Sample Preconcentration in Channels with Nonuniform Surface Charge and Thick Electric Double Layers

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Abstract

Introduction

Recent advances in micro- and nanoscale fabrication technologies have spurred the development of myriad novel devices for bioassays, DNA separation/amplification, and other lab on chip diagnostic techniques[1-5]. However, the small size scales of these devices introduce several obstacles that must be overcome through engineering prowess, chief among them being the necessity for sample preconcentration in bioanalytical micro and nanofluidic devices[6,7]. In this work, we present an alternate method for field amplified sample stacking (FASS) and focusing in nanochannels by taking advantage of the nonuniform ion distributions produced by thick electric double layers (EDLs) in channels with heterogeneous surface charge. We accomplish this by applying a voltage bias to a gate electrode embedded within the channel wall in order to tune the surface charge in a region of the channel, significantly altering the charge density and ionic strength in that region relative to the rest of the channel. Resulting nonuniform electromigration fluxes in the different regions serve to stack charged sample ions at an interface where a step change in zeta potential occurs, providing enhancement ratios superior to those exhibited in traditional microchannel-based FASS[7]. Numerical simulations are performed to demonstrate the phenomenon, and resulting velocity and salt concentration profiles show good agreement with analytical theory-based results.

Use of the COMSOL Multiphysics® software

Simulations of the background electrolyte electroosmotic flow and the electrophoretic stacking of sample ions in the channel were performed using the COMSOL Multiphysics® software. A 2D representation of the channel and salt reservoirs was generated using the COMSOL® software, and a custom mesh with a combination of mapped elements and triangular elements was employed to resolve sub-nanometer gradients within the EDLs surrounding the charged channel and reservoir walls. Background salt ion distributions were modeled with Coefficient Form PDE and Transport of Diluted Species interfaces in order to represent the system of equations from the Poisson-Nernst-Planck model. The resulting ion distributions, which determine the local conductivity and electric field within the fluid, were coupled with the Electric Currents and Creeping Flow interfaces to solve for the electric field and velocity field from conservation of charge and momentum, respectively. Finally, the sample ions were tracked using the Transport of Diluted Species

interface.

Results

We show that these particular stacking and focusing effects only occur in channels with sufficiently large step changes in zeta potential, and for cases in which the EDLs are sufficiently large relative to the channel height. This approach can potentially achieve thousand-fold sample enhancement ratios, notably higher than those limited by conductivity ratios in conventional FASS[7]. Resulting velocity field and ion distributions were validated through comparison with Boltzmann ion distributions and analytical solutions to the Poisson-Boltzmann equation[8].

Conclusion

These results provide encouraging indications that it is possible to perform FASS in nanochannels without using an injected low conductivity plug solution, but by simply inducing conductivity gradients through tailoring of the channel wall surface charge uniformity via embedded electrodes. The resulting enhancement exceeds that of traditional FASS, providing another promising technique for sample preconcentration in nanofluidic devices.

Reference

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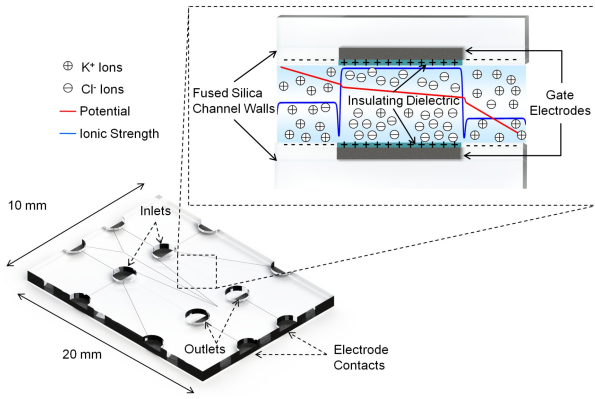
Figures used in the abstract

Figure 1: Figure 1: Schematic illustration of the nanofluidic device with embedded gate electrodes separated from the channel by a thin layer of SiO2. The inset diagram shows representative background electrolyte (BGE) ion distributions for a case with thick electric double layers, a positive zeta potential in the center region, and a negative wall zeta potential. Typical ionic strength and axial electric potential profiles are depicted in blue and red, respectively.
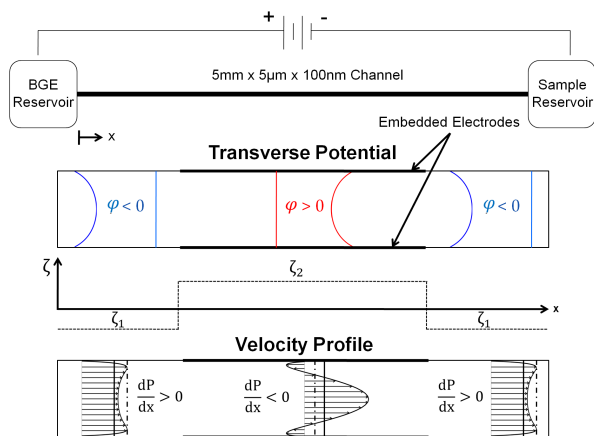

Figure 2: Figure 2: Vertical profiles of transverse potential and velocity in the three channel regions. The velocity profile in the region with the positive zeta potential experiences a favorable pressure gradient and is maximum at the channel center, while the reversed flow at the walls in this region produces an adverse pressure gradient in the other two regions. This leads to a local focusing effect when the fluid leaves the middle region, as the flow in the next region is slowed along the centerline. The area-averaged BGE speed is indicated by solid vertical lines, while the area-averaged sample ion speed is depicted by dash-dot lines (note that the BGE moves left to right and a negatively charged sample moves right to left).
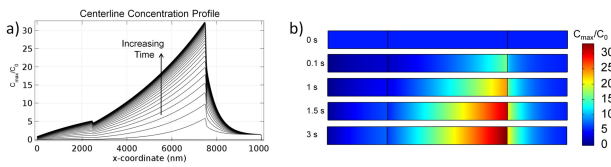
Figure 3: Figure 3: (a) Evolution of centerline sample concentration profile, and (b) concentration surface plots through three seconds of sample concentration. The nominal electric field applied to channel for this simulation was 10,000 V/m, and the zeta potential ratio was set to -2.25 with a BGE concentration of 0.01mM.
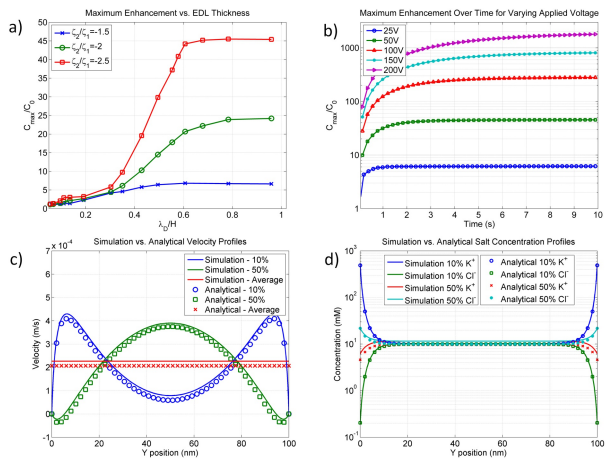

Figure 4: Figure 4: (a) Simulated maximum sample concentration ratio as a function of electric double layer thickness and zeta potential ratio, (b) the transient evolution of the sample enhancement vs. applied axial potential for a -2 zeta potential ratio and a BGE concentration of 0.01 mM, (c) simulated and analytical vertical velocity profiles, and (d) simulated and analytical vertical salt ion profiles for a zeta potential ratio of -0.2 with a BGE concentration of 10 mM.