

# Electrochemical adsorption of a cationic cellulosic polymer by ion pair formation at the interface between two immiscible electrolyte solutions



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## ABSTRACT

The adsorption/desorption process of cationic cellulose polyquaternium-4, PQ4 (Celquat® L-200), at a water/1,2-dichloroethane interface, was investigated using cyclic voltammetry, spectroelectrochemistry, surface pressure–molecular area isotherms and contact angle measurements. The effect of potential and time of polarization, as well as the nature and concentration of the organic electrolyte was analyzed and correlated with the organization of PQ4 at the interface.

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## 1. Introduction

Polyquaternium-4 (PQ4, Scheme 1) is a cationic hydroxyethyl-cellulose dimethyl diallylammonium chloride copolymer with quaternary ammonium groups. This polysaccharide has been widely used in drug and DNA delivery systems [1–3]. The high bioadhesive capacity and low toxicity of these polyelectrolytes make them good candidates for cosmetic and topical preparations combining long residence times at the application site with adequate mechanical properties. For these reasons, the study of surface properties of these substances on diverse interfaces, employed for modeling biological membranes, has been a topic of growing interest. Among them we can mention the solid/liquid, the air/water and the liquid/liquid interfaces.

The first study of polyelectrolyte adsorption at liquid/liquid interfaces was carried out by Osborne et al., who reported Nafion® adsorption with two different adsorbed forms corresponding to a morphological difference associated with the adsorption in the mixed solvent layer [4]. Later, the interfacial behavior of several polyelectrolytes as well as their interactions with different ions at liquid/liquid interfaces has been studied by different authors [5–11]

and much attention has been paid to the investigation of biopolymers adsorption including a polysaccharide heparin [12–16], and the proteins protamine [17–20], insulin [21], hemoglobin [22,23], myoglobin [24], melittin [25], cytochrome c and ribonuclease A [20,26]. Another research topic is that focused on the study of the interactions between polyelectrolytes and membrane components such as phospholipid molecules adsorbed at liquid/liquid interfaces [27,28] or nanoparticles [29].

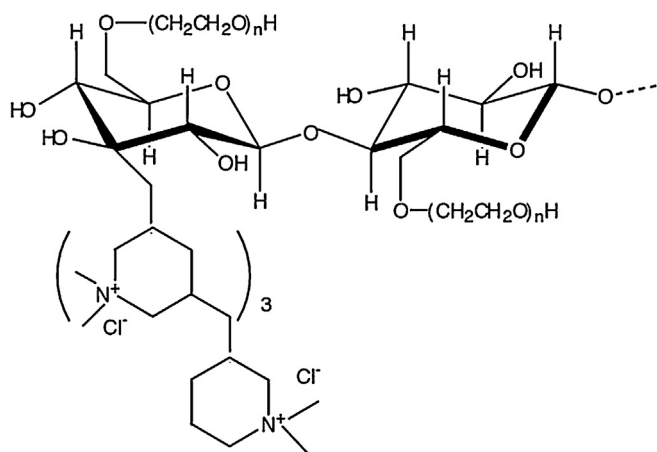
In the present paper we report the voltammetric behavior of polyquaternium-4 (PQ4, Celquat® L200) and, by the combination of several techniques such as cyclic voltammetry, spectroelectrochemistry, surface pressure–molecular area isotherms and contact angle measurements, we postulate the role of organic counter ion and the possible conformation adopted by the polymer at the interface.

## 2. Experimental

### 2.1. Materials and electrochemical cells

All experiments were performed in a four-electrode system using two conventional glass cells of 0.18 cm<sup>2</sup> or 0.83 cm<sup>2</sup> interfacial area for voltammetric or spectroelectrochemical experiments respectively. In both cases, two platinum wires were used as counter-electrodes and the reference electrodes were Ag/AgCl. The reference electrode in contact with the organic solution was

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**Scheme 1.** Molecular structure of the cationic cellulose polyquaternium-4, PQ4 (Celquat® L-200).

immersed in an aqueous solution of 0.010 M tetraphenylarsonium chloride (TPhAsCl) (Sigma) or 0.010 M tetrapentylammonium bromide (TPnABr) (Fluka) + 0.010 M LiCl (Merck p.a.).

The base electrolyte solutions were 0.010 M LiCl (Merck p.a.) in ultrapure water (Milli-Q RiOs 16, Millipore) and tetraphenylarsonium dicarbollylcobaltate (TPhAsDCC) at concentration values in the range between 0.001 M and 0.100 M or 0.010 M tetrapentylammonium tetrakis (4-chlorophenyl) borate (TPnATCIPhB) in 1,2-dichloroethane (DCE, Dorwil p.a.). TPhAsDCC and TPnATCIPhB were prepared by metathesis of TPhAsCl (Sigma) and sodium dicarbollylcobaltate (NaDCC, Strem Chemicals) or TPnABr (Fluka) and potassium tetrakis (4-chlorophenyl) borate (KTCIPhB) respectively. The precipitates were recrystallized from water:acetone mixtures and then dried in an oven at 30 °C for two days.

The polyelectrolyte PQ4 (Celquat® L-200, chloride salt) from National Starch and Chemicals (New Jersey) was added to the aqueous phase at concentrations between 0.025% (w/v) and 0.200% (w/v).

The electrochemical cell used was as follows:

Ag	AgCl	TPhAsCl or TPnABr + LiCl 0.010 M (w)	TPhAsDCC 0.001–0.100 M or TPnATCIPhB 0.010 M (o)	LiCl 0.010 M + PQ4 x% (w/v)  (w)	AgCl	Ag
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## 2.2. Methods

### 2.2.1. Cyclic voltammetry

Cyclic voltammetry and potential pulse experiments were performed using a four-electrode potentiostat, which automatically eliminates the IR drop by means of a periodic current-interruption technique [30]. A wave potential generator (PPR1 Hi-Teck Instruments, UK) and a 10 bit Computer Boards acquisition card connected to a personal computer were also employed.

The potential values  $E$  reported in the voltammograms are the applied potentials between the two Ag|AgCl reference electrodes which are related to the Galvani potential difference ( $\Delta_0^w \varphi$ ) across the interface by

$$E = (\Delta_0^w \varphi) + \Delta E_{\text{ref}}$$

where  $\Delta E_{\text{ref}}$  depends on the reference electrodes and the reference solutions employed.

### 2.2.2. Spectroelectrochemistry

UV-vis absorption spectroelectrochemical experiments were performed according to the parallel beam configuration [31]. The light beam, produced by a white light LED source (LS-1 Ocean Optics), was collimated at the electrochemical interface and directed from the cell to the detector using silica optical fibers (diameter: 600  $\mu\text{m}$  Ocean Optics). Transmission or absorbance spectra were recorded with an HR2000-Ocean Optics spectrometer optimized for the visible range (400–750 nm). The collimated light beam directed to the cell was parallel to the interfacial plane. A small fraction of the light beam, passing through the aqueous phase, is refracted away the interface while the remaining cross section of the beam passed through the organic phase and directed to the spectrometer. In this way, we ensured that the light beam was sensing the organic side of the interface and there was no gap between the interfacial plane and the light beam. Also, as the light beam was bigger than the Nernst diffusion layer, the full interfacial region, with changes of the optical properties, was sensed.

The spectroelectrochemical curves were recorded sampling the organic boundary layer adjacent to the interface during a potential sweep between 0.150 and 0.750 V.

Absorption spectra measurements of aqueous solutions containing 0.010 M NaDCC in absence or in the presence of PQ4 and organic solutions containing 0.010 M TPhAsDCC, were performed on a 1601 Shimadzu UV-vis spectrophotometer, previous to spectroelectrochemical experiments, with the aim of determining the wavelength of maximum absorption ( $\lambda_{\text{max}}$ ) and the molar absorption coefficient,  $\varepsilon$ , for the anion  $\text{DCC}^-$ , in both media. In this way the resulting values were  $\lambda_{\text{max}} = 450 \pm 1 \text{ nm}$  and  $\varepsilon = 355 \pm 3 \text{ M}^{-1} \text{ cm}^{-1}$  regardless of the solvent used and the presence of PQ4.

### 2.2.3. Monolayers at the air–water interface

Surface pressure–area isotherms were recorded with a Mini-trough II from KSV Instruments Ltd. (Helsinki, Finland). The surface tension was measured according to the Wilhelmy plate method, using a platinum plate.

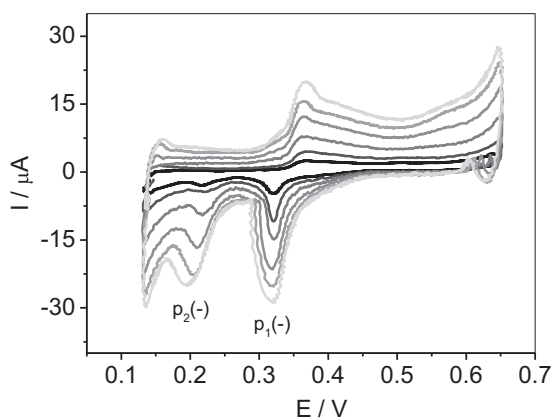
The aqueous subphase, contained in a Teflon trough (364 mm  $\times$  75 mm effective film area), was a 0.010 M LiCl solution.

To prepare PQ4 monolayers at the air–water interface, 35  $\mu\text{L}$  of 0.025% (w/v) PQ4 solution, in water:methanol 1:3, was carefully spread on the surface with a Hamilton micro-syringe. In other experiment a solution containing PQ4/NaDCC mixture was spread on the aqueous surface to evaluate differences in adsorption properties of the polyelectrolyte in its positively charged form or partially neutralized by  $\text{DCC}^-$ . In this case, the volume injected ensured that the molecules of PQ4 spread were kept constant. Before spreading PQ4 or PQ4/NaDCC solutions, the surface of the aqueous subphase was cleaned by sweeping it with a Teflon barrier and then, all surface contaminants were removed by suction from the interface. Cleaning of the surface was checked by recording an isotherm in the absence of PQ4 and verifying a surface pressure value lower than 0.1 mN/m. After spreading, 10 min were allowed for the solvent to evaporate, and then the film was compressed using two barriers, one on each side of the trough, at a compression speed of 5 mm/min while automatic measurement of the lateral surface pressure ( $\pi$ ) was carried out.

All experiments were performed at a temperature of  $25.0 \pm 0.1 \text{ }^\circ\text{C}$ .

### 2.2.4. Contact angle measurements

Contact angles were measured using the sessile drop method with an instrument developed in our laboratory [32]. The analysis of the drop shape and the determination of contact angle values were performed employing an image analysis program. Five measures were carried out for each sample. An aqueous solution containing 0.010 M LiCl and 0.500% (w/v) PQ4 was used to generate the drop,



**Fig. 1.** Cyclic voltammograms for PQ4 at the water/1,2-dichloroethane interface. Aqueous phase composition: 0.010 M LiCl + 0.050% (w/v) PQ4. Organic phase composition: 0.010 M TPhAsDCC.  $\nu = 0.005, 0.010, 0.025, 0.050, 0.075,$  and  $0.100 \text{ V s}^{-1}$ .

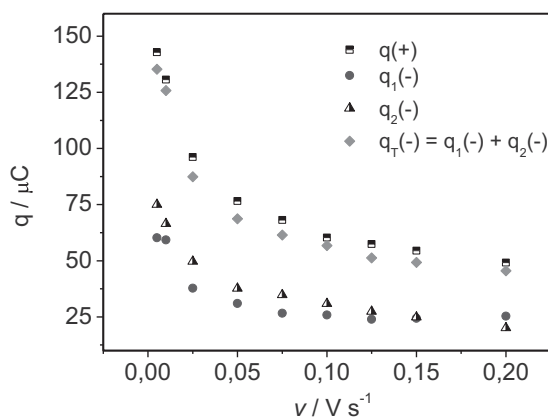
while the solvent DCE gelled with 10.0% (w/v) PVC of high molecular weight with or without 0.020 M TPhAsDCC was employed as support.

### 3. Results and discussion

#### 3.1. Cyclic voltammetry

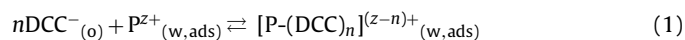
Fig. 1 shows the voltammetric profiles obtained when PQ4 was added to the aqueous phase at a concentration value equal to 0.050% (w/v). During the positive sweep several charge transfer processes take place, while in the negative sweep two well defined current peaks,  $p_1(-)$  at 0.320 V and  $p_2(-)$  at more negative potentials, are observed. The general shape of the profile and the shift of  $p_2(-)$  toward more negative potentials with increasing the scan rate, suggest that the transfer process for PQ4 could involve an activation-controlled interfacial adsorption/desorption mechanism. The first evidence for this hypothesis is the linear dependence of peak current with sweep rate,  $\nu$ , for both negative processes,  $p_1(-)$  and  $p_2(-)$ , when the positive scan is carried out at constant sweep rate while the negative one is performed at different scan rates (data not shown).

With the aim of checking the reversibility of the global process, the total charge accumulated on the forward and reverse scans were calculated from the voltammograms in Fig. 1 and is depicted in Fig. 2 as a function of  $\nu$ . As it can be noted the total



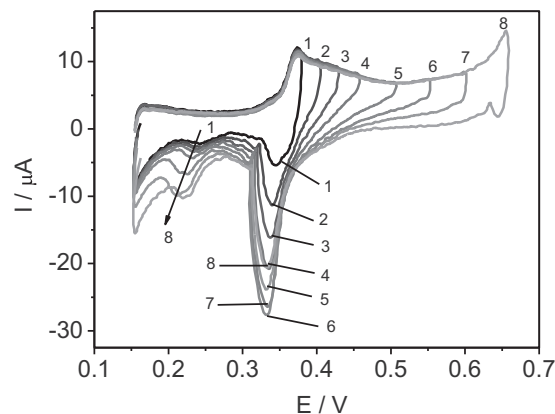
**Fig. 2.** Plot of charge values vs  $\nu$  calculated from voltammograms in Fig. 1 for the positive sweep,  $q(+)$ , and for both processes in the negative sweep,  $q_1(-)$  and  $q_2(-)$ . The total charge in the negative sweep  $q_{T(-)} = q_1(-) + q_2(-)$  is also included.

charge of the positive processes,  $q(+)$ , almost cancels out with the charge resulting from the sum of both negative processes ( $q_{T(-)} = q_1(-) + q_2(-)$ ). Considering the value of charge  $q = 80 \mu\text{C}$ , obtained at  $\nu = 0.050 \text{ V s}^{-1}$ , which is in the middle of the range of calculated charge values, the molecular weight of PQ4 (100,000 g/mol) and the amount of charged groups per mass unit in the polymer ( $1.54 \times 10^{-3} \text{ mol/g}$ , determined by titration), it can be calculated that  $5.38 \times 10^{-12} \text{ mol}$  ( $3.24 \times 10^{12}$  molecules) of polymer are adsorbed. Nevertheless, taking into account the interfacial area ( $A = 0.18 \text{ cm}^2$ ), a molecular area of  $5.55 \text{ nm}^2/\text{molecule}$  is obtained. This value seems to be too small considering the size of these macromolecules, whose reported hydrodynamic diameters values are higher than 100 nm [1]. Similar conclusions could be drawn considering the analysis developed by Herzog et al. [33] based on the comparison between the experimental and the theoretical surface coverage corresponding to a close-packed monolayer ( $\Gamma_{\text{exp}}$  and  $\Gamma_{\text{mon}}$  respectively). According to the experimental  $q$  value obtained in the present paper and the interfacial area, the calculated surface coverage  $\Gamma_{\text{exp}}$  is equal to  $2.99 \times 10^{-11} \text{ mol cm}^{-2}$ , while the theoretical value corresponding to a monolayer calculated according to [33], for a hydrodynamic radius value of 50 nm, is  $\Gamma_{\text{mon}} = 1.84 \times 10^{-14} \text{ mol cm}^{-2}$ . The comparison of both surface coverages indicates that more than a monolayer of polymer is adsorbed or that a smaller molecule is the responsible for the adsorption charge values. These results are the first evidence that the adsorbed species could be the organic anion,  $\text{DCC}^-$ , through a mechanism involving the electrochemical transfer of  $\text{DCC}^-$  from the organic phase to the aqueous side of the interface, where the polyelectrolyte,  $\text{P}^{z+}$ , accumulated or adsorbed, serves as a substrate for the adsorption of the transferred anions on the positive groups in the polymer, according to:



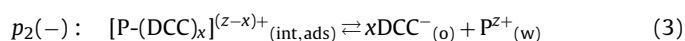
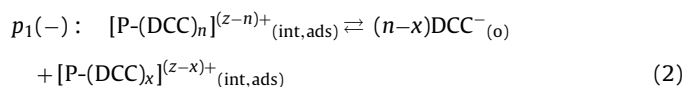
during the positive sweep. When the potential sweep is reversed, the adsorbed anions return to the organic phase through a desorption process, explaining in this way the linear dependence of peak current with  $\nu$ . The interfacial complex formation, according Eq. (1), has been also reported for lysozyme with several lipophilic ions [28,34].

Fig. 3 shows the  $i/E$  profiles resulting from reversing the sweep at successively more positive potentials,  $E_\lambda$ . As it can be noted, the current for  $p_1(-)$  increases with  $E_\lambda$ , reinforcing the hypothesis that the organic anion  $\text{DCC}^-$  plays a fundamental role in this process. Nevertheless, for  $E_\lambda$  values higher than 0.550 V, as the current for  $p_1(-)$  becomes lower, an important increase in current for



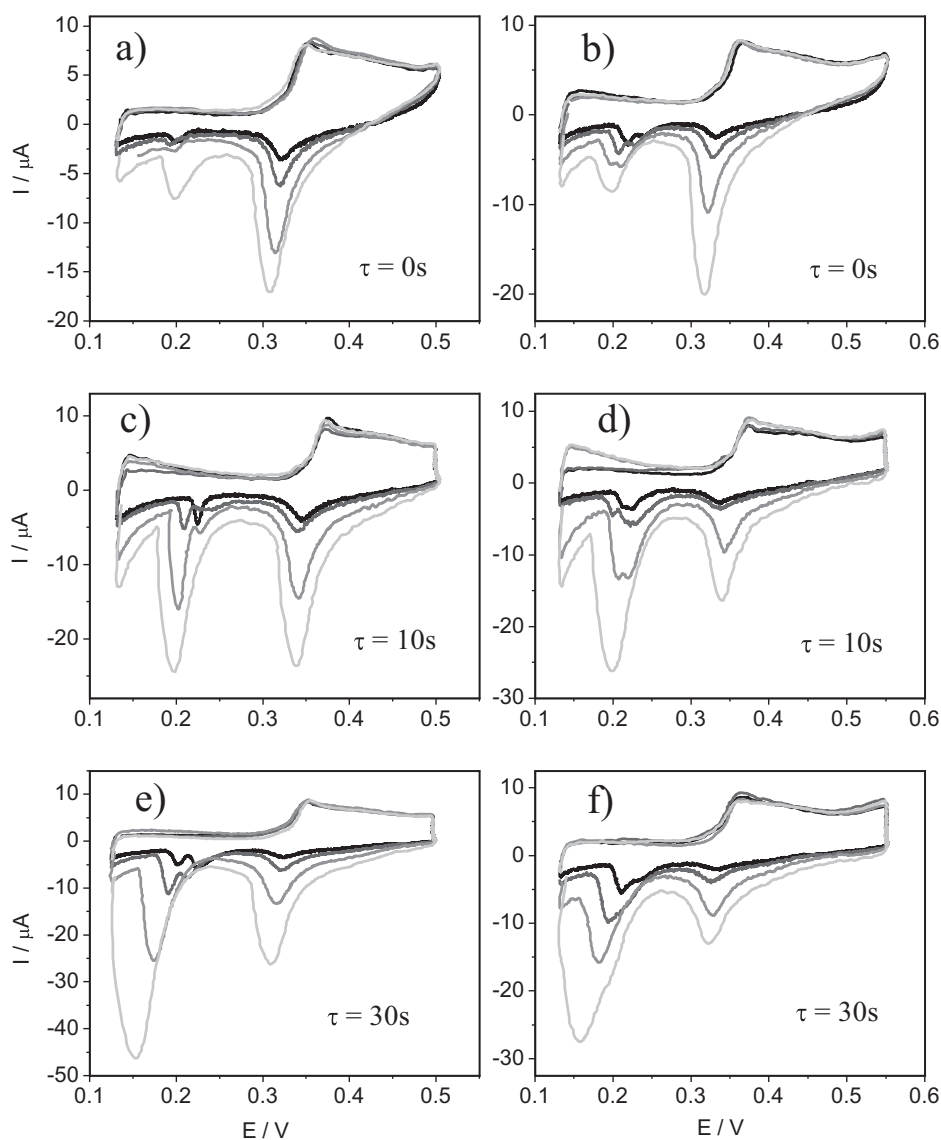
**Fig. 3.** Cyclic voltammograms for PQ4 at the water/1,2-dichloroethane interface, reversing the scan at successively more positive potentials,  $E_\lambda$ . Aqueous phase composition: 0.010 M LiCl + 0.050% (w/v) PQ4. Organic phase composition: 0.010 M TPhAsDCC.  $\nu = 0.050 \text{ V s}^{-1}$ .

$p_2(-)$  is evident together with a potential shift toward more negative values for this second process. One possible explanation for this result arises from considering that at high potential values, where the accumulation of  $\text{DCC}^-$  is enhanced, almost the complete neutralization of the polyelectrolyte occurs and, under these conditions, the  $[\text{P}-(\text{DCC})_n]^{(z-n)+}$  interfacial complex can reorganize and prevail adsorbed at both sides of the interface, with the more polar zones oriented to the aqueous phase and the hydrophobic fragments toward the organic one. In this way the processes corresponding to  $p_1(-)$  and  $p_2(-)$  are the partial desorption of  $\text{DCC}^-$  from the aqueous side of the interface toward the organic phase and the desorption of the cationic polyelectrolyte from organic side of the interface toward the aqueous phases respectively, according to:



The first desorption process, Eq. (2), is favored for low  $E_\lambda$ , while the second one, Eq. (3), prevails at high  $E_\lambda$ , where the interfacial concentration of  $\text{DCC}^-$  is high enough to neutralize almost all the positive charge in the polymer leading to the reorganization of adsorbed species and changing, consequently, their desorption energy value. Moreover, the shift of peak potential corresponding to  $p_2(-)$  toward more negative potentials with increasing  $\nu$  or  $E_\lambda$ , indicates that, as the interfacial coverage increases, the adsorption-desorption process becomes more irreversible.

To analyze the effect of negative sweep rate,  $\nu_{(-)}$ , under controlled interfacial conditions, voltammetric experiments at a constant positive sweep rate, ( $\nu_{(+)} = 0.010 \text{ V s}^{-1}$ ), were carried out for two different  $E_\lambda$  values (0.500 and 0.550 V, Fig. 4a and b). As it can be noted, the shift of  $p_2(-)$  toward more negative potentials with increasing  $\nu_{(-)}$ , takes place only for  $E_\lambda = 0.550 \text{ V}$ , i.e. for high coverages. This result is also observed when the potential is held for increasing periods of time ( $\tau$ ) at  $E_\lambda$  (Fig. 4c–f). Two important conclusions can be extracted from these figures: the potential shift produced by increasing  $\nu_{(-)}$  is enhanced at high  $\tau$  (high coverage) and the conversion of  $p_1(-)$  into  $p_2(-)$  is favored increasing



**Fig. 4.** Cyclic voltammograms for PQ4 at the water/1,2-dichloroethane interface recorded at a constant positive sweep rate, ( $\nu_{(+)} = 0.010 \text{ V s}^{-1}$ ) and two different  $E_\lambda$  values: 0.500 V (a, c and e) and 0.550 V (b, d, and f). Once  $E_\lambda$  was reached, the potential was held during different time,  $\tau$ : 0, 10 and 30 s, then the negative sweep was recorded at different scan rates,  $\nu_{(-)} = 0.005, 0.010, 0.025$  and  $0.05 \text{ V s}^{-1}$ . Aqueous phase composition: 0.010 M LiCl + 0.050% (w/v) PQ4. Organic phase composition: 0.010 M TPhAsDCC.

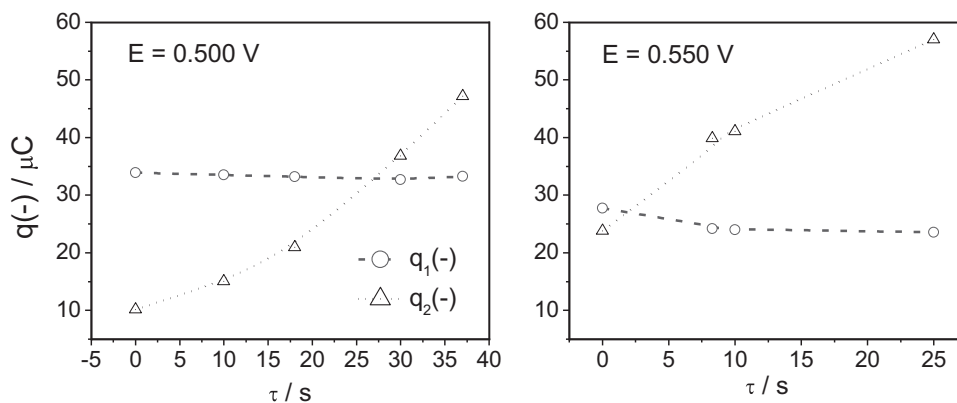


Fig. 5. Plot of charge values vs  $\tau$ , calculated from voltammograms in Fig. 4 for both processes in the negative sweep,  $q_1(-)$  and  $q_2(-)$ .  $E_\lambda = 0.500$  or  $0.550 \text{ V}$ .

$\tau$  and  $E_\lambda$ . Fig. 5 shows the charge values for  $p_1(-)$  and  $p_2(-)$ , calculated from experiments in Fig. 4, as a function of  $\tau$  at  $E_\lambda = 0.500 \text{ V}$  (a) or  $E_\lambda = 0.550 \text{ V}$  (b). As it can be seen, the charge corresponding to  $p_1(-)$  slightly decreases with  $\tau$ , while the charge associated with  $p_2(-)$  increases markedly. For both  $E_\lambda$ , the initial charge for  $p_1(-)$  is higher than that for  $p_2(-)$ , nevertheless as  $\tau$  increases this relation is inverted, being the time for this inversion lower in the case of  $E_\lambda = 0.550 \text{ V}$ . This finding supports the hypothesis about the interconversion of the negative processes, being the first process,  $p_1(-)$ , favored at low potentials and hold time, while the second one,  $p_2(-)$  requires high potentials or hold time, demonstrating a reorganization of the adsorbed species at the interface.

Fig. 6a and b shows the effect of changing the concentration of PQ4 in aqueous phase or  $\text{DCC}^-$  in organic phase respectively. As it can be noted in Fig. 6a the change in PQ4 concentration from 0.025 to 0.200% (w/v), maintaining the concentration of  $\text{DCC}^-$  in organic phase constant at a value 0.010 M, leads to a general increase in current values, i.e. a gradual increase in adsorption charges, but the general shape of the  $i/E$  profile is preserved with the presence of both processes  $p_1(-)$  and  $p_2(-)$ . On the contrary the increase in  $\text{DCC}^-$  concentration, from 0.001 to 0.100 M for PQ4 concentration equal to 0.05% (w/v), produces important changes in the shape of the voltammetric profiles, as can be observed in Fig. 6b. In this case, the current corresponding to  $p_1(-)$  decreases as  $\text{DCC}^-$  concentration increases and vanishes for  $\text{DCC}^-$  concentrations equal or higher than 0.100 M, while the process  $p_2(-)$  becomes the main one for these high concentration values. A possible explanation for this behavior can be found in the basic principles of adsorption of linear polyelectrolytes at interfaces [35]. The segments in an adsorbed polymer may be distributed over trains, loops and tails (Scheme 2), depending on the chain length, the quality of the solvent and ionic strength. It is expected that, for low  $\text{DCC}^-$  concentrations, trains segments predominate at the aqueous side of the interface and, upon polarization, the electrochemical transfer of  $\text{DCC}^-$  anions from the organic to the aqueous phase, followed by the adsorption of  $\text{DCC}^-$  to the positive sites in the polymer, occurs during the positive sweep, according to Eq. (1). When the scan is reversed, the subsequent desorption of  $\text{DCC}^-$  toward the organic phase,  $p_1(-)$ , according to the reverse of Eq. (1) takes place. At high  $\text{DCC}^-$  concentration in the organic phase or high potential values or long hold times, the excess of negative charge, neutralizes the positive sites in the polymer and more segments can be promoted to loops or tails formations toward the organic phase during the positive sweep, which desorbs in the negative sweep during the process  $p_2(-)$ , Eq. (3).

Fig. 7 compares the voltammetric profile obtained for 0.050% (w/v) PQ4 in aqueous phase and two different organic electrolytes in a concentration 0.010 M: TPhAsDCC and TPnATCIPhB.

The potential scales were corrected taking into account standard transfer potential values for both cations used in the organic phase,  $\Delta_\circ^w \varphi_{\text{TPhAs}^+}^0 = -0.364 \text{ V}$  and  $\Delta_\circ^w \varphi_{\text{TPnA}^+}^0 = -0.359 \text{ V}$  [36]. As it can be observed, during the negative sweep, the peak potential for  $p_1(-)$  is markedly dependent on the organic anion, indicating a main participation of this species in the process (desorption of  $\text{DCC}^-$  or  $\text{TCIPhB}^-$ ), on the contrary, the peak potential corresponding to  $p_2(-)$  is almost equal for both systems, demonstrating that the involved species could be the same in both cases (desorption of  $\text{P}^{z+}$  from the organic side of the interface to the aqueous phase).

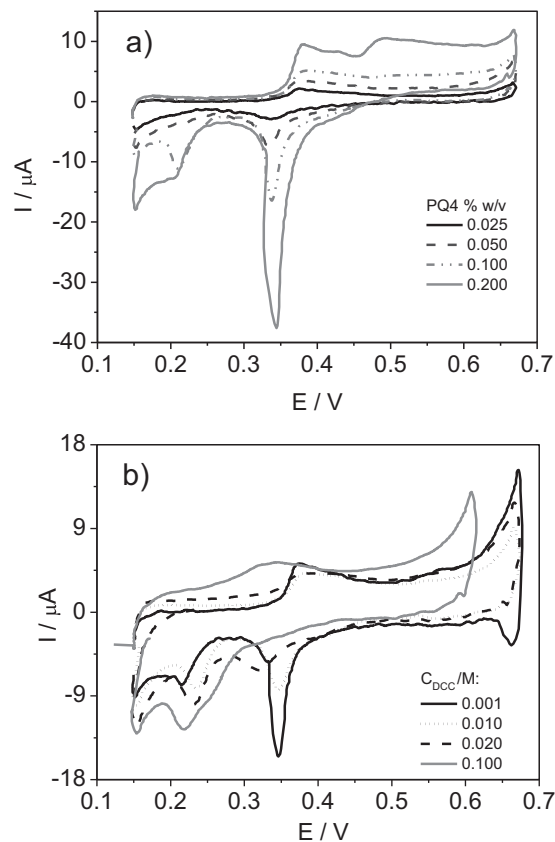
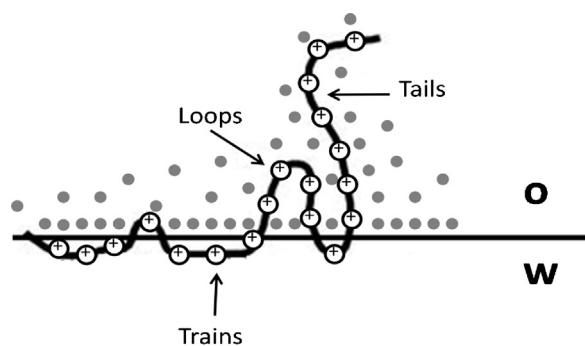
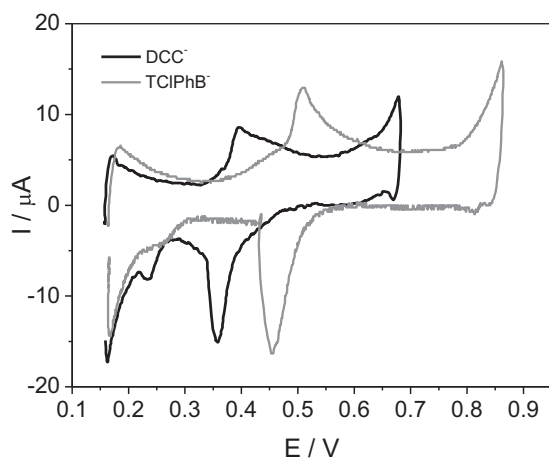


Fig. 6. Cyclic voltammograms changing the concentration of PQ4 at the aqueous phase (a) or the concentration of  $\text{DCC}^-$  at the organic phase (b). Aqueous phase composition: (a) 0.010 M LiCl + 0.025, 0.050, 0.100 or 0.200% (w/v) PQ4; (b) 0.010 M LiCl + 0.050% (w/v) PQ4. Organic phase composition: (a) 0.010 M TPhAsDCC; (b) 0.001, 0.010, 0.020, 0.100 M TPhAsDCC.  $\nu = 0.025 \text{ V s}^{-1}$ .



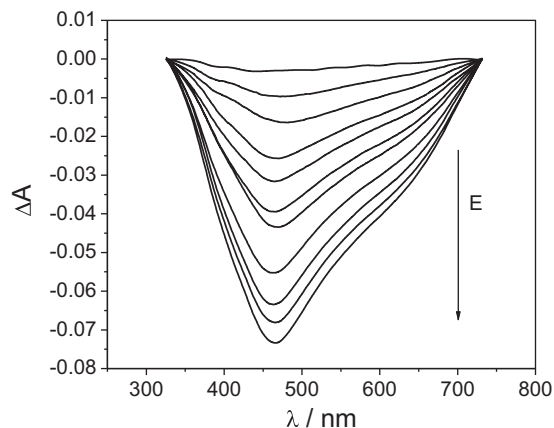
**Scheme 2.** Schematic model for PQ4 adsorption at the organic/water interface. Circles (●) represent the anions  $\text{DCC}^-$ .



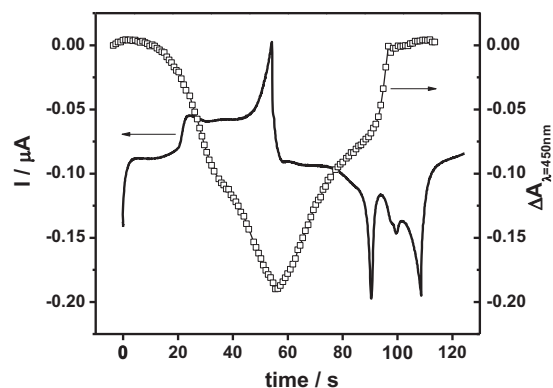
**Fig. 7.** Cyclic voltammograms for PQ4 at the water/1,2-dichloroethane interface changing the organic electrolyte. Aqueous phase composition: 0.010 M LiCl + 0.050% (w/v) PQ4. Organic phase composition: (a) 0.010 M TPhAsDCC; (b) 0.010 M TPhAT-ClPhB.  $\nu = 0.050 \text{ V s}^{-1}$ .

### 3.2. Spectroelectrochemistry

**Fig. 8** shows the UV–vis absorption spectra measured during a potential sweep between 0.150 and 0.750 V, sampling the organic boundary layer adjacent to the interface formed by the organic and aqueous base solutions.  $\Delta A$  values shown in the figure correspond to the difference between the absorbance measured during



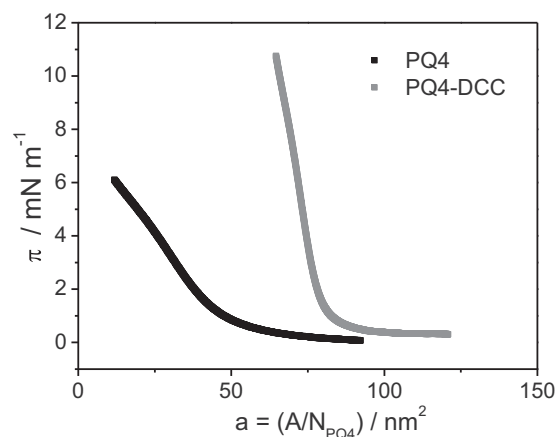
**Fig. 8.** UV–vis absorption spectra ( $\Delta A$  vs  $\lambda$ ) measured within the organic phase, during a potential sweep between 0.150 and 0.750 V at  $\nu = 0.010 \text{ V s}^{-1}$ . Aqueous phase composition: 0.010 M LiCl + 0.050% (w/v) PQ4. Organic phase composition: 0.010 M TPhAsDCC.



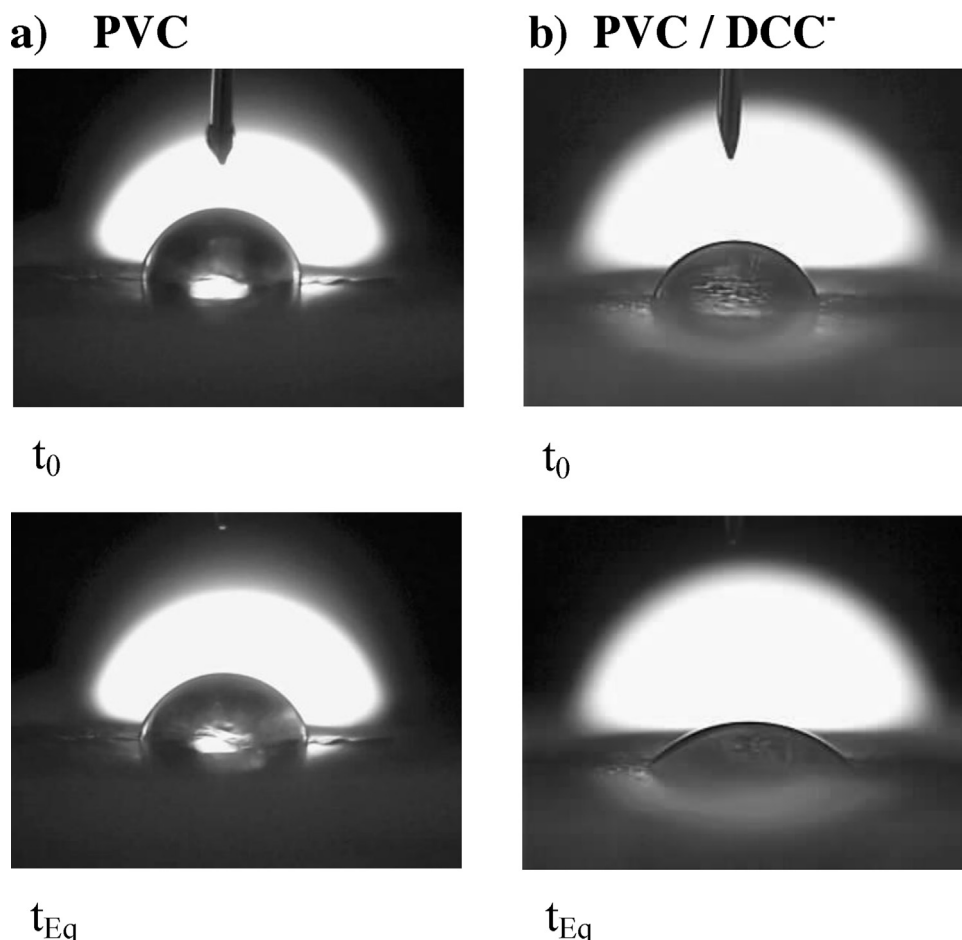
**Fig. 9.** Potentiodynamic  $i/t$  and  $\Delta A_{(\lambda=450 \text{ nm})}/t$  profiles for the system PQ4/ $\text{DCC}^-$  at the water/1,2-dichloroethane interface. Aqueous phase composition: 0.010 M LiCl + 0.050% (w/v) PQ4. Organic phase composition: 0.010 M TPhAsDCC.  $\nu = 0.010 \text{ V s}^{-1}$ .

the potential sweep and the absorbance recorded at open circuit, in this way the negative values of  $\Delta A$  obtained are indicating that the absorbance decreases when the polarization is applied. This decrease of absorbance observed in the organic phase is due to the transfer of  $\text{DCC}^-$  anions to the aqueous phase during the potential sweep. The wavelength of greatest absorbance,  $\lambda_{\text{max}} = 450 \text{ nm}$ , is the same than the observed for the absorption of  $\text{DCC}^-$  in aqueous or organic solutions.

**Fig. 9** shows the optical signal obtained during the positive and negative scans when the organic phase contained TPhAsDCC and the polymer PQ4 was present in the aqueous phase. As can be noted, the absorbance begins to decrease from potential (or time) values corresponding to the process described in Eq. (1), and continues decreasing during the positive sweep, reaching the maximum value at  $E_{\lambda}$ . When the scan is reversed, the absorbance begins to rise, to recover the initial value once the process  $p_1(-)$  has been completed. This result reinforces our hypothesis that only this process corresponds to desorption of  $\text{DCC}^-$  and transfer to the organic phase, while the process  $p_2(-)$  is due to the desorption of the fractions of polymer which penetrated into the organic phase and, as a consequence, no changes in the absorbance values are observed at these potentials.



**Fig. 10.** Surface pressure ( $\pi$ ) as function of the mean molecular area,  $a$ , for PQ4 monolayer at the air–water interface in presence and in absence of  $\text{DCC}^-$ . The  $x$ -axis variable,  $a$ , is calculated as:  $a = A/N_{\text{PQ4}}$ , where  $N_{\text{PQ4}}$  is the number of PQ4 molecules in the area  $A$ . Subphase composition: 0.010 M LiCl. To prepare the monolayer 35  $\mu\text{L}$  of 0.025% (w/v) PQ4 solution, with and without NaDCC, in water:methanol 1:3 was spread on the surface. Compression speed: 5 mm/min.



**Fig. 11.** Images obtained of aqueous sessile drop on the organic gel. Aqueous phase composition: 0.010 M LiCl and 0.500% (w/v) PQ4. Organic phase composition: 10.0% (w/v) PVC in 1,2-dichloroethane without (a) and with (b) 0.020 M TPhAsDCC.

### 3.3. Monolayers at the air–water interface

**Fig. 10** shows the surface pressure–molecular area isotherm obtained at 25 °C for the polyelectrolyte PQ4 in absence or in presence of NaDCC. In both cases the change in the slope observed in the isotherm corresponds to the liftoff due to the displacement of segments in the adsorbed state, during the compression, from predominantly trains configuration, at pressures lower than 5 mN/m (large area values), to loops formation at pressures between 5 and 20 mN/m (lower area values) [35]. It is worthwhile to clarify that collapse point was not reached in these experiments. As it can be observed the presence of DCC<sup>-</sup> favors this last configuration and produces an increase in the surface activity of the polymer, as it was deduced in preceding sections, from the electrochemical experiments, which pointed out that PQ4 prevailed at the aqueous side of the interface at low DCC<sup>-</sup> concentrations, while at high DCC<sup>-</sup> concentration it could penetrate and adsorb at the organic side.

### 3.4. Contact angle measurements

**Fig. 11** shows images obtained for determining the contact angle by the sessile drop method. With the aim of evaluating the effect of DCC<sup>-</sup> on PQ4 adsorption at the interface, experiments were carried out in presence or in absence of this anion in the organic gelled phase, which, in turn, constitute the holder for the aqueous drop. Images were recorded at several times elapsed from the injection of the drop ( $t=0$ ) up to the equilibrium time ( $t_{Eq}=20$  s), at which the shape of the sessile drop kept without changes. **Table 1** summarizes

**Table 1**

Contact angle values measured at zero or equilibrium time, on a support containing the organic phase with PVC or with PVC + TPhAsDCC.

Solid support	Contact angle (°) (time = 0)	Contact angle (°) (equilibrium time)
PVC	84.9	72.7
PVC/DCC <sup>-</sup>	79.4	48.5

the contact angle values obtained for both systems at  $t=0$  and  $t=t_{Eq}$ . We consider that  $t=t_{Eq}$  better describes the affinity between the polymer and the interface, so that, taking this consideration into account, data in **Table 1** indicate that the polymeric solution wets the organic gel more efficiently when DCC<sup>-</sup> is present, revealing the important role of interactions between the positive charges in the polymer and the organic anions, in agreement with the results described above.

## 4. Conclusions

The combination of cyclic voltammetry, spectroelectrochemistry, surface pressure–molecular area and contact angle measurements demonstrates that PQ4 adsorbs at an electrified liquid/liquid interface according to different configurations which depends on the potential and the concentration of the anion in the organic phase (DCC<sup>-</sup>). Taking into account the results obtained in the present paper, we propose the model shown in **Scheme 2** for the adsorption/desorption processes of PQ4. At low potentials and times of polarization, and low DCC<sup>-</sup> concentrations, the

polyelectrolyte adsorbs preferentially at the aqueous side of the interface in trains configuration. Upon polarization,  $\text{DCC}^-$  is transferred in the positive sweep from the organic phase and adsorbs on positive sites in the polymer. When the sweep is reversed a desorption process is evident in the negative sweep corresponding to the transfer of adsorbed  $\text{DCC}^-$  back to the organic phase. When high potentials values are applied to the interface during long polarization times or when  $\text{DCC}^-$  is present at high concentrations in the organic phase, the positive sites in the polymer are almost completely neutralized and these neutral segments can penetrate into the organic phase forming loops or tails. In these cases, another desorption process is evident in the reverse scan which account for the transfer of these segments back to the aqueous phase. In this way, the combination of electrochemical and spectroscopic techniques together with surface pressure–molecular area and contact angle measurements are a valid tool to evaluate the state of polymers at liquid/liquid interfaces.

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