

Molecular Aspects of Transport in Thin Films of Controlled Architecture

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Executive Summary

I. Overview

Molecular transport in thin films is pertinent to a wide spectrum of energy-relevant technologies, especially those critical to molecular separations. Traditional understanding of diffusion and solvent motion has relied on continuum level descriptions, driven primarily by experimental work in macroscopic samples. However, as technology pushes to ever shorter length scales, continuum approaches are not adequate, so it is critical to develop molecular-level structures and concepts to address transport problems. Our laboratory has focused on developing spatially localized chemistries which can produce structures of controlled architecture on the supermolecular length scale -- structures which allow us to control the motion of molecular species with high spatial resolution, ultimately on nanometer length scales. In this project period we have addressed nanofluidic/microfluidic hybrid architectures which, because they are competent to manipulate samples with sub-femtoliter characteristic volumes and attomole sample amounts, extend molecular separations and multidimensional chemical analyses to samples in a size range not previously addressable. In particular our work has focused on the special transport properties of nanocapillary array membranes (NCAMs) using both pressure and electrokinetic driving forces.

II. Highlights from this Project Period

In the current project period we have concentrated on the parallel goals of (1) understanding transport and interfacial chemistry in nanofluidic/microfluidic hybrid architectures, and (2) optimizing the functional utility of nanometer-diameter capillary interconnects between microfluidic layers. The highlights of work carried out during the current project period include (numbered references refer to the list of DOE-supported publications below):

- Optical (laser induced fluorescence, LIF) and electronic characterization of fluid flow in microfluidic/nanofluidic hybrid structures has been coupled to meshless molecular dynamics and compact model simulations to understand the driving forces behind differential ion transport in nanocapillaries. [3,6]
- Transport in single nanopores has been characterized by both optical (4π microscope single molecule fluorescence) and electrical measurements. A robust strategy for the preparation and transfer of thin polymethylmethacrylate (PMMA) films containing single pores was developed and electrical conductivity studies have been implemented with polyelectrolytes. [2,9]
- Voltage and thermally-activated polymer switches have been developed for active control of transport in NCAMs. Thermally-switchable and size-selective transport was achieved by grafting poly(*N*-isopropylacrylamide) (PNIPAAm) brushes onto the exterior surface of a Au-coated polycarbonate track-etched membrane, while poly(hydroxyethylmethacrylate) (PHEMA) has been used for voltage-gated applications. [5,10]
- Molecular recognition (DNAzyme) motifs have been incorporated in the *interior* of nanopores, and their interfacial chemistry has been characterized. These experiments open the way for "flow-through" chemical sensing which time-integrates the analyte signal allowing ultralow limits of detection and operation in a dosimeter format. [4]

- Electrophoretic separations have been coupled to analyte sampling both by LIF and mass spectrometry. Detection of electrophoresis separation products by electrospray mass spectrometry was achieved through direct interfacing of the microfluidic electrophoresis capillary to a mass spectrometer. LIF was used to characterize Pb(II) interactions with a nanopore-immobilized DNAzyme in an NCAM-coupled integrated microfluidic structure. Thus, cation separations have been coupled to molecular beacon detection motifs for the determination of Pb(II) in the challenging matrix represented by electroplating sludge. By changing the DNAzyme to select for other compounds of interest, multiple sensing systems can be incorporated within a single device, thereby achieving great flexibility. [4,7]
- Au colloids have been tested as specific transfer agents to capture components released from NCAMs. Thermodynamic binding parameters were obtained from isotherm data, and the kinetics of Au colloid-adsorbate assembly reactions were acquired in a single-shot image after reactive mixing through an NCAM. Binding to easily manipulated carriers, such as Au colloids facilitates the chip-to-world interface, thereby enabling confirmatory assays by off-chip tools, such as mass spectrometry. [1,8]

III. Summary

The natural range of sample sizes addressed by the studies here is < 1 fmol; a size range which is relevant to two very important classes of problems where molecular separations play a crucial role: samples in which the analyte mass amount is inherently limited, and samples in which some property, e.g. toxicity, cost of acquisition, etc. limits the sample size. The first constraint arises naturally in many biologically oriented studies, especially those in which single cell or sub-single cell phenomena are targeted. The natural economy of living systems dictates that the interesting active components of cellular machinery are often present in exceedingly small amounts. This problem is most acutely portrayed within the context of proteomics, in which the "copy number" problem is well-known. The second category is graphically illustrated by the various classes of toxins, e.g. the potent class of neurotoxins derived from *C. botulinum*, for which the inherently low LD₅₀ values dictate that they be handled in extremely small quantities.

The special challenges posed by separations and analytical determinations in these mass-limited samples dictated the specific focus of our efforts, namely: (1) to understand the unique nature of electrokinetic transport at the nanoscale; and (2) to extend the functional utility of the integrated nanofluidic-microfluidic architectures. To address the first objective we initiated electrical and optical studies of transport in NCAMs and in membranes containing single nanopores. The functional utility of integrated microfluidic devices was extended by developing interfaces for LIF and mass spectrometric detection as well as intelligent molecular gating strategies based on voltage- and thermally-induced free volume transitions in network polymers. Thus, work supported by the DOE in this project period addressed both deep fundamental questions of enduring interest surrounding the special nature of molecular transport at small length scales, as well as questions of great practical utility, such as the capacity to couple molecular and ionic separations in these architectures to powerful detection modalities, i.e. mass spectrometry and laser induced fluorescence, and to extend the capabilities to size-dependent molecular gating by exploiting free volume transitions in network polymers.

IV. Publications Acknowledging DOE Support, 2004-2006

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5. I.S. Lokuge and P.W. Bohn, "Voltage-Tunable Volume Transitions in Nanoscale Films of Poly(hydroxyethylmethacrylate) Surface Grafted onto Gold," *Langmuir* **2005**, *21*, 1979-1985.
6. K. Fa, J.J. Tulock, J.V. Sweedler and P.W. Bohn, "Profiling pH Gradients across Nanocapillary Array Membranes Connecting Microfluidic Channels," *J. Am. Chem. Soc.* **2005**, *127*, 13928-13933.
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9. E.N. Gatimu, J.V. Sweedler and P.W. Bohn, "Nanofluidics and Mass-Limited Chemical Analysis," *Analyst* **2006**, *131*, 705-709.
10. I.S. Lokuge, X. Wang and P.W. Bohn, "Temperature Controlled Flow Switching in Nanocapillary Array Membranes Mediated by Grafted Poly(*N*-isopropylacrylamide) Polymer Brushes Prepared by Atom Transfer Radical Polymerization," *Langmuir*, submitted.