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Solute Transport in Nanochannels with Roughness-like Structures

Guoqing Hu

State Key Laboratory of Nonlinear Mechanics, Institute of Mechanics, CAS
Beijing 100190, China

ABSTRACT

Newfound attention has been given to solute transport in nanochannels. Because the electric double layer (EDL) thickness is comparable to characteristic channel dimensions, nanochannels have been used to separate ionic species with a constant charge-to-size ratio (i.e., electrophoretic mobility) that otherwise cannot be separated in electroosmotic or pressure-driven flow along microchannels. In nanochannels, the electrical fields within the EDL cause transverse ion distributions and thus yield charge-dependent mean ion speeds in the flow. Surface roughness is usually inevitable during microfabrication of microchannels or nanochannels. Surface roughness is usually inevitable during the fabrication of nanochannels. In the present study, we develop a numerical model to investigate the transport of charged solutes in nanochannels with hundreds of roughness-like structures. The model is based on continuum theory that couples Navier-Stokes equations for flows, Poisson-Boltzmann equation for electrical fields, and Nernst-Planck equation for solute transports. Different operating conditions are considered and the solute transport patterns in rough channels are compared with those in smooth channels. Results indicate that solutes move slower in rough nanochannels than in smooth ones for both pressure-driven and electroosmotic flows. Moreover, solute separation can be significantly improved by surface roughness under certain circumstances.

Keywords: Nanochannel, Solute Transport and Separation, Surface Roughness, Numerical Modeling

INTRODUCTION

Nanofluidics offers new possibilities in manipulating molecules mainly because the length scales of the devices shrink to or overlap with the typical dimensions of the electrical double layer (EDL), biological macromolecules, or even ions [1-3]. The drastic increase of the surface-to-volume

ratio means that the surface effects will dominate the motion of fluid, dissolved molecules, and ions in the nanofluidic channels. Newfound attention has been given to analysis, separation, and detection of chemical and biological samples using nanoscale structures or channels. In nanochannels, solute-wall interactions were found to affect both the transport and the hydrodynamic dispersion of charged solutes [4-14]. Recently, nanochannels were implemented to separate ionic species with a constant charge-to-size ratio (i.e., electrophoretic mobility) that otherwise cannot be separated in either electroosmotic or pressure-driven flows along microchannels. Pennathur and Santiago [4, 5] showed that electrokinetic migration of charged species in nanochannels is strongly affected by valence-dependent dynamics of the transverse electric fields and proposed a separation method referred to as electrokinetic separation by ion valence (EKSIV). Garcia et al. [6] experimentally indicated that nanoconfinement of electrokinetic transport results in well-behaved separation of charged and neutral dyes, which differs from that typical of larger fluidic systems. Later, Griffiths and Nilson [7], and Xuan and Li [9] theoretically demonstrated that solute separation can be accomplished in pressure-driven flows through nanochannels due to solute-wall interaction and such pressure-driven separation is efficient in identifying charged solutes with different valences. The ion dispersion associated with the finite EDL thickness in nanochannels has also been investigated by several groups [10-12]. Nevertheless, it is worth noting that all the aforementioned studies were conducted on straight channels with smooth wall surfaces.

Surface roughness exists in most microfluidic and nanofluidic devices as a result of microfabrication processes or adsorption of macromolecules from samples. The amplitude of surface roughness could be only one or two order lower than the channel height in many cases. Salieb-Beugelaar et al. [15] measured surface roughness of the 20 nm deep fused silica nanoslits using AFM and found that the roughness RMS value is between 0.8 and 1.1 nm and holes occur with a depth of down to 8 nm. Just like artificial or random surface roughness

and surface heterogeneity were generated to realize certain flow functions in microchannels [16-18], nanostructures have been fabricated in microchannels and nanochannels to facilitate the separation or preconcentration of biomolecules such as DNA and protein [19, 20]. Kim and Darve [21] performed molecular dynamics simulation to study electroosmotic flows inside nanochannels with different types of surface roughness and showed that the diffusion of water and ions along the direction normal to the wall is significantly reduced near the wall and further decreases inside the roughness structures. Qiao [22] investigated the effects of molecular level surface roughness on the electroosmotic flow in nanochannel and found that the electroosmotic flow is reduced significantly when the EDL thickness is comparable to the height of surface roughness. Due to the computational cost, however, molecular dynamics simulation is limited to solve the problems with small space (~nm) and short time (~ns). It is impractical to use molecular dynamics simulation to directly study the solution transport in a realistic long nanochannel. The solute motion in nanochannels is essentially the complex coupling between solute components and the EDL that introduces large non-uniform transverse electric fields. As the channel size decreases, the presence of surface roughness further complicates the local solute-wall interactions and thus the transverse electromigration of charged solutes in nanochannels. So far no work has been done on solute transport in rough nanochannels. It is necessary to answer whether such surface roughness will improve or degrade separation efficiency of charged solutes in nanochannels.

This article is going to examine the effects of roughness-like structures on the solute transport in nanochannels for both pressure-driven flow and electric field driven flow. We develop a numerical model to investigate the transport of charged solutes in nanochannels with hundreds of roughness-like structures. The model is based on continuum theory that couples Navier-Stokes equations for flows, Poisson-Boltzmann equation for electric fields, and Nernst-Planck equation for solute transports. Different operating conditions, including background electrolyte (BGE) concentrations, structure geometry, and wall zeta potential, are considered.

THEORY AND NUMERICAL MODEL

Assuming a fully developed flow of the BGE (either pressure-driven or electric field driven), the transport of charged solutes in nanochannels is described by Nernst-Planck equation without chemical reactions [23],

$$\frac{\partial c}{\partial t} + \nabla \cdot (c\mathbf{u} - D\nabla c - \mu_{ep}c\nabla\Phi) = 0 \quad (1)$$

where c is the solute concentration, t the time, $\mathbf{u}$ the velocity vector of the BGE, D the molecular diffusion coefficient, and $\mu_{ep} = Dze/k_B T$ the solute electrophoretic mobility with z the valence number, e the charge of a proton

($1.602 \times 10^{-19} \text{ C}$), k_B the Boltzmann constant ($1.381 \times 10^{-23} \text{ JK}^{-1}$), and T the temperature. The electric potential Φ may be conveniently divided into the externally applied potential φ and the internally induced electric potential ψ due to the surface charge of channel walls. Thus Eq. (1) can be rewritten as

$$\frac{\partial c}{\partial t} + (\mathbf{u} + \mu_{ep}\mathbf{E}) \cdot \nabla c = \nabla \cdot (D\nabla c) + \nabla \cdot (\mu_{ep}c\nabla\psi) \quad (2)$$

where $\mathbf{E} = -\nabla\varphi$ is the externally applied electric field. The second term at the right-hand side represents the contribution from transverse electromigration of charged solutes in response to the intrinsic electric field within EDLs. This term is usually negligible in microchannels, but becomes important in nanochannels, which underlies the charge-based separation [4,5,7,9].

Since the time scale of liquid flows in nanochannels is much shorter than that of the solute transport, the steady-state Navier-Stokes equations govern the incompressible flow field,

$$\nabla \cdot \mathbf{u} = 0 \quad (3)$$

$$\rho\mathbf{u} \cdot \nabla \mathbf{u} = -\nabla p + \eta \nabla^2 \mathbf{u} + \rho_e (\mathbf{E} - \nabla\psi)$$

where ρ is the liquid density, p the pressure, η the liquid viscosity, and ρ_e the net charge density. The term $\rho_e (\mathbf{E} - \nabla\psi)$ represents the electrical body force. Assuming a Boltzmann distribution, ρ_e in a symmetric uni-valence electrolyte is given by [24],

$$\rho_e = -2n_0 e \sinh(e\psi / k_B T) \quad (4)$$

where n_0 is the ionic density of the bulk electrolyte. Poisson-Boltzmann equation links the EDL potential ψ to the net charge in confined nanochannels,

$$\nabla \cdot (\epsilon \nabla \psi) = -\rho_e = 2n_0 e \sinh(e\psi / k_B T) \quad (5)$$

where ϵ is the electrolyte permittivity. It is noted that we have neglected in Eq. (5) the effects from the charged solutes on EDL potential since the solute concentration is typically much lower than the ionic concentration of the BGE. A Laplace equation is needed to describe the external electric field applied along the channel,

$$\nabla \cdot (\epsilon \nabla \varphi) = 0 \quad (6)$$

Given the fact that the width (in micrometers) of state-of-the-art nanofluidic channels is usually much larger than the depth (in nanometers), we consider the solute transport in slit nanochannels. A two-dimensional model is sufficient to describe the fluid flow and solute transport in such configurations. Figure 1 shows a scheme of the slit channel in the computational domain (not to scale). The nanochannel under investigation is 180 μm long and 50 nm high, with 150

roughness elements at the bottom surface. Beginning at $30\mu\text{m}$ away from the channel inlet, these evenly distributed elements are 500 nm long and 500 nm apart from each other. Their height is constant while being varied from 1 to 10 nm in the calculations. The charged solute band was initially confined to a $2\mu\text{m}$ uniform band with its center located $X_0 = 20\mu\text{m}$ away from the channel inlet.

Figure 1. Scheme of the solute transport in a slit nanochannel with roughness structures

We use a finite element package Multiphysics 3.2 (Comsol AB Inc.) to numerically solve the partial differential equations (2), (3), (5), and (6). Poisson-Boltzmann equation (5) and the Laplace equation (6) were first solved. A constant zeta potential was imposed to the channel and nanostructure walls for Eq. (5), while the Neumann condition was applied to all other boundaries. For Eq. (6), a potential and a ground were applied at the inlet and the outlet, respectively, while the Neumann condition was applied to all other boundaries. The calculated EDL potential ψ and the electric field $\mathbf{E}$ were used to specify the body force in the Navier-Stokes equations (3), where a neutral condition was imposed at the channel inlet and outlet for electrically-driven flows, a pressure condition at the channel inlet for pressure-driven flows, and a non-slip condition at the channel and roughness walls. Finally, the Nernst-Planck equation (2) was solved with the known potential ψ , electrical field $\mathbf{E}$, and velocity $\mathbf{u}$. In all the cases, the solute was assumed to be initially confined to a $2\mu\text{m}$ -wide uniform band with its center located $20\mu\text{m}$ away from the channel inlet. The solute was then delivered by pressure-driven or electrically-driven flows from the left end to the right end. The zero concentration condition was imposed to the channel ends while the channel walls were impermeable to the solutes.

To estimate the mean migration velocity of the charged solute, we first calculated the motion of its center of gravity X_c with respect to time,

$$X_c = \frac{\int_{\Omega} xc(t)d\Omega}{\int_{\Omega} c(t)d\Omega} \quad (7)$$

where x is the streamwise coordinate and Ω signifies the integration over the whole computational domain. The mean migration speed is then given by

$$U = (X_c - X_0) / \Delta t \quad (8)$$

where X_0 is the initial center position of the solute band, and Δt is the time interval.

RESULTS AND DISCUSSION

In this section, we apply the proposed model to evaluate the effects of surface roughness on solute transport in nanochannels. Multi-block non-uniform meshes with refined grids adjacent to the channel walls and roughness structures were employed in order to resolve the feature within the EDL. The mesh size of the computational domain used in this study was varied and verified until acceptable mesh independence of the solution was achieved. The main factors affecting the separation efficiency, including solute valence z and roughness size, will be examined individually in nanochannels with different BGE concentrations. Unless stated otherwise, the BGE and solute properties used in the simulations are summarized in Table 1. Similar numerical models have previously been used to study the transport of charged solutes in smooth straight nanochannels [8, 9]. The computational results agreed with the analytical results very well.

Figure 2 illustrates the typical distributions of (a) EDL potential and (b) electroosmotic flow field in a rough nanochannel filled with a $100\mu\text{M}$ BGE. Each roughness element is 10 nm high and 500 nm wide. For a symmetrical 1:1 electrolyte with concentration $100\mu\text{M}$ at room temperature, the characteristic EDL thickness $1/\kappa$ is estimated about 30 nm where $\kappa = \sqrt{2e^2 n_0 / \epsilon k_B T}$ is the Debye parameter [24]. Here we introduce a nondimensional channel height κh to characterize the ratio of channel height h to EDL thickness. Since the presence of roughness changes the channel heights locally, the potential distribution and the flow behavior near the roughness steps are expected to be complex due to the sidewalls, as shown in the zoom-in pictures around the roughness elements in Figure 2.

We then compare the solute transport between in rough channels and smooth channels. Figure 3 displays the simulated concentration contours of solutes with valence $z=-1$ and $z=+1$ in a rough channel and a smooth channel in pressure-driven flows with a $100\mu\text{M}$ BGE. Both channels are $180\mu\text{m}$ long and 50 nm high and the roughness elements are 10 nm high. A vacuum of -80 kPa was applied to both channels. It is important to note that the dispersion of the solutes in rough channels is almost the same as that in smooth channels, indicating that the surface roughness does not affect the solute dispersion significantly. As can be seen in Figure 3, the

negatively charged solute and the positively charged solute both move slower in rough channels than in smooth channels. A vacuum of -80 kPa was applied at the outlet of all channels. For all other parameters refer to Table 1 and Figure 2.

Table 1: Summary of the physicochemical properties used in the numerical simulations unless otherwise stated in the text or figure captions

Properties		Values
BGE	Permittivity ε	$80 \times 8.854 \times 10^{-12} \text{ CV}^{-1}\text{m}^{-1}$
	Viscosity η	$1 \times 10^{-3} \text{ kg} \cdot \text{m}^{-1}\text{s}^{-1}$
	Mass density ρ	$1000 \text{ kg} \cdot \text{m}^{-3}$
	Ionic density n_0^a	$10^{-4} \times 10^3 \times 6.022 \times 10^{23} \text{ m}^{-3}$
	Temperature T	298 K
Nano-channels	Length	180 μm
	Height	50 nm
	Zeta potential ζ	-50 mV
Charged solutes	Diffusion coefficient D	$1 \times 10^{-11} \text{ m}^2\text{s}^{-1}$
	Bulk concentration c_0	10 μM
	Half width of initial 1 μm solute band width	
	Center of initial 20 μm solute band X_0	

a) Note: for a typical BGE concentration 0.1 mM, the second power 10^3 is used to convert the BGE ionic concentration $0.1 \text{ mM} = 10^{-4} \text{ mol/L}$ to $10^{-4} \times 10^3 \text{ mol/m}^3$.

Two factors contribute to the difference of solute migration velocities difference between rough channels and smooth channels: the BGE velocity is smaller in rough channels under the external pressure because the roughness reduces the channel height; and the roughness elements retard the solute migration due to the stronger interaction between the channel walls and the solutes. Figure 4 compares the absolute mean migration speeds of solutes in channels with different roughness height and in smooth channels. The same external pressure and electrical potential were applied to drive the solutes in all nanochannels. A vacuum of -80 kPa was used for pressure-driven flows while a 2 V electrical potential for electric field-driven flows. The roughness elements are 1 nm, 5 nm, and 10 nm high, respectively. Figure 4 shows that under the same driving forces the migration speed in a rough channel

can be much slower than that in a smooth channel. Nevertheless, such difference in migration speed becomes less as the roughness height decreases.

Figure 2. Distributions of (a) EDL potential and (b) electroosmotic flow field in a rough nanochannel.

Figure 5 displays the simulated concentration contours of solutes with valence z varying from -2 to $+2$ at $t=1.5\text{s}$ in a $100 \mu\text{M}$ BGE. A vacuum of -80 kPa was applied at the channel outlet to drive the flows. Due to the transverse electromigration effect, the negatively charged walls repel the co-ions ($z=-2$, $z=-1$) to the center of nanochannels, where the BGE has the highest velocity. In contrast, the counter-ions ($z=+1$, $z=+2$) are attracted into the near-wall region where the liquid velocity is less than in the central portion of the channel. As such, the negatively charged solutes always move faster than the neutral one, and the positively charged solutes always move the slowest. Therefore, solutes with different valences can be separated in pressure-driven flows. In the electric field-driven flow, attraction or repulsion between the wall surface and the charged solute are similar. However, the solute transport becomes more complex due to the competition between electroosmosis and electrophoresis.

Figure 3. Comparison of the solute concentration contours in pressure-driven flows in rough and smooth nanochannels.

Since the hydrodynamic dispersion is proportional to the square of the channel transverse dimension in both pressure [25] and electric field-driven flows [26], it becomes trivial in nanochannels. Therefore, we neglect the hydrodynamics dispersion effect and focus mainly on the migration velocity with regard to solute separation. We define a retention parameter U/U_n , i.e., ratio of the mean speed of charged solutes to that of neutral solutes, to measure the separation efficiency. The more deviated from unit, the better the separation efficiency is.

Figure 6 shows the comparison of U/U_n for charged solutes with valences from -2 to +2 in pressure-driven (a) and electric field-driven (b) nanochannel flows. All the migration speeds were calculated using Eqs. (7) and (8). We choose the nondimensional channel height κh as the abscissa. In rough nanochannels, the curves of the retention for pressure-driven flows and electric field-driven flow display a similar trend as those obtained in smooth channels [9]. In pressure-driven flow negatively charged solutes always move faster than neutral ones ($U/U_n > 1$) while positively charged solutes move slower ($U/U_n < 1$). Such trend becomes more significant when κh shrinks (i.e., relatively thick EDL or narrow nanochannel), indicating higher separation efficiency in lower BGE concentration if the channel size is fixed. U/U_n curves of negatively charged solutes reach their extremes at around $\kappa h=5$ while those of positively charged solutes reach their extremes at around $\kappa h=12$. Figure 6(a) shows that counterions can be separated more efficiently than co-ions using pressure-driven flow.

(a) pressure-driven flow

(b) electric field-driven flow

Figure 4. Comparison of the solute migration speeds in rough and smooth channels.

In electric field-driven flow, U/U_n curves also have their extremes at different κh but with crossovers. Moreover, U/U_n curves of the negatively charged solutes gather more closely compared to those in pressure-driven flow, which indicates an inefficient separation. In the present nanochannel with 10 nm high roughness structures, the ratio U/U_n for $z=+2$ solute can be as low as 0.26 for pressure-driven flow and 0.31 for electric field-driven flow. Both values are significantly smaller than those obtained in a smooth nanochannel (0.42 and 0.68, respectively) [9]. The improvement of the separation performance for the counter-ionic solutes with higher valence can be attributed to the increased interaction between solutes

and roughness structures. Such effects, however, are less evident for the co-ionic solutes and counter-ionic solutes with lower valence.

Figure 5. Comparison of the pressure-driven solute transport in a nanochannel at $t=1.5s$. C_{max} always indicates the maximum concentration in each case.

CONCLUSIONS

A numerical model has been developed to study the charged solute transport in nanochannels with surface roughness. Charged solute transport in rough nanochannels was compared to that in smooth nanochannels. Under the same driving forces, the solute migration speed in roughness nanochannels is slower than in smooth nanochannels. We found that similar as in smooth nanochannels pressure-driven flow can separate efficiently solutes with different valences in rough nanochannels. Relatively large roughness elements can significantly improve the optimal separation efficiency in both pressure-driven flows and electric field-driven flows, especially for the counter-ionic solutes with higher valences. It was also found that smaller roughness structures have no notable effects on the solute separation performance.

(a) pressure-driven flow

(b) electric field-driven flow

Figure 6. Comparison of the ratio of the mean migration speed U/U_n for solutes with different valences.

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