Electronic Supporting Information to

Time-resolved pressure-induced electric potential in nanoporous membranes: measurement and mechanistic interpretation

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Demonstration of anti-symmetricity of salt-concentration distribution under linear conditions

Due to (partial) solute rejection, under conditions of pressure-driven flow membrane surfaces behave as solute sources. Understanding the physics of this is simplest in the initial state where concentration gradients have not, yet, had time to develop. The source intensities can be obtained as differences between the solute fluxes entering and leaving very thin layers just outside the membrane surfaces. On the feed side, the entering flux is

$$J_{in}^{(f)} = cJ_v \tag{S1}$$

The solute flux leaving the layer through the membrane in the initial state is equal to

$$J_{out}^{(f)} = cJ_v(1-\sigma_s) \tag{S2}$$

Thus, the source intensity on the feed side is

$$J_{in}^{(f)} - J_{out}^{(f)} = c\sigma_s J_v \tag{S3}$$

On the permeate side, the entering flux is

$$J_{in}^{(p)} = cJ_v(1-\sigma_s) \tag{S4}$$

and the leaving flux is

$$J_{out}^{(p)} = cJ_v \tag{S5}$$

The difference is

$$J_{in}^{(p)} - J_{out}^{(p)} = -c\sigma_s J_v \tag{S6}$$

Thus, the solute sources have the same magnitude and opposite signs. They give rise to antisymmetric solute-concentration profiles. Of course, this is valid as long as the concentration differences remain small (linear approximation).

Polynomial approximation for the bracketed term in Eq(24) valid up to $\tau < 1.4$

$y = -2.172153\text{E-}02x^6 + 1.348534\text{E-}01x^5 - 3.851127\text{E-}01x^4 + 7.086186\text{E-}01x^3 - 9.920583\text{E-}01x^2 + 1.127824\text{E+}00x + 9.258163\text{E-}06$

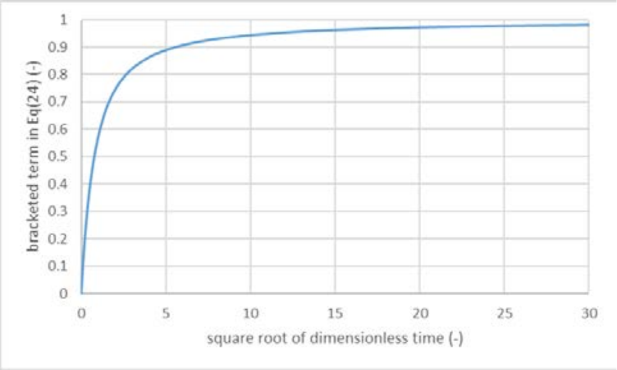

Fig.S1. Time dependence of bracketed term in Eq(24) at long dimensionless times

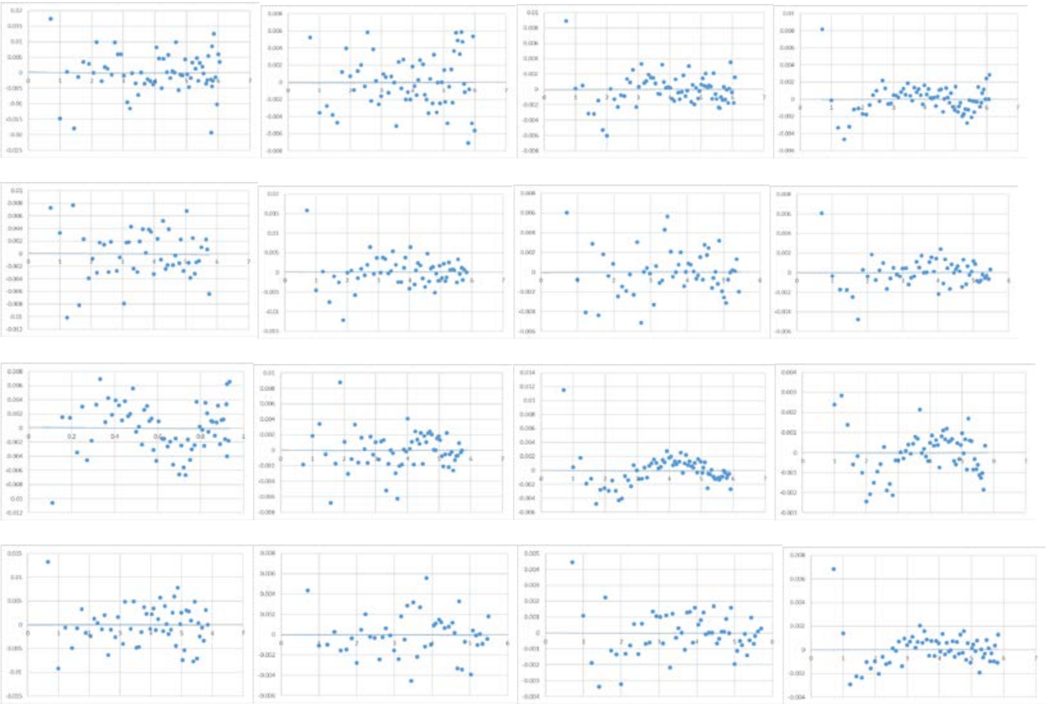

Fig.S2. Relative deviations of experimental data from the theoretical fits for the data shown in Fig.5

Fitting of surface-charge density

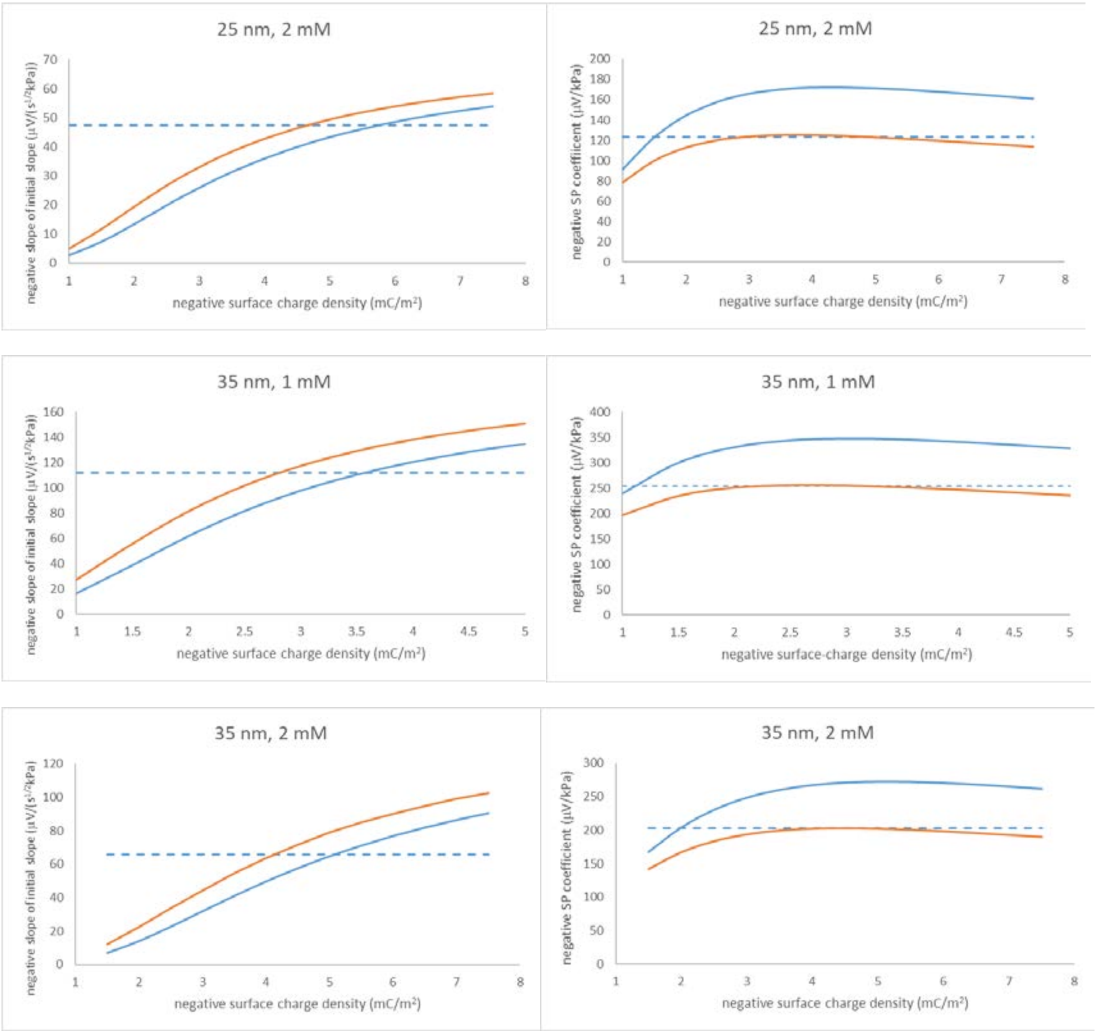

Fig.S3. Theoretical dependencies of slope of initial slope (a) and streaming-potential coefficient (b) on surface-charge density and their comparison with experimental values (horizontal dashed lines): the blue lines were calculated assuming a smooth non-porous nanopore surface, the orange lines were obtained postulating the existence of a “gel” layer on the pore surface.

Estimates of Péclet number

For our model to be applicable, the Péclet number defined by Eq(9) has to be sufficiently small. From the interpretation of measurements of transient pressure-induced potential, we could estimate the surface-charge densities listed in Table 2 of the main text. According to Eq(9),

$$Pe_0 \equiv J_{v0}/2P_m \equiv \frac{r_p^2 \gamma L}{16\eta L \gamma D_p}\Delta p \equiv \frac{r_p^2 \Delta p}{16\eta D K} \qquad \text{(S7)}$$

where K denotes the dimensionless coefficient of reduction of salt diffusivity in nanopores due to electrostatic coion exclusion, D is the bulk salt-diffusion coefficient. By using Eqs(32,37,38) the K coefficient was calculated numerically and found to be between 0.42 (1 mM) and 0.48 (2 mM) with the 25-nm membrane and between 0.55 (1 mM) and 0.67 (2 mM) in the 35-nm membrane. By using these values, for the maximum pressure difference of $\Delta p = 10\ kPa$, the Péclet numbers are about $0.1 \div 0.12$ for the 25-nm membrane and around $0.14 \div 0.17$ for the 35-nm membrane.

Estimates of buildup of osmotic pressure

According to Eq(26), the ratio of maximum osmotic-pressure difference across the membrane (occurring at very long times) to the “driving” hydrostatic-pressure difference is approximately given by

$$2RTc_0\frac{\sigma_s^2\chi_*}{P_m} \approx 2RTc_0\frac{r_p^2\gamma L\sigma_s^2}{8\eta L\gamma D_p} \equiv (2RTc_0)\frac{r_p^2\sigma_s^2}{8\eta DK} \qquad \text{(S8)}$$

The first factor (in parenthesis) is the osmotic pressure in solution, it is about 10 kPa in 2 mM KCl (and two times less in 1 mM KCl). For the surface-charge densities listed in Table 2, the salt reflection coefficients approximately are: 0.6 (25 nm, 1 mM), 0.5 (25 nm, 2 mM), 0.4 (35 nm, 1 mM), 0.3 (35 nm, 2 mM). Using these numbers (and the diffusivity-reduction factors given in the previous section), and taking into account that in our measurements the trans-membrane concentration differences reached about 50% of their maximum values, one can estimate the relative contribution of buildup of osmotic pressure to be about 2.0-2.5% in the case of 25-nm membrane and about 1.3-1.4% in the case of 35-nm membrane.