



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

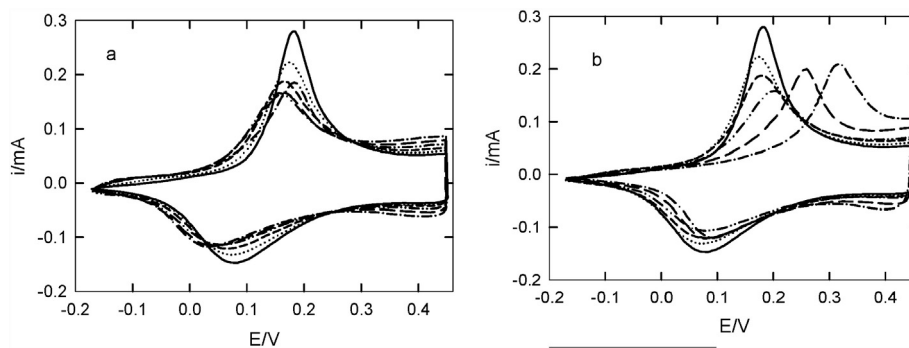


Fig. 1. Voltammetric profiles of (a) $\text{H}_2\text{SO}_4 + \text{NaHSO}_4$ mixtures of constant $\mu = 1 \text{ M}$, and (b) Pure H_2SO_4 . Both at different pH values: (—) 0.02, (.....) 0.32, (—) 0.66, (-.-.-) 1.00, (- - -) 1.33, (-.-.-) 1.66. $Q_T(0.45) = 25 \text{ mCcm}^{-2}$, $v = 0.01 \text{ Vs}^{-1}$.

equilibrium due to electron transfer across it (reaction 2). Charge is transported across the film by a mixed electron-ion diffusion-migration mechanism. The internal phase is in contact with an external solution (phase e or external phase). At the polymer/solution interphase there is ion charge transfer. This is a fast process. In the experimental conditions employed here (i.e. relatively thin films and low sweep rate) these processes can be considered to equilibrate very rapidly as the potential is changed. Therefore, we may consider the whole process to be at equilibrium. In these conditions, the potential drop across the polymeric phase is zero (the potential within the polymer phase is constant).

The total potential drop experimentally measured, E_{exp} , is the sum of that at the metal/polymer interface, E , and that at the polymer/solution interface. We will identify the latter with the Donnan potential difference, E_D . Therefore, E_{exp} can be written as [8]:

$$E_{\text{exp}} = E + E_D. \quad (1)$$

In this system there is a membrane equilibrium between the internal and the external phases. This membrane equilibrium is similar to that between two electrolytic solutions separated by a membrane impermeable to one of the species (fixed sites) [2,3]. In the case of Pani the fixed sites bear a positive charge and they are originated by the protonation of the amine and imine groups of the polymer (see Eqs. (25) and (26) below). In this case, these fixed charged sites are of very limited mobility.

3.2.2. The potential difference at the metal/polymer interface

At the metal/polymer interface takes place the following electrochemical reaction:



where R represents the reduced form (Leucoemeraldine) and Ox the half oxidized form (Emeraldine) of Pani, and ν_e and ν_H are the

stoichiometric coefficients of electrons and protons, respectively. In the case of Pani $\nu_e = 2$ and $\nu_H = 2$. All the literature coincides that, under the experimental conditions employed in this work: relatively thin films and low scan rates, v ($v < 0.05\text{--}0.1 \text{ Vs}^{-1}$), charge transfer (i.e. reaction (2)) controls the whole process. Moreover, reaction (2) is very fast and the voltammetric response during the oxidation of Pani is well represented by the behaviour of confined redox couples with interaction between the redox centres [23].

The redox potential depends on the electrolyte pH by several reasons. First, protons participate in the electron exchange reaction (reaction (2)). This should lead to a decrease of the potential of 0.059 V/decade per pH increase [19,21]. However, as it happens in most electrochemically active macromolecular systems, the redox potential also depends on the pH through the proton binding to the acid-base sites [28,29]. Furthermore, protonated neighbour redox centres interact among each other [17,23]. As the amount of protonated redox centres depends on the electrolyte pH, this interaction energy also depends on the pH.

The experimental values of the average acid dissociation constant of the protonated reduced form (amine groups), $\text{p}K_{\text{aR}}$, lie in the range comprised between $0.5 < \text{p}K_{\text{aR}} < 2.5$ whereas those for the half oxidized (imine groups), $\text{p}K_{\text{aOx}}$, are considered to be between $4.0 < \text{p}K_{\text{aOx}} < 6.0$ ([17,18] and references therein). In a previous work [17] we obtained for thin films under potential control the values of $\text{p}K_{\text{aR}} \approx 1$ and $\text{p}K_{\text{aOx}} \approx 4.5$. These $\text{p}K_{\text{a}}$ values are operational; they were determined in 3.7 M sulphate media. Therefore they may be slightly different in other electrolytes and at different ionic strengths. This means that when the internal pH, pH_i , is low enough both reduced and oxidized forms are fully protonated and when it is relatively high (> 1.5) only the oxidized groups (imines) are still fully protonated, whereas the amine groups are fully deprotonated. Thus, when the polymer is oxidized from the LE form to the E form in electrolytes of different pH values, the number of fixed sites of the E form increases with respect

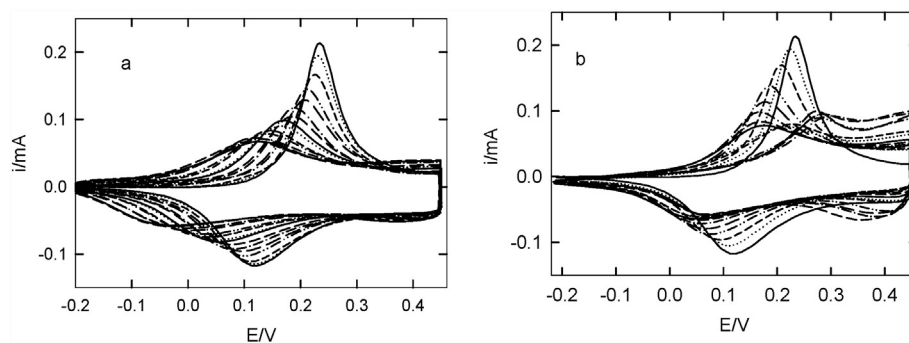


Fig. 2. Voltammetric profiles of (a) $\text{HCl} + \text{NaCl}$ mixtures of constant $\mu = 4 \text{ M}$. Both at different pH values: (---) 1.08, (.....) 0.96, (---) 0.81, (-.-.-) 0.60, (- - -) 0.41, (-.-.-) 0.19, (- - -) 0.02, (---) 0.26, (.....) 0.51, (---) 0.76, (-.-.-) 1.01, (- - -) 1.28 (-.-.-) 1.52, (- - -) 1.80, (---) 2.02 and (b) pure HCl, at different pH values: (---) 0.75, (.....) 0.56, (---) 0.40, (-.-.-) 0.06, (- - -) 0.21, (-.-.-) 0.45, (- - -) 0.68, (---) 0.90, (.....) 1.11, (---) 1.31, (-.-.-) 1.55, (- - -) 1.67, (-.-.-) 1.88, (- - -) 2.01. $Q_T(0.45) = 18 \text{ mCcm}^{-2}$, $v = 0.01 \text{ Vs}^{-1}$.

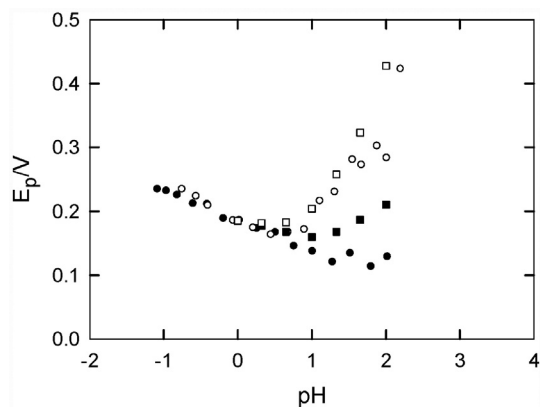


Fig. 3. pH dependence of the peak potential (vs. SCE) in the different solutions. (○) HCl solution, (□) H₂SO₄ solution, (●) HCl + NaCl, μ = 4.0 M, (■) H₂SO₄ + NaHSO₄, μ = 1.0 M.

to the number of fixed sites of the LE form, as the pH increases. In turn, and in the absence of an excess of supporting electrolyte, this fact yields a change of the Donnan potential and the adjustment of the internal concentrations to maintain the electro neutrality inside the polymer. It has been experimentally measured that during the oxidation-reduction cycles there are proton and anion ejection/injection from and into the film (see, for instance, [30–36] and references therein). This is a consequence of the variations in the Donnan potential in order to maintain the electroneutrality inside the film.

In view of the electrochemical equilibrium (2) it is possible to write [4]:

$$\tilde{\mu}_R^i = \tilde{\mu}_{Ox}^i + \nu_e \tilde{\mu}_e^M + \nu_H \tilde{\mu}_H^i \quad (3)$$

In general, for species *i* in phase α , the electrochemical potential can be written as

$$\tilde{\mu}_i^\alpha = \mu_i^{\alpha\theta} + RT \ln a_i^\alpha + P^\alpha \bar{V}_i + z_i F \varphi^\alpha \quad (4)$$

where, μ_i^θ is the standard chemical potential, a_i^α , the activity of species *i* in phase α , *P* is the pressure, \bar{V} the molar partial volume, φ the Galvani potential, and z_i is the charge (if any) of species *i*. Applying Eq. (4) to Eq. (3), it results:

$$\nu_e F (\varphi^M - \varphi^i) = \mu_{Ox}^\theta - \mu_R^\theta + \mu_e^M + RT \ln \frac{f_{Ox}^\alpha}{f_R^\alpha} + RT \ln \frac{\theta_n}{1 - \theta_n} - \nu_H RT pH + P^i (\bar{V}_{Ox} - \bar{V}_R) \quad (5)$$

By convention, μ_H^θ is equal to zero. f_i refers to the activity coefficients and θ_n is the degree of oxidation, then $a_{Ox} = f_{Ox} \theta_n$, and similarly for a_R . The last term is referred to the mechanical work due to the volume change. However, if \bar{V}_{Ox} and \bar{V}_R are independent of the oxidation degree, this term is constant during the oxidation and it may be included in the internal standard potential, E_{int} , arising from the term

$$E_{int} = \mu_{Ox}^\theta - \mu_R^\theta + \mu_e^M \quad (6)$$

Previously [17,29], it was proposed a simple statistical mechanical model, that also takes into account the effect of proton binding on the redox potential of the metal/polymer interface. There, the final expression for the potential reads:

$$E = E_{int} - \frac{\nu_H 2.303 RT}{\nu_e F} pH - \frac{RT}{\nu_e F} \ln \left(\frac{(1 - \theta_{N,R})}{(1 - \theta_{N,Ox})} \right)^2 - \frac{\Delta \varepsilon_m}{\nu_e F} (1 - 2\theta_n) - \frac{RT}{\nu_e F} \ln \left(\frac{(1 - \theta_n)}{\theta_n} \right) \quad (7)$$

$\theta_{N,R}$ and $\theta_{N,Ox}$ are the fractions of bound protons to R and Ox segments, respectively.

The terms in Eq. (7) are due to the following effects: The first term, E_{int} , is due to the polymer standard redox potential in the absence of other effects (such as binding and interactions between the redox centres [17]). The second term is a consequence of the dependence of the electrochemical reaction on the pH. The third term is due to the proton binding (acid-base equilibrium). The fourth term is due to the interaction energy between the redox centres, $\Delta \varepsilon_m$, and the last one is the usual concentration ratio in the Nernst equation. The mechanical work, $P(\bar{V}_{Ox} - \bar{V}_R)$, is included in E_{int} .

The amount of bound protons may be calculated from an expression of the type:

$$\theta_{N,Ox} = \frac{K_{pOx} a_{H^+}^i}{(1 + K_{pOx} a_{H^+}^i)} \quad (8)$$

and similarly for $\theta_{N,R}$. Then, taking into account Eq. (8), the third term of

Eq. (7) may be written as: $-\frac{RT}{\nu_e F} \ln \left(\frac{(1 + K_{pOx} a_{H^+}^i)^2}{(1 + K_{pR} a_{H^+}^i)} \right)$. In a previous work [17] was demonstrated that the pH dependence of the peak potential in the presence of an excess of indifferent electrolyte (see curve (•) in Fig. 3 above) can be explained by Eq. (7). At small pH values the second term in Eq. (7) predominates and E_p decreases with pH. As the pH further increases the third and fourth terms becomes increasingly more important and E_p levels in the range $0.5 < pH < 1.5$ and after it increases ($pH > 1.5$).

3.2.3. The potential difference at the polymer/solution interface

At equilibrium, this potential difference is the well known Donnan potential, E_D . This has been considered in many physical chemistry and electrochemistry books and reviews [6–8]. However, in order to properly consider this magnitude, it is necessary to account not only the ionic equilibrium, but also the osmotic equilibrium between the two phases. That is, the solvent equilibrium between the two phases. To our knowledge, these points have been previously considered but in a very general way (see for instance Refs. [1,4,5]).

3.2.4. Membrane equilibrium

The system was described in Section 3.2.1. In general, the equilibrium condition for constituent *i* between the two phases is:

$$\tilde{\mu}_i^i = \tilde{\mu}_i^e \quad (9)$$

Considering Eq. (4), Eq. (9) can be written for the cations, *c*, as:

$$P^i \bar{V}_c + \mu_c^\theta + z_c F \varphi^i + RT \ln a_c^i = P^e \bar{V}_c + \mu_c^\theta + z_c F \varphi^e + RT \ln a_c^e \quad (10)$$

and similarly for the anions, *a*:

$$P^i \bar{V}_a + \mu_a^\theta - |z_a| F \varphi^i + RT \ln a_a^i = P^e \bar{V}_a + \mu_a^\theta - |z_a| F \varphi^e + RT \ln a_a^e \quad (11)$$

From Eqs. (10) and (11), and assuming $z_c = |z_a| = 1$, we obtain:

$$\pi \bar{V}_c + FE_D = RT \ln \left(\frac{a_c^e}{a_c^i} \right) \quad (12)$$

Being $\pi = P^i - P^e$ and $E_D = \varphi^i - \varphi^e$. A similar expression it is obtained for the anions. Note that if $\pi = 0$ we regain the classical expression of E_D [6] which we will call $E_D(\pi = 0)$. For the solvent, it results:

$$\pi \bar{V}_w = RT \ln \left(\frac{a_w^e}{a_w^i} \right) \quad (13)$$

Eliminating E_D from Eqs. (10) and (11) we obtain:

$$\pi = \frac{RT}{(\bar{V}_a + \bar{V}_c)} \ln \left(\frac{a_a^e a_c^e}{a_a^i a_c^i} \right) \quad (14)$$

Eliminating π between Eqs. (13) and (14), we obtain the membrane equilibrium condition as:

$$a_a^e a_c^e = f_w a_a^i a_c^i \quad (15)$$

where $f_w = \left[\left(\frac{a_w^e}{a_w^i} \right)^Q \right]$ and $Q = \frac{\bar{V}_a + \bar{V}_c}{\bar{V}_w}$.

The Donnan potential can be obtained by eliminating π between Eqs. (10) and (11).

$$FE_D = \left(\frac{RT}{(\bar{V}_a + \bar{V}_c)} \right) \left[\bar{V}_a \ln \left(\frac{a_c^e}{a_c^i} \right) - \bar{V}_c \ln \left(\frac{a_a^e}{a_a^i} \right) \right]. \quad (16)$$

If the activities of anions and cations inside the polymer and the partial molar volumes of anions and cations are known, the above equations will allow to estimate π and E_D . It deserves to point out that only if $f_w = 1$, it is obtained the usual condition for the Donnan equilibrium [6]. An expression for π can be obtained from Flory's model [2,28,37] for polyelectrolyte gels. According to it, π is given by:

$$\pi = \ln(1 - \phi_2) + \phi_2 + \chi_{\text{eff}} \phi_2^2 \quad (17)$$

where ϕ_2 is the volume fraction of the polymer and χ_{eff} is the effective interaction energy (solvent plus electrostatic).

3.2.5. Approximate evaluation of E_D in the case $\pi = 0$

Employing the molar scale of concentrations, C_i , the electroneutrality condition (EC) in each phase may be written as:

$$z_c C_c^e + z_a C_a^e = 0 \quad (18)$$

$$z_c C_c^i + z_a C_a^i + z_F C_F^i = 0 \quad (19)$$

where C_F the concentration of fixed sites and z_c , z_a , and z_F , the charges of the different species. For $\pi = 0$

$$FE_D(\pi = 0) = +RT \ln \left(\frac{a_c^e}{a_c^i} \right) = -RT \ln \left(\frac{a_a^e}{a_a^i} \right). \quad (20)$$

From this equation, employing the EC inside the film, (Eq. (18)), we obtain, for a 1:1 electrolyte, a second order equation from which either C_a^1 or C_c^1 can be obtained. Replacing one of these, and considering ideal conditions (activity coefficients equal to unity), it can be obtained an

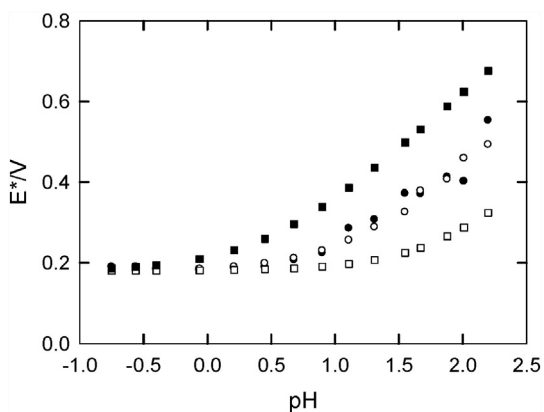


Fig. 4. Experimental E^* data (●) for pure HCl, together with those calculated as described in the text employing Eq.(32) and different values of pK_{AR} : (■) 0.5, (○) 1.0, (□) 2.0. $E_{\text{int}} = 0.180$ V vs. SCE.

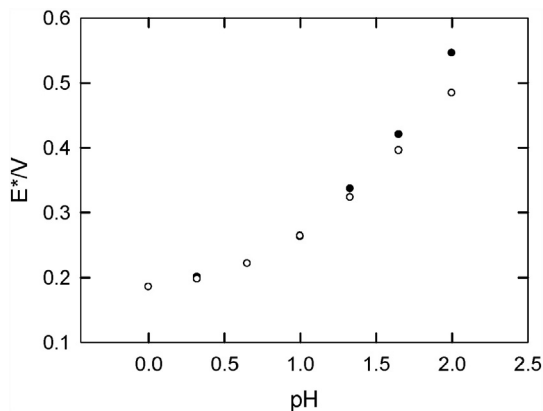


Fig. 5. Experimental E^* data (●) for pure H_2SO_4 , together with those calculated as described in the text employing Eq. (32) (○). $E_{\text{int}} = 0.174$ V, $pK_{AR} = 1$.

approximate expression for the Donnan potential:

$$E_D(\pi = 0) = \left(\frac{RT}{F} \right) \ln \left(\left(1 + \left(\frac{C_F}{2C_s} \right)^2 \right)^{1/2} + \left(\frac{C_F}{2C_s} \right) \right) \quad (21)$$

where C_s is the salt concentration in the external electrolyte. It is not difficult to extend this expression to the case of a mixture of two 1:1 electrolytes with a common anion in the external phase. Also, an equivalent of Eq. (21) may be obtained for a 2:1 electrolyte.

It is interesting to note the following points about E_D : (i) The sign of E_D depends on the charge of the fixed sites. If $z_F < 0$, E_D is negative and vice versa. (ii) E_D increases in absolute value for increasing C_F . (iii) E_D increases for decreasing C_s and (iv) For a mixture of salts, E_D only depends on the ionic strength of the electrolyte in the external phase.

From Eq. (11) or (12), being $\pi = 0$, the activity of any species inside the internal phase may be expressed in terms of E_D and the activity of the external phase. Thus for the case of protons:

$$a_{H^+}^i = a_{H^+}^e \exp \left(- \frac{z_{H^+} E_D F}{RT} \right) \quad (22)$$

or

$$(pH)_i = (pH)_e + \frac{z_{H^+} FE_D}{2.303RT} = (pH)_e + E'_D \quad (23)$$

where, for compactness in the notation, we have defined $E'_D = z_{H^+} FE_D / 2.303RT$.

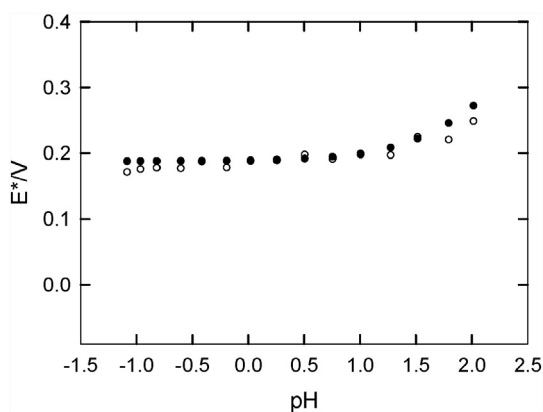


Fig. 6. Experimental E^* data (○) for HCl + NaCl mixtures of constant $\mu = 4$ M, together with those calculated as described in the text employing Eq.(32) and $pK_{AR} = 2.0$, (●). $E_{\text{int}} = 0.187$ V.

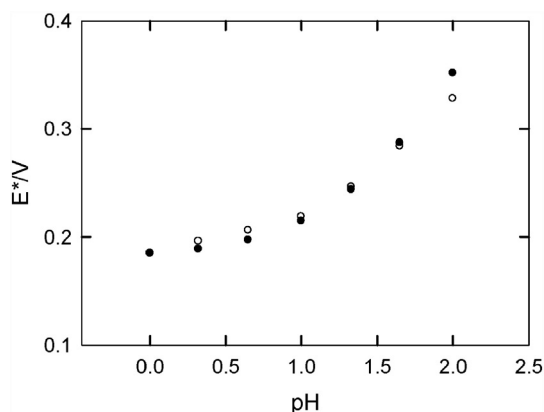


Fig. 7. Experimental E^* data (○) for $H_2SO_4 + NaHSO_4$ mixtures of constant $\mu = 1$ M, together with those calculated as described in the text employing Eq. (23) and $pK_{aR} = 1.5$ (●). $E_{int} = 0.181$ V.

3.2.6. The mechanism of building the concentration of fixed charges in Pani

The amount and type of fixed charges in a polyelectrolytic polymer with weak acid-base sites will depend on the pH and on the oxidation state of the polymer. For Pani in the fully reduced base form (deprotonated form), there will only be $-NH^-$ groups. These groups can be protonated to form $-NH_2^+$ according to the reaction:



where K_{pR} is the protonation constant, K_{aR} is the acid dissociation constant; and obviously $K_{pR} = 1/K_{aR}$.

If the polymer is in a partially oxidized state, the imine groups will also undergo a protonation reaction according to:



Menardo et al. [38] carried out acid base titrations of half oxidized Pani and could separate the contributions of the two forms, attributing to them $pK_{aR} = 2.5$ and $pK_{aOx} = 5.5$. Here, we will consider the values obtained by spectroelectrochemistry, employing thin films under potential control [17,18]: $pK_{aR} \approx 1.0$ and $pK_{aOx} \approx 4.5$.

The protonation constants for reactions (25) and (26) are:

$$K_{pR} = \frac{a_{(-NH_2^+)}}{a_{(-NH^-)}a_{H^+}} = \frac{a_{(-NH_2^+)}}{a_{(-NH^-)}a_{H^+}^e} \exp\left(-\frac{z_{H^+}FE_D}{RT}\right) \quad (27)$$

$$K_{pOx} = \frac{a_{(=NH^+)}}{a_{(=N^-)}a_{H^+}} = \frac{a_{(=NH^+)}}{a_{(=N^-)}a_{H^+}^e} \exp\left(-\frac{z_{H^+}FE_D}{RT}\right) \quad (28)$$

where $a_{(-NH_2^+)}$, etc., are the activities of the corresponding species inside the film. It is clear that K_{pR} and K_{pOx} will differ from the values determined in solution due to the presence of E_D . Note that if the constant K_{pOx} is estimated by measuring the ratio $a_{(-NH_2^+)}/a_{(=N^-)}$, for example, spectroscopically, and it is employed the pH outside the film, the constant will be wrong by a factor $\exp(z_{H^+}E_D F/RT)$. This is an important point to remark because many workers report the pK values determined with the polymer as a film in contact with a solution and actually this is different from that determined with the macromolecules in solution.

In order to estimate E_D with Eq. (21) it is necessary to know the fractions of protonated amines, $x_R = [-NH_2^+]/C^0_R$ and imines, $x_{Ox} =$

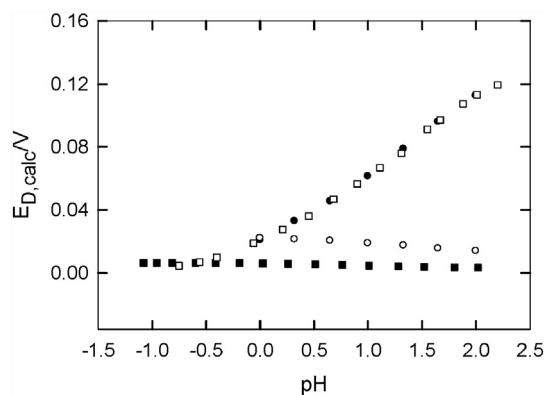


Fig. 8. E_D calculated, as described in the text, (●) pure H_2SO_4 , (○) for $H_2SO_4 + NaHSO_4$ mixtures of constant $\mu = 1$ M, (□) pure HCl, (■) HCl + NaCl of constant ionic strength $\mu = 4$ M. $E_{int} = 0.180$ V.

$[=NH^+ -]/C^0_{Ox}$ at equilibrium, that is, when E_D is the actual value, and C^0_R and C^0_{Ox} are the total amounts of amine and imine sites. This is a difficult task because three quantities, x_R , x_{Ox} and E_D , have to be determined from two equations, Eqs. (27) and (28). However, the three quantities can be estimated by a numerical procedure.

It deserves to remark that our interest is to evaluate the system at the peak potential, where the amount of the LE form equals the amount of the E form. Moreover, as we said above, in the pH range studied in this work, only the protonated reduced species ($pK_{aR} \approx 1$) dissociates as the pH increases; the oxidized species are always protonated in this pH range ($pK_{aOx} \approx 4.5$).

3.2.7. Evaluation of π for the case of Pani in 1 M H_2SO_4 solutions

It is important to compare the magnitude of the osmotic work with the electric one, to ascertain whether or not; the influence of the osmotic term can be disregarded to calculate E_D . The calculation of π for reduced Pani, together with the estimation of the necessary parameters is carried out in the Appendix. The conclusion is that, in this case, π is negligible as compared with E_D , for a wide range of salt concentration values, C_s , in phase 2, and of fixed sites concentration, in phase 1. So, we will work under the assumption that π is negligible.

3.2.8. The relation between the experimental value of E_p and E_D

Replacing Eq. (7) into Eq. (1), for $E = E_p$ and noting that at this potential $\theta = 0.5$ the fourth and fifth terms in Eq. (7) disappear, then we obtain the following expression for the experimental peak potential.

$$E_{p,exp} = E_{int} - \frac{\nu_H 2.303RT}{\nu_e F} \left(pH_e + z_{H^+} \frac{FE_D}{2.303RT} \right) - \frac{RT}{\nu_e F} \ln \left(\frac{(1 + K_{pOx} a_{H^+}^e \exp(-z_{H^+} E_D F/RT))}{(1 + K_{pR} a_{H^+}^e \exp(-z_{H^+} E_D F/RT))} \right)^2 + E_D \quad (29)$$

In the case of Pani, $\nu_H = \nu_e$ and $z_{H^+} = 1$ so E_D cancels out and Eq. (29) becomes:

$$E_{p,exp} = E_{int} - \frac{\nu_H 2.303RT}{\nu_e F} pH_2 - \frac{RT}{\nu_e F} \ln \left(\frac{(1 + K_{pOx} a_{H^+}^e \exp(-z_{H^+} E_D F/RT))}{(1 + K_{pR} a_{H^+}^e \exp(-z_{H^+} E_D F/RT))} \right)^2 \quad (30)$$

This shows that, in electrochemically active polymers where the concentration of fixed sites depends on the pH, the potential may not depend directly on E_D . However, it indirectly depends on E_D through its influence on the binding contribution (last term in Eq. (30)).

Table 1
 pK_{aR} and E_{int} for the different electrolytes.

	HCl + NaCl $\mu = 4$ M	Pure HCl	$H_2SO_4 + NaHSO_4$ $\mu = 1$ M	Pure H_2SO_4
pK_{aR}	2.0	1.0	1.5	1.0
E_{int}/V	0.187	0.180	0.181	0.173

3.3. Analysis of the results. Calculations

3.3.1. Qualitative discussion of the experimental results

The change of the experimental peak potential with the pH of the external solutions is bigger in the solutions of single electrolytes than in those of constant ionic strength (Fig. 3). According to Eq. (30), there is only one reason that explains these differences: The Donnan potential increases as the external ionic force decreases.

According to our previous discussion, the peak potential does not depend directly on the Donnan potential because it cancels out with the dependence on the pH due to the electrochemical reaction (given by the second term of Eq. (30)). However, the potential also depends on the internal pH (third term of Eq. (30)) due to proton binding. Moreover the proton activity inside the polymer does depend on E_D . It has been stated that E_D increases in absolute value for increasing C_F , and also E_D increases for decreasing C_S . In the presence of a large amount of indifferent electrolyte E_D decreases very slowly with the pH due to the decrease of the number of fixed sites. On the other hand, in the absence of supporting electrolyte E_D should increase markedly with decreasing the concentration of the external electrolyte. This is the tendency shown by the experimental values of the peak potential for different external solutions (Fig. 3).

3.3.2. Calculations

In this section we will attempt to fit Eq. (30) to the experimental results. To this end, it is convenient to write Eq. (30) in terms of the pH and the corresponding pKs. It results:

$$E_{p, \text{exp}} = E_{\text{int}} - \frac{\nu_H 2.303RT}{\nu_e F} \text{pH}_e - \frac{RT}{\nu_e F} \ln \left(\frac{1 + 10^{-(\text{pH}_e + E_D - \text{pK}_{aOx})}}{1 + 10^{-(\text{pH}_e + E_D - \text{pK}_{aR})}} \right)^2 \quad (31)$$

It is also convenient to group together in Eq. (31) the experimentally accessible quantities, the $E_{p, \text{exp}}$ and pH_e terms as:

$$\begin{aligned} E^* &= E_{p, \text{exp}} + \frac{\nu_H 2.303RT}{\nu_e F} \text{pH}_e \\ &= E_{\text{int}} - \frac{2.303RT}{\nu_e F} \log \left(\frac{1 + 10^{-(\text{pH}_e + E_D - \text{pK}_{aOx})}}{1 + 10^{-(\text{pH}_e + E_D - \text{pK}_{aR})}} \right)^2 \end{aligned} \quad (32)$$

Then, we will compare E^* with the predicted theoretical result at the right hand side. In principle, E_D could be evaluated by solving Eq. (32) numerically. However, this procedure was not robust enough and convergence could not be reached. So, we will proceed in the following way. In order to calculate E_D from Eq. (21) it is necessary to estimate C_F at $\theta = 0.5$. It can be shown that E_D does not depend much on C_F in the range $2 \text{ M} < C_F < 6 \text{ M}$. Then, only a rough estimation is necessary. From the density of Pani (1.4 g cm^{-3} from Ref. [39]) we get a value of about 10 M for the concentration of monomers. However, the density value just quoted is presumably for the dry polymer. For a polymer embedded in an electrolyte it should be smaller than that. On the other hand, at the peak potential, half of the polymer is in the LE form and the other half in the E form. In the LE form, each monomer has one amine group whereas in the E form, half the monomers have amine groups and half the monomers have imines groups. Then, and according to Menardo et al. [38] in 1 M HCl, only 25% of the amine groups in the LE form are protonated and in the E form 14% of the amine groups and 32% of the imines ones are protonated. Based on these numbers, the maximum amount of protonable amine groups is 1.6 M and 0.75 M for the protonable imine groups. So the total amount of fixed sites is about $C_F = 2.35 \text{ M}$. Then, we will employ this value to calculate E_D and with it, the last term in Eq. (23) for different values of pK_{aR} (see Fig. 4). Despite the approximation made by employing Eq. (21), the agreement is reasonable taking into account that most probably, the values for the acidity constants are different in HCl and in H_2SO_4 solutions. In Fig. 4 we compare the experimental E^* data in pure HCl solution, with

those calculated employing different pK_{aR} values. The best results are obtained for $\text{pK}_{aR} = 1$. The values of E_{int} were determined graphically, shifting the calculated plot vertically for best coincidence with the experimental one. Figs. 5 to 7 show the results obtained for the other electrolytes.

In Table 1 the values of pK_{aR} and E_{int} are assembled for the different solutions employed here.

The following features can be noted. First, the E_{int} values are approximately the same for different solutions, as expected. Second, in the solutions of constant ionic strength the release of the protons, lower acidity constant ($> \text{pK}_a$), seems to be hindered as compared with the pure electrolytes. This can be attributed to a more efficient screening of the solutions of constant ionic strength that stabilizes the bound protons.

Fig. 8 shows the E_D values calculated as described in the text above, with the values of pK_{aR} shown in Table 1 and $\text{pK}_{aOx} = 4.5$. The rationale behind these values is simple: The values of E_D in solutions of the pure electrolytes increase as the pH increases meaning that, despite the fact that the concentration of fixed charges decreases, the concentration of the external solution also decreases making E_D to increase. On the other hand, in solutions of constant ionic strength, E_D slightly decreases as the pH increases. This is due to the fact that the concentration of fixed charged sites decreases whereas the total concentration of the external solution remains constant.

4. Conclusions

The membrane equilibrium at the polymer/solution interface was analyzed and it is concluded that the osmotic work is coupled to the electrical one. If the former is negligible as compared to the latter, it will be valid to apply the classical expression for the Donnan potential (Eq. (20) or Eq. (21)), considering that the activity coefficients may be equalled to one.

Moreover, it is estimated that, in Pani, π is negligible.

The peak potential in the voltammetric response was measured as a function of the pH and the ionic strength. The differences in the change of experimental peak potential with the pH of the external solutions, between single electrolytes and those at high constant ionic strength, are attributed to the change of Donnan potential.

The values of E_D in solutions of the pure electrolytes increase as the pH increases meaning that, despite the fact that the concentration of fixed charges decreases, the concentration of the external solution also decreases making E_D to increase. On the other hand, in solutions of constant ionic strength E_D slightly decreases as the pH increases. This is due to the fact that the concentration of fixed charged sites decreases whereas the total concentration of the external solution remains constant.

The experimental results of the peak potential may be explained through a model that takes into consideration the dependence of the potential on the pH and the Donnan potential. From this analysis the following features can be noted. First, the E_{int} values are approximately the same for the different solutions, as expected. Second, in the solutions of constant ionic strength the release of the protons, lower acidity constant, seems to be hindered as compared with that of the pure electrolytes. This fact can be attributed to a more efficient screening of the solutions of constant ionic strength that stabilizes the bound protons. For the mixtures of the higher μ , it results a lower acidity constant, implying that the screening is more efficient.

Acknowledgments

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Appendix A. Appendix

A.1. Estimation of π for the case of Pani in 1M H₂SO₄ solutions

It is important to compare the magnitude of the osmotic work with the electrical one to ascertain whether or not we can disregard the influence of the osmotic term in E_D calculations. In this Appendix we will attempt to estimate π for the system Pani films in 1 M H₂SO₄ solutions. For the sake of simplicity we will consider here only the reduced polymer. To this end we will employ Eq. (13) for the osmotic pressure and we will assume we may employ molar fractions for the solvent, x_w^α , instead of activities, to estimate x_w^1 and x_w^2 .

The starting point of the calculation is Eq. (15) that in terms of the molar concentrations for the ionic species may be written as:

$$C_a^2 C_c^2 = f_w C_a^1 C_c^1. \quad (\text{A.1})$$

Assuming $f_w = 1$ and employing the EC (Eqs. (17) and (18)) we make a first estimate of either C_c^1 or C_a^1 solving the second order equation that results from replacing either C_a^1 or C_c^1 into Eq. (15). With this

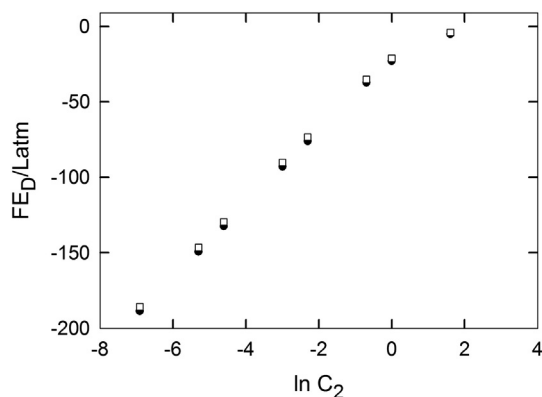


Fig. A.1. E_D (•) and $E_D(\pi = 0)$ (□), as a function of the logarithm of the external concentration, C_2 . $C_F = 2$ M.

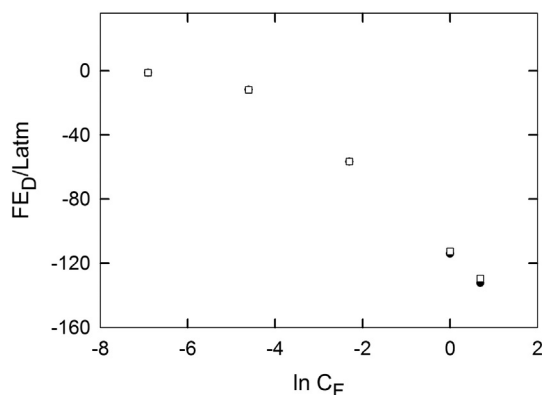


Fig. A.2. E_D (•) and $E_D(\pi = 0)$ (□), as a function of the logarithm of the fixed site concentration C_F . $C_2 = 0.01$ M.

value we calculate the molar fractions of the solvent that can be approximately expressed as:

$$x_w^2 = \frac{55.5}{(55.5 + C_c^2 + C_a^2)} \quad \text{and} \quad x_w^1 = \frac{55.5}{(55.5 + C_c^2 + C_a^2 + C_F)}.$$

C_F was estimated as described in the Section 3.3.2 of the main text. With these values a new f_w is calculated and, employing (Eq. A.1) we recalculate new values of C_c^1 and C_a^1 . Then, the process is iterated to convergence. Three cycles are enough to reach a reasonable convergence. We choose the values of the partial molar volumes as: $\bar{V}_w = 18 \text{ cm}^3$, $\bar{V}_c = \bar{V}_a = 30 \text{ cm}^3$. Employing this procedure, we calculated π , E_D and $E_D(\pi = 0)$ for the characteristic volumes mentioned above assuming an ideal system as a function of C_2 and C_F . It results that the osmotic work is very small compared to the electrical one in all cases. The results of the calculations are summarized in Figs. A.1 to A.3 where we have plotted in the same plot E_D and $E_D(\pi = 0)$ keeping in mind that $FE_D(\pi = 0) = \pi \bar{V}_c + FE_D$.

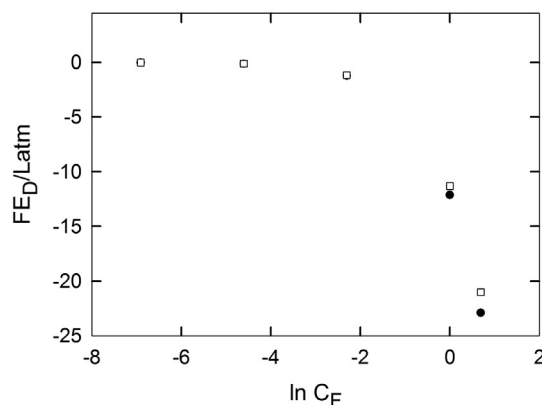


Fig. A.3. E_D (•) and $E_D(\pi = 0)$ (□), as a function of the logarithm of the fixed site concentration C_F . $C_2 = 1$ M.

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