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Study of the zeta potential and streaming current of ultrafiltration membranes in contact with an anionic surfactant

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ABSTRACT

The controlled adsorption of surfactants on ultrafiltration (UF) membranes can modify their surface properties by increasing the fields of applicability. In this context, the understanding of the phenomena involved in the adsorption process of the surfactants is very important. The latter may be accomplished through measurements of the electrokinetic properties of the modified membranes under different conditions. Thus, this work is focused on the study of the streaming current and the zeta potential of polyethersulfone (PES) UF membranes modified with the anionic surfactant sodium dodecyl sulfate (SDS). The study was performed by measuring of the streaming current at the first contact between the membrane and the surfactant. The results obtained show that there are two zones of behavior, for the concentrations under and above the critical micelle concentration (CMC). In the first case a positive current was observed, meanwhile for the concentrations higher than the CMC the current observed was negative. Measurements of zeta potential of the modified membrane showed that the saturation of the membrane was reached at lower concentrations of SDS, and that the adsorption of the surfactant is taking place only on the membrane surface.

Keywords: Ultrafiltration; SDS; Zeta potential; Streaming current

1. Introduction

The adsorption of surfactants on different kind of solids had big attention due to their final applications: removal of pollutants, remediation processes, recuperation of specific compounds, etc. [1–8]. The properties acquired by the modified solid depend on different factors: surfactant properties and concentration, pH of the solution, solid morphology and charge, and concentration of electrolytes [4,5,7]. For example, the modification of ultrafiltration membranes (UF) by surfactant adsorption enlarges their possibilities of application. But the modification of their selectivity depends on the membrane nature as well as surfactant self-arrangement [9–14].

The charge of the membrane surface can be strongly modified by the surfactant adsorption. The surface charge can be obtained by an electrokinetic study: streaming current and zeta potential measurements. There are a few papers that report about this kind of measurements specially in the case of the

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adsorption of surfactants on the UF membranes [15,16].

Thus, this paper is a contribution for understanding the phenomenon of adsorption of the surfactants on UF membranes. To do this, a kinetic study at first contact was performed in order to follow the sodium dodecyl sulfate (SDS) adsorption on the surface membrane as well as the charge variations. This study has also the advantage that the classical adsorption studies are performed in a less time.

2. Theoretical background

UF organic membranes put in contact with an aqueous solution can acquire a surface charge. This surface charge is compensated by counter ions in the solution close to the surface, forming the electrical double layer (EDL). The Gouy-Chapman-Stern-Grahame model describes this charge distribution at the solid/liquid interface [15]. The EDL can be described as two layers: (1) the immobile layer where the charges are fixed on the surface and (2) the diffuse layer where the charges are in the electrolytic solution. The potential between the immobile and diffuse layer is called the zeta potential [15,17].

The movement of the electrolyte on the solid surface creates a streaming potential, having a direct relationship with the zeta potential by the Helmholtz–Smoluchowski equation [15,17,18].

$$\zeta = \frac{dU}{dp} \times \frac{\eta \times \lambda}{\varepsilon \times \varepsilon_0} \tag{1}$$

For planar samples where the surface area is known, the zeta potential can be calculated through the streaming current as follows:

$$\zeta = \frac{dI}{dp} \times \frac{\eta}{\varepsilon \times \varepsilon_0} \times \frac{L}{A} \tag{2}$$

where ζ represents the zeta potential, $\frac{dU}{dp}$ is the differential potential with respect to the differential pressure (streaming potential), $\frac{dI}{dp}$ the differential current with respect to the differential pressure (streaming current), η is the electrolyte viscosity, λ is the specific electrical conductivity of the electrolyte, ε is the permittivity of the solution, ε_0 is the vacuum permittivity, L is the length of the streaming channel, and A is the cross-section.

The charge on the membrane surface, as well as the streaming current and the zeta potential at the first contact between the surfactant solution and the membrane, can provide information on the surfactant adsorption process and allows us to understand the behavior of modified membranes. These parameters can be obtained by measuring the current at specific pressure as a function of time [16].

3. Experimental

3.1. Material and methods

3.1.1. Surfactant solutions

The anionic surfactant SDS, was purchased from Sigma–Aldrich with a purity ≥ 99%. The critical micelle concentration (CMC) of SDS was determined at 25.0°C by conductivity measurements reporting a value of 8.2 mM.

3.1.2. UF membranes and filtration set-up

The membranes used were KOCH UF flat-sheet membranes (HFK$^{\text{TM}}$-328). These membranes consisted of semi-permeable polyethersulfone (PES) on a polyester support with a molecular weight cut-off (MWCO) of 5,000 Daltons.

The membranes were washed before use in order to eliminate membrane preservatives (anti-fungal agents). The cleaning procedure consists of a cycle of milli-Q water—NaOH (3.2×10^{-4} M—1×10^{-3} M)—milli-Q water. Each stage of the cycle was performed between 20 and 30 min at room temperature in an open filtration system, which works with a module in tangential flow.

3.2. Methodology

3.2.1. Streaming Current and zeta potential measurements

The kinetic study at first contact was performed using the SurPASS electrokinetic analyzer (Anton Paar GmbH). All measurements were conducted with an adjustable-gap cell, which allows setting the distance between the two samples of the same membrane at 100 μm. The previously washed membranes were hydrated and cut into pieces of 20 × 10 mm, and then the samples were fixed on the sample holder with double-sided tape. The experiments were carried out at room temperature with 500 mL of KCl 1×10^{-3} M and pH 5.8.

In the kinetic study at first contact, a baseline with the electrolyte was initially obtained. After which, SDS solution at a specific concentration was passed through the system at constant pressure. The surface current variations were registered throughout the experiment in order to record the variations provoked by the surfactant adsorption at the first contact of the SDS solution with the membrane.

The zeta potential variation of the membrane brought into contact with SDS at different concentrations was also monitored. This experiment was performed using a single membrane section for all concentrations consecutively. The evaluation was conducted by the addition of SDS to the electrolyte in order to fix the concentration, after each addition the variation of the zeta potential was recorded. After registration of the membrane zeta potential variation, due to the presence of SDS, the desorption degree was evaluated through consecutive washes with KCl. The concentration of the electrolyte (1×10^{-3} M) in all experiments is maintained constant in order to avoid the contribution of the membrane support to the final measurement of zeta potential.

4. Results

The results obtained of the kinetic study at first contact (variation of the current as a function of time) at 0.4 and 40 mM of SDS are shown in Fig. 1, where the profile of the baseline is also included with the aim of showing clearly, the behavior of the system.

From Fig. 1 two kinds of behavior are observed. At 0.4 mM concentration of SDS, there is an increase in the current with respect to the baseline after 23 s. It is clear that the variation of the current is due to the presence of SDS in the system, which is adsorbed by the membrane. The consequence of the adsorption phenomenon is the increase in the streaming current (positive current) suggesting that the adsorption of the SDS monomers is carried out by the tail (aliphatic chain) leaving the negative-charged head toward the solution. On the other hand, at SDS concentration of 40 mM (Fig. 1b) three regions can be identified. At first an increase in the current is registered, followed by a decrease in the current (to negative values). It is important to say that 40 mM of SDS is higher than the CMC value, in these conditions there is an important quantity of micelles that increase the quantity of negative charges in the system resulting in a decrease in the current, even to negative values. Finally, at the third zone, the current takes positive values closer to that obtained with 0.4 mM of SDS, corresponding when the micelles are dragged out by the flow. Fig. 2 is a graphical representation of the interaction between the membrane channel and the electrolyte in the presence of SDS: for the baseline, when the current has positive values and when the current has negative values.

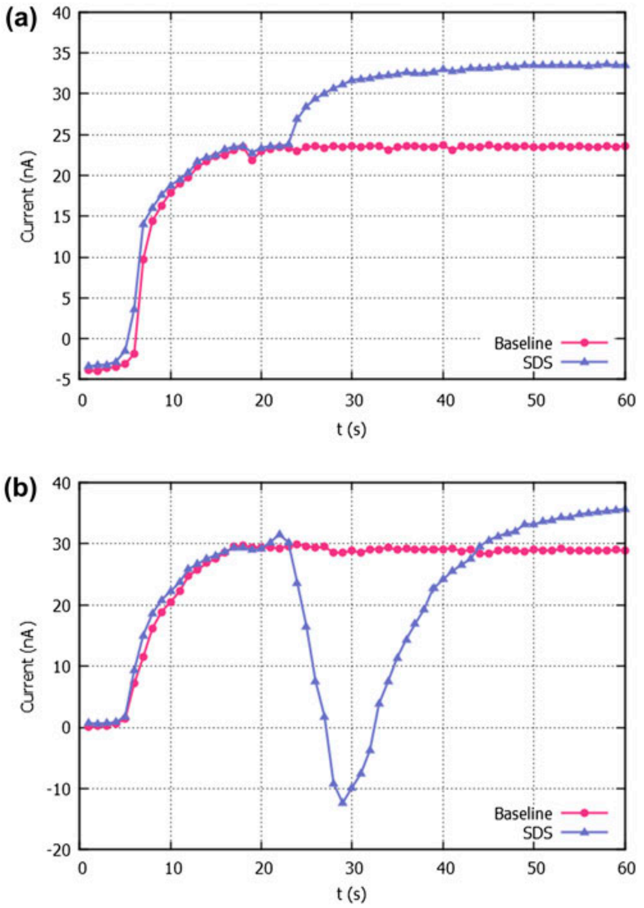

Fig. 1. Current variation as a function of time at first contact of SDS with an UF membrane: (a) [SDS] = 0.4 mM and (b) [SDS] = 40 mM. P = 200 mbar. Baseline: KCl 1.0 mM.

Fig. 2 (a) shows that the membrane in an aqueous media is negatively charged. In the presence of 0.4 mM of SDS (Fig. 2(b)), this one is adsorbed with the tail toward the membrane by increasing the number of negative charges on the membrane surface. When there is a flow in the system (at P constant), the positive counter ions migrate in the direction of flow creating a positive current. At 40 mM of SDS (Fig. 2(c)), the presence of micelles is important with a bigger number of negative charges in the solution, which migrate with the flow with an important increase in the current with negative values.

Fig. 3 shows the variation of the current as a function of time for different concentrations of SDS.

As can be seen in Fig. 3(a) the value of the current is positive in the entire range, reaching eventually a constant value after 15 s. In Fig. 3(b) it can be observed that greater is the concentration of SDS, larger is the value of the negative current for SDS concentrations equal to or greater than the CMC. After which the current rises up until its stabilization.

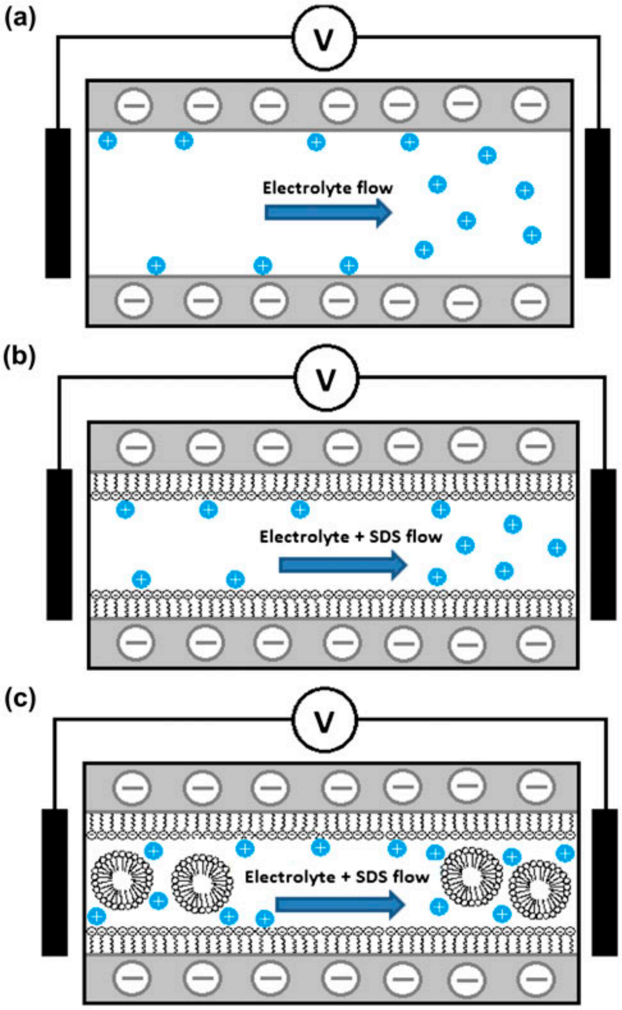

Fig. 2. Graphical representation of the interaction of the UF PES membrane channel with (a) KCl, (b) KCl + SDS 0.4 mM, and (c) KCl + SDS 40 mM. *P* = 200 mbar.

These results also show that below 1.4 mM of SDS, the maximum amount of SDS adsorbed in the membrane surface is achieved in the first 6 s and it is kept constant with time. The maximum amount of superficial charges increases with the concentration of SDS.

In Fig. 3(b), beyond 2 mM the initial adsorption is higher for the lower concentrations in the first 5 s, followed by the decrease in the current, being more pronounced, for higher concentrations due to the increase in the presence of micelles. The maximum amount of current is achieved in the last few seconds, after the rearrangements of the SDS monomer on the surface of the membrane.

The current values at the saturation point are almost the same, even at lower concentrations, indicating that the adsorption is taking place only in the surface area.

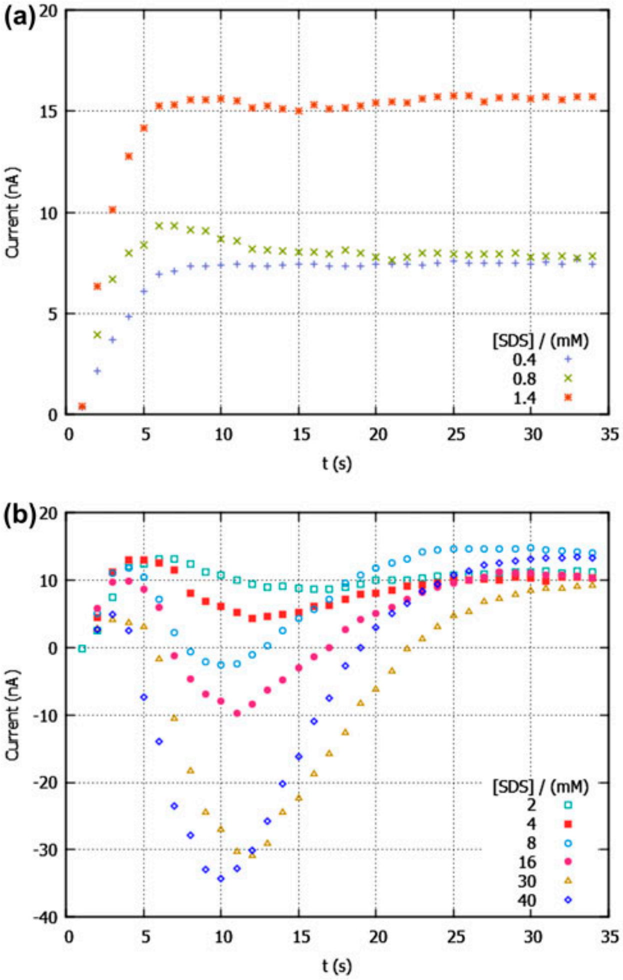

Fig. 3. Variation of the current of the modified membranes as a function of time for concentrations of SDS (a) lower than 1.4 mM and (b) higher than 2 mM. *P* = 200 mbar.

The relationship between the amount of SDS adsorbed and the net charge on the surface is presented in Fig. 4. The punctual charge was calculated using the electric current formula ($q(C) = \text{current}(A) \times \text{time}(s)$).

As can be seen in Fig. 4(a), a lineal relationship occurs at lower concentrations, changing this tendency with the SDS concentration. Fig. 4(b) shows a minimum increase on the charges in the first 5 seconds, followed by a decay of these ones with the augmentation of SDS concentration. Finally the charges rise to positive values.

Fig. 5 shows the variation of the superficial charge as a function of the SDS concentration at different times. (5, 13, and 34 s).

At 5 s the charge increases up to SDS concentration of 1.4 mM, followed by a decrease in the superficial charges when the SDS concentration increased. At 13 s, the behavior observed has the same trend than at 5 s. Nevertheless, the values of the superficial charge

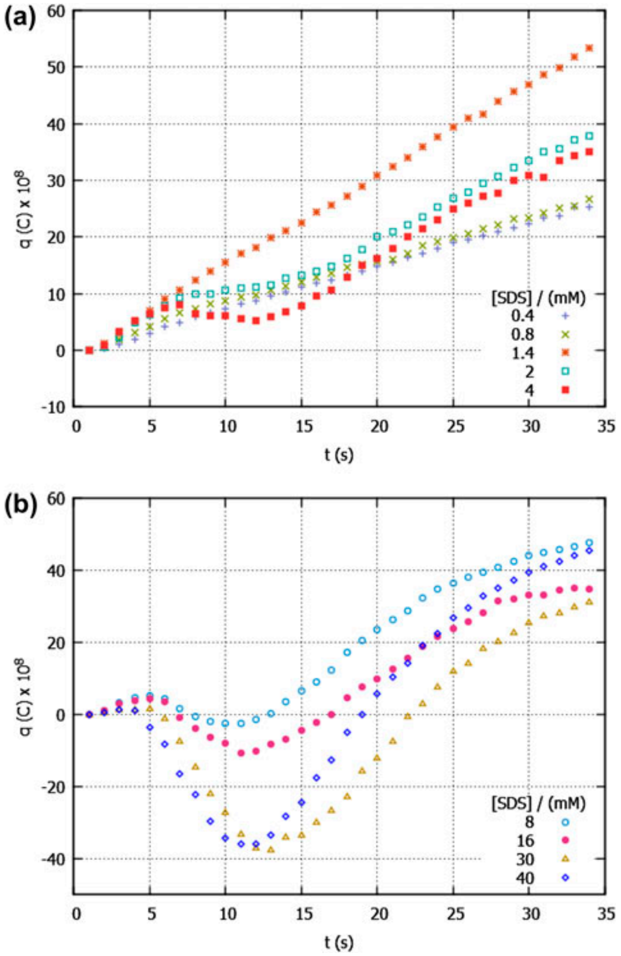

Fig. 4. Superficial charge of modified membranes as a function of time, at different SDS concentrations: (a) lower than the CMC and (b) higher than the CMC. P = 200 mbar.

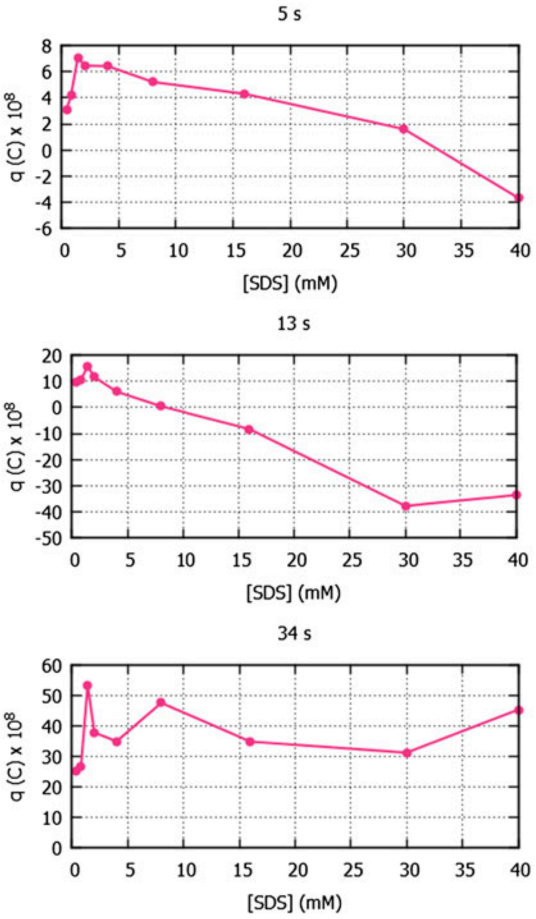

Fig. 5. Superficial charge of modified membranes as a function of the SDS concentration, at different times.

are more negative due to the presence of the micelles. The increase in the charges after 1.4 mM, here, is more pronounced than at 5 s. At 30 and 40 mM, the superficial charge is almost the same.

At 34 s, as well as the 5 and 13 s, the maximum of charge is found at SDS 1.4 mM, followed by a decrease in the superficial charges until 8 mM where the charge rise up again. After which the charges are stabilized, presenting similar values than at 2 mM and 4 mM.

These results indicate that the saturation of the membrane is found at 1.4 mM. The decrease in the charges after this saturation point suggests the surface neutralization of the charges by the same SDS monomers.

The variation of the zeta potential performed for a single membrane section in contact with SDS solutions at different concentrations was evaluated. As can be seen in Fig. 6, at lower concentrations a significant decrease in zeta potential was registered in

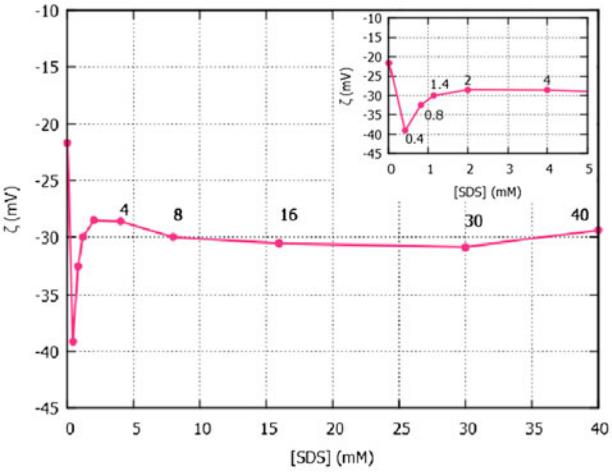

Fig. 6. Variation of zeta potential at equilibrium of modified membranes as a function of SDS concentration.

comparison with the clean membrane. Followed by a stabilization region, until it reaches an equilibrium over 2 mM, after which the zeta potential decreases slightly up to 8 mM. Finally the zeta potential is remained almost constant until high concentrations.

From the zeta potential at equilibrium it can be confirmed that the saturation of the membrane was reached at lower concentrations and the SDS adsorption is taking place only on the surface area. For this reason, the initial decrease in zeta potential is interpreted like the maximum negative charge. Then neutralization begins until equilibrium, which reaches at 2 mM. The decrease in zeta potential around the CMC is due the rearrangement of the adsorbed monomers at the membrane surface.

After the SDS adsorption, consecutive washes with KCl were performed to analyze the degree of desorption. At all concentrations the degree of desorption achieved was similar (zeta potential −23 mV). The zeta potential desorption value found is very close to the average clean membranes (−22 mV) indicating that the surfactant was entirely eliminated from the membrane surface.

5. Conclusions

The kinetic study shows that there are two zones behavior, for the concentrations under and above the CMC. In the first case a positive current was observed suggesting the adsorption of the SDS monomers by the aliphatic chain, meanwhile for the concentrations higher than the CMC the current observed was negative, this is due to the presence of micelles in the system, which were dragged out by the flow.

The current values at the saturation point are almost the same even at lower concentrations indicating that the SDS adsorption is taking place only in the surface area.

The punctual charge calculated from the kinetic data indicates that membrane saturation by SDS takes place at a concentration of 1.4 mM. The decrease in the charges after this saturation point suggests the surface neutralization of the charges by the same SDS monomers.

Measurements of zeta potential of the modified membrane showed that the saturation of the membrane was reached at lower concentrations of SDS, and that the adsorption of the surfactant is taking place only on the membrane surface.

Through these results it was also showed that even after the neutralization of the surface by the same surfactant, the membrane surface has more negative charges in comparison with the clean membrane, therefore the neutralization of charges is incomplete.

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List of symbols

ζ — zeta potential (mV)
$\frac{dV}{dp}$ — differential potential vs. differential pressure (streaming potential) (mV mbar^{-1})
$\frac{dI}{dp}$ — differential current vs. differential pressure (streaming current) (nA mbar^{-1})
λ — specific electrical conductivity of the electrolyte (μScm^{-1})
η — electrolyte viscosity (Pa s)
ε — dielectric coefficient of electrolyte
ε_0 — vacuum permittivity (C^2 J^{-1} m^{-1})
L — length of the streaming channel (m)
A — cross-section of the streaming channel (m)
q — charge (C)

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