Journal of Membrane Science 411–412 (2012) 193–200

Contents lists available at SciVerse ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Electrokinetic characterization of hollow fibers by streaming current, streaming potential and electric conductance

Y. Lanteri[a], P. Fievet[a,*], S. Déon[a], P. Sauvade[b], W. Ballout[a], A. Szymczyk[c,d]

[a] Institut UTINAM, UMR CNRS 6213, Université de Franche-Comté, 16 route de Gray, Besançon Cedex 25030, France
[b] Degremont Technologie – AQUASOURCE, 20 Avenue Didier Daurat, 31029 Toulouse, France
[c] Université Européenne de Bretagne, France
[d] Université de Rennes 1, Institut des Sciences Chimiques de Rennes, UMR CNRS 6226, 263 Av. du Général Leclerc, CS 74205, 35042 Rennes, France

ARTICLE INFO

Article history:
Received 31 January 2012
Received in revised form 10 April 2012
Accepted 20 April 2012
Available online 27 April 2012

Keywords:
Electrokinetic measurements
Streaming current/potential
Zeta potential
Hollow fibers

ABSTRACT

The electrokinetic properties of hollow fiber polymer membranes were investigated from tangential streaming current/streaming potential and electric conductance measurements. The experiments were conducted with a number of fibers n between 1 and 10 and for three fiber lengths l. The quite good linearity of (i) streaming current/potential data versus pressure difference and (ii) streaming current coefficient and "$SP \times G$" (SP: streaming potential coefficient; G: cell electric conductance) data versus n/l shows that expressions of the streaming current and streaming potential derived in laminar flow are also valid for turbulent flux conditions (provided the electrical double layer lies within the laminar sublayer near the surface). The high experimental conductance, the nonlinear dependence of electric conductance on the number of fibers and the variation of streaming potential coefficient with n and l suggest that the solution in which fibers are immersed makes contribution to the cell electric conductance. A non negligible part of the total streaming current is likely to flow through the macroporous body of fibers. Unlike flat membranes, the contributions of the skin surface and the porous body of the fibers to the streaming current cannot be separated for this type of material due to the impossibility of varying channel cross section. The conversion of tangential electrokinetic measurements into zeta-potential of lumen surface is then no more possible. In such cases, it is advisable to carry out streaming current measurements (or to combine streaming potential measurements with electric conductance measurements) because the streaming current (or the product $SP \times G$) is not affected by the cell electric conductance and can then be considered a property of membrane surface.

1. Introduction

The zeta potential originates from the accumulation of charges at a solid–liquid interface where an electrical double layer is formed. It is defined as the electrostatic potential at the hydrodynamic plane of shear. It is an important and reliable indicator of the membrane surface charge that interacts with its surroundings and its knowledge is essential (i) to characterize new membrane materials as well as modified membranes, to study the effect of solution properties (type of ions, ionic strength, pH...) on membrane charge properties, (ii) to control the efficiency of cleaning treatments, (iii) to better understand the rejection mechanisms of charged solutes as well as interactions between the membrane surface and various charged foulants such as macromolecules or colloids... The zeta potential can be determined from the measurement of the streaming potential or streaming current. Streaming potential measurements can be performed in two different ways: by flow through the membrane pores (transversal streaming potential) [1–6] or by flow along the top surface of the membrane (tangential streaming potential) [6–14]. In the case of asymmetric/composite membranes or fine-porous membranes, it is advisable to use the second procedure because it allows avoiding undesirable effects such as the contribution of both supporting layer(s) to the measured signal [15–17] and the membrane potential induced by the concentration difference across the selective layer of the membrane [18–20]. These contributions make the interpretation of experimental data difficult. Unlike streaming potential, streaming current measurements are seldom carried out through membranes due to their unknown pore structure (the calculation of the zeta potential from streaming current requires the knowledge of both the pore length and the membrane porosity). This drawback is eliminated by measuring the streaming current in a channel, the geometry of which is precisely known (typically slit-like channels of 50–500 μm in height), formed by two identical flat membranes facing each

* Corresponding author. Tel.: +33 81 66 20 32; fax: +33 81 66 62 88.
E-mail address: patrick.fievet@univ-fcomte.fr (P. Fievet).

0376-7388/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.memsci.2012.04.031

other. With so large channels, it could have been expected that the Helmholtz–Smoluchowski (H–S) relation is applicable to the interpretation of tangential streaming potential measurements in terms of zeta potential of membrane surface. However, ten years ago, Yaroshchuk and Ribitsch [21] have underlined that in the case of channels whose walls are formed by porous materials soaked with electrolyte solution, a non negligible share of the conduction current involved in the streaming potential phenomenon is likely to flow through the channel walls (i.e. the substrate body). They have shown theoretically that in such cases neither the H–S equation nor related relations accounting for the surface conductivity are suitable to compute the zeta potential because these equations are derived with the implicit assumption that both streaming and conduction currents flow through identical paths. In the case of channels with conducting walls, it was theoretically shown that the correct value of the zeta potential can be inferred either from a series of streaming potential measurements performed at various channel heights (extrapolation method) [14] or directly from coupled streaming potential and electric conductance measurements (coupling method) [9,22]. The influence of porous body conductance was investigated experimentally in refs. [9–12,14] for organic and ceramic membranes. It was found that the magnitude of this effect was quite different from a study to another. Indeed, the ratio of the zeta potential determined from the above-mentioned extrapolation or coupling method (i.e. by taking into account the effect of the porous body conductance) to that calculated via the H–S equation (ζ_{corr}/ζ_{H-S}) was found to be in the range 1–10. Since about five years, the availability of streaming current measurement (in addition to the streaming potential) with the new commercial electrokinetic analysers has enabled a deeper insight into the tangential electrokinetic phenomena with porous substrates. Indeed, Yaroshchuk and Luxbacher [14] have recently shown that the porous structure could make contribution not only to the cell electric conductance (as demonstrated previously) but also to the streaming current and these contributions are considerable especially in the case of membranes with large pores like MF membranes. They have also highlighted that the type of cell used may have a significant influence on measurements of the streaming current or streaming potential. Indeed, the contribution of the support layer of membrane to the measured streaming current (in addition to the measured conductance), and consequently to the streaming potential, may be very different depending on whether the support layer of membrane is or not directly exposed to the pressure drop occurring along the cell. The contribution of the porous body, to a greater or lesser extent, to the streaming current and the type of cell used for electrokinetic measurements could then explain the different ratios ζ_{corr}/ζ_{H-S} reported in literature. The influence of the measuring cell on the electrokinetic measurements was recently demonstrated by Buksek et al. [13] by comparing the results of two differently designed measuring cells but operating on the same principle. Up to now, the tangential technique was very little applied to the characterization of channels of tubular membranes or membrane hollow fibers probably due to the fact that no tangential measuring cell for this type of membranes has been marketed yet. Another possible explanation could be the large hydraulic diameter of channels that prevents the establishment of a laminar flow and the use of standard equations (e.g. the H–S equation) derived from the Hagen–Poiseuille equation (which is used to derive the expression of the streaming current). However, it was demonstrated in ref. [11] that the expression of streaming current usually used in the electrokinetics theory is still applicable even if the flow is not wholly laminar provided the electrical double layer lies within the laminar sublayer near the channel surface.

In this paper, the electrokinetic behavior of a bundle of hollow fibers is studied by streaming current, streaming potential and cell electric conductance under conditions for which the flux is not wholly laminar. To the best of our knowledge, this is the first time that tangential electrokinetic measurements are performed with hollow fiber membranes. It will be shown that, in addition to the contribution of the membrane body to the overall electric conductance, the electrolyte solution around fibers (indeed, in the measuring cell, the permeate compartment is filled up with the measuring solution and the permeate outlet is closed in order to avoid any permeation through fibers during tangential measurements) also makes contribution.

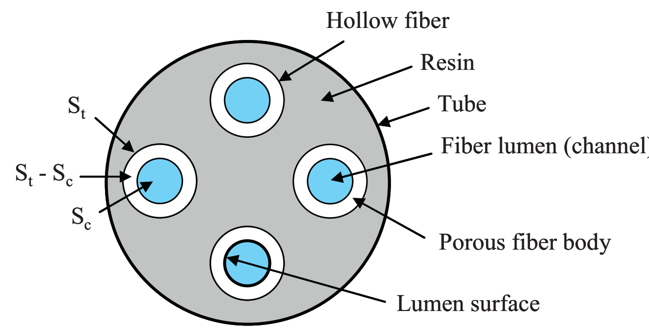

Fig. 1. Schematic cross section view of a bundle of fibers.

2. Theory

Lets us consider a set of n identical fibers immersed in an electrolyte solution, the porous structure of which is hydraulically exposed (Fig. 1 and Table 1). When a solution is forced to flow through the lumen of the fibers, a tangential gradient of hydrostatic pressure occurs inside their porous structure. As recently explained by Yaroshchuk and Luxbacher [14], when the pores are not large enough and/or the electrokinetic properties of their surface are not the same as those of external surface of the porous substrate (in this work, the lumen of the fiber) forming the channel, one has to explicitly account for the streaming current (I_s) occurring inside the pores of the fiber and in the fiber lumen (i.e. the channel). The contribution of the two media to the electric conductance of the system has also to be taken into account. Unlike the streaming current which has a convective nature and arises only where the liquid flow is possible (i.e. inside the channel and membrane pores), the conduction current flows wherever the electric conductivity is non zero. Consequently, if the fibers are immersed in a conducting liquid, it could also contribute to the conductance of the system. The equivalent electrical circuit describing this system consists of three conductances in parallel due to the channels, pores of the fibers and external solution (i.e. the solution around the fibers). The streaming potential ($\Delta\varphi_s$) is given by the ratio of the streaming current (I_s) to the total electric conductance (G) of the system. The expressions for the streaming current, electric conductance, streaming potential and parameter $SP \times G$ (where SP denotes the streaming potential coefficient) are collected in Table 1 for various situations. All symbols are defined in the nomenclature section. The situation A corresponds to the case where the streaming current flows in both the channel (i.e. the lumen of the fiber) and the membrane pores, and conduction current exists in the channel, the membrane pores and also in the external solution around the fibers. That is why the electric conductance of the system is expressed as the sum of three components. However, the expression of the external solution conductance is not derived because its representation is not simple. The situation B considers that the streaming and conduction currents take the same path, namely the channel and membrane pores. The situation C corresponds to the situation where the contribution of the porous structure to the streaming current is negligible but not its contribution to the system electric conductance. Finally, in