

# Electropolymerisation of pyrrole onto aluminium from alkaline solutions containing a surfactant

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## Abstract

Polypyrrole films have been successfully electrodeposited on aluminium substrates from alkaline solutions containing an anionic surfactant (sodium dodecyl sulphate or sodium dodecylbenzene sulfonate). Homogeneous and adherent films were formed under potentiostatic, galvanostatic and potentiodynamic control. The electrochemical response was compared to that obtained with vitreous carbon as a substrate. Studies performed in monomer-free solutions showed that both  $\text{OH}^-$  and  $\text{Na}^+$  play an important role in the redox process. Scanning electron microscopy and atomic force microscopy studies indicated that the presence of surfactants influences the morphology of the polymer producing more homogeneous and less rough films than those formed in absence of surfactants.

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## 1. Introduction

It has been demonstrated that surfactants are effective electrolytes for chemical and electrochemical polymerisation of polypyrrole (PPy), one of the most investigated conducting polymers. Aromatic and very large amphiphilic sulfonate dopants provided the best conductivities, stabilities and mechanical properties to the polymer film [1]. Conducting polymer exchanges ionic species with the electrolyte solution when its redox state changes in order to preserve its electroneutrality. It is well known that this ion exchange depends on the size and nature of the dopants. It has been postulated that large surfactant anions remain immobilised in the polymer matrix and cations are mainly involved in the redox process of the film [2–5]. But the participation of anions with small radius in the redox

process of the films doped with large surfactant molecules has been demonstrated [6–8]. It was found a relevant cation exchange in the first redox process of PPy with dodecylbenzene sulfonate as a dopant and anion exchange in the second one [9].

The concentration of the surfactant plays a role in the electropolymerisation process. Considerable higher diffusion coefficient of ions was reported when the PPy films were formed from surfactant solution above the critical micelle concentration (cmc) [10]. Likewise, a columnar structure of the polymer was explained considering bilayered micelles on the electrode surface. The bilayered micelles adsorbed on the electrode surface are stabilised when the concentration of dopants increases.

There has been an increasing interest in the use of conducting polymers as anti-corrosion coatings. It is well known that in the case of Al, a passive oxide film is formed on the surface, which makes the electropolymerisation process very difficult. A previous work has shown that PPy films can be produced in alkaline solutions onto Al due

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to the instability of the oxide film at these pH values [11]. While PPy formed in acid media is not stable to cycle in alkaline solution, the film formed in alkaline solution is stable without evidence of degradation.

On the other hand, it has been provided that surfactants are good electrolytes for PPy formation onto active metals [12, 13]. Sodium 4,5-dihydroxy-*m*-benzenedisulfonate (Tiron) was used in the electropolymerisation of PPy onto Al and it was postulated that the ion acts as an electron mediator, lowering the potential for polymer electrodeposition [14,15]. This polymer deposition became increasingly patchy at pH higher than 7.

With the above information in mind, the electrochemical preparation of PPy films onto aluminium in aqueous alkaline solutions containing surfactants was checked. Two typical salts for PPy electropolymerisation were tested, sodium dodecyl sulphate (SDS) and sodium dodecylbenzene sulfonate (SDBS). The electrochemical behaviour is compared to that obtained using vitreous carbon as a substrate.

## 2. Experimental details

Aluminium (99.999 %, Aldrich Chemical Company) and vitreous carbon (The Electrosynthesis Co.) rods embedded in a Teflon holder with an exposed area of 0.070 cm<sup>2</sup> were used as working electrodes. Before each experiment, the electrode was polished with successively finer grades of SiC emery papers up to 1000 grits, then degreased with acetone and washed with triply distilled water. Following this pretreatment, the electrode was immediately transferred to the electrochemical cell. All the potentials were measured against a saturated calomel electrode (SCE) and a platinum sheet was used as a counter electrode. The cell was a 20 cm<sup>3</sup> Metrohm measuring cell. Electrochemical measurements (potentiodynamic, potentiostatic and galvanostatic techniques) were done using a linear voltage sweep generator PAR model 175, a potentiostat–galvanostat PAR model 173 and HP 4007 B *x–y* recorder. Scanning electronic microscopy pictures were taken with a Jeol 100. Surface topography changes of the samples were followed by using *ex situ* AFM imaging with Nanoscope III equipment (Digital Instrument, Santa Barbara, CA). Silicon-nitride tips were used under the contact mode by applying different forces in the range 70 nN < *f* < 250 nN.

Measurements were performed in solutions containing 0.25 M Py and 0.05 M of the surfactant (SDS or SDBS) in a purified nitrogen gas saturated atmosphere at 25 °C.

The pH of the solution was adjusted by addition of NaOH. All chemicals were reagent grade and solutions were freshly made in twice distilled water. Pyrrole was purchased from Acros Organics and it was freshly distilled under reduced pressure before use.

## 3. Results

### 3.1. Polypyrrole electropolymerisation

Fig. 1 shows the cyclic voltammograms obtained by electropolymerisation of Py in the presence of 0.05 M SDBS, pH 12, onto Al (Fig. 1a) and onto vitreous carbon (Fig. 1b). The voltammetric curves for the vitreous carbon electrode show a sharp current increase starting at about 0.45 V, indicating the onset of electropolymerisation. Thus, the surfactant allows pyrrole oxidation at a very low potential close to that measured when using others anions in acid or neutral media. When the substrate is Al, pyrrole oxidation initiates at more positive potentials (0.60 V) in the first anodic scan, shifting to more negative potentials in the second one. In the presence of SDS the electropolymerisation curve is similar to that observed with SDBS. The peaks associated with the build-up of electroactive polymeric products are very broad for both substrates. Oxidation and reduction peaks are closer in the case of vitreous carbon. The total charge tends to stabilise in the 10th cycle and the electrodes become covered by an homogeneous, thick and adherent deposit, which can be removed only after mechanical polishing.

Polypyrrole films could be also formed potentiostatically. The current-time responses during deposition differed with

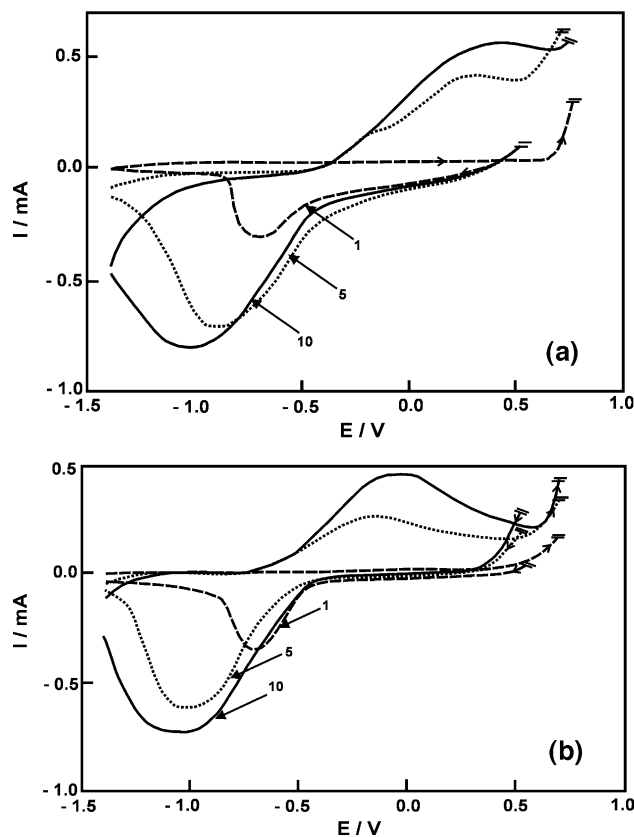


Fig. 1. Cyclic voltammograms obtained with (a) Al and with (b) vitreous carbon electrode in 0.05 M SDBS, pH 12 solution containing 0.25 M Py. Scan rate: 0.05 V s<sup>-1</sup>. Scans 1, 5 and 10 are displayed.

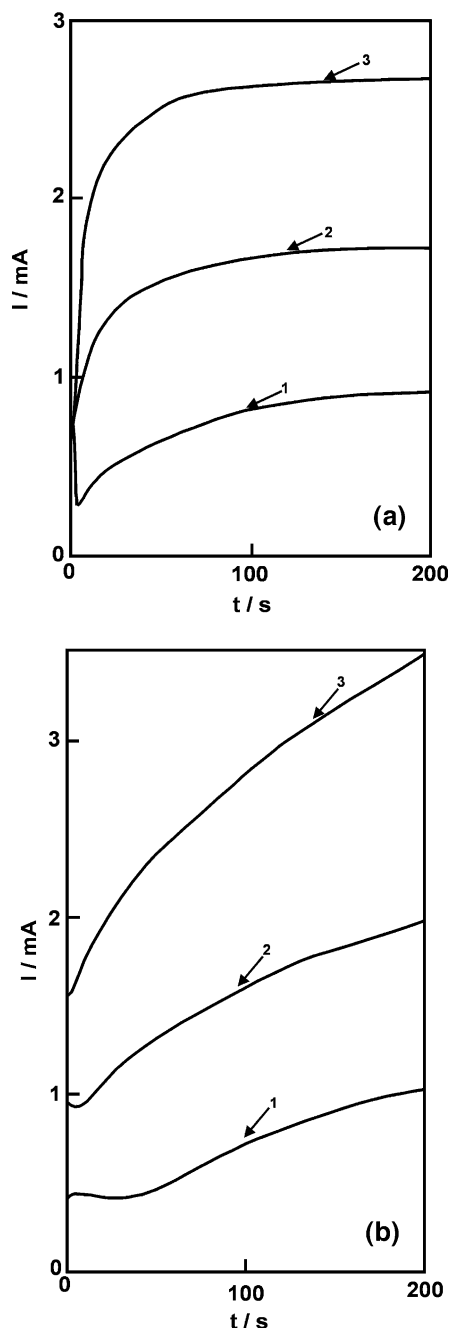


Fig. 2. Chronoamperometric curves obtained on (a) Al and on (b) vitreous carbon electrodes in 0.05 M SDBS, pH 12 solution containing 0.25 M Py, in response to potential steps from  $-1.0$  V to: (1) 0.70 V, (2) 0.90 V and (3) 1.10 V.

the two substrates. A series of chronoamperometric curves obtained during electropolymerisation on Al and on vitreous carbon are shown in Fig. 2, corresponding to different applied potentials from 0.70 to 1.10 V. The results are very similar when SDBS is replaced by SDS. The initial current decay in the case of Al is associated with the formation of the oxide layer under a high field conduction mechanism. After an initial rise, the current attains a constant value. This behaviour may be attributed to a reaction controlled by

charge transfer on the electrode [16], with a first electron transfer from Py to form radical cation species being the rate determining step [17].

For vitreous carbon the current still increases after 4 min polarisation, following an  $I-t^{1/2}$  relationship (Fig. 2b). This behaviour is in accordance with the response predicted for instantaneous nucleation and growth under diffusion control. Another possible way for the formation of the film is the precipitation of soluble intermediates from a supersaturated solution, which are generated during Py oxidation [18].

Strongly adherent PPy films can also be formed under galvanostatic conditions. Fig. 3 shows the chronopotentiometric curves obtained on Al and vitreous carbon in 0.05 M SDBS, pH 12 solution. In the case of vitreous carbon the electropolymerisation reaction starts at relatively very weak

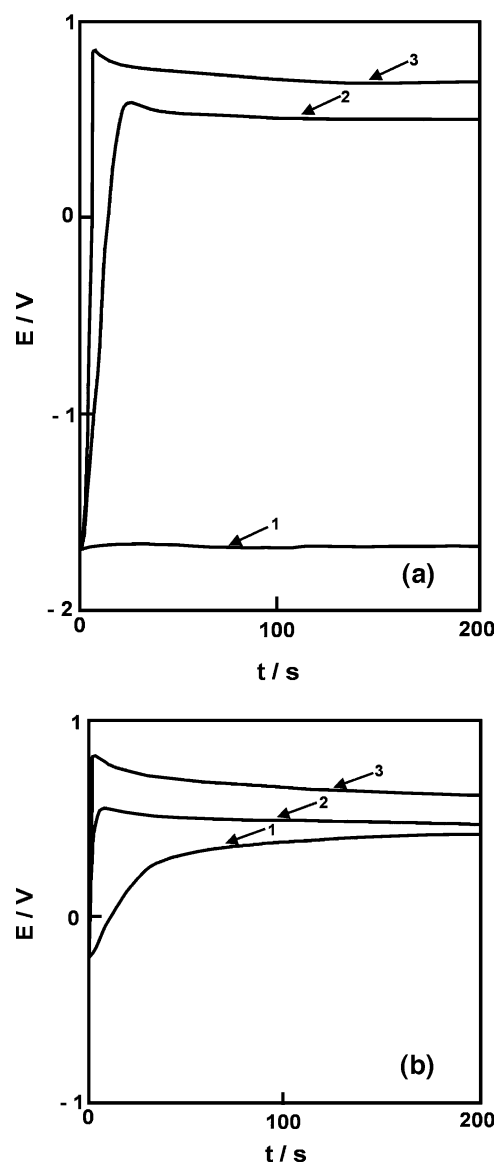


Fig. 3. Chronopotentiometric curves obtained under galvanostatic conditions on (a) Al and on (b) vitreous carbon electrodes in 0.05 M SDBS, pH 12 solution containing 0.25 M Py at: (1)  $7 \mu\text{A}$ , (2)  $70 \mu\text{A}$  and (3)  $700 \mu\text{A}$ .

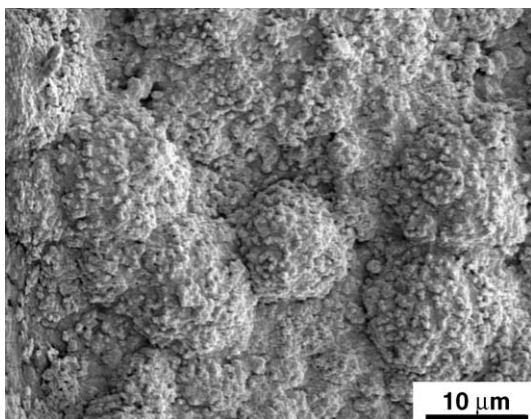


Fig. 4. SEM micrograph of PPY-coated Al. The film was formed at 0.90 V in 0.05 M SDBS, pH 12 solutions containing 0.25 M Py.

current densities ( $0.1 \text{ mA cm}^{-2}$ ). The potential remains at a value that corresponds to the oxidation potential of Py and the subsequent formation of a PPY film. Greater the applied current more positive is the potential plateau and thicker is the film obtained. In the case of Al, at low currents the potential does not exceed  $-1.65 \text{ V}$  indicating that there is no electrodeposition and that Al dissolves (Fig. 3a). At currents higher than  $1 \text{ mA cm}^{-2}$ , the potential rapidly reaches the value of the electropolymerisation potential and a thick, homogeneous and adherent film is formed.

### 3.2. Surface morphology

The scanning electron microscopy (SEM) images for the PPY films formed on Al are shown in Fig. 4. The morphology of the polymer formed at 0.9 V in SDBS (curve 2 in Fig. 2a) and SDS is characterised by the formation of aggregates. The grains are smaller and have a less globular surface than those formed in  $0.1 \text{ M NO}_3^-$ , pH 12 solution [17]. Likewise, the coating formed is smoother and more compact.

Atomic force microscopy provides more details about the surface morphology and allows a quantification of the root mean square roughness (rms) of the films, which is the standard deviation of the height values ( $Z$ ) within the area under analysis and is defined through:

$$R_q = \sqrt{\frac{\sum (Z_i - Z_{ave})^2}{N}} \quad (1)$$

where  $Z_{ave}$  is the average of the  $Z$  values within the given area,  $Z_i$  is the height at point  $i$  and  $N$ : number of points in the area under analysis,  $h_i$ : height at the point  $i$ , and  $\langle h \rangle$  is the average height of the area under analysis.

For the sake of comparison, the AFM images for the film formed in acid media and in alkaline solution containing nitrate are also presented. Fig. 5 shows the images of PPY formed potentiostatically in  $0.1 \text{ M HNO}_3$  (a),  $0.1 \text{ M NaNO}_3$ , pH 12 (b) and  $0.05 \text{ M SDBS}$ , pH 12 (c). The time of electropolymerisation was 30 s.

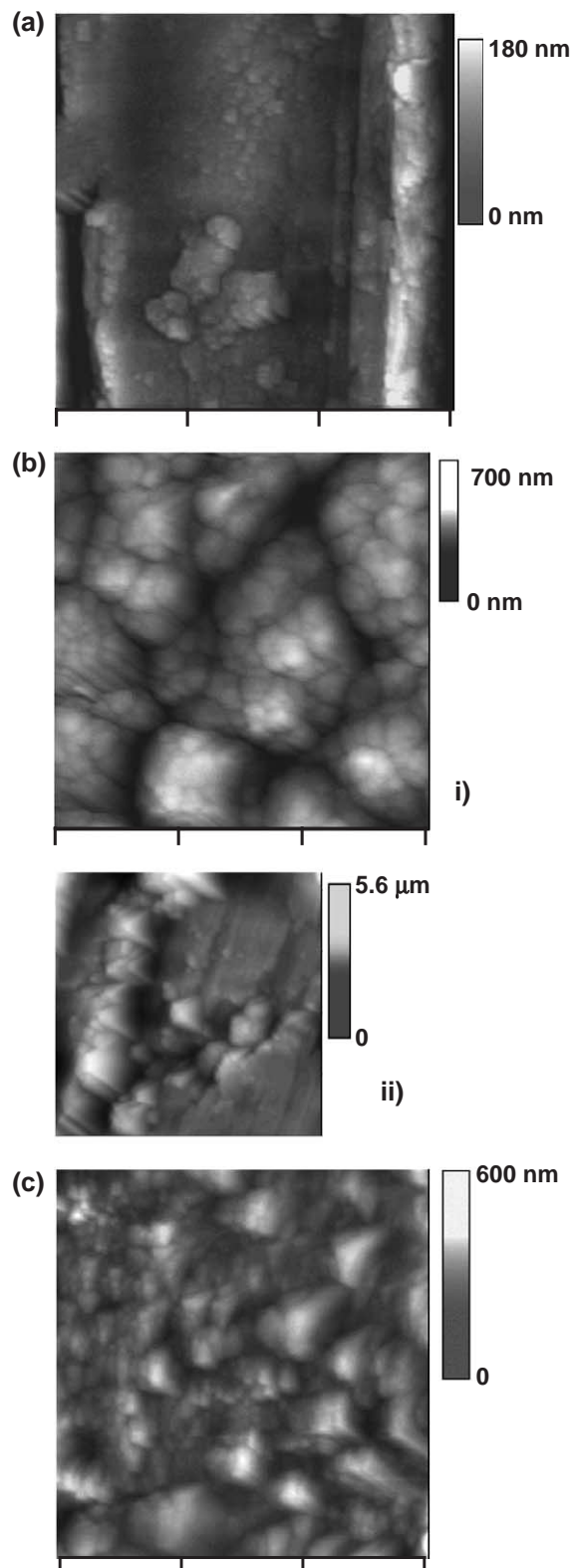


Fig. 5.  $3 \times 3 \mu\text{m}$  AFM images of PPY formed potentiostatically on Al ( $E=0.90 \text{ V}$ ,  $t=30 \text{ s}$ ) in solutions containing 0.25 M Py: (a)  $0.1 \text{ M HNO}_3$ , (b)  $0.1 \text{ M NaNO}_3$ , pH 12 ((i) film on terraces, (ii) irregular growth at ridges), (c)  $0.05 \text{ M SDBS}$ , pH 12.



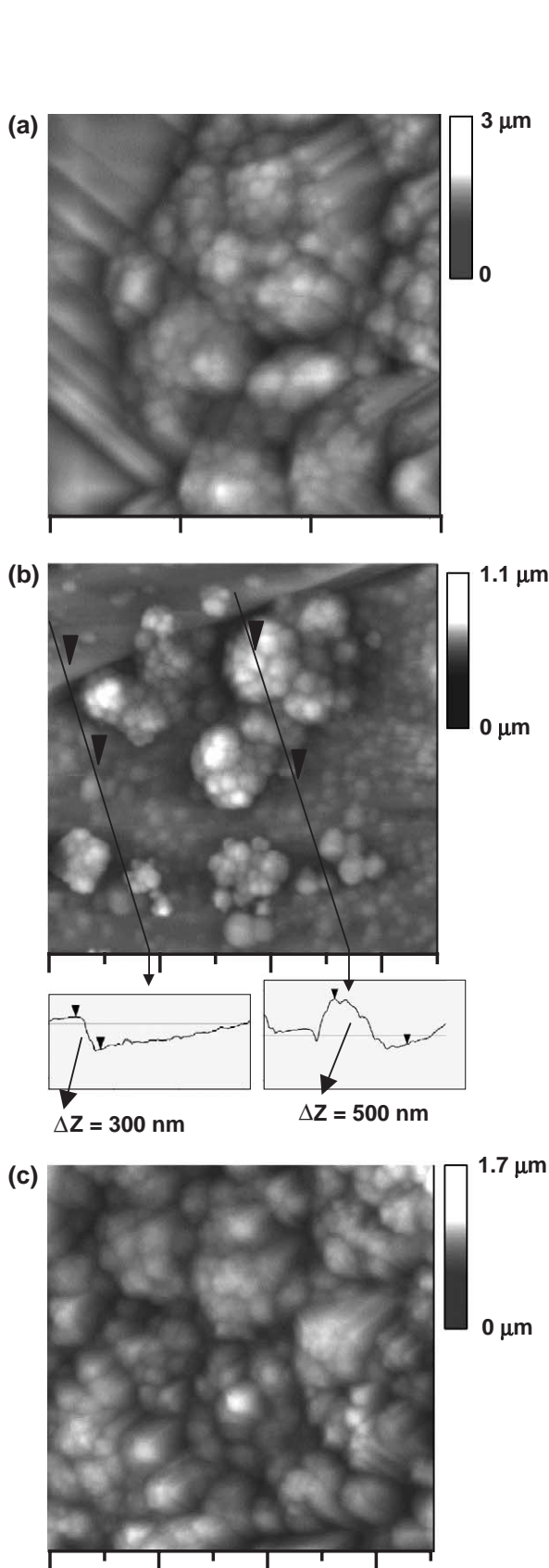


Fig. 6.  $7 \times 7 \mu\text{m}$  AFM images of PPy formed potentiostatically on Al ( $E=0.90 \text{ V}$ ,  $t=2 \text{ min.}$ ) in solutions containing  $0.25 \text{ M Py}$ : (a)  $0.1 \text{ M HNO}_3$ , (b)  $0.1 \text{ M NaNO}_3$ , pH 12, (c)  $0.05 \text{ M SDBS}$ , pH 12.

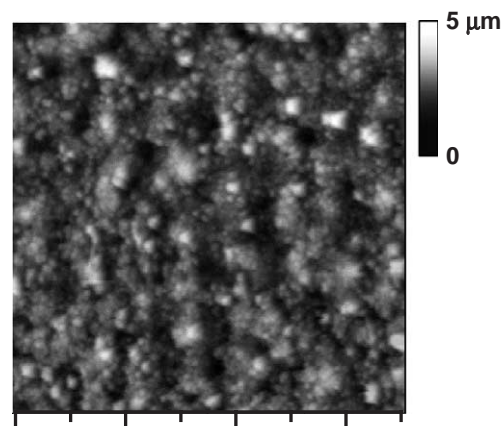


Fig. 7.  $100 \times 100 \mu\text{m}$  AFM image of PPy-coated Al formed at  $0.90 \text{ V}$  in  $0.05 \text{ M SDBS}$ , pH 12.

It can be observed that in the first two cases (Fig. 5a and b.ii), nucleation initiated at the ridges. On the contrary, in the case of SDBS, a very thin polymer film covering the whole substrate surface is observed (Fig. 5c). The growth of polymer in the steps in  $0.1 \text{ M NaNO}_3$  pH 12 solution produced dendritic or columnar shapes that are not possible to be followed by the pyramidal AFM tip. Typical tip effects can be observed in Fig. 5b.ii where the morphology of the tip is most likely to be observed near the ridges. On the other hand in terraces, more homogeneous polymer deposits are well imaged (Fig. 5b.i).

Fig. 6 shows the images of PPy formed potentiostatically in  $0.1 \text{ M HNO}_3$  (a),  $0.1 \text{ M NaNO}_3$  pH 12 (b) and  $0.05 \text{ M SDBS}$ , pH 12 (c) for longer times of electropolymerisation (2 min). The cauliflower structure of the deposits is evident in all images. In the  $\text{NaNO}_3$  solution of pH 12 the cross section analysis shows that some globular structures growth near the step exceeding the mean height of the polymer on terraces. For long time of electropolymerisation the irregular shapes impedes the imaging in large scans. On the contrary for surfactant-doped PPy thicker films structures shows that a relatively smooth uniform surface structure is obtained (see image of  $100 \mu\text{m}$  in Fig. 7).

The mean roughness values measured by AFM through  $R_q$  (Eq. (1)) in  $3 \times 3 \mu\text{m}$  scans are in the range  $30\text{--}50 \text{ nm}$  for the PPy films formed in presence or absence of surfactant. The main difference appears in large scans where the inhomogeneities of the deposits (dendritic or columnar shapes) obtained in absence of surfactants turns it impossible to be followed by the capability of the piezoelectrics in the normal direction to the surface. For longer times of electropolymerisation the rms values in  $3 \times 3 \mu\text{m}$  images are in the order of  $40\text{--}60 \text{ nm}$ . For larger scans in the absence of surfactants the rms value is affected by the convolution between tip and sharp polymeric formations. When the surfactant participates in the electropolymerisation procedure, homogeneous films are formed that can be imaged in large scans (Fig. 7). Typical  $R_q$  values of this films are in the order of  $500 \text{ nm}$ .

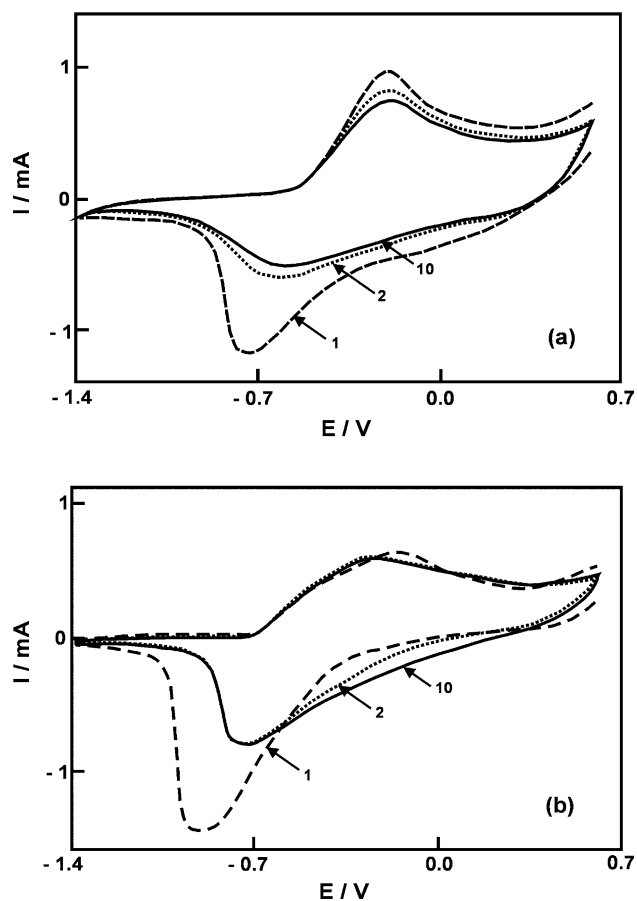


Fig. 8. Cyclic voltammograms of the PPy film on (a) Al and on (b) vitreous carbon electrodes in 0.05 M SDBS, pH 12 solution at  $0.05 \text{ V s}^{-1}$ . The film was formed potentiostatically ( $E=0.90 \text{ V}$ ,  $t=90 \text{ s}$ ) in 0.05 M SDBS, pH 12 solution containing 0.25 M Py. Scans 1, 2 and 10 are displayed.

### 3.3. Redox behaviour of PPy

The redox switching behaviour of the PPy-coated electrodes was examined in monomer-free solutions. The behaviour of PPy formed potentiostatically on Al in a SDBS solution shows reduction and oxidation peaks at  $-0.60$  and  $-0.20 \text{ V}$ , respectively (Fig. 8a). The response for the film formed on vitreous carbon did not differ markedly from that

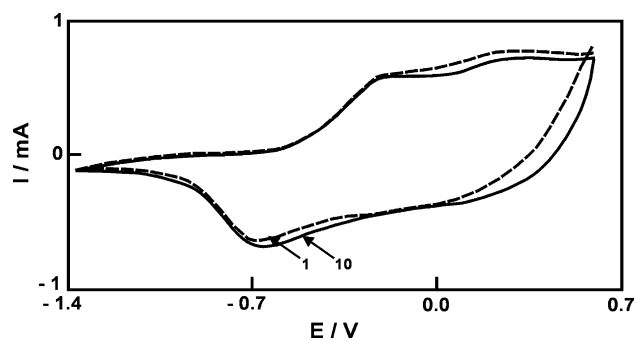


Fig. 9. Cyclic voltammograms of the PPy-coated Al electrode in  $0.1 \text{ M NO}_3^-$ , pH 12 solution at  $0.05 \text{ V s}^{-1}$ . The film was formed potentiostatically ( $E=0.90 \text{ V}$ ,  $t=90 \text{ s}$ ) in 0.05 M SDBS, pH 12 solution containing 0.25 M Py. Scans 1 and 10 are displayed.

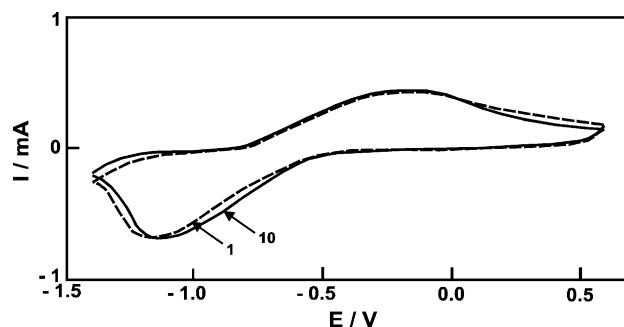


Fig. 10. Cyclic voltammograms of the PPy-coated Al electrode in 0.05 M SDBS, pH 9.5 solution at  $0.05 \text{ V s}^{-1}$ . The film was formed potentiostatically ( $E=0.90 \text{ V}$ ,  $t=90 \text{ s}$ ) in 0.05 M SDBS, pH 9.4 solution containing 0.25 M Py. Scans 1 and 10 are displayed.

obtained on Al (Fig. 8b). For both cases it can be observed that the voltammetric charge decreases until a stabilised curve is achieved and that the reduction peak is shifted to more positive potentials during cycling. The coulombic efficiency over a cycle of charge–discharge is practically 100% for both substrates. The charge cycled corresponds to a 10.1% and 8.7% of the charge used for the deposition of the film on vitreous carbon and on Al, respectively. These values are similar to those obtained employing a PPy modified Al in an alkaline solution containing nitrate [11].

When the PPy-coated Al electrode obtained in the presence of SDBS was transferred and potentiodynamic polarised in a  $\text{NO}_3^-$  solution of pH 12, oxidation and reduction waves appear at the more positive potentials (Fig. 9). This redox couple is associated with the exchange of nitrate.

Further details of the redox process can be obtained by analysing the voltammetric behaviour of PPy formed in 0.05 M SDBS, pH 9.5 solution containing pyrrole, and then cycled in a solution without the monomer. The potentiodynamic response differs from that observed for the film formed and cycled at pH 12, as can be seen in the voltammograms shown in Fig. 10. The  $I/E$  curve shows that reduction and oxidation waves are very broad and that the potential of the cathodic peak remains practically unchanged during cycling. Likewise, the charge measured during deposition of the film is smaller than that measured at pH 12 for the same polymerisation time.

## 4. Discussion

The experimental results indicate that PPy films can be formed on both, Al and vitreous carbon electrodes, in alkaline solutions of surfactants. The electropolymerisation process also takes place in nitrate and sulphate solutions at the same pH [11,19]. These results were explained considering the amphoteric character of the Al oxide. As the solution pH increases, a less protective oxide layer is formed. The present results also indicate that the surfactants are very effective for the electropolymerisation. The

following observations support this conclusion: (a) the process initiates at a very negative potential; (b) it was found that no film formation on Al occurred in nitrate solution at pH 9.5 [11]. On the contrary, Al could be electrocoated with PPy at this pH in the presence of surfactants; (c) the galvanostatic polarisation is not suitable for the preparation of the film in alkaline solutions of nitrate [11], while very adherent coatings are formed using surfactants.

It has been postulated that surfactants act not only as dopants but they also modify the surface conditions, affecting the electropolymerisation process. The cmc of SDS and SDBS in water are 8 and 1.5 mM, respectively, and these values are generally reduced with additions of electrolytes. Thus, it is expected that the high surfactant concentrations used here for electropolymerisation (0.05 M) are well above the cmc. It is known that these molecules form layers or bilayers on surfaces at or near the cmc [20]. The pyrrole is considered to be preferentially dissolved into the micellar assembly [10]. On the other hand, taking into account the hydrophilic character of the Al oxide, it is supposed that the surfactant is adsorbed on its surface with the polar group facing the substrate and the hydrophobic group facing the solution [13]. This adsorption can also take place on metallic Al on surface areas where the oxide presents flaws and defects. This configuration can facilitate the anchoring of monomers and oligomers of Py and the onset of electropolymerisation.

It can be observed that when the electropolymerisation takes place in absence of surfactant ( $\text{HNO}_3$  solution in Fig. 5a and  $\text{NaNO}_3$  solution, pH 12 in Fig. 5b.ii), nucleation initiated at the ridges. On the contrary, when the electropolymerisation was made in SDBS, a very homogeneous polymer film covering the whole substrate surface is observed (Figs. 5c, 6c and 7). The absence of preferential sites of growth in presence of surfactant allows us to infer that there are homogeneously distributed nucleus of growth that produce a higher deposition rate of the polymer. It is likely that the nucleation process is faster than the process associated with the growth of the polymer chain. Thus, the coating formed on Al in the presence of the surfactants is formed by smaller grains and has a smoother and a more compact morphology than that observed in nitrate [19]. Typical roughness values measure through  $R_q$  of these films are of 500 nm in  $100 \times 100 \mu\text{m}$  images (Fig. 7). On the contrary, in the absence of surfactant in the electropolymerisation procedure, the irregularities of the deposit turned it impossible to be followed by the AFM probe in scans larger than 10–20  $\mu\text{m}$ .

The influence of the Al oxide on the electropolymerisation process can be analysed by comparing the results obtained on both Al and vitreous carbon. Considering the potentiodynamic polarisation, the electropolymerisation is faster on the polymer than on the Al oxide (Fig. 1). Considering the early stages of potentiostatic polymerisation, the oxidation of Al occurs first, followed by the

formation of PPy under activation control. Finally, considering the galvanostatic mode for electropolymerisation, higher currents are needed to perform the reaction on Al (Fig. 3). On the other hand, it has been reported that some surfactants act as inhibitors of Al dissolution in acid media because of their adsorption on the metal surface [21–23]. The surfactants checked in the present work slightly inhibit Al corrosion in alkaline media. More details on this issue will be reported in a forward publication.

With respect to the redox process, a reduction process at very negative potentials was attributed to  $\text{Na}^+$  insertion when the PPy formed on vitreous carbon is cycled in a neutral or alkaline solution containing  $\text{NaNO}_3$  [24]. Using Al there was no insertion of the cation of the electrolyte and it has been postulated that  $\text{Al}^{3+}$  (or  $\text{Al}(\text{OH})_4^-$ ) is involved in the charge compensation process [19]. The situation is different when a surfactant is used because the presence of the remaining surfactant in the polymer matrix leads to the participation of the cation of the electrolyte. The cathodic peak in Fig. 8a should be associated with this process. On the other hand, a reduction current in the potential range between 0.0 and  $-0.6$  V can be measured (Fig. 8). When a PPy film synthesised in  $\text{NO}_3^-$ , pH 12, was submitted to a potential cycling in 0.01 M NaOH, a reduction wave was obtained in this potential range, which was attributable to the participation of  $\text{OH}^-$  in the redox process [19]. The same behaviour occurred when the polymer was cycled in the presence of anions that cannot re-intercalate to replace the expelled  $\text{NO}_3^-$ , such as sulphate, acetate or oxalate. Thus, taking into account previous results [19,24], the exchange of  $\text{OH}^-$  would not be excluded in the present case. The transport of  $\text{OH}^-$  during the redox reaction of PPy film agrees with the participation of anions with small radius in the redox process of the films doped with surfactants [6,8,9]. The fact that the transport of  $\text{OH}^-$  takes place at pH 12 is indicated by the comparison with the response at pH 9.5 (Fig. 10), where the current measured in this potential range is very small. At this pH, only the transport of the cation of the electrolyte equilibrates the charge.

The diffusion of  $\text{OH}^-$  through the film causes oxidation of Al [19]. This effect was not observed when the film is formed in the presence of surfactants probably due to the fact that surfactants inhibit the oxide dissolution.

When the electrode covered with PPy electrodeposited in the presence of SDBS was transferred and potentiodynamic polarised in a  $\text{NO}_3^-$  solution, new oxidation and reduction waves appear at more positive potentials (Fig. 9), indicating that the transport of small anions takes place in addition to  $\text{Na}^+$ .

## 5. Conclusions

It is shown that it is possible to obtain conducting and stable PPy films in alkaline solutions containing surfactants. In spite of the electropolymerisation process starts after the

oxidation and passivation of Al, the characteristics of the film formed on Al do not differ markedly from that synthesised on vitreous carbon. Surfactant increases the deposition rate of the polymer and smoother films are obtained. The films are porous to electrolyte ions. The transport of  $\text{OH}^-$  in addition to  $\text{Na}^+$  occurs during the redox process of the polymer formed in SDS and SDBS. It is shown that although the diffusion of  $\text{OH}^-$  takes place, the presence of surfactants inhibits the Al oxide dissolution.

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