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Supporting Information

for

Concentration Gradient Focusing and Separation in a Silica Nanofluidic Channel with a Non-uniform Electroosmotic Flow

by

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SI 1 A Quantitative Study to Identify the Dominant Parameters for the Induced Counter-Electroosmotic Flow

In the main text, we point out that the electroosmotic flow behaviour in Conductivity/Concentration Gradient Focusing systems is complex and governed by several factors including: the (i) variation of the axial electric field, (ii) variation of the electric double layer thickness, (iii) variation of the surface charge density and (iv) viscoelectric effect. The electric field variation was discussed in the main text - electroosmotic force increases with field, hence this first effect aids the recirculation zone formation. The other three effects are strongly coupled so that it is difficult to quantify the influence that each has on the electroosmotic flow from the full protein trapping simulations. Hence, in this section we perform one dimensional simulations on a simplified system to separately quantify the importance that each of these three effects has on the electroosmotic flow, so demonstrating which supports and which hinders the formation of the flow recirculations observed in the protein trapping device

We consider a straight silica nanochannel of 75nm depth, 20 μ m width and 100 μ m filled with a NaCl electrolyte solution. In contrast to the simulations presented in the main text, the bulk concentrations of NaCl at ends of the channel are equal so that there is no concentration gradient applied along the channel's length. A uniform electric field of 2.5×10^5 V/m is imposed in the channel length's direction.

Given that the channel length and width are much longer than the channel depth, we assume that end effects in the channel length's and width's directions are negligible, and hence neglect variations of physical quantities in the channel length's and width's directions. This allows us to employ a one dimensional (1D) model in the channel depth direction. The governing equations in the main text, eqns $1 \sim 4$, are used. We employ three different models at different salt concentrations to quantify the influence that the variation of the salt concentration (double layer thickness), viscoelectric effect and surface charge regulation model have on the electroosmotic velocity (see Table SI 1.1):

- (1) The viscoelectric effect and surface charge regulation model are included.
- (2) The viscoelectric effect is neglected and a constant surface charge density [†] is applied on the surface.
- (3) The surface charge regulation model is included but without the viscoelectric effect.

For model (1), eqns 7 and 8 in the main text are applied to modify the viscosity and diffusivities in response to the local electric field within the electric double layer, while in models (2) and (3) the viscosity and diffusivities are uniform. We apply a symmetry condition on the centreline. On the silica surface, nonslip, non-conductive and ion impenetrable conditions are applied.

[†]The constant surface charge density used is -24.05mC/m^2 which is the average of the low (-11.3mC/m^2) and high (-36.8mC/m^2) values predicted by the surface charge regulation model employed in the main simulations.

Table SI 1.1: The three simplified models considered.

	The Viscoelectric Effect	The Charge Regulation Surface
(1) Model VS	Yes	Yes
(2) Model N	No	No
(3) Model S	No	Yes

SI 1.1 Net Influence of the Salt Concentration

Fig. SI 1.1 shows velocity profiles and flow rates as a function of salt concentration for this purely electroosmotic (no axial pressure gradient) flow. Decreasing the salt concentration results in a thicker electric double layer, lower surface charge density and weaker viscoelectric effect. The model VS results indicate that the net influence of these effects has a positive contribution to the local recirculation flow. The difference in the maximum velocity (at the centreline) and flow rate between the salt concentrations 7mM and 241mM are 165.9% and 145.2%, respectively. Note that, as discussed in the main text, such a higher electroosmotic flow at low salt concentrations tends to reinforce the formation of the recirculation zone, once volume conservation in the channel is considered.

Salt concentrations affects the electric double layer thickness, surface charge and viscoelectric effect. We now examine separately how each of these effects affects recirculation zone formation.

SI 1.2 Influence of the Electric Double Layer Thickness

In the model N, neither the charge regulation surface and viscoelectric effect models are used. Thus, here we independently examine the influence of the variation of the electric double layer thickness on the purely electroosmotic flow. The percentage difference in the maximum velocity and flow rate between the 7mM and 241mM concentrations are 300.9% and 273.0% respectively, which are larger than those for the model VS. This indicates that the gradual increase of the electric double layer thickness from the high to low concentration end reinforces the recirculation zone formation, and also implies that the net effect of the charge regulation surface and viscoelectric effect hinders the recirculation zone formation.

SI 1.3 Influence of the Charge Regulation Surface

Here, we compare the models N and S to examine the effect that just the charge regulation surface model has on the electroosmotic force. Due to a higher/lower surface charge density at the high/low concentration compared to that from the model N, the electroosmotic velocity and flow rate are larger at high concentrations (163 and 241 mM) but lower at low concentrations (7 and 85 mM) for the model S yielding smaller differences (only 100.8% in electroosmotic velocity and 85.3% in flow rate) between the two end concentrations. That is, the charge regulation surface reduces the electroosmotic force difference between the low and high concentration ends and thus retards the formation of the recirculation zones.

SI 1.4 Influence of the Viscoelectric Effect

Finally, we evaluate the influence of the viscoelectric effect on the electroosmotic flow by comparing results from the models VS and S. The electroosmotic velocity and flow rate differences between the low and high concentrations are larger when the viscoelectric effect is considered (see values in Section SI 1.1 and SI 1.3) meaning that the viscoelectric effect aids the formation of the recirculation zones.

Note that the velocity difference between the models VS and S decreases when the concentration decreases. The percentage difference in flow rate between the models VS and S is 42.6% at 241mM, while it is only 7.72% at 7mM, implying that the viscoelectric effect has a much stronger impact on the electroosmotic flow at the high salt concentrations. This is because at the high concentrations the diffuse layer is more compact, the surface charge density is higher, and hence the local electric field normal to the surface within the electric double layer is greater.



Figure SI 1.1: Variations of the (a) electroosmotic velocity as a function of the nanochannel depth position (where 0 and ± 37.5 nm denote to the centreline and surface of the channel, respectively) at various NaCl concentrations (b) electroosmotic flow rate as a function of the NaCl concentration based on different models [in (a), solid curves are model VS; dashed curves are model N; dotted curves are model S].

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