Effect of wall permittivity on electroviscous flow through a contraction

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The electroviscous flow at low Reynolds number through a two-dimensional slit contraction with electric double-layer overlap is investigated numerically for cases where the permittivity of the wall material is significant in comparison with the permittivity of the liquid. The liquid-solid interface is assumed to have uniform surface-charge density. It is demonstrated that a finite wall permittivity has a marked effect on the distribution of ions in and around the contraction, with a significant build-up of counter-ions observed at the back-step. The development length of the flow increases substantially as the wall permittivity becomes significant, meaning that the electric double-layers require a longer distance to develop within the contraction. Consequently, there is a corresponding decrease in the hydrodynamic and electro-potential resistance caused by the contraction. The effect of wall-region width on the flow characteristics is also quantified, demonstrating that the development length increases with increasing wall-region width for widths up to 5 channel widths. © 2011 American Institute of Physics.

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I. BACKGROUND

The flow of aqueous-based solutions in micro-electro-mechanical systems (MEMS) is affected significantly by electrokinetic phenomena.^{9,25,26} Flow at these scales can be driven efficiently by the application of an external electric field, which exerts a force on excess counter-ions present in the liquid adjacent to a charged wall. This type of flow is termed electro-osmosis. Purely pressure-driven electrolytic flows are also affected by electrokinetic phenomena. The flow of ions induces an electric field, which acts to resist the flow motion.²⁶ This phenomenon is known as the electroviscous effect.^{18,21} Electroviscous flows in uniform channels have been studied extensively, including slit-like channels,^{6,13,14} cylinders,^{2,3} and channels with rectangular or elliptic cross-section.^{10,11,21,30,31} Davidson and Harvie⁷ studied electroviscous flow through a contraction-expansion geometry for negligible wall permittivities.

For electroviscous flow in a uniform channel, the axial electric field is constant. This fact, the absence of free charge in the solid region of the channel, and the overall electroneutrality of the system, constrains the transverse electric field to be zero in the solid region. In that case, the permittivity of wall material has no effect on the flow characteristics. Wall permittivity can only affect the flow when the geometry of the channel changes and the normal component of the electric field in the solid influences the flow. Most numerical and analytical models in the micro-fluidic literature either neglect the permittivity of the wall material or treat it as very small. However, in practice, the permittivity ratio between the solid and fluid in MEMS can be significant. The most common MEMS consist of water flowing through glass or polydimethylsiloxane (PDMS), where the permittivity ratio is ~ 0.1 . In circumstances where the working fluid is an organic solvent such as *N,N*-dimethylformamide or acetonitrile, the permittivity ratio is ~ 0.2 .¹⁷ These types of solvents are used commonly as electrolytes in capillary electrophoresis.²²

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Studies that have examined the effect of finite wall permittivity in electrokinetic systems have primarily focussed on electro-osmotic flow. Electro-osmotic flow around a 90° nearly insulated wedge has been studied,^{27,33} demonstrating that field leakage into the wall results in the formation of vortices in the flow. The electro-osmotic flow of water through a glass nano-channel connected by two reservoirs was modelled by Postler *et al.*,²⁰ with permittivity ratio = 0.1, showing that a narrow region of low conductance (or ionic gate) forms at the entrance to the contraction. Other studies have used analytical techniques in the thin Debye-layer limit to investigate electro-osmotic flows over surfaces with finite permittivity for low potential,^{34,37} and moderate potential.³²

No studies have explored the effect of finite wall permittivity specifically on the practically relevant case of electroviscous flow in a non-uniform geometry. Hence, the aim of this study is to analyse numerically the effect of finite wall permittivity on electroviscous flow in a two-dimensional planar 1:4 contraction-expansion channel of finite wall thickness. This type of geometry is chosen to allow direct comparison to the results of Davidson and Harvie.⁷ Despite the simplicity of the geometry, the flow through a contraction-expansion channel is complex, characterised by shearing regions close to the wall and extensional regions along the centre-line. It is, therefore, representative of many types of common lab-on-a-chip circuit elements.¹⁹ This type of geometry is also representative of a membrane nanopore; useful for molecule, ion and DNA sorting.^{4,5,15,28,35,36}

II. PROBLEM STATEMENT

The flow of a 1:1 symmetric electrolyte solution through a slit-like contraction-expansion geometry is considered (Figure 1). The inlet and outlet channel half-width is defined as W , and the contraction channel half-width as $0.25W$, consistent with previous numerical studies.⁷ The mean velocity of the fluid at the inlet is $\bar{V}$, in effect imposing a net flow rate. The fluid is assumed to have constant viscosity μ , constant density ρ , and permittivity ϵ_f . The electrolyte contains cations (n_+) and anions (n_-) with equal diffusivities $D_+ = D_- = D$, and equal valencies $z_+ = -z_- = z$. The average ionic concentration entering the contraction is given by n_0 , representing the local geometric mean of both ion species.^{1,7,8} The walls of the channel are assumed to carry a uniform, constant surface-charge density σ , and the wall material is assumed to have constant permittivity ϵ_w . The width of the solid region of the channel is L_w .

The dimensionless equations governing the flow through the channel are given by the Poisson equation relating the electric potential U to the local charge density $n_+ - n_-$ in the fluid:⁷

FIG. 1. Schematic of contraction-flow geometry with inlet channel half-width W and contraction ratio $0.25W$. The electrolytic fluid flows in the non-shaded region Ω_f , and the shaded region Ω_w is the surrounding solid device, or wall region.

$$\nabla^2 U = -\frac{1}{2}K^2(n_+ - n_-) \quad \text{for } \mathbf{x} \in \Omega_f, \quad (1)$$

the Nernst-Planck equation ensuring conservation of each ion species

$$\frac{\partial n_{\pm}}{\partial t} + \nabla \cdot (\mathbf{u}n_{\pm}) = \frac{1}{ReSc} [\nabla^2 n_{\pm} \pm \nabla \cdot (n_{\pm} \nabla U)] \quad \text{for } \mathbf{x} \in \Omega_f, \quad (2)$$

and the Navier-Stokes equations with an electrical body-force term

$$\frac{\partial \mathbf{u}}{\partial t} + \nabla \cdot (\mathbf{u}\mathbf{u}) = -\nabla P + \frac{1}{Re} \nabla \cdot [\nabla \mathbf{u} + (\nabla \mathbf{u})^T] - \frac{BK^2}{Re^2} (n_+ - n_-) \nabla U \quad \text{for } \mathbf{x} \in \Omega_f, \quad (3)$$

$$\nabla \cdot \mathbf{u} = 0 \quad \text{for } \mathbf{x} \in \Omega_f, \quad (4)$$

where $\mathbf{u}$ is the fluid-velocity vector and P is the pressure. The electric potential in the solid region Ω_w is given by

$$\nabla^2 U = 0 \quad \text{for } \mathbf{x} \in \Omega_w. \quad (5)$$

Equations (1)–(5) have been non-dimensionalised using length scale W , velocity scale $\bar{V}$, ion number-density scale n_0 , electric-potential scale kT/ze , and permittivity scale ϵ_f . The dimensionless numbers present in Eqs. (1)–(4) are defined as

$$Re = \frac{\rho \bar{V} W}{\mu}, \quad (6)$$

$$Sc = \frac{\mu}{\rho D}, \quad (7)$$

$$B = \frac{\rho k^2 T^2 \epsilon_f \epsilon_0}{2z^2 e^2 \mu^2}, \quad (8)$$

$$K = \left[\frac{2z^2 e^2 n_0 W^2}{\epsilon_f \epsilon_0 kT} \right]^{\frac{1}{2}}, \quad (9)$$

where Re is the Reynolds number, Sc is the Schmidt number, K is the dimensionless inverse Debye length (proportional to the ratio of the channel half-width W to the EDL thickness), and B is a material parameter that is fixed for a given liquid at a constant temperature. The constants k , e , and ϵ_0 are the Boltzmann's constant, elementary charge and the permittivity of free space, respectively. The product $ReSc$ represents the Peclet number Pe , which measures the relative importance of ion advection to ion diffusion.

The boundary conditions for the electric potential at the liquid-solid interface are given by^{16,32,34,37}

$$\left. \frac{\partial U}{\partial n_w} \right|_f - \alpha \left. \frac{\partial U}{\partial n_w} \right|_w = \frac{1}{2} K^2 \bar{S}, \quad (10)$$

$$U|_f = U|_w, \quad (11)$$

where the subscripts f and w refer to the fluid and wall regions, respectively, and n_w is the coordinate normal to the channel wall pointing out from the flow (Figure 1). When subscripted with a letter, n represents the normal coordinate; at all other times it refers to ion concentration. The dimensionless number $\alpha = \epsilon_w/\epsilon_f$ is the ratio of the fluid permittivity to the wall permittivity, and $\bar{S}$ is the dimensionless surface-charge density, defined as

$$\bar{S} = \frac{\sigma}{ze n_0 W}. \quad (12)$$

This wall surface-charge density is scaled differently from previous studies to avoid referencing any permittivities, which vary in this study. The new dimensionless charge-density $\bar{S}$ is related to the dimensionless charge density S of Davidson and Harvie⁷ by

$$\bar{S} = \frac{2S}{K^2}. \quad (13)$$

Rescaling the surface-charge density in this fashion yields a dimensionless number identical to the Dukhin number, which measures the importance of bulk-flow conductance relative to the surface conductance. The Dukhin number has been used to describe concentration polarisation at microchannel-nanochannel interfaces.^{15,36}

In this study, the effect of stagnant-layer conduction, in which counter-ions are conducted through a hydrodynamically stagnant layer next to the wall, is neglected. Most numerical and analytical models neglect this effect, although experimental studies demonstrate that this effect can be important in some circumstances.^{12,23} Conduction of counter-ions in the stagnant layer acts to reduce the magnitude of the streaming potential gradient and, therefore, the electroviscous effect.

The boundary condition for the electric potential on the outer edge of the domain is given by

$$\frac{\partial U}{\partial n_e} = 0, \quad (14)$$

where n_e is the coordinate normal to the domain edge parallel to the flow (Figure 1). Equation (14) represents a solid-air interface with no surface-charge density.

The steady, fully developed electroviscous flow solution in a uniform channel is used for the inlet boundary condition. The inlet and outlet lengths are set to $10W$, long enough to ensure that the flow is fully developed before and after the contraction. A uniform staggered grid with 32 mesh cells per unit length W is used to solve the governing equations given by Eqs (1)–(4). Grid refinement calculations on a grid with 16 mesh cells per unit length W yielded differences in the predicted overall pressure drop of less than 3%, and less than 1% for the overall electric-potential drop. The numerical method of Davidson and Harvie⁷ was extended to include a wall-region Ω_w . The liquid-solid interface is co-incident with cell boundaries on the mesh. Equation (1) is solved over the liquid domain Ω_f and Equation (5) is solved over the solid region Ω_w , with the wall boundary condition described by Eq. (10) implemented implicitly. Equations (2)–(4) are solved only in the liquid region Ω_f . The transient simulation is integrated forward in time until the total dimensionless current passing through the inlet to the domain falls below 10^{-8} , consistent with steady electroviscous flow.

For direct comparison with the results of Davidson and Harvie,⁷ the Reynolds number is set to 0.01, the Schmidt number to 1000, and the B parameter to 2.34×10^{-4} . The dimensionless inverse Debye length for this study is fixed at $K=2$, giving overlapping double layers in the inlet and outlet, and in the contraction when the permittivity ratio $\alpha=0$.⁷ The range of permittivity ratios examined is $0.001 < \alpha < 0.5$. The lowest value of $\alpha=0.001$ was chosen, instead of $\alpha=0$, as the present numerical method requires a finite α in order to plot electric-field lines in the wall region Ω_w . Comparisons with the numerical model of Davidson and Harvie,⁷ which does not provide a solution within the wall region Ω_w , showed no discernible difference in the results of $\alpha=0$ and $\alpha=0.001$ within the fluid region Ω_f . The upper limit of $\alpha=0.5$ is chosen based on the permittivity ratios of common microfluidic systems. Typically, the permittivity of the component material ranges from 3 to 8, whereas common working electrolytes have permittivities of ~ 20 – 80 .¹⁶ Hence, the range of physically relevant permittivity ratios is $\lesssim 0.5$.

III. RESULTS

A. Observations

Contour plots of the dimensionless charge density $n_+ - n_-$ and electric potential U , with corresponding electric-field lines, are shown in Figure 2 for dimensionless inverse Debye length $K=2$, dimensionless charge-density $\bar{S}=1$, and three values of permittivity ratio α . For low values of permittivity ratio, the electric-field lines that begin at the front-step continue on through the contraction. As α increases, the field lines originating upstream of the contraction are able to pass through the front-step into the solid region. Also, the potential drop along the contraction decreases as the permittivity ratio α increases.

A significant build-up of counter-ions (negative ions for positive wall charge) occurs at the back-step, an effect that increases markedly as the permittivity ratio α increases. For the lowest value of permittivity ratio depicted, $\alpha=0.001$, there is also a slight build-up of counter-ions at the front-step. For larger values of α , however, this effect is reversed, and a build-up of co-ions (positive for positive wall charge) occurs at the front-step. The distribution of ions observed here bears some similarity to the concentration polarisation effect observed to occur in electro-osmotic flow through nanochannel junctions,^{4,5,15,28,36} with a separation of ion concentration between the entrance and the exit regions of the contraction. However, unlike the present circumstance, for electro-osmotic flow through a contraction with negative (positive) wall charge, there is a depletion of both ion species at the anodic (cathodic) end of the channel, and a corresponding enrichment of both ion species at the cathodic end of the channel.

FIG. 2. Contour plots of dimensionless charge density $n_+ - n_-$, electric potential U and electric-field lines E for dimensionless inverse Debye length $K=2$, dimensionless wall charge $\bar{S}=1$, and permittivity ratios of (a) $\alpha=0.001$, (b) $\alpha=0.1$, and (c) $\alpha=0.5$. The bottom of each channel depicts the charge density, and the top shows the electric potential contours and the corresponding electric-field lines (with arrows), defined as $E = -\nabla U$. The direction of flow is from left to right.

(anodic) end of the channel. Furthermore, it will be shown in Sec. III B that the form of concentration polarisation observed here is a direct consequence of the finite wall permittivity.

Figure 3 shows that the build-up of co-ions at the front-step with increased permittivity ratio α causes a region of low-charge magnitude to extend into and downstream of the entrance

FIG. 3. Dimensionless charge density $n_+ - n_-$ along the centreline of the channel for three different values of permittivity ratio α at dimensionless inverse Debye length $K=2$ and dimensionless wall charge (a) $\bar{S} = 0.5$, (b) $\bar{S} = 1$, and (c) $\bar{S} = 4$. The contraction section of the channel is located at $0 \leq x \leq 5$. The direction of flow is in the positive x direction.

of the contraction. As a consequence, the flow needs a longer distance to develop within the contraction when the permittivity ratio α is significant. To elucidate the effect of flow development on the formation of double layers within the contraction, the dimensionless charge density $n_+ - n_-$ across the middle of the contraction is shown in Figure 4 for various permittivity ratios and wall-charge densities. Also shown is the charge-density profile for fully developed flow in the contraction, calculated with an effective n_0 , and therefore K , to ensure ion conservation.^{1,8} At low wall-charge densities, $\bar{S}$, the magnitude of charge density in the contraction is very low in comparison to the fully developed flow profile, because the flow requires a longer distance to reach full development. This effect increases with increasing permittivity ratio α . This result is important considering that the dimensional Debye length within the inlet when $K=2$ is approximately $\frac{1}{2}W$. As the surface charge density is increased, this effect diminishes and the profile for all permittivity ratios approaches the fully developed profile.

Figure 5 shows the same contour plots and electric-field lines as Figure 2 for a fixed permittivity ratio $\alpha=0.1$, and varying dimensionless charge density $\bar{S}$. For low $\bar{S}$, the charge present in the fluid is low, and the field lines that originate near the front-step pass into the wall region. As $\bar{S}$ increases the charge within the fluid increases, along with the potential drop along the contraction. At high $\bar{S}$, the field lines that originate from the front-step pass into the contraction. It is also evident that the region of low charge-density magnitude that accumulates at the front-step diminishes as the surface-charge density increases.

B. Charge distribution

To understand how the charge distribution within the channel is affected by the permittivity ratio α and the dimensionless surface-charge density $\bar{S}$, reference can be made to the boundary condition placed on the normal potential gradient at the fluid-solid interface. The normal potential gradient in the fluid next to the wall can be written as (Eq. (10))

$$\left. \frac{\partial U}{\partial n_w} \right|_f = \frac{1}{2} K^2 \bar{S} + \alpha \left. \frac{\partial U}{\partial n_w} \right|_w = \frac{1}{2} K^2 \bar{S}_{\text{eff}}, \quad (15)$$

where $\bar{S}_{\text{eff}}$ is the effective surface-charge density (or effective Dukhin number) defined as

$$\bar{S}_{\text{eff}} = \bar{S} + \frac{2}{K^2} \alpha \left. \frac{\partial U}{\partial n_w} \right|_w. \quad (16)$$

Equation (15) is plotted in Figure 6 at dimensionless surface-charge density $\bar{S}=4$ and three permittivity ratios α for a line segment perpendicular to the middle of the front-step, passing from the fluid into the solid. In the fluid region, $x < 0$, the potential gradient normal and into the wall $\left. \frac{\partial U}{\partial n_w} \right|_f$ is plotted. In the solid region, $x > 0$, the quantity $\frac{1}{2} K^2 \bar{S} + \alpha \left. \frac{\partial U}{\partial n_w} \right|_w$ is plotted. At the wall, $x=0$, these quantities are equal. Also, shown is the streaming potential gradient for fully developed flow in the inlet, and the quantity $\frac{1}{2} K^2 \bar{S} + \alpha \left. \frac{\partial U}{\partial n_w} \right|_w$ for each permittivity ratio α , evaluated based on the streaming potential gradient for fully developed flow in the contraction.^{1,8} Contours of dimensionless potential at the entrance and exit to the contraction are also shown in Figure 6, along with the electric-field lines.

Far upstream of the front-step, the potential gradient in the fluid normal to the front-step is equal to the fully developed streaming potential gradient for all values of permittivity ratio α . Similarly, far downstream of the front-step in the contraction, the quantity $\frac{1}{2} K^2 \bar{S} + \alpha \left. \frac{\partial U}{\partial n_w} \right|_w$ for each permittivity ratio approaches the value given by fully developed flow in the contraction. For positive (negative) surface wall-charge density $\bar{S}$, the fully developed streaming potential gradient is negative (positive). This means that the two terms of the quantity $\frac{1}{2} K^2 \bar{S} + \alpha \left. \frac{\partial U}{\partial n_w} \right|_w$ are of opposite sign. Further to this, the second term is directly proportional to α . For negligible α , the quantity $\frac{1}{2} K^2 \bar{S} + \alpha \left. \frac{\partial U}{\partial n_w} \right|_w$ reduces to $\frac{1}{2} K^2 \bar{S}$. As the permittivity ratio increases, this quantity for fully developed flow in the contraction decreases (increases) from $\frac{1}{2} K^2 \bar{S}$ and, at a particular value of α , this quantity is able to change sign to match the direction of the streaming potential gradient.

FIG. 4. Transverse profiles of dimensionless charge density $n_+ - n_-$ halfway along the contraction, $x = 2.5$, for three different values of permittivity ratio α at dimensionless inverse Debye length $K = 2$ and dimensionless wall charge (a) $\bar{S} = 0.5$, (b) $\bar{S} = 1$, and (c) $\bar{S} = 4$. The dotted-dashed line indicates the charge-density profile for fully developed flow in the contraction, with an effective n_0 , and therefore K , chosen to ensure ion conservation.^{1,8}

FIG. 5. Contour plots of dimensionless charge density $n_+ - n_-$, electric potential U , and electric-field lines E for dimensionless inverse Debye length $K = 2$, permittivity ratio $\alpha = 0.1$, and dimensionless wall charges of (a) $\bar{S} = 0.5$, (b) $\bar{S} = 1$, and (c) $\bar{S} = 4$. The bottom of each channel depicts the charge density, and the top shows the electric potential contours and the corresponding electric-field lines (with arrows), defined as $E = -\nabla U$. The direction of flow is from left to right. Note that the contour range is different from that shown in Figure 2.

The implications of the effective surface-charge density on the charge distribution in the vicinity of the front-step can now be drawn: when α is negligible the effective surface-charge density at the wall $\bar{S}_{\text{eff}} = \bar{S}$. The effective surface-charge density constrains the potential gradient in the fluid to be in the opposite direction to the streaming potential gradient, inducing a build-up of counter-ions (negative for positive wall charge) at the front-step. However, when α becomes significant, the effective surface-charge density $\bar{S}_{\text{eff}}$ is of opposite sign to the actual surface-charge density, meaning that the potential gradient in the fluid is in the same direction to the streaming potential gradient, and a build-up of co-ions (positive for positive wall charge) occurs at the front-step. From Eq. (16), it is evident that the permittivity ratio α at which the effective charge density $\bar{S}_{\text{eff}}$ changes sign to match the direction of the streaming potential gradient increases with increasing surface-charge density $\bar{S}$.

Figure 7 plots Eq. (15) for the same values of $\bar{S}$ and α for a line segment perpendicular to the middle of the back-step, passing from the solid into the fluid. In the solid region, $x < 5$, the quantity $\frac{1}{2}K^2\bar{S} + \alpha\frac{\partial U}{\partial n_w}$ is plotted. In the fluid region, $x > 5$, the potential gradient normal and into the wall $\frac{\partial U}{\partial n_w}$ is plotted. Again, the streaming potential gradient for fully developed flow in the outlet is shown, along with the quantity $\frac{1}{2}K^2\bar{S} + \alpha\frac{\partial U}{\partial n_w}$ for each permittivity ratio α , evaluated based on the streaming potential gradient for fully developed flow in the contraction.^{1,8}

FIG. 6. (a) Equation (15) over a line segment perpendicular to the middle of the front-step for dimensionless inverse Debye length $K = 2$, dimensionless surface-charge density $\bar{S} = 4$, and three permittivity ratios $\alpha = 0.001$ (squares), $\alpha = 0.1$ (circles), and $\alpha = 0.5$ (triangles). In the fluid region, $x < 0$, the potential gradient normal and into the wall $\frac{\partial U}{\partial n_w}$ is plotted (closed symbols). In the solid region, $x > 0$, the quantity $\frac{1}{2}K^2\bar{S} + \alpha\frac{\partial U}{\partial n_w}$ is plotted (open symbols). The dotted line represents the streaming potential gradient for fully developed flow in the inlet $\frac{\partial U}{\partial n_w}|_{FD}^{inlet}$. The dashed lines represent the quantity $\frac{1}{2}K^2\bar{S} + \alpha\frac{\partial U}{\partial n_w}|_{FD}^{cont.}$ for each permittivity ratio α , evaluated based on the streaming potential gradient for fully developed flow in the contraction $\frac{\partial U}{\partial n_w}|_{FD}^{cont.}$. Contours of dimensionless potential at the entrance to the contraction are also shown for permittivity ratios (b) $\alpha = 0.001$, and (c) $\alpha = 0.5$, along with the electric-field lines. The dashed line represents the line segment plotted in (a).

For a sufficiently long contraction length to ensure fully developed flow, the quantity $\frac{1}{2}K^2\bar{S} + \alpha\frac{\partial U}{\partial n_w}$ upstream of the back-step for each permittivity ratio is given by the value for fully developed flow in the contraction. Far downstream of the back-step, the potential gradient in the fluid normal to the back-step approaches the fully developed streaming potential gradient for fully developed flow in the outlet. In contrast to the front-step of the contraction, the two terms of the quantity $\frac{1}{2}K^2\bar{S} + \alpha\frac{\partial U}{\partial n_w}$ are of the same sign for the back-step, because n_w is now orientated in the opposite direction. When the permittivity ratio is negligible, $\bar{S}_{eff} = \bar{S}$, and a moderate build-up of counter-ions occurs at the back-step. As α increases, the quantity $\frac{1}{2}K^2\bar{S} + \alpha\frac{\partial U}{\partial n_w}$ for fully developed flow in the contraction increases linearly. Therefore, the effective surface-charge density $\bar{S}_{eff}$ also increases in magnitude, causing the magnitude of the normal potential gradient in the fluid to rise, and, therefore, inducing a larger concentration of counter-ions in the vicinity of the back-step.

FIG. 7. (a) Equation (15) over a line segment perpendicular to the middle of the back-step for dimensionless inverse Debye length $K = 2$, dimensionless surface-charge density $\bar{S} = 4$ and three permittivity ratios $\alpha = 0.001$ (squares), $\alpha = 0.1$ (circles), and $\alpha = 0.5$ (triangles). In the solid region, $x < 5$, the quantity $\frac{1}{2}K^2\bar{S} + \alpha \frac{\partial U}{\partial n_w}|_{FD}^{cont.}$ is plotted (open symbols). In the fluid region, $x > 5$, the potential gradient normal and into the wall $\frac{\partial U}{\partial n_w}$ is plotted (closed symbols). The dotted line represents the streaming potential gradient for fully developed flow in the outlet $\frac{\partial U}{\partial n_w}|_{outlet}^{outlet}$. The dashed lines represent the quantity $\frac{1}{2}K^2\bar{S} + \alpha \frac{\partial U}{\partial n_w}|_{FD}^{cont.}$ for each permittivity ratio α , evaluated based on the streaming potential gradient for fully developed flow in the contraction $\frac{\partial U}{\partial n_w}|_{FD}^{cont.}$. Contours of dimensionless potential at the exit to the contraction are also shown for permittivity ratios (b) $\alpha = 0.001$, and (c) $\alpha = 0.5$, along with the electric-field lines. The dashed line represents the line segment plotted in (a).

C. Flow resistance

The previous analysis demonstrates that a finite wall permittivity leads to a build-up of cations (positive for positive wall charge) in and around the entrance to the contraction. The presence of these ions impedes the development of the flow and reduces the net charge within the contraction. The pressure drop and potential drop along the contraction consequently depend upon the permittivity ratio α . The axial potential gradient, or axial electric field, along the centre of the channel is depicted in Figure 8 for three values of dimensionless wall charge $\bar{S}$, and three values of permittivity ratio α , at dimensionless inverse Debye length $K = 2$. The dotted line with the lower magnitude of axial electric field indicates the fully developed value for both the inlet and outlet. The dotted line with the higher magnitude of axial electric field corresponds to the fully developed value in the contraction. For all values of $\bar{S}$ and α shown, the magnitude of the axial electric field E_x increases from its fully developed state in the inlet as

FIG. 8. Axial electric field E_x along the centreline of the channel for three different values of permittivity ratio α at dimensionless inverse Debye length $K=2$ and dimensionless wall charge (a) $\bar{S} = 0.5$, (b) $\bar{S} = 1$, and (c) $\bar{S} = 4$. The axial electric field is defined as $E_x = -\partial U / \partial x$. The contraction section of the channel is located at $0 \leq x \leq 5$. The direction of flow is in the positive x direction.

the flow moves into the contraction. Through the contraction, the magnitude of axial electric field E_x continues to increase towards the fully developed state in the contraction. As the flow passes out of the contraction into the outlet, E_x decreases to the fully developed state in the outlet.

At the lowest value of dimensionless wall charge shown, $\bar{S} = 0.5$, the contraction is not long enough for the flow to become fully developed for any of the permittivity ratios α depicted. It is also apparent that as α increases the flow takes longer to develop within the contraction, and the maximum value of the axial electric field E_x reached decreases markedly. This means that the potential drop along the contraction is much less for higher values of permittivity ratio α , indicating that the contraction offers less electroviscous resistance to the flow when the electric-field lines penetrate into the wall. At a dimensionless wall charge of $\bar{S} = 1$, the same qualitative behaviour can be observed. However, it is evident that for all values of α , the flow develops more rapidly than for the lower dimensionless wall-charge $\bar{S} = 0.5$. For the lowest value of permittivity ratio shown, $\alpha = 0.001$, the axial electric field E_x is very close to the fully developed value at the end of the contraction. If the wall charge $\bar{S}$ is increased further, to $\bar{S} = 4$, the flow becomes fully developed in the contraction for all values of α shown. It is, therefore, apparent that the development length of the flow increases with increasing α and decreasing $\bar{S}$, consistent with the observed build-up of co-ions (positive for positive wall charge) in and around the contraction entrance. As a consequence, the electroviscous resistance of the contraction decreases with increasing α and decreasing $\bar{S}$.

To quantify the effect of permittivity ratio α on the electroviscous resistance of the contraction, equivalent lengths can be calculated. Two equivalent lengths are considered here: one in terms of a pressure drop along the contraction, and one in terms of a potential drop along the contraction. In this context, an equivalent length is defined as the length of uniform channel W needed to match the potential, or pressure drop, caused by the contraction. These lengths are, therefore, measures of the resistance to the flow caused by the contraction and are analogous to the equivalent length used to describe viscous losses in pipe systems.²⁹ Formally, these lengths $L_{eq,A}$ are defined as

$$L_{eq,A} = \frac{\Delta A_c - L \left. \frac{dA}{dx} \right|_{FD}}{\left. \frac{dA}{dx} \right|_{FD}}, \quad (17)$$

where A can represent either the electric potential or the pressure, ΔA_c is the drop in quantity A over the length L of the channel (including the contraction), and $\left. \frac{dA}{dx} \right|_{FD}$ is the gradient of A in fully developed flow.^{1,8} Equation (17) is valid only if the length L over which ΔA_c is measured starts at a point in the inlet where the flow is fully developed and ends in fully developed flow in the outlet. If these criteria are met then $L_{eq,A}$ is independent of L .

The equivalent length of the flow based on both the pressure and the electric potential is depicted in Figure 9 as a function of dimensionless wall charge $\bar{S}$. At large values of $\bar{S}$, the potential equivalent length varies only minimally with permittivity ratio. Below $\bar{S} = 5$ however, it is evident that contractions with large values of α offer significantly less electro-potential resistance. The same type of behaviour can be observed with the hydrodynamic equivalent length. Interestingly, for all values of α shown, the resistance caused by the contraction in electrokinetic flow is less than that caused by purely hydrodynamic flow. This phenomenon has been shown to occur in electroviscous flow with negligible wall permittivity, attributable to a favourable local potential gradient parallel to the front-step.⁷ However, it is clear that the flow resistance decreases with increasing permittivity ratio α here, despite the fact that the local potential gradient parallel to the front-step decreases (Figure 6).

D. Effect of wall thickness

As the permittivity ratio α becomes significant, the width of the wall region L_w (Figure 1) affects the flow through the contraction. Contour plots of the dimensionless charge density $n_+ - n_-$ and electric potential U for three different values of wall-region width L_w are depicted in

FIG. 9. Equivalent length of the contraction for dimensionless inverse Debye length $K = 2$ and three different permittivity ratios, based on (a) electric potential drop, and (b) hydrodynamic pressure drop. The equivalent length for the hydrodynamic pressure drop has been normalised by the equivalent length of purely hydrodynamic flow through the contraction. For $Re = 0.01$, the hydrodynamic equivalent length given by the numerical model is $L_{visc} = 334$. The data points represent the results of simulations, with dashed lines included to guide the eye.

Figure 10. The potential drop along the contraction decreases with increasing wall-width. A region of low charge magnitude extends further into the contraction as the wall width L_w increases. To explain the observations, reference can be made to the boundary condition placed on the potential gradient normal to the edge of the microfluidic component (Eq. (14)). If the wall-region width L_w is small, the constraint imposed upon the gradient of potential normal to edge of the component will limit the size of the potential gradient in the solid normal to the liquid-solid interface. Consequently, through Eq. (16), the effective surface-charge density $\bar{S}_{eff}$ approaches $\bar{S}$ as the wall thickness decreases. Thus, decreasing the thickness of the wall region is qualitatively similar to decreasing the permittivity ratio α .

To quantify the effect of wall width, the normalised electroviscous equivalent length as a function of wall width L_w is plotted in Figure 11 for two permittivity ratios α . The equivalent length has been normalised by the equivalent length of a contraction with permittivity ratio $\alpha = 0$. For the highest value of dimensionless wall charge $\bar{S} = 4$, no discernible difference can be observed, and the normalised equivalent length varies very little with wall-region width L_w . However, at lower values of $\bar{S}$, the normalised equivalent length of the contraction decreases as the solid region becomes wider. It is also apparent that as the permittivity ratio α increases, the normalised equivalent length decreases, consistent with an effective surface-charge density

FIG. 10. Contour plots of dimensionless charge density $n_+ - n_-$, electric potential U , and electric-field lines $\mathbf{E}$ for dimensionless inverse Debye length $K=2$, dimensionless wall charge $\bar{S}=1$, permittivity ratio $\alpha=0.3$, and wall thicknesses (a) $L_w=0.5$ (b) $L_w=1$, and (c) $L_w=2$. The bottom of each channel depicts the charge density, and the top shows the electric potential contours and the corresponding electric-field lines (with arrows), defined as $\mathbf{E} = -\nabla U$. The direction of flow is from left to right.

$\bar{S}_{\text{eff}} \sim \bar{S}$. This effect becomes less and less noticeable with increasing L_w , suggesting that the flow will become independent of the wall width for $L_w/W \approx 10$.

IV. CONCLUSIONS

Numerical simulations have been carried out to elucidate the effects of finite wall permittivity on electroviscous flow through a slit-like 1:4 contraction-expansion geometry with electric double-layer overlap. The results of the simulations have demonstrated that a finite wall permittivity has a significant effect on the characteristics of electroviscous flow through a contraction.

The effect of finite wall permittivity on the charge distribution can be explained with an *effective* surface-charge density (or local effective Dukhin number). For negligible wall permittivity, the effective surface-density is equal to the actual surface-charge density, leading to a build-up of counter-ions (negative for positive wall charge) at the solid-liquid interface. However, as the wall permittivity becomes significant in comparison with the fluid permittivity, the coupling between the potential gradient normal to the wall in the fluid and the solid becomes important. This has the effect of reducing the effective surface-charge density at the front-step, allowing it to change sign and, therefore, inducing a build-up of co-ions (positive for positive wall charge) in the vicinity. In contrast, the effective surface-charge density at the back-step

FIG. 11. Equivalent length of the contraction based on electric potential drop for dimensionless inverse Debye length $K = 2$ and three different dimensionless wall charges $\bar{S}$, for permittivity ratios (a) $\alpha = 0.1$, and (b) $\alpha = 0.3$. The equivalent length has been normalised by the equivalent length of a contraction with permittivity ratio $\alpha = 0$, denoted by $L_{eq,U}^{(\alpha=0)}$. The data points represent the results of simulations, with dashed lines included to guide the eye.

increases, leading to a higher concentration of counter-ions at the back-step when the wall permittivity is significant. As a consequence, the magnitude of charge at the front-step and in the contraction is very low, and the magnitude of charge at the back-step is very high, for significant wall permittivity. We speculate that the ion distribution shown to occur in and around the contraction may be of use as a microfluidic capacitor, or in an application requiring molecules or ions to be separated based on charge.

It has also been shown that, for a fixed contraction length, both the hydrodynamic and potential resistances along the contraction decrease as the permittivity ratio increases. This effect is most evident at low values of dimensionless wall charge. The decrease in potential drop and pressure drop along the contraction with increasing permittivity ratio is due to the increase in development length of the flow. Increasing the width of the solid part of the channel also increases the development length of the flow. This effect is most pronounced at low values of dimensionless surface charge and high values of permittivity ratio. The effect of decreasing the wall-width is qualitatively similar to decreasing the permittivity of the wall material. Thus, with a finite wall permittivity, it is possible to a certain extent to “control” the development length of electroviscous flow, and therefore the resistance caused by the contraction, by adjusting the size of the solid part of the channel. It is likely that the flow will become independent of the wall-region width at widths greater than ~ 10 channel half-widths.

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- ¹C. J. C. Biscombe, M. R. Davidson, and D. J. E. Harvie, *J. Colloid Interface Sci.* (in press).
- ²W. R. Bowen and F. Jenner, *J. Colloid Interface Sci.* **173**(2), 388 (1995).
- ³D. Brutin and L. Tadrist, *Nanoscale Microscale Thermophys. Eng.* **9**(1), 33 (2005).
- ⁴H.-C. Chang and L. Yeo, *Electrokinetically Driven Microfluidics and Nanofluidics* (Cambridge University Press, New York, 2010).
- ⁵H.-C. Chang and G. Yossifon, *Biomicrofluidics*, **3**(1), 12001 (2009).
- ⁶M. Chun and H. W. Kwak, *Korea-Aust. Rheol. J.*, **15**(2), 83 (2003).
- ⁷M. Davidson and D. Harvie, *Chem. Eng. Sci.* **62**(16), 4229 (2007).
- ⁸D. J. E. Harvie, C. J. C. Biscombe, and M. R. Davidson, *J. Colloid Interface Sci.* (in press).
- ⁹C. Ho and Y. Tai, *Ann. Rev. Fluid Mech.* **30**, 579 (1998).
- ¹⁰J.-P. Hsu, C.-Y. Kao, S. Tseng, and C.-J. Chen, *J. Colloid Interface Sci.* **248**(1), 176 (2002).
- ¹¹D. Li, *Colloids Surf., A* **195**(1-3), 35 (2001).
- ¹²J. Lyklema, *J. Phys.: Condens. Matter* **13**, 5027 (2001).
- ¹³G. M. Mala, D. Li, and J. D. Dale, *Int. J. Heat Mass Transfer* **40**(13), 3079 (1997).
- ¹⁴G. M. Mala, D. Li, C. Werner, and H. Jacobasch, *Int. J. Heat Fluid Flow*, **18**(5), 489, (1997).
- ¹⁵A. Mani, T. A. Zangle, and J. G. Santiago, *Langmuir*, **25**(6), 3898 (2009).
- ¹⁶J. H. Masliyah and S. Bhattacharjee, *Electrokinetic and Colloid Transport Phenomena* (Wiley-Interscience, Hoboken, New Jersey, 2006).
- ¹⁷J. Muzikar, T. van De Goor, B. Gas, and E. Kenndler, *Electrophoresis*, **23**(3), 375, (2002).
- ¹⁸Here, the electroviscous effect refers to the flow resistance caused by the streaming potential gradient. This term is also used the literature to describe the unrelated phenomenon of an increase in suspension viscosity due to electrokinetic effects (Ref. 24).
- ¹⁹M. S. N. Oliveira, L. E. Rodd, G. H. McKinley, and M. A. Alves, *Microfluid. Nanofluid.* **5**(6), 809 (2008).
- ²⁰T. Postler, Z. Slouka, M. Svoboda, M. Pribyl, and D. Snita, *J. Colloid Interface Sci.* **320**(1), 321 (2008).
- ²¹L. Ren, D. Li, and W. Qu, *J. Colloid Interface Sci.* **233**(1), 12 (2001).
- ²²K. Sarmini and E. Kenndler, *J. Chromatogr. A* **792**, 3 (1997).
- ²³R. Schoch, J. Han, and P. Renaud, *Rev. Mod. Phys.* **80**(3), 839 (2008).
- ²⁴J. D. Sherwood, *J. Fluid Mech.* **101**, 609 (1980).
- ²⁵H. A. Stone and S. Kim, *AIChE J.* **47**(6), 1250 (2001).
- ²⁶H. A. Stone, A. D. Stroock, and A. Ajdari, *Ann. Rev. Fluid Mech.* **36**(1), 381 (2004).
- ²⁷S. K. Thamida and H.-C. Chang, *Phys. Fluids* **14**(12), 4315 (2002).
- ²⁸S.-C. Wang, H.-H. Wei, H.-P. Chen, M.-H. Tsai, C.-C. Yu, and H.-C. Chang, *Biomicrofluidics*, **2**(1), 14102 (2008).
- ²⁹F. M. White, *Fluid Mechanics* (McGraw-Hill, Singapore, 1999).
- ³⁰C. Yang and D. Li, *J. Colloid Interface Sci.* **194**(1), 95 (1997).
- ³¹C. Yang, D. Li, and J. H. Masliyah, *Int. J. Heat Mass Transfer* **41**(24), 4229 (1998).
- ³²E. Yariv and A. M. J. Davis, *Phys. Fluids* **22**(5), 052006 (2010).
- ³³G. Yossifon, I. Frankel, and T. Miloh, *Phys. Fluids* **18**(11), 117108 (2006).
- ³⁴G. Yossifon, I. Frankel, and T. Miloh, *J. Fluid Mech.* **620**, 241 (2009).
- ³⁵G. Yossifon, Y.-C. Chang, and H.-C. Chang, *Phys. Rev. Lett.* **103**, 154502 (2009).
- ³⁶T. A. Zangle, A. Mani, and J. G. Santiago, *Langmuir* **25**(6), 3909 (2009).
- ³⁷C. Zhao and C. Yang, *Phys. Rev. E* **80**, 046312 (2009).