Electrokinetics with Tailored Porous Materials: Direct, in Situ Measurement of Phoretic Migration, and Nonlinear Electrokinetic Pumps

J.S. Paustian, R. Nery-Azevedo, and T.M. Squires
Dept. of Chemical Engineering, UC Santa Barbara, CA 93106-5080 USA
E-mail: squires@engineering.ucsb.edu

We will discuss two microfluidic systems in which integrated “tailor-made” porous media enable novel electrokinetic studies.

First, we have developed a method to integrate thin (10 μm) Hydrogel “Microwindow” Membranes (HMMs) into conventional microfluidic devices. These thin hydrogel structures have pores that are small enough to prevent appreciable trans-HMM flows, yet large enough to admit the diffusive passage of solute and solvent. They thus function as exceptionally thin, locally-integrated micro-dialysis membranes: solution reservoirs may be imposed, maintained, or switched on one side of the HMM using conventional microfluidic techniques, while remaining hydrodynamically isolated from the fluid on the other side of the HMM. Rapid diffusion of solutes and solvents across the HMM, however, enables the chemical microenvironment on the “sample” side of the HMM to be sculpted in both space and time. Strong gradients of e.g. salts, pH, solvents and sugars can be directly imposed atop a particulate suspension, and the resulting phoretic migration (e.g. electro-diffusiophoretic, chemi-diffusiophoretic, or even solvophoretic) can be measured directly, enabling many “first of its kind” diffusiophoretic mobility measurements (fig 1a). Furthermore, AC electric fields can be locally introduced through HMMs, enabling in situ electrophoretic measurements on suspensions as the background solution evolves or under imposed gradients (fig 1b).

Second, we drive nonlinear (induced-charge) electro-osmotic flows within anisotropically metallized arrays (fig 1c-d), in a manner that generates high pressures with relatively small applied potentials. Strong fields are established by small AC potentials applied across thin channels, whereas the micropillars’ asymmetry drives strong electro-osmotic flows along the channel. Ultimately, our pressure source operates on the same principle as linear electrokinetic pumps, but can be driven by AC fields.

Fig. 1 Hydrogel microwindow membranes (HMMs), function as microdialysis membranes integrated into channel walls. (left) Particles move solvophoretically under imposed concentration gradients of Ethanol. (center left) AC fields applied between reservoir channels drives AC electrophoretic motion. (center right) A microfabricated, anisotropically metallized array can function as an induced-charge electrokinetic pressure source. (right) Particle tracers move under Induced-charge electro-osmotic flow in the oriented array of Janus posts.

References
Microfluidic Pump Based on Concentration Polarization of Ion-Exchange Beads

T. Heldal¹, N. Mishchuk², T. Volden¹, J.Auerswald³, H. Knapp³
¹Osmotex AG, Alpnach Dorf, Switzerland
²Institute of Colloid Chemistry and Water Chemistry, Kiev, Ukraine
³CSEM SA, Alpnach Dorf, Switzerland

E-mail: trond.heldal@osmotex.ch

The development of modern technologies requires miniaturization of different constituents of equipment, including creation of microsized pumps. One of the effective ways to solve this problem is the use of electroosmosis, which does not need the bulky mechanical devices for the creation of pressure gradient, which is necessary for the appearance of hydrodynamic flow.

The majority of studies of electroosmotic pumping concern liquid flow through porous materials or dense multiparticle systems, where the flow-voltage relation is linear or deviation from linearity is relatively low. However, depending on the voltage and the properties of materials, the liquid velocity can be not only a linear function of the electric field strength (classical or standard electroosmosis), but due to concentration polarization can grow with the field increase overproportionally (the induced charge electroosmosis or “electroosmosis of the second kind” [1-3]).

The present study is concerned with the theoretical and experimental aspects of electroosmosis of the second kind near ordered assembly of ion-exchange microspheres, and its application to directed fluid pumping in microchannels. A micropump was developed using polarizable beads with diameter 50 or 90 microns and three-dimensional gold electrodes placed in a 2 mm long and 0.0750 mm wide channel compartment.

The obtained pump was tested using AC and DC modes. The experiments showed an approximately second order dependence of created flow velocity and pressure on the applied voltage, as can be predicted according the theory of electroosmosis of the second kind. The difference between experimental and theoretical flow rates and pressures is attributed to the hydrodynamic resistance of the channel network.

The possibility of directed pumping using AC signals was confirmed also in agreement with the theory. Although the application of AC current results in lower liquid velocities compared to DC, it brings important advantages such as inhibiting electrolytic bubble formation and pH changes, which is important to obtain reliable operation and to minimize changes to the liquids and solutions to be pumped.

Since the active part of pump was considerably smaller than its passive part, there is a great potential of increasing the liquid velocity and pump pressure by increasing the active part length and surface area.

References
Models of Hydrodynamic Dispersion in an Electrolyte Moving Through a Microchannel During Concentration Polarization

C.P. Nielsen and H. Bruus
Department of Physics, Technical University of Denmark, DTU Physics Building 309, DK-2800 Kongens Lyngby, Denmark

E-mail: chnie@fysik.dtu.dk

We have derived a 1D model for salt transport in a microchannel, which includes the effects of hydrodynamic dispersion by superposed electroosmotic and pressure driven velocity fields, as well as effects of surface conduction in the Debye layers. Some aspects of the model are similar to the celebrated Taylor-Aris model for hydrodynamic dispersion, and for a class of systems the derived model does indeed reduce to the Taylor-Aris result. Earlier Taylor-Aris models of dispersion by electroosmosis [1,2,3] assume that the velocity field does not vary along the axis. In contrast, no such assumption is required in our model. Due to our different solution approach, our model can treat axially varying velocity fields, which makes it well suited for the study of concentration polarization in a microchannel, where large axial variations in the electroosmotic velocity occur. In particular, we have used our model to generalize the results obtained in Ref. [4] for concentration polarization in a microchannel in the limit of negligible advection, to cases where advection does play a significant role. Our study comprises a fully resolved numerical 2D model, Fig. 1(a), a 2D effective-boundary-layer model, Fig. 1(b), and an analytical transversely averaged 1D model, Fig. 1(c). We have shown excellent agreement between the latter two, Fig. 1(d), and currently we are working towards a comparison with the fully resolved numerical 2D model.

Fig. 1 (a) Fully resolved numerical 2D model. (b) Locally electroneutral boundary layer model. (c) Leading terms in the transversely averaged 1D model. (d) I-V curves for the 2D boundary layer model and the 1D model at different Péclet numbers for a microchannel during concentration polarization.

References
1. S. K. Griffiths, R. H. Nilson, Anal. Chem. 2000, 72, 4767
Probing Space Charge and Resolving Overlimiting Current Mechanisms at the Micro-Nanochannel Interface Using Electrochemical Impedance Spectroscopy

J. Schiffbauer, N Liebowitz, S. Park, and G. Yossifon,
Micro-Nanofluidics Laboratory, Faculty of Mechanical Engineering, Technion IIT, Haifa, Israel

E-mail: jarrod.schiffbauer@gmail.com

We present recent results showing the unique electrochemical impedance signatures [1] of a fabricated micro-nanochannel interface device over a wide range of voltages. The system is probed from 0 V to 20 V DC bias, covering the full range of the DC current-voltage response, from Ohmic to far-overlimiting regimes. The evolution of the space charge-nanochannel entrance EDL can be tracked in the high-frequencies, showing a characteristic shift in the phase angle in the limiting regime [2], and an anomalous sharply-peaked minimum in the overall DC resistance. Upon further increase of applied voltage, an abrupt change in the response characteristics occurs, corresponding to a rapid increase in the overall DC resistance to a higher, nearly constant value, with marked qualitative change of the impedance characteristics, and the appearance of a new, localized relaxation. The overlimiting current has two sub-regimes, demarked by the position of the anomalous DC minimum resistance. The lower overlimiting regime appears essentially electro-diffusive in nature, suggesting dominance of surface-conduction mechanisms while the higher overlimiting regime is believed to correspond to an electro-osmosis dominated mechanism [3]. The latter may be accompanied by electro-convective instability of the space charge and associated fast electro-convective vortices [4,5,6] and is distinguished by a region of frequency-dependent negative resistance.

Fig. 1 Fast-sweep IV curve showing response regions (left) and phase angle from electrochemical impedance spectroscopy under DC bias (right) for the same system.

References
Novel Electrochemical Systems for Energy Storage and Water Desalination Leveraging Flow-through Porous Media

M.E. Suss  
Department of Chemical Engineering, MIT, USA  
Faculty of Mechanical Engineering, Technion – Israel Institute of Technology, Israel

The development of inexpensive and robust renewable energy and water desalination systems are two of the major technological challenges faced today. Electrochemical systems leverage ion transport and electrochemical reactions to store and deliver energy or desalinate salt water streams. This talk will focus on my work towards the development of novel systems which implement flow-through porous materials with micron-scale flow dimensions to enhance device performance. Example devices will include hydrogen-bromine laminar flow batteries for large-scale energy storage, flow-through electrode capacitive water desalination, and shock electrodialysis desalination. I will further describe my work on novel experimental techniques for improved characterization of porous electrodes.

Fig. 1: a) Schematic of the architecture of a membraneless hydrogen bromine flow battery with porous flow-through electrodes. b) Polarization curve data demonstrating that use of porous flow-through electrodes enable over 3 X improvement in limiting current density.

Fig. 2: a) Schematic of the architecture of a flow-through electrode capacitive desalination cell. b) Performance of the capacitive desalination cell, demonstrating concentration reductions of the NaCl feed stream of up to 70 mM as well as up to roughly 1 mg/g*min mean sorption rate.

References
Supression of Induced-Charge Electroosmosis by the Addition of Polyethylene Oxide to the Electrolyte

P. García-Sánchez¹, J.J. Arcenegui¹, H. Morgan², A. Ramos¹

¹Depto. de Electrónica y Electromagnetismo, Universidad de Sevilla, Sevilla, Spain.
²School of Electronics and Computer Science, University of Southampton, Southampton, UK
E-mail: pablogarcia@us.es

We report experimental results on induced-charge electrokinetic phenomena with electrolytes containing an added polymer (polyethylene oxide, PEO). Electrorotation of silver nanowires show that the typical frequency of the rotating applied electric field is not affected by the presence of PEO. Electro-orientation of these nanowires is originated by induced charge electroosmotic flow around the particle at low frequency and by the torque on the induced dipole at high frequency [1,2]. No effect of the PEO is found if the frequency of the applied field is high, however, the electroorientation of the metal nanowires at low frequencies is greatly reduced by the addition of PEO. According to our previous results with silver nanowires [1,2], the present experiments are explained if the presence of the polymer decreases the induced-charge electroosmosis (ICEO) while not affecting the electrode-electrolyte surface capacitance. This behaviour can be understood if PEO molecules adhere to the nanowire surface, augmenting the viscous friction within the diffuse layer at the metal-electrolyte interface. We also made experiments to measure the ICEO velocity on a floating electrode as the experiments in [3], see Fig 1. The measurements confirmed that ICEO velocity was drastically reduced by PEO. Additionally, we found that nanowire dispersion is stable for higher electrolyte conductivities when PEO was added. ICEO suppression might be useful in applications where the electroosmotic flow perturbs the manipulation of particles with electric fields.

![Induced-charge electroosmotic velocity on a floating electrode (100 μm wide) for three different values of the electrolyte conductivity. An external electric field (50 V/cm) was applied and the velocity was measured at 35 μm from the electrode edge. Addition of PEO strongly reduces the ICEO velocity.](image)

Fig. 1. Induced-charge electroosmotic velocity on a floating electrode (100 μm wide) for three different values of the electrolyte conductivity. An external electric field (50 V/cm) was applied and the velocity was measured at 35 μm from the electrode edge. Addition of PEO strongly reduces the ICEO velocity.

References
Electrophoresis of Bubbles

O. Schnitzer¹, I. Frankel¹ and E. Yariv¹

¹Technion — Israel Institute of Technology, Haifa, Israel
E-mail: udi@technion.ac.il

Smoluchowski’s formula is inadequate for describing the motion of drops and bubbles, as the no-slip condition underlying its derivation does not apply at a free surface. Electrophoresis of drops and bubbles was analyzed by Baygents & Saville [1] for weak fields. While the weak-field approximation applies to micron-size colloidal particles, it is usually inappropriate for describing drops and bubbles, which are typically much larger, of millimetric dimensions. Other models [2], based upon a small-zeta-potential approximation, predict nil bubble velocity, in contrast to experimental observations.

We here analyze bubble electrophoresis in the thin-double-layer limit, allowing for arbitrary (i.e. non-small) values of the applied-field magnitude and the zeta potential. Following Booth [2] we employ what may be the simplest model problem, namely a spherical gas bubble whose surface charge density is fixed and uniform. The thin-double-layer limit is analyzed using inner-outer asymptotic expansions, the inner region being a Debye diffuse layer in quasi-equilibrium and the outer region constituting an electro-neutral bulk with uniform salt concentration at leading order. As in the classical problem of a solid particle, asymptotic matching with the bulk results in an effective electro-osmotic slip. However, the bubble motion is not determined by the slip mechanism, but rather by the shear-stress balance at the interface, resolution of which requiring in turn analyzing one higher asymptotic order. The interfacial shear is driven by the salt perturbation in the bulk, itself engendered by the electric field and modified by Debye-scale advection.

The resulting macroscale model consists of a set of differential equations in the bulk, governing the leading-order flow and the excess-salt perturbation, together with effective “boundary” conditions representing asymptotic matching with the diffuse-layer fields. The excess salt is thus governed by an advection–diffusion equation together with a Neumann-type condition, which accommodates an effective surface-convection term, rendering a coupling to the Stokes flow. This flow, in turn, is animated by an effective shear-stress condition, wherein surface gradients of the salt perturbation result in a Marangoni-like stress jump. Because of the advection term, the problem is inherently nonlinear and thus does not admit a closed-form solution. We have obtained numerical solutions for arbitrary parameter values, as well as linearized approximations for the respective cases of small zeta potentials, small ions, and weak fields. These resolve the paradoxical prediction of nil velocity in Booth’s analysis [2].

For typical bubble size, the relevant limit is actually that of strong fields. In this singular limit the excess salt is confined within a diffusive boundary layer. The parabolic boundary-value problem governing that layer is solved using integral transforms, eventually leading to a nonlinear boundary-value problem governing the flow field. The bubble velocity scales as the 2/3 power of the applied field. A transformation to a universal flow problem, independent of any parameters, reveals an explicit functional dependence of the scaled bubble velocity upon a specific combination of the zeta potential and the ionic drag coefficient. Both the field scaling and this functional dependence are corroborated via comparison with numerical solutions of the macroscale model.

References
Electrokinetics of Metal Drops Revisited

O. Schnitzer¹, I. Frankel¹, E. Yariv¹
¹Technion — Israel Institute of Technology, Haifa, Israel

E-mail: schnit@technion.ac.il

The electrokinetic response of liquid-metal (e.g. mercury) drops is very different from that of solid particles or non-conducting drops [1]. In particular, their electrophoretic mobilities are unusually high, and electroviscous effects are appreciable even for small Debye lengths. In the seminal analysis by Oshima et al. [2], these anomalies were studied theoretically via a systematic weak-field linearization of the standard electrokinetic model. For all but small zeta potentials, their results (degenerated to thin double layers) disagree with earlier results by Frumkin and Levich (FL), which are based on rather intuitive arguments.

In a recent contribution [3], we revisited metal-drop electrophoresis by considering the limit where the dimensionless Debye thickness $\delta=1/\kappa a$ is asymptotically small. The large velocities unambiguously follow from the requirement of microscale tangential-stress continuity: since the electric potential of a metal is uniform, the strong $O(\delta^{-1})$ viscous stress associated with electroosmotic flow cannot be locally balanced by a Maxwell stress. The analysis results in a coarse-grained model where the electrokinetic transport occurring within the diffuse part of the double layer is represented by effective boundary conditions governing the pertinent fields in the electro-neutral bulk.

The macroscale model is limited to neither weak fields nor small zeta potentials; with the effective removal of scale disparity from the problem, it is fairly straightforward to solve numerically [4]. For weak fields, the linearized macroscale equations admit an analytic solution, yielding a closed-form expression for the electrophoretic velocity. Surprisingly, the result is incompatible with that of Oshima el al. — it actually coincides with that of FL. This discrepancy is related to the dominance of advection on the bulk scale, even for weak fields, which feature cannot be captured by a linear theory. The respective limit of thin double layers and weak applied fields do not commute; the limit process considered in [3] is the one appropriate in most physical scenarios.

The problem of calculating the excess drag on a sedimenting metal drop has also been considered. The thin-double-layer methodology results in an appropriate macroscale model holding for arbitrary Péclet (Pe) numbers. An asymptotic solution at low Pe recovers the comparable result of Oshima et al. [2], while at high Pe, the macroscale model yields the result of FL. A numerical solution for arbitrary Pe bridges the two limiting behaviors.

References
4. O. Schnitzer and E. Yariv, Nonlinear electrokinetic flow about a polarised conducting drop, Phys. Rev. E, 87 041002(R) 2013, see also erratum: 059901(E).