



The effect of membrane equilibrium on the behaviour of electrochemically active polymers



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ABSTRACT

The establishment and effects of the Donnan potential, E_D , at the polymer/external solution interface in Electrochemically Active Macromolecular films, for the particular case of Polyaniline (Pani) is considered both from the fundamental and experimental viewpoints. In particular, it is demonstrated that E_D should be considered together with the osmotic equilibrium and only under special circumstances, i.e. the osmotic pressure is negligible, E_D may be calculated with the classical expression that arises from considering the ionic equilibrium alone. Also, it is demonstrated that, in Pani, the amount of protonated fixed sites depends on the external pH and the Donnan potential.

The electrochemical response of the Pani film/aqueous solution system is studied as a function of the pH and the ionic strength. The parameter used in this work to evaluate the influence of E_D in this kind of systems is the experimental peak potential, $E_{p,exp}$, which is the potential at the maximum current in the voltammetric response. Based on previous models, it is obtained an equation for the $E_{p,exp}$ that allows to interpret the dependence of this parameter on the pH and the ionic strength.

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1. Introduction

When an electrochemically active polyelectrolyte phase is brought in contact with an electrolytic solution, it is established a membrane equilibrium between the two phases. This is similar to a membrane separating two electrolytic solutions which is impermeable to one ionic constituent of one of the solutions [1–4]. The membrane equilibrium comprises an osmotic equilibrium, characterized by the osmotic pressure, π , that is referred to the solvent and by an ionic equilibrium characterized by the Donnan potential, E_D [4].

The membrane equilibrium, and consequently the Donnan potential are present in the majority of film modified electrodes. However, more often than not, the existence of this potential has been overlooked in this type of electrochemical systems. This is acceptable if E_D is negligible, as it happens in systems where the concentration of electrolyte in the external phase is comparable with the concentration of fixed sites in the film. Moreover, considering that E_D is coupled to the osmotic equilibrium [1,4,5] i.e. the solvent equilibrium between the phases, the calculation of E_D just on the basis of the ionic equilibrium may be erroneous by an amount that depends on the osmotic pressure. Then, if the osmotic work is negligible as compared to the electrical one (Donnan), this statement will be correct.

Below, it will be shown that these two quantities (π and E_D) depend on each other. Furthermore, when the fixed sites are weak acid–basic or polyampholite (as in the case of proteins) the amount of fixed sites in the polyelectrolyte will depend on the pH inside; and in turn this will depend on E_D as well as on the pH of the external solution.

Briefly, the Donnan potential, E_D , is a Galvani potential difference that establishes at the interphase between two phases separated by a semi permeable membrane; and it is a consequence of both the ionic equilibrium between them and the existence of immobilized charges (fixed sites) in one of the phases [1–8].

In electrochemically active polymers (EAPs) films [9,10], that is, in those polymers that can be oxidized and reduced reversibly, the existence of a Donnan potential may strongly influence their electrochemical behaviour. On the other hand, the presence of fixed charged sites may be due to different reasons [8]. For example, the polymer has charged sites as in Os(II) bpy polyvinyl pyridine, or it has weak acid–base sites that may become protonated (charged) by protons present in the internal solution, as a consequence of the ionic equilibrium with the external electrolyte. This is the case of many EAPs such as Pani that will be considered in this work.

In the first case, as the polymer is oxidized, the charge of the Os fixed sites increases, leading to a change in the E_D . In the case of Pani, half the protonated amino groups (pK_a about 1) are oxidized to imines ones (pK_a about 4.5) with the consequent changes in the amount of fixed charged sites leading to a change in E_D . Here, the problem is more

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complicated because protons also participate in the electrochemical reaction as is schematically shown below in reaction (2).

In electrochemical systems where the pH and the applied potential are kept constant, the influence of the Donnan potential on the total potential drop has been measured several times by changing the external concentration of indifferent electrolyte [11–16]. Under these conditions the concentration of fixed sites in the film is kept constant. These experiments were analyzed at the peak potential, E_p , that is, the potential at the maximum current in the voltammetric response. The election of this particular potential value has several advantages. The more important one is that, for electrochemically reversible processes in confined redox couples, E_p has a simple thermodynamic meaning. Namely: it is equal to the standard redox potential. These experiments show a slope in the E_p vs. the logarithm of the external salt concentration plot, very close to 0.059 V/decade. This behaviour seems to indicate that under the experimental conditions employed in these works π is very small or constant (see Eq. (12) below).

In this work, we establish an expression for the Donnan potential in the presence of osmotic equilibrium and search under what conditions the osmotic work may be disregarded against the electrical work (Donnan). Then, we study the formation of fixed sites in the case of weak acid-basic fixed groups and how they depend on the electrolyte pH and on the Donnan potential.

As a case of study, we measured the dependence of the peak potential on the ionic strength and the electrolyte pH for an EAP as Pani. Pani was chosen because the quantity of fixed sites depends on the external pH, and also because both, the acid-base equilibrium (see [17,18] and references therein) and its electrochemistry have been thoroughly studied (see [19–23] and references therein). However, it has the disadvantage that protons also participate in the electron exchange reaction, so that a change in the pH produces, not only a change in the number of fixed sites, but also in the potential.

2. Experimental

Pani films were obtained by electro polymerization on Au electrodes by cycling the potential at $v = 0.1 \text{ V s}^{-1}$, between -0.2 V vs. SCE, and the potential corresponding to the beginning of the oxidation of the monomer, around 0.8 V vs. SCE, as described before [24,25]. To improve the adherence and homogeneity of the film, after a few cycles, the positive potential limit was slightly decreased. The electro synthesis solutions were 0.5 M in the monomer in aqueous solution of $3.7 \text{ M H}_2\text{SO}_4$. The geometric area of the wire working electrode was 0.154 cm^2 . Polymer films were grown until the desired voltammetric charge was reached. The voltammetric charge of the films employed in this work, $Q_T(0.45)$, was determined from the integration of the anodic j/E profiles of the voltammetric response in the potential range comprised between -0.20 and 0.45 V vs. SCE.

The polymer films charges were about $Q_T(0.45) = 20 \text{ mC cm}^{-2}$ for the experiments performed with the sulphate solutions and $Q_T(0.45) = 25 \text{ mC cm}^{-2}$ for the chloride solutions. Employing the equivalence given by Gottesfeld et al. [26] for Pani films of $Q/d = 8 \pm 1 \times 10^{-2} \text{ mC cm}^{-2}/\text{nm}$, the thicknesses of these films result to be about 250 nm . This relatively thin film allows fast equilibration of the ionic fluxes within the film.

The electrolyte solutions were prepared from H_2SO_4 , HCl, NaCl and NaOH (Merk, p.a.); aniline (Fluka-Guarantee, puriss. p.a.) and Milli-Q® water. The monomer was distilled under reduced pressure before the preparation of the solutions.

Four different types of electrolytes were employed: a) $\text{H}_2\text{SO}_4 + \text{NaHSO}_4$ aqueous solutions of constant $\mu = 1\text{M}$; b) HCl + NaCl aqueous solutions of constant $\mu = 4\text{M}$; c) pure H_2SO_4 aqueous solutions; d) pure HCl aqueous solutions. The electrolytes were prepared at different pH values, in the range comprised between $-1.0 < \text{pH} < 2.0$. The pH of the constant ionic strength solutions was changed by adding NaOH to a $1 \text{ M H}_2\text{SO}_4$ solution or by mixing the

appropriate amounts of HCl and NaCl. The pH of each one of the solutions was previously measured with a glass electrode adequate for acid media (Ross, Orion Research) by using a pH-meter (Cole-Palmer 59003-15). For the most acid solutions, also a Pd (Pd) electrode in the test solutions was employed to check the glass electrode readings [27].

The experimental set-up for the voltammetric measurements was a conventional three electrode glass cell as described elsewhere [24,25]. The auxiliary electrode was a cylindrical Pt foil. For the chloride solutions, a Saturated Calomel Electrode (SCE) was used as reference electrode. For the sulphate solutions, a 1 M Mercurous sulphate (MSE) was employed as reference electrode. However, all the potentials in the text are referred to the SCE.

The experimental procedure for exchanging electrolytes was the following: after achieving the voltammetric stationary profile in one medium; the electrode was extracted from the cell, washed with the solution of different pH and inserted into another similar cell containing the electrolyte of that pH. The pH was changed in the order of increasing values. Then, the potential was cycled until a stationary j/E profile was obtained. A new polymer film was employed for each one of the four types of electrolytes employed.

Conventional voltammetry was performed using a Pine AFRDE5 bipotentiostat at different sweep rates in the range, $10^{-3} \text{ V s}^{-1} < v < 0.5 \text{ V s}^{-1}$, covering a potential range between -0.20 V and 0.45 V vs. SCE, in the case of chloride solutions, and between -0.63V and 0.02 V vs. MSE, in the case of the sulphate solutions.

3. Results and discussion

3.1. Results

The voltammetric responses of Pani films in $\text{H}_2\text{SO}_4 + \text{NaHSO}_4$ aqueous solutions of constant ionic strength and different pHs are shown in Fig. 1a and in pure aqueous solutions of H_2SO_4 of different pHs are shown in Fig. 1b, respectively. In Fig. 2a and b, it is shown the corresponding voltammetric responses in the HCl + NaCl mixtures of constant ionic strength (Fig. 2a) and in pure HCl (Fig. 2b).

In Fig. 3, the peak potential values are shown for both, the sulphate and the chloride solutions, in single electrolytes and in the mixtures as a function of pH. In the pH range between -1 and 0.5 , E_p decreases with the pH increase for all solutions with approximately a similar slope. For the solutions of pure electrolytes, E_p increases for pH values higher than 1.0 , and it does not depend much on the nature of the anion. For H_2SO_4 solutions of constant ionic strength, the E_p value also increases although less steeply than for the pure electrolytes. For the chloride solutions of constant ionic strength $\mu = 4 \text{ M}$, there is no increase of E_p with the increase of pH, as it was observed by previous workers for these solutions [19,21].

The integrated anodic charges, $Q_T(0.45)$, for all the solutions studied in this work are independent of the pH and the composition of the electrolyte.

3.2. Summary of fundamentals

We consider convenient to summarise some fundamental aspects related to the discussion of the present experimental results. Some of them are well known. However, others have been overlooked in previous works, and others have been recently presented. These questions will be discussed considering Pani as the system example.

3.2.1. The potential difference across the metal/polymer/solution interface in the case of Pani

We will consider the system as a metal base (M) on top of which there is a polyelectrolyte polymer film composed of reduced (R) and oxidized (Ox) chains, embedded in an electrolyte solution (phase i or inter-nal phase). At the metal/polymer interface there is an electrochemical

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