LANGMUR Cite This: Langmuir 2019, 35, 6203–6210

Modulation of the Streaming Potential and Slip Characteristics in **Electrolyte Flow over Liquid-Filled Surfaces**

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ABSTRACT: A significant enhancement in the streaming potential (V_s) was obtained in experiments considering the flow of electrolyte over liquid-filled surfaces (LFSs), where the grooves in patterned substrates are filled with electrolyte immiscible oils. Such LFSs yield larger V_s (by a factor of 1.5) compared to superhydrophobic surfaces, with air-filled grooves, and offer tunability of electrokinetic flow. It is shown that the density, viscosity, conductivity, as well as the dielectric constant of the filling oil, in the LFS, determine V_s . Relating a hydrodynamic slip length to the obtained V_s offers insight into flow characteristics, as modulated by the liquid interfaces in the LFS.

INTRODUCTION

Electrokinetic flows, considering the movement of electrolyte relative to another charged surface, are important for understanding the effects of charge accumulation and dispersion, with applications ranging from power generation $^{1-3}$ to biochemical separations.^{4,5} For instance, in pressure driven flows, the flow of excess ions in the electrical double layer (EDL) near the surface would generate a streaming current and in the absence of such current/open circuit conditions, an ion accumulation related streaming potential (V_s) . The exploration of the use of this phenomenon for energy sources has a long history^{6,7} and has also received much attention recently, from a micro- and nanofluidics perspective.⁸⁻¹⁰ For example, the overlap of the EDLs in nanoscale channels could lead to unipolar flows mimicking battery-like behavior. However, considering that flow and throughput restrictions are a major constraint at the nanoscale,¹¹ we focus our work here on engineered microscale channels for obtaining high V_s .

Fluid flows over smooth surfaces with concomitant no-slip conditions yield low streaming currents and potential. It has been indicated that enhanced electroosmotic mobility, M, may be obtained through the use of patterned^{12,13} or superhydrophobic (SH) surfaces,¹⁴ in both laminar and turbulent flows. The basis is that the aiding of the counterion motion near the surface would enhance the electroosmotic current and the related V_s. From the Helmholtz–Smoluchowski relation,¹⁵

 $M = \frac{\varepsilon \zeta}{r}$, where $\varepsilon \ (=\varepsilon_0 \varepsilon_r; \ \varepsilon_0 = 8.854 \times 10^{-12} \text{ C}^2/(\text{N m}^2)$ is the vacuum permittivity, and ε_r is the relative permittivity) of the electrolyte, ζ is the zeta potential, and η is the viscosity. However, such an increased mobility is based on the requirement that the no-shear/slipping surfaces have a significant charge density which is of a similar magnitude and sign as that of the no-slip surface in fluidic channels.

Traditionally, SH surfaces were fabricated through the use of air to promote slip, e.g., in patterned^{16,17} or nonsmooth surfaces,¹⁸⁻²⁰ with a flat air-electrolyte interface. Through much insight, it was determined that only a charged liquid-air interface could enhance the streaming potential.²¹⁻²³ It was found, for instance, that the V_s for flow over the uncharged liquid-air interface was similar to that of the homogeneously charged smooth surface, with no slip, for low EDL thicknesses and $\zeta^{21,22}$ and may be smaller compared to that obtained from a smooth surface with high ζ^{23} . There is also considerable ambiguity on the electrical character of the air-electrolyte interface as to whether there is an electrical potential due to residual OH⁻ ions.

We circumvent such ambiguity in our work using liquid (of an appropriate ε_r) filled into the interstices of patterned surfaces, fabricated to mimic the SH character. Consequently, a

Received: March 8, 2019 Published: April 16, 2019



Figure 1. Large (a) slip velocities (u_s) as well as (b) electrokinetic streaming potentials $(V_s = V_1 - V_2)$ may be generated through Poiseuille-type electrolyte flow (under a pressure difference $\Delta P = P_2 - P_1$) over a liquid-filled surface (LFS), with interstices/grooves filled with liquids of varying physical parameters, such as the density, dielectric constant, viscosity, etc. The positive and negative charges are indicated by the red and the blue circles. A larger V_s may be generated due to a larger ζ (the ζ potential).



Figure 2. A liquid-filled surface (LFS) was fabricated through (a) lithographic procedures to synthesize a surface with ridges and grooves and subsequent deposition of a uniform parylene film. The grooves are filled with a liquid (immiscible with the electrolyte and with low surface tension), and subsequently, the LFS is planarized. (b) The surface, as indicated through a scanning electron microscope (SEM) image, is defined through the width of the trough (d) and ridge (w), as well as the height (h). (c) Image of a practical LFS, indicating grooves filled with oil.

definitive charge density would be ensured at the flowing electrolyte slipping surface,²⁴ promoting the conditions for obtaining large streaming potentials (Figure 1). The shear plane is generally understood as the location at which the fluid starts to move and would be expected to be located at the liquid–liquid interface and the solid–liquid interface. Figure 1a emphasizes the flow profile (incorporating the slip velocity, u_{sr} as well as the associated slip length, b) over a liquid-filled surface (LFS),²⁵ while Figure 1b depicts the associated electrokinetic flows over the LFS. In this study, we investigate the characteristics of such LFS, which may be used for enhancing the magnitude of the associated V_{sr} . We also show that the use of such surfaces enables a simultaneous decrease of the fluid drag^{26–29} and increased flow^{30,31} coupled to an increase in the V_{sr} .

EXPERIMENTAL SECTION

Fabrication and Characterization of Hybrid Surfaces: The AFS and the LFS. A reference air-filled surface (AFS), consisting of rectangular ridges and troughs, was fabricated through photolithography processes and is shown in Figure 2a. Briefly, a Si wafer (n-type, $\langle 110 \rangle$, thickness 500 μ m, from University Wafer Inc.) was cleaned with acetone and isopropyl alcohol (IPA), rinsed by DI water, and then baked at 180 °C for 5 min. Negative photoresist NR9-3000 was coated on the Si wafer at 3000 rpm for 40 s and then baked at 120 °C for 60 s. The specific pattern was defined through a mask aligner (EVG 620) and developed (using RD6) for 1 min. Subsequently, the resist patterned wafer was subjected to dry etching (using an Oxford Plasmalab 100 RIE/ICP instrument) to yield a trench depth (h) ~95 $\mu m.$ The etched Si wafer was then put in RR2 photoresist remover over ~ 12 h, and any resist residues were further removed (using a PVA TePla PS100 instrument at 120 sccm, 200 W for 90 s). Finally, the grooved surface was coated with Parylene-C (using a PDS 2010 parylene coater) to a thickness of ~ 600 nm. The basis AFS was defined through an air fraction, $\phi_a = \frac{d}{d+w}$, the ratio of the trough width (d) over one period length (d + w). The surfaces were imaged using environmental scanning electron microscopy (ESEM): FEI/ Phillips XL ESEM and the FEI Quanta FEG 250 ESEM, respectively (Figure 2b, AFS; and Figure 2c, LFS). Patterned substrates with various values of ϕ_a were deployed to monitor the effect of air fraction on the V_s (see Section S1 in the Supporting Information).

Due to the oleophilicity of the AFS,³² oils immiscible with water and with low surface tension, e.g., Dupont Krytox GPL 104 (general purpose lubricant), a fluorinated synthetic oil, castor oil, and synthetic motor oils (0W-20 and 20W-50), can be filled into the troughs of the patterned surface to yield an LFS, located at the bottom of the microfluidic channel. The physical parameters for the oils used in the LFS are listed in Table 1. The oil was spread evenly on the surface via a soft brush, and any excess oil was removed from the top of the LFS. Table 1. Parameters^{*a*} of the Oils Filling the Interstices of the Liquid-Filled Surfaces (LFSs)

| oil | $ ho~({ m g/cm^3})$ | $\eta ~({\rm cm}^2/{\rm s})$ | μ (mPa s) | ε | $\gamma (mJ/m^2)$ |
|---------------------|---------------------|------------------------------|---------------|-----|-------------------|
| Krytox 104 | 1.93 | 1.77 | 340 | 2.1 | 18 |
| castor oil | 0.96 | 3.25 | 312 | 4.7 | 39 |
| motor oil 0W-20 | 0.86 | 1.19 | 102 | 2.4 | 30 |
| motor oil 20W-50 | 0.86 | 5.76 | 495 | 2.4 | 30 |

^{*a*}Density, ρ ; kinematic viscosity, η ; dynamic viscosity, μ ; dielectric constant, ε ; and surface tension, γ .

Detailed microscopic examination, e.g., Figure 2c, did not indicate any entrapped bubbles in the grooves. The oil filling was found to be reliable and is stable for the LFS, e.g., compared to the AFS. For instance, the surface energy of the LFS, $E_{\rm LFS} \sim 0.5 \times \gamma_{\rm pary} + 0.5 \times \gamma_{\rm oil} \sim 32 \text{ mJ/m}^2$, is an order of magnitude smaller compared to that of the AFS, $E_{\rm AFS} \sim r \times \gamma_{\rm pary} \sim 290 \text{ mJ/m}^2$ with *r* as the roughness factor (=6.3, from the ratio of the total area to the projected area³²). The excellent liquid-interface stability was also considered previously with surface-immobilized lubricants.³³

Setup for the Measurement of the Streaming Potential (V_s) . The experimental setup is shown in Figure 3a with a schematic



Figure 3. (a) Apparatus used for the measurement of the streaming potential consisting of a syringe pump connected by a tube to the microchannel to provide a constant flow rate to the electrolyte and a pressure gradient. (b) Schematic of the placement of the electrodes (nonpolarizable Ag/AgCl-type) at the ends to measure the streaming potential (V_s) related voltage along the microchannel.

(Figure 3b). A microchannel (11.8 cm in length, 9 mm in width, and 255 μ m in height) was constituted from a top surface (constituted from a polycarbonate coated with silicone) and a bottom AFS or LFS. These two surfaces are separated by a silicone rubber spacer for sealing and adjusting the height of the channel. For the streaming potential (V_s) measurement, electrolyte, i.e., salt water (in the concentration range 0.1-10 mM), prepared by dissolving NaCl into deionized (DI) water, was pumped by a syringe pump through a tube into the microchannel at a constant flow rate and provides a pressure gradient. The pressure drop for the experiment was in the range 200-1200 Pa, with lower and higher pressures yielding unreliable values for the $V_{\rm s}$. The voltages, related to the $V_{\rm s}$, were measured (using a Keithley 2700 Multimeter with input resistance >10 G Ω) through Ag/AgCl electrodes inserted into the two end reservoirs located at the inlet and outlet of the channel. The V_s for each applied pressure was measured six times. Given that the channel length (L) and width (W)are much larger than channel height (h), Poiseuille flow is assumed. The $V_{\rm s}$ was measured in flow at different orientations with respect to the patterned substrate to consider various tensorial aspects.^{22,34}

Measurement of the Pressure. The electrolyte flow rate in the channel, constituted from a rectangular plate geometry,⁹ was modulated through a syringe pump (Figure 3a) and was transduced to an applied pressure (ΔP) based on the Poiseuille relation: $\Delta P = \frac{12 \mu LQ}{wh^3}$ (Q is flow rate, L the channel length of ~11.8 cm, and h the channel height of ~250 μ m). The ΔP over the channel length (where the other end was left open to the atmosphere) motivated the pressure gradient driven flow. For the experiment, the flow rates were chosen as 0.0275 mL/s (corresponding to 200 Pa), 0.055 mL/s (440 Pa), 0.0825 mL/s (670 Pa), 0.11 mL/s (900 Pa), and 0.1375 mL/s

(1130 Pa). Additionally, the calculated pressure drop was checked using a manometer (UEI EM152) by inserting the measurement ports into the two reservoirs of the channel, and corresponded very closely to the values estimated from the Poiseuille relation.

Measurement of the Contact Angle. The electrolyte–oil interfacial energy will influence the interface shape and adhesion force and modifies the interface flow profile and the V_s . The Young relation is as follows:

$$\gamma_{\rm SA} - \gamma_{\rm SL} - \gamma_{\rm LA} \cos \theta = 0 \tag{1}$$

with γ_{SA} , γ_{SL} , and γ_{LA} as the substrate-air, substrate-liquid, and liquid-air surface energy, respectively, and θ as the substrate-liquid contact angle. The contact angles of electrolyte (0.1 mM NaCl solution) with parylene and Si substrate with different oil films were measured using a Ramé-Hart Model 190 contact angle goniometer at 20 °C, for estimating the corresponding γ_{SL} from given γ_{SA} and γ_{LA} (Figure 4). The estimated γ_{SL} values for the various oils are listed in Table 2 (with $\gamma_{SA} = 46 \text{ mJ/m}^2$ for parylene and $\gamma_{LA} = 72 \text{ mJ/m}^2$).



Figure 4. Contact angles measured on a (a) water–parylene and (b) water–GPL 104 interface at ~94.6° and ~68.9°, respectively. These values were used for estimating the corresponding γ_{SL} from a given γ_{SA} (=46 mJ/m² for parylene) and γ_{LA} (=72 mJ/m²).

Table 2. Measured Contact Angles for Oils and Parylene and Calculated Interface Energy $\gamma_{\rm SL}$

| substrate | contact angle | $\gamma_{SL} \ (mJ/m^2)$ |
|------------------|---------------|--------------------------|
| Krytox 104 | 68.86° | -7.97 |
| castor oil | 74.39° | 19.63 |
| motor oil 0W-20 | 82.93° | 21.14 |
| motor oil 20W-50 | 81.01° | 18.75 |
| Parylene-C | 94.6° | 51 |
| | | |

RESULTS AND DISCUSSION

Pressure Induced Flow on the LFS and Related Measurement of the Streaming Potential. We report measurements of the V_s with a 0.1 mM electrolyte concentration, where maximal values of the streaming potential were determined (Figure 5). Here, the observed variation arises from the relation, $V_s = \frac{e\zeta}{\eta\kappa_b}\Delta P$, in terms of the electrolyte dielectric constant (ε), the surface zeta potential (ζ), electrolyte viscosity (η), bulk electrolyte conductivity (κ_b), and pressure drop in the channel (ΔP). Assuming relatively constant ε and η for the electrolyte, the κ_b is proportional to concentration (I),^{4,5} while the $\zeta \approx c1 \log[I] + c2$, where c1 and c2 are constants. The overall effect³⁷ is that the V_s decreases with the I.

A typical response of the measured voltage as a function of flow is indicated in Figure 6a. The voltage increased when the electrolyte was driven through the channel and subsequently attained a steady value $V_{\rm f}$. The difference between $V_{\rm f}$ and the initial voltage, V_0 (in the absence of flow), was defined to be the measured streaming potential, $V_{\rm s}$. The variation of the $V_{\rm s}$



Figure 5. Variation of the streaming potential (V_s) for the air-filled surface (AFS), the GPL-oil-filled LFS, and the castor-oil-filled LFS at different flowing (transverse to the pattern ribs) electrolyte concentrations, I (0.1, 1, and 10 mM), at 1200 Pa. The V_s is fitted to a relation of the form $\sim \log[I]/[I]$.

with applied pressure, transverse to the ridges, is shown in Figure 6b for both the AFS and LFS (with four different filling liquids). Generally, a linear variation between the V_s and the ΔP ,¹⁵ was observed. It was also found that the V_s decreased with increasing ϕ_a for both AFS and LFS (see Figure S1 in the Supporting Information). Interestingly, when ϕ_a is ~0.75, the $V_{\rm s}$ of the GPL-filled LFS is larger than that of the AFS, while the $V_{\rm s}$ of the castor oil-filled LFS is smaller than that of the AFS. Moreover, it was observed, e.g., see Figure S2 in the Supporting Information, that at a given ϕ_a the V_s increased with an increasing number of interfaces, e.g., for groove widths 8, 18, and 40 μ m, with a larger V_s in the former smaller groove width case compared to the latter larger groove width case. While the rationale for such results has yet to be understood, it is likely that surface tension related instabilities would increase the kinetic energy near the interface,³⁵ which in turn induces larger moving velocity and the transduced V_s. Preliminary modeling of the flows, see Section S2 of the Supporting Information, employing a laminar two-phase flow level set model, over a given set of grooves, did seem to indicate a large

perturbation of the velocity or related pressure near the ridgegroove edges with distinct differences for GPL versus castor oil or the motor oils. Such effects may bear on the obtained V_{s} , and related scaling issues are being further investigated. Measurements were also done with the grooves oriented at various angles (e.g., see Figures S3 and S4 of the Supporting Information), where there seems to be evidence of tensorial $slip^{22,34,36}$ and concomitant electrokinetics.

Possible Influence of Oils on the Measured V_s . The selected oils, which serve as lubricants in the LFS, vary in terms of the dielectric constant (ε), dynamic viscosity (η), electrical conductivity (κ), surface tension (γ), and density (ρ), with the individual properties as listed in Table 1. As the V_s may be related to the electrolyte—oil interface shape and influenced by many of such parameters, we first aim to obtain empirical relationships of such an influence through the Buckingham II theorem.³⁸ While the given LFS system is quite complex, as related to the large number of parameters and the multiphysics aspects, the motivation was to make sense of the results through dimensional analysis. Consequently, for a given flow condition, as well as groove fraction and orientation (see Section S1 of the Supporting Information), one may obtain related nondimensionalized groups, namely

$$\Pi_0 = \frac{V_{\rm s}}{\eta^{-0.5} \kappa^{-0.5} \gamma} \tag{2a}$$

or

$$\Pi_1 = \frac{\rho}{\varepsilon^{-1} \eta^3 \kappa \gamma^{-2}} \tag{2b}$$

may be obtained. From fitting the above, with $V_{\rm s}$ from experiment and the values of oil properties, an empirical relationship $\Pi_0 = F(\Pi_1)$ and fit ($R^2 \sim 0.82$) was obtained (Figure 7). A larger (/smaller) $\varepsilon_{\rm oil}$ may be expected to increase (/decrease) the polarizability and increase (/decrease) friction at the oil–water interface³⁹ and modulate the $V_{\rm s}$. A possible correspondence between the η and the $\varepsilon_{\rm r}$ was indicated earlier.⁴⁰

For a better understanding of the obtained V_s variation, we considered the flow profile variation for an LFS taking into



Figure 6. (a) Typical measured voltage response indicating the voltage increase under the action of an applied pressure of 1200 Pa causing the flow of 0.1 mM NaCl solution. The periodic action of the syringe pump is responsible for the increase (flow) and decrease (no flow/Flow Pause) of the measured voltage. The corresponding velocity is indicated on the right-hand side. (b) Linear variation of the streaming potential (V_s) as a function of the applied pressure (ΔP), for various filling liquids/oils, in the LFS. The GPL is a fluorinated synthetic oil while the 0W-20 and 20W-50 are synthetic motor oils. It is to be noted that a larger V_s is obtained using GPL and other oils compared to air in the interstices, i.e., an air-filled surface (AFS).



Figure 7. Experimentally derived correlations between the obtained streaming potential (V_s) on the LFS as a function of nondimensional parameters, through considering the viscosity (η) , electrical conductivity (κ) , surface tension (γ) , density (ρ) , and dielectric constant (ε) of the filling liquid.

account *both* the electrical attributes, such as ε and κ , as well as the nominal fluidic parameters, such as the ρ , η , and γ , of both the impregnated liquid in the LFS as well as at the electrolyte–LFS interfaces.

Influence on Slip, as a Function of Electrical Parameters of the Filling Liquid, in the LFS. One manifestation of a liquid impregnated surface, akin to the LFS discussed in this work, was a slippery liquid infused porous surface.⁴¹ There, the wettability in terms of enhancing the liquid slip was considered. The slip length (b), as determined through the slip velocity (u_s) and the surface shear rate $\left(\frac{\partial u}{\partial y}|_{y=0}\right)$ from the Navier boundary condition, $u_s = b \frac{\partial u}{\partial y}|_{y=0}$, would be dependent on the filling liquid properties.^{26,31} Considering electrical characteristics, we indicate the inverse relation of the V_s to the dielectric constant of oil: ε_{oil} . For a hybrid surface, such as the LFS, consisting of both solid parylene and liquid oil, an effective slip length b_{eff} may be defined.

Using the relations in Belyaev and Vinogradova⁴² and Nizkaya⁴³ et al., we calculated the slip length of the LFS with transverse grooves where we consider the groove orientation, groove fraction, and viscosity ratio. The local slip length for the transverse groove, considering the viscosity of the electrolyte (η_{elect}) and the oil (η_{oil}) and a geometry-dependent function, β , was estimated through⁴³

$$b = w \frac{\eta_{\text{elect}}}{\eta_{\text{oil}}} \beta \tag{3}$$

For deep grooves, as in our case (with a height, *h*, of ~95 μ m, and a width, *w*, of 18 μ m, i.e., with $h/w \ge 1$), $\beta \approx 0.12$. The effective slip length (b_{eff}) was then estimated to be

$$b_{\rm eff} = \frac{L}{2\pi} \frac{\ln\left|\sec\left(\frac{\pi\phi}{2}\right)\right|}{1 + \frac{L}{2\pi b_1^{y}}\ln\left[\sec\left(\frac{\pi\phi}{2}\right) + \tan\left(\frac{\pi\phi}{2}\right)\right]} \tag{4}$$

The calculated $b_{\rm eff}(b)$ for the GPL-oil- and castor-oil-filled LFS is then ~2.5 nm (6.4 nm) and ~2.7 nm (6.9 nm), respectively. The $b_{\rm eff}/b$ ratio is then ~0.4, corresponding closely⁴⁴ to the expected value of ~0.5 (the area fraction); when $b/L \ll 1$, $b_{\rm eff}^{L,\parallel} \simeq \phi b$. If we consider the charge effects at

the gas/oil sectors on flow transport,⁴⁴ then the electroosmotic mobility for a transversely oriented groove was shown to be

$$M_{\perp} = \frac{\varepsilon \zeta}{\eta} \left[1 + \frac{b_{\text{eff}}}{b} \left(\frac{q_2}{q_1} (1 + kb) - 1 \right) \right]$$
(5)

From the literature, the surface charge density is ~-3.6 mC/m² (=q₁) for parylene⁴⁵ and ~-1.8 mC/m² (=q₂) for oil.⁴⁶ Through V_s measurements on the flow of 0.1 mM NaCl solution (with $k \sim (1/30) \text{ nm}^{-1} = 1/\lambda_{\text{D}}$, where λ_{D} is the Debye length) on parylene and PDMS coated *flat* substrates, and $V_{\text{s}} = \frac{\epsilon \zeta}{\eta \sigma} \Delta P$, we estimated that $\zeta_{\text{parylene}} \sim 31.7 \text{ mV}$, and $\zeta_{\text{PDMS}} \sim 26.9 \text{ mV}$. Then, the *enhanced* ζ potential for the bottom surface, $\zeta_{\text{bottom,en}}$, considering the correspondence^{44,47} of the electroosmotic mobility to the V_{s} is

$$\zeta_{\text{bottom,en}} = \zeta_{\text{bottom}} \left[1 + \frac{b_{\text{eff}}}{b} \left(\frac{q_2}{q_1} (1+kb) - 1 \right) \right]$$
(6)

and the concomitant $\boldsymbol{\zeta}$ for the channel is

$$\zeta_{\text{channel}} = 0.5\zeta_{\text{PDMS}} + 0.25(\zeta_{\text{parylene}} + \zeta_{\text{oil}}) \\ \left[1 + \frac{b_{\text{eff}}}{b} \left(\frac{q_{\text{oil}}}{q_{\text{parylene}}} (1 + kb) - 1 \right) \right]$$
(7)

Here, the effective ζ potential of the rectangular channel was defined through $\zeta_{\text{eff}} \left(= \frac{1}{2} \zeta_{\text{bottom}} + \frac{1}{2} \zeta_{\text{top}} \right)$, and for the ζ_{bottom} , a weighted summation²¹ of ζ_{parylene} and ζ_{oil} was assumed. We then estimate that $\zeta_{\text{GPL}} \sim 214$ mV, and $\zeta_{\text{castor}} \sim 66$ mV from the above relation. The larger V_s obtained with the use of GPL oil in the LFS compared with that of obtained by using castor oil could be tentatively ascribed to the larger ζ_{GPL} .

It may also be necessary to consider the issue of *fixed* charges and *mobile* charges on the slipping interfaces.³⁶ In Maduar³⁶ et al., a parameter μ was used to modify the Navier slip boundary conditions, with $\mu = 0$ for fully *mobile* charges and with $\mu = 1$ for *fixed charges*. If there is adsorption of hydroxyl ions, for example, the liquid—oil interface would be charged, and the correspondent V_s is modified to

$$V_{\rm s} = \frac{\varepsilon \zeta}{\eta \sigma} (1 + \mu b_{\rm eff} k) \Delta P \tag{8}$$

Consequently, another reason for the difference in the V_s between the GPL- and castor-oil-filled LFS may be due to differing μ and the fact that $\mu_{GPL} > \mu_{castor}$ due to the smaller dielectric constant of GPL oil ($\varepsilon \sim 2.1$) compared to castor oil ($\varepsilon \sim 4.7$). Considering the continuity of tangential shear stress across the electrolyte (with η of ~ 1 mPa s)-oil (with η of ~ 300 mPa s) interface, it was assumed that the slip is along the oil-electrolyte interface.

An alternate understanding of the influence of charges may be manifested through a charge density (σ) difference, $|\sigma_{\text{parylene}} - \sigma_{\text{oil}}|$, which is expected to yield a longitudinal electric field (E_x) as well as a transverse electric field (E_y), the former of which drives ion motion across the surface (Figure 8). Here, xis in the direction of fluid flow, and y is the orthogonal direction transverse to the direction of the pressure driven flow. It may be expected that, with a large (small) σ_{oil} , the screening of the charge into the flowing electrolyte occurs over a smaller (larger) distance yielding a larger (smaller) ζ . The Langmuir



Figure 8. Schematic of electrokinetic flow over the LFS with varying surface charge densities (σ). As σ_{oil} is less than $\sigma_{parylene}$, the surface conductivity κ_s is smaller for the oil regions. Consequently, driven surface currents, J (both parallel, in the *x*-direction; and perpendicular, in the *y*-direction, to the LFS), serve to enhance the slip and the slip length (b). The b was correlated to the healing length $L_{\rm H} \sim \kappa_{\rm s}/\kappa_{\rm b}$ (the ratio of the surface to the bulk electrical conductivities), the Debye length ($\lambda_{\rm D}$), $\eta_{\rm elec}$, as well as the $\varepsilon_{\rm oil}$ and $\sigma_{\rm oilv}$ through analysis and experiment.

shear plane is then closer (further), implying smaller (larger) u_s and b. We estimated, for the parylene coated Si surface, $\sigma_{\rm parylene}$ at -3.6 mC/m^2 and that of the oil σ_{oil} at -1.8 mC/m^2 . The resultant E_y would be of the form $E_{y,\text{parylene}} \sim \sigma_{\text{parylene}}/\varepsilon_{\text{elec}}$ and $E_{y,oil} \sim \sigma_{oil} / \varepsilon_{elec}$ respectively. If we assume no residual charge at the oil-electrolyte (elec) interface, then from the continuity of electrical displacement and electrical fields across the interface, (i) $\varepsilon_{\text{oil}}E_{y,\text{oil}} = \varepsilon_{\text{elec}}E_{y,\text{elec}}$ and (ii) $E_{x,\text{oil}} = E_{x,\text{elec}}$. Here, the capillary number $(Ca) = \eta v / \gamma$, with η as the dynamic viscosity, v as the characteristic velocity, and the surface tension (γ) , was estimated to be of the order of 10^{-3} , which indicates that the surface tension dominates over the viscous forces. A similar inference could be made through estimating the Bond number (Bo), which relates the difference of the density of the two phases (electrolyte and oil) over a characteristic length, say, the groove width, with respect to the surface tension. Consequently, the pressure driven flow induced viscous force will not significantly deform the liquid-liquid interface.⁴⁸

The deployment of a *hybrid* bottom surface, constituted from both the liquid and the solid with concomitant differing surface charge densities, may be expected to yield concentration polarization⁴⁹ as well as nonuniform conduction⁵⁰ effects over the surface. In electroosmotic flows, the ions contributing to the surface current $(J_x \sim \kappa_s E_x, \text{ with } \kappa_s \text{ being the}$ surface conductivity) in the direction of the flow are replenished through an ion current from the bulk liquid (of conductivity: κ_b) over a length scale (termed a healing length: $L_{\rm H}$) and due to a normal component of the electric field (E_y) . From such ion conservation considerations, $\kappa_s E_x \sim \kappa_b E_y L_{\rm H}$. If E_x and E_y are of comparable magnitudes, then the $L_{\rm H}$ is of the order of κ_s/κ_b .

For flow over the LFS, it may be expected that the E_x or the E_y may contribute to u_s and the resultant surface current, $J_{s,x} \sim \rho_s u_s$, where ρ_s is the *mobile* surface charge density. From an analogy to the arguments presented above, for the E_y induced current dominated case, $\kappa_{\rm b}E_y L_{\rm H} \sim \rho_s u_s$, implying, for a given shear rate $(\partial u/\partial y)$ in the absence of nonlinear effects, the following: ^{51,52}

$$b \sim \frac{\kappa_{\rm b} \sigma_{\rm oil} L_{\rm H}}{\epsilon_{\rm ele} \rho_{\rm s}}$$
(9a)

Alternately, if the longitudinal electrical fields, say $E_{x,\text{elec}}$ (= $E_{x,\text{oil}}$), are more responsible for the fluid slip, then $\kappa_s E_{x,\text{elec}} \sim \rho_s u_{s}$, indicating

$$b \sim \frac{\kappa_{\rm s} \sigma_{\rm oil}}{\varepsilon_{\rm oil} \rho_{\rm s}}$$
 (9b)

Here, a larger *b* or a u_s also seems to be facilitated through a higher σ_{oil} . Additional electrostatic considerations, e.g., related to the screening in the electrolyte, may also be important. It was previously indicated, for instance,⁴⁶ that the magnitude of the associated surface charge density may be independent of oil type and mostly dependent on the aqueous phase/ electrolyte. Indeed, testing with several oils indicates that the correlations indicated in eqs 2a and 2b may be valid. As we use nonpolar oils in the LFS, the molar conductivity is negligible, and the Walden rule relating η to the σ is not applicable.⁵³

At the shear plane, from considering an equivalence of the shear stress, τ (~ $\eta \partial u/\partial y$) to u_s , a direct correlation between the *b* and the η of the electrolyte may be deduced. Indeed, such a correlation and scaling have been previously indicated for liquid slip on air,⁵⁴ through a "gas cushion" model.¹⁶ From the previously deduced $b \sim 1/\varepsilon_{oil}$, we now obtain a significant correlation for the oil–electrolyte interface:

$$b \sim \frac{\eta_{\text{elec}}}{\varepsilon_{\text{oil}}}$$
 (10)

The expression above posits a relation between the measured V_s and the flow characteristics as modulated by the oil-electrolyte interface(s) in the LFS. Consequently, aspects of the surface that promote *b*, e.g., geometry,¹⁶ air bubbles,⁵¹ surface interactions, etc., may all now be utilized for obtaining enhanced V_s .

CONCLUSIONS

In summary, we have indicated that enhanced streaming potentials (V_s) may be obtained through electrolyte flows over liquid-filled surfaces. It was observed that the $V_{\rm s}$ was sensitive to the character of the liquid-in terms of the density, viscosity, and dielectric constant-in the LFS. Moreover, the magnitude and variation of the pressure at the ridge-groove interface seem to be important in determining the enhancement of the V_s over that obtained in air-filled grooves and surfaces. The influence of such local perturbations merits further study, e.g., the modification of the flow profile close to LFS,55 due to the unequal interface energy between electrolyte-parylene (ridge) and electrolyte-oil (groove). A correlation of the slip length (b) to the V_s yields a better understanding of the hydrodynamics inherent in electrokinetic flows. The presented study indicates a path forward²¹ in terms of generating large streaming potentials, through fluid flow in microchannels with a hybrid surface, consisting of both solid and oil interfacing with an aqueous electrolyte, moving beyond smooth walled nanoscale channels.9 Our results and those expected from extending our investigations⁵⁶ may be utilized to gain greater insights with applications ranging from energy conversion^{3,6,9,10,57} to transport in lab-on-a-chip devices^{58,5} and nanosystems.⁶⁰

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.lang-muir.9b00704.

Streaming potential (V_s) measurements as a function of AFS and LFS geometry and computational simulations (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors are grateful for support from the National Science Foundation (NSF: CBET 1606192). We acknowledge the use of the Nano3 facility (NNCI supported with grant number: ECCS-1542148). We also appreciate the assistance of Prof. J. Friend and P. Chen for help with imaging and A. Bhattacharya and Dr. S. Rubin for discussions.

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