

Electroosmotic Flow Rectification in Pyramidal-Pore Mica Membranes

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Electroosmotic flow (EOF) is an electrokinetic phenomenon that occurs when an ionic current is passed through a channel or porous medium that contains excess surface charge.¹ EOF is used to pump fluids through microfluidic devices^{1c} and capillary electrophoresis columns.^{1d} While the pores and channels typically have a symmetrical shape, there is increasing interest in transport through asymmetrical pores² and channels,³ for example conically shaped pores in polymer membranes.⁴

Transport in conically shaped pores is of interest because such pores can act as ion-current rectifiers; i.e., the magnitude of the current flowing through the pore depends on the polarity of the potential difference applied across the membrane (Figure 1).^{4,5} It occurred to us that this phenomenon might produce a corresponding rectification of the EOF rate across the membrane. If this is true, such membranes could be used as EOF rectifiers, yielding high flow rates for one polarity and low flow rates when the polarity is reversed. We report here the first demonstration of this rectified electroosmotic flow effect.

Mica membranes with pyramidally shaped pores prepared by the track-etch method⁶ were used (Figure 2). The membranes were 10.4 μm thick and contained 10^5 heavy-ion induced damage tracks per cm^2 .⁷ While this is the first example of pyramidal pores in mica, the chemical etching procedure⁷ is similar to that used to etch conically shaped pores in polymer membranes.⁸ Briefly, this entails placing a solution that etches the damage tracks (10 M HF) on one side of the membrane and a solution that neutralizes the etchant (10 M NaOH) on the opposite side.⁷ Because chemical etching of mica yields pores with a rhomboidal cross section (Figure 2A),⁹ the pores have a pyramidal shape with the base opening of the pyramid facing the etch solution and the tip opening facing the stop solution. Figure 2B shows a replica of such a pyramidal pore prepared by chemical vapor deposition of carbon within the pore¹⁰ and dissolution of the membrane.⁷

We report the sizes of the base and tip opening in terms of the length of the major axis, l_{maj} , of these rhomboidal openings (Figure 2A). Since the major angle, α_{maj} , is $\sim 120^\circ$,⁹ the length of the minor axis can be calculated. The sizes of the base and tip openings of the pyramidal pores were controlled by varying the etch time and measured by electron microscopy.^{7,10} Pores with four different sizes of the base and tip openings were investigated here (Table 1). A control membrane with symmetrical, as opposed to pyramidally shaped, pores was also prepared.⁷

Transport measurements were made by mounting the membrane between the two halves of the permeation cell¹¹ described previously. The feed half-cell contained ~ 3 mL of a solution that was 10 mM in phenol and 10 mM in phosphate buffer, $\text{pH} = 7.0$. The permeate half-cell initially contained only buffer. The area of the exposed membrane was 0.78 cm^2 . As per our prior work, the phenol is used as an electrically neutral probe to measure the EOF rate from the feed to the permeate.^{1c} This was accomplished by periodically measuring the UV absorbance of the phenol in the permeate solution and making plots of moles of phenol transport vs time (Figure 3). The slope of this line is proportional to the flux of phenol across the membrane.

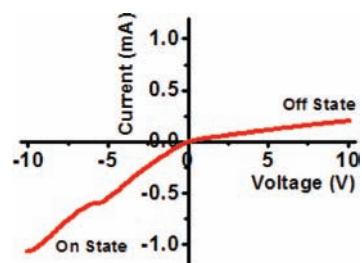


Figure 1. Current–voltage curve for a pyramidal-pore mica membrane demonstrating ion-current rectification (10 mM phosphate buffer, $\text{pH} 7.0$). l_{maj} for the tip and base were 17 and 122 nm, respectively (Table 1).

Table 1. EOF Velocities and Ion-Current and EOF Rectification Ratios for the Membranes Studied Here

Tip l_{maj} (nm)	Base l_{maj} (nm)	v_{eof} (mm/s)		r_{eof}	r_{ic}
		Base-to-Tip	Tip-to-Base		
17	122	3.8	0.37	10.3	5.3
35	244	1.7	0.35	4.9	2.7
52	366	0.55	0.32	1.7	1.3
70	488	0.32	0.23	1.4	1.2
11	11	12	12	1.0	1.0

EOF was driven through the membrane by using a Pt electrode in each half-cell solution to pass a current of 100 μA through the pores. Because mica surfaces have excess negative charge,⁹ EOF is in the direction of cation migration. For this reason, the cathode was in the permeate solution for all EOF experiments.

The objective of these studies was to determine whether the ion-current rectification effect observed in these pyramidal-pore membranes yields a corresponding rectification in the EOF rate. The “off” state for these ion-current rectifiers occurs at positive values of applied potential, E_m (Figure 1), which corresponds to the cathode being in the solution adjacent to the nanopore tip. When an EOF transport experiment was done with a current having this polarity (EOF from base to tip), a high flux state was obtained (Figure 3A). When the polarity of the current was reversed, corresponding to the “on” state (Figure 1, EOF from tip to base), a much lower flux state was observed. Similar results were obtained for all of the pores investigated here.

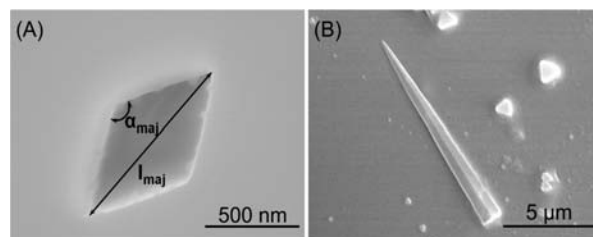


Figure 2. Electron micrographs of (A) the base opening of a pore in a mica membrane and (B) a carbon replica of a pyramidal mica pore.

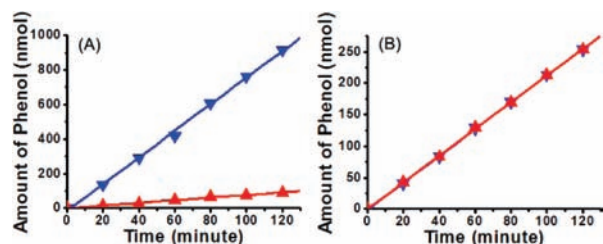


Figure 3. Plots of nmol of phenol transported vs time from EOF experiments on two mica membranes. (A) Asymmetric-pore membrane (as per Figure 1). (▼) Transport from base to tip; (▲) transport from tip to base. (B) Membrane containing symmetrical pores with $l_{\text{maj}} = 11$ nm. (▼▲) correspond to the two directions of EOF through this membrane.

These results show for the first time that asymmetric pores can act as EOF rectifiers. Symmetrical pores in mica show neither ion-current nor EOF rectification (Figure 3B, Table 1).

To explain EOF rectification, we briefly review ion-current rectification in asymmetric pores.^{2,5,12} According to Ramírez et al.¹² if an asymmetric pore has excess anionic surface charge (like mica) and the tip opening is sufficiently small, the tip will preferentially transport cations and reject anions. This high cation transference number causes the electrolyte to be depleted from the solution in the pore tip when the “off” state polarity (Figure 1) is applied.¹² This causes the resistivity of the solution in the pore tip to increase, yielding the lower “off” state current. In contrast, when the “on” state polarity is applied, the electrolyte accumulates in the pore tip.¹² This causes the resistivity of the pore-tip solution to decrease, yielding the higher “on” state current.

The velocity of electroosmotic flow, v_{eof} , is also related to solution resistivity, ρ ,^{1c}

$$v_{\text{eof}} = -\epsilon \zeta J_{\text{app}} \rho / \eta \quad (1)$$

where ϵ and η are the permittivity and viscosity of the solution, respectively, J_{app} is the constant applied current density, and ζ is the zeta potential of the pore wall.^{1c} Equation 1 predicts that the high solution ρ of the “off” state will produce a high v_{eof} and the low solution ρ of the “on” state will produce a low v_{eof} , and this is exactly what we observe experimentally (Figure 3A, Table 1).

We quantified these results by calculating the “on” and “off” state v_{eof} values. The slopes of the transport lines (e.g., Figure 3A) provided the rate of phenol transport in the presence of the applied current, N_i . The rate of diffusion, N_{diff} , was also measured by doing analogous experiments with no applied current. N_i and N_{diff} were then used to calculate the enhancement factor, E ,^{1c,7}

$$E = N_i / N_{\text{diff}} \quad (2)$$

which was used to calculate the Peclet number, Pe .^{1c}

$$E = Pe / (1 - \exp(-Pe)) \quad (3)$$

Pe is related to v_{eof} via^{1c}

$$v_{\text{eof}} = PeD/l \quad (4)$$

where l is the membrane thickness, and D is the diffusion coefficient for phenol.⁷

The v_{eof} values obtained are shown in Table 1.¹³ Note first that v_{eof} increases with decreasing pore size. This is because v_{eof} increases with pore resistance, which is higher for smaller pores.⁷ The extent of EOF rectification was quantified by defining a parameter called the EOF rectification ratio, r_{eof} , which is v_{eof} for the “off” state polarity divided by v_{eof} for the “on” state polarity. We see that r_{eof} also increases with

decreasing pore size (Table 1). This is certainly reasonable since the chance of achieving the requisite high cation transference number¹² is greater in a smaller pore.

The extent of ion-current rectification is quantified by the ion-current rectification ratio,⁵ r_{ic} , defined here as the absolute value of the current at -10 V divided by the current at $+10$ V. The r_{ic} values (Table 1) show that, like r_{eof} , ion-current rectification is greater in smaller pores. We also see that r_{eof} scales with r_{ic} . This is because both phenomena derive from the change in pore-solution resistivity with the sign of E_m . The proportionality between r_{eof} and r_{ic} indicates that a simple measurement of r_{ic} (Figure 1) can be used to predict whether a membrane will be a good EOF rectifier. Furthermore, because r_{ic} increases with decreasing ionic strength,¹⁴ r_{eof} should show a similar dependence.

We have demonstrated here a new electrokinetic phenomenon: EOF rectification in membranes containing asymmetric pores. As theory predicts, and as we have shown experimentally, EOF rectification is observed in pores that show the more familiar ion-current rectification.^{2,4,5,12} Because v_{eof} increases with increasing solution resistivity (eq 1) and ion-current decreases with resistivity, the “off” state for the current is the high velocity state for EOF. The extents of both ion-current and EOF rectification increase with charge density on the pore wall. As a result, mica is an especially propitious material for such rectifiers since the anionic charge density¹⁵ exceeds by a factor of ~ 2 the charge density on the more commonly studied polymeric membranes.¹⁶

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Supporting Information Available: Details of the nanopore fabrication and characterization methods, the transport measurements. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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