

Electrostatic Correlation Effect on Electroosmotic Flow through a Hydrophobic Nanochannel with Laterally Mobile Surface Charge

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1. INTRODUCTION & OBJECTIVE

Electroosmotic flow (EOF), which occurs when electrolytes move over a charged surface due to an externally applied electric field, is considered the most efficient mode of transport in micro- and nano-channels, such as those found in lab-on-a-chip devices [1]. Ion transport in nanoscale systems is crucial for physiological processes, energy harvesting, biosensing, and more [2]. Experiments with foam films [3] show electric fields driving surface charges oppositely, enhancing shear stress. Ion adsorption makes surface charges mobile under external fields [4]. Silkina et al. [2] modeled electroosmotic flow in nanotubes using electrohydrodynamic slip to account for charge mobility. Bazant et al. [5] showed through a continuum model that the double-layer structure of concentrated multivalent electrolytes aligns with Monte Carlo and density functional theory findings.

In this study, we analyze how electrostatic correlations affect the electroosmotic flow (EOF) of multivalent electrolytes in a hydrophobic nanochannel with laterally mobile surface charges. We also account for the finite size of ions by adjusting the electrochemical potential. A semi-analytical solution is obtained for a low applied electric field.

2. MATHEMATICAL MODEL

We consider the electroosmotic flow (EOF) of multivalent electrolyte through a nanochannel of height $2h$ under an external electric field \mathbf{E}_0 . The hydrophobic and uniformly charged (σ) walls of the channel are considered to possess laterally mobile surface charges.

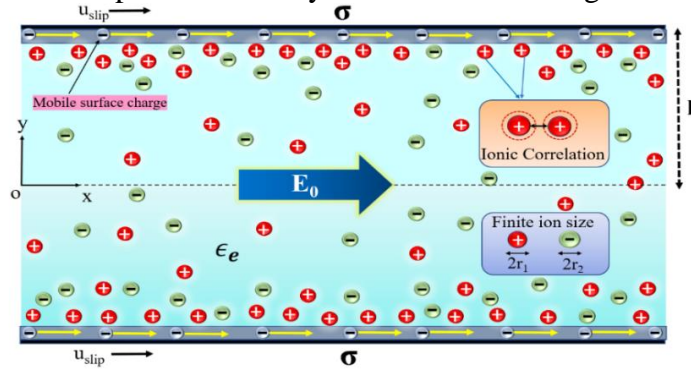


Figure 1: Schematic of the EOF through a nanochannel with hydrophobic walls
The governing equations and boundary conditions are given as [6]

$$Re[\mathbf{u} \cdot \nabla \mathbf{u}] + \nabla p - \nabla \cdot [(\nabla \mathbf{u}) + (\nabla \mathbf{u})^T] + \frac{(\kappa h)^2}{2} \rho_e \nabla \phi = 0, \quad \nabla \cdot \mathbf{u} = 0 \quad \text{for fluid flow}$$

$$\nabla \cdot \mathbf{J}_i = 0, \quad \mathbf{J}_i = \mathbf{u} n_i - \frac{1}{Pe_i} n_i \nabla \mu_i, \quad \mu_i = z_i \phi + \ln n_i + \mu_i^{ex} \quad \text{for ion transport}$$

$$\delta_c^2 \nabla^4 \phi - (\kappa h)^2 \nabla^2 \phi = \frac{(\kappa h)^4}{2} \rho_e, \quad \delta_c = 0.35 (Z^2 \kappa l_B)^{\frac{2}{3}} \left(\frac{eh}{2\pi Z^3 \epsilon_e \phi_0 l_B^2 |\sigma|} \right)^{\frac{1}{8}} \quad \text{for electric potential}$$

$$\text{At the walls: } u_{slip} = \lambda_s^{eff} \left[-\frac{\partial u}{\partial y} + \alpha_s \sigma E_0 \right], \quad v = 0, \quad \hat{\mathbf{n}} \cdot \mathbf{J}_i = 0, \quad \hat{\mathbf{n}} \cdot \nabla \phi = -\sigma, \quad \hat{\mathbf{n}} \cdot \delta_c \nabla (\nabla^2 \phi) = 0$$

At the centreline: $\frac{\partial u}{\partial y} = 0$, $v = 0$, $\frac{\partial n_i}{\partial y} = 0$, $\frac{\partial \phi}{\partial y} = 0$, $\frac{\partial^3 \phi}{\partial y^3} = 0$ (symmetry)

A fully developed fluid flow condition is applied along the inlet and outlet of the channel. Here, Re , $\rho_e (= \sum z_i n_i)$, $\kappa = \sqrt{2eI_\infty / \epsilon_e \phi_0}$ are respectively the Reynolds number, space charge density, and inverse of the electrical double layer (EDL) thickness. Pe_i and μ_i denote the Peclet number and electrochemical potential of i^{th} ionic species. We consider BMCSL model [6] for excess electrochemical potential μ_i^{ex} . The non-dimensional correlation length $\delta_c = \kappa l_c$ is scaled by κ^{-1} . The Bjerrum length $l_B = e / 4\pi \epsilon_e \phi_0$ and Z is the magnitude of the counterion valency. The effective slip length λ_s^{eff} is given by [7]

$$\lambda_s^{eff} = \frac{\lambda_s^0}{1 + 3\pi d_h \lambda_s^0 (1 - \alpha_s) \left(\frac{\epsilon_e \phi_0}{e} \right) |\sigma|}$$

where, α_s and d_h are respectively the surface charge mobility and diameter of the mobile charges.

The coupled set of governing equations are solved numerically with aid of finite volume method. The governing equations are discretized over a staggered grid arrangement and the discretized equations are solved through SIMPLE (Semi-Implicit Method for Pressure-Linked-Equation) algorithm. Based on the first order perturbation approximation we have also derived a semi-analytical solution for the electroosmotic velocity.

3. RESULTS & HIGHLIGHTS OF IMPORTANT POINTS

This mean-field continuum model captures the layered structure of the electric double layer (EDL) resulting from surface charge overscreening. Reversal of electroosmotic flow (EOF) is observed in concentrated multivalent electrolytes when the walls are highly charged, as seen in various EOF experiments. The reversal becomes more pronounced with increased surface charge mobility due to opposing friction from laterally mobile physisorbed ions. However, as hydrodynamic slippage on the wall increases, the reversal diminishes because convection dominates. Additionally, the finite size of ions significantly impacts EOF in concentrated electrolytes with high surface charge density.

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