simple statistical thermodynamics treatment, we will model its apparent formal potential distribution.

2. The Potential Distribution Function from Experimental Results

To study the electrochemical response of these materials, we made a layer of an electroactive material (for example, a conducting polymer film) on top of an inert electrode, and the ensemble is the working electrode in an electrochemical cell. By some suitable means, the current density, i, versus applied potential, E, is determined.

The electroactive material can be described as an ensemble of redox centers Red (reduced) and Ox (oxidized) homogeneously distributed in a matrix which supports them. The redox switching of the film takes place by applying potential. Applying a positive potential, we oxidize the material according to the reaction

$$Red \leftrightarrow Ox^+ + e \qquad (1)$$

Reaction 1 occurs at the metal/polymer interface. We will assume that the charge-transfer reaction is very fast, so at each potential reaction 1 can be considered at equilibrium. Equilibrium is also assumed at the polymer/solution interface. To avoid the consideration of membrane potentials, we will assume that an infinitely supported situation can be achieved.[16] For simplicity, we have also assumed that the charge of Ox, $z_{ox} = 1$ and that Red is neutral. Under these conditions, the Nernst equation can be applied

$$E = E^{\circ\prime} + (RT/F) \ln\left(\frac{c_{ox}\gamma_{ox}}{c_{red}\gamma_{red}}\right) = E_a^{\circ\prime} + (RT/F) \ln\left(\frac{c_{ox}}{c_{red}}\right) \qquad (2)$$

where $E^{\circ\prime}$ is the formal potential,[5b] the γ's are the activity coefficients of the redox centers, c_{ox} and c_{red} are the molar fraction concentrations of Ox and Red, and $E_a^{\circ\prime}$ is the apparent formal potential

$$E_a^{\circ\prime} = E^{\circ\prime} + (RT/F) \ln(\gamma_{ox}/\gamma_{red}) \qquad (3)$$
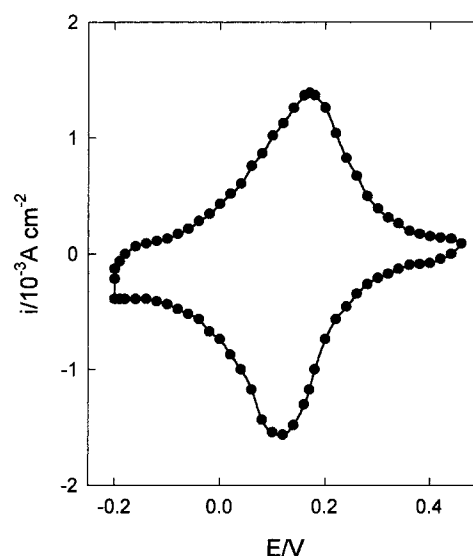
The total concentration of redox centers, c_T is

$$c_{ox} + c_{red} = c_T \qquad (4)$$
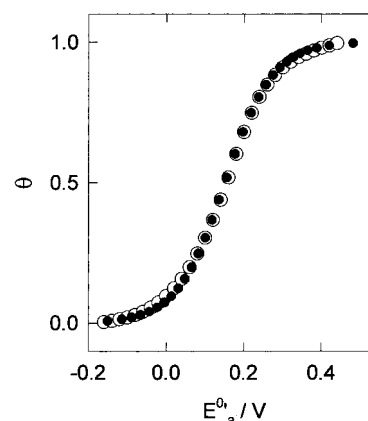
Employing the fraction of oxidized centers, which is the titration fraction, $\theta = c_{ox}/c_T$, we can write eq 2 as

$$E = E^{\circ\prime} + (RT/F) \ln\left[\frac{\theta\gamma_{ox}}{(1-\theta)\gamma_{red}}\right] = E_a^{\circ\prime} + (RT/F) \ln\left[\frac{\theta}{1-\theta}\right] \qquad (5)$$

The relation between $E_a^{\circ\prime}$ and θ, can be obtained analyzing the response of the current density, i, as a function of the

Figure 1. Voltammetric response of POAP in 1 M H$_2$SO$_4$ + 0.5 M Na$_2$SO$_4$. Film charge: 4.6 mC cm^{-2}. Sweep rate: 0.05 V s^{-1}.


Figure 2. Typical θ vs $E_a^{\circ\prime}$ plot for POAP in 1 M H$_2$SO$_4$ + 0.5 M Na$_2$SO$_4$: (○) experimental and (●) calculated with the paramenters resulting from the fit to eq 39.

potential applied to the system, E. In Figure 1, this behavior is shown for an electroactive (redox) polymer film of poly-*o*-aminophenol (POAP)[17] during a linear potential cyclic scan. We will analyze here only the positive half potential cycle. The oxidation charge as a function of the applied potential, $Q(E)$, can be obtained by integrating the i/E profile. The fraction of oxidized polymer, as a function of the applied potential, is obtained from the ratio of $Q(E)$ to the maximum oxidation charge, Q_T. That is, $\theta = Q(E)/Q_T$. Then, and assuming that the electrochemical process is reversible, $E_a^{\circ\prime}$ is obtained as a function of θ by applying eq 5 (Figure 2).

In conducting polymers, the voltammetric response shows a large contribution of capacitive current and a marked hysteresis between the anodic and the cathodic sweeps.[18] This could be overcome by employing, instead of the voltammetric response, the potential dependence of the low-frequency capacitance, $C_{LF} = iv^{-1}$, where v is the sweep rate, obtained from impedance measurements. Also, the charge could be obtained directly from chronocoulometric experiments.

It is observed in Figure 2 that the shape of the curve is sigmoidal. This indicates that there is not a unique value of $E_a^{\circ\prime}$ but, instead, a distribution of them. In the ideal case (no interaction), a step function,[4c] i.e., $E_a^{\circ\prime} = E^{\circ\prime}$, should be obtained (Figure 3).

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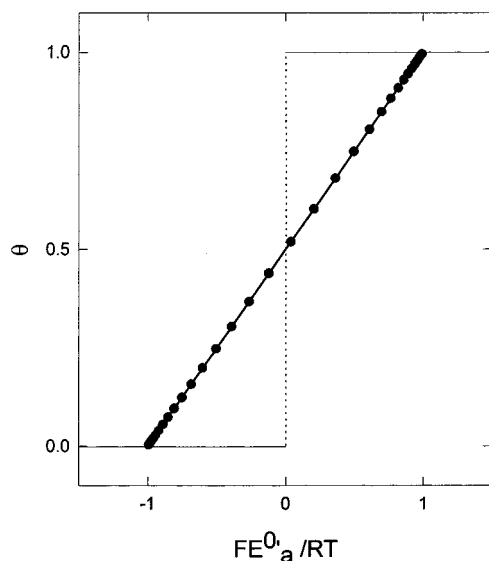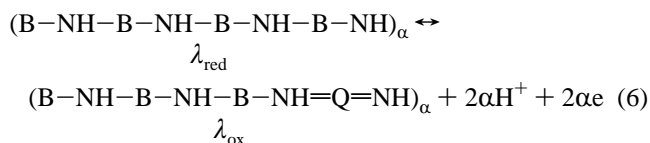

Figure 3. Calculated redox potential distribution function, θ vs $F E_a^\circ/RT$, plots with $q_{red}/q_{ox} = 1$: (- - -) the Langmuir case from eq 27 and (-·-) the Bragg−Williams model from eq 32. $w = 2 \times 10^9$, $N = 1.2 \times 10^{14}$ cm^{-2}.

3. Theory

Model. We will consider that the polymer film contains N_{ox} and N_{red} redox centers, the total number of them, $N = N_{ox} + N_{red}$ is constant. The conversion of Red to Ox occurs through reaction 1. This process can be visualized as an electron binding process by which an electron is added to Ox to form a Red center and vice versa. The process can be analyzed within the framework of lattice statistics. Analogously to the binding of gas particles onto a two-dimensional lattice, Red plays the role of the occupied sites here, Ox the role of the empty sites, and the applied potential the role of the chemical potential of the external gas.

The situation just described is similar to that of the electrochemical reaction between reactants and products adsorbed on electrodes,[5b,19] where each one of the electrochemically active species is in equilibrium with the corresponding one in the solution. Usually, the interaction among the adsorbed species is taken into account by applying a suitable adsorption isotherm to the reactants and products. However, in the case of confined redox couples, the redox centers are fixed, localized in the polymer matrix; i.e., there is no equilibrium between the chemical species constituting the redox centers in the polymer and those in the solution side. There are no chemical species Red and Ox in the solution.

To take into account the expansion/contraction of the polymer, we will further consider that the polymer is composed of units of different length.[7b] These units have different lengths according to whether they are associated to an oxidized or a reduced redox center. At this point, we will consider that there are M_{ox} units associated to the oxidized form and M_{red} units associated to the reduced one. The total number of units $M = M_{ox} + M_{red}$ is constant. As an example, we will consider the redox switching of Pani. For this polymer, the first oxidation reaction of the reduced form can be roughly represented as[20]

$$(B-NH-B-NH-B-NH-B-NH)_\alpha \leftrightarrow$$
$$\lambda_{red}$$
$$(B-NH-B-NH-B-NH=Q=NH)_\alpha + 2\alpha H^+ + 2\alpha e \quad (6)$$
$$\lambda_{ox}$$

where α is the number of redox centers necessary to make an Ox or Red unit. It seems reasonable to consider that α is the same for the reduced and oxidized units. From the point of view of chemical structure, the present situation can be visualized by attributing different lengths, λ_i, to the several amine (reduced) and imine (oxidized) groups and to the associated benzoid, B, and quinoid, Q, rings, forming the units.

As the polymer is progressively oxidized, some of the Red units convert into the Ox ones, and assuming that $\lambda_{red} < \lambda_{ox}$, the polymer will expand. We will assume that the deformation is homogeneous. As the polymer expands, a state of tension (mechanical stress), τ, develops in the polymer film. Thus, for a Red unit to be converted into an Ox one, an extra mechanical work, $\tau \, d\lambda$, has to be performed on the system. In ref 11a, it is reported the polymer expands in one direction. In a similar way to the pulling of a wire, we will consider that the dimensional change in the polymer is preponderant in one dimension. Then, for modeling purposes, we will consider that the expansion/contraction of the polymer occurs in one dimension.[7b] Therefore, τ is a force, and λ is a length.

According to the above definitions, the following relations can be established:

$$M_{ox} = \alpha N_{ox} \quad (7)$$

$$M_{red} = \alpha N_{red} \quad (8)$$

The total number of units, M, is

$$M = M_{ox} + M_{red} = \alpha N = \alpha (N_{ox} + N_{red}) \quad (9)$$

The total length, λ, of the polymer is given by

$$\lambda = M_{ox} \lambda_{ox} + M_{red} \lambda_{red} = \alpha N_{ox} \lambda_{ox} + \alpha N_{red} \lambda_{red} \quad (10)$$

Thermodynamic Analysis of the Redox Potential for Confined Redox Couples Including Mechanical Work. The thermodynamic analysis of the redox potential of a system, in which also mechanical work is performed, has been already done.[12a] We will carry out the analysis for the particular case of the metal/polymer interface. We will first consider the open circuit potential of the system. For this purpose, let us consider the following galvanic cell:

Cu/base electrode/polymer/solution/reference electrode/Cu

where Cu represents the copper terminals of a potentiometer and the base electrode is an inert metal capable of exchange electrons with the polymer (Pt for instance).

The differential of the Helmholtz free energy of the system base electrode + polymer, A, can be written, at constant temperature, as

$$dA = \tau \, d\lambda + \mu^*_{ox} \, dN_{ox} + \mu_{red} \, dN_{red} + \mu^*_{el} \, dN_{el} \quad (11)$$

It should be noted that, in eq 11, the term $\tau \, d\lambda$ plays the role of the $p \, dV$ term (pressure times the differential of a volume) in the three-dimensional problem. $d\lambda$ is obtained by differentiating eq 10, $d\lambda = \alpha \lambda_{red} \, dN_{red} + \alpha \lambda_{ox} \, dN_{ox}$. The μ^*_i's are the corresponding electrochemical potentials. We have taken into account the fact that because the Red species is uncharged, its electrochemical potential is equal to the chemical potential, $\mu_{red} = \mu^*_{red}$. The three differentials at the rhs of eq 11 can be expressed in terms of the degree of advancement, $d\xi$, of reaction 1

$$d\xi = dN_{ox} = - dN_{red} = dN_{el} \quad (12)$$

Replacing eq 12 into eq 11 and considering that, at equilibrium, $dA/d\xi = 0$ results in

$$\Delta^{m,p}\phi = \phi^m - \phi^p = [\mu_{ox} - \mu_{red} + \mu_{el} + \tau\alpha(\lambda_{ox} - \lambda_{red})]/F \tag{13}$$

where $\Delta^{m,p}\phi$ is the Galvani potential difference at the metal/polymer interface. Since we are considering that the Galvani potential difference at the polymer/solution interface, $\Delta^{p,s}\phi$, is constant; the applied potential, E, differs from $\Delta^{m,p}\phi$ by a series of constant terms, C. That is

$$\Delta^{m,p}\phi = E + C \tag{14}$$

Then, we may write eq 13 as

$$(E + C)F = \mu_{ox} - \mu_{red} + \mu_{el} + \tau\alpha(\lambda_{ox} - \lambda_{red}) \tag{15}$$

The chemical potentials of Ox and Red can be written as

$$\mu_{ox} = \mu_{ox}{}^\circ + RT \ln(\gamma_{ox}\theta_{ox}) \tag{16}$$

and

$$\mu_{red} = \mu_{red}{}^\circ + RT \ln[\gamma_{red}(1 - \theta_{ox})] \tag{17}$$

$\mu_i{}^\circ$'s are the standard chemical potential of the centers. Then eq 15 becomes

$$E = E_a^{\circ\prime} + (RT/F) \ln\left[\frac{\theta_{ox}}{(1 - \theta_{ox})}\right] \tag{18}$$

with

$$E_a^{\circ\prime} = E^{\circ\prime} + \tau\alpha(\lambda_{ox} - \lambda_{red})/F + (RT/F) \ln\left(\frac{\gamma_{ox}}{\gamma_{red}}\right) \tag{19}$$

where

$$E^{\circ\prime} = (\mu_{ox}{}^\circ - \mu_{red}{}^\circ + \mu_{el})/F \tag{20}$$

and the constant term, C, has been included in $E^{\circ\prime}$. In what follows, to keep the notation simpler, we will omit the constant C, keeping in mind that it is included in $E^{\circ\prime}$.

Equation 18 is the Nernst equation in the presence of mechanical work. The apparent formal potential, eq 19, results dependent on the state of stress of the polymer.

Some Simple Statistical Thermodynamic Models for Confined Redox Couples. We will first consider the Langmuir case of noninteracting sites with no mechanical work. The polymer phase can be considered as a subsystem composed of N_{el} electrons, N_{red} reduced centers, and N_{ox} oxidized centers. The electrons in the polymer phase are in equilibrium with those at the metal phase contacting the polymer. The thermodynamic state of the polymer is fixed by the applied potential that determines the concentrations of Ox and Red. Under these conditions, the differential of the Helmholtz free energy of the polymer phase can be written as[7b]

$$dA = \mu^*_{ox} dN_{ox} + \mu_{red} dN_{red} + \mu^*_{el} dN_{el} \tag{21}$$

Since the polymer phase is electroneutral, the electrical contributions to μ^*_{ox} and μ^*_{el} cancel, and eq 21 can be written as

$$dA = \mu_{ox} dN_{ox} + \mu_{red} dN_{red} + \mu_{el} dN_{el} \tag{22}$$

In view of equilibrium 1, eq 22 is transformed into

$$dA = (\mu_{ox} - \mu_{red} + \mu_{el}) dN_{el} = F(E + C) dN_{el} \tag{23}$$

the last equality has been written according to eq 14.

The partition function for this system, $Q(N_{ox}, N, T)$, is simply[7b]

$$Q(N_{ox}, N, T) = q_{red}{}^{N - N_{ox}} q_{ox}{}^{N_{ox}} N!/N_{ox}!(N - N_{ox})! \tag{24}$$

where q_{red} and q_{ox} are the internal partition functions of Red and Ox, respectively, and functions of the temperature only. According to eq 23

$$F(E + C) = (\partial A/\partial N_{el})_{N,T} = -(\partial \ln Q/\partial N_{el})_{N,T} \tag{25}$$

So that

$$FE = FE^{\circ\prime} + RT \ln[\theta/(1 - \theta)] \tag{26}$$

with

$$E^{\circ\prime} = (RT/F) \ln(q_{red}/q_{ox}) \tag{27}$$

and $\theta = N_{ox}/N$. Since $E^{\circ\prime}$ is a function of the temperature only, a plot of θ versus $E^{\circ\prime}$ gives a step function (Figure 3).

Second, we will consider the mean field approximation for interacting sites with no mechanical effects. In this case, the analogy with the mean field approximation is to consider a mixture of redox centers Ox and Red, which are in equilibrium through reaction 1. This is equivalent to the Van Laar model of regular solutions.[7b] The thermodynamic equation describing the polymer phase (eq 23) is applicable.

Assuming the centers are homogeneously distributed, it is very easy to write the partition function in the mean field approximation for such a system.[7b] The canonical partition function, Q, is

$$Q(N_{ox}, N_{red}, T) = [q_{red} \exp(ur_{RR}/2RT)]^{N_{red}} \times$$
$$[q_{ox} \exp(ur_{OO}/2RT)]^{N_{ox}} (N_{ox} + N_{red})! \times$$
$$\exp(wN_{OR}/2RT)/N_{ox}!N_{red}! \tag{28}$$

where u is the coordination number of the lattice, N_{OO}, N_{RR}, and N_{OR} are the numbers of nearest neighbors pairs, and r_{OO}, r_{RR}, and r_{OR} the corresponding interaction energies of the OO, RR, and OR neighbors, respectively. q_{ox} and q_{red} are the internal partition functions of each site. Within the mean field approximation

$$N_{OR} = uN_{ox}N_{red}/(N_{ox} + N_{red}) \tag{29}$$

and

$$w = r_{OO} + r_{OR} - 2r_{RR} \tag{30}$$

Taking the natural logarithm of eq 28, differentiating it with respect to N_{ox}, keeping in mind that $dN_{ox} = dN_{el}$, and applying eq 25, we have

$$F(E + C) = \ln N_{ox} - \ln[q_{ox} \exp(ur_{OO}/2RT)] -$$
$$uw(1 - N_{ox})^2/2RT(N_{ox} + N_{red})^2 - \ln N_{red} -$$
$$\ln[q_{red} \exp(ur_{RR}/2RT)] - uw(1 - N_{red})^2/2RT(N_{ox} + N_{red})^2 \tag{31}$$

leading to an apparent formal potential

$$FE_a^{\circ\prime} = (\ln q'_{red} - \ln q'_{ox} - uw/2RT + uw\theta_{ox}/2RT) \tag{32}$$

where we have written $q'_{red} = q_{red} \exp(ur_{RR}/2RT)$, $q'_{ox} = q_{ox} \exp(ur_{OO}/2RT)$, $\theta_{ox} = N_{ox}/(N_{ox} + N_{red})$, $\theta_{red} = N_{red}/(N_{ox} + N_{red})$, and $\theta_{ox} + \theta_{red} = 1$.

In the present case, the apparent formal potential depends linearly on θ_{ox} (Figure 3). This result is equivalent to that obtained from the models of Laviron[5b] and Anson[19a] for adsorbed redox centers in equilibrium with the solution. This is not surprising since in those models the Frumkin isotherm is employed, which is based on the mean field approximation.

Now we will describe a statistical model which takes into account *mechanical effects*. For simplicity, we will not take into account the interaction between neighboring centers. From eq 11, the differential of the Helmholtz free energy for the polymer can be written as

$$dA = \tau(\lambda_{ox} dM_{ox} + \lambda_{red} dM_{red}) + \mu^*_{ox} dN_{ox} + \mu_{red} dN_{red} + \mu^*_{el} dN_{el} \quad (33)$$

Expressing M_{red} in terms of M and M_{ox} (eq 9), considering M is constant, and recalling eq 23, we can write eq 33 as

$$dA = \tau (\lambda_{ox} - \lambda_{red}) dM_{ox} + F(E + C) dN_{el} \quad (34)$$

Assuming that the conversion of units and the binding of sites are statistically independent, we can write the canonical partition function as the product of the contribution of the units times the contribution of the sites

$$Q(M_{ox},M,N_{ox},N,T) = Q_N Q_M \quad (35)$$

where

$$Q_M(M_{ox},M,T) = M! j_{ox}^{M_{ox}} j_{red}^{(M-M_{ox})}/(M - M_{ox})! M_{ox}! \quad (36)$$

refers to the units. j_{ox} and j_{red} are the internal partition functions of the units associated to the Ox and Red centers, respectively. According to eq 7 to 9, eq 36 can be written as

$$Q_M(\alpha N_{ox},\alpha N,T) = (\alpha N)! j_{ox}^{\alpha N_{ox}} j_{red}^{\alpha(N-N_{ox})}/[\alpha(N - N_{ox})]!(\alpha N_{ox})! \quad (37)$$

Q_N refers to the centers and is given by eq 24. Under these conditions, it can be shown that

$$F(E + C) = (\partial A/\partial N_{ox})_{N,N_{ox},T} = -\alpha RT \ln(j_{ox}/j_{red}) + \alpha RT \ln[\theta/(1 - \theta)] + RT \ln(q_{red}/q_{ox}) + RT \ln[\theta/(1 - \theta)] \quad (38)$$

The two first terms on the rhs come from the derivative of Q_M and the others from the derivative of Q_N.

According to our definition of $E_a^{\circ\prime}$ (see eq 3), the terms in eq 38 can be grouped as

$$E_a^{\circ\prime} = -(\alpha RT/F) \ln(j_{ox}/j_{red}) + (\alpha RT/F) \ln[\theta/(1 - \theta)] + (RT/F) \ln(q_{red}/q_{ox}) \quad (39)$$

A graphical representation of eq 39 for different values of the parameters α and j_{ox}/j_{red} are shown in Figures 4 and 5, respectively. It can be seen from Figures 4 and 5 that the distribution function is sigmoidal in shape. Furthermore, since α is the number of redox centers associated to a unit, increasing its value leads to a wider apparent potential distribution (Figure 4). In the particular case of $\alpha = 0$, there are no mechanical effects, and the ideal distribution (step function) is obtained. On the other hand, j_{ox}/j_{red} reflects the intrinsic relative mechan-
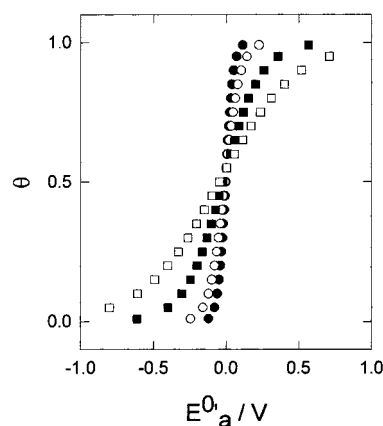
Figure 4. Calculated, θ vs $E_a^{\circ\prime}$ according to eq 39: ($\bullet$) $\alpha = 1$, ($\circ$) $\alpha = 2$, ($\blacksquare$) $\alpha = 5$, and ($\square$) $\alpha = 10$. $q_{red}/q_{ox} = 1$, $j_{ox}/j_{red} = 1.2$.
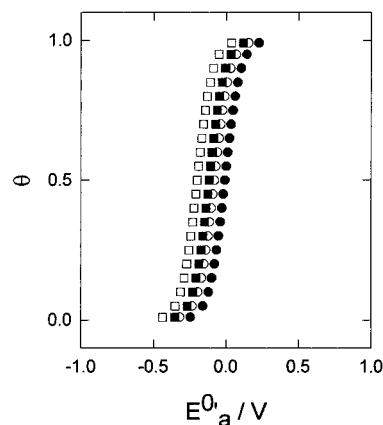
Figure 5. Calculated θ vs $E_a^{\circ\prime}$ according to eq 39: ($\bullet$) $j_{ox}/j_{red} = 1.2$, ($\circ$) $j_{ox}/j_{red} = 5$, ($\blacksquare$) $j_{ox}/j_{red} = 10$, and ($\square$) $j_{ox}/j_{red} = 50$. $q_{red}/q_{ox} = 1$, $\alpha = 1.2$.

ical stability of the units in the absence of stresses.[7b] $j_{ox}/j_{red} > 1$ implies that the oxidized form is mechanically more stable and, therefore, the oxidation is easier, as is reflected in Figure 5 for increasing values of j_{ox}/j_{red}.

Equation 39 can be employed to tentatively inquire about the magnitude of the parameters α, j_{ox}/j_{red}, and $E^{\circ\prime}$. To this end, we fitted the results of Figure 2 to eq 39, considering $n = 2$.[18a,b] A two-parameter fitting gives $\alpha = 3.15 \pm 0.044$ and $-(\alpha RT)/(nF) \ln(j_{ox}/j_{red}) + (RT)/(nF) \ln(q_{red}/q_{ox}) = 0.1514 \pm 0.0028$. A three-parameter fitting and splitting of the latter into j_{ox}/j_{red} and $E^{\circ\prime} = (RT)/(nF) \ln(q_{red}/q_{ox})$ gives $j_{ox}/j_{red} = 0.970$ and $E^{\circ\prime} = 0.1533$ V. However, because j_{ox}/j_{red} is very close to unity, the uncertainty is relatively high. The results of the fit are compared with those of the experiments in Figure 2. The agreement is very good.

As diagnostic criterion for the presence of stress/strain during the redox switching, the following can be employed: if the experimental plot of θ versus $E_a^{\circ\prime}$ is sigmoidal in shape, one could presume stresses are present. If, however, these plots are linear, only neighbor interactions with no mechanical effects are to be expected.

At this point, some remarks should be made. First, in the derivation we assumed, for simplicity, $n = 1$. This is the reason that n does not appear in all the equations. Obviously, to take into consideration the possibility that $n \neq 1$, all the RT terms should be divided by n. Second, it should be borne in mind that although they have been not explicitly included in the present treatment, a part of the interaction energy between redox centers is lumped into τ as a part of the energy employed to

convert Red to Ox. Finally, the present model can be improved in several ways. The model including mechanical effects could be combined with that considering interaction between the redox centers. On the other hand, it is known that during oxidation these materials (electroactive polymer films) incorporate anions.[21] This process could be taken into account by considering a further binding equilibrium between the oxidized centers and the anions in the solution.

3. Conclusions

The current/potential response during the redox switching of electroactive polymers derived from substituted arylamines can be interpreted in terms of a sigmoidal distribution of apparent formal potentials. Also, during the redox switching, this kind of polymers shows expansion and contraction. The thermodynamic analysis of such systems, allowing for mechanical stresses during the expansion and contraction, leads to the appearance of a distribution of apparent formal potentials.

It is shown that the concept of electron binding can be applied to describe the redox switching of an electroactive polymer. On the basis of this simple concept, statistical thermodynamic models can be applied to describe the distribution of apparent formal potentials during the redox switching of this kind of polymers. In particular, a simple model, based on the mean field approximation, including interaction between near neighbors, leads to a linear distribution of the apparent formal potential. On the other hand, a statistical thermodynamical model, including the development of strains during the redox switching, successfully describes the experimental sigmoidal distribution of apparent formal potentials.

References and Notes

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