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Electrokinetic characterization of composite membranes from streaming current measurements

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ABSTRACT

The effect of the streaming current flowing through the porous supports of composite membranes during tangential electrokinetic measurements was investigated theoretically. It was shown that neglecting this additional path for streaming current may have dramatic implications in the interpretation of the experimental data and on the determination of the membrane zeta potential. Experimental measurements of both streaming current and streaming potential were performed with a composite polymer membrane. By carrying out measurements for various channels heights it was possible to determine the streaming currents flowing through the channel and the membrane supports. This allowed us to assess separately the zeta potential of the membrane surfaces and that of their porous supports.

1. INTRODUCTION

Assessing the zeta potential of membranes is particularly attractive because this quantity is correlated with the mechanism of salt rejection. Moreover, zeta potential is very sensitive to any change in surface properties and it can therefore serve as a probe for various studies in material science dealing with adsorption phenomena, surface ageing, membrane fouling...

In membrane science, a standard method for zeta potential determination consists in the measurement of the streaming potential either through the membrane pores (transversal mode) or along the skin layer (tangential mode). However, several works have pointed out the difficulties associated with the interpretation of streaming potential data for the determination of zeta potential of composite membranes (Yaroshchuk 2002, Fievet 2003).

Alternatively, it has been proposed to measure the streaming current along the skin layer of membranes since its interpretation is complicated neither by surface conductance nor by conduction through the porous sublayers (membrane supports) of the membranes (Luxbacher 2006). However, it has been recently shown with monolayer porous membranes that a non negligible part of the streaming current may circulate through the membrane body (Yaroshchuk 2010). In this case, the zeta

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potential can no longer be obtained from a single streaming current measurement and its accurate determination requires performing a series of streaming current experiments with different channel heights.

In the first part of this work we shall illustrate theoretically the effect of the additional streaming current flowing through the membrane supports and we will show that neglecting it may have dramatic implications in the interpretation of the experimental data and on the determination of the membrane zeta potential. The additional streaming current due to the contribution of membrane supports can be viewed as a parasite signal which adds to the streaming current in the channel. Nevertheless, unlike streaming potential the dependence of streaming current coefficient on the channel height turns out to be linear, which makes possible to provide insight into the electrokinetic properties of both the top surface and the underlying support. This will be shown experimentally with a composite membrane consisting of a polyethersulfone layer on a polyester backing material.

2. THEORY

In the standard electrokinetic theory it is implicitly assumed that the channel through which electrokinetic measurements (streaming current and / or streaming potential) are performed has impermeable walls. In this case, and if the channel height (h_{ch}), i.e. the distance between the two identical membrane samples facing each other, is much larger than the Debye length, the streaming current (I_s) is linked to the zeta potential (ζ) by the following well-known relation:

$$I_s = -\frac{W h_{ch} \varepsilon_0 \varepsilon_r \Delta P}{\eta L} \zeta \tag{1}$$

where W is the channel width, ε_0 is the vacuum permittivity, ε_r the dielectric constant of the test solution, ΔP the pressure difference between channel ends, η the dynamic viscosity of the test solution and L the channel length.

Composite membranes consist of a skin layer on a porous support (which can be composed of one or several sublayers). If supports of the membrane samples are exposed to the hydrodynamic flow during electrokinetic experiments (it seems to be the case with measuring cells currently available with commercial electrokinetic analyzers), then a streaming current is likely to occur also within the porous supports. From an electrical point of view the system behaves as a parallel circuit and the experimental streaming current (I_s^{tot}) is therefore the sum of the current flowing through the channel (I_s^{ch}) and that flowing through the membrane supports ($I_s^{\sup}$). In this case Eq. (1) no longer holds and should be replaced by (Yaroshchuk 2010):

$$I_s^{tot} = I_s^{ch} + 2I_s^{\sup} = -\left(\frac{W h_{ch} \varepsilon_0 \varepsilon_r \Delta P}{\eta L} \zeta_{surf} + \frac{2W h_{\sup}^{eff} \varepsilon_0 \varepsilon_r \Delta P}{\eta L} \zeta_{\sup} \right) \tag{2}$$

where ζ_{surf} and $\zeta_{\sup}$ are the zeta potentials of the membrane surface and membrane support, respectively, and $h_{\sup}^{eff}$ the effective height on which the streaming current flows through a single membrane support ($h_{\sup}^{eff}$ depends on the structural features of the support, i.e. its thickness, porosity and tortuosity).

The electric conductance of the system (G_{cell}) is given by the ratio between the streaming current and the streaming potential (ΔV_s) and can be expressed as follows (provided that the surface conductance is negligible):

$$G_{cell} = -\frac{I_s^{tot}}{\Delta V_s} = \frac{H}{L}\left(h_{ch}\lambda_0 + 2h_{\sup}^{eff}\lambda_{\sup}\right) \tag{3}$$

where λ_0 and $\lambda_{\sup}$ are the electric conductivities of the test solution in the channel and in the porous supports, respectively.

3. EXPERIMENTAL SECTION

Composite membranes (HFK-131, Koch Membrane Systems) composed of a polyethersulfone skin-layer on a polyester support were used. Prior to measurements, membranes were washed with ultra pure water (milli-Q quality) and were sonicated (2x20 minutes) in order to remove preservatives.

A SurPASS (Anton Paar GmbH) electrokinetic analyzer was used to perform both streaming current and streaming potential measurements. All measurements were conducted with an adjustable-gap cell with which it is possible to vary the distance between the two membrane samples without dismounting the cell. Membrane samples (dimensions: L = 20 mm and W = 10 mm) were fixed on sample holders using double-sided adhesive tape. The channel height was varied between ~40 and 120 μm by means of micrometric screws and its value was determined from volume flow rate measurements by using the Hagen-Poiseuille relation. Streaming current and streaming potential were measured with a pair of Ag/AgCl electrodes by applying pressure differences up to 300 mbar in alternating directions (which helps to limit electrode polarization).

A 0.001 M KCl solution was used as the electrolyte and pH was adjusted with a 0.1 M HCl solution.

4. RESULTS AND DISCUSSION

Let us first consider a theoretical membrane whose surface and porous support have different electrokinetic properties. The pH dependence of the zeta potential of the surface and the support are shown in Figs. 1a and 1b by the full lines and the open symbols, respectively (the trends were chosen arbitrarily).

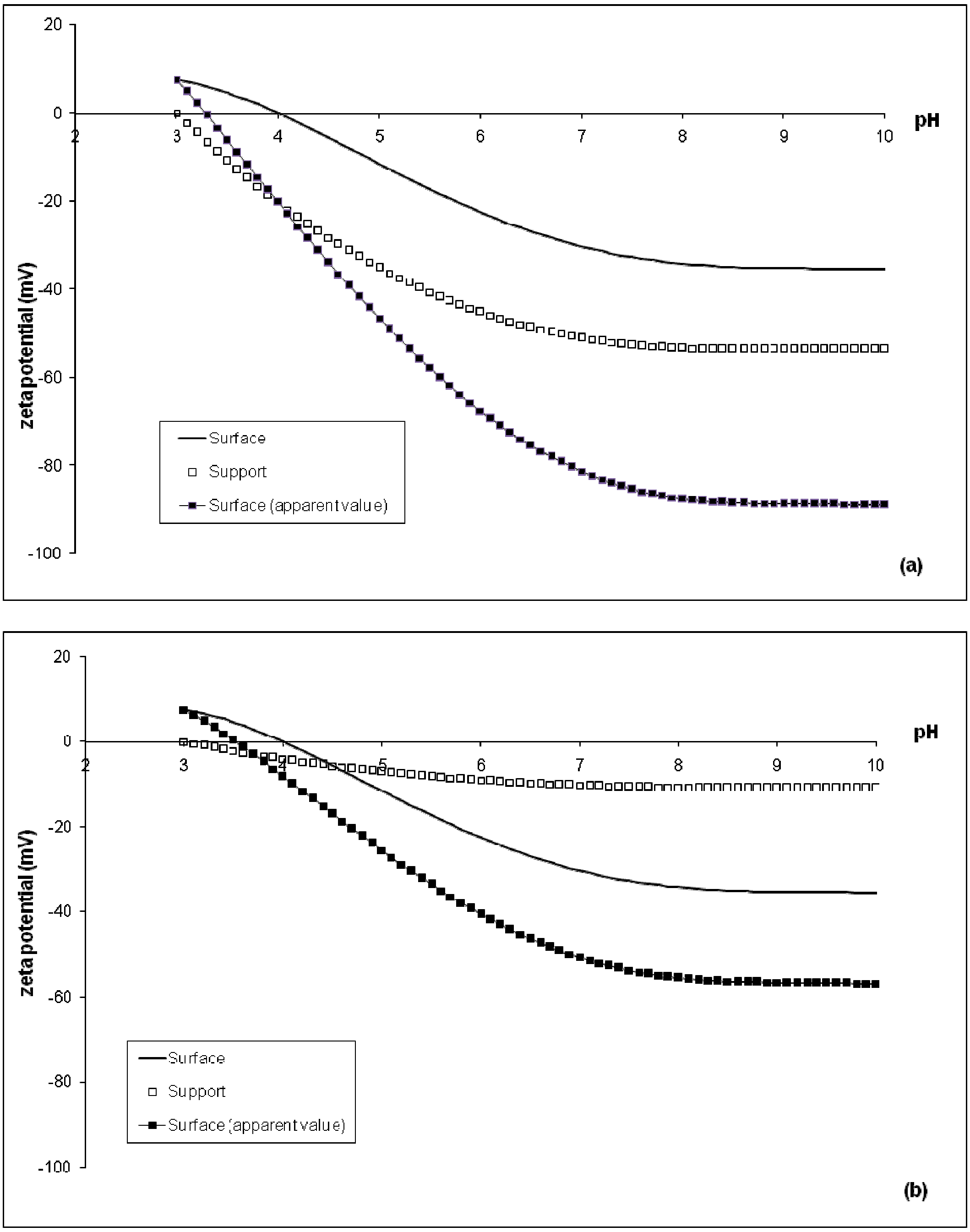

Fig. 1 pH dependence of the apparent zeta potential (i.e. computed from Eq. (1)) of the surface of theoretical membranes (full symbols) having support layers with different zeta potentials (open symbols) and comparison with the exact zeta potential of the membrane surfaces (full lines). Calculations were performed with $h_{\sup}^{eff} = h_{ch}$ = 100 μm.

Eq. (2) was then used to compute the total streaming current coefficient ($I_s^{tot}/\Delta P$), that is the experimental quantity that could be measured by performing experiments with a single channel height. In both figures we set $h_{\sup}^{eff} = h_{ch}$ = 100 μm.

In Figs. 1a and 1b we also show the pH dependence of the apparent zeta potential (closed symbols) that would be inferred from a streaming current experiment if the contribution of membrane supports to the total streaming current was not taken into account (i.e. if I_s^{tot} instead of I_s^{ch} was used in Eq. (1) to compute the zeta potential of the membrane surface). The comparison with the exact zeta potential of the membrane surfaces (shown by full lines in Figs. 1a and 1b) clearly shows that misleading conclusions, both in terms of zeta potential value and isoelectric point (i.e. the pH for which the zeta potential is zero), can be drawn if the streaming current flowing through the membrane supports is not taken into account. Figs. 1a and 1b also show that the properties of the underlying membrane support (its zeta potential but also its structural features) can significantly affect the value of the apparent zeta potential that would be obtained from the (erroneous) use of the well-known Eq. (1).

Fig. 2 shows the experimental streaming current coefficient measured with HFK-131 membranes at various channel heights (h_{ch}). Results obtained with the full membrane, i.e. the membrane with both its top layer and underlying support, are shown by closed symbols.

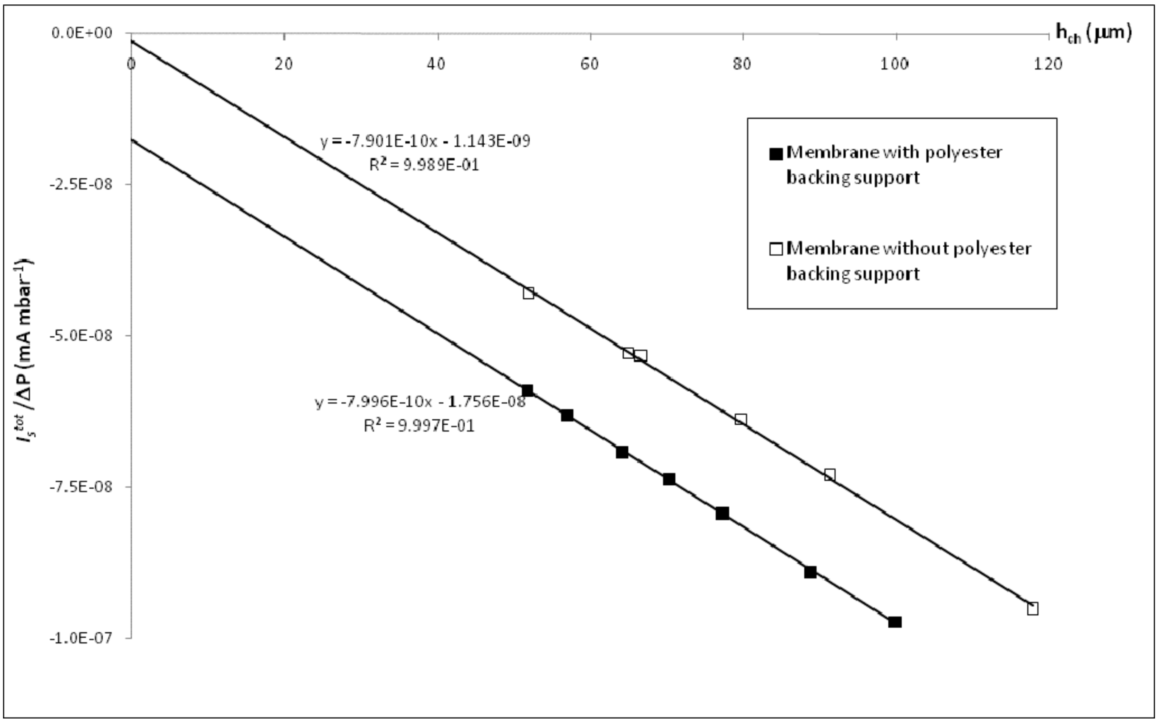

Fig. 2 Streaming current coefficient ($I_s^{tot}/\Delta P$) versus channel height (h_{ch}) measured with HFK-131 membrane with (closed symbols) and without its backing support (open symbols); 0.001 M KCl solution at pH 5.5.

As expected the total streaming current measured through the cell varies linearly with the channel height. However, the line does not pass through the origin, which gives evidence that an additional streaming current flows through the membrane supports (the value of this latter is obtained by extrapolation at zero channel height).

We performed similar measurements after having peeled off carefully the backing polyester material of the membrane (of course it is impossible to remove the support entirely and a part of it remains "attached" to the skin layer made of polyethersulfone). Figure 2 clearly shows that the streaming current flowing through the membrane body becomes negligible since the intercept is now near zero.

As mentioned previously, the electrical conductance of the system (G_{cell}) can be obtained from streaming current combined with streaming potential measurements. Fig. 3 shows the variation of G_{cell} with the channel height for the membrane composed of the polyethersulfone layer on the polyester support.

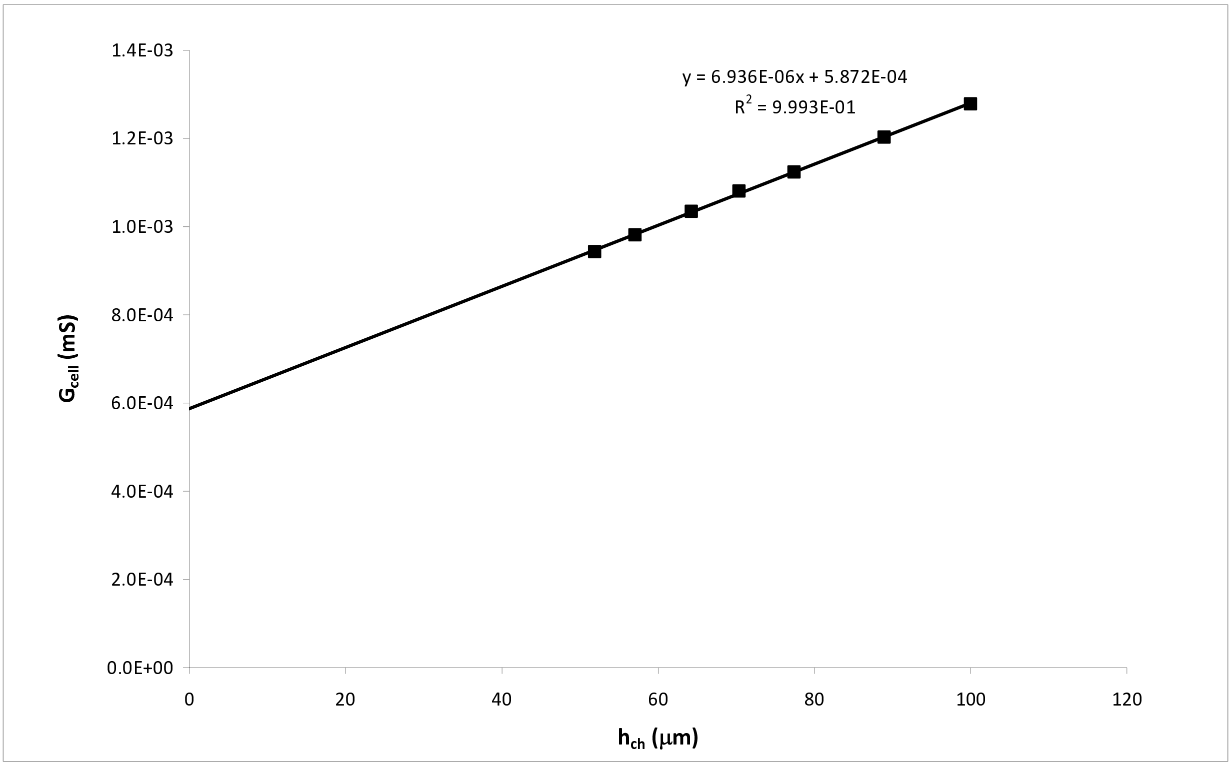

Fig. 3 Electric conductance (G_{cell}) versus channel height (h_{ch}) measured with HFK-131 membrane with its polyester support; 0.001 M KCl solution at pH 5.5.

As expected from Eq. (3), the cell conductance varies linearly with the channel height. The electric conductivity of the solution in the channel can inferred from the slope. We found 139 μS cm^{-1}, which is in good agreement with the electric conductivity measured in the bulk solution (150 μS cm^{-1}). Assuming that the electric conductivity of the electrolyte solution in the porous support is similar to that in the channel, the extrapolation of the electric conductance at zero channel height allows the assessment of the effective height on which the streaming current flows through a single membrane support (see Eq. (3)). We obtained $h_{\sup}^{eff}$ = 42 μm.

Knowing $h_{\sup}^{eff}$, it is further possible to determine the effective zeta potential of the membrane support (ζ_{sup}) by means of Eq. (2) and the streaming current coefficient value extrapolated at zero channel height (Fig. 2). Also, the zeta potential of membrane surfaces (ζ_{surf}) can be obtained straight from the slopes of lines obtained in Fig. 2. We obtained ζ_{surf} = - 21 mV and ζ_{sup} = -5 mV in 0.001 M KCl solution at pH 5.5. It can be noted in Fig. 2 that the slope of $I_s^{tot}/\Delta P = f(h_{ch})$ obtained with the "peeled" membrane is very close to that obtained with the complete membrane. Measurements performed with both membranes therefore lead to similar values of the surface zeta potential, which confirms the quality of the present streaming current measurements.

CONCLUSION

We investigated theoretically the effect of the additional streaming current flowing through the porous supports of composite membranes and gave illustrations of the error made in the interpretation of electrokinetic data when streaming current in the porous substrates is neglected. Moreover, the zeta potentials of both the surface and the porous support of a composite polymer membrane were assessed experimentally from a series of streaming current and streaming potential measurements performed at various channel heights. This study therefore suggests that advanced electrokinetic measurements can provide significant insight into important issues in membrane science including membrane ageing, fouling and functionalization.

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