Research Objective:

Ultimately, there is a need for miniature analytical instrumentation that is hand-portable or used for remote in-situ monitoring and includes the necessary analysis processes to provide quantitative analysis of multiple targets with minimal possibilities of interference. Ideally, these instruments will have analysis times of seconds to minutes and be relatively inexpensive so that they can be massively deployed. One approach for this analytical instrumentation for liquid phase analysis is to develop microfabricated fluidic devices with appropriate functionality. Over the past decade, significant advances have been made in this area, particularly for the analysis of biomolecules, but further research and development is needed to produce robust, miniature instruments capable of analyzing environmental samples. This proposal attempts to further the development of these liquid phase analysis devices by providing low- and high-pressure pumps that can be easily incorporated into microfluidic devices. Such devices would be capable of executing well-recognized characterization methodologies that include sample filtering to exclude particulate matter, concentration of target molecules by solid phase extraction, and target analysis by liquid chromatography. If these capabilities were integrated into a miniature platform, a very powerful analytical tool would be available for EM to use as an emplaced sensor for assessing subsurface contaminant transport, performing in-situ wide area site remediation, and monitoring in a variety scenarios. A key component of these instruments is a robust, high performance, low cost, low power pump, and this proposal sets out to develop and optimize such a pump.

Research Progress and Implications:

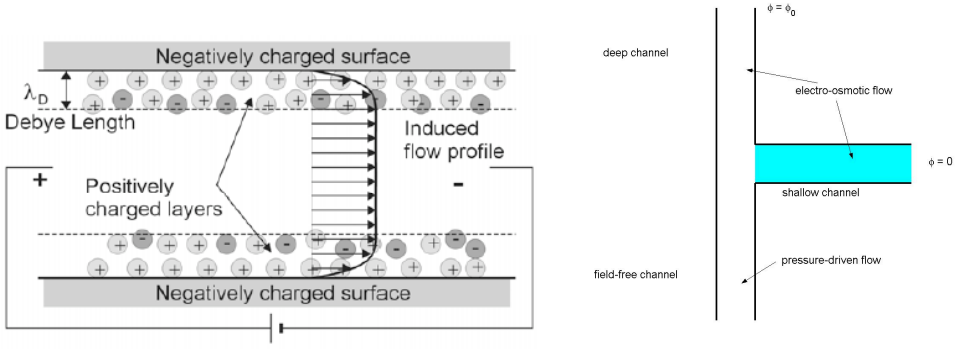
Below we document our progress as of two years of effort on this project. Our results indicate that it will clearly be possible to integrate electrokinetically driven pumps into microfluidic devices for performing liquid phase chromatographic separations, potentially in the field or in situ. Such capabilities will greatly enhance the ability to intelligently collect samples or to monitor remediation efforts.

Hydraulic pumping devices using nanoscale features

Electroosmotic transport of fluid in a microchannel arises due to a separation of electrical charges near the solid-fluid interface at the channel walls. On glass substrates, for example, this separation occurs due to the negatively charged silanol groups residing on the channel surface. Consequently, positive ions in the solution phase are drawn towards the solid-fluid interface leading to the formation of a non-neutral diffuse layer (Debye layer) as illustrated in Figure 1a. Upon application of an axial electric field in the channel, this non-neutral Debye layer experiences a net force resulting in the electroosmotic motion of the adjacent neutral fluid. The streamline velocity in this case, increases from a value of zero at the channel wall and approaches a value of $U_0 = \varepsilon \zeta E_a / \mu$ beyond the Debye layer where ε is the dielectric constant of the medium, ζ is the electric potential relative to the bulk at the solid-fluid interface, μ is the fluid viscosity and E_a is axial electric field in the channel. Note that the variation in the velocity field occurs in the

transverse direction across a length scale given by the thickness of the Debye layer $\lambda_D=(\varepsilon kT/2n_0z^2e^2)^{1/2}$ (typically of the order of 10 nanometers).

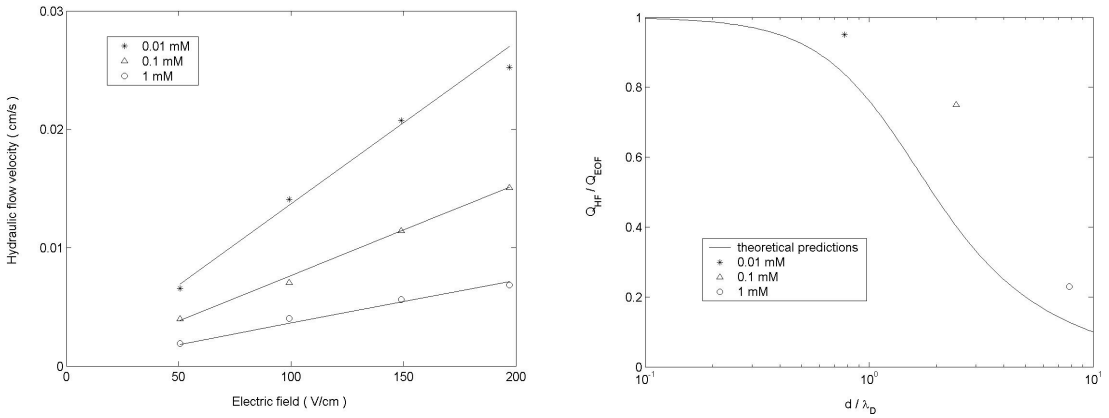
In most microchip applications, the channel dimensions are typically many orders of magnitude greater than the Debye layer thickness in the system leading to a nearly uniform fluid velocity ($=U_0$) across the channel cross-section. However, if the channel depth is made comparable to λ_D, the average velocity in the conduit may be reduced. As a consequence, when an electric field is applied along a channel layout as shown in figure 1(b), a mismatch in the fluid flow rates in the deep and the shallow sections will lead to a pressure-driven flow in the electric field-free region.



(a) (b)

Figure 1. (a) Electroosmotic flow in a glass microfluidic conduit. (b) Schematic diagram for a hydraulic pump employing a combination of a deep and shallow

To demonstrate this idea, experiments were performed on glass microchips using sodium tetraborate buffers at ion concentrations varying between 20μM and 20mM. The channel depth in the shallow and the deep sections of the microchip were chosen to be 2μm and 200nm, respectively while the channel width in both these sections was about 20μm. The fluid velocity in the system was determined using the neutral dye, Rhodamine B (base) that was detected via the laser induced fluorescence (LIF) technique. As may be seen from the results presented in figure 2, a hydraulic pressure-driven flow can be induced in the field-free channel for such a design that scales linearly with the electric field strength in deep channel section. Further, this flow velocity is observed to increase with a

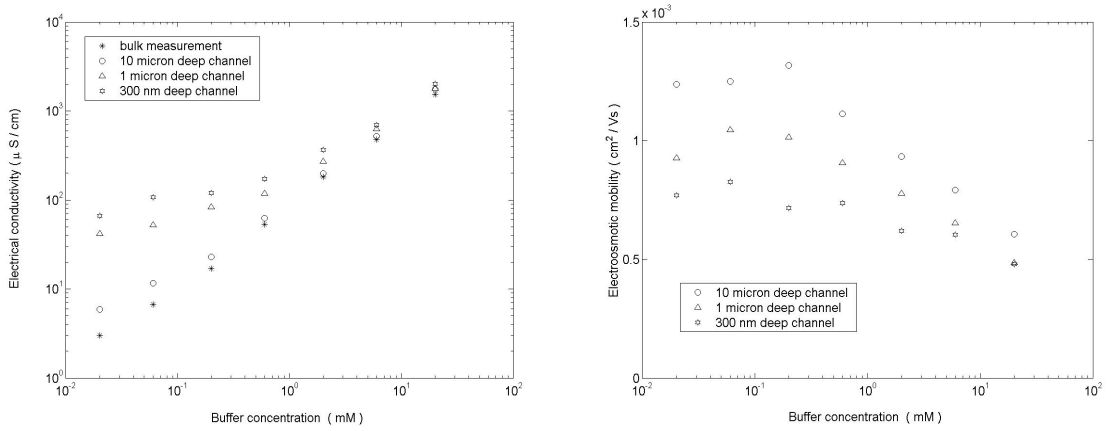


(a) (b)

Figure 2. (a) Observed variation in the hydraulic flow velocity under different operating conditions. (b) Observed dependence of the ratio of hydraulic flow rate (Q_{HF}) to

reduction in buffer ion concentration due to an increase in the electroosmotic mobility in the system. The surprising part, however, was the fact that the experimentally observed hydraulic flow rates were greater than the theoretical predictions made using the Debye layer theory (see figure 2(b)). Upon detailed investigation, it was noticed that while the electrical conductivity of the buffer in the deep section matched the bulk conductivity measurements, the observed conductivity in the shallow section was far greater than this value. Preliminary calculations suggested that such a mismatch in the electrical conductivity could account for the enhanced hydraulic flow rates in the device.

To understand the observations presented above, a more detailed study of the electrokinetic properties of chemically etched channels on glass substrates was undertaken. The electrical conductivity and the electroosmotic mobility of sodium tetraborate were measured in the channels varying the extent of overlap of the Debye layers around the top and the bottom walls of the channel. As may be seen from figure 3(a), the electrical conductivity of fluid increases significantly from its bulk value under conditions when thickness of the Debye layer becomes comparable to the channel depth (shallow channels or dilute buffers). The electroosmotic mobility measured in these systems also shows a significant dependence on both the channel depth and the buffer



(a) (b)

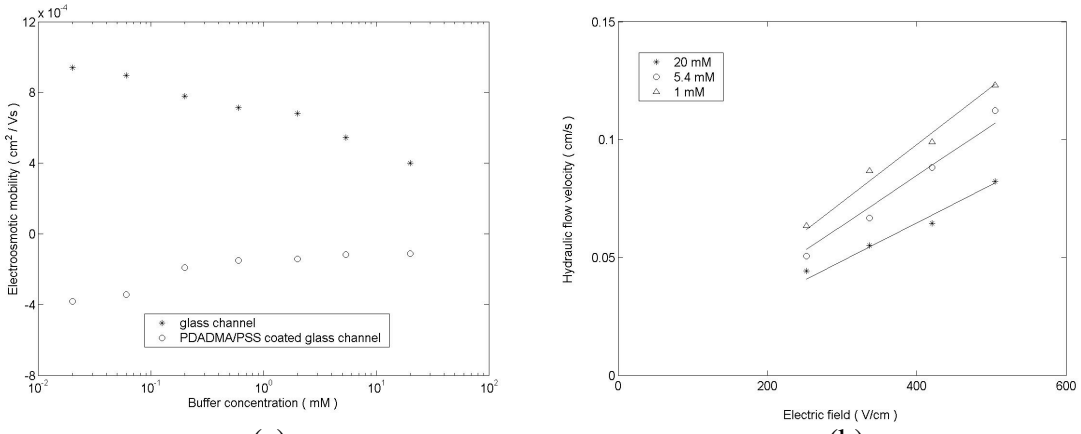
Figure 3. Electrokinetic measurements in chemically etched glass channels.

concentration. These observed variations in the electrokinetic properties with different system parameters are currently being investigated in view of the Debye layer theory. An understanding of the electrokinetic phenomena in these devices is essential for designing efficient electroosmotic pumps described previously.

Hydraulic pumping devices with surface modified structures

The working principle underlying the design of hydraulic pumping devices described above is essentially a mismatch in the electroosmotic mobility in an electrically connected channel network. Alternative to employing shallow microfabricated structures, this mismatch may also be introduced by modifying the channel surface in a

particular section of the fluidic network. For example, a hydraulic pressure-driven flow may be induced in the field-free section of the channel layout shown in figure 1(b) by coating side-arm section with a polyelectrolyte (such as poly-diallyl-dimethylammonium, PDADMA) instead of fabricating it shallow. In fact, such a device may be expected to outperform the devices with shallow microfabricated sections if a cationic coating, such as provided by PDADMA, is used. To test the feasibility of this strategy, the electroosmotic mobility of sodium phosphate buffer in a glass channel was measured both before and after coating with PDADMA. As may be seen from figure 4(a), the electroosmotic flow is indeed reversed upon introduction of the surface modification. Proceeding further, the hydraulic flow velocity was measured in a microchip based on the design depicted in figure 1(b) with the side-arm coated with PDADMA. The hydraulic flow generated in such a device was observed to scale with the electric field strength in the channel as expected. Further, the pumping performance was enhanced for dilute buffers due to a larger difference in the electroosmotic mobilities in the coated and the uncoated channel sections.



(a) (b)

Figure 4. (a) Effect of PDADMA coating on the electroosmotic mobility of sodium phosphate buffer in glass microchips. (b) Performance of a surface modified hydraulic pumping device under different operating conditions.

Planned Activities:

Our future work on this project will be focused in two main directions:

- The first one will be a comprehensive investigation of the electrokinetic measurements in the micron and the sub-micron deep glass channels in view of the Debye-layer theory. The objective in this case will be to build a quantitative model that could explain the variation in electroosmotic flow rates as well as the increased electrical conductivity with the extent of overlap of the Debye-layers around the adjacent channel walls.

- We are also currently working on demonstrating pressure-driven open-channel liquid chromatography on a microchip that has an in-house hydraulic pumping capability.

In this case, we will be exploring the performance of such devices employing the shallow microfabricated structures as well as those relying on the PDADMA surface coating strategy. The channel layout that will be investigated for the purpose has been depicted in figure 5. An important parameter that will be optimized in this design is the channel depth in the different sections of the fluidic network. Simple scaling laws suggest that this depth profile will significantly influence the strength of the hydraulic back-flow in the different sections of the microchip thereby affecting the pressure-gradient generated in the field-free separation channel.

Information Access:

N. J. Petersen, and D. Dutta, J. P. Alarie, J. M. Ramsey, Molecular Transport Through Nanoscale Channels, HPLC 2004, Philadelphia, PA, June 13-18, 2004 (invited).