



pH dependence of the voltammetric response of Polyaniline



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ABSTRACT

Voltammetric studies of Polyaniline (Pani) films were carried out in solutions of 3.7 M sulphate solutions of constant ionic strength and pH values comprised in the range between -0.6 and 3.0 . The results show that if the voltammetric results are properly corrected by capacitive currents, according to Feldberg's model, it will be possible to obtain the potential dependence of the faradaic oxidation degree.

The integrated anodic and cathodic charges are practically equal and independent of the electrolyte pH, in the range $-0.6 < \text{pH} < 2.0$. The pH dependence of the current peaks is qualitatively explained by the change in the interactions between the redox centres as a consequence of the changes in their protonation.

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1. Introduction

Polyaniline (Pani) is an interesting electrochemically active macromolecule both, in the field of basic science as well as by its possible applications. In the reduced state, it is not conducting and in its half oxidized state, in electrolyte solutions of sufficiently low pH, it is electrochromically conducting. Besides, as other electrochemically active macromolecules, Pani has many real and potential applications such as sensors, electrochromic materials, actuators, batteries, membranes and so on [1].

Many workers have studied the redox commutation of Pani modified electrodes and measured the dependence of the voltammetric parameters, potential and current peak values, on the electrolyte pH [2–11].

In the case of conductive polymers such as Pani, polypyrrole and polythiophene, the current response contains two components: one capacitive, and another pseudocapacitive, due to charge transfer. The first can be observed in the j vs. E profile as a plateau after the charge transfer reaction has finished. The presence of this capacitive contribution, added to the faradaic one, makes the experimental current/voltage response to differ from the pure faradaic one. Then, the experimental parameters such as peak, potential and current, and charge do not have their usual significance. Many years ago, Feldberg [12] proposed a model that allows formally interpreting the voltammetric response in the presence of this capacity. *The capacitive current cannot be separated from the faradaic one just from voltammetric measurements.* Recently, this model was applied to describe the voltammetric response of Pani in acid media [13].

Although the faradaic and capacitive currents cannot be separated; it is possible, based on Feldberg's model, to obtain the fraction of oxidized polymer due to the faradaic process alone as a function of the applied potential. Then, from this relationship it is possible to obtain the peak potential and the shape of the j vs. E response for solutions of different pHs, as well as the pH dependence of these parameters, free from the capacitive contribution.

After the corrected oxidation degrees have been determined, the electrochemical parameters of the charge transfer reaction, that is, the peak potential, the shape of the faradaic current-voltage response and the faradaic charge dependence on the electrolyte pH, may be analyzed. This will be done below.

In this work, it is measured the voltammetric j vs. E response of Pani film modified electrodes, during steady state cycling, as a function of the electrolyte pH, in the range $-0.6 < \text{pH} < 3.0$. After correction for the capacitive contribution it is possible to obtain the true faradaic oxidation degree, as a function of the applied potential at different pHs. From these data it is possible to apply a similar analysis to one described earlier, to explain both, the peak potential and the j_F vs. E response dependence on the electrolyte pH [14].

2. Experimental

The base electrodes were gold wires 2 cm long and of 0.5 mm radius. Pani films were obtained by electro polymerization on Au electrodes [15,16]. The electrosynthesis were carried out by cycling the potential at 0.10 V s^{-1} between -0.20 V vs. SCE and a positive potential limit set at the beginning of the monomer oxidation (around 0.70 – 0.80 V). Polymer films were synthesized in solutions 0.5 M in the monomer in aqueous solution of $3.7 \text{ M H}_2\text{SO}_4$. To improve the adherence and homogeneity of the film, after a few cycles, the positive potential limit was

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slightly decreased. A conventional three electrode glass cell was employed [15,16]. After the synthesis, the films were washed with pure water and cycled in 3.7 M H₂SO₄ solution, until the stationary voltammetric profile is achieved.

Solutions were made of Milli-Q purified water, NaOH and H₂SO₄ (Carlo Erba, RPE-ACS), both were employed as received. Aniline (Fluka- Guarantee, puriss. p.a.) was distilled under reduced pressure before using. The *pH* of the solutions was previously measured with a glass electrode (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 [17]. A saturated calomel electrode (SCE) was employed as reference electrode. Sometimes, a Molar Mercurous Sulphate Electrode (MSE) was also employed. However, all the potential in the text are referred to the SCE.

A potentiostat TEQ-03 was employed for all the electrochemical experiments at different sweep rates in the range, $10^{-3} \text{ V s}^{-1} < \nu < 0.5 \text{ V s}^{-1}$,

As a measure of the film thickness, it was employed the integrated charge from $E = -0.20 \text{ V}$ up to 0.45 V , recorded in 3.7 M H₂SO₄ solution at 0.1 V s^{-1} , it will be named $Q_T(0.45)$ (see below).

Most of the experiments were carried out with polymer films of charges about 20 mC cm^{-2} . Employing the equivalence given by Gottesfeld et al. [18] for Pani films of $Q/d = 8 \pm 1 \times 10^{-2} \text{ mC cm}^{-2}/\text{nm}$, the thicknesses of these films, d , result to be about 250 nm. These relatively thin films allow fast equilibration of the ionic fluxes within de film.

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 the new *pH*. The *pH* was changed in the order of increasing values. Then, the potential was cycled until a stationary j vs. E profile was obtained.

3. Results

3.1. Voltammetric results

Voltammetric studies of Pani films were made as a function of the sweep rate, polymer charge and different electrolyte *pH*s. At the *pH*s comprised in the range $-0.6 < \text{pH} < 2.0$, the peak current is linearly dependent on the sweep rate, ν , the peak potential is independent of ν and the charge scales with the film thickness.

In a previous work in 3.7 M H₂SO₄ [14], it was demonstrated that the current/potential relationship may be formally represented by an electrochemically reversible process, of a confined redox couple with interaction between the redox centres [19].

In Fig. 1, it is shown the steady state cycling j vs. E response of Pani films, in different *pH* electrolytes.

The features of Fig. 1 are as follows: In the *pH* range comprised between $-0.6 < \text{pH} < 1.0$, as the *pH* increases, the current and the potential of the anodic peak decrease and the voltammograms becomes wider. In this *pH* range, the “capacitive” current plateau is practically independent of the *pH*. At higher *pH*s, between $1.0 < \text{pH} < 2.0$, the current and the potential peak values reach a minimum. Then, as the *pH* further increases, the current peak increases and the potential peak shifts in the positive direction.

During the cathodic scan, in the range comprised between $-0.6 < \text{pH} < 1.0$, the cathodic peak current decreases and the potential peak shifts in the negative direction. As the *pH* increases beyond about 2.0, and immediately after the positive switching potential, it is noted an increase of the cathodic current, suggesting the beginning of a different reduction process. As the *pH* increases further, this current increases and a broad peak shows up at about 0.3 V. It is clear that, at *pH* about 2.0 and beyond, the electrochemical oxidation process of the polymer

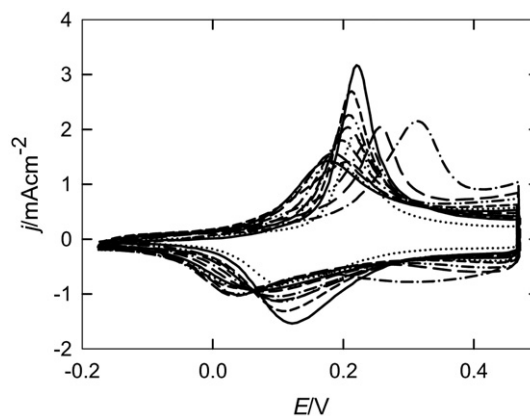


Fig. 1. Steady state cycling linear potential sweep voltammograms of Pani films in electrolytes of different *pH*s. $Q_T(0.45) = 20.0 \text{ mC cm}^{-2}$ at $\nu = 0.01 \text{ V s}^{-1}$ measured in H₂SO₄ + HNaSO₄, ionic strength 3.7 M. (—) *pH* = -0.67 , (.....) -0.62 , (---) -0.38 , (-.-.-) -0.01 , (- - -) 0.15 , (-.-.-) 0.47 , (- - -) 0.93 , (—) 1.25 , (.....) 1.60 , (---) 1.82 , (-.-.-) 2.16 , (- - -) 2.52 (-.-.-) 3.01 .

changes. In what follows we will not consider *pH*s > 2 . In Fig. 2 it is shown the dependence of the experimental peak potential, E_p , on the *pH* of the external solution.

In Fig. 3, it is shown the dependence of $Q_T(E)$ on the potential for different *pH* values.

In Fig. 4, it is shown the dependence of the integrated anodic and cathodic charges on the *pH*. The cathodic ones are practically coincident with the anodic charges. These results show that, in the range $-0.6 < \text{pH} < 2.0$, the integrated charge is practically independent on the *pH*. Then, as the *pH* increases beyond 2.0, the charge slightly increases.

3.2. Calculation of the oxidation degree, θ

The oxidation degree will be calculated from the voltammetric response. The starting point is Feldberg's model. According to it, the total voltammetric charge, $Q_T(E)$, can be written as the sum of the capacitive charge, Q_C , and that due to the charge transfer, named faradaic charge, Q_F , then:

$$Q_T(E) = Q_C(E) + Q_F(E) \quad (1)$$

Eq. (1) is based on the fundamental assumptions of Feldberg model [12], these can be resumed as follows: *i*) The integral capacitance of the polymer, C_d , is proportional to the faradaic charge. Thus, $C_d = aQ_F$,

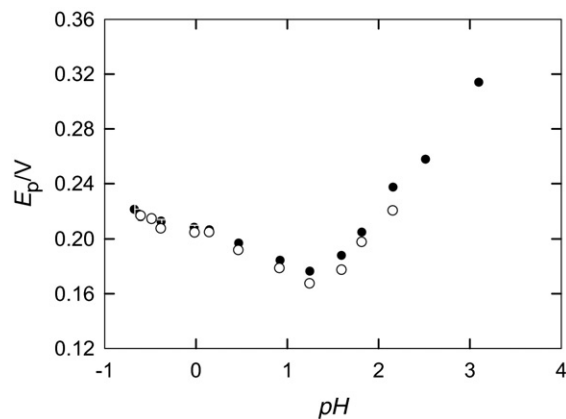


Fig. 2. Dependence of the peak potential, E_p , on the electrolyte *pH*. (●) Experimental values, from Fig. 1. (○) Values corrected with Feldberg's model, from data reported below in Fig. 7.

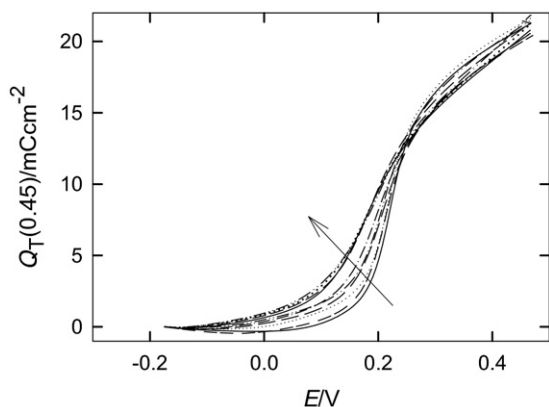


Fig. 3. Dependence of $Q_T(E)$ on the potential for different pH values. $Q_T(0.45) = 20.0 \text{ mC cm}^{-2}$ at $v = 0.01 \text{ V s}^{-1}$ measured in $\text{H}_2\text{SO}_4 + \text{HNaSO}_4$ solutions of ionic strength 3.7 M . (—) $pH = -0.6$, (.....) -0.48 , (---) -0.38 , (-.-.-) -0.01 , (- - -) 0.15 , (-.-.-) 0.47 , (- - -) 0.93 , (-) 1.25 , (.....) 1.60 , (-.-.-) 1.82 . The arrow indicate the direction of increasing pH .

where a is a proportionality constant. Also, the integral capacitance can be written as $C_d = Q_C / (E - E_z)$, being E the applied potential and E_z the potential of zero charge of the oxidized material. *ii*) The differential capacitance of the conducting form of the polymer is independent of the applied potential. *iii*) The differential capacitance of the base electrode is negligible.

These assumptions allows writing the capacitive charge as:

$$Q_C(E) = a(E - E_z)Q_F(E) \quad (2)$$

So, the total charge, Q_T , can be written as:

$$Q_T(E) = (1 + a(E - E_z))Q_F(E) \quad (3)$$

From this equation the total current, j_T , can be obtained by differentiation with respect to the time:

$$j_T(E) = (1 + a(E - E_z))j_F + vaQ_F(E) \quad (4)$$

where, $v = dE / dt = \text{constant}$.

As a consequence of the existence of a capacitance, the voltammetric current is not zero at high potentials, even when the faradaic process has finished. Then, at potentials high enough, $E > E_L$, where $j_F = 0$; the current is only capacitive and it follows that:

$$Q_F(E > E_L) = Q^0 \quad (5)$$

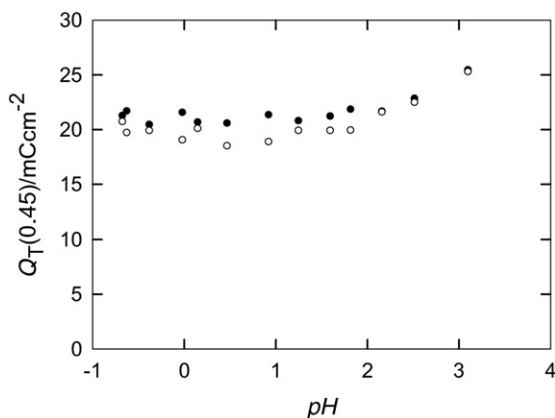


Fig. 4. Integrated charges, $Q_T(0.45)$, of the voltammograms shown in Fig. 1, as a function of the electrolyte pH . (●) anodic, (○) cathodic.

where Q^0 is the maximum faradaic charge. From Eq. (5), it follows that

$$j_T(E > E_L) = vaQ^0 \quad (6)$$

and,

$$Q_T(E > E_L) = Q^0(1 - aE_z) + aQ^0E \quad (7)$$

In Fig. 5 it is shown a plot of $Q_T(E)$ as a function of E . There, it is seen the portion for $Q_T(E > E_L)$ that gives a straight line of slope $C_d = aQ^0$ and ordinate $aQ^0(a^{-1} - E_z) = C_{d\sigma}$. Although the parameters a , Q^0 and E_z cannot be obtained from voltammetric experiments, it is possible to obtain C_d and σ (see Fig. 5). Fig. 3 shows that, for potentials higher than 0.3 V , the straight traces are practically coincident and parallel. Therefore, and also considering Fig. 4, we will consider that both C_d , and σC_d are pH -independent. The resulting values are: $C_d = 22.89 \text{ mF cm}^{-2}$ and $\sigma C_d = 12.13 \text{ mC cm}^{-2}$.

Taking into account the definition of $\theta(E) = Q_F(E) / Q^0$, Eq. (3) may be written as:

$$Q_T(E) = \theta(E)Q^0 + \theta(E)aEQ^0 - \theta(E)aE_zQ^0 \quad (8)$$

or, employing the definitions of C_d and σ

$$Q_T(E) = \theta(E)C_d(\sigma + E) \quad (9)$$

From Eq. (9), θ can be obtained from the voltammetric results.

From the Feldberg's parameters, θ as a function of the potential may be calculated at different pH s (Fig. 6). From these values, the derivative $d\theta/dE = j_F/vQ^0$ can be calculated, and a sort of normalized faradaic voltammogram is obtained.

It is interesting to compare the values of θ with the charge quotient $x = Q_T(E) / Q_T(0.45)$, where arbitrarily it has been chosen the value of 0.45 V as the anodic limit. Neither the shape nor the potential of the inflection point (the peak potential) would coincide. The values of θ steadily approach the limiting value of unity whereas the x values do not.

4. Discussion

As it was said at the Introduction section the main purpose of the present work is twofold: First, to obtain the faradaic oxidation degree. Second, to explain the dependence of the shape of the j_F vs. E response as the pH is changed.

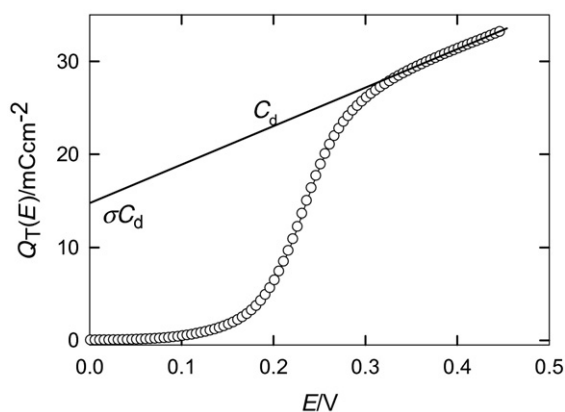


Fig. 5. Voltammetric charge of a Pani film, in $3.7 \text{ M H}_2\text{SO}_4$ solution, as a function of the applied potential. (○) experimental results; the line, fit to the upper points according to Eq. (7), showing the slope, C_d , and the ordinate, σC_d . $v = 0.1 \text{ V s}^{-1}$, $Q_T(0.45 \text{ V}) = 33 \text{ mC cm}^{-2}$.

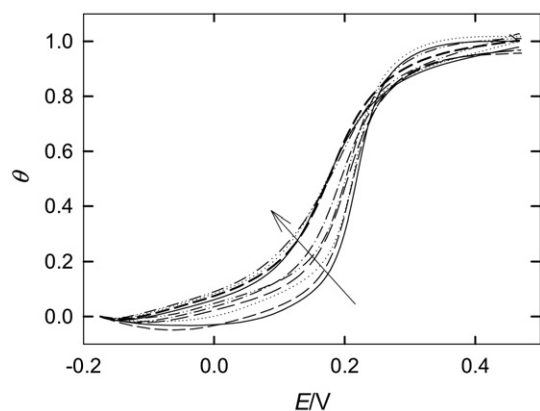


Fig. 6. Anodic oxidation degree, θ , for different pH s calculated as described in the text, for the data of Fig. 1. (—) $pH = -0.67$, (.....) -0.48 , (---) -0.38 , (-.-.-) -0.01 , (- - -) 0.15 , (-.-.-) -0.47 , (- - -) 0.93 , (-) 1.25 , (.....) 1.60 , (-.-.-) 1.82 . The arrow indicate the direction of increasing pH .

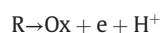
4.1. The shape of the j_F vs. E response

To explain the shape of the j_F vs. E response it is enough to consider the derivative of the data in Fig. 6: $d\theta/dE = j_F / vQ^0$, where j_F is the faradaic current and Q^0 the maximum faradaic charge. Fig. 7 shows this derivative. It is worth remarking here that j_F alone cannot be obtained from the voltammetric experiments. For comparison, the potentials corresponding to the current peaks in Fig. 7 are also shown in Fig. 2.

In Fig. 7 it is shown that the behaviour of the j_F vs. E response is similar to that of the j_T vs. E response: as the pH increases the current decreases and the peak becomes wider.

4.2. Theoretical analysis of the results of Fig. 5

The results shown in Fig. 6 could be analyzed on the basis of an expression for the potential based on a statistical mechanical model obtained before [18]. First, we will consider the electrochemical reaction per redox centre as:



where R and Ox represents the reduced and oxidized redox centres. The model considers the binding of protons to the polymer chains and the

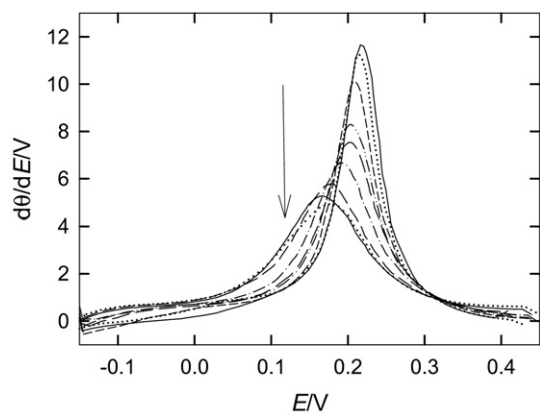


Fig. 7. Derivatives $d\theta/dE$ vs. E from Fig. 5, for different pH s. (—) $pH = -0.67$, (.....) -0.48 , (---) -0.38 , (-.-.-) -0.01 , (- - -) 0.15 , (-.-.-) -0.47 , (- - -) 0.93 , (-) 1.25 , (.....) 1.60 . The arrow indicate the direction of increasing pH .

electrostatic interaction among the protonated redox centres:

$$E = E_{int} - \frac{v_H 2.303RT}{v_e F} pH_i - \frac{RT}{v_e F} \ln \left(\frac{(1-\theta_{N,R})}{(1-\theta_{N,Ox})} \right)^2 - \frac{\Delta\epsilon}{v_e F} (1-2\theta) - \frac{RT}{v_e F} \ln \left(\frac{(1-\theta)}{\theta} \right) \quad (10)$$

$\theta_{N,R}$ and $\theta_{N,Ox}$ are the fractions of bound protons to R and Ox segments, respectively and v_e and v_H are the stoichiometric numbers of the electrons and protons in the electrochemical reaction, pH_i is the pH inside the polymer. At high ionic strength, pH_i differs very little from the pH outside [14].

The different terms in Eq. (10) 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 [14]). 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 related to the interaction energy between the redox centres, $\Delta\epsilon$, and the last one is the usual concentration ratio in the Nernst equation. The mechanical work, is included in E_{int} .

The interaction parameter, $\Delta\epsilon$, is defined as $\Delta\epsilon = \frac{1}{2} N_{Av} c (\epsilon_{OO} + \epsilon_{RR} - 2\epsilon_{OR})$ where c is the number of next neighbours redox centres, ϵ_{OO} is the interaction energy between two next neighbour oxidized centres, similarly for two reduced and one oxidized and one reduced centres. If $\Delta\epsilon$ is assumed to be due only to repulsions between protonated redox centres, three limiting situations will be recognized, in the case of Pani ($pK_{a,R} \approx 0.5$ and $pK_{a,Ox} \approx 4.5$): i) All R and Ox centres are protonated (as it would happen at $pH < 0$), then $\Delta\epsilon = 0$. ii) All R are deprotonated and all Ox are protonated, in the range $1 < pH < 3$, then $\Delta\epsilon = \epsilon_{OO}$ and positive. iii) If all R and Ox are deprotonated ($pH > 5.5$), then it will be $\Delta\epsilon = 0$. In the case where the electrochemical process can be represented as a confined interacting reversible redox couple, the peak current should decrease and the Full Width at Half Maximum (FWHM) should increase when the interaction energy becomes more positive, as it happens here.

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

$$\theta_{N,Ox} = \frac{K_{aOx}^{-1} a_{H^+}^i}{(1 + K_{aOx}^{-1} a_{H^+}^i)} \quad (11)$$

where K_{aOx} is the acid constant of the Ox sites, and similarly for $\theta_{N,R}$. Then, taking into account Eq. (11), the third term of Eq. (10) may be written as: $-\frac{RT}{v_e F} \ln \left(\frac{(1 + K_{aOx}^{-1} a_{H^+}^i)}{(1 + K_{aR}^{-1} a_{H^+}^i)} \right)^2$. Thus, Eq. (10) results:

$$E = E_{int} - \frac{v_H 2.303RT}{v_e F} pH_i - \frac{RT}{v_e F} \ln \left(\frac{(1 + K_{aOx}^{-1} a_{H^+}^i)}{(1 + K_{aR}^{-1} a_{H^+}^i)} \right)^2 - \frac{\Delta\epsilon}{v_e F} (1-2\theta) - \frac{RT}{v_e F} \ln \left(\frac{(1-\theta)}{\theta} \right) \quad (12)$$

It is clear that by fitting the data of Fig. 6 with Eq. (12) it is possible to obtain $\Delta\epsilon$ as a function of pH and the constants K_{aOx} and K_{aR} . This was done, for θ vs. E data obtained spectroscopically [14]. For the present data, it was done the same analysis (Fig. 6) and the results are practically coincident with those previously reported [14].

For the coming analysis, it is needed to know the interaction parameter, $\Delta\epsilon/v_e F$, dependence on the electrolyte pH (see also Fig. 8 in ref. [14]).

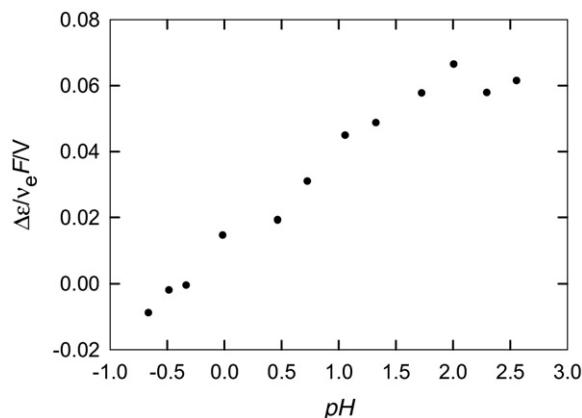


Fig. 8. $\Delta\varepsilon_m/v_e F$ vs. pH according to the analysis given in ref. [14] of the data of Fig. 6.

4.3. A theoretical expression for the faradaic current

In Eq. (12), at constant pH , the second and third terms are constant. The derivative of E with respect to θ results:

$$\frac{dE}{d\theta} = \frac{RT}{v_e F} \left[\frac{1 + \frac{2\Delta\varepsilon}{RT}(1-\theta)\theta}{(1-\theta)\theta} \right] = \frac{RT}{v_e F} + \frac{2\Delta\varepsilon}{v_e F} \frac{(1-\theta)\theta}{(1-\theta)\theta} \quad (13)$$

Then, the faradaic current is obtained from the inverse of the derivative of E with respect to θ multiplied by νQ^0 . It results:

$$j_F = \nu Q^0 \frac{v_e F}{RT} \left[\frac{(1-\theta)\theta}{1 + \frac{2\Delta\varepsilon}{RT}(1-\theta)\theta} \right] \quad (14)$$

Eq. (14) is equal to other expressions for the current of reversible confined redox couples with interactions between the redox centres [13,20–22]. It can be shown [20–22] that the maximum in the current occurs at $\theta = 0.5$. Therefore, explicit expressions for the peak current and potential can be obtained by setting $\theta = 0.5$ in Eqs. (14) and (12), respectively.

4.4. The dependence of j_F on $\Delta\varepsilon$

Now, we will set to explain the dependence of the faradaic current on $\Delta\varepsilon$. The starting point is Eq. (13). For simplicity, we will employ values at the peak current, that is for $\theta = 0.5$. Then Eq. (14) reads:

$$\left[\frac{dE}{d\theta} \right]_{\theta=0.5} = \frac{4RT}{v_e F} + \frac{2\Delta\varepsilon}{v_e F} \quad (15)$$

Considering $\Delta\varepsilon/v_e F$ as the variable, Eq. (15) is the equation of a straight line. We obtained $dE/d\theta$ at the peak employing the data of Fig. 6, reading the values at the peak ($\theta = 0.5$) for each pH . In Fig. 9, we show a plot of $dE/d\theta$ at the peak against $\Delta\varepsilon/v_e F$. A linear relationship is obtained. The slope and the ordinate are 1.963 and 0.093 V^{-1} , respectively that are very close to those expected theoretically. This shows that Eq. (13) represents adequately the experimental results (see Fig. 9).

Above we have demonstrated that: (i) The total charge is practically independent of pH in the range $-0.6 < pH < 2.0$. (ii) That the capacitive current is independent of the pH . This allows to conclude that also that the total faradaic charge, Q^0 , should be independent of pH . (iii) The peak of faradaic current decreases as the pH increases. The half width of the peak increases as the pH increases. And (iv) the interaction energy, $\Delta\varepsilon$, increases as the pH increases. Then, according to Eq. (14) as $\Delta\varepsilon$ increases

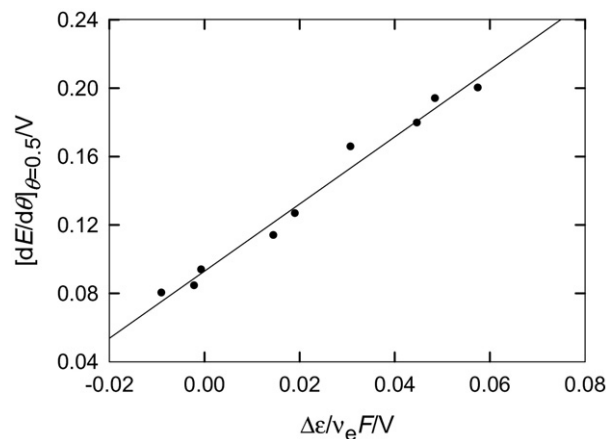


Fig. 9. Plot of the inverse of $d\theta/dE$ at the peak, obtained by deriving the data of Fig. 6, as a function of $\Delta\varepsilon$ from Fig. 8.

the peak current decreases. All these features are shown in the j vs. E profiles as a function of the pH shown in Fig. 1.

5. Conclusions

The experimental results show that: (i) The peak current and potential decrease as the pH increases in the range comprised between $-0.6 < pH < 1.5$. In this regions the “capacitive” current plateau is practically independent of the pH . (ii) At higher pH s both the peak current the peak potential levels off and then increases again. (Fig. 2). As the pH increases beyond about 1.5, also the anodic current peak and the current at the capacitive plateau increase. (iii) During the cathodic scan in the range comprised between $-0.6 < pH < 1.5$ the cathodic peak current decreases and the potential peak shifts in the negative direction. As the pH increases beyond about 1.5, it is noted an increase of the cathodic current just after the positive switching potential. Finally, this current increase becomes a broad peak at about 0.3 V. (iv) The voltammetric anodic charge is independent of the pH in the range $-0.6 < pH < 1.5$. As the pH increases beyond 1.5, the charge slightly increases (Fig. 5).

Although the faradaic and capacitive current contributions cannot be separated, it is possible to obtain the faradaic oxidation degree as a function of the potential from the voltammetric data. Deriving the oxidation degree with respect to the potential it is possible to obtain the shape of the faradaic current/potential response.

The analysis of the results employing a previous model shows that:

- (i) The interaction energy between the redox centres increases with the pH . As the voltammetric charge is independent of the pH , the change of the voltammetric response in the range $-0.6 < pH < 1.0$ is due to a change in the interaction energy that makes the current peak to decrease and to become wider.

Acknowledgments

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