Induced Charge Electro-osmosis over Controllably Contaminated Electrodes

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Recent studies of nonlinear electrokinetic phenomena have shown that the standard theory generally overpredicts measured slip velocities, sometimes by orders of magnitude. Thin ($O$(nm)) dielectric contaminant layers over the driving surface provide a natural mechanism for electrokinetic suppression. We describe experiments of induced charge electro-osmosis over gold electrodes ‘contaminated’ with silica layers of controlled thickness for nearly a thousand distinct conditions, in a system that enables direct comparisons between theoretical predictions and experimental measurements. Both the magnitude and the frequency dependence of the measured slip velocity are captured quantitatively over the entire range of experiments by accounting for both the physical capacitance of the dielectric layer and its surface chemistry. More generally, the system described here enables the quantitative EK characterization of a wide variety of surfaces, electrolytes, and experimental conditions, and will prove invaluable for the rational design and prediction of electrokinetic systems.

Electrokinetic (EK) effects involve the interaction between electric fields, electrolytic ions, fluid flows and particle motion, and have a history dating back two centuries [1]. Recent years have seen a resurgence of interest in EK effects, including protein, DNA, and particulate separations, directed assembly of colloidal particles, and transport in micro- and nanofluidic devices [2].

Despite this long history and sustained interest, the most basic elements of electrokinetics have remained largely unstated. The Helmholtz-Smoluchowski (HS) equation,

$$ u_s = -\frac{\varepsilon_w \zeta_{eq} E}{\mu}, $$

relates the electro-osmotic flow (EOF) velocity, $u_s$, to the electrostatic potential drop, $\zeta_{eq}$, across the diffuse layer of ions that screen a charged surface. Here $\varepsilon_w$ and $\mu$ are the permittivity and viscosity of the electrolyte, respectively (Fig. 1a). $\zeta_{eq}$ is generally difficult to manipulate experimentally, since it is generally set by surface chemistry [3], although some direct control has been shown in flow-FET systems [4]. While (1) is in principle predictive, its role in practice has most commonly been interpretive: given a measured $u_s$, (1) is used to infer $\zeta_{eq}$. The design of increasingly complex microfluidic devices, however, will require reliable predictions for EK flows under a wide range of conditions.

A variety of nonlinear EK effects have been explored and exploited in recent years, including AC [5] and travelling wave electrokinetic flows [6], electrokinetic instabilities due to concentration gradients [7] and through electrochemical membranes [8], and induced charge electrokinetics (ICEK) [9–11] for transporting and mixing fluid in microchannels. All involve an applied field that perturbs the electrolyte (e.g., induces a charged double layer over a polarizable inducing surface), and then forces the perturbations into motion. An important advantage is that small AC potentials applied to closely-spaced electrodes can produce large fields without electrolysis and drive steady nonlinear electrokinetic flows. Furthermore, the standard Poisson-Nernst-Planck (PNP) equations for ion transport make quantitative predictions for the steady flows driven by AC fields, which can be directly compared against experimental measurements. Any discrepancies indicate physico-chemical effects that are missing from the standard model.

While measured ICEK effects generally show qualitative agreement with theoretical predictions [10, 12], both qualitative and quantitative discrepancies have been reported [11, 13]. In particular, measured nonlinear electrokinetic flows in a variety of systems [13] are generally slower than the standard model predicts, sometimes by orders of magnitude. Various mechanisms have been proposed to explain this discrepancy, including Stern layers [14], steric interactions between double-layer ions [13, 16] and non-continuum effects.

Contamination of the inducing (metal) surface provides a natural mechanism for ICEK flow suppression [9]. To investigate this, we deliberately and systematically contaminate ICEK inducing surfaces with silica (SiO$_2$) films of known thickness ($O$(10 nm)), and compare the measured ICEO flow against theory. We measure ICEO flow profiles for 987 distinct experimental conditions, in which we vary electrolyte composition and concentration, electric field strength and frequency, and silica film thickness. In all cases, our system enables quantitative comparisons with the predictions of the PNP standard model. A naïve theory (computed as though no contaminant were present) fails in a manner reminiscent of many ICEK experiments [11, 13]. Accounting for the physical capacitance of the dielectric improves the agreement, but discrepancies remain. Including the ‘buffer capacitance’ of known surface chemical reactions yields an unprecedented quantitative agreement between theory and experiment over the entire range of experiments.

Such impressive agreement validates our experimental system and the theory developed for this parameter regime. Our system can easily be adapted to drive strongly nonlinear induced double layers, enabling direct and systematic measurements of the breakdown of the standard model. Furthermore, our system enables the EK characterization of any material that can be deposited as a planar film atop a metal surface, under a variety electrolytes and driving conditions, enabling the rational optimization of surface materials for EK applications.

We begin with the standard description of ICEO, in which
an applied field induces a charged screening cloud around a polarizable surface, and then drives that induced cloud into electrokinetic motion. A suddenly applied electric field initially intersects normal to an (equipotential) metal strip (Fig. 1b), driving ions in solution toward the metal surface. In the absence of electrochemical (Faradaic) reactions, positive ions accumulate near the field source, and negative ions near the field sink, to form a dipolar induced double layer (IDL) at steady state, leaving a tangential bulk electric field that drives the IDL into EOF flow as in (a).

\[ u_s = \frac{-\varepsilon_w E^2 x}{2\mu (1 + \tau_c^2 \omega^2)} \]  

where \( \tau_c = \varepsilon_w \langle |x| \rangle / \sigma \lambda_D \), and \( \sigma \) is the electrolyte conductivity. Explicit numerical calculations (COMSOL AB) are in excellent agreement with (3).

We now describe our experiments (Fig. 2a). We coated molecularly smooth fused silica plates (University Wafer) with a silane-thiol monolayer (as in [17], but with 575 mTorr O\(_2\) plasma exposure) to make an adhesion/wetting layer. We then patterned 50 x 900 \( \mu \)m electrodes by depositing 200 \( \AA \) of gold at 0.5 Å/s via electron beam evaporation with subsequent lift-off of the photoresist. We then evaporated silica films of various thickness (33, 66, or 100 nm) on the same day, to prevent fouling of the electrode surface.

Using soft lithography [18], we microfabricated PDMS channels of length 1 cm, height 100 \( \mu \)m, and width 300 \( \mu \)m, which we ozone-bonded to the substrate so that the microelectrode was located at the midpoint of the microchannel and oriented perpendicular to it (Fig. 2a). We designed the electrode to minimize stray asymmetric flows due to capacitive coupling with the microscope [19]. Fluid ports were punched at the channel ends with 26 gauge Luer stubs (McMaster-Carr). Stainless steel pins (New England Small Tube, 23 gauge) were inserted to act as fluidic vias and driving electrodes.

Electrolytes of concentration 10, 1, 0.1, and 0.01 mM KCl or NaCl were made by diluting a 10 mM stock solution of the salt dissolved in Milli-Q water. 520 nm fluorescent mi-
crospheres (Bangs Laboratories, FS03F/5069) were added to each electrolyte (0.02 wt%) to serve as flow tracers for micro-particle image velocimetry (μPIV).

Syringes were connected to the stainless steel pins via Tygon tubing, and an electrolyte of given ionic strength and composition (starting with the lowest ionic strength) was flowed into the channel. Syringes were then removed, and the ends of the tubing were placed in an electrolyte reservoir to avoid stray capillary pressure gradients. Electric leads were attached to the stainless steel pins and driven with a sinusoidal potential (Agilent 33220A function generator, amplified by a Trek PZD350 M/S). For each electrode/electrolyte combination, an automated system (Labview, National Instruments) applied AC potentials from 50 - 150 V to the stainless steel pins at frequencies from 100 Hz - 30 kHz. Between runs, the channel was flushed with at least 1 mL of the next electrolyte. Fluorescence microscope video microscopy (Andor iXon 885, Nikon TE2000-U with 20X ELWD, 0.45 NA objective) was used to record microsphere positions and μPIV algorithms were used to determine velocity profiles (Fig. 2c), which were corrected for the finite depth of focus of the optics [20]. A detailed description of similar experimental protocols is given in [19].

Since we expect (and observe) no flow perpendicular to the applied field, we average in the y-direction to obtain the mean velocity profile across the field of view (Fig. 2d). The slope, \( u' \), of this profile over the central 20 \( \mu \)m of the electrode was recorded [21]. 987 trials had a velocity above the error threshold (set so that Brownian motion of the tracer particles accounts for less than 20% of the observed velocity [20]).

Fig. 3a shows measured slip velocities \( u' \), scaled by \( u'_0 = -\varepsilon_w E^2/2\mu \) from the naive ICEO theory (as if the metal were clean), plotted versus frequency (scaled by \( \tau_c = \varepsilon_w \langle \sigma | x_v \rangle / \sigma \lambda_D \), with \( | x_v | = 10 \mu \)m at the edge of the region of interest). Measured velocities at low frequencies (\( \tau_c \omega < 1 \)) are 10-1000 times slower than predicted by theory, and the frequency dependence is poorly captured by the theory.

Of course, the naïve theory omits the silica contaminant, which splits the total potential drop, \( \Delta V = Ex \), between the double-layer \( \zeta_d = Ex/(1 + \delta) \), which contributes to ICEK flow, and the dielectric \( \Delta V_d = \delta Ex/(1 + \delta) \), which does not [9]. Here \( \delta = \varepsilon_w d/\varepsilon_d \lambda_D \) is the ratio of the linear double layer to dielectric layer capacitances, where \( \varepsilon_d = 4.6 \) and \( d \) are the permittivity and thickness of the silica layer. Here, \( \delta \) ranged from 0.18-566. The dielectric reduces both \( u_s \) and \( \tau_c \):

\[
\tau_{phys} = \tau_c (1 + \delta)^{-1}, \quad u_{phys} = u_s (1 + \delta) \quad .
\]

Scaling the measured velocities to account for the physical dielectric improves agreement (Fig. 3b), yet significant scatter remains even between experiments with the same \( d \). The nonlinear double layer capacitance, \( C_{DL} = \varepsilon_w/\lambda_D \cosh(\varepsilon \zeta_d/2k_BT) \), here leads to at most 20% changes, which is insufficient to account for these discrepancies. A missing mechanism thus remains.

Silica surfaces contain silanol groups which can react with hydronium (\( H^+ \)) ions in the double layer via

\[
\text{SiOH} \rightarrow \text{SiO}^- + \text{H}^+, \quad (5)
\]

which we assume to be in quasi-equilibrium with the hydronium ion concentration in the double layer. An increase (decrease) in \( \zeta_d \) lowers (raises) \( [H^+] \) in the double layer, which shifts the equilibrium in (5) to the left (right). The surface thus acts to “buffer” changes in the double layer \([H^+]\), introducing a buffer capacitance in parallel with the double layer [22]:

\[
C_{buff} = \frac{e^2 N_s}{k_B T} \left( \frac{K_a a_H \exp(-\varepsilon \zeta / k_B T)}{K_a + a_H \exp(-\varepsilon \zeta / k_B T)} \right)^2 ,
\]

FIG. 3: (Color online) Normalized slip velocity vs. dimensionless frequency. Data points are coded by silica film thickness: (●) 33 nm, (■) 66 nm, (♦) 100 nm. Solid lines represent theoretical predictions. (a) \( u'\) scaled by the naive ICEO theory, ignoring the dielectric. Inset: Neglecting the dielectric layer, all of the potential difference \( \Delta V \) between the electrode and the bulk electrolyte occurs over the double layer. (b) \( u'\) scaled assuming the dielectric acts only as a physical capacitor, in series with the double layer. Inset: The physical capacitance of the dielectric layer reduces \( \zeta_d \) by \( (1 + \delta)^{-1} \), where \( \delta = C_{DL}/C_d \). (c) \( u'\) scaled accounting for both surface chemistry (via buffer capacitance \( C_{buff} \)) and the physical capacitance. Inset: Surface chemistry immobilizes some ions that would otherwise contribute to EK flows, further reducing \( \zeta_d \) by \( C_{buff}/C_d \). 99% of all measurements (representing 987 distinct conditions) lie within a factor of 3 of this theory.
where $N_s$ is the silanol site density, $K_a \sim 10^{-6}$ is the equilibrium constant for (5), and $a_H$ is the activity of $H^+$ in the bulk electrolyte. A related model for ion adsorption [23] was found to better fit early ACEO measurements [14].

Accounting for both buffer and physical capacitances yields an induced zeta potential $\zeta_i = E_x / (1 + \delta + \beta)$, where $\beta = C_{\text{buff}} / C_\ell$. The theoretical slip velocity and RC time become

$$u'_{BP} = \frac{u'_o}{1 + \delta + \beta}, \quad \tau_{BP} = \frac{1 + \beta / \delta}{1 + \delta + \beta} \tau_e.$$ 

(7)

Here $N_s$, $a_H$ and $\zeta_{eq}$ are specific to the experimental system and are required to calculate $C_{\text{buff}}$. Reasonable bounds are known: $N_s \leq 7.8 \text{ nm}^{-2}$ and $-50 \leq \zeta_{eq} \leq -25 \text{ mV}$ [3]. The in-channel pH of the electrolyte was determined to be $\leq 4$ via fluorescent indicators.

Since $\zeta_i$ is generally low in our experiments (0.2-10.3 mV), and $N_s$ and $\zeta_{eq}$ do not vary significantly between experiments, a single value for $C_{\text{buff}}$ is expected for all experiments. Indeed, setting $C_{\text{buff}} = 24 \text{ mF m}^{-2}$ yields remarkable agreement, capturing both the magnitude and frequency dependence of the theory for 987 experiments (Fig. 3c). 99% of the data lie within a factor of three of theory. Additionally, the above parameter bounds yield a consistent magnitude for $C_{\text{buff}}$. By contrast, poor fits are obtained using a linear Stern layer (in series with the double layer and dielectric) instead of $C_{\text{buff}}$.

A curious trend appears at low frequencies (Fig. 3c), in which theory underpredicts measurements, for the highest salt concentrations ($10 \text{ mM KCl and NaCl}$). While the cause is unknown, the high mobilities of $H^+$ and $OH^-$ (which set $C_{\text{buff}}$) relative to salt ions (which do not) may play a role.

Induced zeta potentials in these experiments were relatively small ($\zeta_i < k_B T/e$), and well described by the linear theory. A variety of interesting effects (e.g. nonlinear capacitance, modified charging dynamics, ion crowding, and flow reversal) arise in the nonlinear regime ($\zeta_i > k_B T/e$) [6, 13, 16]. Our system enables a continuous transition between linear and nonlinear systems, and an important future direction will be to interrogate nonlinear induced double layers.

To summarize, we have demonstrated an unprecedented agreement between theoretical predictions and experimental measurements of ICEO flow over controllably contaminated surfaces. Values from nearly a thousand distinct experiments, representing a wide range of conditions, collapse onto a single theoretical curve that accounts for the physical dielectric contaminant and its surface chemistry.

Of course, understanding how contaminants reduce ICEK velocities does not mitigate this velocity reduction. Having elucidated these mechanisms, however, we can suggest strategies to maximize ICEK more generally by using thin surface coatings (to minimize $C_{\ell}$) and low ion reactivity (to minimize $C_{\text{buff}}$), e.g. self-assembled alkane-thiol monolayers. Our experimental system is remarkably general, and enables the rapid EK characterization of any material that can be deposited as a thin film atop a planar electrode, under a range of conditions and electrolytes. High-throughput searches to optimize materials for ICEK systems are thus within reach.

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