Analytical study of AC electroosmotic mixing in 2-dimensional microchannel with time periodic surface potential

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ABSTRACT

This work reported an analytic study of AC electroosmotic flows with a view to control the degree of mixing in a rectangular microchannel. Only with spatially non-uniform zeta potential distribution, fluid particles travel back and forth along a vortical flow field developed inside a microchannel. Although complex patterns of electroosmotic vortical flows can be obtained by various types of non-uniform zeta potential distributions, fluid particles always follow regular paths due to a laminar flow limit. To further facilitate the mixing of sample fluid, we propose a scheme that the zeta potential distribution was temporally non-uniform as well. General solutions for both the double layer potential distribution and the AC electroosmotic flow field are analytically determined by solving the unsteady Stokes equation with an electrostatic body force. As an illustrative example, we consider a case where two different types of non-uniform zeta potential distributions alternate with each other and the effects of both the AC frequency and the frequency of the alternation of the two zeta potential distributions on flow characteristics are examined using the Poincaré sections. Conclusively, one can either enhance or prevent mixing compared to a static electroosmotic flow, which is in line with previously demonstrated experimental works. Thus, the results presented would be an effective mean for controllable electroosmotic flow in a microfluidic platform.

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INTRODUCTION

Electrokinetic forces have been widely utilized for the transport of sample liquid and controlling flow in micro/nanochannel network devices.^{1–3} Electroosmosis driven by electrokinetic forces plays an important role in transporting, mixing, and separating samples in numerous micro/nanofluidic systems. The electrokinetic motion of sample liquid is caused by the bulk movement of an electrolyte solution past a stationary solid surface in the presence of an external applied electric field. The spontaneous separation of ions at a solid/liquid interface forms a nanoscale layer, called the electrical double layer (EDL), and the ions adjacent to the surface are attracted to the oppositely charged substrate. In an ideal electroosmotic flow, the velocity profile would be plug-type and the mean velocity is independent of the cross-sectional area of the microchannel (or the

capillary). In a pressure-driven flow, however, the velocity profile is parabolic and the mean flow rate would depend on the channel cross-sectional area. Thus, the electroosmotic flow offers significantly less deleterious dispersive effects than pressure-driven flow and the valveless control of flow direction is presented with appropriate switching of the applied electric field. However, the Reynolds number of typical microfluidic devices is extremely small and thus achieving a sufficient mixing in electroosmotic microchannel flow can be often a challenging problem.

The micro-mixer scheme employing complex mechanical structures in such low Reynolds number environment has been demonstrated in a wide variety of schemes.^{4–7} Such designs effectively created chaotic mixing in a pressure-driven microchannel flow. However, the complex structure can cause fouling or clogging of

solute molecules, especially for large molecules at high concentrations, and typically need multilayer fabrication techniques, which turns the mixers less attractive to bio-analysis system designers. On the other hand, to enhance electroosmotic mixing in a microchannel, one just needs to control the local magnitude and direction of electroosmotic flow by manipulating either the distribution of zeta potential at the wall or the applied external electric field.^{8–13} Controlling the electric conditions does not require a complex microchannel structure and can prevent the fouling problems. A number of studies to date have shown the applications of controlling the zeta potential manipulation. Anderson and Idol proved that a vortical motion in electroosmotic flow could be achieved with non-uniform zeta potential distribution in a capillary.¹⁴ Ajdari analyzed various electroosmotic flow patterns induced by non-uniform zeta potentials along an undulated microchannel.^{15–17} He also investigated the aspect ratio of channel length to channel height for the electroosmotic flow profile. Recently, Qian and Bau, using an analytical solution of complex electroosmotic flows induced by the non-uniform and time periodic zeta potential with a uniform DC electric field,¹⁸ derived the chaotic advection in the electroosmotic flow.

The application of an AC electric field affects the fluid dynamics of a sample liquid in a more subtle way. Depending on the frequency of the AC electric field, the charge relaxation in the EDL and the resulting electrokinetic process can produce more complex patterns of electroosmotic flows. Electroosmotic flows caused by the AC electric field have been studied by several researchers.^{12,19–23} Barragan and Bauza experimentally studied the influences of superimposing an AC electric field to DC electroosmotic behavior in a cation-exchange membrane system.²⁰ Dutta and Beskok precisely analyzed the effect of uniform zeta potential and buffer concentration on the AC electroosmotic flow.²¹ Electrokinetic processes were developed to rapidly stir microflow stream using the AC electric field.¹² However, physical parameters used in these studies, such as geometric size and strength of electric field, were much larger than recent conditions of electroosmotic flow in a microchannel. While chaotic microvortices were generated around a small conductive ion-exchange granule when moderate AC and DC electric fields were applied, the spherical types of agitator were hardly applicable to recent microchannel geometry.²² The analytical solution of three-dimensional AC electroosmotic flow was also presented in a closed-end rectangular microchannel and the induced backpressure was derived.²³ However, since all these previous studies except the one by Oddy *et al.*¹² did not focus mainly on the mixing problem in a microfluidic system, the electroosmotic mixing characteristics were not rigorously presented.

In this work, we analytically investigate electroosmotic flows produced in a 2-dimensional straight rectangular microchannel by applying the AC electric field. The zeta potential distributions on the top and the bottom surfaces of the microchannel are time-periodic and spatially non-uniform. The zeta potential distribution is time-periodic in a sense that we periodically change the zeta potential distributions. This active control of non-uniform zeta potential has been experimentally demonstrated by field effect control, also known as the Ionic Field Effect Transistor (IFET) concept,^{24–33} while surface modification is only capable of spatially non-uniform patterning. The fabrication process of IFET includes

gate electrode patterning, insulation layer deposition, and connecting the gate electrodes to the circuit that can control external electrical potentials. The completed platform enables one to control the surface zeta potential not only spatially but also temporally. Specifically, the experimental observations of electroosmotic flow using temporally varied zeta potential were previously reported for the effect of frequency on mixing.^{8,10,11} Thus, the presenting analytical study can fundamentally support these results in a more detailed manner. In this work, the patterns of the electroosmotic flow developed in the microchannel are thus governed by three factors: the frequency of the AC electric field, the pattern of non-uniform zeta potential distribution, and the period for changing the zeta potential distribution. We study the effects of these factors by analytically solving the governing equations for the electroosmotic velocity field. The EDL potential developed inside a microchannel is first determined by solving the linearized Poisson-Boltzmann equation. The zeta potential distribution is not uniformly constant but periodic. The electrostatic force that governs the electroosmotic velocity field is determined by multiplying the double layer charge density by the external AC electric field. The unsteady Stokes equation augmented with the electrostatic body force is solved analytically using periodic and no-slip boundary conditions. After studying the AC electroosmotic flow fields under various types of non-uniform zeta potential distributions, we consider cases in which two different types of non-uniform zeta potential distributions alternate with each other. Electroosmotic flow characteristics are strongly influenced by the frequency of the alternation of the two zeta potential distributions. By plotting Poincare sections of the resulting flow fields, the effects of both the AC frequency and the frequency of the alternation of the zeta potential distributions on the mixing of sample liquid are discussed.

MATHEMATICAL MODEL

Basic equations

Consider a two-dimensional microchannel with a gap distance $2H$. The zeta potential distributions on the microchannel surfaces are non-uniform but periodic along the longitudinal direction with the period L . The non-uniform zeta potential distributions over the length L are given by $f_1(x)$ and $f_2(x)$ for the top and the bottom surfaces, respectively. The non-uniform zeta potential distribution can be achieved either by coating the microchannel surfaces with different materials³⁴ or by installing arrays of microelectrodes beneath the microchannel surfaces.^{27,28,35} The microchannel is filled with an electrolyte solution, and thus an EDL is formed near the microchannel surface. The AC electric field is applied externally along the longitudinal direction (Fig. 1). Since the pattern of electroosmotic flow field in the microchannel is governed by the distribution of electrostatic body forces in the EDL, the electroosmotic flow field is also periodic along the longitudinal coordinate x with the period L . Since the Reynolds number of the flow in the microchannel is small, the flow field is governed by the unsteady Stokes equations and continuity equation

$$\rho \frac{\partial \mathbf{v}}{\partial t} = -\nabla p + \mu \nabla^2 \mathbf{v} + \rho^E \mathbf{E}, \quad (1)$$

FIG. 1. Schematics for the AC electroosmotic flow between two parallel surfaces. Here ω is the frequency of the external AC electric field, ψ is the surface potential, $\mathbf{v}$ is electroosmotic velocity, and $f(x)$ is the arbitrary function with period L , where L is the microchannel length and H is the height of the microchannel.

$$\nabla \cdot \mathbf{v} = 0. \quad (2)$$

Here, $\mathbf{v}$ and p denote the velocity and the pressure fields, respectively, ρ the fluid density, and μ the fluid viscosity. The last term in Eq. (1), product of the electrical charge density ρ^E and the electric field $\mathbf{E}$, represents the electrostatic body force. In general, the charge density ρ^E and the electric field $\mathbf{E}$ must be determined by solving the Poisson equation and the charge conservation equations. However, when the electrical charge density barely deviates from its equilibrium state under the influence of an external electric field, which is the case in our system, ρ^E and $\mathbf{E}$ can be determined independently. The electrical charge density ρ^E is determined by solving the linearized Poisson-Boltzmann equation

$$\nabla^2 \psi = -\frac{\rho^E}{\epsilon} = \kappa^2 \psi. \quad (3)$$

Here ψ is the EDL potential, κ is the inverse Debye length, and ϵ is the fluid permittivity. We assume that the zeta potentials at the microchannel surfaces are small (~ 25 mV). Without this assumption, one can fully solve the Poisson-Boltzmann equation for analyzing electroosmotic flow.^{36,37} In a straight microchannel shown in Fig. 1, the electric field $\mathbf{E}$ is given by $\mathbf{E} = E e^{i\omega t} \mathbf{e}_x$ where ω is the frequency of the AC electric field applied externally. As shown in Eq. (3), the electrical charge density ρ^E is linearly proportional to the EDL potential ψ and thus $\rho^E \mathbf{E}$ term in Eq. (1) is equal to $-\epsilon \kappa^2 \psi \mathbf{E}$.

Electrical double layer

The solution for the linearized Poisson-Boltzmann equation is obtained using the periodic boundary conditions

$$\psi|_{x=0} = \psi|_{x=L}, \quad (4a)$$

$$\frac{\partial \psi}{\partial x} \bigg|_{x=0} = \frac{\partial \psi}{\partial x} \bigg|_{x=L}, \quad (4b)$$

and the boundary conditions at the top and the bottom surfaces.

The zeta potential distributions at $y=H$ and $y=-H$ are given by arbitrary functions $f_1(x)$ and $f_2(x)$, respectively. The functions $f_1(x)$ and $f_2(x)$ are expressed as Fourier series

$$\psi|_{y=H} = f_1(x) = \frac{\alpha_0}{2} + \sum_{n=1}^{\infty} [\alpha_n \cos \lambda_n x + \beta_n \sin \lambda_n x], \quad (5a)$$

$$\psi|_{y=-H} = f_2(x) = \frac{\gamma_0}{2} + \sum_{n=1}^{\infty} [\gamma_n \cos \lambda_n x + \delta_n \sin \lambda_n x], \quad (5b)$$

where

$$\alpha_n = \frac{2}{L} \int_0^L f_1(x) \cos \lambda_n x dx, \quad n = 0, 1, 2, \dots, \quad (6a)$$

$$\beta_n = \frac{2}{L} \int_0^L f_1(x) \sin \lambda_n x dx, \quad n = 1, 2, \dots, \quad (6b)$$

$$\gamma_n = \frac{2}{L} \int_0^L f_2(x) \cos \lambda_n x dx, \quad n = 0, 1, 2, \dots, \quad (6c)$$

and

$$\delta_n = \frac{2}{L} \int_0^L f_2(x) \sin \lambda_n x dx, \quad n = 1, 2, \dots, \quad (6d)$$

where $\lambda_n = 2n\pi/L$. Using the method of separation of variables, the solution of Eq. (3) is obtained as

$$\begin{aligned} \psi(x, y) = & A_0 \cosh \kappa y + B_0 \sinh \kappa y \\ & + \sum_{n=1}^{\infty} [(A_n \cosh \mu_n y + B_n \sinh \mu_n y) \cos \lambda_n x \\ & + (C_n \cosh \mu_n y + D_n \sinh \mu_n y) \sin \lambda_n x], \end{aligned} \quad (7)$$

where $\mu_n^2 = \lambda_n^2 + \kappa^2$. The coefficients in Eq. (7) are given by

$$A_0 = \frac{\gamma_0 + \alpha_0}{4 \cosh \kappa H}, \quad B_0 = \frac{\gamma_0 - \alpha_0}{4 \sinh \kappa H},$$

$$A_n = \frac{\gamma_n + \alpha_n}{2 \cosh \mu_n H}, \quad B_n = \frac{\gamma_n - \alpha_n}{2 \sinh \mu_n H},$$

$$C_n = \frac{\gamma_n + \beta_n}{2 \cosh \mu_n H}, \quad D_n = \frac{\gamma_n - \beta_n}{2 \sinh \mu_n H}.$$

Electroosmotic flow field

After determining the electrostatic body force term $\rho^E \mathbf{E} = -\epsilon \kappa^2 \psi \mathbf{E}$ using Eq. (7), we solve the unsteady Stokes equations [Eqs. (1) and (2)]. Since the electroosmotic flow developed in the microchannel shown in Fig. 1 is an incompressible two-dimensional

flow, the flow field can be conveniently determined by introducing the stream function $\Psi(x, y, t)$ such that

$$v_x(x, y, t) = \frac{\partial \Psi}{\partial y} \quad (8a)$$

and

$$v_y(x, y, t) = -\frac{\partial \Psi}{\partial x}. \quad (8b)$$

After expressing Eq. (1) in terms of the stream function Ψ by using Eqs. (8a) and (8b), we eliminate the pressure term to obtain the equation for the stream function,

$$\rho \frac{\partial}{\partial t} \nabla^2 \Psi = \mu \nabla^4 \Psi - \epsilon \kappa^2 E \frac{\partial \Psi}{\partial y} e^{i\omega t}. \quad (9)$$

Note that the solution for Ψ in Eq. (9) and the resulting velocity field are complex-valued functions. Also, pure electroosmotic flow was considered in this work so that the pressure gradient [$\nabla p = 0$ in Eq. (1)] was neglected and the periodic boundary conditions [Eqs. (4a) and (4b)] released any induced pressure in the domain. Actual solutions are obtained by taking real parts of the complex-valued solutions. We solve Eq. (9) after recasting it into

$$\nabla^2 \Psi = \Phi(x, y) e^{i\omega t} \quad (10)$$

and

$$\nu \nabla^2 \Phi - i\omega \Phi = \alpha \frac{\partial \Psi}{\partial y}, \quad (11)$$

where $\nu = \mu/\rho$ and $\alpha = \epsilon \kappa^2 E/\rho$. The solutions for Φ and Ψ are obtained by using the method of separation of variables. As we put explicitly in Eq. (10), the stream function and the resulting velocity field are periodic functions of time with the same frequency as the AC electric field applied externally. In other words, the solution does not contain any transient behavior that would develop before the velocity field reaches a periodic steady state. Since the EDL potential ψ is periodic along the coordinate x , the stream function Ψ and the resulting velocity field have the same periodic character along the coordinate x . In addition to the periodic conditions, the velocity field satisfies the no-slip boundary conditions,

$$\mathbf{v}(x, H) = \mathbf{0} \quad (12a)$$

and

$$\mathbf{v}(x, -H) = \mathbf{0}. \quad (12b)$$

The final form of the solution for the stream function Ψ is listed in Appendix A. Differentiating the stream function with respect to x or y , we obtain the velocity field for the corresponding AC electroosmotic flow. When the applied electric field is a DC field, i.e., $\mathbf{E} = E\mathbf{e}_x$, the stream function for the resulting DC electroosmotic flow is also listed in Appendix B.

RESULTS AND DISCUSSION

Electroosmotic flows with spatially non-uniform zeta potential

We consider AC electroosmotic flow fields under various types of non-uniform zeta potential distributions. The zeta potential distributions used for $f_1(x)$ and $f_2(x)$ in Eqs. (5a) and (5b) are shown in Fig. 2. Five different types of periodic square wave functions are considered. In all cases, the zeta potential varies between $-\zeta$ and ζ . Since the EDL potential ψ satisfies the linearized Poisson-Boltzmann equation, both the electrostatic body force term and the resulting velocity field are linear to ζ . In this work, we present the electroosmotic velocity field normalized with the Smoluchowski velocity ($\epsilon \zeta E/\mu$) so that our velocity results are independent of the value for ζ that appears in $f_1(x)$ and $f_2(x)$.

Electroosmotic velocity fields under various combinations for the zeta potential distributions are shown in Fig. 3. Using the square wave functions shown in Fig. 2, we consider six different pairs for $f_1(x)$ and $f_2(x)$: (a) II-I; (b) I-I; (c) III-I; (d) IV-IV; (e) V-IV; and (f) IV-I. The square wave functions are approximated by summing the first 15 terms in the Fourier series shown in Eqs. (5a) and (5b). We set the dimension of the microchannel as $L/H = 4$ and $\kappa H = 100$. Since the domain in this study has micrometer scale, the condition of $\kappa H = 100$ gave the thickness of EDL of 10 nm (i.e., ~ 1 mM electrolyte concentration) inside $1 \mu\text{m}$ scale microchannel. These physicochemical conditions were practically valid so that we can use $\kappa H = 100$. In addition to this, the size of grid for evaluating flow field was $1/50$ and, thus, the variation inside EDL was negligible in this work. Various types of vortex motions are observed depending on the zeta potential distribution used. Fluid particles not only circulated along vortex flows but also change their direction periodically with the same frequency as the AC electric field. The arrows shown in Fig. 3 represent the velocity vectors determined at $t = 0$. The same velocity vectors will be obtained at $t = 2n\pi/\omega$, and at $t = (2n + 1)\pi/\omega$, the velocity vectors will be the opposites of those shown in Fig. 3. Note that the circular paths observed in Fig. 3 coincide with the streamlines in the electroosmotic flow that would be developed under the same zeta potential distributions but with the DC electric field $\mathbf{E} = E\mathbf{e}_x$. Under

FIG. 2. Various types of zeta potential distributions used for the investigating electroosmotic flow field where ζ_0 is the absolute value of zeta potential.

FIG. 3. AC electroosmotic flow patterns in the two parallel surfaces for zeta potential distributions at lower and upper surface which are given by Fig. 2 of (a) II-I, (b) I-I, (c) III-I, (d) IV-IV, (e) V-IV, and (f) IV-I at $t=0.0$. Here, $\kappa H = 10^2$, $\omega = 10^1$ Hz, $H = 100.0 \mu\text{m}$, $L = 400.0 \mu\text{m}$, and $\zeta_0 = -25$ mV. This flow does not have a net flow in any direction.

the AC electric field $\mathbf{E} = E e^{i\omega t} \mathbf{e}_x$, fluid particles travel back and forth along portions of the streamlines of the DC electroosmotic flow field. The length of the circular path along which a given fluid particle travels back and forth decreases as the frequency of the AC electric field increases. The effects of the AC frequency on the path length of the fluid particle are shown in Fig. 4. Under the AC electroosmotic flow field shown in Fig. 3(b), we study the motion of 20 fluid particles initially placed at $(x = L/4, -H < y < H)$. As we follow the motion of 20 fluid particles for $0 < t < 20$, we mark their positions at every Δt . The results at two different AC frequencies are shown. When $\omega \equiv \omega/2\pi = 10^2$ Hz (the left plot in Fig. 4), the tracer follows only its regular orbit. Since an inertia effect is

FIG. 4. The particle's trajectories of the flow in two parallel surfaces when the non-uniform zeta potential is time-independent. The physical conditions are the same as Figs. 3(a) and 3(b), respectively. Each column has the same ω value (10^2 Hz, 10^0 Hz, DC). The initial positions of tracers are $(0.0, -0.95 + 0.1i)$, $i = 0, 1, \dots, 19$.

neglected in this work, the particle tracer cannot escape the way even if AC electric field is applied. Under the frequency, the tracer could not complete even one cycle of circulation. As ω decreased ($\omega \equiv \omega/2\pi = 10^0$ Hz), the tracer gradually completes the circulation and the third figures show the continuing rotation with DC electric field condition. At a glimpse, the second and the third figures are the same plots. But the particles travel along the circular path counterclockwise and clockwise in the second figure due to the AC electric field. With DC electric field in the third figure, the particles only have a counterclockwise or clockwise direction. Thus, the two figures have totally different basic phenomena.

Since fluid particles in AC electroosmotic flow essentially travel along the streamlines in the DC electroosmotic flow field under the same zeta potential distribution, it is useful to study the DC electroosmotic flows under various physical conditions before we study the AC electroosmotic under the same physical conditions. In addition to the pattern of the zeta potential distribution, the ratio L/H of the microchannel also strongly affects the pattern of streamlines in DC electroosmotic flows. In Fig. 5, we show the streamlines in DC electroosmotic flows at different values of L/H . Under three different conditions for the zeta potential distributions, cases (a) to (c) in Fig. 3, the effects of L/H on the pattern of streamlines are shown. When $L/H = 1$, the vortex near the top surface does not interact with the vortex near the bottom surface. However, as the ratio L/H increases, the vortices near the top and the bottom surfaces tend to merge into a larger vortex when the two vortices are co-rotating. When the ratio L/H is larger than 4, the formation of a larger vortex that fills the gap of the microchannel is clearly observed in cases (a) and (c). Similar results have been reported by Ajdari's work.¹⁷

Electroosmotic flow both with spatially and time-varying non-uniform zeta potential

Since the spatially non-uniform zeta potential unavoidably generates the isolated rotation point, that is elliptic points, the particles could not escape once they are trapped in the elliptic point. Therefore, it is important to turn the elliptic point movable or to reduce the number of elliptic points for increasing mixing quality. An almost non-interacting flow pattern in the first part of Fig. 5 in each row is developed when L becomes shorter than the channel gap. Shown in the first and second row, the two extrema, that is the centers of rotation get closer to merging into one extremum point when L extends. The charge modulation length will determine the number of elliptic points in the flow field. If the two flow patterns are alternatively changed (one may have many elliptic points while the other may have few), we can therefore achieve a complicated flow pattern. In this manner, Qian and Bau induced the chaotic advection by appropriate time modulation of the surface zeta potential with the DC electric field.¹⁸ They concluded that it was sufficient to induce complex flow field exclusively with the DC electric field. Building on their work, we investigate the effects of the AC electric field on the microchannel system that has both spatially and time-varying non-uniform zeta potential. We proceed to change the surface potential in a manner similar to the work by Aref and Balachandar³⁸ and Qian and Bau.¹⁸ As for the time-periodic zeta potential distributions assigned at the top and

FIG. 5. The contour plots of stream function as a function of L/H . Physical conditions are the same as Figs. 3(a)–3(c), respectively. Each column has the same L/H values, 1, 2, 4, and 8.

the bottom surfaces, we use two different types of zeta potential distributions alternately. We assume that the first type of zeta potential distribution is maintained over the initial half period of the time period and the second type is maintained over the time period's second half. Under this method, the total zeta potential can be varied as a function of time with the period T . That is to say, when the flow patterns alternate between A and B, the total flow field would be given by the stream function of

$$\Psi(x, y, t) = h_A(t)\Psi_A(x, y, t) + h_B(t)\Psi_B(x, y, t),$$

where

$$h_A(t) = \begin{cases} 1, & kT < t < kT + \frac{T}{2}, \\ 0, & kT + \frac{T}{2} < t < (k+1)T, \end{cases} \quad (13)$$

and

$$h_B(t) = \begin{cases} 0, & kT < t < kT + \frac{T}{2}, \\ 1, & kT + \frac{T}{2} < t < (k+1)T. \end{cases}$$

Thus, different types of flow field are generated following the zeta potential type in each period. The critical assumption behind Eq. (13) was equilibrium time constant (or charge relaxation time) of EDL $\ll$ any time-scale in this work. The structure of EDL should change with time but one can use pseudo-steady state condition if equilibrium time constant of EDL is much smaller than T or $1/\omega$, which are two time scales in this work. Among various driving physics for restructuring EDL, diffusion is the slowest process. Because typical value of diffusion constant of ion is $O(10^{-9}) \text{ m}^2/\text{s}$, it takes about $O(10^{-9})$ – $O(10^{-5}) \text{ s}$ to reach another steady state. [Typical value of EDL thickness is 10^{-9} – 10^{-7} m and $\tau = L^2/D$, where L is the thickness of EDL and D is the diffusion constant, leading $\tau = O(10^{-18})/O(10^{-9}) = O(10^{-9})$ or $O(10^{-14})/O(10^{-9}) = O(10^{-5})$.] If T or $1/\omega$ is smaller than $O(10^{-5})$ which is the slowest equilibrium time constant of EDL, one

needs to solve full time-dependent salt conservation equations numerically, i.e., $\frac{\partial C^\pm}{\partial t} = D\nabla \cdot (\nabla C^\pm + \frac{ez}{k_B T} C^\pm \nabla \psi)$ together with $-\nabla^2 \psi = ez(C^+ - C^-)$ which eventually gives the charge density ρ^E as a time dependent quantity. Therefore, the mathematical procedures in this work do not violate the physical reality with this assumption.

For the first example, the AC electroosmotic flow fields depicted in Figs. 3(a) and 3(b) are used to test the effects shown in Fig. 6. We maintain the flow field in Fig. 3(a) for the time interval $0 < t < T/2$, switch to the flow field in Fig. 3(b) for the time interval $T/2 < t < T$, and then switch back to the flow field in Fig. 3(a). This process is repeated with a period T . The first flow pattern has two elliptic points, and the second one has four points. In this case, we depict only in the range of $0 < x < L/2$, since the used flow patterns have the geometrical period of $L/2$.

Though there are numerous experimental criteria presenting the quality of mixing such as detecting the concentration of fluorescent dye, there were few theoretical measures. One of the most frequently used theoretical criteria is the Poincaré section. The Poincaré section informs us which flow pattern is more complex. If the section has lots of vacancies, it means the particles move freely in the limited region. But if the section is filled with dots, it presents a flow field that has good mixing quality. We plot the Poincaré section at various frequencies as shown in Fig. 6 with 20 initial insertion points. Each column has the same AC frequency of ω which has the values of 0 Hz, 10^0 Hz , 10^2 Hz , and 10^4 Hz , and each row has the same zeta potential alternation period of T which has the values of 0.1 s, 1 s, and 10 s. The flow is getting complicated as T increases by comparing each row shown in Fig. 6. When T is small, the particles move freely along the regular path. As T increases, the tracer moves beyond the regular path and bursts into the chaotic motion. When T is extremely large, it is obvious that the path becomes regular, which we do not represent since those

FIG. 6. The Poincaré sections of AC electroosmosis when the non-uniform zeta potential is time-periodically changed between flow patterns depicted in Figs. 3(a) and 3(b). The initial positions of particle tracers are the same as Fig. 5. Each row has the same zeta potential changing period (T), 0.1 s, 1 s, and 10 s. And each column has the same ω ; 0.0 Hz (DC electric field), 10^0 Hz, 10^2 Hz, and 10^4 Hz.

results are physically the same as the case of time-independent zeta potential distribution. Comparing the first through the fourth column of Fig. 6, we can observe both unstable and stable flow fields as a function of ω . Although T is high enough to gain good mixing in the DC electric field case in the first plot of the third row, high ω gives an extremely stable flow field shown in the fourth plot of the third row. Essentially, the Poincaré section usually has the closed and unfolded path as shown in the DC cases of the first column in Fig. 6. However, since we have two different time variables, AC frequency and zeta potential modulation, the Poincaré

section has a folded and overlapped path in the case of the AC electric field. Particularly, there are three phase dimensions in the DC case, x , y , and T , as shown by Qian *et al.*, and four phase dimensions in the AC case, x , y , T , and ω , as our work shows. Therefore, it is no wonder that the AC electric field gives more complex flow fields than the DC electric field.

By using another electroosmotic flow pattern shown in Figs. 3(a) and 3(d), Fig. 7 is generated. Each row and column had the same T and ω value of Fig. 6, respectively. While Fig. 3(d) has eight elliptic points, Fig. 3(a) has two elliptic points. Since the elliptic points change

FIG. 7. The Poincaré sections when the varying flow patterns are Figs. 3(a) and 3(d). Other physical quantities are the same as Fig. 6.

further than the previous example, we expect faster and more vigorous mixing than in the case of Fig. 6. We plot the Poincaré section with the same initial insertion points during 2000 time periods. As shown in Fig. 7, a similar effect of the AC frequency in the first example is observed. The AC electroosmotic flow field is quite stable at a high ω value. And as T increases, the flow field is getting complex and good mixing is achieved when T is 10 s in the third row. At first glance, one could not notice the difference between the first (DC case) and the second figure (AC case, $\omega = 10^0$ Hz) of the third row because the Poincaré section does not give the information about time-evolving patterns. From these results, we can observe that the chaotic motions are achieved due to the additional time periodic modulation of surface zeta potential. However, the flow instability can be reduced by adjusting the AC frequency even with non-uniform surface zeta potential.

Quantitative investigation on AC electroosmosis instability

Though we have few theoretical criteria to measure flow complexity, we set up a simple quantitative method using the Poincaré section. In this work, we introduce a simple and easy, but well-described scheme to quantify the flow complexity. Kang and Kwon³⁹ suggested a measure which considered the entropy information of the tracer particles.⁴⁰ The system which has high complexity gives high entropy value and vice versa. This concept also can be applied to determine mixing quality in the micromixer. The number density of particles in finite numbers of discretized cells in the Poincaré section represents the mixing quality. By using the number density, the mixing entropy S is defined as follows:

$$S = - \sum_{i=1}^{N_t} n_i \log n_i. \quad (14)$$

In the definition of mixing entropy, N_t is the total number of discretized areas of Poincaré section, i is the index for the cell, and

n_i is the number density of tracer particle in the i th cell. Since S itself does not have any practical quantity, the normalized degree of mixing σ is introduced as a measure of mixing as follows:

$$\sigma = \frac{S - S_0}{S_{\max} - S_0}. \quad (15)$$

The minimum value of entropy is S_0 when the tracer particles are initially inserted to a mixer. In contrast, when all the cells have an evenly distributed number of particles after flowing through a mixer, S has maximum value, $S_{\max}$. It denotes that σ is 1 in an ideal mixing and 0 at the inlet condition. For example, the region $-H < y < H$, $0 < x < L/2$ was discretized into 100×100 unit rectangular cells in Fig. 7. In only 20 cells, 400 000 tracer particles are initially introduced. Each 20 unit cells have 20 000 particles and another 9980 unit cells have 0 particles. With this condition, $S_0 = -20 \times (20\,000 \times \log 20\,000) = -1.720\,41 \times 10^6$ by using Eq. (14). After complete mixing, we assume that 10 000 unit cells each have 40 particles. Then $S_{\max} = -10\,000 \times (40 \times \log 40) = -640\,824$. For the case of DC at $T = 0.1$, S has a value of $-881\,400$, then $\sigma = (-881\,400 + 1\,720\,410) / (-640\,824 + 1\,720\,410) = 0.7771$ by using Eq. (15). The plot in Fig. 8(a) shows the mixing entropy results from the Poincaré section in Fig. 7 as a function of AC electric field frequency. As ω approaches zero, it means that the AC electric field becomes the DC electric field and it gives a certain quality of the flow complexity. In the plot, we place the result of the DC electric field at $\omega = 10^{-2}$ Hz because we cannot present zero value with a logarithmic scale. As ω increases from the zero, the entropy is gradually increased which is not clearly visible in the plot. We defined the frequency which gives the maximum σ value as an optimal AC frequency value. Moreover, the optimal frequency σ is getting lower and finally it reaches a non-moving circumstance (over $\omega = 10^4$ Hz). For better demonstration, we calculated area fraction (black area/white area) from the Poincaré plot as shown in Fig. 8(b). It clearly showed that there is an optimum frequency around O (10^{-1}) to O (1) Hz for

FIG. 8. The results of (a) normalized mixing entropy and (b) area fraction (black/white) shown in Fig. 7: x-axis as AC frequency is logarithmically scaled.

enhancing mixing and higher frequency higher than 100 Hz would suppress the mixing. These results were in-line with previous experimental work that the mixing efficiency varied as a function of frequency.¹⁰ Since the same plot is almost obtained from the first example of the Poincaré section shown in Fig. 6, we do not show the plot. Experimental researchers can use this result with various physical quantities for their own experimental expediency.

SUMMARY AND CONCLUSION

The characteristics of the DC electroosmosis have been well-established in the past. However, the electroosmotic experiments are usually conducted using the DC electric field accompanied with the AC electric field. The DC electric field is used for the purpose of net flow transport, while the AC electric field gives more convenient experimental conditions such as preventing the unnecessary electrolysis and unpredictable Joule heating. Accordingly, the effect of the AC electric field to the electroosmotic flow pattern should be investigated. Here, we describe the AC electroosmotic flow with spatially and time-periodically non-uniform zeta potential distribution under the rigorous consideration of the EDL potential. To obtain the solution to this problem, we use the Debye-Hückel approximation⁴¹ and neglect the deformation of the counter-ion cloud.⁴² However, this analysis sufficiently proves the possibility of controlling electroosmotic flow instability using the frequency of applied AC electric field. We track the motion of passive tracer particles over many time periods. The cases were categorized as follows:

- (1) DC electric field + spatially non-uniform zeta potential (no temporal variation): See the DC case in Fig. 4 (3rd column). Tracers trapped in their loop (i.e., island) so that there is no mixing.
- (2) AC electric field + spatially non-uniform zeta potential (no temporal variation): See $\omega = 100$ Hz and 1 Hz case in Fig. 4 (1st and 2nd column). Tracers trapped in their roundtrip path so that there is no mixing.
- (3) DC electric field + time-periodic zeta potential (no spatial variation): If there is no special variation of zeta potential, the flow field should be plug type flow (i.e., no circulation) with just oscillation as a function of frequency of time-periodic zeta potential, regardless of DC or AC electric field. Thus, there is no mixing in this case.
- (4) AC electric field + time-periodic zeta potential (no spatial variation): Similar to case (iii), there is no circulation so that the mixing does not occur.
- (5) AC electric field + time-periodic spatially non-uniform zeta potential: This is the case of Figs. 6 and 7 and the mixing efficiency was shown in Fig. 8.

In summary, time periodic spatially non-uniform zeta potential is essential to obtain (or control) good mixing efficiency. AC electric field can enhance the efficiency. From these results, we conclude that extraordinary stable flow field is achieved at the high frequency of the AC electric field even if there is a time-periodic modulation of zeta potential distribution. In the range of the AC frequency from 10^{-1} Hz to 1 Hz, the AC electroosmotic flow gives rise to almost the same or slightly better mixing quality than the DC electroosmotic flow without consideration of zeta potential modulation. These results are in-line with previous experimental demonstration^{8,10,11} that the frequency plays a critical role of controlling the mixing in

microfluidic environment. Note that direct (or quantitative) comparisons with previous experimental literature were difficult mainly because practical electroosmotic micromixers usually require net flow (i.e., continuous flow domain), while theoretical analysis has usually focused on the case of no net flow. Thus, the patterns of electroosmotic flows were completely different in experimental study and analytic study. However, one quantitative comparison can be given for the frequency of AC electric field or alternation of zeta potential. Previous experimental work also reported that there is an optimal frequency of alternating non-uniform zeta potential.¹⁰

Unstable flow patterns are unquestionably required for the sample mixing devices. On the other hand, the stable flow patterns favor the sample separation, extraction, and focusing which require quiescent control of the electroosmotic flow. Furthermore, when both stable and unstable electroosmotic flow fields are simultaneously required, one may easily control the stability by just adjusting the AC frequency. Although the ideal electroosmotic flow usually gives plug and stable flow, it is difficult to achieve the perfect plug flow because of the unavoidable distortion of channel structure or natural surface defects by experimental deficient. Applying high frequency of the AC electric field can help to produce highly stable flow patterns despite the deficiency without any additional devices or geometrical structures.

This work proposes a concept that can allow one to control the electroosmotic flow in microfluidic components such as micromixer, micro-separator, or micro-extractor by adjusting the frequency of the AC electric field. The analytical solution that we obtained here can be used as meaningful methods to achieve more controllable electroosmotic flow in microfluidic systems.

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APPENDIX A: STREAM FUNCTION OF AC ELECTROOSMOTIC FLOW

The details of the analytical solution of the stream function are as follows:

$$e^{i\omega t}\Psi(x, y) = \frac{\alpha}{\kappa^2(\kappa^2\nu - i\omega)} \left\{ \frac{\nu}{i\omega} \left(\hat{A}_0 \cosh \sqrt{\frac{i\omega}{\nu}} y + \hat{B}_0 \sinh \sqrt{\frac{i\omega}{\nu}} y \right) + \kappa(A_0 \sinh \kappa y + B_0 \cosh \kappa y) + \sum_{n=1}^{\infty} [(\bar{A}_n \cosh \lambda_n y + \hat{A}_n \cosh \hat{\mu}_n y + \mu_n B_n \cosh \mu_n y) \cos \lambda_n x + (\bar{B}_n \sinh \lambda_n y + \hat{B}_n \sinh \hat{\mu}_n y + \mu_n A_n \sinh \mu_n y) \cos \lambda_n x + (\bar{C}_n \cosh \lambda_n y + \hat{C}_n \cosh \hat{\mu}_n y + \mu_n D_n \cosh \mu_n y) \sin \lambda_n x + (\bar{D}_n \sinh \lambda_n y + \hat{D}_n \sinh \hat{\mu}_n y + \mu_n C_n \sinh \mu_n y) \sin \lambda_n x] \right\}, \quad (A1)$$

where Ψ is the stream function and $\hat{\mu}_n = (\lambda_n^2 + i\omega/\nu)^{1/2}$. The AC electroosmotic velocity field is obtained using the definition of stream function as Eqs. (8a) and (8b)

The eight unknown coefficients are determined by the no slip boundary conditions [Eqs. (12a) and (12b)]. The condition gives eight linearly solvable equations from two velocity components, two Eigen functions at both plates. The values of the coefficients are

$$\hat{A}_0 = -B_0 \kappa^2 \sqrt{\frac{i\omega}{\nu}} \sinh \kappa H \operatorname{csch} \sqrt{\frac{i\omega}{\nu}} H, \quad (\text{A2.1})$$

$$\hat{B}_0 = -A_0 \kappa^2 \sqrt{\frac{i\omega}{\nu}} \cosh \kappa H \operatorname{sech} \sqrt{\frac{i\omega}{\nu}} H, \quad (\text{A2.2})$$

$$\hat{A}_n = B_n \mu_n \frac{(-\lambda_n \cosh \mu_n H \sinh \lambda_n H + \mu_n \cosh \lambda_n H \sin \mu_n H)}{(\lambda_n \cosh \hat{\mu}_n H \sinh \lambda_n H - \hat{\mu}_n \cosh \lambda_n H \sin \hat{\mu}_n H)}, \quad (\text{A2.3})$$

$$\hat{B}_n = -A_n \mu_n \frac{(\mu_n \cosh \mu_n H \sinh \lambda_n H - \lambda_n \cosh \lambda_n H \sin \mu_n H)}{(\hat{\mu}_n \cosh \hat{\mu}_n H \sinh \lambda_n H - \lambda_n \cosh \lambda_n H \sin \hat{\mu}_n H)}, \quad (\text{A2.4})$$

$$\hat{C}_n = D_n \mu_n \frac{(-\lambda_n \cosh \mu_n H \sinh \lambda_n H + \mu_n \cosh \lambda_n H \sin \mu_n H)}{(\lambda_n \cosh \hat{\mu}_n H \sinh \lambda_n H - \hat{\mu}_n \cosh \lambda_n H \sin \hat{\mu}_n H)}, \quad (\text{A2.5})$$

$$\hat{D}_n = -C_n \mu_n \frac{(\mu_n \cosh \mu_n H \sinh \lambda_n H - \lambda_n \cosh \lambda_n H \sin \mu_n H)}{(\hat{\mu}_n \cosh \hat{\mu}_n H \sinh \lambda_n H - \lambda_n \cosh \lambda_n H \sin \hat{\mu}_n H)}, \quad (\text{A2.6})$$

$$\bar{A}_n = B_n \mu_n \frac{(-\mu_n \cosh \hat{\mu}_n H \sinh \mu_n H + \hat{\mu}_n \cosh \mu_n H \sin \hat{\mu}_n H)}{(\lambda_n \cosh \hat{\mu}_n H \sinh \lambda_n H - \hat{\mu}_n \cosh \lambda_n H \sin \hat{\mu}_n H)}, \quad (\text{A2.7})$$

$$\bar{B}_n = A_n \mu_n \frac{(-\hat{\mu}_n \cosh \hat{\mu}_n H \sinh \mu_n H + \mu_n \cosh \mu_n H \sin \hat{\mu}_n H)}{(\hat{\mu}_n \cosh \hat{\mu}_n H \sinh \lambda_n H - \lambda_n \cosh \lambda_n H \sin \hat{\mu}_n H)}, \quad (\text{A2.8})$$

$$\bar{C}_n = D_n \mu_n \frac{(-\mu_n \cosh \hat{\mu}_n H \sinh \mu_n H + \hat{\mu}_n \cosh \mu_n H \sin \hat{\mu}_n H)}{(\lambda_n \cosh \hat{\mu}_n H \sinh \lambda_n H - \hat{\mu}_n \cosh \lambda_n H \sin \hat{\mu}_n H)}, \quad (\text{A2.9})$$

$$\bar{D}_n = C_n \mu_n \frac{(-\hat{\mu}_n \cosh \hat{\mu}_n H \sinh \mu_n H + \mu_n \cosh \mu_n H \sin \hat{\mu}_n H)}{(\hat{\mu}_n \cosh \hat{\mu}_n H \sinh \lambda_n H - \lambda_n \cosh \lambda_n H \sin \hat{\mu}_n H)}. \quad (\text{A2.10})$$

APPENDIX B: STREAM FUNCTION OF DC ELECTROOSMOTIC FLOW

We solve the DC electroosmosis system on the purpose of comparing the AC electric field case. The solution method is also the stream function analysis and the separation of variable. Details are as follows:

$$\begin{aligned} \Psi(x, y) = & \frac{\alpha}{\nu \kappa^4} \left\{ \kappa (A_0 \sinh \kappa y + B_0 \cosh \kappa y) \right. \\ & + \sum_{n=1}^{\infty} \left[(\bar{A}_n \cosh \lambda_n y + \mu_n B_n \cosh \mu_n y + \tilde{A}_n y \cosh \lambda_n y) \cos \lambda_n x \right. \\ & + (\bar{B}_n \sinh \lambda_n y + \mu_n A_n \sinh \mu_n y + \tilde{B}_n y \sinh \lambda_n y) \cos \lambda_n x \\ & + (\bar{C}_n \cosh \lambda_n y + \mu_n D_n \cosh \mu_n y + \tilde{C}_n y \cosh \lambda_n y) \sin \lambda_n x \\ & \left. \left. + (\bar{D}_n \sinh \lambda_n y + \mu_n C_n \sinh \mu_n y + \tilde{D}_n y \sinh \lambda_n y) \sin \lambda_n x \right] \right\}, \quad (\text{B1}) \end{aligned}$$

$$\text{where } \bar{A}_n = 2B_n \mu_n \frac{[-\cosh \mu_n H (H \lambda_n \cosh \mu_n H + \sinh \mu_n H) + H \mu_n \sinh \lambda_n H \sinh \mu_n H]}{(2H \lambda_n + \sinh 2\lambda_n H)}, \quad (\text{B2.1})$$

$$\bar{B}_n = 2A_n \mu_n \frac{[H \lambda_n \sinh \lambda_n H \sinh \mu_n H + \cosh \lambda_n H (-H \mu_n \cosh \mu_n H + \sinh \mu_n H)]}{(2H \lambda_n - \sinh 2\lambda_n H)}, \quad (\text{B2.2})$$

$$\bar{C}_n = 2D_n \mu_n \frac{[-\cosh \mu_n H (H \lambda_n \cosh \mu_n H + \sinh \mu_n H) + H \mu_n \sinh \lambda_n H \sinh \mu_n H]}{(2H \lambda_n + \sinh 2\lambda_n H)}, \quad (\text{B2.3})$$

$$\bar{D}_n = 2C_n \mu_n \frac{[H \lambda_n \sinh \lambda_n H \sinh \mu_n H + \cosh \lambda_n H (-H \mu_n \cosh \mu_n H + \sinh \mu_n H)]}{(2H \lambda_n - \sinh 2\lambda_n H)}, \quad (\text{B2.4})$$

$$\tilde{A}_n = 2A_n \mu_n \frac{(\mu_n \cosh \mu_n H \sinh \lambda_n H - \lambda_n \cosh \lambda_n H \sinh \mu_n H)}{(2H \lambda_n - \sinh 2\lambda_n H)}, \quad (\text{B2.5})$$

$$\tilde{B}_n = 2B_n \mu_n \frac{(\lambda_n \cosh \mu_n H \sinh \lambda_n H - \mu_n \cosh \lambda_n H \sinh \mu_n H)}{(2H \lambda_n + \sinh 2\lambda_n H)}, \quad (\text{B2.6})$$

$$\tilde{C}_n = 2C_n\mu_n \frac{(\mu_n \cosh \mu_n H \sinh \lambda_n H - \lambda_n \cosh \lambda_n H \sinh \mu_n H)}{(2H\lambda_n - \sinh 2\lambda_n H)}, \quad (\text{B2.7})$$

$$\tilde{D}_n = 2D_n\mu_n \frac{(\lambda_n \cosh \mu_n H \sinh \lambda_n H - \mu_n \cosh \lambda_n H \sinh \mu_n H)}{(2H\lambda_n + \sinh 2\lambda_n H)}. \quad (\text{B2.8})$$

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