Coupling between proton binding and redox potential in electrochemically active macromolecules. The example of Polyaniline

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ABSTRACT

In this work it is investigated the coupling between the redox potential and the extent of proton binding in electrochemically active polymers, for the particular case of Polyaniline (Pani). To this purpose, the degree of oxidation of the polymer was measured by spectrophotometry changing the external potential applied to Pani films, in solutions of different pH values. The knowledge of the oxidation degree for the different applied potentials allows determining the apparent formal redox potential. For Pani, in the hypothetical case of absence of interactions between the redox centres, the apparent formal redox potential should be independent of the oxidation degree and it should decrease linearly with the pH with a slope of 0.059 V, at room temperature. The values of the apparent formal redox potential, experimentally obtained, show that the pH dependence is not as expected from the redox equation. This fact implies interactions between the redox centres and some sort of coupling between the redox potential and the state of binding of the polymer. By employing a simple statistical mechanic model is possible to evaluate the interaction energy between the redox centres and also the acid dissociation constants of both, the oxidized and reduced forms. The values obtained for both dissociation constants agree with some reported in the literature. The application of the model also allows explaining the observed relationship between the apparent formal redox potential and the electrolyte pH.

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1. Introduction

Electrochemically active macromolecules (EAM) are substances that can be oxidized and reduced in a reversible way. These macromolecules, both natural and synthetic, have received a great deal of attention. The interest in natural EAM, mostly metalloproteins, is due to its obvious importance in biochemical reactions [1]. On the other hand, the interest in synthetic EAM, mostly in polymers, is due to its potential applications in several fields [2–5].

These macromolecules can be characterized by several properties such as their redox potential, the state of binding, the state of tension (deformation) and the extension of their screening. The redox potential is related to the possibility of the macromolecule to transfer electrons to a suitable redox couple in the same solution or to an electrode submitted to a suitable potential. The state of binding refers to the amount of bound species (mainly ions) on different sites of the macromolecule. The screening refers to the weakening of the electrostatics interactions between the fixed charged sites of the macromolecule due to the ionic atmosphere surrounding them. In this context, the state of tension refers to

conformational deformation that appears in the macromolecule as a consequence of interactions between parts of it.

In a previous work [6], it was shown that a variety of experimental results on EAM can be explained by the existence of couplings among the state of tension, the state of binding, the extension of screening and the redox potential. That is, if one of these states changes, all the others will change too. The vast majority of EAM are polyelectrolytes, and there are many examples of couplings of these types that can be attributed to its polyelectrolytic nature. It is well known that polyelectrolytic macromolecules show couplings among the degree of binding, generally of protons, and its state of deformation [7–9] and screening [10–12]. Deformation can be also induced by redox potential changes [13,14], and changes in the ionic strength of the electrolyte (screening effects) can modify the redox potential in both, natural [15] and synthetic macromolecular systems [16]. Finally, the concept of coupling between the redox potential and proton binding widely spread [17–19]. This coupling is of paramount importance to understand the redox behaviour of proteins, substances in which their redox activity may depend on small changes of the binding ion activity [19–22].

Polyaniline (Pani) is a relatively simple synthetic polymer, as compared with natural EAM, and its electrochemical behaviour is relatively well understood. The aim of this work is to rationalize,

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employing a simple modified a statistical mechanics model, the effect, experimentally observed, of proton binding on the redox potential of Pani.

Although simpler than many natural EAM, Pani presents an additional difficulty for the model: its redox potential depends directly on the proton activity in the solution, because protons participate in the redox reaction (Scheme 1). And, as protons also participate in a binding equilibrium with the macromolecule, the redox potential should indirectly depend on the solution pH through the coupling effects mentioned above.

In the present work, the coupling between proton binding and the redox potential of Pani, as a particular case of EAM, is experimental and theoretically studied. The experimental investigation of this coupling requires the determination of the oxidation degree of the polymer film in electrolytes of different pHs. Contrary to many electrochemical systems, for conducting polymers as Pani, the oxidation degree cannot be simply obtained from the voltammetric or chronoamperometric results because there is a capacitive contribution to the electrochemical current response [23,24]. So, in this work, the oxidation degree is obtained by UV–Visible spectroelectrochemical measurements.

On the other hand, a simple statistical mechanic model is developed to link the redox potential with the oxidation degree and the solution pH. The model allows the analysis of the experimental results to determine the proton binding constants of the reduced and the oxidized forms of the polymer, and also other parameters, such as differences in the interaction energy between the redox centres, as a function of the electrolyte pH.

2. Materials and methods

Pani films were electro synthesized onto Indium Tin Oxide (ITO) plates (R_s = 5–15 Ω cm, Delta Technologies). These plates were glued to a metallic contact with epoxy silver resin. The top and sides of the metallic plate were covered with an insulating varnish as shown in Fig. 1. The active area of the polymer film onto the ITO plate was around 1.0 cm^2. The electro synthesis was carried out by cycling the potential at 0.1 V s^{-1} between −0.200 V vs. a saturated calomel electrode (SCE) and a positive potential limit set at the beginning of the monomer oxidation (around 0.700–0.800 V). To improve the adherence and homogeneity of the film, the positive potential limit was slightly decreased after a few cycles. After the synthesis, the film was washed with pure water and cycled in 3.7 M H$_2$SO$_4$ solution during some minutes and then introduced in the spectrophotometric cell. This was a square quartz cell (Spectrocell, 1 cm side) in which the electrode was inserted perpendicular to the light path. Inside the cell it was placed a Pt plate that serves as the counter electrode, and a fine capillary connected to an external reference electrode (see Fig. 1). This was also a SCE, which was
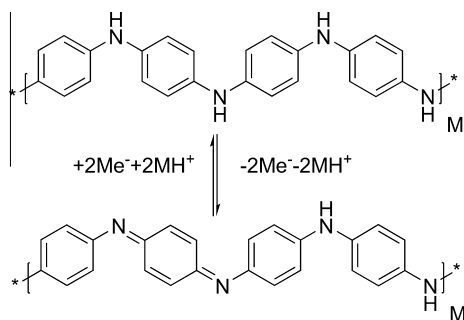
employed throughout the work; all potentials in the text are referred to it. The absorbance of the film electrodes was monitored over a period of several hours and no change was noticed, meaning the Pani film covering ITO plates was stable during that time.

Solutions were made of Milli-Q purified water and NaOH and H$_2$SO$_4$ (Carlo Erba, RPE-ACS). The latter were employed as received. A potentiostat TEQ-03 was employed for all the electrochemical experiments.

Spectra were taken with an Agilent model 8453E diode array spectrophotometer in the spectral range comprised between 300 nm and 900 nm and in the potential range between −0.200 and 0.450 V.

Electrolytic solutions of different pH and constant ionic strength of 3.7M of H$_2$SO$_4$ + HNaSO$_4$, were employed. For pH > 1, the pH was measured with a glass electrode adequate for acid media (Ross, Orion Research) by using a pH-meter (Cole-Palmer 59003-15). For pH ⩽ 1, the pH was measured using a Pd(Pd) hydrogen electrode [25].

Before starting the experiments with each one of the solutions of different pH values, the Pani – covered electrodes were polarized at −0.200 V during 20 min to completely reduce and age the Pani films [26,27]. Afterwards, the potential was increased in steps of 0.010–0.025 V and held at that potential value for 5 min, to reach ionic equilibrium with the electrolytic solution. Then the spectrum was taken.

As a measure of the film thickness, it was employed the integrated charge from E = −0.200 V up to 0.450 V, Q_T (0.45) [24]. Experiments were done with films of charge about Q_T (0.450) = 32 mC cm^{-2}.

3. Results

In Fig. 2 it is shown the voltammetric response of a typical Pani film between the potential limits −0.200 V and 0.450 V. During the positive half potential scan the reduced form of Pani (Leucoemeraldine, L) is oxidized to the half oxidized form (Emeraldine, E).

The spectra of Pani for different applied potentials, at pH = −0.60, are shown in Fig. 3. These spectra show three main characteristic bands in the wavelength range 300–900 nm. The band at 320 nm is attributed to the $\pi \rightarrow \pi^*$ transitions characteristic of the benzenoid ring units in the polymer. Also, it might be attributed to the band gap in the reduced polymer. This band is the main one for the L form; besides a second broad and small band is observed at about 850 nm. As the polymer is oxidized, the band at 320 nm steadily decreases, a band starts growing at about 400 nm, and the band with a maximum at around 850 nm in the reduced state, shows a gradual increase and shift to 750 nm. These bands are attributed to the polarons and bipolarons associated to the formation of the quinoid units due to the oxidation of the amine to imine groups. Further discussions about the band assignments in Pani spectra are available in several works [28–31].

As the band at 320 nm steadily decreases as the polymer is oxidized; the absorbance changes in this region may be employed to quantify the fraction of oxidized polymer. The relative absorbance change will be defined as:

$$\Delta A(E)_R = \frac{A(E) - A_{0.45}}{\Delta A_T} \qquad (1)$$

where $A(E)$ is the absorbance at the potential E, $\Delta A_T = A_{-0.2} - A_{0.45}$ is the total absorbance change and $A_{-0.2}$ and $A_{0.45}$ are the absorbances at E = −0.2 V and 0.45 V.

Consequently, the degree of oxidation of the polymer, θ_n, can be expressed as:

$$\theta_n = 1 - \Delta A(E)_R \qquad (2)$$

Scheme 1. Redox commutation for the first redox couple of Pani (only the base forms are shown).

+2Me⁻+2MH⁺   -2Me⁻-2MH⁺