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Effect of Adsorption of Charged Macromolecules on Streaming and Membrane Potential Values Measured with a Microporous Polysulfone Membrane

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ABSTRACT

Changes in streaming and membrane potentials measured across a commercial microporous polysulfone membrane as a result of the adsorption of differently charged macromolecules were studied. Measurements were carried out with different NaCl solutions (10^{-3} M to 5×10^{-2} M) and their mixtures with a polyanion (dextran sulfate or DS) and a polycation (diethylaminoethyl or DEAE-dextran). From electrokinetic and electrochemical measurements, information about characteristic membrane parameters (transport number and ionic permselectivity) and membrane/solution interactions (zeta potential) can be obtained. Results show how the adsorption of charged particles affects the electrical parameters of the membrane and also its hydraulic permeability. The concentration dependence of these parameters was also studied.

Key Words. Streaming potential; Membrane potential; Macromolecules adsorption; Zeta potential; Permselectivity

INTRODUCTION

The permeate flux decline normally observed during the microfiltration of macromolecules by membranes, which is attributed to their adsorption/deposition on the membrane, mainly depends on the interactions of solute components with the membrane, and it is directly related to the charge density of the membrane (1–3). However, this parameter not only depends on the membrane material but also on the particular operating conditions of the filtrate solution (pH and ionic strength). Electrokinetic and electrochemical parameters, such as streaming and membrane potentials, can be used to study the transport of electrolyte solutions across membranes and also to get information about the electrical interactions at the membrane/solution interface (4–6), which means that the electrical nature of the adsorbed particles can be known in an easy and fast way. "Streaming potential" is the electrical potential difference measured at both sides of a porous membrane as a result of the liquid flow through the pores under a pressure difference; it is an experimental parameter indicative of the electrical interactions between membrane surface and solutions (7, 8). On the other hand, when a membrane separates two electrolyte solutions with different concentrations, an electrical potential difference can be measured; it is normally called "membrane potential," and it depends on the different mobilities of the ions in the membrane. Both parameters strongly depend on the value and electrical character (positive or negative) of the membrane charge and, for this reason, are a source of information about the charged particles adsorbed/deposited in the membrane.

The effect of adsorption on a membrane (membrane fouling) of two charged macromolecules, with similar molecular weights but of opposite charge, on the streaming and membrane potential values measured through a commercial polysulfone microporous membrane is studied in this paper for different NaCl solutions. From the experimental data, characteristic parameters, such as the cation transport number in the membrane, the ionic permselectivity, and the zeta potential, which was obtained by means of the Helmholtz–Smoluchowski expression, were determined. The concentration dependence of these parameters was also studied. A comparison with the values obtained for an unfouled membrane for the same NaCl solutions shows the influence of the adsorbed macromolecules on these parameters. It was found that the adsorption of both kinds of charged particles changes the effective charge in the membrane, but permselectivity results show that the positive adsorbed macromolecule presents a higher effect in the exclusion of co-ions although, in both cases, the permselectivity strongly decreases when the salt concentration is increased.

EXPERIMENTAL

Materials

A microporous polysulfone membrane from DDSS (Dow Denmark Separation System) was used. Measurements were carried out using NaCl solutions and also their mixtures with two oppositely charged macromolecules: dextran sulfate or DS, which has negative charges, and diethylaminoethyl dextran (DEAE-dextran) with positive charges, supplied by Pharmacia Fine Chemical (Sweden). Both are derivatives of dextran, a high molecular weight polymer (M_w approximately 500,000) of D-glucopyranose synthesized from sucrose. The negative charge for dextran sulfate comes from SO_3^- groups (the sulfur content of the macromolecule is approximately 17%); the positive charge for DEAE-dextran is due to NH^+ groups (the nitrogen content is approximately 3.2%). The concentration of macromolecules was always 0.5 g/L, while five different NaCl solutions (10^{-3} M, 5×10^{-3} M, 10^{-2} M, 2×10^{-2} M, and 5×10^{-2} M) were used. In all cases the measurements were performed at a constant temperature (25.0 ± 0.4)°C and neutral pH (pH = 7.0 ± 0.4). To avoid changes in the membrane due to pressure during the streaming potential measurements, which could affect its transport properties, the PS membrane was maintained for 1 hour under a pressure difference of 8 atm, which was higher than those used in the experiments. Previous to streaming potential measurements, one of the membrane surfaces was kept in contact for 4 days with NaCl solutions containing each of the macromolecules, but the system was cleaned every 4 hours with distilled running water. It was assumed that in this case the charged particles would be mainly adsorbed on the membrane surface (9).

Experimental Setup

Streaming and Concentration Potential Measurements

The experimental system used in streaming and membrane potential measurements is shown in Fig. 1. It basically consists of two loops (Compartments 1 and 2) to control the concentration of the solution at both sides of the membrane, which were the high and low pressure sides in streaming potential measurements or the constant and variable concentration sides in membrane potential experiments, respectively. Measurements were carried out in a crossflow cell which was made of acrylic with two holes in the center of each half-cell in which to place the Ag/AgCl electrodes. The potential difference between both half-cells due to the transmembrane pressure gradient, ΔE_p, or the concentration gradient, ΔE_c, was measured by means of a high impedance voltmeter with the

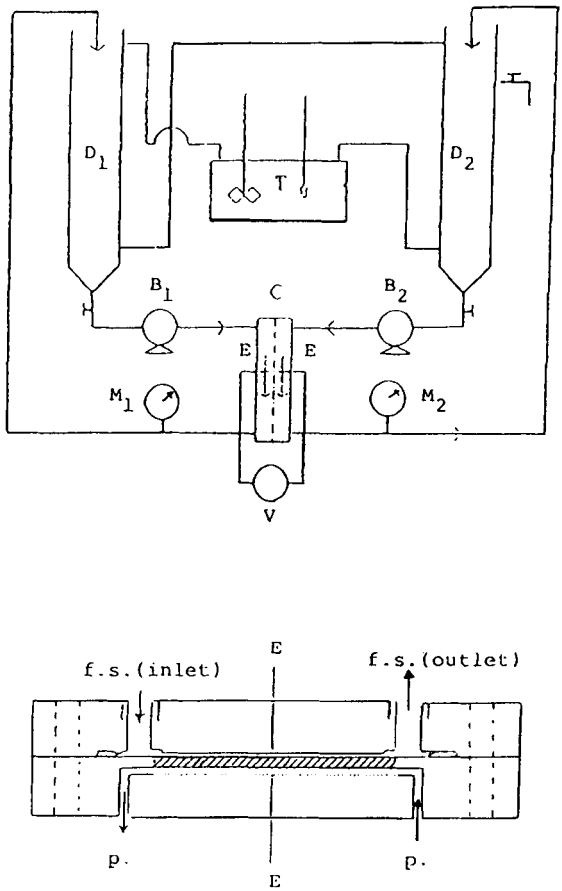

FIG. 1 Experimental equipment for streaming and membrane potential measurements. C: measuring cell; V: voltmeter; E: Ag/AgCl electrodes; D: solution tanks; B: pumps; M: manometers; T: thermostat. Measuring cell: f.s.: feed solution (Compartment 1); p: product (Compartment 2).

electrode placed in Compartment 2 grounded, which means that $\Delta E = E(1) - E(2)$. The solution tank in Compartment 1 had a capacity of 2 L. To minimize the effect of concentration polarization at the high pressure side, the speed of the circulating solution was approximately 115 cm/s (10). The capacity of the solution tank and the pump output in Compartment 2 were 150 cm^3 and 136 cm^3/min, respectively. Solute concentrations in both compartments (C_1 and C_2) were determined by conductivity mea-

surements using a radiometer CDM-3 conductivity meter. In both experiments the charged macromolecules were added to Compartment 1.

Streaming potential was measured for pressure differences between 1 and 5 atm. At the same time the volume flux, J_v, through the membrane due to the corresponding transmembrane pressure difference was also measured. Membrane potentials, ΔE_c, were measured while maintaining the NaCl concentration constant at one side of the membrane (C_1) and gradually changing the concentration at the other side (C_2) from 10^{-4} M to 10^{-1} M.

RESULTS AND DISCUSSION

Membrane hydraulic permeability, $L_p = (J_v/\Delta P)$, can be obtained from volume flux–transmembrane pressure difference relationships, such as those shown in Fig. 2 for the water flux measured after using NaCl solutions and those containing DS and DEAE-dextran. As a result of the filtration of charged macromolecules, a reduction in water permeability across the membrane was found: 48% for the solutions with dextran sulfate and 53% for those with DEAE-dextran. This decrease in the hydraulic permeability of the polysulfone membrane is due to the adsorption of

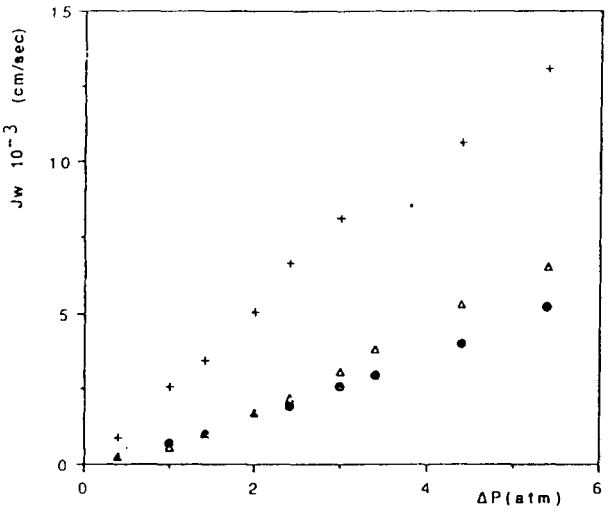

FIG. 2 Water flux versus transmembrane pressure difference for three membrane samples. Clean PS membrane (+), fouled DS membrane (△), and fouled DEAE-dextran membrane (●).

particles (membrane fouling) and shows how the filtration of macromolecules affects the transport properties of clean microporous membranes.

Streaming potential values, $\Delta\phi_{st}$, measured with both charged macromolecule solutions as a function of the transmembrane pressure difference, ΔP, are shown in Fig. 3 for two different NaCl concentrations ($C = 5 \times 10^{-3}$ M and 2×10^{-2} M). These results indicate a change in the sign of $\Delta\phi_{st}$ values depending on the solution considered: negative with the dextran sulfate solution and positive with the dextran-DEAE solution. In a previous paper (11) it was found that the polysulfone membrane can be considered to be a neutral membrane, which means it does not present any net fixed charge although it can exhibit a weak negative character in chlorine solutions, as can also be observed from the values shown in Fig. 3. As a result of the adsorption of DS on the polysulfone membrane, more negative values for the streaming potential were obtained, which indicates that the DS fouled membrane has a higher negative charge than the clean PS membrane. The positive $\Delta\phi_{st}$ values obtained with the DEAE-dextran fouled membrane indicate a positive charge due to the adsorption of the polycation DEAE-dextran.

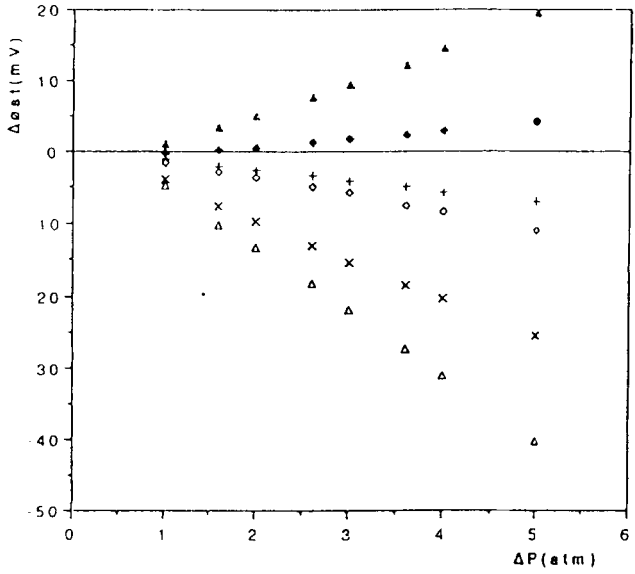

FIG. 3 Streaming potential as a function of the transmembrane pressure difference at two NaCl solutions. Fouled membranes, DS: (△) $C = 5 \times 10^{-3}$ M, (◇) $C = 2 \times 10^{-2}$ M; DEAE-dextran: (▲) $C = 5 \times 10^{-3}$ M, (◆) $C = 2 \times 10^{-2}$ M; clean PS membrane: (×) $C = 5 \times 10^{-3}$ M, (+) $C = 2 \times 10^{-2}$ M.

From the slope of the straight lines indicated in Fig. 3, the streaming potential coefficient, $\gamma_{st} = (\Delta\phi_{st}/\Delta P)$, can be obtained for each system and salt concentration. Figure 4 shows γ_{st} values as a function of the NaCl concentration. These results also indicate the strong dependence on concentration of the streaming potential coefficient, which is always more significant at low concentrations (10^{-3} M $< C <$ 10^{-2} M), while at high concentrations an almost constant value is reached. This kind of behavior is due to the higher number of counterions in the pore liquid when high salt concentrations are used, which reduces the effect of the membrane charge (12, 13).

Zeta potential, ζ, is the parameter commonly used in colloid science to characterize solid/liquid interfaces and, for porous neutral membranes or capillary systems, it can be obtained from streaming potential results using the Helmholtz–Smoluchowski expression (14):

$$\zeta = (\chi\eta/\epsilon_0\epsilon_r)(\Delta\phi_{st}/\Delta P) = \chi\eta\gamma_{st}/\epsilon_0\epsilon_r \quad (1)$$

where ϵ_0 is the permittivity of a vacuum, ϵ_r is the relative dielectric constant of the solvent, χ is the conductivity, and η is the viscosity of the solution. Variation with NaCl concentration of zeta potential values are shown in Fig. 5 for the three membranes studied. The more negative character of the DS fouled membrane with respect to the clean PS mem-

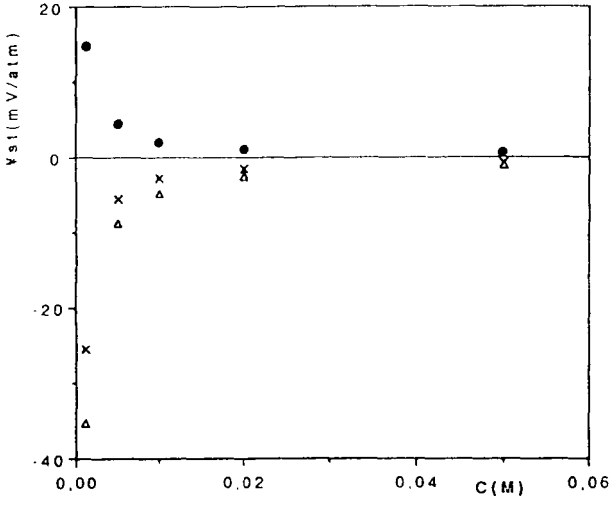

FIG. 4 Streaming potential coefficient versus NaCl concentration for the different membranes: clean PS (×), fouled DS (△), and fouled DEAE-dextran (●).

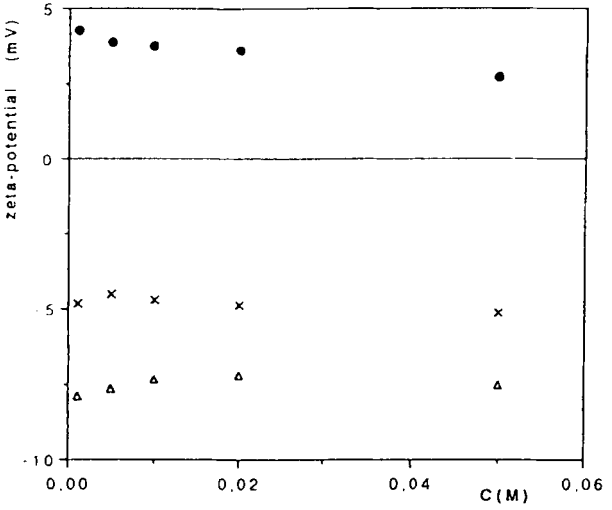

FIG. 5 Zeta potential versus NaCl concentration for the different membranes: clean PS (×), fouled DS (△), and fouled DEAE-dextran (●).

brane previously indicated is clearly shown in this figure. In both cases the ζ values are almost independent of concentration, but a slight decrease of ζ values when the concentration increases was found for the DEAE-dextran fouled membrane. This can be attributed to the increase of the number of counterions in the solutions filling the membrane pores which results in a decrease of the net membrane charge.

Membrane potential versus $\ln(C_1/C_2)$ for the different membranes studied are shown in Fig. 6 for $C_1 = 10^{-2}$ M. Some differences can also be observed in this figure between both fouled membranes, but quite similar values were obtained for the clean PS and the DS fouled membranes, which shows that the adsorption of the polyanion DS hardly affects the mobility of ions in the PS membrane. Membrane potential basically consists of two parts: 1) a diffusion potential due to the different mobilities of the ions in the membrane, and 2) a Donnan potential on each membrane/solution interface. When the external concentrations are higher than the concentration of fixed charge in the membrane (X), the Donnan potential can be neglected. For all cases with external concentrations higher than 10^{-3} M, linear relationships between membrane potential and $\ln(C_1/C_2)$ were obtained, which indicates that $C >> X$, and the membrane potential is mainly due to a diffusion potential across the membrane. This can be expressed as a function of the mobility of the ions in the membrane (or

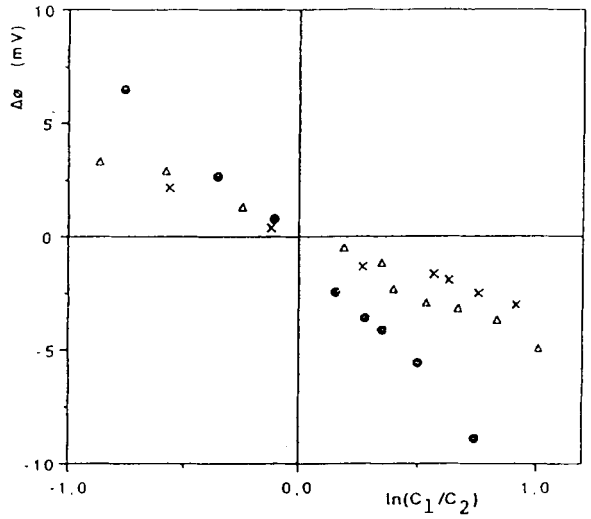

FIG. 6 Membrane potential versus $\ln(C_1/C_2)$ for the different membranes at constant NaCl concentration $C_1 = 10^{-2}$ M: clean PS (×), fouled DS (△), and fouled DEAE-dextran (●).

the transport numbers) by means of (15):

$$\Delta\phi = (RT/F)([u_+ - u_-]/[z_+u_+ + u_-z_-]) \ln(a_1/a_2) \qquad (2)$$
$$= (RT/F)([t_+/z_+] - [t_-/z_-]) \ln(a_1/a_2)$$

where u_i and t_i are the mobilities and transport numbers of the ions in the membrane, respectively; z_+ and z_- are their valencies; a_1 and a_2 are the mean activities of the solutions at each side of the membrane; R and F are the gas and Faraday constants, and T is the temperature of the system. Taking into account that $t_+ + t_- = 1$, the cation or anion transport number in the membrane can be obtained by Eq. (2) from membrane potential experimental data.

Variations of t_+ values with the external constant concentration C_1 for both fouled membranes are shown in Fig. 7. These results show that t_+ values for the DS fouled membrane are slightly higher that those corresponding to free solution (16), t_+^0, which agrees with a small negative fixed charge in the membrane as a result of the adsorption of DS, as was previously obtained from streaming potential results. However, t_+ values obtained with the DEAE-dextran fouled membrane are much lower than in free solution, which represents an exclusion of Na^+ ions (membrane co-ions) due to a positive charge in the membrane. It also agrees with the

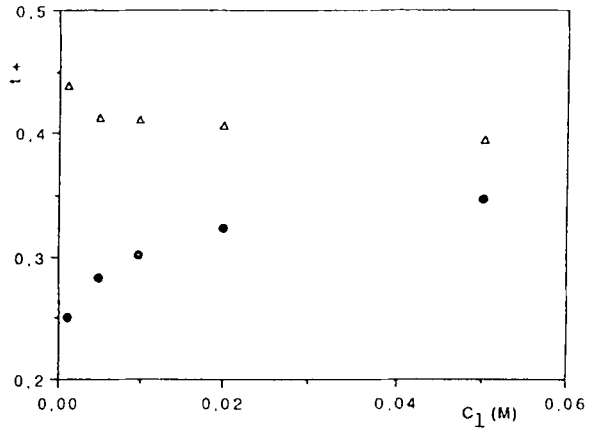

FIG. 7 Cation transport number as a function of the external constant concentration C_1. Fouled DS membrane (△) and fouled DEAE-dextran (●).

results obtained for this membrane from streaming potential measurements. For both fouled membranes there is a clear dependence of t_+ values with NaCl concentration for the interval between 10^{-3} M and 10^{-2} M, but almost constant values are reached at high concentrations (10^{-2} M $< C < 5 \times 10^{-2}$ M).

The permselectivity P_i of a membrane, which is a measure of the membrane selectivity of the counterions over the co-ions, can be obtained from transport numbers (15):

$$P_{s^i} = (t_i - t_i^0)/(1 - t_i^0), \qquad (i = +, -) \tag{3}$$

Variation with concentration of the permselectivity of both membranes (cationic or P_{s^+} for the DS fouled and anionic or P_{s^-} for the DEAE-dextran fouled) is presented in Table 1. The results show that the DS fouled membrane presents a very low exclusion of co-ions (the membrane hardly affects Cl^- transport), but the effect of the DEAE-dextran fouled membrane over Na^+ ions is significantly higher. However, in both cases there is a loss of selectivity when the concentration increases. This is due to the higher number of co-ions in the pore solution which decreases the effectiveness of the membrane–solution electrical interactions.

In conclusion, we can state that the filtration of saline solutions containing charged macromolecules through a microporous polysulfone membrane strongly reduces its hydraulic permeability due to the adsorption/deposition of macromolecules in the membrane (around 50%). This fact

TABLE 1
Variation with NaCl Concentration of the Permselectivity to Cation, P_{s+}, and Anion, P_{s-}, for DS and DEAE-Dextran Fouled Membranes, Respectively

C (M)	DS membrane, P_{s+}	DEAE membrane, P_{s-}
0.001	0.078	0.350
0.005	0.036	0.280
0.01	0.033	0.225
0.02	0.027	0.170
0.05	0.013	0.102

also affects the membrane effective charge as can be seen from streaming and membrane potential results, the membrane showing a negative character when a polyanion such as dextran sulfate is adsorbed but, for similar solution conditions (NaCl concentration and pH), it behaves as a positively charged membrane due to the adsorption of a polycation such as DEAE-dextran. Different parameters such as zeta potential, transport numbers, and membrane ionic permselectivity were also obtained. The results show a higher exclusion of co-ions for the positively charged DEAE-dextran fouled membrane than for the DS fouled one. The concentration dependence of these parameters shows a significant variation at low concentrations (10^{-3} M to 10^{-2} M) but almost constant values at high concentrations (10^{-2} M to 5×10^{-2} M) as a result of counterion inclusion in the pore liquid, which reduces the effect of the membrane charge. Both kinds of measurements allow determination of the sign of adsorbed particles in membranes during microfiltration.

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