Experimental Investigation of Induced-Charge 
Electro-Osmosis

by

Jeremy Asher Levitan

Submitted to the Department of Mechanical Engineering
in partial fulfillment of the requirements for the degree of
Doctor of Philosophy

at the

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Abstract

We analyze the general phenomenon of induced-charge electro-osmosis (ICEO), nonlinear electro-osmotic slip generated when an electric field acts on its own induced charge around a polarizable surface, in the context of microfluidics. Simple ICEO flows are first observed around a platinum wire in a polymer microchannel. While convenient for scaling analysis of resulting flows, this geometry proved difficult to analyze because of sensitivity to measurement height. This motivated the development of microfabrication techniques for the creation of electroplated metal structures with clean surfaces for ICEO flow characterization.

ICEO flows are analyzed in a simple geometry, with an electroplated metal cylinder and two outer electrodes on a glass substrate. ICEO flow velocities scale as $V^2$, where $V$ is the potential drop across the outer electrodes, and decay monotonically with increasing frequency. Flow velocity also decays with increasing electrolyte concentration. Fixed-potential ICEO, with non-zero fixed charge on the polarizable surface, is demonstrated around a metal cylinder. A range of electrolyte solutions are tested in ICEO flow geometries and measured velocities scale well with effective salt diffusivity.

Finally, we propose ICEO microfluidic systems as solid-state pumps and mixers for a variety of possible applications.

Thesis Supervisor: Martin Z. Bazant
Title: Associate Professor
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Chapter 1

Introduction

This thesis presents an experimental investigation of induced-charge electro-osmosis (ICEO), the nonlinear electro-osmotic slip created when an electric field acts on its own induced charge around a polarizable metal object. Though this thesis largely presents experimental results, the reader will also find predictions for scalings of ICEO flows with voltage, frequency, and electrolyte chemistry. This chapter provides an outline of this thesis, followed by an introduction to the relevant physics.

1.1 Organization of the Thesis

Chapter 1 discusses the relevant physics behind ICEO flows. Chapter 2 presents a brief introduction to two experimental techniques employed herein, particle-image velocimetry and impedance spectroscopy. Chapter 3 explores ICEO flows around a platinum wire in a polymer microchannel. Chapter 4 presents fabrication processes for the creation of electroplated metal structures, with clean surfaces, for electrokinetics. The following two chapters explore ICEO flows in these structures, first at zero fixed charge on the metal structure, then allowing for non-zero charge. Chapter 7 explores the relationship between solution chemistry and resulting fluid flow. Chapter 8 examines the colloidal manipulation in ICEO flows. Chapter 9 discusses possible applications of ICEO flows in microfluidics. Chapter 10 summarizes the results of this thesis.

1.2 Relevant Background

Electrokinetics provides one of the most plausible alternatives to mechanical pumping in microfluidics. This section follows the introduction to electrokinetics and ICEO from [Squires & Bazant(2004)], while expanding the discussion of frequency dependence of steady-state ICEO flow profiles, which will prove useful in understanding experimental results in subsequent chapters.
Consider a surface with charge density $q$ in an aqueous solution with mobile positive and negative ions. Electrostatic interactions between the surface charge and mobile ions will lead to the development of a screening cloud of oppositely-charged ions near the surface, an electrochemical 'double layer', which screens out the excess surface charge exponentially from the surface, yielding an electrostatic potential profile

$$\phi = \frac{q}{\varepsilon} e^{-\kappa z} \equiv \zeta e^{-\kappa z}. \quad (1.1)$$

Here $\varepsilon$ is the permittivity of the solution and the 'zeta potential',

$$\zeta \equiv \frac{q}{\kappa}, \quad (1.2)$$

is the potential drop across the double layer, where $\kappa^{-1}$ is the Debye screening length (the width of the double layer), defined for a symmetric $z:z$ electrolyte as

$$\kappa^{-1} \equiv \lambda_D = \left( \frac{2c_0 z^2 e^2}{\varepsilon k_B T} \right)^{-1/2}, \quad (1.3)$$

with bulk ion concentration $c_0$, ion charge $e$, valence $z$, Boltzmann constant $k_B$, and temperature $T$.

An electric field applied tangentially across the screening cloud results in a body force on the charged parcels of fluid and a resulting fluid slip. The fluid appears to move as a plug flow just outside the Debye length, with slip velocity given by the classical Helmholtz-Smoluchowski formula,

$$u_s = \frac{\varepsilon}{\eta} E_{||}, \quad (1.4)$$

where $\eta$ is the fluid viscosity and $E_{||}$ is the tangential component of the bulk electric field.

This basic electrokinetic phenomenon gives rise to two related effects, electro-osmosis and electrophoresis. Electro-osmotic flow occurs when an electric field is applied down a channel with surface charge, such as an electric field down a glass capillary. The fluid slip, given by Eq. 1.4, gives rise to a plug flow in the capillary, shown in Fig. 1-1(a).

In the case of a suspended particle in solution, the slip results in motion of the particle, electrophoresis, and is shown in Fig. 1-1(b).

### 1.3 Induced-Charge Electro-Osmosis

#### 1.3.1 Qualitative description

The basic phenomenon of induced charge electro-osmosis can be understood from Figure 1-2. Immediately after an external field $E = E_0 \hat{z}$ is applied, an electric field is set up so that field lines
Figure 1-1: Left: A charged solid surface in an electrolytic solution attracts an oppositely-charged ‘screening cloud’ of width $\sim \lambda_D$. An electric field applied tangent to the charged solid surface gives rise to an electro-osmotic flow, with magnitude given by Eq. (1.4). Right: An electric field applied to an electrolytic solution containing a suspended solid particle gives rise to particle motion called electrophoresis, with velocity equal in magnitude and opposite in direction to Eq. (1.4). From [Squires & Bazant(2004)].

Figure 1-2: The evolution of the electric field around a solid conducting cylinder immersed in a liquid electrolyte, following the imposition of a background DC field at $t = 0$ (a), where the field lines intersect normal to the conducting surface. Over a charging time $\tau_c = \lambda_D a / D$, a dipolar charge cloud forms in response to currents from the bulk, reaching steady state (b) when the bulk field profile is that of an insulator. The resulting zeta potential, however, is nonuniform. From [Squires & Bazant(2004)].
intersect a conducting surface at right angles (Fig. 1-2(a)). Mobile ions in the solution move in response to applied fields, and a current \( j = \sigma E \) drives positive ions into a charge cloud on one side of the conductor \((z < 0)\), and negative ions to the other \((z > 0)\), thereby an opposite charge on the conducting surface is induced to maintain the equipotential surface. A dipolar charge cloud thus develops, charging until no field lines penetrate the double-layer in steady state (Figure 1-2b). In steady state, the tangential field \( E_{\parallel} \) drives an electro-osmotic slip velocity (Eq. 1.4) proportional to the local double-layer charge density, driving fluid from the 'poles' of the particle towards the 'equator'. The same flow can be driven using an AC field, as can be seen by the fact an oppositely-directed field induces an oppositely-charged screening cloud, so that the net flow (dependent on the product of the field and the charge) remains the same.

**Steady ICEO Around an Uncharged Conducting Cylinder**

Consider an isolated, uncharged conducting cylinder of radius \( a \) immersed in an electrolyte solution with \( \kappa a \ll 1 \). An external electric field \( E_0z \) is suddenly applied at \( t = 0 \), and charges within the conductor arrange themselves so that the conducting surface forms an equipotential surface, giving a potential

\[
\phi_0 = -E_0z \left(1 - \frac{a^2}{r^2}\right).
\]

(1.5)

Electric field lines intersect the conducting surface at right angles, as shown in Figure 1-2(a). Positive ions are driven with the local electric field and negative ions are driven opposite. Due to the non-zero electrolyte conductivity \( \sigma \), a non-zero current

\[
j = \sigma E
\]

(1.6)

is driven along field lines, and ions are transported up to the cylinder surface. In the absence of electrochemical reactions at the conductor/electrolyte interface (i.e. sufficiently low potentials whereby the cylinder is 'ideally polarizable'), mobile solute ions accumulate in a screening cloud adjacent to the solid/liquid surface. The conductor's surface charge density \( q \) — induced by the growing screening cloud — changes in a time-dependent fashion, via

\[
\frac{dq(\theta)}{dt} = -j_\perp = \sigma E \cdot \hat{r}.
\]

(1.7)

Using the approximate linear relationship (1.2) between surface charge density and zeta potential, this can be expressed as

\[
\frac{d\zeta(\theta)}{dt} = \frac{\sigma}{\epsilon_{wK}} E \cdot \hat{r}.
\]

(1.8)
A dipolar charge cloud grows, since positively-charged ions are driven into the charge cloud on the side of the conductor nearest the field source \((z < 0\) in this case), and negatively-charged ions are driven into the charge cloud on the opposite side. As ions are driven into the charge cloud, field lines are expelled, thereby reducing the ionic flux into the charge cloud.

The system reaches a steady state configuration when all field lines are expelled \((\mathbf{r} \cdot \mathbf{E}(a) = 0)\). This occurs when the electrostatic potential outside of the charge cloud is given by

\[
\phi_f = -E_0 z \left( 1 + \frac{a^2}{r^2} \right),
\]

shown in Figure 1-2(b). The steady-state configuration corresponds to a cylinder whose zeta potential varies with position according to

\[
\zeta(\theta) = -\phi_f(a) = 2E_0 a \cos \theta.
\] (1.10)

While the steady-state electric field has no component normal to the charge cloud, it does have a non-zero tangential component, given by

\[
\hat{\theta} \cdot \mathbf{E} = -2E_0 \sin \theta.
\] (1.11)

This tangential field drives an induced-charge electro-osmotic flow, with slip velocity given by equation (1.4), where the (spatially-varying) surface potential \(\zeta\) is now given by equation (1.10). Because the charge cloud is itself dipolar, the tangential field drives the two sides of the charge cloud in opposite directions—each side away from the poles—resulting in a quadrupolar electro-osmotic slip velocity

\[
u_s = 2U_0 \sin 2\theta \hat{\theta}
\] (1.12)

where \(U_0\) is the natural velocity scale for ICEO,

\[
U_0 = \frac{\epsilon_0 E_0^2 a}{\eta}.
\] (1.13)

One power of \(E_0\) sets up the 'induced-charge' screening cloud, and the second drives the resultant electro-osmotic flow.

The fluid motion in this problem is reminiscent of studies by Taylor [Taylor(1966)] whereby a fluid drop of one conductivity immersed in a fluid of another conductivity and subjected to an external electric field. By analogy, we find the radial and azimuthal fluid velocity components of the fluid flow outside of the cylinder to be

\[
u_r = 2\frac{a(a^2 - r^2)}{r^3} U_0 \cos 2\theta
\] (1.14)
\[
\phi_\theta = \frac{2a^3}{\pi^3} U_0 \sin 2\theta.
\] (1.15)

1.3.2 Time-Dependence of Double Layer Charging

A significant feature of induced-charge electro-osmotic flow is its dependence on the square of the electric field. This has important consequences for AC fields: if the direction of the electric field in the above picture is reversed, so are the signs of the induced surface charge and screening cloud. The resultant ICEO flow, however, remains unchanged: the net flows generically occur away from the poles and toward the equator. Therefore, induced-charge electro-osmotic flows persist even in an AC applied fields given that the driving frequency is sufficiently low such that the induced-charge screening clouds have time to at least partially form.

It is thus of interest to examine the time-dependence of induced-charge electro-osmotic flows. In each of the following examples, we consider equivalent circuit models with time-dependent voltage source with potential given by the real part of a complex potential, \( \phi = \phi_0 e^{i\omega t} \). For all elements, we examine its impedance, \( Z \), as the ratio of the voltage drop across the device to the current flowing through the device. For instance, the impedance of a purely resistive element would be its resistance. In general, the impedance of an element can be a complex function of frequency.

1.3.3 Impedance Models of Equivalent Electrical Circuits

Model 1: Gouy-Chapman Model

We consider the equivalent circuit shown in Fig. 1-3(a). The double layer is modeled as a capacitor, \( C_d \), and the bulk electrolyte as a resistor, \( R \). The total impedance of the circuit (using complex variable notation) is then

\[
Z = \frac{i\omega RC_d + 1}{i\omega C_d}
\] (1.16)

We recognize \( \tau_c = RC_d \) as the critical charging time for the double layer to form around the
cylinder. The zeta potential is then given by the product of the current and the impedance of the double layer capacitance, $Z_{dl} = \frac{1}{i\omega C_d}$. Assuming a background potential of $\phi$ across the whole cell, we have

$$\zeta = \frac{\phi}{1 + i\omega \tau_c} \quad (1.17)$$

The assumptions inherent in this model of the double layer (i.e. linear capacitance) break down at large voltages (where the zeta potential is large relative to the thermal voltage $kT/e$). In the experiments to be presented in subsequent chapters, the driving voltages are well into the nonlinear regime, where the linear circuit models, such as Gouy-Chapman, lack theoretical justification. A modification would be to allow for a nonlinear differential capacitance, $C_D(\zeta)$, e.g., as predicted by Gouy-Chapman theory [Bazant et al.(2003)]. In the nonlinear regime $\zeta > 2kT/e$, the capacitance goes up, and thus the charging slows down, compared to the linear model, although this mainly affects the low frequency response.

In general, nonlinearity violates the circuit model by causing ion concentrations in time and space, both in the bulk and in the double layers. One consequence is the adsorption of neutral salt in the diffuse layer, which depletes bulk concentration with slow, diffusive relaxation [Bazant et al.(2003)]. Bulk concentration gradients can give rise to diffusio-osmotic flows [Anderson(1989)], which would generally act against the primary electro-OSMOTIC flow. Further, once concentration gradients appear, the electrochemical and fluid problems may become coupled, since the bulk Péclet number may not be small. We have estimated the double-layer Péclet number to be 0.03, so the bulk Péclet number should be roughly $0.03a/\lambda = 150$, which is quite large. Clearly, at some point, bulk advection-diffusion will have to be addressed in nonlinear electrokinetics.

**Model 2: Stern Model**

In the Stern model of the double layer, shown in Fig. 1-3(b), we model the double layer as two capacitors in series - the diffuse double layer capacitance, $C_d$, which contributes to electrokinetic flow, and a compact, or Stern layer, capacitance, $C_s$, of adsorbed ions. The bulk electrolyte is modeled as a resistor, $R$. The total cell impedance is

$$Z = \frac{i\omega RC_s C_d + C_d + C_s}{i\omega C_d C_s} \quad (1.18)$$

and the zeta potential is then given by

$$\zeta = \frac{\phi}{(1 + \delta) + i\omega \tau_c} \quad (1.19)$$

where $\delta = C_d/C_s$.

**Model 3: Constant-Phase Angle Impedance**
Consider the equivalent circuit shown in Fig. 1-3(c). The double layer is modeled by a constant-phase angle element, 
\[ Z(\omega) = \frac{A}{(i\omega)\beta} \]
with phase angle \( \beta \) and resistance \( A \). The bulk electrolyte is modeled as a resistor, \( R \). The total cell impedance is

\[ Z = \frac{R(i\omega)\beta + A}{(i\omega)\beta} \tag{1.20} \]

and the zeta potential is given by the potential drop across the constant phase angle element

\[ \zeta = \frac{\phi}{1 + \frac{A}{A(i\omega)\beta}}. \tag{1.21} \]

### 1.3.4 ICEO Around a Conducting Cylinder in a Sinusoidal AC Field

We then calculate the frequency-dependence of the time-average slip velocity for sinusoidal applied fields. We represent the electric field using complex notation

\[ E = E_0 e^{i\omega t} \hat{z}, \tag{1.22} \]

where the real part is implied.

**Model I: Simple Capacitor Model of the Double Layer**

For a time-dependent zeta potential with a simple capacitor model of the double layer, as shown in Fig. 1-3(a),

\[ \zeta = 2E_0 a \cos \theta \text{Re} \left( \frac{e^{i\omega t}}{1 + i\omega \tau_c} \right). \tag{1.23} \]

The resulting induced-charge electro-osmotic slip velocity is then

\[ u_s = 2U_0 \sin 2\theta \left[ \text{Re} \left( \frac{e^{i\omega t}}{1 + i\omega \tau_c} \right) \right]^2 \hat{r}, \tag{1.24} \]

where \( U_0 = \frac{eE_0 a}{\eta} \) is the typical ICEO slip velocity, with time-averaged slip velocity

\[ \langle u_s \rangle = \frac{U_0 \sin 2\theta}{1 + \omega^2 \tau_c^2} \hat{r}. \tag{1.25} \]

In the low-frequency limit \( \omega \tau_c \ll 1 \), the double-layer fully develops in phase with the applied field. In the high-frequency limit \( \omega \tau_c \gg 1 \), the double-layer does not have time to charge up, attaining a maximum magnitude \( \sim 1/(\omega \tau_c)^2 \) with a \( \pi/2 \) phase shift.

**Model II: Stern Layer Capacitance**

Returning to the equivalent circuit shown in Fig. 1-3(b), the zeta potential is given by

\[ \zeta = 2E_0 a \cos \theta \text{Re} \left( \frac{e^{i\omega t}}{1 + \delta + i\omega \tau_c} \right). \tag{1.26} \]
The resulting induced-charge electro-osmotic slip velocity is found to be

\[
\mathbf{u}_s = 2U_0(1 + \delta) \sin 2\theta \left[ \text{Re} \left( \frac{e^{i\omega t}}{1 + i\omega \tau_c} \right) \right]^2 \hat{\theta},
\]

(1.27)

with time-averaged slip velocity

\[
\langle \mathbf{u}_s \rangle = \frac{U_0 \sin 2\theta(1 + \delta)}{(1 + \delta)^2 + \omega^2 \tau_c^2} \hat{\theta}.
\]

(1.28)

To gain better insight into the function of the second capacitance, we define a rescaled critical time \( \tau_c^0 = \tau_c/(1 + \delta) \) and observe that

\[
\mathbf{u}_s = 2U_0 \sin 2\theta \left[ \text{Re} \left( \frac{e^{i\omega t}}{1 + i\omega \tau_c^0} \right) \right]^2 \hat{\theta},
\]

(1.29)

with time-averaged slip velocity

\[
\langle \mathbf{u}_s \rangle = \frac{U_0 \sin 2\theta}{1 + \delta(1 + (\omega \tau_c^0)^2)} \hat{\theta}.
\]

(1.30)

In the low-frequency limit \( \omega \tau_c^0 \ll 1 \), the double-layer fully develops in phase with the applied field, with magnitude \( \sim 1/(1 + \delta) \). In the high-frequency limit \( \omega \tau_c^0 \gg 1 \), the double-layer does not have time to charge up, attaining a maximum magnitude \( \sim (1 + \delta)^{-1}/[1 + (\omega \tau_c^0)^2] \) with a \( \pi/2 \) phase shift.

Therefore, the addition of the Stern layer capacitance explains both a reduction in the magnitude of the resulting velocity as well as a shift in the time-scale by \( 1 + \delta \). The Stern model can also be used to explain the behavior of capacitive coatings on electrodes in ICEO flows as well as parasitic coatings due to contamination during device operation.

**Model III: Constant Phase Angle Impedance**

We introduce an impedance element defined by \( Z(\omega) = \frac{A}{(\omega \tau_c)^\beta} \) and examine its dynamics, with a bulk resistance in series. Because of the peculiar units involved in \( \omega \beta \), we non-dimensionalize \( \omega \) by \( \tau_c \).

The zeta potential is given by

\[
\zeta = 2E_0a \cos \theta \text{Re} \left( \frac{e^{i\omega t}}{1 + (R/A)(i\omega \tau_c)^\beta} \right).
\]

(1.31)

The resulting induced-charge electro-osmotic slip velocity is found to be

\[
\mathbf{u}_s = 2U_0 \sin 2\theta \left[ \text{Re} \left( \frac{e^{i\omega t}}{1 + (R/A)(i\omega \tau_c)^\beta} \right) \right]^2 \hat{\theta},
\]

(1.32)
and the time-averaged slip velocity

\[ \langle u_x \rangle = \frac{U_0 \sin 2\theta}{1 + (R/A)^2 (\omega \tau_c)^{2\beta}} \theta. \]  

(1.33)

In the low-frequency limit \( \omega \tau_c \ll 1 \), the double-layer fully develops in phase with the applied field. In the high-frequency limit \( \omega \tau_c \gg 1 \), the double-layer does not have time to charge up, attaining a maximum magnitude \( \sim 1/(\omega \tau_c)^{2\beta} \).

**Discussion of Frequency Response for Different Double Layer Models**

The resulting equations for the time-averaged fluid slip velocity are all of the form \( \langle u_x \rangle = U_0 \sin(2\theta) P(\omega) \theta \), where \( P(\omega) \) encompasses the entire frequency dependent characteristic of the slip velocity. Fig. 1-4 plots this function for each of the three models. The standard single capacitor model of the double layer (solid line) shows the fastest decay. The Stern model (diffuse capacitor and compact double layer capacitance) begins with half the amplitude of the other models, and has a much slower decay than either of the two other models. Two examples of the constant phase angle model are shown in the Figure. In the first example, \( \beta = 0.5 \) is used, which corresponds to a Warburg-type impedance model for a diffusive process. The second example is \( \beta = 0.8 \), which is consistent values of \( \beta \) from various references, including [Green et al. (2002)], and may correspond to the influence of charging of roughened surfaces. As expected, the \( \beta = 0.5 \) curve (dash-dotted line) shows the shallowest decay. The velocity still is roughly one-quarter of the peak velocity at a dimensionless frequency of 5. The \( \beta = 0.8 \) curve (dotted line) shows steeper decay, which approximates the Stern model for the double layer, though only through the specific choices of \( \delta \) and \( \beta \) used in the illustration. Both constant
phase angle models predict slower velocities at low frequency (below $\omega\tau_c = 1$) and then transitions to predict higher velocities above $\omega\tau_c = 1$.

**A Note About the Difference in Frequency Dependence Between AC Electro-Osmosis and ICEO**

We conclude this chapter by examining the frequency dependence of AC electro-osmosis, the non-linear electrokinetic flow around two planar electrodes immersed in an electrolyte solution. The system is modeled with total impedance $Z = \frac{\omega\tau_c + 2}{\omega\tau_c}$. The potential drop across the double layer is then scales as

$$\zeta \sim \text{Re} \left( \frac{e^{i\omega t}}{i\omega\tau_c + 2} \right). \quad (1.34)$$

and the local (tangential) electric field scales with the potential drop across the bulk fluid resistor, such that

$$|E| \sim \text{Re} \left( \frac{e^{i\omega t}i\omega\tau_c}{i\omega\tau_c + 2} \right). \quad (1.35)$$

The resulting induced-charge electro-osmotic slip velocity is found to scale as

$$u_s \sim \left[ \text{Re} \left( \frac{e^{i\omega t}}{i\omega\tau_c + 2} \right) \right] \left[ \text{Re} \left( \frac{e^{i\omega t}i\omega\tau_c}{i\omega\tau_c + 2} \right) \right] \bar{\theta}, \quad (1.36)$$

with the time-averaged slip velocity

$$\langle u_s \rangle \sim \frac{\omega\tau_c}{\omega^2\tau_c^2 + 4} \bar{\theta}. \quad (1.37)$$

We should note that ACEO is a specific example of the much more general phenomenon of ICEO, though ACEO appeared first in the literature.

Because the driving electric field is determined by the local potential drop across the bulk resistance, frequency dependence appears in the numerator, resulting in zero velocity at DC and a peak velocity at $\omega\tau_c = 2$, a very different frequency character than demonstrated by ICEO flows with any of the three impedance models herein. In these two examples, we observe that ICEO can have a much more general frequency response than ACEO at electrode arrays.
Chapter 2

Experimental Methods for Microfluidics

This chapter presents two experimental methods used in characterizing ICEO flows – particle image velocimetry and impedance spectroscopy. Particle-image velocimetry enables extraction of quantitative information from image pairs captured from movies of experiments. Impedance spectroscopy yields information about the double layer charging dynamics, as a function of frequency and voltage. Both of these tools enable analysis of experimental data.

2.1 Particle Image Velocimetry

Particle image velocimetry (PIV) is a non-intrusive optical diagnostic technique which tracks the displacements of collections of tracer particles to characterize flow fields [Adrian(1996)]. Micro-particle image velocimetry (μPIV) has been implemented to map velocity fields within microfluidic devices. μPIV utilizes fluorescent microscopy coupled with specialized cross-correlation algorithms to yield vectors with micrometer spatial resolution [Santiago et al.(1998)].

In the experiments in this thesis, small (500 nm) fluorescent seed particles (G500, Duke Scientific, CA) with peak excitation and emission at 468 nm and 508 nm, respectively, or 1 μm fluorescent seed particles (F8823, Molecular Probes, Eugene, OR) with peak excitation and emission at 505 nm and 515 nm, respectively, were loaded into polymer microchannels at a volume loading fraction of between 0.5% and 0.01%. The neutrally buoyant polystyrene spheres were suspended in electrolyte solutions with screening lengths between 7 nm and 1 μm.

Figure 2-1 shows a representative raw image from an experiment. A 100 μm diameter platinum wire is centered in the image. Florescent tracer particles are adsorbed to the wire surface, seen as large clumps at the edges of the wire and, more clearly, as individual tracers nearer the center. The
background noise, mostly attributable to fluorescent particles adsorbed to the platinum surface, is observed in this figure. Background subtraction was performed to remove the fluorescence due to stuck particles and improve signal-to-noise ratio (SNR). Images were synchronously collected onto a CCD camera at 30 frames per second as movie files (AVI format) and exported as individual digital image files (TIFF format). Individual frames were analyzed with a cross-correlation µPIV software [Devasenathipathy(2003)]. For the steady flows (driven by an AC field) in this thesis, the correlations were ensemble averaged to obtain substantially higher SNR. The interrogation spots for the reported measurements were between 16 and 64 pixels in the horizontal and vertical directions, depending on the experiment, and with 50% overlap. In the image shown in Fig. 2-1, a vector-to-vector spacing of 24 µm was obtained in the image plane.

A sample PIV measurement of the velocity profile in an optical slice is shown in Fig. 2-2. The total field of view is 474×355 µm. The wire is vertically aligned at a horizontal position of 400 (pixels). The width of the wire is approximately 200 pixels. Some asymmetry in the velocity profile is evident, which may be due to the loading of the tracer particles, from left to right, which seems to leave more trapped particles on the left, close to where the wire touches the channel wall. There are also clearly errors in the PIV measurement itself, which causes some cells to have much smaller velocity than neighboring cells. By ensemble averaging over many image pairs, we are able to make fairly accurate measurements of the velocity profile transverse to the wire, with relative error less than 10%.

In AC electrokinetic experiments, the advection of the tracer particles should track the true streamlines with reasonable accuracy. Linear electrophoretic transport of the carboxylate-modified fluorescent microspheres is negligible for the applied electric field alternating at 300 Hz. The Brow-
Figure 2-2: A sample velocity profile obtained by particle-image velocimetry, for a horizontal slice of the channel near the tip of the wire, as shown in Fig. 3. The wire is roughly 200 pixels wide and centered near the 400 pixel position.

The standard displacement estimate for the particles over the measurement time interval is approximately 0.1 μm and is reduced by ensemble averaging (the error scales as the square root of the number of image pairs analyzed multiplied by the number of particles in each interrogation spot) to less than 5% of the measured displacement throughout the flow field. Additional discussion on the behavior of the tracer particles is contained in Chap. 8.

2.2 Impedance Measurement

Various models are advanced in the electrokinetics literature for the double layer as a means to achieve better fit between measurements and theory. As shown in the previous chapter, the model of the double layer can have a significant effect on the predicted frequency response of the experimental system. As part of our experimental analysis we constructed a parallel plate impedance cell and measured the impedance in two different electrolytes at voltage amplitudes of 10mV, 25mV, 50mV, and 100mV.

2.2.1 Experimental Setup

Glass wafers with a 500Å gold/500Å chromium bilayer were patterned with a high-resolution transparency mask using standard 1 μm OCG825 resist and gold and chromium etch chemistries to produce a 25mm diameter gold pad with electrical connections to a 10mm square gold pad for
electrical contact. Two gold pads were placed facing each other with a 100μm thick delrin washer holding de-ionized water or 1 mm KCl solution. The two plates were held together with a plastic c-clamp. Metal wires were connected to the gold contact pads via conductive epoxy.

The two electrical connections were used for a two-probe impedance measurement using a Solartron SI 1287 Electrochemical Interface to a Solartron SI 1260 Impedance/Gain-Phase Analyzer (Solartron Instruments, Hampshire, UK). Tests were run at various voltage amplitudes from 10mV to 100mV, in both KCl and deionized water.

### 2.2.2 Results

Figures 2-3 and 2-5 show bode plots for the deionized water and KCl electrolytes, respectively. Fig. 2-3 shows results in deionized water. At high frequencies, the cell impedance looks purely resistive, which is expected. At low frequencies, the phase angle settles to approximately -65 degrees. Between roughly 1Hz and 100Hz, the phase angle is approximately 45-50 degrees, which may be indicative of a diffusive process dominating this frequency regime. This range of frequencies includes the frequency corresponding to the charging frequency for the double layers spaced by 100μm. The four different voltage values are evident here, with groupings at both 10 and 25mV and at 50 and 100mV, though the main differences are slight phase angle differences between 1Hz and 100Hz, and a slight decrease in bulk resistivity measured at higher voltages.

Fig. 2-5 shows a similar structure. At low frequencies, the phase angle is approximately 60 degrees. The range of frequencies where the phase angle is near 45 degrees begins at a higher frequency in KCl than in deionized water, which may be due to a higher charging frequency for the Debye layer, consistent with a thinner Debye length in KCl (10nm versus greater than 100nm in deionized water). The bode plot for the weak electrolyte also settles to purely resistive behavior at a higher frequency than for deionized water.

By subtracting off the bulk resistivity values (at high frequency), we arrive at Figures 2-4 and 2-6. For deionized water, we see roughly two linear trends. At very low frequencies, the decay slope is approximately 0.6. At higher frequencies, the slope is 0.9. In KCl, the slope is 0.7. These values are similar to those reported in, for instance, [Ramos et al. (2003)] for similar metals. Had the decay slope been identically 1, the double layer could be treated as purely capacitive.

The structure of both the 0.1 mM KCl and DI water experiments are very similar. Both show a plateau over a middle range of frequencies at phase angles near 45 degrees, which is consistent with a Warburg impedance model of a diffusive-dominated process, perhaps reactions at the electrodes. Unfortunately, this only serves to complicate the impedance model for the double layer and is beyond the scope of the present work.
Figure 2-3: Bode plot with DI water.

Figure 2-4: Impedance of DI water.
Figure 2-5: Bode plot with 0.1 mM KCl solution.

Figure 2-6: Impedance of 0.1 mM KCl solution.
Chapter 3

Experimental Investigation of Induced-Charge Electro-Osmosis on a Platinum Wire in a Microchannel

This chapter examines ICEO flow around a platinum wire laid transverse in a polymer microchannel. This chapter was previously published, in part, in [Levitan et. al.(2005)].

3.1 Experimental Setup

As a simple first experiment to illustrate ICEO at a non-electrode metal surface in a microfluidic device, we considered the experimental setup shown in Fig. 3-1. A platinum wire of circular cross section was attached to the wall of a polymer microchannel containing low concentration KCl electrolyte. An AC voltage was applied from distant ends of the channel (without any electrical connections to the wire) to produce an oscillating background electric field transverse to the wire.

To visualize the flow, small (500 nm) fluorescent seed particles (G500, Duke Scientific, CA) with peak excitation and emission at 468 nm and 508 nm, respectively, were loaded into the microchannel at a volume loading fraction of 0.01%. The neutrally buoyant polystyrene spheres were suspended in 1mM KCl solution (prepared from granular Malinckrodt AR KCl), which has a screening length of $\lambda \approx 10$ nm. The solution was loaded into the channel with a syringe through a hollow metal fitting, which also served as the ground electrode.

The open end of the channel, at a distance 1 cm away from the ground electrode, was capped
Figure 3-1: Experimental setup. A platinum wire is transverse in a polymer microchannel. The channel is filled with dilute KCl and two metal wires are placed in the distant channel ends, 1 cm apart. The wires are connected to a function generator. Inverse optics microscopy synchronously captures images onto a CCD camera.

with a 1 mm diameter gold wire which served as the second electrode for the oscillating voltage, applied across the channel using a function generator (33220A, Agilent, Palo Alto, CA) connected through a power amplifier (Model 50/750, Trek, Medina, NY). This setup enabled the application of between 0 and 750V with a maximum frequency of 3MHz, but the experiments reported here were restricted to \( \leq 100 \text{ V} \) at \( \leq 500 \text{ Hz} \). The typical electric field in the channel was thus in the range, \( 0 - 100 \text{ V/cm} \), which corresponded to an approximate background voltage drop across the 100 \( \mu \text{m} \) wire of \( 0 - 1 \text{ V} \).

An inverted microscope (Axiovert 200M, Karl Zeiss, Germany) was used to follow the tracer particles in the microchannel. The illumination source was a broad spectrum 100W mercury lamp (LEJ GmbH, Germany). The fluorescent spheres were imaged through a cube filter consisting of a band-pass excitation filter (450-490 nm), dichroic mirror with a cut-off wavelength of 510 nm and a barrier long-pass emission filter (515 nm). The 10X objective (numerical aperture of 0.25) had a measurement depth of 28 \( \mu \text{m} \) as compared to the 200 \( \mu \text{m} \) depth of the device [Meinhart et al.(2000)]. The images were recorded onto a CCD camera (DFW-V500, Sony, Japan) with a 640 X 480 pixel array and 8-bit read-out resolution. The field of view corresponding to the CCD pixel sheet size and the magnification is 474 X 355 \( \mu \text{m} \)in the object plane.
3.2 Fabrication of Polymeric Microchannels

Molds for the microfluidic channels were made by spin-coating negative resist (Microchem SU-8 2050) onto 4 inch silicon wafers and patterned with high-resolution transparency masks. The patterned resist layer was then hard-baked. The top layer of the device was cast as a thick layer of 5:1 part A:B GE Silicones (GE Silicones RTV 615) using the master mold. The layer was cured for approximately 40 minutes at 80°C. Ports were punched through this thick layer using 20 gauge luer stub adapters. The bottom layer of the device was 20:1 A:B GE Silicones, spun-coat at 4000 rpm onto a #1 glass 24X50mm cover slip, and cured for 40 minutes at 80°C. The top layer was cleaned with isopropyl alcohol and dried with nitrogen. For additional details for soft-lithographic fabrication of microchannels, the reader is referred to Refs. [Unger et al.(2000), Whitesides et al.(2001)].

The experimental channel was 200 μm thick, 1 mm deep, and 1cm long, as shown in Fig. 3-1. The AC voltage was applied across the longest dimension of 1 cm. The 1 mm long section of 100 μm diameter platinum wire was cut and cleaned in acetone and isopropyl alcohol and then placed in the center of the channel on the top section. The top section was then placed on the bottom layer and the assembled layers were cured for an additional 1 hour at 80°C. Devices were also fabricated using Dow Corning Sylgard 184 with similar results. Various orientations of the platinum wire in the channel, for instance laid vertically in the channel, were also achieved via this process.

Fig. 3-2 shows two SEM images of the polymeric microchannel. In Fig. 3-2(a), the wall and surface of the PDMS microchannel can be seen. Note the exceptionally smooth surfaces on the PDMS surface in the valley. The surface becomes the upper boundary of the PDMS microchannel once it is capped with glass, and also becomes the surface to which the platinum wire is attached. Near the lower edge of the image, polymeric debris is visible. In Fig. 3-2(b) we see a close-up of the polymer microchannel wall. Note that even at this magnified scale, the bottom surface appears smooth, though we can make out faint evidence of stuck, agglomerated fluorescent tracer particles in the valley. The sidewall has surface roughness on order of a few microns.

3.3 Numerical Simulation

This section is presented to complete the discussion of the experiments around a platinum wire. However, it should be noted that the simulations in this section were conducted by Yuxing Ben.

We consider a microchannel formed in a cavity of an insulating material and containing perfectly conducting electrodes at each end and a metal cylinder in its center. The microchannel is filled with a binary electrolyte solution. A potential difference is applied between the two outer electrodes. The applied electric field acts on its own induced charge cloud around the metal cylinder to produce fluid slip.
Outside the double layer, the electric potential, \( \phi \) satisfies the Laplace equation

\[
\nabla^2 \phi = 0, 
\tag{3.1}
\]

where the electric potential is specified on the outer electrodes, the cylinder surface is taken to be equipotential at voltage \( V \), and the remaining boundaries are insulating. The double layer charging around the cylinder is governed by

\[
\sigma \frac{\partial \phi}{\partial n} = C \frac{\partial \zeta}{\partial t} = \frac{d}{dt} (V - \phi) 
\tag{3.2}
\]

where \( \sigma \) is the fluid bulk conductivity, \( C \) is the capacitance of the double layer, and \( \frac{\partial}{\partial n} \) denotes the normal derivative. The zeta potential, \( \zeta \), is defined as the potential drop of the cylinder surface relative to the bulk.

To simplify analysis, we assume the capacitance of the double layer is linear, has uniform thickness, \( \lambda \), and permittivity \( \epsilon \), and is given by \( C = \epsilon / \lambda \). The conductivity \( \sigma = \epsilon D / \lambda^2 \) simplifies the charging problem to

\[
\frac{\partial \phi}{\partial n} = \frac{\lambda}{D} \frac{d}{dt} (V - \phi) 
\tag{3.3}
\]

The fluid mechanics problem is governed by low Reynolds number flow

\[
\mu \nabla^2 u = \nabla p 
\tag{3.4}
\]

where \( \mu \) is the fluid viscosity, \( u \) the fluid velocity, and \( p \) the fluid pressure. The fluid is also taken to be incompressible. That is, \( \nabla \cdot u = 0 \).

We non-dimensionalize the governing equations by choosing characteristic length \( X = a \), char-
acteristic time $T = \alpha a/D$, characteristic velocity $U_{ICEO} = \epsilon E^2 a/\mu$, with $E$ the applied electric field, characteristic pressure as $P = \mu U_{ICEO}/a$, and characteristic voltage $\Phi = E a$. We denote non-dimensional variables and operators with $\tilde{}$.

The governing equations simplify to

$$\tilde{\nabla}^2 \tilde{u} = \tilde{\nabla} \tilde{p} \quad (3.5)$$
$$\tilde{\nabla} \cdot \tilde{u} = 0 \quad (3.6)$$
$$\tilde{\nabla}^2 \tilde{\phi} = 0 \quad (3.7)$$
$$\tilde{\nabla}^2 \tilde{\phi} = 0 \quad (3.8)$$

In the actual experimental geometry, the wire diameter is 100 $\mu m$ and the total channel height is 200 $\mu m$. We define $\alpha = a/L$ as the non-dimensional aspect ratio of the channel geometry. The height of the channel is fixed at 4 (in non-dimensional units). The boundary condition for potential at the outer electrodes is $\tilde{\phi} = \phi/\epsilon a = \phi/V a L = L/a = 1/a$. We recognize that the boundary conditions governing the electric potential are independent of actual applied potential, but resulting velocities scale, by inspection, as $E^2$ (or $V^2$).

For the remainder of this section, for convenience, we drop the $\tilde{}$ in our analysis, but deal with dimensionless formulations for all governing equations. The boundary conditions for electric potential on all insulating surfaces is given by $\frac{\partial \phi}{\partial n} = 0$ and the boundary condition on the cylinder itself reduces to $\frac{\partial \phi}{\partial n} = \frac{\partial \phi}{\partial t}$.

We analyze the cylinder charging problem in Fourier space, so that the boundary condition becomes:

$$\frac{\partial \phi}{\partial n} = i \omega \phi \quad (3.9)$$

where $\phi = \phi_r + i \phi_i$, with $\phi_r$ and $\phi_i$ representing the real and imaginary parts of $\phi$ respectively.

We note that $\frac{\partial \phi_r}{\partial n} = -\omega \phi_i$ and $\frac{\partial \phi_i}{\partial n} = \omega \phi_r$, with both $\phi_r$ and $\phi_i$ satisfying Laplace’s equation.

On the cylinder surface, the velocity is given by

$$u_x = -\frac{1}{2} |\phi| \frac{\partial \phi}{\partial x} \quad (3.10)$$
$$u_y = -\frac{1}{2} |\phi| \frac{\partial \phi}{\partial y} \quad (3.11)$$

These equations (for $\phi_r$, $\phi_i$, $u_x$ and $u_y$) set up a complete set of non-dimensional governing equations which are then solved in FEMLAB (Comsol AB, Burlington, MA). The electric potentials are solved first and then the Navier-Stokes equation. Fig. 3-3(a) shows a numerical simulation of
the experimental geometry with an electric field initially applied at \( t = 0 \). A short time later (i.e. at \( t > t_c = \lambda a/D \), where \( \lambda \) is the Debye screening length, \( a \) is the radius of the wire and \( D \) the ion diffusivities), the double layer has fully charged and no electric field lines are normal to the wire. Simulation results are shown in Fig. 3-3(b). The action of this tangential electric field acting on its own induced charge creates fluid slip at the cylinder surface, symmetric about the midsection of the cylinder. The near boundaries set the height of the fluid rolls. The resulting fluid flow simulation is shown in Fig. 3-3(c).

The model equations cannot be solved analytically for the experimental geometry, so accurate numerical solutions are obtained by the finite-element method. The electrochemical and fluid problems decouple, so one solves first for the (complex) electrostatic potential to obtain the zeta potential distribution on the wire and then for the (time-averaged) Stokes flow resulting from the ICEO slip. The number of elements is 4547 with 503 boundary elements. Mesh density is refined around the cylinder and increased gradually with a growth factor of 1.3. A typical solution takes a few seconds on a laptop computer.

Sample numerical solutions are shown in Fig. 3-3. For reference, the real part of Fourier-transformed electrostatic potential, \( Re(\Phi) \), is shown in (a) for the moment the voltage is initially applied, after relaxation of electrons on the metal wire, but before any ionic relaxation in the electrolyte. This is also the limit of high frequency, \( \omega \gg 1 \) (i.e. dimensional frequencies \( > \tau_0^{-1} \)). In the opposite limit, \( \omega \ll 1 \), since the double-layer is completely charged at all times, \( Re(\nabla \Phi) \) in (b) is expelled from the wire, and \( Im(\Phi) \) is zero. The time-averaged flow in (c) shows two closed circulation rolls driven by ICEO slip on the wire, which draws in fluid along the field axis and ejects it into the middle of the channel. In this regime, the wire acts like a patterned metal surface on the wall generating half of the quadrupolar ICEO flow for an isolated wire.

The spatial structure of the flow depends on the AC frequency. At intermediate frequencies, \( \omega \approx 1 \), \( Re(\nabla \Phi) \) in (d) shows remnants of normal component due to incomplete charging. Rather than causing the field to wrap smoothly around the wire as in (b), the field \( Re(\nabla \Phi) \) in (d) exhibits regions close to the wall where the tangential component changes direction, pointing toward the wall. This changes the structure of the flow considerably, as shown in (e). The time-averaged fluid velocity shows a new stagnation point on each side of the wire, which separates in the incoming flow into one large vortex in the bulk as before and another smaller vortex against the wall.

### 3.4 Results

We begin by studying the spatial profile of the velocity from \( \mu \)-PIV near the tip of the wire at a driving frequency of 300 Hz. The raw data is shown in Fig. 3-4 for applied voltages ranging from 35 to 100 V. At higher voltages bubbles form at the electrodes at low frequency, and at smaller voltages
Figure 3-3: Numerical simulations of induced-charge electro-osmosis in the experimental geometry. Field lines from the real part of $\nabla(\Phi)$ are shown at high frequency ($\omega = \infty$) in (a) and at low frequency ($\omega = 0.0001$) in (b). Streamlines of the time-averaged ICEO flow in (c) for the latter case show two large vortices which draw in fluid toward the wire and expel it into the channel. At an intermediate frequency, $\omega = 1$, $Re(\nabla(\Phi))$ in (d) and flow in (e) have different profiles due to incomplete double-layer charging, which produces small, counter-rotating vortices near the wall. The arrows in (a), (b) and (d) indicate the direction of $Re(\nabla(\Phi))$ (which oscillates) and those in (c) and (e) indicate the (steady) time-averaged flow direction. Simulations were performed by Yuxing Ben.
velocities are too small to measure accurately with our \( \mu \)-PIV setup.

The inverted optics microscope records images of fluorescent tracer particles in an optical slice roughly 20 \( \mu \)m thick, set by the relatively long focal depth. To record the data, the optical slice is adjusted so as to appear just below the tip of the wire, with a clear stagnation point in the flow at the center. As shown in the sample image in Fig. 2-1, the optical slice also cuts partly through the top of the wire, since a thin central strip of the wire surface appears blurred. As such, we estimate the center plane of the slice to be \( h = 7.5 \) \( \mu \)m. Finally, to compare with the theory, we also adjust the horizontal position of the PIV data so that the velocity extrapolates to zero at \( x = 0 \). This is consistent with both the visual identification of the axis of the wire and the 12 \( \mu \)m size of the PIV averaging cells.

Before attempting a quantitative comparison, we show in Fig. 3-4(b) that the data collapses well when scaled to the typical ICEO velocity, \( U_{\text{ICEO}} \). This demonstrates that the overall velocity scales like the square of the applied voltage, as expected. The flow profiles at the smallest voltages, \( V = 35 \) V and 40 V, show some deviation from the collapse, but this may be due to larger relative error in the \( \mu \)-PIV measurement and division by a smaller \( V^2 \). Indeed, for \( V < 35 \) V, it is difficult to obtain a consistent value of the velocity, since many cells do not record a well defined tracer-particle displacement between successive images.

We first compare to the simplest model of only a linear diffuse-layer capacitor \((\beta = 1, \delta = 0)\), which contains no empirical fitting parameter. The theoretical velocity profile in Fig. 3-4(b) clearly has the same shape as the experimental data, but its magnitude is too large by roughly a factor of three. In the case of model (b) with \( \delta = 1 \), which also allows for a surface capacitance, the fit is not very different for this data. In the DC limit, the theoretical velocity is reduced by a factor \((1 + \delta)^{-1} \), but this effect is roughly canceled here by a slower decay with frequency. We conclude that the data cannot be described quantitatively by the linear capacitor model (at all frequencies), although the shape of the flow profile is captured quite well. Similar conclusions have also been drawn from experiments on AC electro-osmosis at electrode arrays [Ramos et al.(1999), Green et al. (2002), Studer et al.(2002), Studer et al.(2004)].

To obtain a better fit, we follow Green et al. [Green et al. (2002)] and consider model (c) with a constant-phase-angle impedance. Electrochemical impedance spectra for solid electrodes typically yield values of \( \beta \) in the range 0.7 to 0.9 [Kerner & Pajkossy(2000)]. Measurements for KCl in contact with Ti/Au/Ti sandwich electrodes yield \( 0.75 \leq \beta \leq 0.82 \), depending on the ion strength and the applied voltage [Green et al. (2002)]. For our KCl/Pt system, we make a reasonable choice of \( \beta = 0.8 \) based on these values.

Once we have chosen \( \beta = 0.8 \), we fit two parameters to the experimental data, \( \delta \) and \( \omega_c \), even though this scheme has questionable physical justification. The additional degree of freedom makes a huge difference, as we are able to achieve an excellent fit with \( \delta = 1.5 \) and \( \omega_c = 320 \) Hz, as shown
Figure 3-4: ICEO velocity versus position at different voltages across 1.0 cm and 300 Hz driving signal (solid circles). Lines show simulation results for the velocity profile at $h = 7.5 \mu$m above the wire surface with different $\beta$ and $\delta$ values (a) Raw data, (b) Velocities are scaled by $U_{\text{ICEO}}$. In (b), $\beta$ and $\delta$ are labeled on the figure, $\omega_z = 320Hz, 640Hz, 320Hz$ respectively for the solid, dash and dash-dot lines.
in Fig. 3-4(b). We have also checked that a fairly good fit can be achieved with other choices of \( \beta \), including the purely capacitive case, \( \beta = 1 \), as long as we still keep the two independent parameters, \( \omega_c \) and \( (1 + \delta) \), to scale frequency and velocity, respectively. We caution the reader, therefore, not to view our data as providing direct support for the constant-phase-angle impedance model. Instead, the availability of a second parameter to rescale the velocity seems to be the main reason for the improved fit.

The results are similar for the dependence of the velocity on voltage and frequency, sampled at the velocity maximum in the above profiles, at roughly 22 \( \mu \text{m} \) from the wire axis. The voltage dependence in Fig. 3-5(a) has the correct \( V^2 \) trend in the capacitor models but the magnitude of the flow is overestimated, while the \( \beta = 0.8 \) impedance model (due to its two free parameters) gives an excellent fit to the data. The frequency dependence in Fig. 3-5(b) shows roughly the expected decay at high frequencies like \( (\omega_c/\omega)^2 \), as well as a persistence of the flow toward the DC limit of zero frequency. (In the simulations, the very low-frequency regime shows flow reduction due to simple screening of the electrodes [Bazant et al. (2003)].) The capacitor models, extrapolated from our fits, over-estimate the velocity in the DC limit, but the discrepancy is improved by increasing \( \delta \), as expected. The impedance model again gives a reasonable fit to the data, although the shape of the frequency profile seems better described by the capacitor models (if rescaled by a larger \( \delta \)).

### 3.5 Discussion

Overall, we find reasonable agreement between theory and experiment, sufficient to conclude that we have in fact observed ICEO. This is an interesting result on its own, since it demonstrates the same physical mechanism as AC electro-osmosis around an inert (non-electrode) metal surface with a very different frequency response, including steady electro-osmotic flow in the DC limit. The flow scales with the square of the applied voltage, and the shape of the velocity profile and the frequency dependence are consistent with the basic theory of ICEO. Similar flows were first observed around mercury drops in AC electric fields [Gamayunov et al. (1992)], but the theory was never tested quantitatively, beyond confirming the scaling of the flow with the field squared. Microfluidics and \( \mu \)-PIV allows the novel possibility of controlled measurements of the complete flow field, as experimental conditions are varied.

Some difficulties arise in making quantitative comparisons between theory and experiment, as in many previous studies of linear and nonlinear electrokinetics. We find that the standard capacitor model tends to overpredict the velocity by at least a factor of two under the conditions studied here. This is clearly due in part to the large applied voltages across the wire (up to 1 Volt) which can not be reasonably transferred to the double layer, as assumed by the simple theory. It may also have to do with the inadequate description of double-layer charging dynamics, even in the linear regime.
Figure 3-5: Dependence of velocity on (a) the applied voltage (across 1cm) at a fixed frequency of 300Hz and on (b) frequency at a fixed voltage of 50 V. Solid circles are experimental data 22μm from the wire axis and h = 7.5μm above the wire, and the lines correspond to theoretical predictions with different values of β and δ. The characteristic frequency is chosen to be ωc = 320, 640, 320Hz, respectively, for the solid, dash, and dash-dot lines.
We have obtained good quantitative agreement between theory and experiment using an empirical model of the double-layer impedance, $Z \propto (i\omega)^{\beta}$, based on a constant phase angle $\beta = 0.8$ as in Ref. [Green et al. (2002)]. The good fit, however, seems more easily attributed to the introduction of an ad hoc fitting parameter to rescale the velocity than to any clear physical mechanism. We also find this model unsatisfactory since it is not derived from the same microscopic transport equations as the Helmholtz-Smoluchowski slip formula, although perhaps closer attention must be paid to boundary conditions. It might be more self-consistent to attribute this kind of impedance to the compact layer, while retaining classical Gouy-Chapman theory in the diffuse layer.

There is also the question of the concentration dependence of ICEO flow, which we have not addressed here. We have observed very little concentration dependence for $c < 1$ mM and decreasing flow speed with increasing concentration for $c > 1$ mM—but a more careful experimental study of the effect of ionic strength is needed, as has recently been done for AC electro-osmosis [Green et al. (2002), Studer et al. (2004)].

As mentioned above, the driving voltage in our experiments is well into the nonlinear regime, where all linear circuit models lack theoretical justification. A simple modification would be to allow for a nonlinear differential capacitance, $C_D(\zeta)$, e.g., as predicted by Gouy-Chapman theory [Bazant et al. (2003)]. In the nonlinear regime $\zeta > 2(1 + \delta)kT/e$, the capacitance goes up, and thus the charging slows down, compared to the linear model, although this mainly affects the low frequency response.

The more general effect of nonlinearity is to violate the circuit approximation by causing ion concentrations to vary in time and space, both in the bulk and in the double layers. One such effect is the adsorption of neutral salt in the diffuse layer, which causes a depletion of bulk concentration with slow, diffusive relaxation [Bazant et al. (2003)]. Such bulk concentration gradients would generate diffusio-osmosis [Anderson (1989)], which generally would act against the primary electro-osmotic flow. A similar mechanism is behind Dukhin’s celebrated analysis of the nonlinear electrophoretic mobility of highly charged particles [Dukhin (1993)]. Once concentration gradients appear, the electrochemical and fluid problems may become coupled, since the bulk Péclet number may not be small. We have estimated the double-layer Péclet number to be 0.03, so the bulk Péclet number should be roughly $0.03\sigma/\lambda = 150$, which is quite large. Clearly, at some point, bulk advection-diffusion will have to be addressed in nonlinear electrokinetics.

A related effect is surface conduction of ions through the diffuse layer [Dukhin (1993)]. The relevant dimensionless parameter is the Bikerman-Dukhin number, defined as the ratio, $\sigma_s/\sigma L$, where $\sigma_s(\zeta)$ is the surface conductivity. This number can also be understood as controlling the relative number of ions in the diffuse layer compared to the bulk, which plays a crucial role even in one-dimensional electrochemical dynamics without surface conduction, and a somewhat different dimensionless number is needed in time-dependent problems [Bazant et al. (2003)]. The effect of the
Dukhin number has been calculated for the nonlinear electrophoresis of highly charged particles in weak AC fields [Murtsovkin(1996)], but in our experiments it is the induced charge on an initially uncharged metal surface which is large. In that case, one must consider the nonlinear dynamics of the diffuse charge, which is generally ignored in electrokinetic theory.

The generic effect of surface conduction is to “short-circuit” the polarization of the double layer on a metal surface, thus reducing the induced zeta potential and the ICEO flow. In our experiments, it may be that some of the flow reduction which we have attributed to surface capacitance ($\delta = 0.5-1.0$) may instead be due to surface conduction and diffusio-osmosis. Indeed, the local Dukhin number, inferred from our simple model of the double layer polarization, can be as large as $10^3$ in our experiments. Sorting out this matter will require additional experiments and more sophisticated mathematical modeling.

Another nonlinear effect is the breakdown of ideal polarizability, perhaps first discussed by Murtsovkin in the context of AC electrokinetics [Murtsovkin & Mantrov(1990)]. Faradaic reactions at the metal surface can become important, as the induced zeta potential is increased, eventually stealing current from the capacitive charging process. This is yet another means of “short circuiting” which can reduce the magnitude of ICEO flow. Some recent experiments have even observed flow reversal in AC electro-osmosis [Studer et al.(2004), Lastochkin et al.(2004)], which could have something to do with Faradaic processes at the electrodes (e.g. modeled as in Ref. [?]). In our case of an isolated metal surface, we did not observe any flow reversal.

We close by noting that, even in the simple linear regime, our simulation of the experimental geometry in Fig. 3-3 demonstrates an interesting effect: The spatial structure of ICEO flow in an asymmetric geometry can be controlled simply by changing the AC frequency. In contrast, for AC electrokinetics in more symmetric geometries, such as colloidal spheres [Gamayunov et al.(1986), Murtsovkin(1996), Gamayunov et al.(1992)] or linear electrode arrays [Ramos et al.(1998), Ramos et al.(1999), Brown et al.(2001)], changing the AC frequency affects only the magnitude, but not the spatial structure of the flow. The ability to control the flow profile by simply varying the frequency, without changing the locations or potentials of the electrodes, might be useful in microfluidics. For example, particles might be trapped for detection or analysis in a convection roll at one frequency and then swept away to another channel at another frequency. The remarkable nonlinear sensitivity of ICEO flows to voltage, frequency and geometry merits further experimental and theoretical investigation.
Chapter 4

Fabrication of Induced-Charge Electrokinetic Devices

This chapter discusses the development of the fabrication process for creation of induced-charge electro-osmotic microfluidic devices. Emphasis is made to distinguish between our fabrication process herein and other possible methods for fabrication.

The basic ICEO device is comprised of two components—a polymeric microchannel that defines the actual flow geometries, including inlet and outlet ports, possible multiple channels intersecting, etc., and a base substrate which contains electrical controls for application of electric fields as well as structures for generating induced-charge electro-osmotic flows. The fabrication process for the polymeric channels has been discussed previously in Chap. 3. However, we begin this chapter by discussing further methods for fabricating the polymeric channels, including additional choices in photoresist.

The remainder of the chapter is then dedicated to fabrication processes for the base layer, substrates with electrical connections and structures for generating electrokinetic flow. These structures can be substantially planar, can rise through a portion of the microfluidic channel, or can traverse the entirety of the channel. These structures can be single cylinders, ellipses, or more complicated geometries, and these structures can be arranged in various patterns. Electrical connection can also be provided to these structures. The range of possibilities for ICEO device geometry is nearly endless. Microfluidic mold and substrate wafer fabrication was performed in the Microsystems Technology Laboratory at MIT, while polymer device fabrication was performed in the Hatsopoulos Microfluidics Laboratory at MIT.
4.1 Alternative Manufacturing for Polymeric Channels

Microfluidic channels were prepared using standard soft lithographic techniques [Whitesides et al. (2001), Unger et al. (2000)] with PDMS or similar polymer cast from hard photoresist master molds. For thick structures, molds for micro-fluidic channels were made by spin-coating negative resist (Microchem SU-8 2050) onto 3 inch silicon wafers and patterned with high-resolution transparency masks. Microchem SU-8 resists can be spun-coat in layer thicknesses from approximately 5 μm to over 200 μm with multiple coats. The manufacturer provides detailed data sheets and process plans for achieving desired thicknesses. Best results with SU-8 resist were achieved for channel heights between 30 μm and 200 μm. SU-8 master molds yield near-vertical sidewalls (with achievable slope of less than 3°). However, SU-8 processing is notoriously difficult. Processing takes longer than traditional resists, is more susceptible to peeling, cracking, and bubbling, and improper processing can easily allow for variations in resist thickness.

Thinner resists, due to their processing simplicity, have been utilized for polymeric channel fabrication in subsequent chapters. The devices in Chap. 3 were cast with SU-8 resist, whereas the devices shown in the remainder of this thesis have been capped with channels made with AZ9260 resist (Clariant Chemicals, Somerville, NJ). Single spun-coat layers can reach 11 μm. Additionally, this resist can be spun-coat in multiple coats, achieving a maximum resist thickness of 30 μm. Newer photoresist, such as AZ 50XT or 100XT, enable single coat film thicknesses greater than 50 μm.

The general process flow for the microchannel fabrication is shown in Fig. 4-1. A clean base wafer is patterned with a thick photoresist (1) and (2). The wafer is treated with chloro-trimethyl-silane to prevent PDMS adhesion to the mold, and PDMS is cast (3) and cured and the channel is then peeled off (4). Inlets and outlets are punched using luer stub adapters (5). The entire structure is cleaned with isopropyl alcohol and dried with a nitrogen gun and sealed on a glass slide pre-coated with a thin layer of partially cured PDMS in (6) and filled with fluid in (7).

Prior to depositing the resist, the base silicon wafer is typically cleaned in a piranha bath (H₂SO₄:H₂O₂) for ten minutes, rinsed in deionized water, and spun dry. For thick SU-8 resist, the wafers are additionally dehydrated on a hot plate for one hour. For thin resist, the wafers are dehydrated using an HMDS oven. This deposits a thin monolayer of adhesion promoter for thin resists. The general purpose of the dehydration steps is to improve adhesion of the photoresist polymer to the substrate. The photoresist is then deposited with a spin coater. For multi-layer deposition with thin resists, a fifteen minute pre-bake between depositions is performed in an oven at 95°C. After all layers have been deposited, the thin resist multilayer is baked at 95°C for a total of one hour. The wafers are then exposed on a mask aligner according to standard recipes (for AZ9260, this requires four 5 second exposures with a 5 second relaxation in between). Exposure times vary from a few seconds for thin resists to approximately one minute for 200 μm SU-8 resist. SU-8 wafers undergo an additional post-exposure bake prior to developing. The wafers are developed (SU-8 in
Figure 4-1: Process flow for creation of polymer microchannels. Starting from the top, a photoresist master mold is patterned (1) and (2); PDMS is cast (3); PDMS is peeled off and ports are punched (4) and (5); The PDMS is sealed onto a glass slide with thin PDMS (6); The device is filled with fluid (7).
PGMEA and AZ9260 in AZ440 developer), rinsed in deionized water, and spun dry. The AZ resist wafers are post-baked at 95°C for between 30 minutes and 1 hour. Fig. 4-2 shows a schematic of an as-fabricated PDMS chip.

4.2 Patterned Metal Features

Having discussed the fabrication of the polymeric microchannels, we now turn our attention to fabrication of the base substrate, incorporating metal electrodes and, perhaps, a tall metal structure for driving electrokinetic flows. Various authors have developed process plans for fabricating tall electroplated structures. Typically, these process plans are for a narrow range of possible deposition materials. For instance, [Lu(2003), Voldman(2001)] both discuss processes for fabrication of electroplated gold structures. Both these processes, however, are designed to create a device that operates via electrostatics. The resulting surfaces are of poor quality, are covered with organic contaminants (resist residues), and are, therefore, unsuitable for ICEO.

ICEO requires electrically conductive surfaces. Surface contamination provides an additional capacitance acting in series with the double layer capacitance and reduces the overall flow velocity while shifting the characteristic frequency of the system. The addition of organic contaminants also opens the opportunity for fouling of the device with additional adsorbed substances. Hence the
process plan must ensure removal of all organic contaminants during the cleaning process. This is especially critical when using SU-8 resists, which are notoriously difficult to remove.

Fig. 4-3 illustrates the process plan. These fabrication processes were developed for transparent substrates to enable the experiments to be analyzed using fluorescence microscopy, although the processing is compatible with standard silicon processing techniques. The 4 inch glass wafers (Mark Optics, Santa Ana, CA) were cleaned in piranha bath for 10 minutes, rinsed in deionized water, spun dry, and dipped in buffered oxide etch for ten seconds, and transferred to a barrel oxygen plasma asher for 2 minutes. This minimal plasma ash has greatly improved adhesion of the subsequent metal deposition steps, (1) in the figure.

A metal bi-layer is then deposited via e-beam evaporation (2). The metal bi-layer consists of a thin adhesion layer and a layer of the metal surface that will be in contact with solution. We have had success with 500Å Cr/500Å Au layers and 1000Å Ti/4000Å Au layers. The only difference for processing with different bi-layers is that subsequent processing steps need to be adjusted for the adhesion layer. For instance, Cr will survive a short (< 10 minute) piranha etch, while Ti will not. For this reason, Ti is an unacceptable choice for an adhesion layer when SU-8 is used as the resist plating mold. The thickness of the evaporated layers contributes little to device performance, but thicker base layers may result in longer device lifetimes. For instance, chromium is very reactive in KCl and, in some experiments, outer electrode structures appear to have plated from one electrode to the other.

The top metal layer is then patterned using standard photoresists (OCG825) and etch chemistries. Gold was etched in a Transene TFA gold etchant solution, which etches at approximately 28Å/s at 25°C. The wafers are rinsed in deionized water and spun-dry (3). This patterning step defines the electrodes and the seed layer and any electrical connections for the electroplated structure.

To create the metal posts, a thick resist layer is deposited, which forms the mold for electroplating (4). The resist processing steps are identical to those presented above for fabrication of the polymer microchannels. Typically, the molds for the polymer microchannels and the plating mold are processed simultaneously to achieve comparable thicknesses. Once the resist has been patterned, the wafers are barrel ashed for two minutes to remove any organic material on the exposed metal surfaces (to ease electroplating). The wafers are then inserted into an electroplating bath (Orotemp 24C, Technic, Inc, PA) of a gold salt solution at 65°C. The wafer is connected as the anode and a gold foil is connected as the cathode to a pulsed plating supply. A ten-percent duty cycle with 0.1 ms on and 0.9 ms off is applied to plate into the resist mold (5). Typical plating times are two to three hours for 40 μm, however plating times will vary strongly with solution temperature and driving current. The larger the desired plating area, the higher the current required. For the devices fabricated in this thesis, 25mA was employed.

Following the plating process, the wafers are rinsed in deionized water and then the plating mold
is stripped (6). SU-8 resist needs to be stripped in piranha in order to remove organic materials from the plated geometry sidewalls and base. Standard resists can be stripped in either acetone or piranha. Special attention must be made to the choice of adhesion layer to prevent underetching of the plated structures during resist removal and possible lift-off of all devices. Once the resist is stripped, the adhesion layer is etched, using the top metal layer as the mask (7). Standard etching solutions are used. The wafers are rinsed in deionized water and spun dry.

Finally, the electroplated structures are protected with a standard thick photoresist which is applied with a cotton swap. The wafers are baked in an oven at 95°C for fifteen minutes and then diced using a diesaw. Final release steps can be accomplished by rinsing the devices in acetone, followed by a final deionized water rinse and nitrogen dry. Fig. 4-4 shows a schematic of a completed structure.

The choice of photoresist for the plating mask determines the sidewall shape of the plated structure. Referring to Fig. 4-5, we see the effect of three different types of photoresists on the creation of a mold for the electroplating process. Figs. 4-5(1) and (2) are positive and negative photoresists, respectively. Exposure of a circle results in a conical structure with sidewall slope of $36^\circ$. In (3), we have exposure of SU-8, a negative resist, which yields sidewall slopes of approximately $3^\circ$. As has been previously discussed, the more vertical sidewalls which come with plating into an SU-8 mold come with a commensurately more difficult task of removing the resist mold itself.

4.3 Fabrication Results

Fabricated metal posts are visualized by SEM in Figs. 4-6 and 4-7 in order to investigate surface quality resulting from the process. In (a), the post is $12\mu m$ in height and $100\mu m$ in diameter. The post is in the shape of a diamond which is a result of the low-resolution transparency masks that were used in fabrication. The surface roughness evident on the upper, rounded surface (roughness is on order 1 $\mu m$), though the sidewalls look very smooth. Surface roughness is undesirable because ions or particles may stick to the surface during ICEO, thus reducing system performance. In (b), the post is $12\mu m$ in height and $150\mu m$ in diameter. This post was fabricated using a higher-resolution transparency mask and is much more round than (a). Again, note the rough upper surface and relatively smooth sidewalls. The thin base layer of chromium is located under the post and, therefore, assists in adhesion of the plated geometry to the substrate.

Fig. 4-7 shows two close-up images of electrolated structures. Starting with (a), we see clear evidence of the sloped sidewall from the standard resist process. In (b), we see examples of the roughness of the upper surface and, after several ICEO experiments, adhesion of tracer particles sed in PIV measurements. The faint grey circles are the fluorescent tracer particles and the white particles are, presumably, metal salt. SEM images were captured as TIFF images using a Phillips
Figure 4-3: Process plan for electroplated devices. Starting at the top, (1) cleaning the wafer; (2) deposition of the metal bilayer; (3) patterning the top metal layer; (4) depositing the resist mold; (5) plating into the mold; (6) stripping the plating mold; (7) etching the adhesion layer.
Figure 4-4: Schematic of an as-fabricated ICEO electroplated device on a transparent substrate.

Figure 4-5: Various photoresist profiles after patterning with a simple square mask. (1) Standard positive result. Plating results in structures which are narrower at the substrate. (2) Negative resist. Plating results in structures which taper away from the substrate. (3) SU-8 resist. This resist can yield near-vertical sidewalls, but is difficult to remove.
Figure 4-6: Electroplated metal posts. (a) Diamond structure at 350X magnification. (b) Round post at 650X magnification.

Figure 4-7: Electroplated metal posts. (a) Undercut and slope of sidewalls, shown at 1500X magnification. (b) Roughness of top surface, at 8000X magnification.
XL30, FEG-SEM in a shared facility at MIT.

4.4 Discussion

We have developed methods for manufacturing ICEO devices on transparent substrates, and successfully demonstrated the fabrication of functioning ICEO devices. Special attention was paid to ensure that posts could withstand cleaning steps necessary to remove organic residues following electroplating mold removal. The process is capable of yielding electroplated devices with heights from just a few microns up to hundreds of microns, though cleaning processes for higher posts are more problematic.
Chapter 5

ICEO Flows in Electroplated Devices – Section I: ICEO Quadrupolar Flows

5.1 Introduction

This chapter describes ICEO experiments around electroplated gold cylinders centered between planar gold control electrodes in PDMS microchannels. Various device geometries were fabricated using the techniques described in Chapter 4 in order to characterize ICEO flows in this geometry.

5.2 Experimental Setup

We consider the experimental setup shown in Fig. 5-1. A 12 μm tall 100 μm diameter electroplated gold diamond and electrodes on a glass substrate (as shown in Fig. 4-6(a)) were capped with a 12 μm tall polymer channel with length 1 cm and width 1 mm. Two electrodes are formed from a 500Å gold/500Å chromium bilayer, and were 1mm apart. The electroplated post was aligned in the center of the fluid channel. The channel was filled with de-ionized water loaded with 1 μm fluorescent tracer particles (Molecular Probes, Eugene, OR) in a volume loading fraction of 200:1 deionized water to fluorescent tracer fluid. An AC voltage was applied at the outer electrodes to produce an oscillating background electric field in the polymer channel. The flow was visualized by tracking fluorescent tracer particles through an inverted optical microscope in a slice through the post, allowing for quantitative comparisons with theory. Applied voltages at the external electrodes ranged between 0 and 10V, at frequencies from 50 Hz to 6 kHz.
5.3 Numerical Solution

Numerical solutions were performed by Yuxing Ben.

As in Chapter 3, these specific device geometries were numerically simulated using the finite-element method with the software package FEMLAB. Details of the method are presented in Chapter 3. While ideal geometries have been studied analytically, these simulations account for actual geometries resulting from the fabrication process, including the tapered post geometry and the influence of the polymer channel walls on the fluid flow. The numerical simulations utilized 197977 degrees of freedom, 27912 elements, 10238 boundary elements, 763 edge elements, with a minimum element quality of 0.0555. A typical simulation takes up to a few minutes to solve.

Fig. 5-2 shows four numerical results for the shape of the velocity profile. The velocity values are averaged through 6 μm in the channel (to account for depth of focus of the microscope). For this particular geometry with a 100 μm diameter post, we calculate \( \omega_c = 32 \) Hz. Starting with (a), we have the velocity profile in the DC limit. In (b), the driving frequency is 32 Hz. In (c), the driving frequency is 320 Hz and in (d) the driving frequency is 3.2 kHz. As in Chap. 3, we see a large change in the structure of the flow with increased frequency. Partly due to the non-circular cross section, the edges of diamond post preferentially charge first, which occurs even at high frequencies. The basic roll structure starts from a symmetric roll at DC, with rolls centered on each diagonal face, and moves towards four smaller rolls at the poles. Additionally, streamlines near the cylinder in the high frequency limit show three-dimensional corkscrew paths in simulation, which has been observed in experiment.
5.4 Experimental Results

We analyze the voltage dependence, at a fixed 100 Hz driving frequency, on the resulting magnitude of the ICEO flow. Simple ICEO theory predicts that velocity should scale as the driving voltage squared (corresponding to the induced zeta potential scaling as the voltage drop across the cylinder times the same driving voltage). As in the case of our experiments around the metal wire (Chap. 3), we examine the velocity dependence on the voltage applied at the outer electrodes, and utilize PIV techniques to capture a quantitative picture of the flow. We examine the data using a variety of fits including quadratic fits, log fits, and we introduce a whole field scaling parameter to examine the scaling of the entire flow field velocity as a function of the applied voltage. Maximum measured flow velocities were approximately 50 μm/s.

ICEO theory predicts a quadratic dependence on applied voltage (or electric field). Fig. 5-3 shows the experimental data (solid circles) for velocity as a function of applied voltage at a fixed point and a quadratic fit (solid line) with 2 free parameters, the coefficient of the quadratic term and a constant offset. The y-axis shows the velocity in dimensionless form, scaled by $U_{ICEO}$ at 100 V/cm for a 100 μm diameter wire, and the x-axis is the applied voltage (in Volts).

For each fit herein, we compute the $R^2$ error, which is the ratio of the sum of the square errors and the sum of the square errors relative to the mean, adjusted for the number of free parameters.
in the model. A perfect fit corresponds to \( R^2 = 1 \). For Fig. 5-3, \( R^2 = 0.98 \). The fit is given by 
\[ p(x) = p_1 x^2 + p_2, \]
where \( p_1 = 2.4 \times 10^{-5} \pm 0.3 \times 10^{-5} \) and \( p_2 = 7 \times 10^{-7} \pm 10^{-4} \). The two dashed lines in the figure are the 95% confidence intervals for the fit. Nearly all the data points are contained in the confidence intervals. The data at \( V = 7V \) is substantially outside the window of statistical significance and was discounted in the fit. The data value at \( V = 9.5V \) is slightly higher than the confidence interval (even despite the confidence intervals broadening at higher voltages). Further, we notice a slight scatter of the data around the fit. Whereas simple theory predicts a monotonic increase of velocity with applied voltage, the real experimental data includes some apparently random noise.

Studer [Studer et al. (2004)] suggests that a two-line fit may yield better agreement with data in nonlinear electrokinetics than a quadratic fit. Fig. 5-4 shows the line for low velocity data has nearly a flat slope, and at some critical voltage, the velocities increase linearly. In our data (solid circles), the curves naturally break up at approximately \( V = 5V \), though a similar result can be achieved by breaking the curves at \( V = 4.5V \). The lower portion is described by a line of slope \( m = 4.3 \times 10^{-5} \pm 2.5 \times 10^{-5} \), with \( R^2 = 0.75 \). The upper region is described by a line with slope \( m = 3.4 \times 10^{-4} \pm 0.4 \times 10^{-4} \), with \( R^2 = 0.97 \). As before, the data at \( V = 7V \) is excluded. The solid lines are the fit and the dotted lines are the 95% confidence intervals. The lower line has random residuals until \( V = 3V \), then systematically underpredicts the velocities with the values at both \( V = 3V \) and \( V = 4V \) being outside or at the extreme of the confidence intervals. The upper

Figure 5-3: ICEO velocity versus voltage at 100 Hz (solid circles with error bars). The solid lines show a quadratic fit of the data. The dashed lines show 95% confidence intervals.
Figure 5-4: ICEO velocity versus voltage (solid circles). The two lines show a fit of the velocity profile suggested by [Studer et al.(2004)]. The dashed lines are 95% confidence intervals for the two linear fits.

line trends in residuals, starting with overpredicting at $V = 5.5V$, then underpredicting two points at $V = 6V$ and $V = 6.5V$, overpredicting a single point at $V = 7.5V$, and then underpredicting two points at $V = 8V$ and $V = 8.5V$, before settling into a random scatter. The lack of randomness of residuals, combined with broad confidence intervals at the upper end of the velocity spectrum, suggest that better fits (i.e. quadratic, as above) may be possible. However, the exceptionally high value of $R^2$ in the upper region merits entertaining the possible linear dependence of velocity on applied voltage, at least at applied voltages above $V = 5V$.

Fig. 5-4(a) plots the log of velocity (scaled to the $U_{ICEO}$ for an applied electric field of 100V/cm on a 100 $\mu$m diameter post) (solid circles). Our interest here is to determine, via a least squares fit to a line, whether the slope of the velocity versus voltage curve is truly quadratic. The solid line is the fit with slope $m = 2.3 \pm 0.2$, and the dotted lines the 95% confidence intervals. As in the case of the two line fit, despite having an $R^2 = 0.98$ value, the fit first underestimates the velocity at three points, then overestimates at four consecutive points, before settling into a nearly random scatter of residual errors. While the slope of the fit is $m = 2.3$, this is an exceptionally close value to the quadratic dependence of flow velocity on applied voltage predicted from theory.

Fig. 5-4(b) plots the data (solid circles) and a power law fit (solid line) with exponent $m = 2.3$ from the log fit above. The dotted lines, again, show the 95% confidence intervals. We achieve reasonable $R^2 = 0.94$, yet the fit shows substantial trending in residuals. At low voltages, the fit
systematically underpredicts. At moderate voltages \((V = 3V - 5V)\), the model overpredicts, before settling into underpredicting, again, at higher voltages. As in the previous fits, the data at \(V = 7V\) was excluded from the fit. The fit is given by \(p(x) = p_1 x^{2.3} + p_2\), where \(p_1 = 9.5 \times 10^{-6} \pm 1.2 \times 10^{-6}\) and \(p_2 = 8 \times 10^{-5} \pm 2 \times 10^{-4}\). As in the case of the first two fits in this chapter, there is a substantial range of values for the constant offset.

All of the previous fits feature the velocity at a single fixed point in the fluid flow. Because the PIV data calculates the velocity values for the whole imaging field, it is useful to define a metric that can measure the trend in scaling of the entire flow field. The whole field metric computes the mean of the ratio of the velocity field to the velocity field at \(V = 9.5V\) (where we achieved a maximum global velocity value). The whole field scaling parameter should achieve a range of values between 0 and 1, achieving a maximum of unity at \(V = 9.5V\). Mathematically, the whole field scaling parameter is a mean of the norm of all real, non-zero velocity vectors, scaled relative to the velocity at the same
position at $V = 9.5V$.

Fig. 5-6(a) shows the whole field scaling parameter as a function of applied voltage (solid circles) and a quadratic fit (solid line). The dotted lines are 95% confidence intervals for the fit. For the whole field scaling, $R^2 = 0.91$, which is consistent with a quadratic dependence of flow velocity on applied voltage. In Fig. 5-6(b), we plot the whole field scaling parameter as a function of applied voltage (solid circles) along with a linear fit (solid line). The dotted lines are 95% confidence intervals for the fit. For this fit, $R^2 = 0.92$, a slight increase over the goodness of fit for the quadratic scaling. This is, presumably, a consequence of the method for computing the whole field scaling parameter, and can be partly alleviated by implementing a threshold value for the velocities, below which we exclude the velocities in the field. For instance, implementing a threshold value of 20 $\mu$m/s velocity increases $R^2$ to 0.94 for the quadratic fit, while reducing $R^2$ for the linear fit. The resulting fits are very sensitive to the choice of threshold value, though the result still suggests that the velocity dependence on applied voltage is quadratic.

![Figure 5-7](image)

**Figure 5-7:** Raw velocity data taken on a diagonal slice through the metal post. In (a), the exact slice of the data is shown as a white line. In (b), velocity data is shown as a function of position at various voltages between 3.5 and 10V. The solid line is the result from simulation. No fitting parameters are used.

Fig. 5-7 shows the raw velocity data scaled to $U_{ICEO}$ for each voltage (solid circles) taken through a diagonal slice of the diamond-shaped electroplated post, as shown in Fig. 5-7. The solid line is the solution of a finite-element simulation of the same geometry (including the taper of the post) with no fitting parameters. Due to the taper of the electroplated post, we are unable to visualize the maximum velocity values (near the mid-plane of the channel, adjacent to the cylinder), and, therefore, must compare the theoretical predictions in the tails of the curve to simulation. The vector-to-vector spacing is 12.1 $\mu$m. There is good agreement between the predicted velocity results from simulation and experiment. Note that the experimental data collapses well, with roughly $1/V^2$. The scatter in the data largely occurs at smaller voltages where the denominator in the non-dimensionalization assumes large(r) numbers.
Fig. 5-8 shows the raw velocity data scaled to the predicted ICEO velocity (solid circles), this time through a slice passing near the equators of the diamond post. The solid line again represents the solution of a finite-element simulation of the same geometry (with taper). As in Fig. 5-7, we are unable to compare simulation with experimental values near the cylinder wall because of the taper. However, the tails of the curve show good agreement between theory and experiment. Further, the data collapses well to $1/V^2$, except at lower voltages, where we expect the scatter to be significant. The vector-to-vector spacing is $9 \mu m$.

We now analyze the dependence of flow velocity on driving frequency, while voltage is held fixed. The simple capacitance model for ICEO predicts that velocity decays with frequency squared.

In this section, we analyze this dependence of flow velocity on frequency, at fixed applied voltage. The characteristic frequency is $32$ Hz, so we sample a range of dimensionless frequencies from 1 to 200. As in the previous section, various fits will be explored, including powerlaw fits, log fits, and an examination of the whole field scaling parameter.

Fig. 5-9(a) shows the velocity data at a fixed position in the flow field, scaled to $U_{ICEO}$ at $V = 10V$, as solid circles and a two parameter power law fit as a solid line. The two dotted lines are the 95% confidence intervals. $R^2 = 0.8$, and the fit takes the functional form $p(x) = ax^b$, where $a = 3.3 \times 10^{-2} \pm 1.8 \times 10^{-2}$ and $b = 0.44 \pm 0.01$. The relatively low $R^2$ value yields a greater than 50% range in $a$. However, the narrow range of $b$ suggests a good fit of the exponent. The discretization in the solid line in the image is due to a low number of points used in plotting the fit. The fit overpredicts velocity at nearly all frequencies. A few data points give uncharacteristically weak velocities (for instance, $3.5$ kHz gives near-zero velocity).

Fig. 5-9(b) adds a third free parameter to the model, a constant offset, though the resulting $R^2$ value remains unchanged. The power law exponent has a larger range than before (roughly 100%
Figure 5-9: Dimensionless velocity versus frequency (solid circles). In (a), a 2 parameter power law fit is employed. In (b), a constant value is added to the model. Fits are shown by solid lines. Dotted lines are 95% confidence intervals.

Having performed power law fits, we can analyze a linear fit of the log of the data and frequency. Velocity data is again scaled relative to \( U_{ICEO} \). Fig. 5-10(a) shows the linear fit as a solid line. The solid circles are the data and the dotted line represents the 95% confidence bounds. The goodness of fit is \( R^2 = 0.83 \), a slight improvement over the prior fits. The slope of the curve is \(-0.63\). We observe scatter on both sides of the fit, outside the confidence bounds and two point trends in underprediction or overprediction of the data. The higher frequency data (where velocities tend to be smaller) fall better into the confidence bounds, presumably because velocities at high frequencies are all at or near zero. The relatively low decay exponent is inconsistent with the models explored in Chap. 1. A decay exponent of \(-0.63\) represents a very weak decay and corresponds to a constant phase angle impedance element with exponent 0.3.

Fig. 5-10(b) replots the power law fit with constant offset, but fixes the value of the exponent at the best fit from Fig. 5-10(a), \( b = 0.63 \). For this fit, \( R^2 = 0.84 \). We have achieved a maximum in \( R^2 \), though the quality of the fit is still moderate. Because the log fit only analyzes the decay of the velocity in the tails of the curve, we identify that the power law fit underpredicts the initial velocities at low frequencies. The confidence bounds are much more narrow than in prior fits and the fit does a better job of capturing a majority of the data points, though it still underpredicts and
Figure 5-10: Dimensionless velocity versus frequency (solid circles). In (a), log of the data is fit with a straight line, slope is $m = -0.63$. In (b), the data is fit with a two parameter power law fit with exponent $b = -0.63$.

overpredicts in pairs. Overall, the agreement between the fit and the data is good.

Figure 5-11: Whole field velocity scaling parameter versus frequency (solid circles). In (a), solid line is a power law fit. In (b), the log of the data is fit with a straight line, shown as the solid line. In both images, the dotted lines are 95% confidence intervals.

Fig. 5-11 plots the whole field scaling parameter as a function of frequency. Fig. 5-11(a) shows experimental data (solid circles) and a power law fit (solid line). Confidence intervals are shown by the dotted lines. For this fit, $R^2 = 0.87$. Fig. 5-11(b) plots the data on a log fit, with $R^2 = 0.89$ and slope $m = 0.22$. Both fits show relatively good agreement with the data, though fit (a) systematically overpredicts at higher frequencies. Once again, we see the effects of the choice of threshold value for velocity. Because we are fitting the decay of velocity with frequency, we are most concerned with velocity values at higher frequencies, which unfortunately tend to be small. This eliminates the possibility of choosing a large threshold velocity value, which improved the fit results for the voltage dependence.

This thresholding is certainly one cause of the discrepancy between the velocity decay with frequency at a single point versus in the whole field. Another, though certainly related cause, goes
back to the methods used to calculate velocities. The PIV method yields a projected velocity vector with both $x$- and $y$-components of velocity. From these components, we calculate a velocity norm, which has the effect of increasing all measured velocities. This is particularly troublesome with smaller velocities (i.e. those found at high frequencies) since the velocity norm will always yield a small, non-zero velocity value, which inhibits the analysis of the tails of the velocity-frequency curves.

### 5.5 Discussion

As in Chap. 3, we find agreement between theory and experiment, sufficient to again conclude that we have observed ICEO. The flow scales with the square of the applied voltage and the shape of the velocity profile decays with frequency, though notably less steep than predicted by theory.

Additional difficulties presented themselves in making quantitative comparisons between theory and experiment, as with many previous electrokinetic studies\cite{Studer et al. (2004), Ramos et al. (1998)}. While simulation results provided consistent velocity values which closely matched the experimental results, we are limited in our ability to compare the entire velocity profile to simulation results (including the position and magnitude of peak velocities) due to the experimental geometry utilized herein.

As in the studies of the wire geometry, we are imaging on a plane which samples a substantial portion of the cross-section of the channel geometry. The sloped sidewall of the electroplated post and the non-zero vector-to-vector PIV spacing combine to again yield a roughly $6 \, \mu m$ region of uncertainty and we are therefore unable to compare velocity values to simulation and theory within $6 \, \mu m$ of the post. As a result, we lose the ability to assess comparisons between theory and simulation of the surface slip and peak velocities and are left to fit data to the tails of simulations and theories. A return to SU-8 processing holds the possibility for electroplated structures with steep slopes, enabling analysis up to and including the post surface.

Additional difficulties arise, as in the wire analysis, due to the very large voltages across the wire (up to 1 Volt) which cannot be reasonably transferred to the double layer. The inadequacy of our present linear model to explain applied voltages in excess of a few times the thermal voltages impairs comparison between theory and experiment. Further, because of the complicated geometry of the diamond post, including concentration of electric field lines at the poles and equators of the geometry, due to small radius of curvature, the charging dynamics may be even more complicated than in the wire experiment, which may be a factor in the disparity between theory and experiment. One solution is such as employed in Fig. 5-4, where we split the voltage spectrum at roughly twenty times the thermal voltage. There we have achieved excellent agreement between data and fit at higher voltages.
Various fitting models were also employed in this analysis. The basic theory predicts quadratic dependence of velocity on voltage, and we observed excellent goodness-of-fit for the second-order polynomial fits, with and without a constant offset. Fits on a log-scale suggest that the data is best fit with a power law, where the exponent is only slightly larger than 2. Analysis of the whole velocity field supports the quadratic scaling of velocity with applied voltage.

Various fitting models employed in this analysis show that the ICEO flow velocity does decrease with frequency. The decay is best described by curves with exponents on order 0.63, however, this is inconsistent with both the basic model of ICEO (which predicts a decay with the square of frequency) or a constant phase angle impedance model (which would suggest that $\beta = 0.31$) and inconsistent with our measured $\beta = 0.8$ from impedance spectroscopy. Further, the whole field scaling parameter, as a function of frequency, decays at an even shallower $m = 0.22$, which cannot be reconciled with any of the theories for the double layer charging dynamics. Analysis of the minimum detectable velocity from PIV would suggest a natural threshold for discarding velocity values, and may enable better analysis of the velocity-frequency decay curves.
Chapter 6

ICEO Flows in Electroplated Devices – Section II: ICEO Pumping Flows

6.1 Introduction

The previous chapters analyzed a metal cylinder electrically isolated from the outer electrodes, thereby prescribing a fixed zero charge on the cylinder. In this chapter, however, we analyze flows around a cylinder whose potential is fixed at a non-zero value, relative to the driving electrodes.

Consider a cylinder of radius $a$ centered between two electrodes which are spaced a distance $L$ apart. Assume that $L \gg a$, so that we may assume a uniform background field. We specify the potential on the cylinder to be $V_0$, and $V$ and $-V$ on the outer electrodes. The bulk electric field is then $E_b = 2V/L$. As discussed in [Squires & Bazant(2004)], in order to maintain the cylinder at constant potential, an average zeta potential $\zeta = V_0 - V_{\text{background}}$ is induced on the cylinder via charge transfer from the external circuit (the circuit which fixes the cylinder potential), where we take $V_{\text{background}}$ to be identically zero from symmetry (for instance, a cylinder symmetrically placed between two electrodes help at 0 and $V$ would see $V_{\text{background}} = V/2$. An equal and opposite double layer develops, which is driven by the tangential electric field at the cylinder surface, giving rise to a total tangential fluid slip velocity

$$U_{\text{total}} = U_{\text{ICEO}} + \frac{4\epsilon V}{\eta L} \sin(\theta)V_0$$  \hspace{1cm} (6.1)

via the classical Helmholtz-Smoluchowski slip, where, as before, $\epsilon$ is the permittivity of the fluid, and $\eta$ is the fluid viscosity. Note that the cylinder potential $V_0$ only enters the equation linearly, so that,
with a fixed cylinder potential, the time-averaged flow profile only sees the standard quadrupolar ICEO flow.

This fixed-potential ICEO introduces a new level of local control of fluid streamlines. If the sign of the cylinder potential is varied in phase with the outer electrode voltages, a steady flow past the object can be achieved. The fluid slip velocity from fixed-potential ICEO has the same sign as the cylinder potential. So, in our simple example above, a cylinder held at the same potential as one of the outer electrode (as the outer electrode potential oscillates), would continue to move fluid towards that electrode in an oscillating field. In that case, Eqn. 6.1 reduces to $U_{\text{total}} = U_{\text{ICEO}} + 4 \frac{V^2}{L} \sin(\theta)$, and we have a steady flow past the cylinder in AC. In our simple example, a cylinder with fixed potential $V = 0$ can still yield a steady pumping flow in AC if it is arranged assymetrically between two electrodes at $V$ and $-V$ respectively.

### 6.2 Experimental Setup

Fixed-potential ICEO flow geometries may be fabricated using identical methods for the standard ICEO devices, as in Chap. 4, with only minor modification to the design of the devices. Electrical connection must be made between the center cylinder and an external circuit, so additional pads, such as those that connect the outer electrode to a driving circuit must be patterned, as in Fig. 4-4. A simple manner of testing fixed potential ICEO involves connecting the center post to one of the outer electrodes via a thin metal wire. Such a device is shown in Fig. 4-6(b), with a 35 μm wide gold wire extending away from the 150 μm diameter cylinder.

A 150 μm electroplated gold cylinder with height 12μm flat outer control electrodes, and a 35 μm wide metal wire running parallel to the 2 control electrodes were fabricated on a glass substrate. The device was capped with a 12μm tall polymer channel with length 1cm and width 1mm. The outer electrodes and metal wire were formed from a 500Å gold/500Å chromium bilayer, and the outer electrodes were 1mm apart. The channel was filled with de-ionized water loaded with 1μm fluorescent tracer particles (Molecular Probes, Eugene, OR) in a volume loading fraction of 200:1 deionized water to fluorescent tracer particles. An AC voltage was applied to the outer electrodes and to the wire connected to the center cylinder such that the potential of the left electrode and the cylinder were held equal. The flow was visualized by tracking fluorescent tracer particles through an inverted optics microscope in a slice perpendicular to the cylinder major axis, allowing for quantitative comparisons with theory. Applied voltages on the external electrodes were 5V, 10V, and 15V, at frequencies of 50Hz, 100Hz, and 250Hz.
6.3 Numerical Simulation

Numerical solutions were provided by Yuxing Ben.

Fig. 6-1 shows three streamlines for velocity in a fixed potential geometry. Fig. 6-1 (a) and (b) show velocity streamlines from the FEMLAB simulation at dimensionless frequencies 0 and 3, respectively, corresponding to a real frequency of DC and 150Hz. Fig. 6-1 (c) shows streamlines from experimental results at 15V and 100Hz, corresponding to a dimensionless frequency of 2.

Figure 6-1: Flow profiles of fixed potential ICEO via simulation (a) and (b), and via streak images of experiments (c).

Flow in all simulations is from right-to-left. Between Fig. 6-1(a) and (b), with increasing frequency, the accompanying roll structure set up by ICEO flow moves a large recirculation region from the poles of the cylinder toward the leading edge of the cylinder. In the streamline from an experiment, we see a similar flow characteristic, wider at the leading edge and narrower, though more uniform, at the trailing edge (appearing almost like a steady, uniform flow past the cylinder). The experimental streamlines do not exhibit evidence of the roll structure, however. Additionally, the experimental streamlines show evidence of up-down symmetry breaking, presumably due to the presence of the thin metal wire, visible in the image extending down from the cylinder. This feature was absent in the simulations.
6.4 Results

Fig. 6-2 shows peak measured velocity (in \( \mu m/s \)) for the 150\( \mu m \) diameter gold cylinder. Peak velocity was approximately 200 \( \mu m/s \) at 15 V and 100 Hz. At 250 Hz, we observe a change in the direction of the flow, resulting in streamlines that drew fluid in from the sides of the channel and expels fluid towards the outer electrodes. This cannot be reconciled with our present model.

Flows for driving frequencies 50 Hz and 100 Hz show a monotonic increase of velocity with applied cylinder potential. Simple scaling suggests that flow velocity should scale as \( V^2 \). While the trend for 100Hz does show non-linearity of velocity with applied voltage, it would be premature to conclude that it varies with the square of the applied voltage, due to the limited number of data points. The velocity values for 50Hz, however, show a clean linear trend. The velocity field for 250 Hz shows a reversal in flow direction at approximately \( V = 10V \).

6.5 Discussion

We conclude that we have indeed observed fixed-potential ICEO flows around an electroplated gold post in a microchannel at least at low voltage and frequency. The flows exhibit some of the features expected from theory and simulation, yet fail to adequately demonstrate the non-linear dependence of flow velocity on applied voltage, as expected. The standard picture of fixed-potential ICEO
presumes that zeta potentials in excess of 1V can be applied across the double layer, and therefore may be inadequate for capturing the behavior in these experiments.

Previous studies have observed flow reversal at higher voltages, for instance [Studer et al. (2004)]. Therein, the authors observed an as-yet unexplained reversal in flow direction at elevated voltages, which also depends on concentration. Other extensions to ACEO also predict flow reversal at high potentials, including in traveling-wave electro-osmosis [Ramos et al. (2005)]. Additional studies of traveling-wave electro-osmosis demonstrate a change in flow structure at elevated frequencies, consistent with the experiments presented in this thesis [Cahill et al. (2004)]. Despite the apparent universality of flow reversal in experiments, the lack of theoretical explanation seems unsatisfactory.

Faradaic charging has been advanced as an explanation for flow reversal at high voltages in ACEO [Lastochkin et al. (2004)]; however, the choice of materials and the lack of in-phase electrochemical impedance suggest this is not the case in our present experiments.

Fixed-potential ICEO shows exceptional promise for applications of ICEO in microchannels. Flow velocities are large. Device geometries and electrical connections are simple, and can be straightforward to fabricate. Fundamentally, fixed-potential ICEO is a similar concept to FlowFETs [Schasfoort et al. (1999)] while enabling nonuniform surface slip. Additional experiments should be undertaken for an ICEO device that allows for independent control of both the cylinder potential and the electrode potentials, and the entire system should be analyzed over a range of different operating frequencies and voltages. The same flow velocity characterization done for the standard quadrupolar flow profile should also be repeated for fixed potential flows. It is expected that with judicious experimentation and analysis, fixed-potential ICEO may offer great utility in a range of applications.
Chapter 7

Dependence of ICEO Flows on Solution and Interface Chemistry

7.1 Introduction

The previous chapters have analyzed ICEO flow velocities around a variety of geometries in various configurations, as a function of both applied voltage and frequency. In this chapter, we focus on the effect of solution and interface chemistry on flow velocity. In particular, we develop scaling arguments for the effect of solution chemistry and examine the applicability of these scaling laws to a range of electrolytes.

7.2 Scaling Arguments

As discussed briefly in the last section of Chap 3, early experiments demonstrated a dependence of ICEO flow velocity on electrolyte concentration. The first sets of experiments around a metal wire were performed in KCl over a range of concentrations. The initial observable trend was a reduction in measured flow velocities at concentrations above 1 mM. Later experiments were performed in de-ionized water with similar or higher velocities achieved.

We derive scaling arguments for velocity as a function of electrolyte concentration, salt and ion diffusivity, and ion valence.

Recall that that the charging frequency for a metal post with radius $a$ in an electrolyte with diffusivity $D$ and screening length $\lambda$ is given by $\omega_c = \frac{D}{2\pi \lambda a}$. We define $D_0$, $c_0$, and $z_0$ as reference diffusivity, concentration, and valence, respectively. We further define $\omega^0_c = \frac{D_0}{2\pi \lambda_0 a}$ as the critical charging frequency. We look for functional forms of $\omega_c(D, z, c)$.

We reintroduce $\lambda = \left( \frac{2\pi \epsilon c_0}{kT} \right)^{-\frac{1}{2}}$, where $z$ is the ion valence, $c$ is the concentration, $\epsilon$ is the
permittivity, \( k \) is the Boltzmann constant, and \( T \) temperature. We define \( \lambda_0 = \left( \frac{2e^2 \varepsilon_0}{kT} \right)^{-\frac{1}{2}} \) as the reference Debye screening length. Further, define \( \lambda(c) \) as the Debye screening length at concentration \( c \) with valence \( z_0 \) and \( \lambda(z) \) as the Debye screening length in solution with valence \( z \) and concentration \( c_0 \). So, \( \lambda(c) = \lambda_0 (c/c_0)^{-\frac{1}{2}} \) and \( \lambda(z) = \lambda_0 (z_0/z) \).

Additionally, the basic frequency-dependent ICEO theory suggests that velocity as a function of frequency at fixed voltage obeys \( U(\omega) = \frac{U_0}{1 + (\omega/\omega_0)^2} \), where \( U_0 = U(\omega) = 0 \). Combining these equations with the functional forms of \( \lambda(z) \) and \( \lambda(c) \), we derive three scaling rules:

\[
U(\omega, c) = \frac{U_0}{1 + \left( \frac{\omega}{\omega_0} \right)^2 \left( \frac{c}{c_0} \right)}
\]

\[
U(\omega, D) = \frac{U_0}{1 + \left( \frac{\omega}{\omega_0} \right)^2 \left( \frac{D}{D_0} \right)^2}
\]

\[
U(\omega, z) = \frac{U_0}{1 + \left( \frac{\omega}{\omega_0} \right)^2 \left( \frac{z}{z_0} \right)^2}
\]

### 7.2.1 Trend I: Electrolyte Concentration

Consider two sets of experiments in the same electroplated geometry using the same electrolyte, but different concentration. From Eqn. 7.1, we have the ratio of the two fluid velocities is

\[
\frac{U(c_1, \omega)}{U(c_2, \omega)} = \frac{1 + (\omega/\omega_0)^2 c_2/c_0}{1 + (\omega/\omega_0)^2 c_1/c_0}.
\]

For \( c_1 > c_2 \), we have \( U(c_1) < U(c_2) \), consistent with previous electrokinetic results (for instance, [Studer et al. (2004)]). For \( c_1 \to \infty \), with finite \( c_2 \), \( U(c_1) \to 0 \). In the dilute limit, \( U(c_1) = U(c_2) \cdot [1 + (\omega/\omega_0)^2 c_2/c_0] > U(c_2) \), as expected. Also note that at DC, there is no effect of concentration dependence on resulting fluid velocities.

### 7.2.2 Trend II: Salt Diffusivity

Again, consider two equivalent molar solutions of two different salts of the same valence. The first solution has salt diffusivity (or ion diffusivity) \( D_1 \) and the second \( D_2 \). From Eqn. 7.2, we have the ratio of the two fluid velocities is

\[
\frac{U(D_1, \omega)}{U(D_2, \omega)} = \frac{1 + (\omega/\omega_0)^2 (D_0/D_2)^2}{1 + (\omega/\omega_0)^2 (D_0/D_1)^2}.
\]

For \( D_1 \to 0 \), \( U(D_1) = 0 \). For \( D_1 \to \infty \), \( U(D_1) = [1 + (\omega/\omega_0)^2 (D_0/D_2)^2]U(D_2) > U(D_2) \). In general, for \( D_1 > D_2 \), \( U(D_1) > U(D_2) \). As above, we similarly recognize that at DC there is no effect on resulting fluid velocities.
7.2.3 Trend III: Valence

Consider two equivalent molar solutions of two different salts with the same diffusivity, but different valences. The first solution has valence \( z_1 \) and the second has valence \( z_2 \). From Eqn. 7.3, the ratio of the two fluid velocities is

\[
\frac{U(z_1, \omega)}{U(z_2, \omega)} = \frac{1 + (\omega/\omega_0)^2(z_2/z_0)^2}{1 + (\omega/\omega_0)^2(z_1/z_0)^2}.
\]  

(7.6)

Therefore, \( U(z_1 > z_2) < U(z_2) \). Also, as \( z_1 \to \infty \), \( U(z_1) = 0 \).

7.3 Experimental Results

We analyze the scaling of the velocity field as a function of solution chemistry. The first example is concentration dependence. Additionally, various electrolytes are examined at the same concentration.

7.3.1 Concentration Dependence

We analyze the dependence of velocity on electrolyte concentration in a simple 1-1 electrolyte, KCl. This electrolyte is widely used in the electrokinetics field, for instance [Ramos et al.(1998)] and has been the focus of a study in [Studer et al.(2004)]. KCl is a canonical choice because of its ready dissociation in water up to exceptionally large concentrations (4.8 M), as well as its small ion size [Silbey & Alberty(2001)]. The relatively equal sizes of the ions allows the assumption of identical diffusivities for the anion and cation, as well.

We examine the same electroplated diamond post from Chapter 5 with driving voltage \( V = 10V \) and \( \omega = 100Hz \) over a range of electrolyte concentrations. Fig. 7-1(a) shows the whole field scaling parameter, defined previously in this thesis, as a function of ion concentration (solid circles) in KCl.
around a metal post. We are only concerned with the relative magnitude of the flow and how that magnitude scales as a function of concentration. The power law fit is shown as a solid line. The dotted lines are 95% confidence intervals. The character of the data is such that we see rapid decrease in velocity values over one order of magnitude (though a second decade is included in the data collection). Peak velocity scaling parameters decay from near unity to 0.5 at 10 mM. For this fit, \( R^2 = 0.91 \). Fig. 7-1(b), shows the same velocity scaling parameters on a log scale (solid circles) and fit a line through the data points. Relatively good agreement is achieved with this linear fit, with \( R^2 = 0.98 \), and the slope is \( m = -0.28 \).

Revisiting Eqn. 7.4, for KCl concentrations of 1 mM and 10 mM, the velocity at \( c = 10 \) mM should be roughly one-tenth that of the velocity at \( c = 1 \) mM. The whole field scaling parameter is 0.9 at 1 mM and 0.2 at 10 mM, so, while the trend is correct, the absolute magnitude of the relative velocities may be off.

### 7.3.2 Effect of Electrolyte Type

Until now, we have only examined KCl, a salt that readily dissociates in water. Fig. 7-2 shows actual velocity values for two electrolytes, KCl and CaCO₃, at different concentrations.

Calcium carbonate is only slightly soluble in solution (with solubility product constant, \( K_{sp} = 4.5 \times 10^{-9} \)), meaning that some solid salt still likely exists in solution and all ions are not dissociated. The maximum molarity for full dissociation of salt is given by \( \sqrt{K_{sp}} = 6.7 \times 10^{-5} \text{ M} \).
[Silbey & Alberty(2001)]. So, for concentrations of calcium carbonate above roughly 0.1 mM, some solid exists in solution.

The solubility of the salt should affect velocity in a few ways. The first is that the behavior of calcium carbonate should closely resemble the behavior of water in the dilute limit. Second, the behavior of calcium carbonate should approach the behavior of potassium chloride in the concentrated limit. Both of these trends are apparent in the figure. A limited number of actual data points makes further analysis difficult (for instance, answering the question, does the rate of decay for velocity with increasing concentration of calcium carbonate similar to that for potassium chloride?).

However, the trend is consistent – CaCO₃ is less soluble, so the concentration of salt is lower and the velocity larger. These are not suitable electrolytes for examining valence dependence, though, since CaCO₃ does not fully dissociate. Additional experiments will likely validate this trend.

Fig. 7-3 shows velocity data for various 1 mM electrolytes in the diamond electroplated post geometry at the same frequency and voltage (10V at 100Hz). We identify the slightly soluble salt CaCO₃ and identify three groups of salts which merit further examination. The first incorporates KCl, KI, and NaCl, all salts that readily dissociate in water. The second group includes KHCO₃, NaOH, NaBr, and NaI. All these salts also readily dissociate in water. The final group includes two 2-1 electrolytes, MgCl₂ and CaCl₂, and NaHCO₃.
### Size and diffusivity of ions

<table>
<thead>
<tr>
<th>Ion</th>
<th>Ionic Radius (nm)</th>
<th>Diffusivity [$10^{-1} \text{cm}^2 \text{s}^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>K⁺</td>
<td>0.234</td>
<td>1.957</td>
</tr>
<tr>
<td>Na⁺</td>
<td>0.190</td>
<td>1.334</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>0.194</td>
<td>1.584</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.145</td>
<td>1.412</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>0.079</td>
<td>2.032</td>
</tr>
<tr>
<td>I⁻</td>
<td>0.115</td>
<td>2.045</td>
</tr>
<tr>
<td>Br⁻</td>
<td>0.094</td>
<td>2.080</td>
</tr>
<tr>
<td>OH⁻</td>
<td>0.152</td>
<td>5.273</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>0.207</td>
<td>1.185</td>
</tr>
<tr>
<td>CO₃²⁻</td>
<td>0.189</td>
<td>1.846</td>
</tr>
</tbody>
</table>

Table 7.1: Ion Size and Diffusivities

### Diffusivity of salts

<table>
<thead>
<tr>
<th>Salt</th>
<th>Diffusivity [$10^{-1} \text{cm}^2 \text{s}^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl</td>
<td>1.99</td>
</tr>
<tr>
<td>KI</td>
<td>2.00</td>
</tr>
<tr>
<td>NaCl</td>
<td>1.61</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>1.71</td>
</tr>
<tr>
<td>KHCO₃</td>
<td>1.48</td>
</tr>
<tr>
<td>NaOH</td>
<td>2.13</td>
</tr>
<tr>
<td>NaBr</td>
<td>1.63</td>
</tr>
<tr>
<td>NaI</td>
<td>1.61</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>1.67</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>1.25</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>1.78</td>
</tr>
</tbody>
</table>

Table 7.2: Salt Diffusivity

### Predicted and Measured Relative Velocities

<table>
<thead>
<tr>
<th></th>
<th>KCl</th>
<th>KHCO₃</th>
<th>KI</th>
<th>NaBr</th>
<th>NaCl</th>
<th>NaHCO₃</th>
<th>NaI</th>
<th>NaOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl</td>
<td>1</td>
<td>1</td>
<td>1.2</td>
<td>0.99</td>
<td>0.40</td>
<td>1.1</td>
<td>1.2</td>
<td>1.3</td>
</tr>
<tr>
<td>KHCO₃</td>
<td>1</td>
<td>1</td>
<td>0.86</td>
<td>0.66</td>
<td>0.94</td>
<td>3.4</td>
<td>0.95</td>
<td>1.9</td>
</tr>
<tr>
<td>KI</td>
<td>1</td>
<td>1</td>
<td>1.1</td>
<td>5.2</td>
<td>1.1</td>
<td>2.9</td>
<td>1.3</td>
<td>6.7</td>
</tr>
<tr>
<td>NaBr</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0.56</td>
<td>1.2</td>
<td>1.3</td>
<td>1</td>
<td>0.43</td>
</tr>
<tr>
<td>NaCl</td>
<td>1</td>
<td>1</td>
<td>1.2</td>
<td>2.3</td>
<td>1</td>
<td>0.76</td>
<td>0.88</td>
<td>1.2</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>1</td>
<td>1</td>
<td>0.84</td>
<td>0.33</td>
<td>0.74</td>
<td>0.74</td>
<td>0.53</td>
<td></td>
</tr>
<tr>
<td>NaI</td>
<td>1</td>
<td>1</td>
<td>0.88</td>
<td>1.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaOH</td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 7.3: Predicted and measured relative velocities. For each electrolyte pair, the two values (from left to right) represent the predicted velocity ratio from salt diffusivity and the measured velocity ratio from experiment.
### Discussion

We define a charge-weighted mean of the diffusivity as $D_{salt} = \frac{(z_+ + z_-)D_+D_-}{z_+D_+ + z_-D_-}$. Two tables of relevant salt and ion data are presented in Tables 7.1 and 7.2. Data is collected from [CRC Press(2005)] and supplemented by [webelements.com]. Utilizing the data in these Tables, along with the scaling trends above, we compile a table of relative velocities for various ionic species, as a function of the salt diffusivity and individual ion diffusivities, taking $\omega/\omega_c^0 = 3$ and $D_0 = 1 \times 10^{-5}$ cm$^2$ s$^{-1}$. These tables are shown as Table 7.3 - 7.5.

Table 7.3 presents the predicted and measured velocity ratios for electrolyte pairs based on salt diffusivity. For most electrolyte pairs find reasonable agreement between the predicted trend and actual velocity values. Some discrepancy exists between the measured and predicted velocities with NaOH, presumably due to the high hydroxide ion diffusivity. Other issues appear with KHCO$_3$, where the model underpredicts the relative velocity for NaCl and NaBr. We cannot explain these anomalous results from our scaling arguments.

Turning to Table 7.4, we again find excellent agreement between the trend and the actual data. Again, however, we find anomalous behavior with KHCO$_3$, but only for two electrolytes, NaCl and NaI. Reliance only on the cation diffusivity seems to oversimplify the trend, grouping all Na$^+$ and K$^+$ electrolytes together.
Referring to Table 7.5, we find anomalous behavior with two different electrolytes, NaOH and NaBr. The OH\(^{-}\) ion diffusivity is much larger than the other anions and cations utilized in the experiment, however the velocity measured puts NaOH in the middle of the range of velocities, as opposed to at the lower end. The Br\(^{-}\) ion has the second highest diffusivity.

In all of the Tables, however, we observe widespread disagreement between the magnitudes of the predicted and measured flow. While the scaling arguments were capable of predicting, for the most part, the ionic salt which would yield faster ICEO flow, the magnitudes were off by large percentages in nearly all instances. This scaling analysis was unable to capture all the trends (specifically in the case of OH and HCO\(_3\) ions). Further, the scaling argument is certainly not quantitatively accurate, as it generally underpredicts the velocity ratios for all species. We recognize that the simple scaling arguments were based on a simple capacitive model of the double layer, which is inconsistent with the impedance spectra captured in Chapter 2. So, while the trends are roughly correct, a more physical model needs to be developed. Further, additional experiments may be conducted to validate the scalings with ion valence.

Additionally, we have identified another physical constant of the salt which determines its ICEO flow behavior – solubility. In simple solutions of most 1-1 salts, solubility is not a concern. However, in various biological systems and other more complicated salts, solubility may greatly affect performance of ICEO flow devices by producing fluid velocities that on first appearance may seem inconsistent with predicted theory, but upon closer examination make sense in light of solubility product constants, as previously discussed.
Chapter 8

Colloidal Manipulation in ICEO Flows

8.1 Introduction

In previous chapters have observed ICEO flow around metal cylinders with Particle-Image Velocimetry techniques (PIV). As discussed in Chap. 2, PIV assumes that tracer particles are passive tracers, i.e. that they advect with the flow. In this chapter, we re-examine the various forces on a dielectric tracer particle and examine variations in measured ICEO flow profile and velocities with different tracer particles and tracer particle concentrations.

8.2 Forces on Dielectric Tracers

In our experiments, the advection of the tracer particles should track the true fluid velocity streamlines with reasonable accuracy. Linear electrophoretic transport of the carboxylate-modified fluorescent microspheres is negligible for the applied electric field alternating at 300 Hz. The Brownian displacement estimate for the particles over the measurement time interval is approximately 0.1 \( \mu m \) for 0.5\( \mu m \) spheres and smaller for 1 \( \mu m \), and is reduced by ensemble averaging (the error scales as square root number of the number image pairs analyzed multiplied by the number of particles in each interrogation spot) to less than 5% of the measured displacement throughout the flow field.

The dielectric tracer particles, with slight negative surface charge, can also be subject to dielectrophoretic (DEP) forces, those resulting from gradient electric fields acting on (primarily) dielectric particles. The dielectrophoretic velocity is \( \frac{\epsilon}{6\eta} r^2 \nabla |E|^2 \) \cite{Morgan & Green(2003)}, where \( \epsilon \) is the dielectric constant of the electrolyte, \( \eta \) is the viscosity of the fluid, and \( r \) is the radius of the tracking particle, while the ICEO velocity is of order \( \frac{1}{\eta} E^2 a \), where \( a \) is the radius of the wire. The ratio of the two
velocities is thus estimated by the ratio of tracer size to wire size, squared: \( U_{DEP}/U_{ICEO} \sim r^2/a^2 \), as long as the gradient of the electric field is of order \( E/a \) (which is reasonable in the absence of any sharp corners). This ratio is roughly \( 10^{-4} \), so we do not expect any significant effect DEP of the tracer particles.

In microfluidic systems with strong electric fields and high conductivity fluids, Joule heating can be significant. As discussed by Ramos et al., this heating can result in secondary flow profiles at large fields and at large frequencies (typically above 10kHz), although our experiments are at lower frequencies < 1 kHz [Ramos et al.(1998)]. Given the highest electric field of \( 10^4 \text{V/m} \) and a conductivity of \( 0.01 \text{Sm}^{-1} \) in our setup, the power dissipation per volume \( \sigma E^2 \) can be estimated to be \( 10^5 \text{W/m}^3 \). The volume of the microchannel is \( 2 \times 10^{-9} \text{m}^3 \), which implies a typical power consumption of \( 2 \text{mW} \), similar to the estimate in [Ramos et al.(1998)]. We further calculate the temperature gradient by \( \Delta T \sim \frac{\sigma V^2}{k} \), where \( k \) is the thermal diffusion coefficient. For water, \( k \) is \( 0.6 \text{Jm}^{-1}\text{s}^{-1}\text{K}^{-1} \), and substituting a voltage of \( 10 \text{V} \) peak to peak leads to a temperature rise of \( 0.2^\circ \text{C} \). Electrothermal motion due to Joule heating typically requires larger temperature changes and higher frequencies [Morgan & Green(2003)], so we conclude that this is also not an important effect in our experiments.
Figure 8-2: Fluorescent microspheres. (a) sulfonated polystyrene. (b) sulfonated polystyrene with polymer chain and carboxylic acid.

8.3 Experimental Setup

We consider the experimental setup shown in Fig. 5-1. A 100 $\mu$m diameter electroplated gold cylinder with height 12 $\mu$m shown in Fig. 4-6(a)), was capped with a 12$\mu$m tall polymer channel with length 1cm and width 1mm. Two outer electrodes were formed from a 500Å gold/500Å chromium bilayer 1mm apart. The electroplated post was aligned in the center of the fluid channel. The channel was filled with de-ionized water loaded with 1$\mu$m fluorescent tracer particles (Molecular Probes, Eugene, OR) in various volume loading fractions. An AC voltage was applied at the outer electrodes to produce an oscillating background electric field across the post. The flow was visualized by tracking fluorescent tracer particles through an inverted optical microscope in a slice through the post, allowing quantitative comparisons with theory. The flow velocity was analyzed at 10V and 50Hz.

Two different 1 $\mu$m diameter tracer particles were analyzed to determine if different flow velocities were observable with different tracers at various concentrations. The first tracer is the standard carboxylate-modified latex sphere, whose chemical structure is shown in Fig. 8-2(b), and utilized in flow analysis in the prior sections. The second tracer is a sulfate-modified sphere, whose chemical structure is shown in Fig. 8-2(a). Both possess similar surface charge and are stable to low pH. The carboxylate-modified spheres have higher negative surface charge than the sulfate-modified spheres. The sulfate-modified sphere is relatively hydrophobic.

8.4 Results

Fig. 8-3 shows measured peak velocity as a function of sphere diluteness for the two tracer particles (circles for carboxylate-modified spheres and squares for sulfate-modified spheres). The carboxylate-spheres show much larger variation with concentration. It should be noted that the discussion in Chap. 2 assumed that the tracer particles operate truly passively, advecting with the fluid flow. A literature search in the field of PIV has turned up no studies of the effect of particle concentration in the fluid flow or even the choice of particles themselves. The existing PIV literature seems content to show qualitative agreement between the resulting flow profile and the expected flow profile.
The data in Fig. ?? suggest a much richer experimental space. The behavior of the carboxylate- and sulfate-modified spheres are markedly different. The peak velocity for the sulfate-modified spheres occurs in the dilute limit, while the peak velocity for the carboxylate-modified spheres is at 100:1 concentration. In fact, the change in measured velocity with particle concentration is substantially less in the carboxylate-modified spheres. Both types of spheres show an unusual increase in velocity at high concentrations (50:1) and then a reduction at even higher concentrations (25:1). The variations are inconsistent with the prevailing assumption that the particles track the fluid flow, and suggest that forces which we have previously discounted via scaling arguments are, in fact, altering the motion of the tracer particles and presumably the background flow. This conclusion merits further study. While this effect may be minimized in PIV for pressure-driven flows, a baseline examination of the resulting flow profile with the same experimental conditions and variations in particle concentration should be performed to verify PIV's accuracy in each experimental setup. This should eliminate any uncertainty about just what is being measured via the motion of the tracer particles.

Electrophoretic mobility for both types of spheres were tested in both de-ionized water and 1mM KCl using a ZetaPALS/Zeta Potential Analyzer (Brookhaven Instruments Corp., Holstville, NY). Solutions were prepared with 200:1 volume loading of fluid:tracer particles. For each solution, 200 measurements were made. The carboxylate spheres had a higher mobility than the sulfate spheres in de-ionized water, but lower mobility in KCl. The measured zeta potential (inferred from a Huckel model, assuming thin double layers) increased by nearly 60% from the de-ionized water to dilute KCl. The results are summarized in Table 8.1.
<table>
<thead>
<tr>
<th>Solution</th>
<th>Mobility [\mu m/s/V/cm]</th>
<th>Zeta Potential [mV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>carb./DI</td>
<td>-4.31 ± 0.11</td>
<td>-55.15 ± 1.42</td>
</tr>
<tr>
<td>carb./KCl</td>
<td>-6.21 ± 0.12</td>
<td>-79.44 ± 1.54</td>
</tr>
<tr>
<td>sulf./DI</td>
<td>-3.75 ± 0.09</td>
<td>-48.03 ± 1.17</td>
</tr>
<tr>
<td>sulf./KCl</td>
<td>-8.02 ± 0.05</td>
<td>-102.58 ± 0.58</td>
</tr>
</tbody>
</table>

Table 8.1: Mobilities and Zeta Potential of Tracer Particles in Solution

8.5 Colloidal Manipulation in ICEO Flows

Previously, we have maintained that particle concentration should have no effect on the resulting ICEO flow profile. However, we have seen evidence in various particle systems, shown above, that both particle type (i.e. surface charge) and concentration can effect resulting measured flow velocities. Experimentally, we have also seen evidence of particle concentration affecting flows. Fig. 8-4 shows an example of an experimental geometry loaded with two different concentrations of loading particles. In the low concentration limit, the particles tend to aggregate into traps at the point of predicted maximum flow velocity (near 45 degrees on the cylinder surface). In the high concentration limit, the particles no longer demonstrate trapping and instead yield a very different flow structure that shows large global flow from the equator to the poles, and particle clumping along streamlines leading away from the cylinder along the poles. The clustering of tracer particles near the sharpest corners of the diamond are reminiscent of Faradaic trapping of particles in ACEO [Wu et al.(2005)].

The various flow structures established by variations in particle concentration hint at a much richer possibility for colloidal manipulation using ICEO flows. As discussed in [Squires & Bazant(2004)], ICEO and induced-charge electrophoretic phenomena (ICEP) can occur in dielectrophoretic systems with high electric field gradients and can lead to hydrodynamic interactions between colloidal particles. More generally, ICEP flows demonstrate the same size dependence as ICEO flows (with flow velocity depending on colloid particle size), which suggests possible applications of ICEP in colloidal separation and manipulation. At the least, it suggests a possible range of experiments on fluids with two sizes of particles or two surface charges, such as the sulfate- and carboxylate-modified latex spheres.

8.6 Discussion

Our assumption that tracer particles are passive is inconsistent with the experimental results. While the data are reproduceable using the same concentration of tracer particles, the data in the previous chapters should be recognized as having been taken with a specific loading of tracer particles. Dif-
Different loadings of tracer particles would presumably give a different flow velocity, and perhaps flow profile. These results certainly merit additional investigation. New PIV experiments should examine these questions about particle passiveness and determine the influence of particle concentration in a variety of experimental settings. In particular, it is proposed that additional tests with tracer particles in both a diamond geometry (sharp corners) and cylindrical geometry (blunt corners) be carried out to determine the effect of particle concentration on measured velocity. Additionally, examination of particle concentration effects in two-color or two-size PIV should also be explored.
Chapter 9

Microfluidic Applications of
Induced-Charge Electro-Osmosis

Increased access to microfabrication technologies has spurred growing interest in the possibilities and the benefits of miniaturization in chemical analysis and biomedical screening. Microfluidics holds the promise of ultra-fast biological assays, analysis of ultra-dilute samples, and characterization of a previously unrealized compounds. In principle, these advances could be fully miniaturized, enabling new implantable medical devices and readily-available medical diagnostics, but there is still a need to develop robust techniques for pumping and mixing in portable microfluidic devices. Conventional pressure-driven flows are commonly used in microfluidics [Laser & Santiago(2004)], as long as the channel dimensions are not too small (> 10μm), and they possess the advantage of being robust and easy to operate, regardless of the fluid composition. Nevertheless, pressure-driven flows have poor scaling with miniaturization and do not offer simple local control of flow direction and circulation.

The pressure gradient needed to maintain a constant fluid velocity increases as the inverse square of the channel width, and rather bulky (non-portable) pressure sources are often required.

Electrokinetics offers an alternative means to pressure gradients to drive microflows, which is gaining increased attention [Squires & Bazant(2004), Stone et al.(2004)]. Perhaps the best known example of electrokinetics is the electrophoresis of charged colloidal particles [Anderson(1989)], where an applied electric field acts on diffuse double-layer charge to produce fluid slip. By the same mechanism, an electric field applied down a glass or polymer microchannel can drive a plug-like flow in capillary electrophoresis. Standard electrokinetic effects are linear in the applied field, which presents some disadvantages for microfluidics, especially in miniaturization. Aside from being fairly weak, linear electro-osmotic flows suffer from the requirement of direct current, and thus electrochemical reactions at the electrodes, to maintain a steady flow. Alternating current suppresses reactions and thus can allow larger driving voltages without bubble formation or sample contami-
nation by reaction products, but linear flows time-average to zero net velocity in alternating fields. Another problem for miniaturization is the large voltage requirement of linear electro-osmosis, since the voltage is applied globally down the channel, rather than locally across the channel. As a result, to achieve typical electric fields over 100 V/cm, one must apply over 100 Volts down a centimeter-long microfluidic channel. It would be preferrable for portable or implantable microfluidics to use the much smaller voltages (1-10V) supplied by micro-batteries by applying fields locally at the scale of the channel width. Nonlinear electrokinetic phenomena provide a promising alternative mechanism for flow control in microfluidic devices. The first nonlinear electrokinetic phenomenon described in the microfluidic literature was AC electro-osmosis at micro-electrode arrays, independently discovered by Ramos et al. [Ramos et al.(1998), Ramos et al.(1999)] and Ajdari [Ajdari(2000)] and studied extensively since then [Brown et al.(2001), Studer et al.(2002), Studer et al.(2004), Green et al.(2000), Ramos et al.(2003), Morgan & Green(2003)]. Similar flows were also observed by Nadal et al. [Nadal et al.(2002)] around a dielectric stripe on an electrode and by Thamida and Chang [Thamida & Chang(2002)] at a dielectric corner.

9.1 ICEO for Solid-State Pumping and Mixing in Microfluidics

One of the more commonly used methods for driving fluid flows in microfluidic systems is the use of pressure gradients. Consider a channel of length $L$, and square cross-section with side $w$ and area $w^2 = A$, containing fluid of viscosity $\mu$. Viscous flow theory dictates that a pressure drop of $\Delta P$ applied down the length of the channel will result in a resulting parabolic flow profile, with characteristic mid-channel velocity of $u = \Delta P/\mu Lw^2/8$. Immediately, one recognizes several adverse scaling issues with microfluidic systems. Namely, as the length of the channel increases, the resulting pressure drop required to maintain constant velocity increases. Similarly, as the width of the channel shrinks, the resulting velocity scales as $w^2$.

In the laboratory, these drawbacks are not so limiting. Scientists and engineers can now purchase relatively high pressure tanks, metering equipment for pressurized air, and the like. However, for truly portable applications, the adverse pressure scaling necessitates ever larger pressure control equipment for ever shrinking dimension of the microfluidic device. As a result, alternative means of pumping fluids in microchannels have been explored.

Various applications of microfluidics requires the mixing of two or more fluid streams and a variety of current experimental methods have been shown to adequately mix fluids. However, current methods of mixing tend to rely on pressure driven background flows and, therefore, fall victim to the same lack of portability that plagues application of pressure-driven flows to microfluidic settings outside of the laboratory space. Several methods demonstrated in conventional pressure-driven
microfluidic systems for mixing can also be exploited using ICEO as the background fluid pumping mechanism. Further, ICEO opens up new possibilities for local control over fluid streamlines and, thus, fluid mixing. Recent articles ([Squires & Quake(2005), Stone et al.(2004)]) review various techniques for pumping in microfluidics.

**Review of Fluid Mixing Techniques in Microfluidics**

Having already discussed the issues with pressure-driven flows in microfluidics (including the adverse pressure scalings and inability to create portable devices), much work has been done on various electrokinetic alternatives for moving fluids. Standard DC electro-osmosis has been widely employed [Gimsa(1999), Dutta et. al.(2002)] to move fluids down microfluidic channels. More complicated flow-FET structures enable the manipulation of the surface charge, and hence electro-osmotic flow velocity, via buried control electrodes [Lee et al.(1990), Gajar & Geis(1992), Schasfoort et al.(1999)].

AC electro-osmosis is a widely studied ([Ajdari(1995), Ajdari(1996), Ajdari(2000), Ajdari(2001), Brown et al.(2001), Gonzalez et al.(2000), Green et al.(2000), Morgan & Green(2003), Ramos et al.(1998), Ramos et al.(2003), Studer el al.(2002), Studer et al.(2004)]) technique previously discussed in this thesis. Utilizing an array of planar electrodes, AC electro-osmosis yields zero flow velocity at DC and flow velocities decay above the driving frequency. Subsequent contamination by materials in the flow stream can effect the charging time (increasing the characteristic frequency) and cause driving circuitry fixed to operate at one frequency to fail. Newer variants like traveling wave electro-osmosis utilize more complicated driving signals, but the fundamental limitations remain. It operates in AC, at low voltages, and in a wide range of fluids. AC electro-osmosis is attractive for many of the same reasons as ICEO. However, the necessity for periodic arrays and particular driving frequencies, and the relatively large device footprint, makes it less attractive than ICEO for most applications.


For mixing, various methods have also been developed. Each method requires a large background flow field, typically from a pressure-driven flow. Much work has focused on structures within the flow that split and recombine fluid streams, which enhances diffusion [Wang et al.(2002), Hong et al.(2004)]. Another alternative is to create chaotic streamlines via transverse pressure gradients [Stroock et al.(2002)]. Finally, cross-channel mixers have been developed, which employ the creation of oscillating fluid flow transverse to a channel flow direction [Tabeling et al.(2004)]. A complete review of mixing techniques in microfluidics can be found in [Ottino & Wiggins(2004)].

Chap. 7 details fixed-potential ICEO, which generates flow velocities in excess of 100μm/s with control velocities below 15V. We demonstrated the ability to pump from right-to-left by electrically
connecting the center electroplated post to the left electrode. In other fixed-potential geometries,
we have demonstrated flow velocities of approximately 1mm/s with driving voltages near 50V.

Fig. 9-1 shows the layout for a microfluidic device based on ICEO. The device takes two fluid
streams and pumps them into a Y-Channel, where the streams are mixed, then pumped out the
tail end. Beginning with the pumping stages, single fixed-potential devices produce reasonable flow
velocities, but decay quickly in space. One solution is to create an array of fixed-potential posts,
as seen in the Figure. Electrical connections can be made independently to the center post or, as
shown in the image, the posts can be electrically connected to the outer electrodes. In this case, the
number of independent control lines can be reduced drastically, and the need for adjacent positive
and negative electrodes is eliminated, reducing an adverse ac electro-osmosis-like backflow. The
geometry shown in the image is not ideal. Pumping efficiency and velocities can be improved by
tailoring the post geometry, electrode shape and spacing, and other geometric parameters. A more
uniform flow can be envisioned by having multiple posts between each electrode pair, instead of one
single pair. Such a device is shown in Fig. 9-2. The complexity of the governing equations and
full three-dimensional simulations suggests that the best way to design a near-optimized pump is to
merely fabricate and then test the device. This is, therefore, a goal of future research.

The mixer stage is seen in the center of the image. We envision mixing being accomplished
via two fixed-potential ICEO devices. Simulations performed in FEMLAB suggest high rates of
mixing by creating fast circulation between two laminar streams moving through a channel. As the
fluids convect down the channel, the two ICEO devices move fluids from one stream and passes
it through the adjacent stream, substantially speeding up diffusive mixing times. A schematic of
the mixer stage is shown in Fig. 9-3, consisting of a fixed-potential ICEO structure operating with
background electric field applied transverse to the background flow velocity. Fig. 9-4 shows three
time-lapse images of the simulation around a two ICEO mixing stage. Fluid is being pumped into the Y-channel via pressure gradients. The top stream is fluid with concentration $c = 1$. The bottom fluid has concentration $c = 0$. The plots show a measure of mixing, $\text{clog}(c)$ which attains a maximum at $c = 0.5$, when the two streams are perfectly mixed. From the image, we expect enhancement of mixing via ICEO.

9.2 Applications of ICEO in Biology

One of the biggest advantages of ICEO over other methods for pumping fluids is the ability to locally control fluid streamlines with low voltages. This opens up a host of possible applications which becomes the subject of this final section of Chapter 9. We discuss two applications: intra-ocular pressure regulation and constant-flow drug delivery.

9.2.1 Intra-Ocular Pressure Regulation

Glaucoma is a disease which results in loss of vision due to damage to the optic nerve from excess pressure within the eye. The eye has a natural pathway for vitreous humor to drain out of the eye, regulating internal pressure. However, over time, as people age, proteins can clog this pathway, impairing the eye's natural pressure regulation mechanism. Fig. 9-5 shows an image of the eye's
Figure 9-3: Schematic of an ICEO mixer stage. The y-channel brings two fluid streams across a transverse fixed-potential ICEO device.

anatomy, from [National Eye Institute(2005)]. We see the optic nerve at the back of the eye, and the majority of the eye filled with vitreous humor, a solution that is greater than 99% water, with small proteins and sugars. Basically, this is an ideal solution for ICEO. At the front of the eye, we see the cornea and the iris. Fluid drains through the trebecular meshwork near the intersection of the cornea and the iris to regulate the internal pressure of the eye. When the eye can no longer drain fluid, excess pressure builds up which may damage the optic nerve.

There are three main treatments for glaucoma. The first is eye drops, which restore some drainage ability. In more severe cases, doctors may perform a trebeculectomy, where a laser is used to reintroduce small holes into the meshwork. This surgery is successful in a large portion of the patients who undergo the procedure, but, more often than not, has to be performed multiple times as the laser holes will clog as well. A more complicated surgery involves the creation of a small flap in the eye to aid in drainage [National Eye Institute(2005)].

All of these treatments have moderate success rates, but the surgeries have to be performed multiple times and eye medications have to be taken by a patient for a lifetime following a diagnosis. We propose an innovative solution using ICEO as a pumping means to work with the favorable pressure gradient within the eye (relative to the outside) to pump small amounts of fluid continuously out of the eye. The flow velocities/volumes are consistent with what we have already demonstrated in the lab. The open research questions are how to create an ICEO device that is not susceptible
to bio-fouling. Since the natural cause of glaucoma is this build up of proteins, we presumably have to design an ICEO system that can withstand proteins flowing through the device, both without clogging the flow channel and without sticking to the electrode surfaces, and thereby affecting the performance of the device.

We propose the evaluation of various surface treatments on the ICEO electrodes to reduce the sticking of charged particles (as seen in our still images) during device operation. An ICEO device standard can be fabricated with control electrodes, and device performance can be characterized as a function of coatings. Additionally, the performance of the coatings, including ability to reduce biofouling, toughness, and adhesion, can be characterized. This should enable a wide-range of commercial applications of ICEO, including the glaucoma example.

9.2.2 Implantable Drug Delivery

The second example we will present is that of implantable drug delivery systems. The current state-of-the-art in implantable drug delivery systems are devices from Medtronics and Codman which pump drugs through a narrow catheter for intrathecal drug delivery. These devices are comprised of a reservoir, a pump, and a catheter. The reservoir and pump are implanted in the abdomen and the catheter threads from a port in the pump to the spine. While effective for delivery of pain medications, including morphine, and spasticity medications, including baclofen, these devices have significant drawbacks. The large distance between the pump and catheter, combined with the relatively low flow rate for the devices, requires a one to ten day lag between changes in dosing of the medication and the time it reaches the patient, depending on the delivery rate and concentration of the medication. By this time, the patient is no longer being monitored in a medical setting, and this can pose a danger to the patient. Additionally, the device is very bulky, due to the large amount of dilutant required to be stored in a reservoir. Further, high concentrations of medication in these devices can allow for the formation of granuloma tissue at the tip of the implanted catheter, which, in rare instances, can act like a mass on the spinal cord and cause paralysis [Bennett(2005)].

ICEO presents a possible alternative method for direct delivery of drugs into the body. ICEO, due to its compact nature, can be combined with a small reservoir of concentrated drug, and implanted near the desired point of drug delivery. Not only can ICEO be utilized for delivery of pain and spasticity medications, but it also opens the possibility to do localized delivery of chemotherapeutic agents, as well as agents that, when metabolized, are cardio- or hepatotoxic, reducing overall systemic shock. Localized drug delivery has received much research attention (for instance, see the review articles of [Tao & Desai(2003), LaVan et al.(2003)]), yet has still not produced a viable commercial device. ICEO offers an intriguing possibility for localized drug delivery, due to its ability to pump and mix, locally, suggesting in-vivo titrating of drugs prior to dispensing, and allows for control over dispensing the drug safely to the patient.
9.3 Discussion

ICEO has been demonstrated in this thesis as a viable means for pumping and mixing a variety of fluids, including low- to moderate-strength electrolyte solutions. A wide range of commercial applications become apparent for ICEO due to its ability to pump and mix via low level locally-applied electric fields. We have discussed two potential applications - glaucoma treatment and localized drug delivery, though these should not be read as the only possible applications. For both of these to become reality, additional research must be undertaken, including optimization of pumping (and perhaps mixing) in microfluidics using ICEO, and an investigation of means for passivating surfaces within the ICEO devices to reduce the risk of contamination and bio-fouling. However, the general promise of the applications discussed herein do not depend on the eventual prototypes for optimal pumping and mixing, which have yet to be demonstrated.
Figure 9-4: Simulation of mixing with an ICEO device at three different times.
Figure 9-5: Anatomy of the eye. From [National Eye Institute(2005)]
Chapter 10

Conclusion

This thesis has explored induced-charge electro-osmosis (ICEO) in various experiments in microfluidics. We have developed analytical forms for the frequency dependence of ICEO using various models of the electric double layer, and have investigated scaling of ICEO flows in experiments around a platinum wire in a microchannel. Based on the limitations in analyzing that geometry, including the inability to measure flow velocities independent of position above the metal wire, we developed a fabrication processes for the creation of electroplated geometries for ICEO.

We analyzed experiments around electroplated gold posts in a microchannel and examined the scaling of flow velocity with voltage and frequency. We developed analytical expressions for the scaling of flow velocity with concentration, salt diffusivity, and electrolyte ion valence, and analyzed those trends in a variety of electrolyte solutions. This thesis also examined fixed-potential ICEO and colloidal manipulation with ICEO. Finally, we discussed some possible applications of ICEO in microfluidics.

Overall, the phenomenon explored in experiments exhibits many of the identifying characteristics of ICEO and non-linear electrokinetics, in general, most specifically the quadratic dependence of fluid velocity on applied voltage. However, we lose quantitative accuracy between the theory and experiment due to the concern about the relatively high applied voltages. In short, while the theory captures the most general behavior seen within this thesis, it is inadequate for explaining the behavior of the double layer at such large applied electric fields.

Despite what was accomplished in this thesis, this is not the end of the story. ICEO shows great potential for a variety of commercial applications. And the exploration of the fundamental science of ICEO is not complete. Explorations of surface coatings, effect of the post material itself, and two-color PIV investigations around sharp plated shapes still remain unexplored.

I hope that this thesis will show the reader that ICEO is an exciting new mechanism for manipulating fluids at the small scale and inspire us all to continue the investigation. I will never forget
the excitement I felt the first time I observed an ICEO flow in the lab, and I hope many others are able to experience that, too.
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