Nanoscale

Paper

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, AD 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:

$$-\nabla(\varepsilon_0\varepsilon_r\nabla\phi) = \rho_e \quad \text{Eq. 1}$$

$$\rho_e = F\sum_i c_i z_i \quad \text{Eq. 2}$$

Where ϕ is the electric potential and ρ_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:

$$\phi = V1 \text{ at AB} \quad \text{Eq. 3}$$

$$\phi = 0V \text{ at CD} \quad \text{Eq. 4}$$

$$\phi = \zeta_w \text{ at channel wall AD and BC} \quad \text{Eq. 5}$$

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.

$$\nabla N_i = 0 \quad \text{Eq. 6}$$

$$N_i = -D_i\nabla c_i - z_i\mu_i c_i\nabla\phi + c_i v_{EOF} \quad \text{Eq. 7}$$

$$\mu_i = \frac{D_i}{RT} \quad \text{Eq. 8}$$

Where N_i, D_i, μ_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:

$$n \cdot N_i = 0 \text{ at channel walls AD and BC} \quad \text{Eq. 9}$$

Fig. 1 Schematic of modelling EOF in nanochannels. The nanochannel is 2d in height and L in length. Electric potential is applied between the entrance and outlet of the nanochannel.

Tab. 1 Constants and parameters used in the simulation

Parameter	Value and Unit	Description
μ	0.9×10^{-3} [Pa*s]	Viscosity of electrolyte
ρ	1000 [kg/m^3]	Density of water
ε_r	80[1]	Dielectric constant of water
ε_0	8.854×10^{-12} [F/m]	Permittivity of vacuum
z_1	1[1]	Valence of K^+
z_2	-1[1]	Valence of Cl^-
e	1.602×10^{-19} [C]	Unit charge
F	9649 [C/mol]	Faraday Constant
D_1	1.29×10^{-9} [m^2/s]	Diffusion coefficient of K^+
D_2	1.77×10^{-9} [m^2/s]	Diffusion coefficient of Cl^-
R	8.314[J/mol/K]	Gas constant
k_b	1.381×10^{23} [J/K]	Boltzmann constant
T	298[K]	Temperature

$$c_i = c_{i\infty} \text{ at entrance AB and outlet CD} \quad \text{Eq. 10}$$

Here $c_{i\infty}$ 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.

$$-\nabla P + \mu\nabla^2 v_{EOF} - \rho_e\nabla\phi = 0 \quad \text{Eq. 11}$$

$$\nabla \cdot v_{EOF} = 0 \quad \text{Eq. 12}$$

where ρ is the density, P is the pressure, μ 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:

$$v_{EOF} = 0, \text{ at channel wall AD and BC} \quad \text{Eq. 13}$$

$$P = 0, \text{ at inlet AB and outlet CD} \quad \text{Eq. 14}$$

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 $10^{-4}M$ 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.

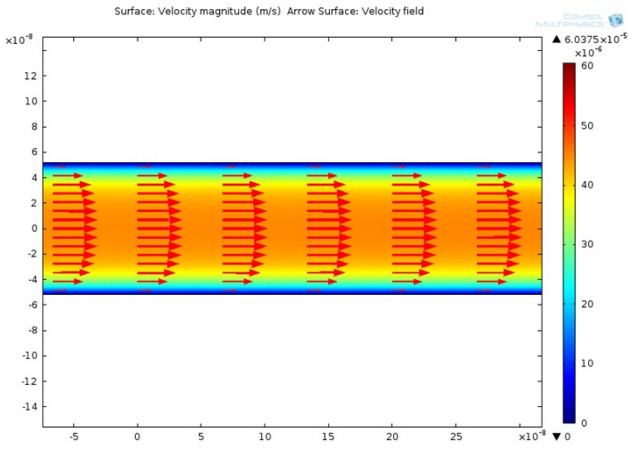

Fig. 2 EOF field inside a nanochannel of 104 nm high with 10^{-3}M KCl solution loaded under an electric field of 25 V/cm.

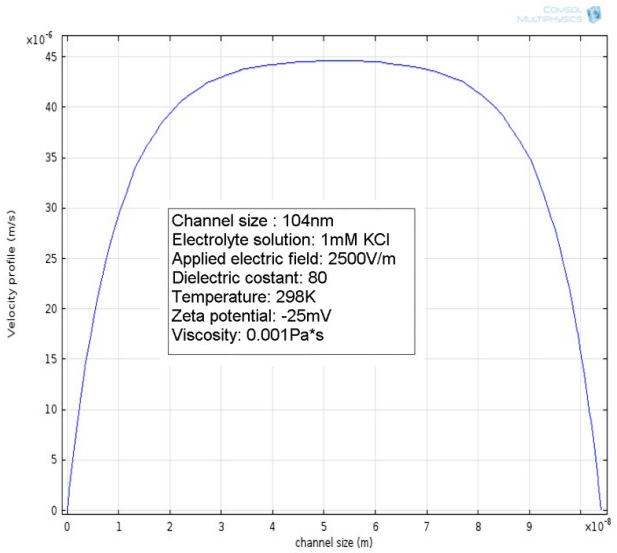

Fig. 3 EOF profile inside a nanochannel of 104 nm high with 10-3M KCl solution loaded under an electric field of 25 V/cm by Comsol 4.3b.

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. 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.

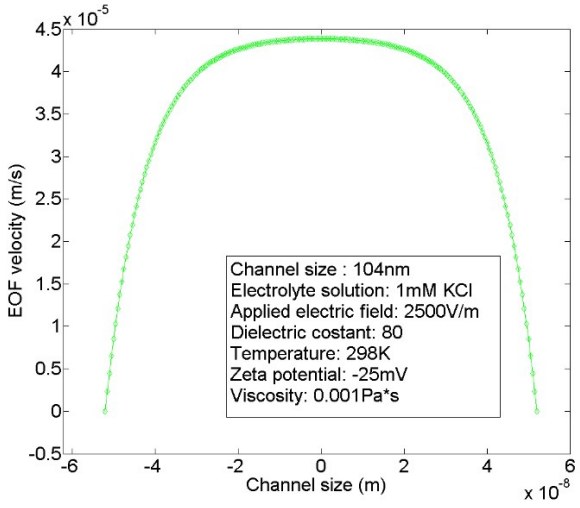

Fig. 4 EOF velocity profile in a nanochannel of 104 nm high with 10^{-3}M KCl solution loaded under an electric field of 25 V/cm plotted based on the analytical solution by Matlab software.