# Redox commuting properties of polyaniline in hydrochloric, sulphuric and perchloric acid solutions

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### ABSTRACT

In the present work we have studied the pH dependence of the voltammetric response of polyaniline (Pani) in three different electrolytic media: HCl, $H_2SO_4$ and $HClO_4$ at constant ionic strength.

The electrochemical stability of Pani as a function of the pH is different for the three electrolytes. As the pH increases, the stability limit decreases in the order HCl > $HClO_4$ > $H_2SO_4$.

The voltammetric data were analyzed based on a theoretical expression for the redox potential as a function of the oxidation degree of the polymer. This analysis allows obtaining the acid dissociation constant for the three electrolytes, and an interaction parameter that reflects the change in the interaction energy between the redox centres of the polymer as the pH is increased. Particularly interesting is the HCl system, in which the pH can be increased up to about 5.0 without loss of the electrochemical activity.

A further proof that the current *vs.* potential response may be represented by a reversible confined redox couple with interactions comes from the pH dependence of the peak current for the three electrolytes.

As expected, the acid dissociation constants of the reduced and oxidized polymer do not depend much on the nature of the anions studied here.

## 1. Introduction

Polyaniline (Pani) is an interesting conducting polymer (CP) both from the fundamental and the applied viewpoints. Its applications range from batteries to actuators, including optoelectronic devices, sensors, membranes, *etc.* [1–6]. Also, the fundamental aspects have aroused much interest, in particular its redox commuting properties.

Pani can be obtained in three oxidation states: leucoemeraldine (LE), its reduced one, emeraldine (E), its half-oxidized one, and perni-graniline (P), its completely oxidized state. Only the E form in its protonated state (ES) is electrically conducting. As all the CPs, Pani is an electrochemically active polymer and it can be reversibly oxidized from the LE to the E state.

The oxidation-reduction of macromolecules is accompanied by other processes that make them to behave very differently from other, more simple, molecules. Together with the electron transfer there are changes in the state of swelling, the state of protonation, and the state of screening of the charged fixed sites, that are accompanied by ionic movements in and out of the polymeric phase. All these processes are coupled to the electron transfer. In particular, for Pani, the redox potential is coupled to, among others, the protonation state. It has been

demonstrated theoretically and experimentally that the redox potential depends on the pH not only through the proton binding to the acid-base sites of the polymer but also through the interaction between the protonated redox centres [7,8].

In Fig. 1, the half oxidation of Pani in its base and salt forms are represented, as well as the acid-base equilibrium between them. Note that the number of protons involved in each electrochemical reaction depends on the state of protonation of the polymer before and after the oxidation. Moreover, these structures do not represent all the possible forms of Pani, since there is a wide range of pH (0 < pH < 4) in which the macromolecule is partially protonated, that is, there are protonated and non-protonated centres both in the reduced and the oxidized polymer. In previous works, we employed a statistical thermodynamic model to explain the dependence of the redox potential and the voltammetric current on the pH, considering coulombic interactions between the protonation centres [8,9]. The results of this analysis were compared with experimental data obtained from the voltammetric response of Pani in $H_2SO_4$ [9]. In the present context, it should be point out that many properties of Pani also depend on the nature of the anions that screen the interactions between the centres. It is well documented that the growth, morphology and properties of synthesized Pani
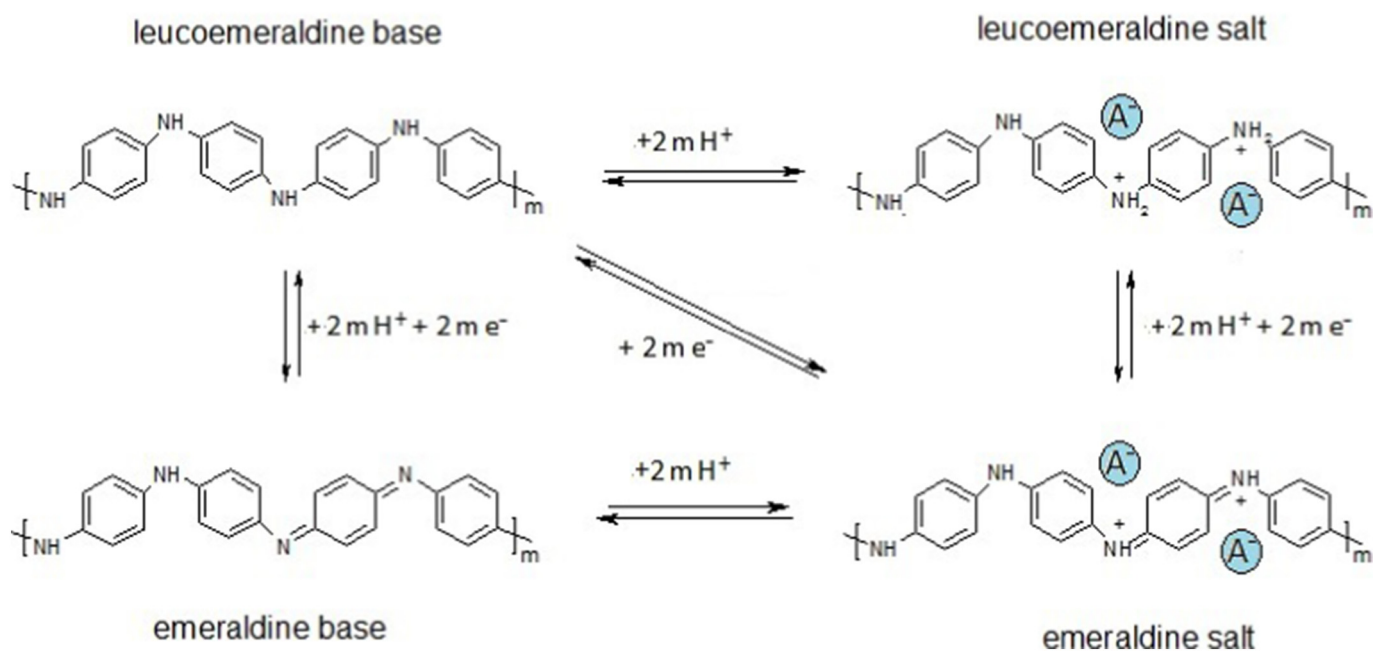
Fig. 1. Representation of the redox commutation for the first redox couple of Pani in its base and salt forms and the acid-base equilibrium between them.

depend on the nature of the acid present in the solution [10–12]. The conductivity of Pani also depends on the type of anion of the acid during the protonation of the base form of emeraldine [13–16]. Moreover the electrochemical behavior of Pani, particularly the voltammetric one, depends on the accompanying anion [17,18].

For this reason we considered interesting to study the pH dependence of the voltammetric response of Pani in acid solutions with different anions: $H_2SO_4$, HCl and $HClO_4$. A similar analysis of the voltammetric results to that described earlier for the case of Pani in $H_2SO_4$ solutions allows determining the influence of the pH on the interaction energy between the redox centres in the presence of the different anions. From this analysis, it is also possible to estimate the average acid dissociation constants of the protonated amino and imino groups in the different media.

## 2. Experimental

Pani films were electrosynthesized on gold wires by cycling the potential at $0.1\,V\,s^{-1}$ between $-0.2\,V$ and $0.75\,V$ vs. SCE [19], until the peak current of the first redox couple was about $2\,mA\,cm^{-2}$. The electrosynthesis solutions were 0.5 M in the monomer in aqueous solution of 3.7 M $H_2SO_4$. The geometric areas of the working electrodes were between 0.150 and 0.314 $cm^2$.

As a measure of the film thickness, it was employed the integrated charge from $E = -0.2\,V$ up to 0.45 V vs. SCE, $Q_T(0.45)$, in $H_2SO_4$ 3.7 M monomer free solution [20]. All the experiments were carried out with polymer films of charges between 20 and 25 $mC\,cm^{-2}$. Employing the equivalence given by Gottesfeld et al. [21] for Pani films of $Q/d = 8 \pm 1 \times 10^{-2}\,mC\,cm^{-2}/nm$, the thicknesses of these films, $d$, result to be between 250 and 300 nm. These relatively thin films allow fast equilibration of the ionic fluxes within de polymer.

After the synthesis, the films were washed with the electrolyte and cycled in 3.7 M $H_2SO_4$ solution at $0.1\,V\,s^{-1}$ between $-0.2\,V$ and 0.45 V vs. SCE during some minutes, and then introduced into the cells. For the measurements in HCl and $HClO_4$ we employed a saturated calomel electrode (SCE) as reference electrode and for the measurements in $H_2SO_4$ a 1 M mercurous sulphate electrode. However, all potentials in the text are referred to the SCE.

A potentiostat PARC Model 273 equipped with a data logger Dataq DI-710-UH was employed for all the electrochemical experiments.

Solutions were made of Milli-Q purified water, NaOH, $H_2SO_4$, HCl and $HClO_4$ (Carlo Erba, RPE-ACS). The latter were employed as received. Aniline (Fluka-Guarantee, puriss. p.a.) was distilled under reduced pressure before using. Electrolytic solutions of different pH and constant ionic strength, $\mu$, were employed: $H_2SO_4$ + $NaHSO_4$, $\mu = 3.7\,M$; $HClO_4$ + $HClO_4$, $\mu = 4\,M$ and HCl + NaCl, $\mu = 4\,M$. The solutions pH was previously measured with a glass electrode (Ross, Orion Research) by using a pH-meter (Cole-Palmer 59003-15). For the most acidic solutions, also a Pd (Pd) electrode was employed to check the glass electrode readings [22].

The experimental procedure for exchanging the electrolytes was the following: after achieving a 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 the new pH. The solutions were changed in order of increasing pH values. Then, the potential was cycled until a stationary $i$ vs. $E$ profile was obtained. After cycling the polymer at the different pHs, the solution was replaced with the most acidic one to compare the voltammetric profile with the initial response and evaluate if there were irreversible changes or any loss of the electrochemical activity of the film.

## 3. Results and discussion

In order to inquire about the pH dependence of the redox commuting properties of Pani films in solutions of different anions, voltammetric measurements in acid solution of constant ionic strength in the range $-1 < pH < 5$ were carried out. All measurements were made in solutions of high ionic strength since, under these conditions, the pH of the internal and external solutions can be considered to be equal [23].

For the analysis of the voltammetric parameters, we will consider, unless otherwise stated, the anodic current profile. Also, we will refer only to the first redox couple, since it is known that films cycled up to potentials after the second couple, corresponding to the pernigraniline formation, rapidly degrade and lose activity.

### 3.1. $H_2SO_4$ + $NaHSO_4$ solutions, $\mu = 3.7\,M$

In Fig. 2, it is shown the $i$ vs. $E$ response in $H_2SO_4$ + $NaHSO_4$

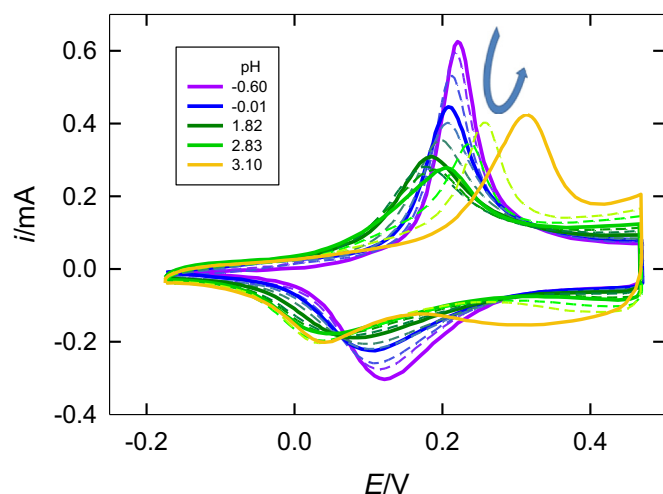**Fig. 2.** Stationary cyclic voltammetry of a Pani film in $H_2SO_4$ + $NaHSO_4$, $\mu = 3.7\,M$ at different pHs. $Q_T(0.45) = 20.0\,mC\,cm^{-2}$, $\nu = 0.01\,V\,s^{-1}$. The arrow indicates the direction of increasing pHs.



**Fig. 4.** Stationary cyclic voltammetry of a Pani film for successive scans in $H_2SO_4$ + $NaHSO_4$ mixtures at pH = 4. $\nu = 0.01\,V\,s^{-1}$. The arrow indicates successive scans.

solutions of different pHs.

It is seen that the current *vs.* potential response depends on the pH. As the pH increases, in the range $-0.6 < pH < 1.25$, the peak potential shifts in the negative direction whereas the peak current decreases. In the range $1.25 < pH < 2.16$ both the peak potential and the peak current increase with the pH. In Fig. 3a it is shown the anodic integrated charge as a function of the potential. Fig. 3b shows $Q_T(0.45\,V)$ as a function of the pH. Both anodic and cathodic charges remain equal and approximately constant in the pH range comprised between $-1 < pH < 3.0$.

For pH > 4.0, the second oxidation peak merges with the first one and the voltammetric response changes irreversibly: in a few scans the integrated charge decreases meaning that the film degrades (Fig. 4).

### 3.2. HCl + NaCl, solutions of ionic strength $\mu = 4\,M$

In Fig. 5, it is shown the current *vs.* potential response for a Pani film in HCl + NaCl media of $\mu = 4\,M$. In the range $-1 < pH < 3$, both potential and current peaks decrease with the pH. As the pH increases beyond 3, the peak current increases but the peak potential remains practically constant. It is remarkable that, in this media, Pani can be reversibly oxidized from the LE form to the E form even at pH = 5 without any loss of the electrochemical activity. In Fig. 6a, the integrated anodic charge it is shown as a function of potential. Both anodic and cathodic $Q_T(0.45\,V)$ values remain equal and approximately
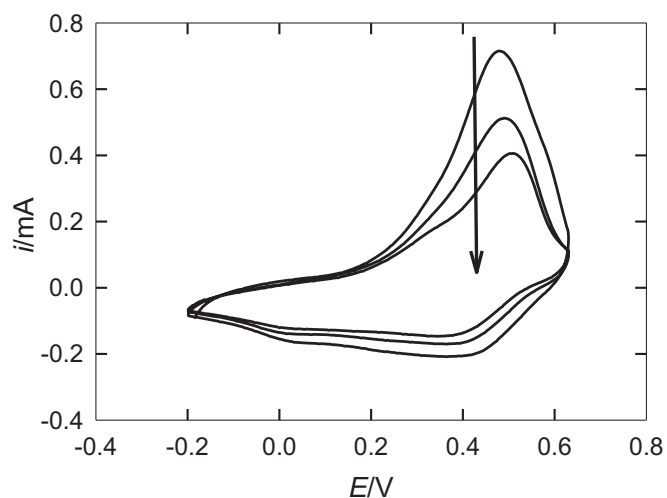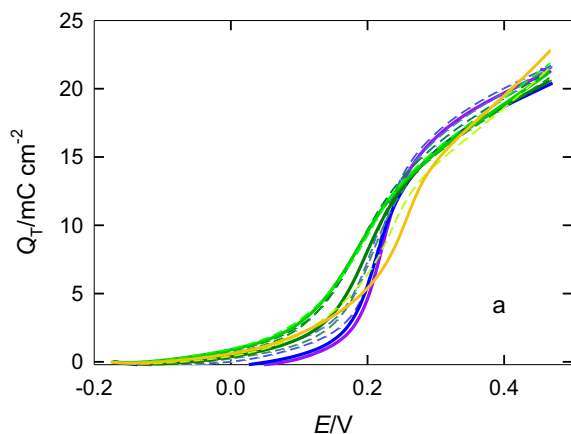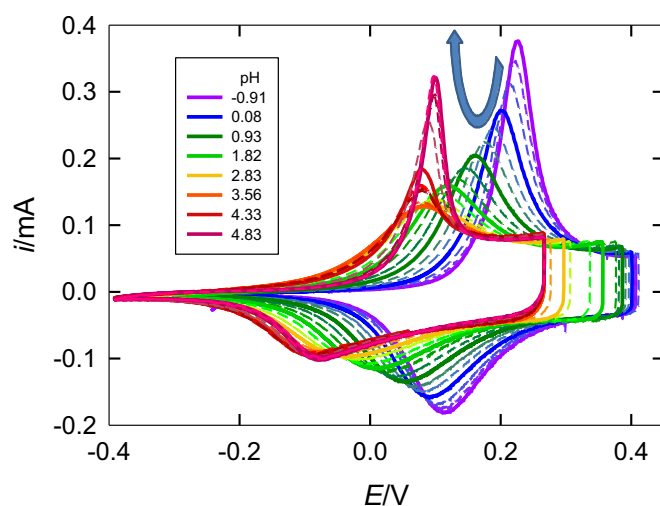


**Fig. 5.** Stationary cyclic voltammetry of a Pani film in HCl + NaCl, $\mu = 4\,M$ at different pHs. $Q_T(0.45) = 24\,mC\,cm^{-2}$, $\nu = 0.01\,V\,s^{-1}$. The arrow indicates the direction of increasing pHs.
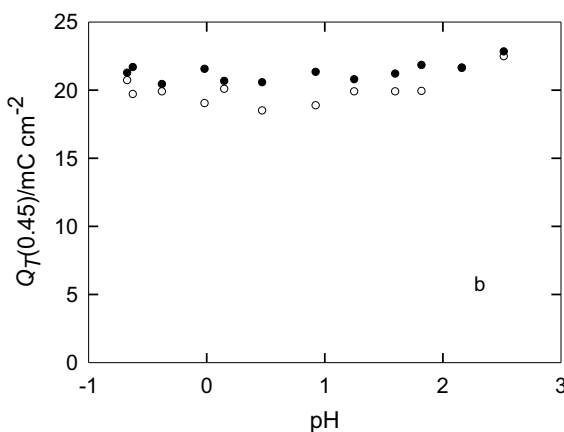


**Fig. 3.** (a) Anodic charge as a function of the potential. Symbols are the same as in Fig. 2. (b) Charge, $Q_T(0.45)$, as a function of pH, (●) anodic, (○) cathodic.

**Fig. 6.** (a) Anodic charge as a function of the potential. Symbols are the same as in Fig. 5. (b) Charge, $Q_T(0.45)$, as a function of pH, (●) anodic, (○) cathodic.
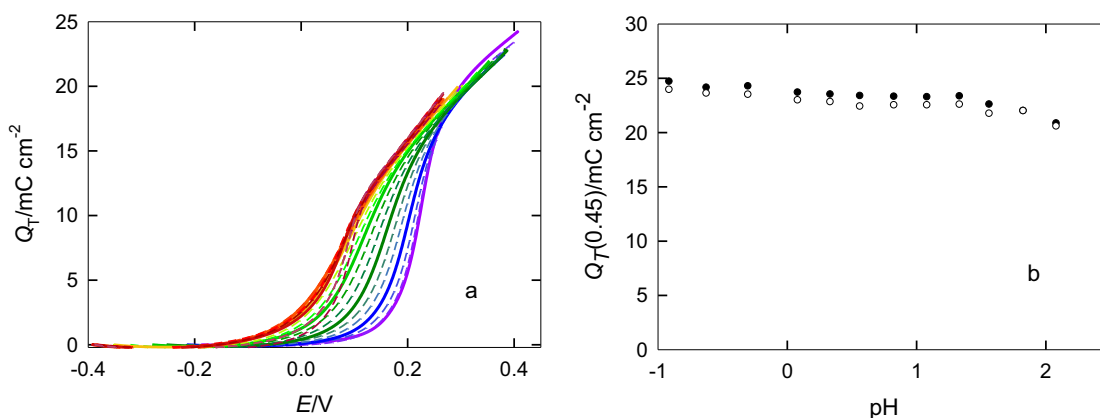
constant as the pH increase in the range studied here (Fig. 6b).

In HCl solutions, there are not irreversible changes in the voltammetric response even at pH = 5.0. After cycling the film at different pHs, if the electrolytic solution is replaced for the most acidic one, the same initial response is recovered.

### 3.3. HClO₄ + NaClO₄ solutions of ionic strength $\mu$ = 4 M

Fig. 7 shows the voltammetric profiles of a Pani film in solutions of HClO₄ + NaClO₄, $\mu$ = 4 M at different pHs. In Fig. 8, it is shown the anodic charge as a function of potential (a) and the anodic and cathodic integrated charges, $Q_T(0.45$ V), as a function of the pH (b). The general behavior is similar to that of the other acids.

In this electrolyte, for pHs higher than 4.5, the electrochemical response practically disappears. However, if the pH is decreased to the initial value, the original profile is recovered.

### 3.4. pH dependence of the redox potential in the different acid solutions

A molecular model that relates the redox potential to the pH and the oxidation degree has been developed previously [7]. In this model, the polymer is considered as chains of polymer units carrying each one four monomer units (see Fig. 1). In the completely reduce state, each polymer unit has four amino groups (R), only two of which are redox centres, and can be oxidized to imino ones (Ox). All groups (redox centres or not) are proton binding sites, so they may be protonated
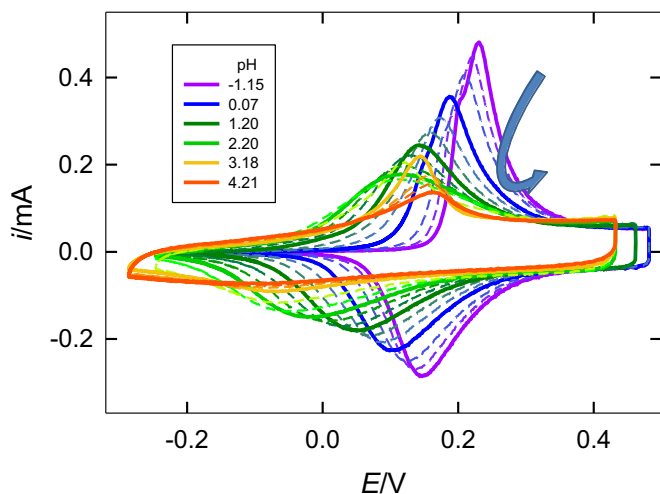
according to its corresponding acid dissociation constant, $K_a$, value and the external pH. Also, it is considered that there are interactions between the groups and that the strongest contribution to it comes from the repulsions between the protonated amino and imino closest neighbours. This electrostatic interaction is screened by the counterions present in the internal solution in the polymer. Assuming that the redox centres and the binding sites are statistically independent and applying the Mean Field Approximation [24] the partition function of the redox centres and the binding sites are calculated. Then, the free energy of the system is obtained and from it the redox potential:

$$E = E_{int} - \frac{RT}{F}\ln\frac{(1-\theta_R)}{(1-\theta_{Ox})} + \frac{\Delta\varepsilon}{F}x_{Ox} - \frac{3cN_{Av}}{2F}(\varepsilon_{RR}-\varepsilon_{OR}) - 2.303\frac{RT}{F}pH$$
$$- \frac{RT}{F}\ln\left(\frac{1-x_{Ox}}{x_{Ox}}\right) \tag{1}$$

$E_{int}$ is related to the internal partition functions of the redox centres, $N_{Av}$ is Avogadro's number, $c$ is the number of closest neighbours of the redox centres, $\varepsilon_{RR}$, $\varepsilon_{OO}$ and $\varepsilon_{OR}$ are the interaction energies between neighbour pair of sites R-R, Ox-Ox, and R-Ox, respectively and $\Delta\varepsilon$ is given by the expression:

$$\Delta\varepsilon = cN_{Av}(\varepsilon_{OO}+\varepsilon_{RR}-2\varepsilon_{OR}) = C(\theta_{Ox}^2+\theta_R^2-2\theta_{Ox}\theta_R) = C(\theta_{Ox}-\theta_R)^2 \tag{2}$$

where $C$ is a constant that depends on the ionic strength and the temperature (a detailed description of the derivation of Eq. (2) is given in Refs. [7] and [9]).

The second term of Eq. (1) is related to the influence of the proton binding on the redox centres and the third and fourth terms to the logarithm of the ratio of the activity coefficients of the reduced and oxidized groups. Finally, the last two terms are referred to the usual concentration dependence of the potential in the Nernst equation.

In Fig. 9 are shown the values of the peak potentials, $E_p$, as a function of the pH for the different electrolytic media. It is appreciated in this figure that the dependence of $E_p$ with the pH is not linear due to the effect of the acid-base equilibrium and the interaction between the redox centres. Also, it is seen, that at very low pHs (pH < 0) there is no difference in the redox potential for the three acids; as the pH is increased, differences are noted.

### 3.5. pH dependence of the interaction parameter, $\Delta\varepsilon$

According to Eq. (1), a plot of $E + \frac{RT}{F}\ln\left(\frac{1-x_{Ox}}{x_{Ox}}\right)$ against $x_{Ox}$ gives a straight line of slope $\Delta\varepsilon/F$. Typical plots are shown in Fig. 10. As commented in previous works, $x_{Ox}$ cannot be obtained directly from voltammetric measurements due to the presence of a capacitive current superposed to the faradaic one, so a procedure based on a model must be employed (see Ref. [9] and references therein).
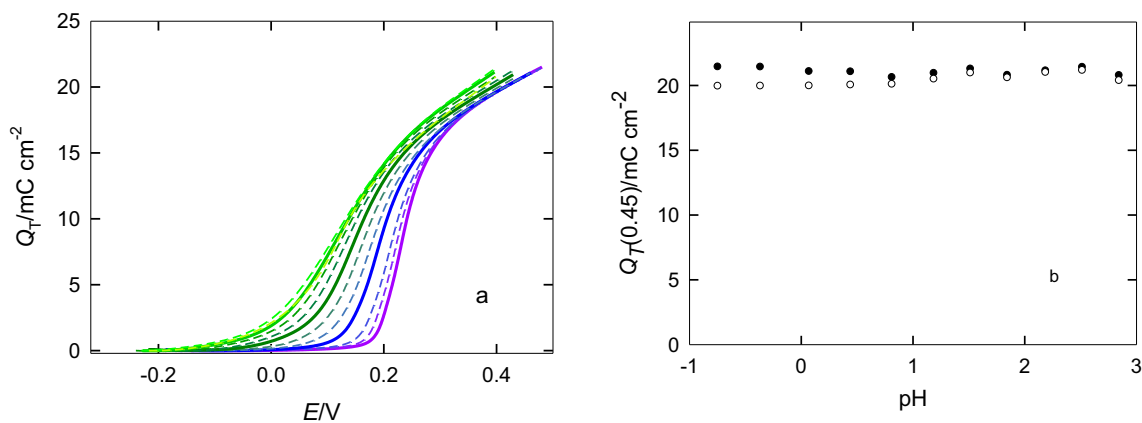


**Fig. 7.** Stationary cyclic voltammetry of a Pani film in HClO₄ + NaClO₄, $\mu$ = 4 M, at different pHs. $Q_T(0.45)$ = 22 mC cm$^{-2}$, $v$ = 0.01 V s$^{-1}$. The arrow indicates the direction of increasing pHs.

**Fig. 8.** (a) Anodic charge as a function of the potential. Symbols are the same as in Fig. 7. (b) Charge $Q_T(0.45)$ as a function of pH, (●) anodic (○) cathodic.
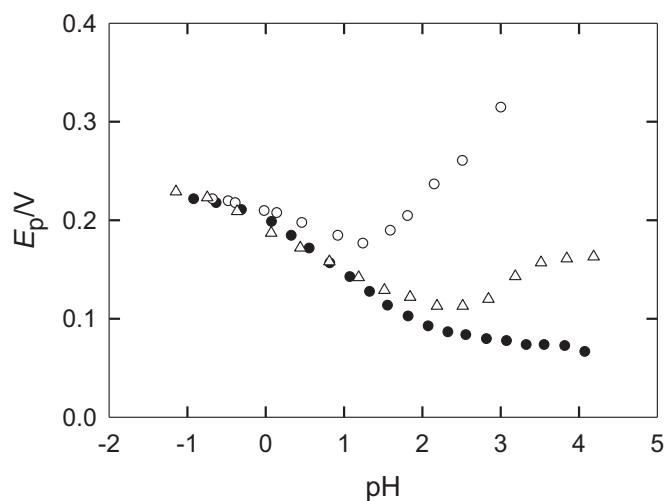


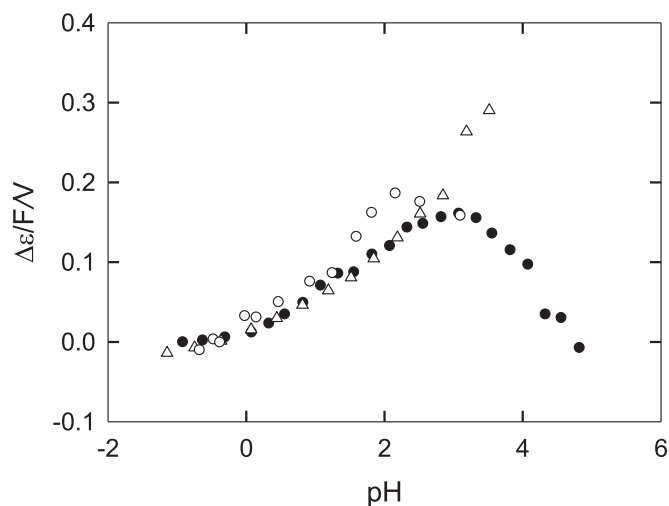**Fig. 9.** Peak potential as a function of the pH in solutions of constant ionic strength. (Δ) HClO$_4$, (●) HCl, (○) H$_2$SO$_4$.



**Fig. 11.** $\Delta\varepsilon/F$ as a function of pH in (Δ) HClO$_4$, (●) HCl and (○) H$_2$SO$_4$ solutions.

of the polymer: if $\theta_{Ox} > \theta_R$, then $\Delta\varepsilon > 0$. The $K_a$ values of Pani have been measured [25]. For the reduced form $pK_{aR} \approx 0.5$ and $pK_{aOx} \approx 4.0$ for the oxidized one. This means that, at very low pHs (pH < 0.0), both species are fully protonated and $\Delta\varepsilon \approx 0$. As the pH increases, $\Delta\varepsilon$ increases and it reaches a maximum at about pH $\approx$ 2.5–3.5 due to the fact that all the reduced centres are deprotonated whereas the oxidized ones are still fully protonated. For pH > 4.5 both forms becomes deprotonated and, therefore, $\Delta\varepsilon \approx 0$ again (see Fig. 11).

It is interesting to comment here that, as a consequence of the wider range of pH in which the redox response of the polymer is stable, in HCl solutions it is observed a decrease of $\Delta\varepsilon$ at pHs higher than 3, whereas this is not seen for the other two acids.

### 3.6. Dependence of the peak current on the interaction parameter

In previous works [9,20], we found that the current response of Pani can be represented as a reversible electrochemical reaction of a confined couple with interaction between the redox centres and the faradaic current density, $j_F$, can be written as a function of the oxidation degree, $x_{Ox}$, as:

$$j_F = \nu Q^0 \frac{F}{RT}\left[\frac{(1-x_{Ox})x_{Ox}}{1 + \frac{\Delta\varepsilon}{RT}(1-x_{Ox})x_{Ox}}\right] \qquad (3)$$

where $\nu$ is the sweep rate and $Q^0$ is the maximum faradaic charge. Since the faradaic current cannot be obtained from the voltammetric
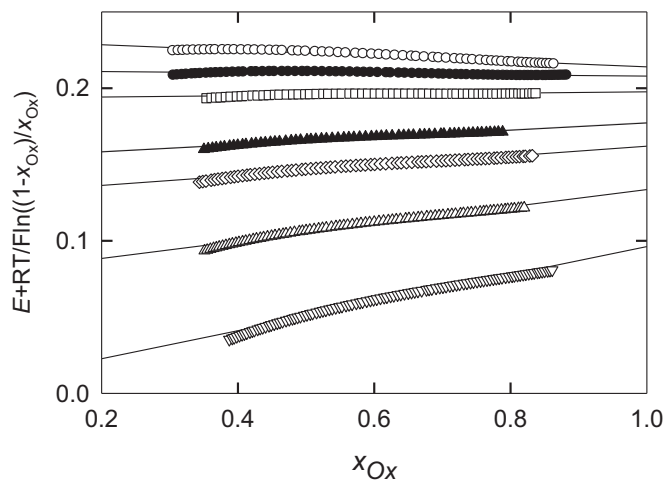


**Fig. 10.** $E + \frac{RT}{F}\ln\left(\frac{1-x_{Ox}}{x_{Ox}}\right)$ against $x_{Ox}$ plots for HCl + NaCl solutions. Data and conditions are the same as in Fig. 5. pHs from top to bottom: −0.91, −0.30, 0.08, 0.56, 1.08, 1.56, 2.83.

The values of $\Delta\varepsilon/F$ obtained are shown in Fig. 11 as a function of the pH for the three electrolytes.

In Eq. (2), it is shown that the interaction parameter depends on the difference of the protonation degrees of the oxidized and reduced forms
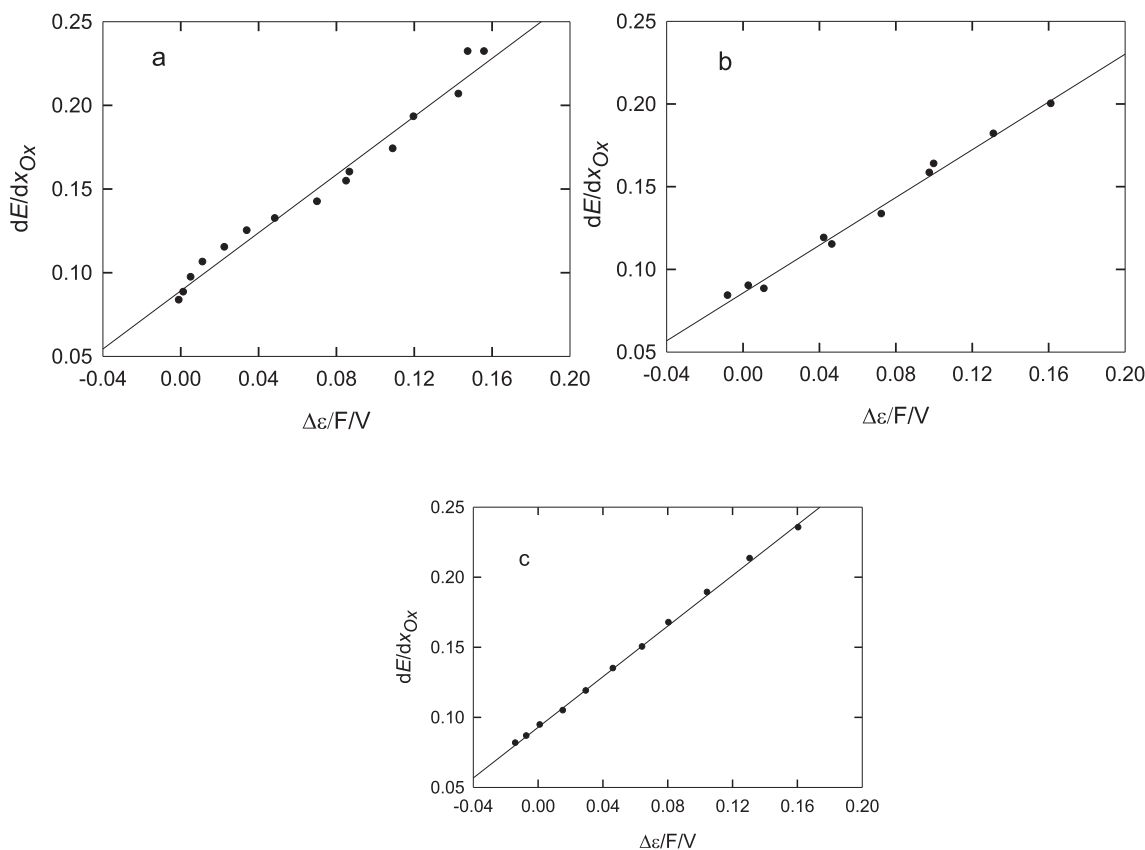
**Fig. 12.** $dE/dx_{Ox}$ evaluated at $x_{Ox} = 0.5$ as a function of the interaction parameter, $\Delta\varepsilon$. (a) HCl, (b) $H_2SO_4$ and (c) $HClO_4$.

measurements [20] but the faradaic oxidation degree can, we will employ, instead of the current density, the derivative $v\,Q^0 dx_{Ox}/dE$, that is equal to $j_F$. This derivative can be obtained from a $E$ vs. $x_{Ox}$ plot as that shown in Fig. 6 of Ref. [9] at any desired $x_{Ox}$. For convenience, we choose $x_{Ox} = 0.5$; replacing this value in Eq. (6), it results:

$$\left[\frac{dE}{dx_{Ox}}\right]_{x_{Ox}=0.5} = \frac{4RT}{F} + \frac{\Delta\varepsilon}{F} \tag{4}$$

Considering $\Delta\varepsilon/F$ as the variable, Eq. (4) is the equation of a straight line. The calculated values of $dE/dx_{Ox}$ at $x_{Ox} = 0.5$ for the data of Figs. 3a, 6a, and 8a against $\Delta\varepsilon/F$ at each pH are shown in Fig. 12. A linear plot is obtained for the three acids.

According to Eq. (4), at 298 K, the slope should be 1 V and the ordinate 0.1 V. The values in Table 1 are close to these figures.

These results show that the proposed model to explain the pH dependence of the current based on the change of the interaction parameter, previously verified in $H_2SO_4$, is also valid for the other two acids studied here. Therefore, we may employ this model to estimate the acid dissociation constants of the reduced and oxidized polymers in the three media.

### 3.7. Estimation of the acid dissociation constants

Eq. (2), together with data of Fig. 11, provides a method to estimate

**Table 1**
Slopes and ordinates of the plots given in Fig. 12 for the different acids.

|  | Slope/V | Ordinate/V |
|---|---|---|
| $HClO_4$ | 0.90 | 0.093 |
| HCl | 0.87 | 0.089 |
| $H_2SO_4$ | 0.72 | 0.086 |

$K_a$ of both the oxidized and reduced centres. Assuming that the proton binding equilibrium of each species can be represented by a Langmuir isotherm:

$$\theta_j = \frac{a_{H^+} K_{p,j}}{1 + a_{H^+} K_{p,j}} \tag{5}$$

where the subindex $j$ represents either R or Ox, $a_{H^+}$ is the proton activity inside the polymer and $K_p$ is the protonation constant. As usual, $K_p = K_a^{-1}$. Replacing Eq. (5) into Eq. (2), it is obtained:

$$\Delta\varepsilon = C\left[\left(\frac{a_{H^+}}{K_{a,Ox} + a_{H^+}}\right) - \left(\frac{a_{H^+}}{K_{a,R} + a_{H^+}}\right)\right]^2 \tag{6}$$

Data of Fig. 11 can be fitted to Eq. (6) to get the corresponding $K_a$ values. A non-linear least squares procedure based on the Levenberg-Marquardt method was employed. Fig. 13 shows the fits for the data obtained in HCl and $H_2SO_4$, and the resulting $K_a$ values are presented in Table 2. $K_{a,Ox}$ for $HClO_4$ cannot be obtained because the $\Delta\varepsilon$ vs. pH plot given in Fig. 11 shows no maximum, even at pH ≈ 4. However, it can be assured that this $pK_{a,Ox}$ value should be bigger than 4.5.

### 4. Conclusions

The voltammetric response of Pani as a function of the pH was studied in three different electrolytic media: HCl, $H_2SO_4$ and $HClO_4$.

The electrochemical stability of Pani as a function of the pH is different for the three electrolytes. As the pH increases, the redox stability limit decreases in the order HCl > $HClO_4$ > $H_2SO_4$.

The interaction parameters and the acid dissociation constants were obtained for the three electrolytes and they do not depend much on the nature of the acids studied in this work. However, only in HCl, it is possible to reversibly oxidize the polymer up to pH ≈ 5 without loss of its electrochemical activity. For this system it is possible to observe the
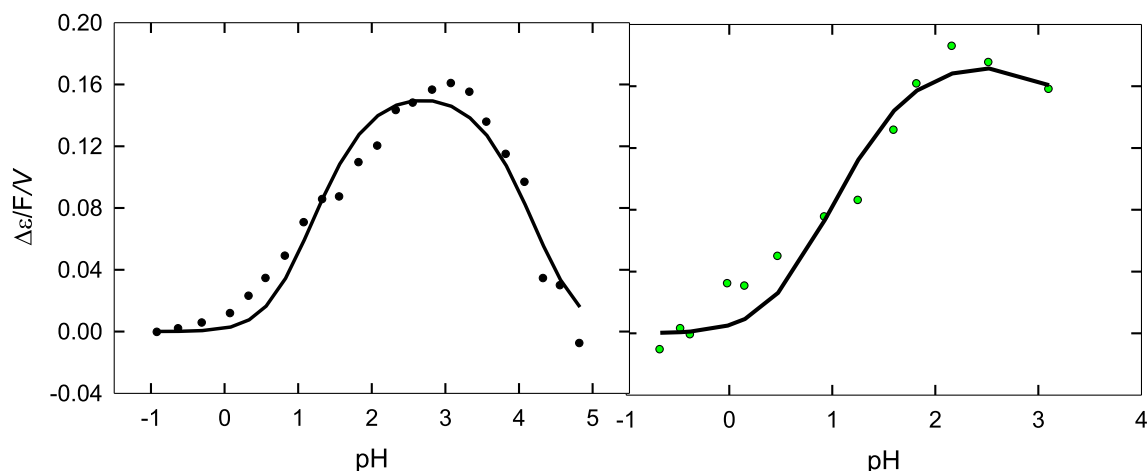
**Fig. 13.** $\Delta\varepsilon/F$ as a function of pH in HCl (●) and H$_2$SO$_4$ (●). Results from the fit to Eq. (6) (—).

**Table 2**
$pK_a$ values fitted with Eq. (6).

|        | $pK_R$ | $pK_{Ox}$ | C/J    |
| ------ | ------ | --------- | ------ |
| HCl    | 0.90   | 4.49      | 0.1596 |
| H$_2$SO$_4$ | 0.69   | 4.32      | 0.1823 |
| HClO$_4$ | 0.86   | > 4.5     |        |

decrease of the interaction parameter as the pH is increased beyond pH ≈ 3 (Fig. 11).

The analysis of the pH dependence of the peak current in the three media offers further proof that the current response can be represented as a reversible confined redox couple with interactions between the centres.

### Acknowledgements

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