Microchannel electrokinetics of charged analytes in buffered solutions near floating electrodes

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We present both experimental and numerical studies of nonlinear electrokinetic flow of buffered solutions seeded with dilute analytes in a straight microchannel (0.6 \( \mu \text{m} \) high, 250 \( \mu \text{m} \) wide, and 9000 \( \mu \text{m} \) long) with a 0.15 \( \mu \text{m} \) high 60 \( \mu \text{m} \) wide electrode situated at the bottom center of the channel. Such studies will enable a fundamental understanding of nonlinear transport effects of ions in electrolyte systems with a significant Debye screening layer. Initial experimental studies have shown an order of magnitude increase of concentration near the electrodes, but numerical studies have so far failed to accurately predict such behavior in these flow regimes. Experimentally, using conventional fluorescence microscopy, we investigated the concentration gradient (as well as the associated electroosmosis, induced-charge electro-osmosis, and electrophoresis) of the charged analyte near the floating electrode as a function of analyte (1 to 10 \( \mu \text{M} \) fluorescein and bodipy) and buffer (1 to 10 mM borate and phosphate) concentrations and an externally applied voltage drop (50 to 100 V) along the channel. We have implemented a nonlinear continuum kinetics model of the system involving the electric potential, the buffer flow velocity, the pressure, and the four ionic concentration fields and compared the resulting numerical simulations with experiments.
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Induced-charge electro-osmosis: UCSB experimental setup I

(a) electrodes
(b) microscope objective

Phosphate Fluorescein
buffer with dye
microchannel

Extreme aspect ratios – Debye layer overlap

- $L = 9000.00 \, \mu m$
- $w = 250.00 \, \mu m$
- $l = 60.00 \, \mu m$
- $H = 0.50 \, \mu m$
- $\lambda_D = 0.03 \, \mu m$

un-biased Pt electrode
Induced-charge electro-osmosis: UCSB experimental setup II

- Inverted fluorescence microscope
- Mercury lamp
- Optical filter cubes
- Microchip stage
- Data analysis
- CCD
- Power supply

Diagram:
- Microchip
- Fluorescence dye
- Objective
- Filter cube
- Dichromatic mirror
- Emission filter
- Ocular
- CCD camera/eyepiece

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Department of Micro- and Nanotechnology
The continuum description of the electric screening in electrolytes: the double layer

- **Governing equations**
  - **Navier-Stokes equation** \( u \) \( \rho [\partial_t u + (u \cdot \nabla) u] = -\nabla p + \eta \nabla^2 u - Ze(c_+ - c_-) \nabla \phi \)
  - **Incompressibility** \( \rho \) \( \nabla \cdot u = 0 \)
  - **Electrostatic Maxwell eq.** \( \phi \) \( \nabla \cdot (\varepsilon \nabla \phi) = -Ze(c_+ - c_-) \)
  - **Nernst-Planck equation** \( J \) \( J_i = -\frac{D_i}{k_B T} c_i \nabla \mu_i + u c_i \)
  - **Continuity equation** \( c \) \( \nabla \cdot J_i = -\partial_t c_i \)

**Diagram:**
- Bulk electrolyte
- Debye layer
- Stern layer
- Charged wall

\( \lambda_D \sim 30 \text{ nm} \)
Induced-charge electro-osmosis: Basic principle

- An external potential difference is applied (+$V_0$ and $-V_0$) to electrolyte
- Induced polarization charge appears in the metallic electrode
- Ions in the electrolyte screens out the $E$-field normal to the electrode
- The tangential $E$-field drives an ionic current along the dielectric
- The moving ions drags the liquid along the dielectric
- Flow‐rolls are consequently induced in the electrolyte
Induced-charge electro-osmosis: UCSB experimental setup III

(a) 3D view:
- Inlets
- Microchannel

(b) Top-down view:
- Floating electrode

(c) Microscope view:
- Floating electrode
- Microchannel view
- $+V_0$
- $-V_0$
- $v_{eo}$
- $E$
- $l$
- $w$
Experimental parameters and calibration of fluorescent detection

### Experimental Parameters

<table>
<thead>
<tr>
<th>Electric Fields</th>
<th>Ion/Analyte Densities</th>
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<tbody>
<tr>
<td>± 13.3 kV/m</td>
<td>1 mM / 1 mM</td>
</tr>
<tr>
<td>± 26.6 kV/m</td>
<td>1 mM / 100 mM</td>
</tr>
<tr>
<td>± 39.9 kV/m</td>
<td>1 mM / 10 mM</td>
</tr>
<tr>
<td>± 53.2 kV/m</td>
<td>1 mM / 1 mM</td>
</tr>
<tr>
<td>± 66.5 kV/m</td>
<td>10 mM / 1 mM</td>
</tr>
<tr>
<td>± 79.8 kV/m</td>
<td>10 mM / 100 mM</td>
</tr>
<tr>
<td>± 93.1 kV/m</td>
<td>10 mM / 10 mM</td>
</tr>
<tr>
<td>± 106.4 kV/m</td>
<td>10 mM / 1 mM</td>
</tr>
<tr>
<td>± 119.7 kV/m</td>
<td>10 mM / 1 mM</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Electrode Geometries</th>
<th>Analytes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ellipsoid</td>
<td>Rhodamine 6G (positive)</td>
</tr>
<tr>
<td>circle</td>
<td>Bodipy DiSulfonate</td>
</tr>
<tr>
<td>Square</td>
<td>Fluorescein (negative)</td>
</tr>
</tbody>
</table>

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Platinum Electrode, BDP

**Normalized Maximum Intensity**

Voltage

- 1mM / 100μM
- 1mM / 10μM
- 10mM / 100μM
- 10mM / 10μM
Real-time CCD recordings of one experiment

Transverse average of the fluorescence signal

Flow direction

Top view

$-V_0$

$+V_0$

Electrode

$-V_0$

$+V_0$

$+V_0$

$-V_0$

x
Theoretical model: the 2D computational domain

Extreme aspect ratios

- $L = 9000.00 \, \mu m$
- $l = 60.00 \, \mu m$
- $H = 0.50 \, \mu m$
- $\lambda_D = 0.03 \, \mu m$
Theoretical model: Induced-charge electro-osmosis in microchannels

The symmetry is broken by the EO-flow from the surrounding walls.
Theoretical model: potential, pressure and velocity profiles

The potential $\phi$

$t = 0$

$t \to \infty$

The pressure $p$

$Q_{eo}$ $Q_p$

$Q$

$+V_0$ $-V_0$

$-4500 \mu m$ $0 \mu m$ $4500 \mu m$
Dye concentration: comparing simulation with experiment

\[ c^{(d)}(x) \text{ [m}^{-3}] \]

(a) \[ c_{0(b,-)} = 10 \, \mu M \]
\[ c_{0(b,+)} = 11 \, \mu M \]
\[ c_{0(d)} = 1 \, \mu M \]

(b) \[ c_{0(ph)} = 1 \, mM \]
\[ c_{0(BDP)} = 1 \, \mu M \]

Flow directions: +\(V_0\) and -\(V_0\) for different voltages: 5V, 10V, 15V, 20V, 25V, 30V, 50V, 75V, 80V, 90V.
Concluding remarks

- Experimental setup for observing induced-charge electro-osmosis (ICEO) in micro/nanochannels
- Transient development of dye concentration has been measured
- Theoretical model combining EO flow with ICEO has been established for extreme aspect ratios
- Qualitative agreement between experiments and numerical simulation has been achieved
- A good basis for further ICEO studies have been developed and successfully tested
Theoretical model

\[ c^{(0)}(x) \text{ [m}^3\text{]} \]

100 \( \mu \)M buffer
1 \( \mu \)M dye

\( x \text{ [m]} \times 10^{-3} \)

15V 10V 5V 20V 25V
Theoretical model