Experimentally-validated theory for the effective zeta potential in microchannel with gate electrodes

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ABSTRACT

In this work we develop and experimentally validate a model to estimate the effective zeta potential, ζ in a microchannel with a nonuniformites. Specifically, we present a robust numerical method to simulate a current monitoring experiment in a channel with two different zeta potentials. Next, we perform experiments to validate our model using a silica-PMDS microchannel system with a nonuniform zeta potential due to a Ti-Au gate electrode that covers 50% of the channel. We show that our theory accurately captures the salient features of our experiments, thereby offering a useful tool to predict effective zeta potential in a channel with nonuniform zeta potential.

Keywords: zeta potential, microfluidics, gate electrode, current monitoring, flow control

1 INTRODUCTION

There is a growing interest in selectively tuning the surface charge within micro- and nanofluidic channels for flow control applications, thus it is important to develop effective tools and methods to characterize fundamental properties of these complex systems. Theoretical characterization of wall properties in fluidic channels is generally difficult due to the sensitivity of the zeta potential, ζ to small differences in chemistry and treatment of surfaces [6]. Therefore, ζ in microchannels is generally obtained via the solution displacement method of current monitoring [2]. In this method, monitoring the current change as a low concentration buffer c_1 is replaced by a more concentrated buffer c_2 ($c_2 > c_2$) allows for the determination of mean electroosmotic flow velocity, which is directly proportional to ζ in channels with homogenous surfaces by the Helmholtz-Smoluchowski relation [3]. In a network of microchannels with nonuniform ζ, such as those with patterned addressable electrodes on the surface, it is useful to define an effective zeta potential, ζ_{eff} that allows us to determine the mean electroomotic flow velocity. However, measuring ζ_{eff} using the current monitoring technique is not straightforward in the case of non-uniform ζ, since nonuniformities in ζ lead to internal pressure gradients and non-uniform electromigration fluxes [6] [5]. Therefore, we have developed a robust model to derive ζ_{eff} in a channel with nonuniform zeta potential for any buffer concentration ratio $\gamma = c_2/c_1$ and any value of externally applied electric field. To validate our model, we fabricated a silica-PDMS microchannels system with a nonuniform zeta potential in the form of a gate electrode that covers 50% of the channel. We show that our theory agrees very well with experimental data and accurately predicts the value of ζ_{eff}

2 THEORY

We consider a straight microchannel, of length $2L$, width w and height H, connected to two reservoirs and having an insulated electrode at the bottom of length $2cL$ ($c \leq 1$). We assume that a voltage differenceΔ V across the channel is applied. Because of the embedded eletrode, the channel walls will have a non-uniform ζ, which we model as:

$$\begin{cases} \zeta_{UP}(x) = \zeta_1 \\ \zeta_{DW}(-L < x < -cL, cL < x < L) = \zeta_1 \\ \zeta_{DW}(-cL < x < cL) = \zeta_2 \end{cases} \quad (1)$$

2.1 Mean flow

The mean flow $\bar{u}$ along the channel can be obtained solving the incompressible Stokes equation of motion, taking the Smoluchowski equation as slip condition at the channel wall ($EDL/H << 1$), and enforcing continuity so that the flow rate is the same for each section of the channel. It is thus easily demonstrated that

$$\bar{u} = -\frac{\epsilon E_0 \zeta_1}{\eta}\left(1 + \frac{c}{2}(\frac{\zeta_2}{\zeta_1} - 1)\right) \quad (2)$$

where $E_0 = \frac{\Delta V}{2L}$, ϵ is the permittivity of water and η is the fluid viscosity. We define the effective ζ, ζ_{eff}, as the value of a uniform fictitious ζ such that the mean flow is the same before and after the discontinuity $\bar{u} = \frac{\epsilon E_0 \zeta_{eff}}{\eta}$, where

$$\zeta_{eff} = \zeta_1\left(1 + \frac{c}{2}(\frac{\zeta_2}{\zeta_1} - 1)\right) \quad (3)$$

As described in the introduction, ζ_{eff} is an important parameter in the characterization of such channels its experimental characterization is the main goal of our

work. In the next section, we will derive the mathmatical model that, once fit to experimental data, will allow us to determine ζ_{eff} for any system as described above.

2.2 Governing Equations

We follow the mathematical model of Bharadwaj and Santiago[4] to accurately simulate a current monitoring experiments. We assume an electrolyte system of two fully ionized ions, n^+ and n^-, which represent the buffer cations and anions in the background electrolyte, respectively. W use the Stokes equation, neglecting fluid inertia at these low Reynolds numbers[6], coupled with the convective diffusion equation to form a closed set of equations for the ion concentrations, electric potential, and fluid flow:

$$\begin{cases} \frac{\partial n^+}{\partial t} + \vec{v}\cdot\nabla n^+ = D^*\nabla^2 n^+ \\ (z^+\nu^+ - z^-\nu^-)F\nabla\cdot(n^+\nabla\phi) = (D^+ - D^-)\nabla^2 n^+ \\ \bigtriangledown p = \eta\bigtriangledown^2\vec{v} \end{cases} \tag{4}$$

where $\vec{v} = (u, v)$ is the velocity vector field, p is the pressure field, ϕ the electric potential, $z^\pm$, $\nu^\pm$ and $D^\pm$ are the valence, mobility and diffusivity of the two ion species, and $D* = \frac{z^+\nu^+D^- - z^-\nu^-D^+}{z^+\nu^+ - z^-\nu^-}$. Since $\frac{H}{w} << 1$ we solve for the flow between two parallel infinite plates. We assume the effect of the metal electrode is changing the zeta potential a function of x, so that the slip condition on the velocity field on the upper and lower surfaces of the channel are, respectively:

$$\begin{aligned} u_{UP} &= -\zeta_{UP}(x)\tfrac{\epsilon}{\eta}E(x, y = +H) \\ u_{DW} &= -\zeta_{LW}(x)\tfrac{\epsilon}{\eta}E(x, y = -H) \end{aligned} \tag{5}$$

where $E(x, y = \pm H)$ is the local electric field at the wall that depends on the electric potential ϕ, $E = -\nabla\phi$. To relate the ζ to buffer concentration at the wall we can use the well-known Grahame's equation, assuming the surface charge σ_0 is constant over different concentrations, a good first-order approximation for low potentials and dilute systems [3]

$$\sigma_0 = 2\sqrt{2n^+k_BT\epsilon}\sinh\left(-\frac{e\zeta}{2k_BT}\right) \tag{6}$$

where e, k_B and T are the elementary charge, the Boltzmann constant and the temperature, respectively. The model is completed imposing a potential difference across the channel, no externally applied pressure gradient, and continuity. In the current monitoring simulation the density number is identically equal to n_0^+, at the beginning of the experiment ($t = 0$), except for the left side of the channel where it is set to be γ times larger:

$$\begin{aligned} n^+(t = 0, -L < x \le L, y) &= n_0^+ \\ n^+(t, x = -L, y) &= \gamma n_0^+ \end{aligned} \tag{7}$$

2.3 Numerical solution and results

We developed both one dimensional and two dimensional semi-analytical and numerical methods to solve the above set of equations. For the one dimensional formulation, we approximated the derivatives in time with a first order implicit scheme, while the derivative in space was approximated using a Chebyshev derivative matrix. The 2D formulation is based on a finite difference scheme. Our simulations of current monitoring revealed that the discontinuity in the surface potential induces a recirculation of the velocity field near the electrode, which in turn changes the streamwise velocity profile, as shown in Figure 1. This fact can results in an incorrect estimate ofζ, especially for large values of γ.

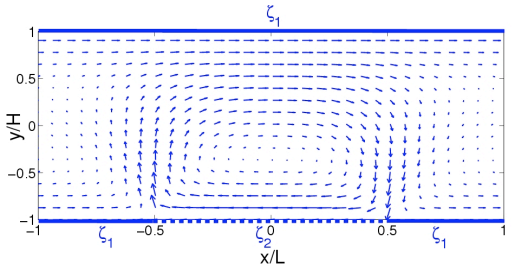

Figure 1: Velocity field obtained by a 2D numerical simulation when ζ potential at the electrode is -3 times the one at the channel surface. From this figure, the presence of a recirculation zone near the electrode is clear.

Figure 2(a) shows a numerical simulation of a typical current monitoring experiment for $\frac{\zeta_2}{\zeta_1} = -3.2$, an electrode coverage of 50%, and various concentration ratios γ.

The cause of the distorted shape of this current vs. time curve (which should typically be a straight line, a linear slope, and a straight line [2]) is the nonuniform velocity field around the electrode, which results in a time-dependent velocity (see Figure 2(b)). This behavior is more sprominent for larger values of γ and will result in a larger difference between the estimated and actual value of ζ_{eff} (Eq. 3) The black dots on the curves of Figure 2(a), represent the time when current reaches its equilibrium value. As can be seen, this displacement T increases with the concentration ration γ. Thus, if we calculate the effective ζ from the average velocity $\bar{u} = \frac{L}{T}$ and the well-known Smoluchowski equation $\bar{u} = \frac{\epsilon E_0\zeta_{eff}}{\eta}$ we obtain a smaller value than the actual effective zeta potential in the channel used during the simulation, note that the error between the two values increases with the concentration ratio.

We have calculated the percentage error between the evaluation of the effective zeta potential using the results from the current monitoring simulation for a concentration ratio range of 1 to 10, and a surface potential ratio from -1 to -4. Note that the percentage error ranges

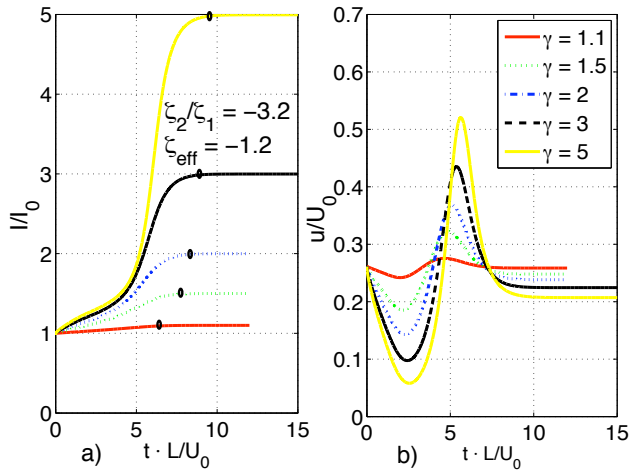

Figure 2: a) Current monitoring simulation with ζ potential discontinuity $\frac{\zeta_2}{\zeta_1} = -3.2$ resulting in a actual effective ζ potential of $\frac{\zeta_{\text{eff}}}{k_B T} = -1.2$. Electrode coverage: $c = \frac{1}{2}$ various γ. Nondimensional results with respect to the initial current in the channel I_0 and to the reference velocity $U_0 = \frac{\zeta_0 \epsilon E_0}{\eta}$. To give an idea of how much the displacement time change with the concentration ratio of the current monitoring, on each curve the point of 99% of jump between the two level of current has been higlighted with a black point. b) Mean velocity of channel flow. Simulation obtained with the 2D finite difference scheme.

from 0, for low concentration and surface potential ratios, to almost 50% for high concentration and surface potential ratios (Figure 3).

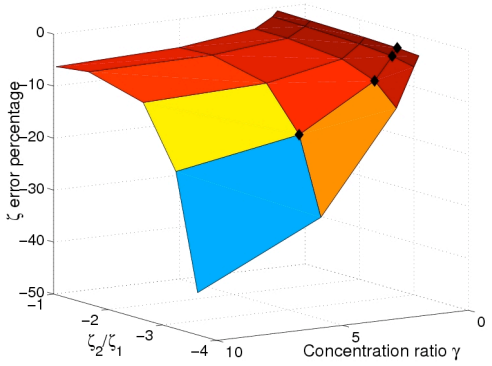

Figure 3: Percentage error on ζ_{eff}. Peclet number: $Pe = \frac{U_0 L}{D*} = 210$. Electrode coverage:$c = \frac{1}{2}$. Black dots represent the error we obtain if we evaluate the ζ potential from the current monitoring shown in Figure 2(a) with the classic method: with the higher concentration ratio current monitoring (yellow solid line in Figure 2(a)) we have an error up to the 25%.

3 EXPERIMENTAL VALIDATION

In order to validate the theory presented in the previous section, we designed and fabricated straight microfluidic channels with embedded metal electrodes that could be addressed by an external power supply, thus changing the zeta potential in certain sections of the microfluidic channel. We designed and fabricated all microchannel devices using glass slides and polydimethylsiloxane (PDMS) channels. The width and depth of the channels are 200 μm and 25 μm, respectively, and the length is 12 mm. Metal electrodes (50 nm titanium, 140 nm gold, and 50 nm titanium evaporated on the glass slide using a Metal evaporator) covered 50% of the channel and were subsequently covered with 800 nm of PECVD oxide. An image of the device is shown in Figure 4.

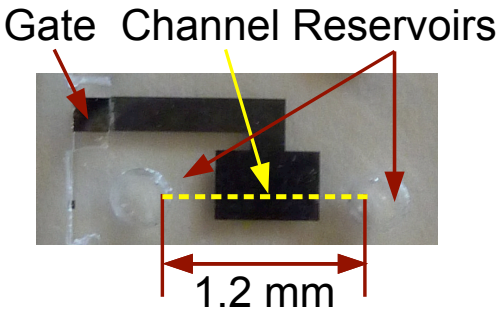

Figure 4: Image of experimental device used in this study. A straight PDMS channel was attached to a glass slide with a Ti-Au-Ti (50nm, 140nm and 50nm respectively) electrode (covered with 800 nm PECVD oxide) covering 50% of the channel. An alligator clip is attached to the side of the chip, which allowed for gate voltage to be applied. Additionally, 10 V were applied via a separate sourcemeter (Keithley 2410, Keithley Inc.) to the inlet of the channel (and ground to the outlet), and the resulting current through the channel was monitored by an electrometer (Keithley 6517, Keithley Inc.) and recorded (using Labview) as different concentration buffers were placed into the inlet well.

All solutions were prepared with de-ionized filtered water (Millipore, Inc.). Sodium acetate buffer pH 4, KCl and NaCl solutions at various concentrations were used as the buffer in all experiments. For current monitoring experiments, concentrations of 1mM, 2mM and 10mM were used, to create concentration ratios of 2 and 10. All solutions were filtered with PTFE syringe filters prior to use. Our experimental procedure is detailed elsewhere[8], we applied 10V between in the inlet and outlet of the channel and 600V to the gate electrode. In order to determine ζ of the bare channels, we performed current monitoring on a channel without an embedded

electrode, and in order to solve for the zeta potential of the channel with an applied field to the gate, a three capacitor model was used [7].

4 RESULTS AND DISCUSSION

Figure 5 shows a direct comparison of experimental and simulated current monitoring experiments. In this case, for an applied gate voltage of 600 V, ζ_2/ζ_1 is calculated to be -2.1. Although the concentrations of 1 mM to 2 mM and 1 mM to 10 mM were used, the simulation matched the conductivity ratios to the lowest and highest experimental current measured, which in this case were 1.3 and 5.5, respectively. From the figure, we first note that the current for the larger γ reaches a steady state value much later than for the lower concentration ratio (steady state times indicated by black diamonds on the graph). This validates our theory that the naive use of the current monitoring method induces an error in the estimate of ζ at large γ. Our model predicts very well the shape of the current curve at both values of γ. We attribute the discrepancies to uncertain knowledge of the values of D^+ and the ions in the buffer.

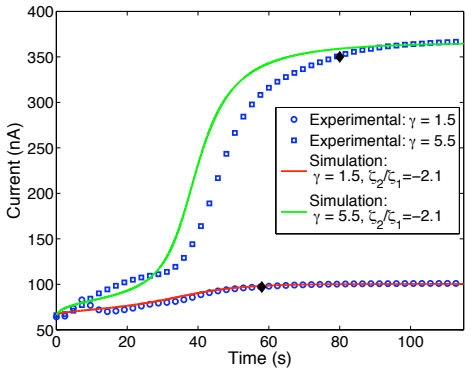

Figure 5: Comparison of a current monitoring experiment and simulation. Concentration ratios are set by the ratio of highest measured current and lowest measured current. Simulations are in good agreement with theory, especially the inflection points of the data, emphasized by black diamonds.

In conclusion, we have shown that current monitoring experiments can lead to erroneous estimates of effective zeta potentials in cases of nonuniform zeta potentials.

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