



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



J.S. Riva, R. Iglesias, L.M. Yudi\*

INFIQC, Instituto de Investigaciones en Fisicoquímica de Córdoba, Departamento de Física Química, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Ala 1, Pabellón Argentina, Ciudad Universitaria, 5000 Córdoba, Argentina

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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].

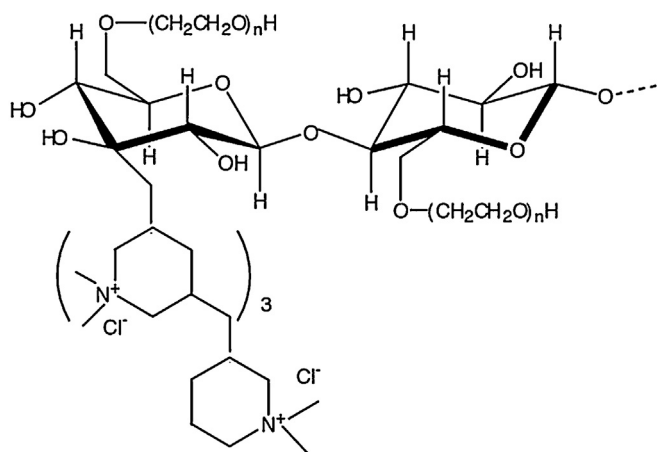
In the present paper we report the voltammetric behavior of polyquaternium-4 (PQ4, Celquat® L200) and, by the combination of several techniques such as cyclic voltammetry, spectroelectrochemistry, surface pressure–molecular area isotherms and contact angle measurements, we postulate the role of organic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

\* Corresponding author. Tel.: +54 0351 4334169/80; fax: +54 0351 4334188.  
E-mail addresses: [mjudi@fcq.unc.edu.ar](mailto:mjudi@fcq.unc.edu.ar), [mabelyudi@hotmail.com](mailto:mabelyudi@hotmail.com), [mabelyudi@gmail.com](mailto:mabelyudi@gmail.com) (L.M. Yudi).



**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,  $\epsilon$ , for the anion  $\text{DCC}^-$ , in both media. In this way the resulting values were  $\lambda_{\text{max}} = 450 \pm 1 \text{ nm}$  and  $\epsilon = 355 \pm 3 \text{ M}^{-1} \text{ cm}^{-1}$  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,

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