Direction dependence of displacement time for two-fluid electroosmotic flow

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Electroosmotic flow that involves one fluid displacing another fluid is commonly encountered in various microfluidic applications and experiments, for example, current monitoring technique to determine zeta potential of microchannel. There is experimentally observed anomaly in such flow, namely, the displacement time is flow direction dependent, i.e., it depends if it is a high concentration fluid displacing a low concentration fluid, or vice versa. Thus, this investigation focuses on the displacement flow of two fluids with various concentration differences. The displacement time was determined experimentally with current monitoring method. It is concluded that the time required for a high concentration solution to displace a low concentration solution is smaller than the time required for a low concentration solution to displace a high concentration solution. The percentage displacement time difference increases with increasing concentration difference and independent of the length or width of the channel and the voltage applied. Hitherto, no theoretical analysis or numerical simulation has been conducted to explain this phenomenon. A numerical model based on finite element method was developed to explain the experimental observations. Simulations showed that the velocity profile and ion distribution deviate significantly from a single fluid electroosmotic flow. The distortion of ion distribution near the electrical double layer is responsible for the displacement time difference for the two different flow directions. The trends obtained from simulations agree with the experimental findings. © 2012 American Institute of Physics. [doi:[10.1063/1.3665721](https://doi.org/10.1063/1.3665721)]

I. INTRODUCTION

In recent years, lab-on-a-chip devices have found numerous applications in chemical analysis and biomedical diagnosis. Lab-on-a-chip is basically the technology that integrates microfluidic, mechanical, electromagnetic, and/or optical system on a microscale chip to perform various tasks. Compared with conventional laboratory test, lab-on-a-chip provides several advantages, including extremely low consumption of reagents and production of chemical waste, a more rapid analysis and a significant improvement in performance.

Transportation of fluids, such as a test sample or reagent, is often a key element in a lab-on-a-chip device. One of the methods to deliver fluid in microchannel is by electroosmotic flow. Electroosmotic flow is caused by an electrokinetic phenomenon, whereby flow of fluids is induced by an applied electric field. In a practical microfluidic system, electroosmotic flows with two or more types of fluids are frequently encountered. Displacement flow refers to the process of one fluid flowing and displacing another fluid in a channel. Displacement time is the time required for a fluid to fully displace another fluid which resides in the microchannel initially. Gan *et al.*¹ reported that the displacement time for the displacement flow of two aqueous solutions of different concentrations is direction dependent. In other words, the time required for a low concentration solution to displace a high concentration is not the same as the time required for a high concentration solution to displace a low concentration solution. Hitherto, no theoretical or numerical studies have been conducted to explain this phenomenon.

This paper presents an in-depth investigation on the displacement time difference in two fluids electroosmotic displacement flow in glass and polydimethylsiloxane (PDMS) microchannels. A numerical model for two fluids displacement electroosmotic flow is introduced to describe and explain the direction dependence of the displacement time.

II. THEORY AND LITERATURE REVIEW

A. Electrokinetic phenomenon

When certain solid is placed in contact with a liquid, surface charge is developed at the interface. There are a few mechanisms of charge development at the interface; some examples are difference in the affinity of the two phases for electrons or ions, ionization of surface groups, and physical entrapment of non-mobile charges in one phase.² These charge development processes lead to the buildup of an electric charge at the solid surface, which creates an electrostatic field that affects the ions distribution in the liquid phase. The separation of charges that occurs at the interface between the solid and fluid phases forms an electrical double layer (EDL).

The EDL can generally be divided into two major regions. The region where immobile counter-ions (ions of opposite charges to the surface) are strongly attached to the solid surface is called the Stern layer. The region next to it with mobile and diffuse ions is called the diffuse layer. The diffuse layer has a non-zero net charge because of the high concentration of counter-ions as compared with co-ions (ions with the similar charges to the surface). It can move under an applied electrical field and drag the bulk of the fluid to flow through viscous force, thus inducing electroosmotic flow. A slipping or shear plane is conceptually introduced to separate the mobile fluid from fluid that remains attached to the surface. Electrostatic potential at this plane is called the zeta potential or ζ -potential.

B. Two-fluid displacement flow

Two-fluid displacement flow is commonly encountered in various microfluidic systems and experiments. Current monitoring technique is a popular method to measure zeta potential in a displacement flow involving two solutions with a small difference in concentration, typically 5%.³ When a solution is displacing another solution with lower or higher concentration, the resistance in the microchannel changes and, thus, inducing observable electrical current changes. When the solution has fully displaced another solution, the current reaches a steady value because the resistance in the microchannel is now constant. By monitoring the current changes in real time, the time for the current to reach a steady value (i.e., the displacement time) can be determined. The zeta potential can then be calculated through the displacement time with the Smoluchowski slip velocity equation. The idea of utilizing displacement flow of solutions with small (5 to 7.5%) concentration difference has been adapted and improved by other researchers^{4–6} to measure the zeta potential of a channel wall.

Displacement flow with a larger concentration difference has been reported. Mampallil *et al.*⁷ demonstrated that the surface charge of glass/PDMS channel wall can also be obtained with two-fluid displacement flow, with the ratio of concentration between the two solutions ranged from 2:1 to 10:1. The surface charge was assumed to be constant regardless of the concentration of the solutions. All displacement flows measured were uni-directional with high concentration solution displacing low concentration solution. Recently, Tang *et al.*⁸ performed a theoretical investigation on electroosmotic displacement flow involving two or more fluids. Asymptotic cases where a fluid is displaced by a very high or a very low conductivity solution have been considered. Hitherto, for the displacement flow involving solutions with large concentration difference, there are no systematic investigations on the difference in displacement time between the two different displacement directions.

C. Electroosmotic flow model

Conventional modeling techniques for electroosmotic flow can be categorized into three major groups, namely, slip-velocity model, Poisson-Boltzmann (PB) model, and Poisson-Nernst-Planck (PNP) model. Slip velocity model is the simplest model, whereby the velocity variation in the thin EDL is neglected. The velocity at the wall of the microchannel is approximated by the Smoluchowski slip velocity, v_{slip}

$$v_{slip} = -\frac{\varepsilon\zeta E}{\mu}, \quad (1)$$

where ε is the permittivity, ζ is the zeta potential, and μ is the viscosity of the fluid. The model has been adopted by various researchers⁹ due to its simplicity in computation.

More sophisticated models that take into account the change of variables in the EDL are the PB model and the Nernst-Planck (NP) model. PB model assumes that the positive and negative ion distributions at the vicinity of the wall are given by Boltzmann distribution

$$c_{\pm} = c \exp\left(\mp \frac{e\psi}{k_b T}\right), \quad (2)$$

where $c_{\pm}$ is the concentration of positive or negative ion, c_0 is the bulk concentration of solution, e is the elementary charge, ψ is the static electric potential, k_b is the Boltzmann constant, and T is the temperature. After obtaining the ion distribution, Navier-Stokes (NS) equation can then be solved separately to obtain the velocity field.^{10–12}

In contrast, PNP model describes the ion distribution in the liquid according to the Nernst-Planck equations for positive and negative ion species

$$\frac{\partial c_{\pm}}{\partial t} + \nabla \cdot [-D_{\pm} \nabla c_{\pm} - z_{\pm} u_{m\pm} F c_{\pm} \nabla(\phi + \psi)] = -\mathbf{u} \cdot \nabla c_{\pm}, \quad (3)$$

where $D_{\pm}$ is the diffusion coefficient of positive or negative ion, $z_{\pm}$ is the ion charge number of positive or negative ion, $u_{m\pm}$ is the mobility of positive or negative ion, F is the Faraday constant, ϕ is the applied electric potential, and $\mathbf{u}$ is the fluid velocity. The Nernst-Planck equation has to be solved simultaneously with the NS and Poisson equations to obtain the flow field because the electric potential, positive/negative ion concentration, and flow velocity are strongly coupled together.

For the slip velocity model, the boundary condition at the wall is set to a slip velocity, which is proportional to a prescribed zeta potential value. It does not rely upon nor provides any information on ions distributions, including those next to the wall. Thus, for a situation where the ions (and charges) distributions next to the wall are changing, it could not be expected to provide accurate predictions. Flows with zeta potential which varies along the channel can be modelled with a modified slip velocity model.¹³ However, the derivation of the slip velocity expression requires the Debye-Hückel approximation, which is only valid for small surface potential and it assumes that there are no external perturbations such as diffusion or convection effect on the ion distribution in the electrical double layer. It is also not accurate for very small diameter channel where there is overlapping of EDL.

PB and PNP models define the boundary of the model at the shear plane of the EDL, which is the plane at which the fluid particles start moving. Therefore, a non-slip condition for velocity is set at the wall boundary. The boundary conditions at the channel wall for potentials distribution and ion concentration are normally specified in terms of the zeta potential of the solution.^{14–16} During the displacement flow of two solutions, diffusion occurs at the interface of these two solutions and therefore the zeta potential (which is related to the concentration of

the solution) in this interface region cannot be defined explicitly. Internal pressure gradient generated¹⁷ at the interface also affects the flow field and the ion distribution near the wall, thus further complicating the specification of boundary conditions as required by PB and PNP models.

Alternatively, instead of specifying the boundary condition at the wall, the boundary condition along the line of symmetry (at the bulk of the fluid) can be specified in terms of the bulk concentration of the solution which reflects the characteristics at the channel wall.^{18,19} However, the boundary condition at the bulk cannot be clearly defined to characterize the conditions at the wall around the vicinity of the interface for the two flowing solutions: there are two characteristic concentrations to start with and the conditions are not at steady state due to diffusion and convection induced by internal pressure gradient at the interface.

Therefore, modelling any flow phenomena which involve perturbation of the ion distribution in EDL that would lead to changes in zeta potential is a challenging task. This perturbation can be expected for flows involving dissimilar fluids and flows in nanochannels.

III. METHODS AND MATERIALS

A. Materials and equipment

In this study, 1 mM KCl solutions were prepared by dissolving KCl salt (Merck) in deionized water. KCl solution of 0.2 mM, 0.5 mM, 0.7 mM, and 0.95 mM were prepared by diluting the 1 mM KCl solutions accordingly. The properties of all solutions were measured with a conductivity meter (IONCheck 65, Radiometer Analytical) and pH meter (AccumetAR20, Fisher Scientific). The measured conductivities for 0.2 mM, 0.5 mM, 0.7 mM, 0.95 mM, and 1 mM KCl solutions were 31.8 $\mu\text{S}/\text{cm}$, 74.3 $\mu\text{S}/\text{cm}$, 104.3 $\mu\text{S}/\text{cm}$, 137.6 $\mu\text{S}/\text{cm}$, and 147.0 $\mu\text{S}/\text{cm}$, respectively. Measured average pH for all solutions was 5.5.

The microchannel employed was polyimide coated fused silica micro-capillary (Polymicro Technologies) with a nominal diameter of either 20 μm , 75 μm , 100 μm , or 150 μm . Micro-capillaries with length of 6 cm, 8 cm, and 10 cm were measured and cut with Shortix Column Cutter (SGT Ltd). Two Teflon reservoirs were fabricated with diameter and depth of 2 cm. The micro-capillary was connected between the two reservoirs. The diameters of the reservoirs were sufficiently large to avoid noticeable liquid level changes during the course of the experiment. This ensures that the back pressure arising from the difference of liquid level in the reservoirs is negligible.²⁰

Besides the glass micro-capillaries, rectangular (PDMS microchannels were also employed as a comparison with the glass micro-capillaries. Each of the PDMS microchannels is 5.5 cm long, and the width and depth of the microchannel are 100 μm and 45 μm , respectively. The PDMS microchannels were fabricated through soft lithography technique with a negative photoresist SU-8 master, which has the protruding microchannel pattern with the required dimensions on a silicon wafer. The PDMS was first prepared by mixing the base and the curing agent at 10:1 weight ratio. Half of the mixture was then poured onto the master, while the remaining was poured into a petry dish. The master formed the three walls of the rectangular microchannel in PDMS while the PDMS slab from the petry dish provided the fourth surface required to form a closed microchannel. They were cured at 80°C for 1 h. The cured PDMS slab from the petry dish was bonded with oxygen plasma treatment to a piece of glass slide to increase the overall rigidity of the PDMS microchannel. The cured PDMS channel on the master was peeled and holes were punched at the inlet and outlet of the channel. The PDMS channel was then bonded to the PDMS slab with oxygen plasma treatment to form a closed four-walled PDMS microchannel. The reservoirs (diameter of 2 cm and height of 0.5 cm) were fabricated from PDMS and attached to the inlet and outlet of the microchannel.

A high voltage power supply (CZE1000R, Spellman) was employed to provide the electric field for inducing electroosmotic flow. The current was monitored by a picoammeter (Keithley 6485), which was connected in series to the micro-capillary (see Fig. 1). A LABVIEW program

FIG. 1. Schematic diagram of experimental setup for current monitoring method.

was written to control the two devices and to obtain the voltage and current data through a data acquisition card (PCI-6052E, National Instrument).

B. Experimental methods

All glass micro-capillaries were flushed with acetone followed by deionized water and KCl solution before use. Flushing was performed through a syringe filled with the required fluid that was connected to the micro-capillary through a silicone tubing. PDMS microchannels were flushed with KCl solution only. For a low concentration fluid displacing a high concentration fluid, after flushing, the microchannel was filled with 1 mM KCl solutions (see Fig. 1). Reservoir 2 was also filled with 1 ml of 1 mM KCl solution. Reservoir 1 was then filled with KCl solution with a lower concentration (0.2 mM, 0.5 mM, 0.7 mM, or 0.95 mM). Subsequently, voltages of 500 V, 1000 V, or 1500 V were applied across the two reservoirs to generate electroosmotic flow across the glass micro-capillary. For the PDMS microchannel, a voltage of 330 V is applied. Similarly, the displacement flow of a high concentration fluid displacing a low concentration fluid was conducted in a similar fashion. In this case, the lower concentration KCl solutions were filled in the microchannel and reservoir 2 while 1 mM KCl solution was filled in reservoir 1 instead.

Experiments were conducted with various concentration ratios between the two solutions, lengths and diameters of microchannel. Each set of parameters was conducted at least five times to obtain consistent and reliable results.

The effect of Joule heating in our investigation can be ignored. It is caused by volumetric heating when an electric field is applied across a conductive media such as electrolyte. However, if the concentration and conductivity of the electrolyte are low, the temperature rise due to Joule heating is negligible.²¹ A conservative estimate of temperature rise from Joule heating can be derived from the energy balance between the energy generation, E_g , and the energy storage, E_{st} , in the liquid as

$$E_g = E_{st},$$

$$\frac{V^2}{R} \Delta t = \rho V_c C_p \Delta T, \quad (4)$$

where V is the applied voltage difference, Δt is the total time the voltage is applied, R is the electrical resistance per unit volume, ρ is the liquid density, V_c is the total liquid volume, C_p is the specific heat of the liquid, and ΔT is the average temperature change of the liquid.²² The worst case scenario given by the parameters investigated is an estimated temperature rise of 0.27 °C only, which is negligible.

FIG. 2. Current-time curve for displacement flow of 0.2 mM and 1 mM KCl solutions in glass micro-capillary.

IV. EXPERIMENTAL RESULTS

Fig. 2 shows an example of the current-time curve for the displacement flow of 1 mM and 0.2 mM KCl solutions in the glass micro-capillary. The case of 1 mM KCl displacing 0.2 mM KCl is depicted by the ascending curve while the case of 0.2 mM KCl displacing 1 mM KCl is represented by the descending curve. The time for the current to reach a steady value is the time required for the fluid from reservoir 1 to fully displace the fluid in the micro-capillary. It can be observed clearly that the displacement times for the two cases are indeed different.

FIG. 3. Displacement time for 1 mM KCl with (a) 0.2 mM, (b) 0.5 mM, (c) 0.7 mM, and (d) 0.95 mM KCl for flows in both directions in glass micro-capillary with diameter of 100 μ m and length of 8 cm under applied voltage of 1000 V. Error bars indicate the standard deviations.

TABLE I. t -score for displacement time of various solutions pairs at 3 voltages applied in glass micro-capillary.

Solution pairs	Voltage applied		
	500 V	1000 V	1500 V
0.2 mM and 1 mM	18.87	25.35	13.08
0.5 mM and 1 mM	6.11	11.09	13.07
0.7 mM and 1 mM	4.46	5.85	8.95
0.95 mM and 1 mM	1.30	3.20	1.06

Fig. 3 shows the displacement time for different pairs of solutions under various voltages for glass micro-capillary of 100 μm in diameter and 8 cm in length. Student's t -test was performed on the data to examine if the mean displacement times of these two different directions are significantly different. Let T_{HL} is the displacement time for high concentration solution displacing low concentration solution and T_{LH} is the displacement time for low concentration solution displacing high concentration solution. The null hypothesis H_0 states that T_{LH} is not larger than T_{HL} while the alternative hypothesis H_1 states that T_{LH} is larger than T_{HL} . The t -score can be calculated as

$$t = \frac{\bar{T}_{LH} - \bar{T}_{HL}}{\sqrt{\frac{s_{LH}^2}{n} + \frac{s_{HL}^2}{n}}}, \quad (5)$$

where $\bar{T}_{LH}$ is the sample mean of T_{LH} , $\bar{T}_{HL}$ is the sample mean of T_{HL} , s_{LH} is the sample standard deviation of T_{LH} , s_{HL} is the sample standard deviation of T_{HL} , and n is the number of sample.

Table I shows the t -score calculated from the experimental data. With 5 samples from each group of data, the degree of freedom is 8. The critical t -score for a significance level of 0.005 in a one-tailed test is 3.36. With the exception of 0.95 mM and 1 mM solution pair, all solutions pairs show t -scores higher than the critical t -score. This implies that the probability for the observed time difference to be caused by sampling or random error is very small (less than 0.5%) for the displacement flow of 0.2 mM, 0.5 mM, and 0.7 mM with 1 mM. Therefore, the null hypothesis H_0 is rejected in favor of the alternative hypothesis H_1 for these three pairs of solutions.

For a better comparison of time differences between different pairs of solutions, percentage time difference is calculated as $(T_{LH} - T_{HL})/T_{LH} \times 100\%$ and plotted with respect to percentage concentration difference, see Fig. 4(a). As the concentration between the two solutions increases, the percentage displacement time difference increases. Each pair of solutions show approximately similar percentage time difference at the three voltages applied. Therefore, the percentage time difference is not dependent on the applied voltages. The average percentage time differences for 0.95 mM, 0.7 mM, 0.5 mM, and 0.2 mM KCl with 1 mM KCl are 4.3%, 13.4%, 19.4%, and 28.4%, respectively.

These results also show that in a conventional current monitoring method, which involves displacement flow of solution with 5% concentration difference, the difference in displacement time between the two different flow directions is not significant (less than 5%). Therefore, zeta potential which is calculated based on displacement time should be almost similar regardless of flow directions in this case.

Displacement flows with three pairs of solutions were also performed with glass micro-capillaries of different lengths and diameters with applied voltage fixed at 1000 V. Similar trend which shows displacement time difference increases with increasing concentration difference was obtained, see Figs. 4(b) and 4(c). Despite changing the diameter and length of the micro-capillary, the percentage displacement time difference is approximately the same for a

FIG. 4. Percentage time difference between displacement time in both directions for KCl solution with various percentage of concentration differences at various (a) voltages (with micro-capillary length of 8 cm and diameter of 100 μm), (b) micro-capillary diameters (length was fixed at 8 cm), and (c) micro-capillary lengths (diameter was fixed at 100 μm).

particular concentration difference. Therefore, diameter and length of micro-capillary do not seem to affect the time difference significantly.

The experimental results based on displacement flow with similar solution pairs in PDMS microchannels were shown in Fig. 5(a). 6.5% and 13% displacement time difference were observed for 50% and 80% concentration difference, respectively. However, the time difference was significantly lower than glass microcapillary at similar concentration difference (see

FIG. 5. (a) Displacement time in PDMS microchannel with KCl solutions of various percentage concentration differences under applied voltage of 330 V over channel length of 5.5 cm and (b) comparison between percentage time difference for PDMS channel and glass micro-capillary (6 cm) at various concentration differences.

FIG. 6. Simulation domain and coordinate system for axisymmetric analysis.

Fig. 5(b)). Contrary to glass micro-capillary, the displacement time in PDMS channel from opposite directions does not differ significantly at 30% concentration difference. This shows that the observed time difference is dependent on the material of the channel.

V. NUMERICAL MODEL

In the literature, no numerical and theoretical studies have been performed to study the displacement time difference reported in Sec. III. Conventional models which prescribe a constant zeta potential or bulk concentration cannot describe adequately the two fluid displacement flow because as they do not consider the changes of ion concentration near the EDL due to diffusion and convection. When one fluid is displacing another fluid under electroosmotic flow, the zeta potential along the microchannel and ion distribution are expected to be constantly changing due to the dissimilar concentration between the two fluids with constant perturbation from diffusive and convective effects.

We conducted a numerical simulation with finite element method (FEM) based on the PNP model with modified boundary conditions to explain the displacement time difference phenomenon in two fluid displacement flow. The model is implemented on COMSOL Multiphysics software. We consider a straight cylindrical microchannel with diameter of 20 μm and length of 160 μm . Since the flow is axisymmetrical about the centre axis of the cylindrical channel, an axisymmetric analysis is conducted, see Fig. 6.

To capture the fine details necessary to describe the two fluid displacement flow, strongly coupled governing equations for fluid flow, ion distributions, wall potential, and applied electric potential have to be solved simultaneously. As such, a large amount of computer memory is required. Thus, due to the limitation of memory availability, the length of the model has to be much less than (500 times smaller) the physical length of the channel employed in the experiments. However, since it is experimentally shown that the displacement time difference is not dependent on the length of the capillary or the voltage applied, the numerical model will provide a good representation, at least qualitatively and in the expected trends, of the experimental flow behavior.

A. Governing equations

Electric field is applied across the two reservoirs to generate electroosmotic flow and current travels across the channel. Charge conservation requires that the divergence of current density $\mathbf{i}$ is equal to zero

$$\nabla \cdot \mathbf{i} = 0. \quad (6)$$

In an aqueous solution, the charge carriers are the solute ions. Therefore, in a binary electrolyte system, the current density $\mathbf{i}$ can be related to the transport of ions as follows:

$$\nabla \cdot [\sigma \nabla \phi + F(z_+ D_+ \nabla c_+ + z_- D_- \nabla c_-) - \mathbf{u} F(z_+ c_+ + z_- c_-)] = 0, \quad (7)$$

where solution conductivity $\sigma = F^2(c_+u_{m+} + c_-u_{m-})$. The current density consists of three components: electro-migrative current, diffusive current, and convective current. The electro-migration of ion is the major contributor to the current observed in the current monitoring experiments and it is often called the conduction current. The diffusive current due to concentration gradient along the channel is very small in our case because the diffusion coefficients of K^+ and Cl^- ions are almost similar. The convective current is several orders of magnitude smaller than the conduction current and is often neglected in the current monitoring experiment.²² Our simulation confirms that the diffusive and convective components are very small and can be neglected without sacrificing accuracy of the simulation results. Therefore, Eq. (7) can be reduced to the Laplace equation (Eq. (8)), which governs the applied electric potential distribution ϕ ,

$$\nabla \cdot (\sigma \nabla \phi) = 0. \quad (8)$$

Since the conductivity of the simulation domain is changing during the displacement flow, the solution conductivity σ is not a constant but varies with concentrations of ions.

The static wall potential distribution ψ is given by the Poisson equation

$$\nabla \cdot \nabla \psi = \frac{\rho_e}{\epsilon_r \epsilon_0}, \quad (9)$$

where net charge density $\rho_e = F(c_+ - c_-)$. It is important to highlight here that the electrical potential is not specified or forced to obey Poisson-Boltzmann equation which is only valid at steady state condition for single fluid electroosmotic flow. In two fluid displacement flow, the concentration of the solutions in the channel is not constant, and thus the zeta potential of the channel wall is constantly varying and should not be prescribed *a priori*. Therefore, the wall potential must be allowed to vary according to the local net charge density, which is governed by the positive and the negative ions.

The distributions of positive and negative ions (c_+ and c_-) in Eq. (9) are not specified but are to be solved by the Nernst-Planck equation

$$\frac{\partial c_+}{\partial t} + \nabla \cdot [-D_+ \nabla c_+ - z_+ u_{m+} F c_+ \nabla (\phi + \psi)] = -\mathbf{u} \cdot \nabla c_+, \quad (10)$$

$$\frac{\partial c_-}{\partial t} + \nabla \cdot [-D_- \nabla c_- - z_- u_{m-} F c_- \nabla (\phi + \psi)] = -\mathbf{u} \cdot \nabla c_-. \quad (11)$$

Equations (10) and (11) show that ion distribution changes are governed by three components, namely, diffusive, electro-migrative, and convective component. The electro-migrative terms consist of two parts: the component due to applied electric field and the component due to the static wall potential, which are summed based on the principle of superposition of electrical potential.

Equations (12) and (13) are, respectively, the Navier-Stokes equation for incompressible Newtonian fluid and the continuity equation which govern the flow field $\mathbf{u}$ and pressure p

$$\rho \frac{\partial \mathbf{u}}{\partial t} + \rho (\mathbf{u} \cdot \nabla) \mathbf{u} = -\nabla p + \mu \nabla^2 + \rho_e [-\nabla (\phi + \psi)], \quad (12)$$

$$\nabla \cdot \mathbf{u} = 0. \quad (13)$$

The last term of Eq. (11) is the body force caused by the applied potential and wall potential on the fluid near the wall with net charge density ρ_e . For microfluidics, the inertial term can be neglected without significant loss of accuracy since Reynolds number is less than 1 (Stokes flow). The values of the various parameters employed are listed in Table II.

TABLE II. Symbols and values of parameters in numerical models.

Parameter	Symbol (unit)	Value
Faraday constant	$F/C \text{ mol}^{-1}$	96485
Relative permittivity	ϵ_r	80
Permittivity of free space	$\epsilon_0/\text{Fm}^{-1}$	8.85×10^{-12}
Bulk concentration	$c_0/\text{mol m}^{-3}$	0.01
Diffusion coefficient of K^+ ion	$D_+/\text{m}^2 \text{ s}^{-1}$	1.957×10^{-9}
Diffusion coefficient of Cl^- ion	$D_-/\text{m}^2 \text{ s}^{-1}$	2.032×10^{-9}
Ion mobility of K^+	$u_{m+}/\text{s mol kg}^{-1}$	7.903×10^{-13}
Ion mobility of Cl^-	$u_{m-}/\text{s mol kg}^{-1}$	8.206×10^{-13}
Ion charge number of K^+ ion	z_+	+1
Ion charge number of Cl^- ion	z_-	-1
Temperature	T/K	298
Electron charge	e/C	1.602×10^{-19}
Boltzmann constant	$k_b/\text{m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$	1.381×10^{-23}
Density of water	$\rho/\text{kg m}^{-3}$	1000
Viscosity of water	$\mu/\text{kg m}^{-1} \text{ s}^{-1}$	8.90×10^{-4}
Avogadro constant	N_A/mol^{-1}	6.022×10^{23}

The simulation domains are meshed with 21 000 quadrilateral elements. The electrostatic potential, ion concentration, and applied potential are discretized with second order elements, while the pressure and velocity are discretized with linear elements. The elements are set to be finer near the wall to capture the changes of various variables near the EDL. Convergence test has been performed with higher number of elements for steady-state solutions and the numerical error is found to be negligible with the mesh employed.

B. Boundary and initial conditions

Boundary conditions for the simulation with displacement flow of a single fluid with concentration 0.01 mol m^{-3} (0.01 mM) are summarized in Table III. The solution concentration in this numerical study is two order smaller than the experimental solution concentration. This is because concentration as high as 1 mM will require very fine mesh at the vicinity of the shear plane to resolve the steep change in ion concentration, pressure, and velocity due to the extremely thin EDL layer. This would require excessive amount of computation time and memory that our current computational resources will not allow. However, we note that the characteristic length scale of EDL is given by the Debye length,

$$\lambda_D = \left(\frac{\epsilon_r \epsilon_0 k_b T}{2 z^2 e^2 N_{Ac_0}} \right)^{1/2}, \quad (14)$$

λ_D for a 0.01 mM solution is calculated to be 97.2 nm, which is still much smaller than the radius of the simulation domain (10 μm). Therefore, no overlapping of EDL is expected and the simulation should give a good representation of the flow of higher concentration solution in a micro-channel. Thus, for this preliminary study to provide an understanding of the mechanism of the two fluid displacement flow behavior, there will be no loss of generality by setting the solution concentration for the simulation at 0.01 mM.

A voltage of 2 V is applied across the inlet and outlet of the microchannel. The resultant electric field is 125 V cm^{-1} which is equivalent to the experimental scenario of applying 1000 V over an 8 cm long micro-capillary. Insulation and symmetrical boundary conditions are applied at the channel wall and along the line of symmetry, respectively. It is assumed that there is no specific ion absorption on the wall and the wall charge is constant during the course

TABLE III. Summary of boundary conditions for steady state numerical model for single fluid electroosmotic flow.

Variable	Condition	Boundary
Applied potential ϕ	$\phi = 1V$	Inlet
	$\phi = 0$	Outlet
Electrostatic potential ψ	$\mathbf{n} \cdot \nabla \phi = 0$	Wall, axis of symmetry
	$\mathbf{n} \cdot \nabla \psi = 0$	Inlet, outlet, axis of symmetry
	$\mathbf{n} \cdot \nabla \psi = -\frac{0.7 \times 10^{-3}}{\epsilon_r \epsilon_0}$	Wall
Positive ion concentration c_+	$c_+ = c_0 \exp\left(-\frac{e\psi}{k_b T}\right)$	Inlet, outlet
	$\mathbf{n} \cdot (-D_+ \nabla c_+ - z_+ u_{m+} F c_+ \nabla(\phi + \psi) + \mathbf{u} c_+) = 0$	Wall, axis of symmetry
Negative ion concentration c_-	$c_- = c_0 \exp\left(\frac{e\psi}{k_b T}\right)$	Inlet, outlet
	$\mathbf{n} \cdot (-D_- \nabla c_- - z_- u_{m-} F c_- \nabla(\phi + \psi) + \mathbf{u} c_-) = 0$	Wall, axis of symmetry
Flow velocity $\mathbf{u}$ and pressure p	$p = \frac{2c_0 F k_b T}{e} \cdot \left[\cosh\left(\frac{e\psi}{k_b T}\right) - 1 \right]$	Inlet, outlet
	$\mathbf{u} = 0$	Wall
	$\mathbf{n} \cdot \mathbf{u} = 0$	Axis of symmetry

Note: $\mathbf{n}$ = unit vector normal to the boundary.

of the two fluid displacement flow process. The surface charge σ_w of glass was assumed to be -0.7 mC/m^2 in a solution with concentration of 0.01 mM .²³

The inlet and outlet of the microchannel are connected to the reservoirs. Neglecting the entrance and exit effects, the positive and negative ion concentration profiles at the inlet and outlet are assumed to follow the Poisson-Boltzmann distribution. Assuming that there is no viscous stress at the inlet and outlet, the steady state pressure at the inlet and outlet can be derived by solving the NS equation

$$0 = -\frac{\partial p}{\partial r} - \frac{\partial \psi}{\partial r} \rho_e. \quad (15)$$

Substituting the positive and negative ion concentrations (Boltzmann distribution Eq. (2)) and integrating Eq. (15) once yield,

$$p = \frac{2c_0 F k_b T}{e} \left[\cosh\left(\frac{e\psi}{k_b T}\right) - 1 \right]. \quad (16)$$

No slip boundary condition is specified at the wall.

The numerical solving process is summarized in Fig. 7. First, the wall static potential distribution and ion distribution are solved with Poisson equation and NP equation, by assuming no fluid flow and no applied electric field. After obtaining the ion distribution, Laplace equation can then be solved to obtain the applied electric potential distribution. Finally, the continuity and NS equations are solved to obtain the flow field and pressure in the channel. Convective component due to fluid flow and electromigrative component due to applied electric field are then added to NP equation. All these equations are then solved simultaneously to obtain the steady state solution of a single fluid electroosmotic flow. The solving and iteration processes are handled by the stationary solver of COMSOL and convergence is obtained within 25 iterations.

After obtaining the steady state solutions for a single fluid flow, boundary conditions at the inlet are modified to model the time-dependent flow condition of two fluid displacement flow. The steady state solution is set as the initial condition. The inlet boundary condition for c_+ , c_- , and p in a displacement flow with 0.002 mol m^{-3} solution displacing 0.01 mol m^{-3} solution

FIG. 7. Flowchart of numerical solving process.

(80% concentration difference, concentration ratio $R = 5$) are modified according to Table IV. However, setting this boundary condition will induce inconsistency with the boundary condition of the steady state solution. To resolve this inconsistency, the value of ion concentration is ramped down from the steady state value $c_0 = 0.01 \text{ mol m}^{-3}$ to $c_0/5 = 0.002 \text{ mol m}^{-3}$ in an arbitrarily short time (0.0001 s). The time-dependent solution for the flow of 0.002 mol m^{-3} solution (inlet reservoir) displacing 0.01 mol m^{-3} solution (outlet reservoir) can be obtained.

The simulation of displacement flow in the other direction can be performed similarly by first obtaining the steady state solution of a single fluid flow for 0.002 mol m^{-3} solution. Subsequently, the inlet boundary condition is similarly modified by ramping up from the steady state value $c_0/5 = 0.002 \text{ mol m}^{-3}$ to $c_0 = 0.01 \text{ mol m}^{-3}$ in 0.0001 s. Displacement flows with other pair of solutions (0.005 mol m^{-3} or $0.0095 \text{ mol m}^{-3}$ with 0.01 mol m^{-3}) are performed in a similar manner.

TABLE IV. Changes in inlet boundary conditions for two-fluid displacement flow (R = concentration ratio between two solutions).

Variable	Inlet boundary condition
Positive ion concentration c_+	$c_+ = \frac{c_0}{R} \exp\left(-\frac{e\psi}{k_b T}\right)$
Negative ion concentration c_-	$c_- = \frac{c_0}{R} \exp\left(\frac{e\psi}{k_b T}\right)$
Flow velocity $\mathbf{u}$ and pressure p	$p = \frac{2c_0 F k_b T}{eR} \left[\cosh\left(\frac{e\psi}{k_b T}\right) - 1 \right]$

FIG. 8. Numerical results showing (a) flow rate and (b) displacement of fluid interface in the displacement flow of 0.01 mM and 0.002 mM solutions. Single fluid flows for each of the two solutions are shown for reference.

C. Numerical results

The flow rate Q for the displacement flow of 0.01 mM and 0.002 mM (80% concentration difference) is obtained by integrating the x -velocity over the cross section area of the channel. The flow rate for the displacement flow of these two directions changes with time and is bounded by the two single fluid flow rates (see Fig. 8(a)). The displacement of the fluid interface X is defined as

$$X = \int u_{av} dt, \quad (17)$$

where the average x -velocity $u_{av} = Q/A$, where A is the cross section area of the channel. Therefore, X can be obtained by integrating the flow rate with respect to time (or area under the curve of Fig. 8(a)) and dividing it by A .

The displacement time can be obtained by determining the time required for the fluid interface to travel 1.6×10^{-4} m which is the length of the microchannel (see Fig. 8(b)). The displacement times for 0.01 mM and 0.002 mM solutions (in the single fluid flow) are 0.2345 s and 0.156 s, respectively. The displacement increases linearly with time for a single fluid flow. However, for two fluid displacement, the displacement-time relationship is shown to be non-linear. The displacement time for the case of 0.002 mM displacing 0.01 mM (T_{LH}) and the case of 0.01 mM displacing 0.002 mM (T_{HL}) are 0.194 s and 0.1745 s, respectively. The simulation result shows that $T_{LH} > T_{HL}$ and this trend agrees with our experimental findings. The percentage time difference between the flows of these two directions is 11.2%.

Fig. 9 shows a comparison between current-time curve obtained from the experimental and simulation results. As the length of channel and applied voltage are different in both cases, comparison is achieved through normalization of parameters. The experimental and numerical currents are normalized with the maximum and minimum currents in the experiment and simulation, respectively, such that all values of current fall between 0 and 1. The numerical displacement time for both cases of 0.002 mM displacing 0.01 mM and 0.01 mM displacing 0.002 mM are normalized with the time to reach the steady current for the former case. The experimental displacement time for the displacement flow of 0.2 mM and 1 mM is normalized in a similar manner. The numerical results show that the time for a high concentration solution displacing low concentration solution is indeed shorter than the displacement time for the flow in the reverse direction. This numerical trend agrees with the experimental results. However, as expected, quantitative agreement is not good as the solution concentrations in both cases differ.

Despite of the lack of good quantitative agreement between the experimental results and simulations, these simulations do reveal the mechanism for the time difference in two fluid displacement flow with large concentration difference. Figs. 10(a) and 10(b) show the time evolution of positive and negative ion concentration distributions at $x = 0.8 \times 10^{-4}$ m (half of the channel length) during the two-fluid displacement flow. These curves are snapshots of

FIG. 9. Comparison between experimental and numerical results for displacement flow of two solutions with 80% concentration difference. Currents are normalized with maximum and minimum currents. Time is normalized with the time for the descending curve to reach a steady current.

concentration profiles when the bulk concentrations (concentrations at the line of symmetry) are 0.002 mM, 0.004 mM, 0.006 mM, 0.008 mM, and 0.01 mM.

The steady state concentration profiles for a single fluid flow is illustrated in Figs. 10(a) and 10(b) as the curve $t=0$. Positive ion concentration decreases and negative ion concentration increases with increasing distance from the wall. The concentrations of positive and negative ions coincide at edge of the EDL where the net charge becomes zero. Beyond the EDL, the steady state curves are flat and there is no concentration variation. The plug-like ionic concentration and velocity profile agree with conventional electroosmotic models. The solution with a lower concentration produces a thicker EDL and results in a higher flow rate.

The concentration and velocity profiles for two fluid displacement flow deviate significantly from the typical plug-like profile of a single fluid electroosmotic flow. Solutions with different concentration flow at different velocities. To maintain continuity, a pressure gradient is

FIG. 10. Positive and negative ion distributions $x = 0.8 \times 10^{-4}$ m for the flow of (a) 0.002 mM displacing 0.01 mM and (b) 0.01 mM displacing 0.002 mM. Full curves represent negative ion and dashed curves represent positive ion.

FIG. 11. Snapshots of velocity vector plot for flow of (a) 0.002 mM displacing 0.01 mM and (b) 0.01 mM displacing 0.002 mM. Numerical results show that velocity profiles in two fluid displacement flow deviate from the plug-like profile of a typical electroosmotic flow.

generated and velocity profile is no longer plug-like (see Fig. 11). The velocity profile is a combination of the plug-like profile of electroosmotic flow and the parabolic profile due to pressure driven flow. The variation of velocity and the diffusion induced by the concentration gradient at the interface of the two fluids influence the ion distributions due to the presence of the convective and diffusive components in the Nernst-Planck equation. Positive and negative ion concentrations are shown to vary with distance even beyond the edge of EDL (see Figs. 10(a) and 10(b)) while maintaining zero net charge (positive ion and negative ion curves overlap).

The ion concentration profiles for the flows in both directions are plotted together in Fig. 12 for easy comparison (only negative ion is shown). The concentration at the edge of EDL is higher than the bulk concentration for the case of 0.002 mM displacing 0.01 mM, whereas the concentration at the edge of EDL is lower than the bulk concentration for the case of 0.01 mM displacing 0.002 mM. A lower ion concentration near the wall results in a thicker EDL and hence higher flow rate. The reverse is true if ion concentration is higher near the wall. It is this different distortion of ionic concentration profile at the EDL that induces the displacement time difference.

FIG. 12. Comparison of negative ion distributions between both flow directions at bulk concentration of 0.004 mM, 0.006 mM and 0.008 mM at $x = 0.8 \times 10^{-4}$ m. Full curves represent the case of high concentration displacing low concentration and dashed curves represent the case of low concentration displacing high concentration.

Simulations for the displacement flow of 0.0095 mM and 0.005 mM solutions with 0.01 mM solution (5% and 50% concentration differences) have also been performed. Percentage time difference for the displacement flow of solutions with 50% concentration difference is computed to be 2.9%, while the time difference for the case of 5% concentration difference is negligible (less than 1%). This shows that the displacement time difference reduces with decreasing concentration difference. This trend is logical and agrees with the experimental results. The percentage time differences obtained from the experiments and simulations are not expected to be the same because the concentrations of solutions between simulations and experiments are different.

VI. CONCLUSION

Electroosmotic displacement flow involving two dissimilar fluids is commonly encountered in microfluidics. The flow direction dependence of displacement time was investigated experimentally. The displacement time was determined with current monitoring method. The time required for a high concentration solution to displace a low concentration solution is less than the time required for a low concentration solution to displace a high concentration solution. It was found that the percentage displacement time difference increases with increasing concentration difference. If the concentration difference between the two solution is large (>30% for glass channel and >50% for PDMS channel), the displacement time difference between these two directions is not negligible. The percentage time difference can be as high as 28.4% if the concentration ratio between the two solutions is 5:1. The percentage time difference appears to be constant regardless of the length or diameter of the channel and the voltage applied.

A numerical model has been proposed to investigate and simulate this phenomenon. Simulation results show that the velocity profile and ion distribution differ significantly from those of single fluid electroosmotic flow. The distortion of ionic profiles near the EDL is responsible for the displacement time difference for two different flow directions. The percentage time difference increases with increasing concentration difference. The trends obtained from simulation results agree qualitatively and explain the mechanism of the experimental findings.

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- ¹H. Y. Gan, C. Yang, Stephen, Y. M. Wan, G. C. Lim, and Y. C. Lam, *J. Phys.: Conf. Ser.* **34**(1), 283 (2006).
- ²R. J. Hunter, *Zeta Potential in Colloid Science: Principles and Applications* (Academic, London, 1988).
- ³X. Huang, M. J. Gordon, and R. N. Zare, *Anal. Chem.* **60**, 1837 (1988).
- ⁴Z. A. Almutairi, T. Glawdel, C. L. Ren, and D. A. Johnson, *Microfluid. Nanofluid.* **6**(2), 241 (2009).
- ⁵A. Sze, D. Erickson, L. Ren, and D. Li, *J. Colloid Interface Sci.* **261**(2), 402 (2003).
- ⁶T. Vishal, K. B. Sharath, and J. K. Brian, *Electrophoresis* **30**(15), 2656 (2009).
- ⁷D. Mampallil, D. v. d. Ende, and F. Mugele, *Electrophoresis* **31**, 563 (2010).
- ⁸S.-W. Tang, C.-H. Chang, and H.-H. Wei, *Microfluid. Nanofluid.* **10**(2), 337 (2010).
- ⁹Y. Hu, C. Werner, and D. Li, *Anal. Chem.* **75**(21), 5747 (2003).
- ¹⁰S. Arulanandam and D. Li, *Colloids Surf., A* **161**(1), 89 (2000).
- ¹¹G. Y. Tang, C. Yang, J. C. Chai, and H. Q. Gong, *Int. J. Heat Mass Transfer* **47**(2), 215 (2004).
- ¹²D. Yang and Y. Liu, *Colloids Surf., A* **328**(1–3), 28 (2008).
- ¹³H.-C. Chang and L. Y. Yeo, *Electrokinetically Driven Microfluidics and Nanofluidics* (Cambridge University Press, New York, 2010).
- ¹⁴L. M. Fu, J. Y. Lin, and R. J. Yang, *J. Colloid Interface Sci.* **258**(2), 266 (2003).
- ¹⁵S. Bhattacharyya and A. K. Nayak, *Colloids Surf., A* **339**(1–3), 167 (2009).
- ¹⁶H. M. Park and Y. J. Choi, *Int. J. Heat Mass Transfer* **52**(19–20), 4279 (2009).
- ¹⁷A. E. Herr, J. I. Molho, J. G. Santiago, M. G. Mungal, T. W. Kenny, and M. G. Garguilo, *Anal. Chem.* **72**(5), 1053 (2000).
- ¹⁸H. S. Kwak and E. F. Hasselbrink Jr., *J. Colloid Interface Sci.* **284**(2), 753 (2005).
- ¹⁹T. J. Craven, J. M. Rees, and W. B. Zimmerman, *Phys. Fluids* **20**(4), 043603 (2008).
- ²⁰D. G. Yan, C. Yang, and X. Y. Huang, *Microfluid. Nanofluid.* **3**(3), 333 (2007).
- ²¹G. Tang, D. Yan, C. Yang, H. Gong, J. C. Chai, and Y. C. Lam, *Electrophoresis* **27**(3), 628 (2006).
- ²²S. Arulanandam and D. Li, *J. Colloid Interface Sci.* **225**(2), 421 (2000).
- ²³S. H. Behrens and D. G. Grier, *J. Chem. Phys.* **115**(14), 6716 (2001).