### Nanoscale

**Electronic supplementary information (ESI):**

Simulation of electroosmotic flow (EOF) in nanochannels.

**Numerical simulation of EOF in nanochannels**

Fig. 1 shows a 2D computational domain of the numerical study with channel height of 2d and channel length of L. AB is the entrance of the nanochannel and CD is the outlet boundary, and BC are the channel walls. The governing equations and boundaries are as follows:

**Electric field.** In the nanochannel area, Poisson equation must be solved in order to calculate the electric potential distribution:

\[-\nabla (e_{r}\varepsilon_{r}\nabla \phi) = \rho_{e}\]

Eq. 1

\[\rho_{e} = F \sum c_{i}z_{i}\]

Eq. 2

Where \(\phi\) is the electric potential and \(\rho_{e}\) is the charge density, \(F\) is the Faraday constant. \(c_{i}\) and \(z_{i}\) are the ionic concentration and valence of \(K^{+}\) and \(Cl^{-}\) respectively. The boundary conditions are:

\[\phi = V1 \text{ at AB} \]

Eq. 3

\[\phi = 0V \text{ at CD} \]

Eq. 4

\[\phi = \xi_{w} \text{ at channel wall AD and BC} \]

Eq. 5

**Ionic concentration field.** The thickness of electric double layer is comparable with the channels size and electric double layers are likely to get overlapped in nanochannels, consequently, Nernst-Plank equation should be applied to study the concentration field.

\[\nabla N_{i} = 0 \]

Eq. 6

\[N_{i} = -D_{i}\nabla c_{i} - z_{i}\mu_{i}\frac{\nabla \phi}{\varepsilon_{r}} + c_{i}v_{EOF}\]

Eq. 7

\[\mu_{i} = \frac{D_{i}}{RT}\]

Eq. 8

Where \(N_{i}\), \(D_{i}\), \(\mu_{i}\) are the flux, diffusion coefficient and ion mobility of \(K^{+}\) or \(Cl^{-}\) respectively. \(v_{EOF}\) is the EOF velocity inside the nanochannel, \(R\) is the gas constant. And the following boundary conditions are applied:

\[n \cdot N_{i} = 0 \text{ at channel walls AD and BC} \]

Eq. 9

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**Tab. 1 Constants and parameters used in the simulation**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value and Unit</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\mu)</td>
<td>(0.9 \times 10^{-3}) [Pa*s]</td>
<td>Viscosity of electrolyte</td>
</tr>
<tr>
<td>(\rho)</td>
<td>1000 [kg/m³]</td>
<td>Density of water</td>
</tr>
<tr>
<td>(\varepsilon_{r})</td>
<td>80[1]</td>
<td>Dielectric constant of water</td>
</tr>
<tr>
<td>(\varepsilon_{o})</td>
<td>8.854 \times 10^{-12} [F/m]</td>
<td>Permittivity of vacuum</td>
</tr>
<tr>
<td>(z_{1})</td>
<td>1[1]</td>
<td>Valence of (K^{+})</td>
</tr>
<tr>
<td>(z_{2})</td>
<td>-1[1]</td>
<td>Valence of (Cl^{-})</td>
</tr>
<tr>
<td>(e)</td>
<td>1.602 \times 10^{-19} [C]</td>
<td>Unit charge</td>
</tr>
<tr>
<td>(F)</td>
<td>9649 [C/mol]</td>
<td>Faraday Constant</td>
</tr>
<tr>
<td>(D_{1})</td>
<td>1.29 \times 10^{-5} [m²/s]</td>
<td>Diffusion coefficient of (K^{+})</td>
</tr>
<tr>
<td>(D_{2})</td>
<td>1.77 \times 10^{-9} [m²/s]</td>
<td>Diffusion coefficient of (Cl^{-})</td>
</tr>
<tr>
<td>(R)</td>
<td>8.314 [J/mol/K]</td>
<td>Gas constant</td>
</tr>
<tr>
<td>(k_{b})</td>
<td>1.381 \times 10^{-23} [J/K]</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>(T)</td>
<td>298[K]</td>
<td>Temperature</td>
</tr>
</tbody>
</table>

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\[c_{i} = c_{i,0}\] at entrance AB and outlet CD

Eq. 10

Here \(c_{i,0}\) is the concentration of the bulk solution.

**Flow field.** Stokes equation and the continuity equation are solved in order to calculate the flow field inside the nanochannel. Here, we assumed that the fluid is incompressible and the flow inside the nanochannel is laminar flow due to the low \(Re\) number, and no pressure is applied between the entrance and the outlet of the nanochannel.

\[-\nabla P + \mu \nabla \cdot v_{EOF} - \rho_{e} \frac{\nabla \phi}{\varepsilon_{r}} = 0\]

Eq. 11

\[\nabla \cdot v_{EOF} = 0\]

Eq. 12

where \(\rho\) is the density, \(P\) is the pressure, \(\mu\) is the dynamic viscosity of the electrolyte solution. The boundary conditions at channel walls are nonslip due to the viscos effect and no pressure at the channel ends:

\[v_{EOF} = 0\] at channel wall AD and BC

Eq. 13

\[P = 0\] at inlet AB and outlet CD

Eq. 14
The numerical simulation was conducted by using Comsol 4.3b. The channel size effect, ionic concentration effect and the applied electric field effect on the EOF velocity in nanochannels are studied systematically by using this model. Tab. 1 lists the parameters and constants used in the simulation. In the numerical studies, ionic concentration from $10^{-5}$M to 0.5 M, channel height from 20 nm to 300 nm, externally applied electric field ranging from 12.5 V/cm to 50 V/cm were tried. The zeta potential values are from the experimental results.

According to the analytical solution in a nanochannel of 104 nm high with $10^{-3}$M KCl solution loaded under an electric field of 25 V/cm. From Fig. 3 and Fig. 4 one can see that the velocity profiles are almost identical, which means that the direct numerical model we set is reliable.

Fig. 2 is an example of EOF field inside a nanochannel of 104 nm high with $10^{-3}$M KCl solution loaded under an electric field of 25 V/cm, the color scale and the arrow depict the velocity field. Fig. 3 is a velocity profile in the cross section of this nanochannel.

The analytical solutions (Eq.1 to Eq.7 in the paper) can also be used to predict EOF velocity profiles in nanochannels directly by using Matlab. Fig.4 is an example of EOF profile plotted according to the analytical solution in a nanochannel of 104 nm high with $10^{-3}$M KCl solution loaded under an electric field of 25 V/cm.

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Fig. 2: EOF field inside a nanochannel of 104 nm high with $10^{-3}$M KCl solution loaded under an electric field of 25 V/cm.

Fig. 3: EOF profile inside a nanochannel of 104 nm high with $10^{-3}$M KCl solution loaded under an electric field of 25 V/cm by Comsol 4.3b.

Fig. 4: EOF velocity profile in a nanochannel of 104 nm high with $10^{-3}$M KCl solution loaded under an electric field of 25 V/cm plotted based on the analytical solution by Matlab software.