

## Ionic Diffusion Processes in Polypyrrole

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As técnicas de deflexão de um feixe-sonda e microbalança de cristal de quartzo foram usadas para estudar a troca de espécies móveis durante a reação redox em polipirrol (PPy) dopado com o surfactante aniônico dodecilbenzenosulfonato (DBS). Combinando estas técnicas com a voltametria cíclica foi possível determinar qualitativamente as espécies iônicas envolvidas nos processos de difusão. Os resultados mostraram que o ânion dopante DBS<sup>-</sup> permanece no filme e que a eletroneutralidade é conservada por inserção/deinserção de cátions e ânions do eletrólito durante o processo de oxidação-redução do PPy/DBS em solução aquosa 0,1 M de KCl, KClO<sub>4</sub> ou CsCl. Comprovou-se que os cátions têm um papel predominante neste processo.

Probe Beam Deflection and Quartz Crystal Microbalance techniques were used to study the exchange of mobile species during the redox reaction in polypyrrole (PPy) doped with an anionic surfactant, dodecylbenzenesulfonate (DBS<sup>-</sup>). These techniques, combined with Cyclic Voltammetry, permit the qualitative determination of the ionic species involved in the diffusion processes. Results show that during the oxide-reduction of PPy/DBS in 0.1 M aqueous solutions of KCl, KClO<sub>4</sub> or CsCl, the doping anion, DBS<sup>-</sup>, remains in the film and the electroneutrality is preserved by the insertion/expulsion of cations and anions from the electrolyte solutions. The cations were found to play a predominant role.

**Keywords:** polypyrrole, dodecylbenzenesulfonate, cyclic voltammetry, electrogravimetry, mirage effect

### Introduction

Electronic conducting organic polymers have generated great interest in view of their possible technological applications<sup>1-7</sup>. Their backbone is an essentially conjugated double-bonded system that can undergo redox reactions. There is agreement in the literature that oxidation and reduction of the polymeric backbone of polymers such as polypyrrole (PPy) are accompanied by the diffusion of ions from the solution into or out of the film to maintain the electroneutrality.

In a previous investigation of the electrochemical properties of PPy doped with dodecylsulfate (PPy/DBS)<sup>8</sup>, we observed that cations have an important role in the ionic diffusion processes when the polymer is switched between its reduced and oxidized states. When the pyrrole backbone is reduced, *i.e.* becomes neutral, the DS<sup>-</sup> anions are immobilized in the polymeric matrix and the cations of the electrolyte diffuse into the film. Several processes have already been observed using the Quartz Crystal Microbalance technique (QCM)<sup>8</sup>: (i) when the polymer is oxidized, *i. e.* becomes positive, cations are expelled, and (ii) at

overoxidation potentials ( $E > 0.0$  V vs. SCE) anions diffuse into the material.

The aim of the present work is to study the diffusion processes of PPy doped with dodecylbenzenesulfonate (PPy/DBS) using Probe Beam Deflection (PBD)<sup>9</sup> and QCM coupled with cyclic voltammetry.

## Experimental

Polypyrrole films were grown onto working electrodes at a constant anodic current of  $1 \text{ mA cm}^{-2}$  in an aqueous solution containing  $0.05 \text{ M}$  pyrrole and  $0.025 \text{ M}$  sodium dodecylbenzenesulfonate. The electropolymerization charge for the polypyrrole films used in the PBD experiments was  $360 \text{ mC cm}^{-2}$  (estimated thickness of  $2.5 \text{ }\mu\text{m}^{10}$ ), and  $22.5 \text{ mC cm}^{-2}$  (estimated thickness of  $0.16 \text{ }\mu\text{m}^{10}$ ) for QCM experiments. The reason for choosing these values for the electropolymerization charges was based on previous investigations<sup>8,10,11</sup>. After deposition, the films were rinsed with triply-distilled water and placed in an electrochemical cell with  $0.1 \text{ M}$  monomer-free aqueous solutions of  $\text{KClO}_4$ ,  $\text{KCl}$ , or  $\text{CsCl}$  as electrolytes.

Electrochemical experiments were done under potentiodynamic conditions, using an EG&G PAR model 273 potentiostat-galvanostat. All potentials were measured with reference to a saturated calomel electrode (SCE). Change of mass and deviation of the laser beam were recorded simultaneously with the respective variation of current as a function of potential. During all experiments the cell atmosphere was maintained under a dry nitrogen flux.

### QCM experiments<sup>8</sup>

Pt wire was used as counter electrode. The working electrode was an "AT-cut"  $6 \text{ MHz}$  quartz crystal ( $16 \text{ mm}$  in diameter) with a gold layer deposited in key form on both sides (active area =  $0.2 \text{ cm}^2$ ). This piezoelectric element was mounted in a Teflon holder and the gold layer, which was in contact with the electrolytic solution, was attached to both the oscillator circuit and the potentiostat, and thereby, to ground. The resonance frequency shift was measured with a Stanford Research System model SR620 universal counter and the data was recorded on a HP model 7046B X/Y recorder.

### PDB experiments<sup>9</sup>

Platinum foils ( $1.0 \times 1.0 \text{ cm}$ ) were used as working and counter electrodes. The electrochemical cell was a glass cuvette with parallel windows. The mirage detection assembly was composed of a  $1 \text{ mW}$  He-Ne laser beam probe ( $\lambda = 632.8 \text{ nm}$ ) with a spot diameter of  $80 \text{ }\mu\text{m}$ . The beam was set parallel to the working electrode and focused by a convergent lens ( $f = 10 \text{ cm}$ ). In all experiments the laser beam was positioned as close as possible to the electrode surface by using a stepped motor. The distance between the

center of the laser beam and the electrode was determined to be  $120 \pm 5 \text{ }\mu\text{m}$  using the same procedure as in reference 12. Laser beam deflections were detected using a UDT PIN SPOT/2D position sensor.

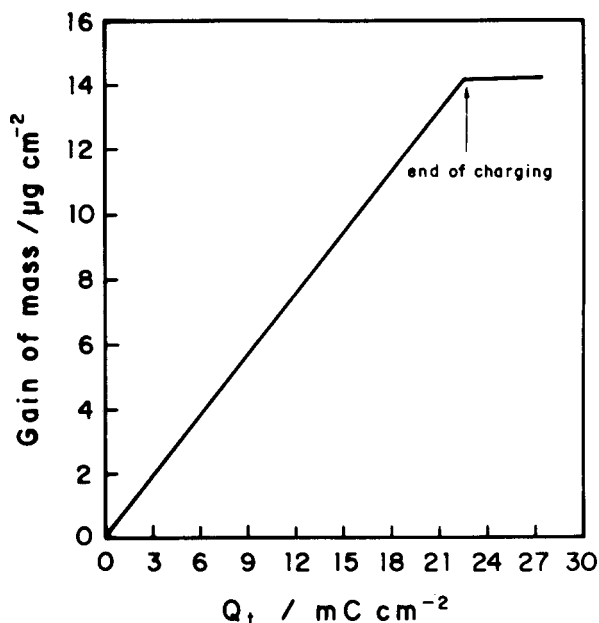
## Results and Discussion

### Electrogravimetric experiments

Figure 1 shows the evolution of the mass as a function of charge during the synthesis of a polypyrrole film in the presence of dodecylbenzenesulfonate. In contrast to the electropolymerization of pyrrole in the presence of dodecylsulfate<sup>8</sup>, which shows two different curve regions (nucleation and film growth), only polymer film growth was observed. The dark color of the film obtained suggests that the electropolymerization process formed an oxidized film.

In order to determine the degree of doping the following assumptions were made: (i) the polymerization reaction consumes two electrons per molecule of monomer<sup>12,13</sup>, and the polymerization charge is represented by  $Q_p = n Z F$ , (where  $n$  is the number of moles of electropolymerized monomer,  $Z$  is the number of electrons, and  $F$  is the Faraday); (ii) only one electron is involved in each oxidation step, and the oxidation charge due to doping is  $Q_{ox} = \frac{n F}{x}$  ( $x^{-1}$  is the degree of doping).

We can thus write the total charge of the process,  $Q_t$ , as:



**Figure 1.** QCM responses recorded during the galvanostatic deposition of PPy films in  $0.05 \text{ M}$  pyrrole and  $0.025 \text{ M}$  sodium dodecylbenzenesulfonate. Deposition current:  $I = 1 \text{ mA cm}^{-2}$ .

$$Q_t = Q_p + Q_{ox} = nF \left( 2 + \frac{1}{x} \right) \quad (1)$$

and the total mass charge for the process,  $\Delta m$ , is expressed as<sup>8</sup>:

$$\Delta m = n \sum_i MW_i = n \left( MW_{Py} + \frac{1}{x} MW_{DBS^-} - 2AW_{H^+} \right) \quad (2)$$

In Eq. 2,  $MW_i$  is the molar mass of species  $i$ , which is 67 g for pyrrole and 325 g for dodecylbenzenesulfonate, and  $AW_i$  is the molar mass of the proton.

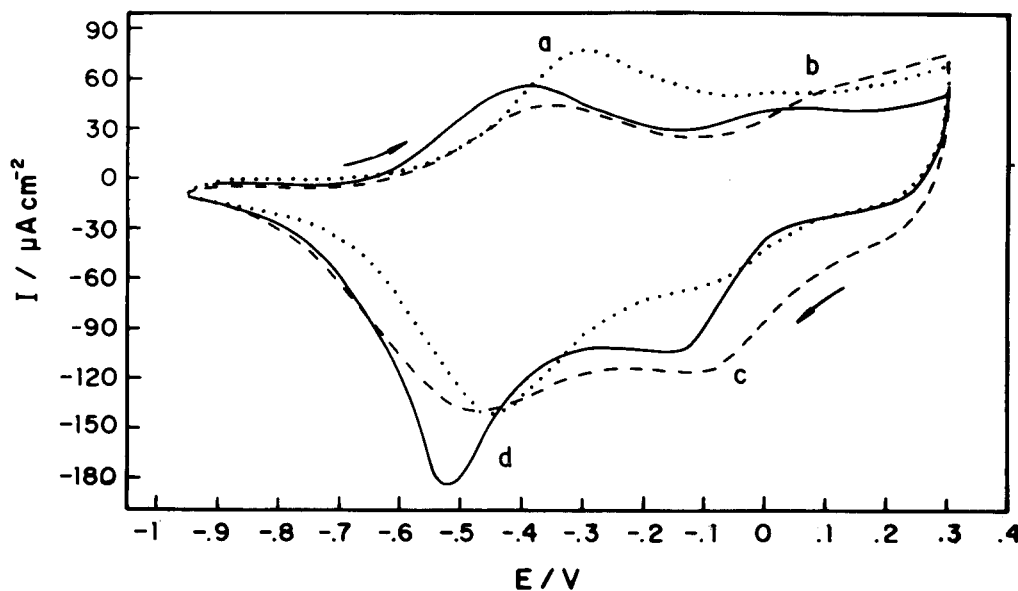
Using the data represented in Fig. 1 the value for the change in mass as a function of the charge variation during the electropolymerization process,  $\frac{\Delta(\Delta m)}{\Delta Q_t}$  was determined as  $0.62 \text{ mgC}^{-1}$ . Using eqs. (1) and (2) the doping level was calculated to be 20%.

Figure 2 shows the cyclic voltammograms of PPyDBS films (estimated thickness  $0.16 \mu\text{m}$ ) obtained in 0.1 M KCl,  $\text{KClO}_4$ , and CsCl aqueous solutions, during linear scan voltammetry at  $20 \text{ mVs}^{-1}$ . The potential range was chosen so that the two successive charge transfers were observed. The electrochemical responses were in good agreement with previous observations for PPy doped with amphiphilic anions<sup>8,10,11</sup>. The differences in the voltammograms indicate that the nature of the anions and cations affects the polymer redox behavior; in other words, it influences voltammogram shapes, redox peak potentials and currents. As the anion or cation hydration radius is increased, the redox peak potentials move to higher potentials and the redox

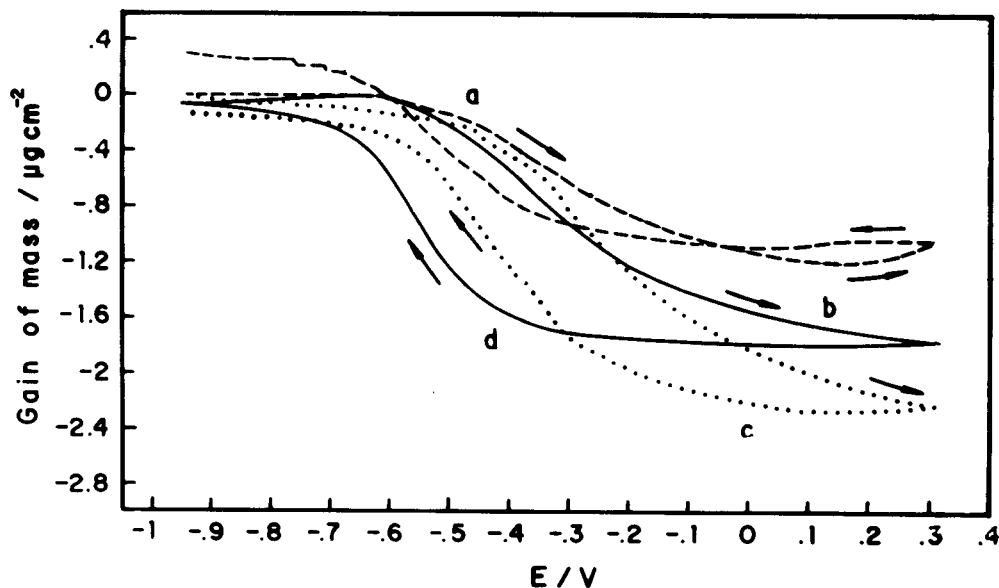
peak currents extend over larger values for both charge transfers. However, the calculated oxidation charges are not affected very much. The oxidation charges for a film cycled in KCl and  $\text{KClO}_4$  solutions were identical ( $Q_{ox} = 1.4 \text{ mCcm}^{-2}$ ), whereas in CsCl solution  $Q_{ox} = 1.8 \text{ mCcm}^{-2}$ .

Figure 3 shows the mass variation during the potentiodynamic experiments of Fig. 2. During the anodic sweep in the  $\text{KClO}_4$  and CsCl electrolyte solutions, the mass of the polymer film decreased and then stabilized. During the cathodic sweep the mass increased and returned to its initial value. In the KCl electrolyte solution, the mass variation was different from that observed in the case of  $\text{KClO}_4$  and CsCl electrolyte solutions; during oxidation above 0.2 V (vs. SCE) the mass of the film increased indicating an anion insertion. Furthermore, a net gain in the mass of the polymer film was observed at the end of the cathodic sweep.

These mass variations suggest that the cations of the electrolyte, and not the anions, play the major role in the redox process; the cations are expelled and inserted during oxidation and reduction, respectively. However, to rationalize the difference in behavior of the polymer film in each electrolyte it is also necessary to consider the role of the anions. The observed difference in the electrogravimetric behavior of a polymer film in electrolytes containing the same anion can be explained in the following manner. In both solutions there is an anion/cation insertion/expulsion process at the end of the anodic sweep. With KCl and CsCl electrolytic solutions, the anion insertion process occurring at the end of the anodic sweep is masked by the cation expulsion process because the weight of the cation exceeds that of the chloride ion. In contrast, when cycling in the  $\text{KClO}_4$  electrolyte the anion insertion is clearly observed



**Figure 2.** Cyclic voltammograms recorded at  $v = 20 \text{ mVs}^{-1}$  for a PPyDBS film (estimated thickness of  $2.5 \mu\text{m}$ ) in 0.1 M (—) KCl, (---)  $\text{KClO}_4$  and (.....) CsCl solutions.



**Figure 3.** E- $\Delta m$  potentiodynamic profiles recorded during the voltammetric sweeps of Fig. 2, in 0.1 M (—) KCl, (---) KClO<sub>4</sub> and (.....) CsCl solutions. Letters a, b, c and d correspond to the redox waves indicated in Fig. 2.

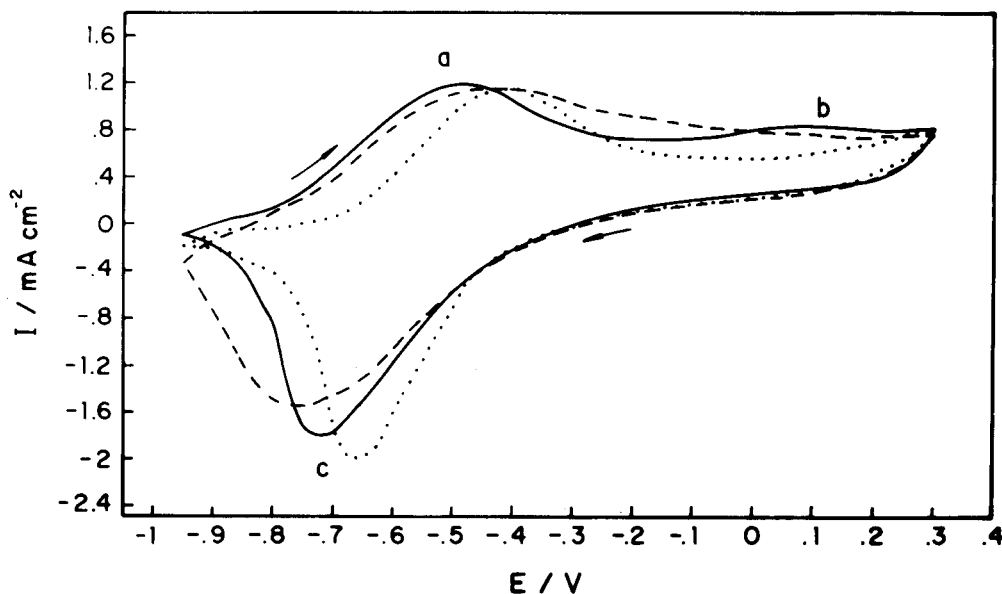
because the weight of the anion is significantly greater than that of the potassium cation.

#### PBD experiments

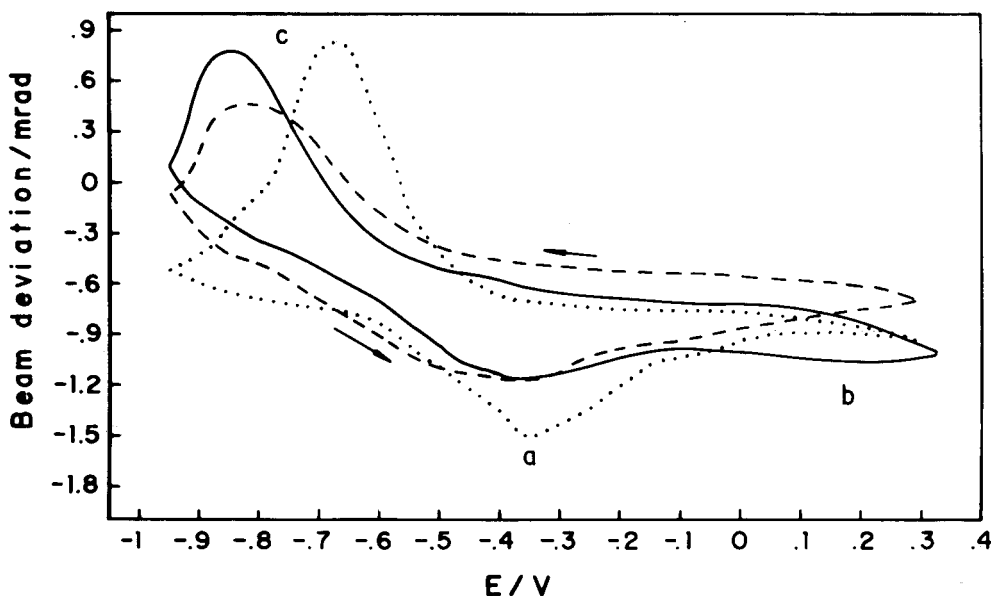
The relationship between the angular deviation,  $\theta$ , and the flux density of the ionic species that participate in the diffusional processes,  $J_i$ , is:  $\theta = -\sum h_i J_i$  13,14 for each species  $i$ , contributing to the beam deviation, where  $h_i$  is proportional to the variation of the refractive index with the concentration, and is normally positive. If a species diffuses

from the polymer into the solution,  $J_i > 0$ , the refractive index of the bulk solution will be smaller than that in the interface. This results in a negative deviation of the laser beam.

Figures 4 and 5 represent the cyclic voltammograms and PBD signals, recorded simultaneously with the linear scan voltammetry at  $20 \text{ mVs}^{-1}$ , for PPy/DBS films (estimated thickness of  $2.5 \mu\text{m}$ ). In the cyclic voltammograms the second transfer process is less distinct than in Fig. 2, where the studied film was thicker. The PBD curves



**Figure 4.** Cyclic voltammograms recorded, at  $v = 20 \text{ mVs}^{-1}$  for a PPy/DBS film (estimated thickness of  $0.16 \mu\text{m}$ ) in 0.1 M (—) KCl, (---) KClO<sub>4</sub> and (.....) CsCl solutions.



**Figure 5.** E- $\theta$  potentiodynamic profiles recorded during the voltammetric sweeps of Fig. 4, in 0.1 M (—) KCl, (---) KClO<sub>4</sub> and (.....) CsCl solutions. Letters a, b and c correspond to the redox waves indicated in Fig. 3.

are similar for the three experiments. During the anodic sweep between -0.95 V and the potential of the first transfer oxidation peak, the negative deviation of the laser beam shows that the predominant process occurring involves the movement of species from the film into the solution. Therefore, the predominant process is the expulsion of cations. After the first oxidation peak, the PBD negative deviation decreases, indicating that either the cations cease to flow out of the film and/or that anions enter the film. However, for the KCl electrolyte a further negative PBD deviation was observed before the second oxidation peak, showing a further expulsion of the cations which ceases at the end of the cycle. The behavior during the cathodic sweep is the inverse, *i.e.* the positive deviation of the laser beam shows that the cations are reinserted into the film and cease their inflowing motion after the reduction peak of the first electron transfer.

In a previous investigation<sup>14</sup> we established that if the current varies linearly with the scan rate, and the laser beam deviation is proportional to the square root of the scan rate, there is no kinetic delay due to the film and only the diffusion process is responsible for the beam deviation. This was confirmed for the PPyDBS films by carrying out cyclic voltammetry at different scan rates (5, 10, 20, 50, 80, 100 mVs<sup>-1</sup>) and simultaneously following the laser beam deflections.

## Conclusions

Using the three complementary techniques, Cyclic Voltammetry, Mirage Effect (Probe Beam Deflection) and Electrogravimetry (Quartz Crystal Microbalance), made possible the qualitative analysis of the ionic species that

participate in the diffusional processes in the redox reactions of PPy/DBS. These results show that the dopant (DBS<sup>-</sup>) is immobilized in the polymer matrix and charge electroneutrality is maintained by the diffusion of electrolytic ions. The results show that the cations are the predominant diffusing species in the redox process of PPyDBS. The nature of both the cations and ions affected the voltammogram shapes, redox peak potentials and currents.

Further work based on the PBD technique is currently in progress in our laboratory in an attempt to obtain quantitative information about diffusion phenomena and variations of the refractive index with electrolyte concentrations. Further results will be published shortly.

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