A New Method to Determine Zeta Potential and Slip Coefficient Simultaneously

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Liquid slip at hydrophobic surfaces in microchannels has frequently been observed. We present here an analytical solution for oscillating flow in a parallel-plate microchannel by combining electrokinetic transport phenomena with Navier's slip condition. Results suggest that the apparent and true zeta potential for a typical electrolye solution can differ by more than an order of magnitude with only a 1% slip. From our analysis, we propose a new method to measure simultaneously the true zeta potential and slip coefficient.

I. Introduction

In general, electrically neutral liquids have a distribution of electrical charges near a surface because of a charged solid surface. This region is known as the electrical double layer (EDL) which induces electrokinetic phenomena. The effect of the EDL during an externally applied pressure gradient is to *retard* liquid flow, resulting in a streaming potential; whereas, in the absence of an external pressure gradient, EDL induces fluid flow when an external electric field is applied (electroosmotic pumping). EDL is primarily a surface phenomenon; its effects tend to appear when the typical dimension of a channel is of the same order as the EDL thickness.[1]

Previous work in the area focuses mainly on the electrokinetic transport phenomenon that is responsible for "electrokinetic flow". However, liquid slip at hydrophobic surfaces has often been observed at this length scale.[2−5] Further, hydrophobic materials have become increasingly attractive for use in fabrication of micropatterned devices.[6,7] Thus, the physics of microfluid involving electrokinetic phenomena and liquid slip is needed for design and operation of microfluid flow in MEMS devices. However, determination of liquid slip and zeta potential in electrokinetic transport phenomena requires separate experiments. Our objective in this paper is to report a new method to determine zeta potential and slip coefficient simultaneously for parallel plate microchannels in a single experiment. We also provide analytical solutions for fully developed laminar electrokinetic flow of liquids subjected to a sinusoidal pressure gradient or a sinusoidal external electric field with Navier's slip condition in an infinitely extended parallel-plate microchannel.

II. Controlling Equations and Boundary Conditions

We consider the boundary value problem for oscillating liquid flow in an infinitely extended parallel-plate microchannel. A Cartesian orthonormal coordinate system (x, y, z) is used where the z-axis is taken to coincide with the microchannel central axis. All field quantities will be taken to depend on the y-direction coordinate y, and time t. The boundary value problem with relevant field equations and boundary conditions are shown below.

A. Electrical Field. The total potential U at the location (y, z) at a given time t is taken to be

$$U \equiv U(y, z, t) = \psi(y) + [U_0 - zE'_z(t)] \quad (1)$$

where $\psi(y)$ is the potential due to the double layer at the equilibrium state (i.e., no fluid motion and no applied external field), U_0 is the potential at $z = 0$ [i.e., $U_0 \equiv U(y, 0, t)$] and $E'_z(t)$ is the spatially uniform, time-dependent field. The potential, eq 1, is symmetric on the y-axis (independent of x). The time-dependent flow to be studied here is assumed to be sufficiently slow such that the charge distribution along the y-direction is relaxed at its steady state. Further, it is assumed that any induced magnetic fields are small enough to be negligible such that the electric field may still be defined as $-\nabla U$ (Shadowitz[8]); this definition may then be used to obtain the Poisson equation

$$\nabla^2 U = -\frac{\rho}{\epsilon} \quad (2)$$

where ρ is the net charge density and ϵ is the permittivity of the medium. Substituting eq 1 into 2 yields the Poisson equation

$$\frac{\partial^2 \psi(y)}{\partial y^2} = -\frac{\rho}{\epsilon} \quad (3)$$

The conditions imposed on $\psi(y)$ are

$$\psi(\pm a) = \psi_s \quad (4)$$

where ψ_s and a are the surface potential at the plate wall and the half-height of channel, respectively. For the sake of simplicity, we focus on a symmetric, binary electrolyte with univalent charges. The cations and anions will be identified as species 1 and 2, respectively. Based on the assumption of thermodynamic equilibrium, the Boltzmann equation provides the local charge density ρ_i of the ith species as

$$\rho_i = z_i e n_\infty \exp\left[-\frac{z_i e \psi}{kT}\right] \quad (i = 1, 2) \quad (5)$$

where z_i is the valence of the ith species, e is the elementary charge, n_∞ is the ionic concentration in equilibrium electrochemical solution at the neutral state where $\psi = 0$, k is the

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Boltzmann constant, and T is the absolute temperature. Invoking the Debye−Huckel approximation for low surface potential, $z_i e \psi / kT \ll 1$, we have $\sinh(z_0 e \psi / kT) \approx z_0 e \psi / kT$, and the total charge density follows from eqs 3 and 5 as

$$\rho = \sum_{i=1}^{2} \rho_i = \frac{-2 n_\infty z_0^2 e^2}{kT} \psi \tag{6}$$

where we have used $z_1 = -z_2 = z_0$. Finally, the definition of the reciprocal of the double layer thickness for a (z_0/z_0) electrolyte is given by

$$\kappa = \sqrt{\frac{2 n_\infty e^2 z_0^2}{\epsilon kT}} \tag{7}$$

and inserting eq 6 into eq 3 results in

$$\frac{\partial^2 \psi(y)}{\partial y^2} = \kappa^2 \psi \tag{8}$$

B. Hydrodynamic Field. The axial electric field will induce a body force $\rho E_z'$, and the modified Navier−Stokes equation becomes

$$-\frac{1}{\mu}\frac{\partial p}{\partial z} + \frac{\partial^2 v}{\partial^2 y} + \frac{1}{\mu}\rho E_z' = \frac{1}{\nu}\frac{\partial v}{\partial t} \tag{9}$$

where we take the pressure gradient, $\partial p / \partial z \equiv \partial p / \partial z(t)$, to be position-independent; μ is the viscosity and ν is the kinematic viscosity of the liquid. The boundary conditions for the velocity field are

$$v(a, t) = \beta \frac{\partial v}{\partial y}(a, t), \frac{\partial v}{\partial y}(0, t) = 0 \tag{10}$$

where β is the slip coefficient. We also call $-\beta$ the slip length. The electric current density along the microchannel may be integrated over the channel cross-section to give the electric current

$$i(t) = 2 \int_0^a \rho v \, dy + \frac{2 z_0 e D}{kT} \int_0^a (\rho_1 - \rho_2) E_z' \, dy \tag{11}$$

where D is a diffusion coefficient. The first term on the right side of eq 11 is due to bulk convection and the second term is due to charge migration (Masliyah[9]). Because of the assumption of an infinitely extended microchannel, a contribution to eq 11 due to concentration gradients vanishes. Using eq 5 and the identities, $z_1 = -z_2 = z_0$, we have $\rho_1 - \rho_2 = 2 z_0 e n_\infty \cosh(z_0 e \psi / kT)$. The Debye−Huckel approximation implies that $\cosh(z_0 e \psi / kT) \approx 1$ and $\rho_1 - \rho_2 = 2 z_0 e n_\infty$. With this simplification, eq 11 reduces to

$$i = 2 \int_0^a \rho v \, dy + \frac{2 z_0^2 e^2 n_\infty D}{kT}(2a) E_z' \tag{12}$$

and the flow rate can be written as

$$q = 2 \int_0^a v \, dy \tag{13}$$

C. The Normalized Equations. We provide here the normalized governing equations and boundary conditions. Using a yet unknown characteristic velocity, $\langle v \rangle$, we define the following normalized quantities:

$$V = \frac{1}{\langle v \rangle} v, \; Y = \frac{1}{a} y, \; \Psi = \frac{z_0 e}{kT}\psi, \; E_z = \frac{z_0 e a}{kT}E_z', \; Z = \frac{1}{a} z \tag{14}$$

for eqs 6, 8, 9, and 12. The normalized counterparts of eqs 8 and 4 become respectively

$$\frac{\partial^2 \Psi}{\partial Y^2} = K^2 \Psi$$

$$\Psi(\pm 1) = \Psi_s \tag{15}$$

whereas eqs 9, 10, 12, and 13 become respectively

$$-\frac{\partial P}{\partial Z} + \frac{\partial^2 V}{\partial Y^2} - \Psi E_z = \frac{\partial V}{\partial T}$$

$$V(1,\tau) = B\frac{\partial V}{\partial Y}(1,\tau)$$

$$\frac{\partial V}{\partial Y}(0,\tau) = 0$$

$$I = -2 \int_0^1 \Psi V \, dY + \frac{\mu D}{a^2 n_\infty kT}E_z = -2 \int_0^1 \Psi V \, dY + 2\frac{\Sigma}{K^2}E_z$$

$$Q = 2 \int_0^1 V \, dY \tag{16}$$

In deriving eqs 15 and 16, the following normalized quantities have been used

$$\bar{\rho} = \frac{\rho}{2 z_0 n_\infty e}, \; K = \kappa a, \; P = \frac{a}{\mu \langle v \rangle}p, \; \tau = \frac{\nu}{a^2}t$$

$$I = \frac{1}{2 z_0 n_\infty e a \langle v \rangle}i, \; \Sigma = \frac{z_0^2 e^2 \mu D}{\epsilon k^2 T^2}, \; B = \frac{\beta}{a} \tag{17}$$

where Σ is a normalized conductivity and B is a normalized slip coefficient. As well, the expression for the characteristic velocity is identified as

$$\langle v \rangle = \frac{2 n_\infty a kT}{\mu} \tag{18}$$

This expression for $\langle v \rangle$ was originally obtained by Hu et al.[10] [see their eq 32]. Finally, the following normalized quantities are also being given here:

$$\Omega = \frac{a^2}{\nu}\omega, \; \bar{\Omega} = \Omega\frac{\mu}{\bar{\mu}}, \; \bar{\tau} = \frac{\bar{\nu}}{a^2}t, \; Q = \frac{q}{\langle v \rangle a} \tag{19}$$

where the parameters ω and q are the frequency of the external oscillating field and volumetric flow rate, respectively. The parameters $\bar{\mu}$ and $\bar{\nu}$ are the apparent viscosity and apparent kinematic viscosity, respectively; they are written with overbars as opposed to the true viscosity μ and kinematic viscosity ν (without overbars).

III. The Analytical Solution

An analytical solution will be sought for a sinusoidal periodicity in the electrohydrodynamic fields and that is best addressed by using complex variables. Thus, a general field quantity X may be defined as the real part of the complex number $X^* e^{j\Omega\tau}$ as

$$X = \text{Re}[X^* e^{j\Omega\tau}] \tag{20}$$

where X^* is complex, $j = \sqrt{-1}$, Ω is the normalized frequency of oscillation [defined in eq 19], and τ is the normalized time [defined in eq 17]. The phase angle ϕ is defined as

$$\phi = \tan^{-1}\frac{\text{Im}(X^*)}{\text{Re}(X^*)} \tag{21}$$

where $\text{Im}(X^*)$ and $\text{Re}(X^*)$ are the imaginary and real part of X^*, respectively. An alternative representation of eq 20 is

$$X = \text{Re}[|X^*| e^{j(\Omega\tau + \phi)}] \tag{22}$$

where $|X| = |X^*|$ and $|X^*| = \sqrt{\text{Im}^2(X^*) + \text{Re}^2(X^*)}$. With the notation of eq 20, we shall seek the solution of the boundary value problem for the following specific dependencies

$$-\frac{\partial P}{\partial Z} = \text{Re}[P^* e^{j\Omega\tau}], \; E_z = \text{Re}[E_z^* e^{j\Omega\tau}] \tag{23}$$

We consider the class of solutions where the amplitudes of the pressure gradient and the electric field could be frequency-dependent, i.e., $P^* \equiv P^*(\Omega)$ and $E_z^* \equiv E_z^*(\Omega)$. The solution for Ψ will then follow from eq 15 and V from the first two parts of eq 16. Thus

$$V = \text{Re}[V^* e^{j\Omega\tau}] \tag{24}$$

where $V^* \equiv V^*(Y,\Omega) = V_P^*(Y,\Omega)P^*(\Omega) + V_E^*(Y,\Omega)E_z^*(\Omega)$. The expression for $V_P^*(Y,\Omega)$ and $V_E^*(Y,\Omega)$ will be given at the end of this section. The normalized electric current will follow from eq 16 and may be written as

$$I = \text{Re}[I^* e^{j\Omega\tau}] \tag{25}$$

where $I^* \equiv I^*(\Omega) = I_P^*(\Omega)P^*(\Omega) + I_E^*(\Omega)E_z^*(\Omega)$. The volumetric flow rate q is defined as $q = 2 \int_0^a v \, dy$. Using the definition in eq 19 as well as eqs 23 and 24, we obtain the normalized flow rate Q as

$$Q = \text{Re}[Q^* e^{j\Omega\tau}] \tag{26}$$

where $Q^* \equiv Q^*(\Omega) = Q_P^*(\Omega)P^*(\Omega) + Q_E^*(\Omega)E_z^*(\Omega)$. During pressure-driven flow, the amplitude of the streaming potential $E_z^*(\Omega)$ is found by setting $I^* = 0$ in eq 25. Thus

$$E_z^*(\Omega) = -\frac{I_P^*(\Omega)}{I_E^*(\Omega)}P^*(\Omega) \text{ for } I^* = 0 \tag{27}$$

During pressure-driven-flow, eq 27 may be substituted into eqs 24 and 26 to determine the normalized liquid velocity and the volumetric flow rate, respectively. Alternatively, the velocity, current, and flow rate during electroosmosis follow from eqs 24, 25, and 26 by setting $P^*(\Omega) = 0$ in those equations. The relevant quantities in eqs 24−26 are listed below:

$$V_P^*(Y,\Omega) = \frac{1}{j\Omega}\left[1 - \frac{\cosh(Y\sqrt{j\Omega})}{\cosh(\sqrt{j\Omega}) - B\sqrt{j\Omega}\sinh(\sqrt{j\Omega})}\right]$$

$$V_E^*(Y,\Omega) = \frac{\Psi_s}{K^2 - j\Omega}\left[\left(BK\frac{\sinh(K)}{\cosh(K)} - 1\right)\right.$$
$$\left.\frac{\cosh(Y\sqrt{j\Omega})}{\cosh(\sqrt{j\Omega}) - B\sqrt{j\Omega}\sinh(\sqrt{j\Omega})} + \frac{\cosh(KY)}{\cosh(K)}\right]$$

$$I_P^*(\Omega) = \frac{-2\Psi_s}{j\Omega\cosh(K)}\left\{\frac{\sinh(K)}{K} - \right.$$
$$\frac{1}{\cosh(\sqrt{j\Omega}) - B\sqrt{j\Omega}\sinh(\sqrt{j\Omega})} \times$$
$$\left.\left[\frac{\sinh(K+\sqrt{j\Omega})}{2(K+\sqrt{j\Omega})} + \frac{\sinh(K-\sqrt{j\Omega})}{2(K-\sqrt{j\Omega})}\right]\right\}$$

$$I_E^*(\Omega) = \frac{-2\Psi_s^2}{(K^2 - j\Omega)\cosh(K)}\left\{\frac{1}{\cosh(K)}\left(\frac{1}{2} + \frac{\sinh(K)\cosh(K)}{2K}\right) + \right.$$
$$\left(BK\frac{\sinh(K)}{\cosh(K)} - 1\right) \times \frac{1}{\cosh(\sqrt{j\Omega}) - B\sqrt{j\Omega}\sinh(\sqrt{j\Omega})}$$
$$\left.\left[\frac{\sinh(K+\sqrt{j\Omega})}{2(K+\sqrt{j\Omega})} + \frac{\sinh(K-\sqrt{j\Omega})}{2(K-\sqrt{j\Omega})}\right]\right\} + 2\frac{\Sigma}{K^2}$$

$$Q_P^*(\Omega) = \frac{2}{j\Omega}\left(1 - \frac{1}{\sqrt{j\Omega}}\frac{\sinh(\sqrt{j\Omega})}{\cosh(\sqrt{j\Omega}) - B\sqrt{j\Omega}\sinh(\sqrt{j\Omega})}\right)$$

$$Q_E^*(\Omega) = \frac{2\Psi_s}{K^2 - j\Omega}\left\{\frac{\sinh(K)}{K\cosh(K)} + \right.$$
$$\left.\left(BK\frac{\sinh(K)}{\cosh(K)} - 1\right)\frac{1}{\sqrt{j\Omega}\cosh(\sqrt{j\Omega}) - B\sqrt{j\Omega}\sinh(\sqrt{j\Omega})}\right\} \tag{28}$$

When $\Omega \to 0$, eq 28 reduces to those of steady state.

$$V_P^*(Y, 0) = \frac{1 - Y^2 - 2B}{2}$$

$$V_E^*(Y, 0) = \frac{\Psi_s}{K^2}\left[\frac{\cosh(KY)}{\cosh(K)} - 1 + BK\frac{\sinh(K)}{\cosh(K)}\right]$$

$$I_P^*(0) = \frac{-2\Psi_s}{K^2}\left[1 - \frac{\sinh(K)}{K\cosh(K)} - BK\frac{\sinh(K)}{\cosh(K)}\right]$$

$$I_E^*(0) = \frac{-2\Psi_s^2}{K^2\cosh(K)}\left\{\frac{1}{\cosh(K)}\left(\frac{1}{2} + \frac{\sinh(K)\cosh(K)}{2K}\right)\right.$$
$$\left. - \frac{\sinh(K)}{K} + B\frac{\sinh^2(K)}{\cosh(K)}\right\} + 2\frac{\Sigma}{K^2}$$

$$Q_P^*(0) = \frac{2}{3} - 2B$$

$$Q_E^*(0) = \frac{2\Psi_s}{K^2}\left[\frac{\sinh(K)}{K\cosh(K)} - 1 + BK\frac{\sinh(K)}{\cosh(K)}\right] \tag{29}$$

If the slip coefficient $B = 0$, all quantities become those of the electrokinetic flow with no slip condition. If $\Psi_s = 0$ and $B = 0$, all quantities become those of macroflow with no EDL effect and no slip.

IV. Results and Discussion

We note that when $K \gg 1$ and hence $\sinh(K)/\cosh(K) \approx 1$, combining eqs 27 and 29 yields an expression of the form

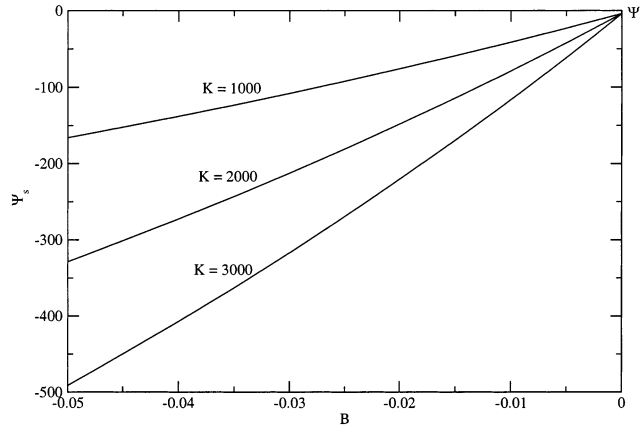$$\frac{\Delta U}{\Delta P'} = \frac{-\Psi_s(1 - BK)}{-B\Psi_s^2 + \Sigma} \tag{30}$$

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Figure 1. Comparison of the apparent zeta potential $\bar{\Psi}_s$ with the true zeta potential Ψ_s using eq 32.

where ΔU and $\Delta P'$ are normalized potential and pressure difference between the two ends of microchannel, respectively. If $B = 0$, eq 30 reduces to the well-known relationship for zeta potential measurement

$$\frac{\Delta U}{\Delta P'} = \frac{-\bar{\Psi}_s}{\Sigma} \qquad (31)$$

where we have used $\bar{\Psi}_s$ as the apparent zeta potential to differentiate from the true potential Ψ_s in eq 30. An expression between the apparent zeta potential $\bar{\Psi}_s$ and true potential Ψ_s can be obtained by equating eqs 30 and 31:

$$\bar{\Psi}_s = \frac{\Psi_s(1 - BK)\Sigma}{-B\Psi_s^2 + \Sigma} \qquad (32)$$

Equation 32 is employed to illustrate the effect of slip coefficient on the apparent zeta potential in Figure 1 for different K values from a given set of parameters that represents a typical system. We have selected the normalized conductivity and the normalized surface potential to be $\Sigma = 3.85$ and $\Psi_s = -3.9$, respectively. These parameters represent, in the dimensional case, a surface potential of -100 mV (Debye−Huckel approximation gives good agreement with experiments when zeta potential is up to 100 mV[11]) and a diffusion coefficient $D \approx 2 \times 10^{-9}$ m²/s for an infinitely diluted KCl electrolyte.[12] In Figure 1, we see that the effect of slip length on the apparent zeta potential increases as K increases. Specifically, when $K = 1000$ with a 1% slip ($B = -0.01$), the apparent zeta potential $\bar{\Psi}_s$ is larger than the true zeta potential Ψ_s by an order of magnitude.

Let us examine if a value of $K = 1000$ indeed reflects physical reality. For a typical electrolyte solution, κ can be expressed as

$$\kappa = \sqrt{\frac{2e^2 z_0^2 n_\infty}{\epsilon kT}} \qquad (33)$$

If we assume $\epsilon = 6.95 \times 10^{-10}$ C²/Nm², $T = 298$ K, $e = 1.602 \times 10^{-19}$ in eq 33, we could express $\kappa = z_0\sqrt{M} \times 3.29 \times 10^9$, where M is molar concentration of a (z_0: z_0) electrolyte. The calculated values of K are shown in Table 1 for typical electrolyte solutions used in the literature. It is apparent that K is usually much larger than 1000. Thus, the difference between the apparent and true zeta potential can be more than an order of magnitude.

Our analysis suggests a new method to determine the true zeta potential and slip coefficient simultaneously. Using eq 30

TABLE 1: K Values for Typical Electrolyte Solutions Used in the Literature

ref	solution	concentration (mM)	K
13	Na_2HPO_4	40	1316
13	KH_2PO_4	40	3290
14	$Na_2B_4O_7 \cdot 10H_2O$	10	6580
14	$NaHCO_3$	54	7645
15	KCl	10	3290

and the expression of flow rate in eq 29, we could design an experiment to measure both Ψ_s and B simultaneously. From the expression in eq 30

$$\frac{\Delta U}{\Delta P'} = \frac{-\Psi_s(1 - BK)}{-B\Psi_s^2 + \Sigma}$$

the normalized potential ΔU and pressure difference between the two ends of microchannel $\Delta P'$ are measurable quantities; K and Σ can be obtained from the properties of the electrolyte solutions and channel wall dimension [cf eq 17]. Thus, only the slip coefficient B and zeta potential Ψ_s are unknowns. An additional equation is then required to solve for these two quantities. Such an equation can be obtained from the measurable steady-state flow rate $Q^*(0)$:

$$Q^*(0) = Q_P^*(0)P^*(0) + Q_E^*(0)E_z^*(0)$$

where

$$Q_P^*(0) = \frac{2}{3} - 2B$$

$$Q_E^*(0) = \frac{2\Psi_s}{K^2}\left[\frac{\sinh(K)}{K\cosh(K)} - 1 + BK\frac{\sinh(K)}{\cosh(K)}\right]$$

$$E*_z(0) = -\frac{I*_P(0)}{I*_E(0)}P^*(0)$$

$$I_P^*(0) = \frac{-2\Psi_s}{K^2}\left[1 - \frac{\sinh(K)}{K\cosh(K)} - BK\frac{\sinh(K)}{\cosh(K)}\right]$$

$$I_E^*(0) = \frac{-2\Psi_s^2}{K^2\cosh(K)}\left\{\frac{1}{\cosh(K)}\left(\frac{1}{2} + \frac{\sinh(K)\cosh(K)}{2K}\right) - \frac{\sinh(K)}{K} + B\frac{\sinh^2(K)}{\cosh(K)}\right\} + 2\frac{\Sigma}{K^2}$$

$$P^*(0) = \frac{\Delta P}{\Delta Z}$$

It is apparent that the only nonmeasurable quantities are again B and Ψ_s. Thus B and Ψ_s can be determined simultaneously between these expressions. Alternatively, because

$$E_z^*(0) = \frac{\Delta U}{\Delta Z} \qquad (34)$$

E_z^* can be calculated from experimental values of ΔU and ΔZ without solving for $I_P^*(0)$ and $I_E^*(0)$. This allows easier calculation of B and Ψ_s.

V. Conclusions

We have presented an analytical solution of an oscillating microfluid in a parallel-plate microchannel by com-

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bining electrokinetic effect with liquid slip. Our results suggest that, for a typical electrolyte solution, the true and apparent zeta potential can differ by at least an order of magnitude with a 1% slip. From our analysis, we propose a new method to measure simultaneously the zeta potential and slip coefficient.

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