Electroosmotic Flow in Heterogeneous Microchannels

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INTRODUCTION

Studies of electroosmotic flow in microchannels are of great interest to engineers and scientists in the emerging microfluidics and biochip areas. Examples include miniaturized flow injection analysis systems (1, 2), DNA amplification, clean up, separation, and detection (3, 4). Most surfaces obtain the electrical charge when they are brought into contact with a polar medium. This may be caused by ionization, ion adsorption, or ion dissociation. The surface charge, in turn, influences the ion distribution in the microchannel, forming the electrical double layer (EDL) (5). If an electrical field is applied tangentially to the EDL, an electrical body force is exerted on the excess counter-ions in the diffuse layer of the EDL. The ions will move under the influence of the applied electrical field, pulling the liquid with them. The liquid movement is carried through to the rest of the liquid in the channel by viscous force, resulting in an electroosmotic flow.

The driving force for the electroosmotic flow in microchannels depends on the local net-charge density and the strength of the externally applied electrical field. The net-charge density is dependent on the EDL field and hence on the zeta potential, ζ; the electroosmotic flow behavior in turn is dependent on the zeta potential. Generally, the zeta potential is a function of the ionic valence, the ionic concentration of the electrolyte solution, and the surface properties of the microchannel wall. For a system with a simple electrolyte solution and a homogeneous channel wall, the zeta potential is considered constant. However, in practice, the liquids involved in various biochips using the electroosmotic pumping to transport liquid or perform other operations are solutions containing biological particles (e.g., DNA and protein). The adhesion of these particles to the channel wall will cause the nonuniform zeta potential along the channel, depending on the distribution and the extent of the adhered particles on the wall. Therefore, the understanding of the flow behavior in such a situation is important for manipulating the flow in biochip devices.

Several researchers (6–10) have investigated the effects of variable zeta potential on electroosmotic flow. Anderson and Idol (6) developed an infinite-series solution for flow in a cylindrical microchannel with a zeta potential varying as a cosine or sine function in the flow direction. Long et al. (7) considered the similar type of zeta potential variation in planar and cylindrical capillaries and developed approximate solutions by considering the heterogeneity as the small perturbations to the velocity. Herr et al. (8) experimentally investigated the flow field of the electroosmotic flow and the sample dispersion rate in open capillaries with a step change in zeta potential (i.e., ζ1 = 0 and ζ2 > 0) and presented a simple model for the fluid velocity and the dispersion rate. It should be noted that the zeta potential change resulting from bioadhesion varies over a range of values along the microchannel. This may bring in more complex effects on electroosmotic flow than the system considered in Ref. (8). Stroock et al. (9) studied two types of surface-charge change in rectangular channels. One is the surface-charge variation along a direction perpendicular to the applied electrical field, which generates a two-directional electroosmotic flow. Another is the surface-charge variation along a direction parallel to the electrical field, which generates a recirculating flow. Potoček et al. (10) investigated the influence of the discrete step change in zeta potential (similar to Ref. (8)) on the velocity profile of the electroosmotic flow by considering the zeta potential change between two steps. The above-mentioned works all assumed thin electrical double layer and, hence, did not completely consider the effects of EDL field and the variation of the EDL filed on the velocity field, except using the electroosmotic velocity as the boundary condition. The thin EDL assumption is valid only for systems...
with high ionic concentrations. It is known that the electrical body force responsible for electroosmotic flow depends on the local net-charge density. Therefore, a more general treatment to the effects of zeta potential or EDL variation on electroosmotic flow should consider the local net-charge density change along the channel. This requires solving for the Poisson–Boltzmann equation, which governs the EDL field.

In this work, we examine the numerical solutions of electroosmotic flow in a cylindrical microchannel with a nonuniform zeta-potential distribution. Without assuming a thin EDL field, the nonlinear Poisson–Boltzmann equation and the momentum equation were solved numerically. The influences of the heterogeneous section size and the direction of the zeta-potential change on the flow rate, the velocity profile, and the induced-pressure distribution are discussed. In this paper, we present two cases of electroosmotic flow in a heterogeneous microchannel 10 cm long. In the first case, the microchannel has 100 sections equal in size and the zeta potential linearly changes from 10 to 200 mV over the 100 sections. In the second case, the microchannel has 100 sections unequal in size and the zeta potential linearly changes from 10 to 200 mV over the 100 sections. In this case, the section size (i.e., the length of the section) is determined by the equation

\[
L_i = f L_{i-1}, \tag{1}
\]

where \(L_i\) is the length of the \(i\)th section and \(f\) is a constant chosen as 1.1. Since the objective here is to investigate qualitatively the effects of the heterogeneous section size on the electroosmotic flow behavior, the specific choice of the function in Eq. [1] will not affect the generality of the results.

**ELECTRICAL DOUBLE LAYER IN CYLINDRICAL MICROCHANNEL**

According to the theory of electrostatics, the relationship between the electrical potential, \(\psi(r)\), and the net-charge density per unit volume, \(\rho_e\), at any point in the liquid is described by the Poisson equation

\[
\frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \psi}{\partial r} \right) = -\frac{\rho_e}{\varepsilon \varepsilon_0}, \tag{2}
\]

where \(\varepsilon\) is the dielectric constant of the solution and \(\varepsilon_0\) is the permittivity of vacuum. Assuming that the equilibrium Boltzmann distribution is applicable, the ion number concentration per unit volume in an electrolyte solution is of the form

\[
n_i = n_{i,\infty} \exp \left( \frac{z_i e \psi}{k_B T} \right), \tag{3}
\]

where \(n_{i,\infty}\) and \(z_i\) are the bulk ionic concentration and the valence of type \(i\) ion, respectively, \(e\) is the charge of a proton, \(k_B\) is Boltzmann’s constant, and \(T\) is the temperature. The net volumetric charge density, \(\rho_e\), is proportional to the concentration difference between cations and anions, for symmetric electrolyte solution such as KCl (\(z : \tilde{z} = 1 : 1\)) solution, given by

\[
\rho_e(r) = e \sum z_i n_{i,\infty} \exp \left( \frac{z_i e \psi}{k_B T} \right) = -2 \tilde{z} e n_{\infty} \sinh \left( \frac{\tilde{z} e \psi}{k_B T} \right). \tag{4}
\]

Substituting the equation for the net-charge density into the Poisson equation [2], and introducing the dimensionless variables

\[
\psi^* = \frac{\tilde{z} e \psi}{k_B T}, \quad r^* = \frac{r}{a},
\]

where \(a\) is the radius of the microchannel, the nondimensional Poisson–Boltzmann equation can be written as

\[
\frac{1}{r^*} \frac{\partial}{\partial r^*} \left( r^* \frac{\partial \psi^*}{\partial r^*} \right) = \kappa^2 a^2 \sinh(\psi^*), \tag{5}
\]

where \(\kappa\), the Debye–Hückle parameter, is defined as

\[
\kappa = \left( \frac{2 n_{\infty} \tilde{z}^2 e^2}{\varepsilon \varepsilon_0 k_B T} \right)^{1/2}
\]

and \(1/\kappa\) is the characteristic thickness of the EDL. Because of the symmetry of the EDL field in the cylindrical microchannel, Eq. [5] is subjected to the nondimensional boundary conditions

\[
\begin{align}
r^* &= 0, & \frac{\partial \psi^*}{\partial r^*} &= 0, \tag{7a} \\
r^* &= 1.0, & \psi^* &= \frac{\tilde{z} e \xi}{k_B T}, \tag{7b}
\end{align}
\]

where the zeta potential, \(\xi\), is a measurable electrical potential at the shear plane (i.e., the boundary between the compact layer and the diffuse layer of the EDL). The equation of electrical potential is a nonlinear partial differential equation that must be solved numerically. Taylor series expansion was used to linearize the nonlinear source term on the right-hand side of Eq. [5] as

\[
\sinh \psi^* = \sinh \psi^* + \psi^* \cosh \psi^* - \psi^* \cosh \psi^* - \psi^* \cosh \psi^* - \psi^* \cosh \psi^*, \tag{8}
\]

where \(\psi^*\) is the value for \(\psi^*\) obtained in the previous iteration (11). A numerical finite difference scheme was used to discretize the governing differential equation and the resulting system of algebraic equations was solved using the Gauss–Seidel iterative technique, with successive overrelaxation employed to improve the convergence time (12). Since the electrical potential field varies dramatically within a small distance of the channel walls, variable grid spacing (13) was employed to ensure that the grid spacing was refined enough to capture the sharp gradients. Once the electrical potential field \(\psi^*(r^*)\) has been found, the net-charge density can be determined by Eq. [4].
ELECTROOSMOTIC FLOW FIELD IN THE CYLINDRICAL MICROCHANNEL

The motion of an aqueous electrolyte solution in the microchannel is governed by the Navier–Stokes equations for incompressible fluid flow,

$$\rho \left[ \frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right] = -\nabla P + \mu \nabla^2 \mathbf{u} + E \rho_e. \quad [9]$$

where \( \mathbf{u} \) is the velocity vector, \( \mu \) is the viscosity, \( \rho \) is the density of the fluid, \( \nabla P \) is the induced-pressure gradient (as discussed later), \( \rho_e \) is the local net-charge density, and \( E \) is the electrical field strength applied to the microchannel. If we assume that the flow is steady and fully developed, then the velocity component is described by

$$u_r = 0, \quad [10a]$$
$$u_\theta = 0, \quad [10b]$$
$$u_z = u_z(r). \quad [10c]$$

With this assumption, the unsteady term and the inertial term on the left-hand side of Eq. [9] drop out and the equation of motion is reduced to

$$\frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial u_r}{\partial r} \right) = -\nabla P + E \rho_e. \quad [11]$$

Substituting Eq. [4] for the net-charge density into Eq. [11] and introducing the following nondimensional variables,

$$u^*_z = \frac{u_z}{U}, \quad r^* = \frac{r}{a},$$

where \( U \) is an arbitrary reference velocity, the nondimensional equation of motion can be obtained:

$$\frac{1}{r^*} \frac{\partial}{\partial r^*} \left( r^* \frac{\partial u^*_z}{\partial r^*} \right) = \frac{2n \varepsilon_e a^2}{\mu U} E \sinh(\psi^*) + \frac{a^2}{\mu U} \frac{\partial p}{\partial z}. \quad [12]$$

Equation [12] is subjected to the no-slip and symmetric boundary conditions:

$$r^* = 0, \quad \frac{\partial u^*_z}{\partial r^*} = 0, \quad [13a]$$
$$r^* = 1.0, \quad u^*_z = 0. \quad [13b]$$

CONSIDERATION OF HETEROGENEOUS SECTIONS

For the electroosmotic flow of a homogeneous liquid through different sections of a microchannel, certain conditions must be satisfied. Because of the uniform bulk liquid properties along the flow path, and assuming negligible effects of the surface conductance, the electrical current and the applied field strength are constant axially. The remaining key condition is the constant volume flow rate or the continuity condition. Consider a heterogeneous channel with two equal-size sections, each with a different zeta potential and the same pressure at the both ends of the channel. It can be understood easily that, if the zeta potential is higher, the EDL field will be stronger and hence the electroosmotic flow rate will be larger. If, for example, the high zeta-potential section is in the downstream and the low zeta-potential section is in the upstream, the liquid in the downstream section would have a higher electroosmotic velocity, and the liquid in the upstream section would have a lower velocity. This will cause different flow rate in different sections and hence violate the continuity condition. The practical solution is that a vacuum tends to form between these two sections since the liquid in the downstream section is moving faster than that in the upstream section. Because of the same pressure (i.e., atmospheric pressure) at the both ends of the channel, a negative pressure is induced between these two sections. This induced negative pressure will generate a positive pressure gradient for the downstream section to slow the flow and a negative pressure gradient for the upstream section to increase the flow rate. In this way, the continuity condition will be satisfied. This is also why Eq. [12] has an induced-pressure gradient term.

The induced-pressure gradient will introduce more complexity into the numerical solution. First, the Possion–Boltzmann equation has to be solved to find the electrical-potential distribution in each section along the channel, \( \psi(r, z) \). Once the electrical potential is found, the net-charge density can be determined by Eq. [4]. Second, a guess value of the induced-pressure gradient profile is chosen for the first 99 sections (from left to right). With this guess value, the equation of motion can be solved for these sections and the volumetric flow rate in these sections can be determined by

$$Q_i = \int u_i(r) \cdot 2\pi r \, dr, \quad [14]$$

where \( Q_i \) is the volumetric flow rate and \( u_i(r) \) is the local velocity for the \( i \)-th section, respectively. During this process, the pressure gradient for the first section is fixed and the pressure gradients for the other sections are adjusted to satisfy the continuity condition:

$$Q_i = Q_{i-1}, \quad i = 2, 3, \ldots, 99. \quad [15]$$

Finally, because of the same pressure at the both ends of the channel, the pressure gradient in the last section has to be determined by the condition

$$\nabla P_{100} = -\frac{1}{L_{100}} \sum_{i=1}^{99} \nabla P_i \cdot L_i, \quad [16]$$

where \( \nabla P_i \) is the pressure gradient of the \( i \)-th section. With this pressure gradient, the equation of motion can be solved for the last section and the volumetric flow rate for this section can be
determined by Eq. [14]. The continuity condition, \( Q_1 = Q_{100} \), has to be checked again at this moment. If the continuity condition is not satisfied, the pressure gradient for the first section has to be adjusted and the above procedure repeated until the continuity condition is satisfied.

RESULTS AND DISCUSSIONS

The above equations and the matching boundary conditions for the EDL field and the flow field were solved numerically. KCl electrolyte solution is used as the testing liquid and the following physical properties of KCl electrolyte solution were used: \( \varepsilon = 80, \varepsilon_0 = 8.854 \times 10^{-12} \text{ CV}^{-1} \text{ m}^{-1}, \) and \( \mu = 0.90 \times 10^{-3} \text{ kg m}^{-1} \text{s}^{-1} \) (14). An arbitrary reference velocity of \( U = 1 \) mm/s was used to nondimensionalize the velocity.

Figure 1 shows the dependence of the electroosmotic flow rate on the diameter of the microchannel. As the diameter increases, the flow rate increases. The variations of the section size and the trend of the zeta-potential change in the flow direction will not affect this result. As discussed previously, the velocity of the electroosmotic flow and hence the flow rate depend on the zeta potential. In this paper, the zeta potential changes from 10 to 200 mV along the channel. As clearly seen from Fig. 1, for the system with equal-size sections, the flow rate generated with the average zeta potential, the average value of the maximum and the minimum zeta potentials, is the same as the flow rate for the case with a linearly increasing zeta-potential distribution and the case with a linearly decreasing zeta-potential distribution in the flow direction. Therefore, for the case of equal section size, the average zeta potential can be used to evaluate the electroosmotic flow rate in a microchannel with a nonuniform zeta-potential distribution. For comparison, the flow rates for homogeneous microchannels with a zeta potential of 200 and 10 mV, respectively, are also plotted in Fig. 1.

However, for the case of unequal section size, the flow rates are different when the trend (i.e., increase or decrease) of the zeta-potential change along the flow direction changes. When the zeta potential linearly decreases in the flow direction, the flow rate is smaller than that in the system with a linearly increasing zeta-potential distribution in the flow direction. This is because when the zeta potential decreases in the flow direction, the lower zeta potential takes a large portion of the microchannel as the section size increases in the flow direction (i.e., \( L_1 = 7.26 \times 10^{-4} \) mm, \( \zeta_1 = 200 \) mV; \( L_{100} = 9.1 \) mm, \( \zeta_{100} = 10 \) mV). This means a weaker EDL field in this portion of the channel. On the other hand, in the system with an increasing zeta-potential distribution in the flow direction, the higher zeta-potential sections occupy a large portion of the channel (i.e., \( L_1 = 7.26 \times 10^{-4} \) mm, \( \zeta_1 = 10 \) mV; \( L_{100} = 9.1 \) mm, \( \zeta_{100} = 200 \) mV). This implies a stronger EDL field in this portion of the channel. The flow rate depends on the EDL field and hence will be smaller in the system with a decreasing zeta-potential distribution in comparison with that in the system with an increasing zeta-potential distribution. The influence of the electrical field strength on the flow rate exhibits a similar behavior, as shown in Fig. 2 and can be understood similarly.

Figure 3 shows the velocity field (upper) and the induced pressure field (lower) in a microchannel with a linearly decreasing zeta-potential distribution and the equal-size sections. For a simple electroosmotic flow in a microchannel with uniform zeta potential, the pluglike velocity profile is expected. However, if the zeta potential is nonuniform, such as specified in this work, the net-charge density within the liquid varies axially. Meanwhile, the applied electrical field strength (V/m), which depends on the electrical current and the conductivity of the electrolyte solution, is constant axially. Consequently, the electrical body force generating the electroosmotic flow, which depends on the net-charge density and the electrical field strength, is different from section to section.
This would imply different volumetric flow rates for different sections. For example, if the zeta potential is lower in a section, the electrical force exerted on the fluid would be smaller and hence the generated flow rate is lower. For an incompressible liquid, the continuity condition requires the same flow rate throughout the microchannel. In order to achieve the same flow rate as that in the next section, with a higher zeta potential, a negative pressure gradient (the pressure decreases in the flow direction) is introduced to increase the flow rate. As seen in Fig. 3, the pressure starts decreasing from a maximum pressure to the atmospheric pressure at the exit when the zeta potential is lower than 105 mV, the average value of the maximum and the minimum zeta potential of the microchannel. The nearly parabolic velocity profile was found for the downstream sections with lower zeta potentials (e.g., \( \zeta = 10 \) mV), since the dominant driving force in these sections is the induced-pressure gradient. For the upstream sections with higher zeta potentials, because of the presence of the negative-pressure gradient in the downstream sections and the same atmospheric pressure at the both ends of the microchannel, a positive-pressure gradient (the pressure increases in the flow direction) must exist to slow down the flow in these upstream sections. As shown in Fig. 3, for the sections with higher zeta potentials (e.g., \( \zeta = 200 \) mV), the electroosmotic velocity profile is distorted by the positive-pressure gradient.

If the zeta potential increases in the flow direction, the distorted electroosmotic velocity profiles in the high-zeta-potential sections, and the nearly parabolic velocity profiles in the low-zeta-potential sections were also found. As shown in Fig. 4, the pressure distribution in the flow direction is different from that shown in Fig. 3, since the directions of the zeta-potential variation in these two cases are opposite. The variation of the induced pressure in this case can be understood in a similar way.

However, for a microchannel with unequal-size sections (the section size increases in the flow direction in this paper), when the zeta potential decreases from 200 to 10 mV in the flow direction, the electroosmotic velocity profile in the higher zeta-potential sections (e.g., \( \zeta = 200 \) mV) is distorted more significantly, as shown in Fig. 5, in comparison with that in the system with equal-size sections. This is because a major portion of the channel has lower zeta potentials in this case and hence the flow rate is smaller than that of the equal-section-size system, as seen in Fig. 1. Therefore, for the sections with the same high zeta potentials, in order to reach this small flow rate, a bigger induced-pressure gradient is required, resulting in the more distorted velocity profile.

Figure 6 shows that the induced-pressure field depends on the direction of the zeta-potential variation and the section size distribution. As discussed earlier, for the sections with higher zeta potentials, the induced-pressure gradient is positive (the pressure increases) and for the sections with lower zeta potentials, the induced-pressure gradient is negative (the pressure decreases). Therefore, when the zeta potential decreases from 200 to 10 mV in the flow direction, the pressure first increases from the atmospheric pressure until the zeta potential reaches a specific value, and then the pressure decreases from a maximum value to the atmospheric pressure at the exit. When the zeta potential increases from 10 to 200 mV, the pressure decreases first from the atmospheric pressure until the zeta potential reaches a specific value, and then the pressure increases from a minimum value to
The atmospheric pressure at the exit. This specific zeta potential depends on the section size distribution. For the case of equal section size, this specific zeta potential is the average value of the maximum and the minimum zeta potentials; however, for the case of unequal section size, this value is between the maximum and the minimum zeta potential and can be determined by the numerical results.

Also in Fig. 6, we can see that the induced pressure in the case of equal section size is bigger than that in the case of unequal section size. This is because for the unequal-section-size
The zeta potential changes more quickly over a very small distance. For example, in the case of decreasing zeta potential, the zeta potential decreases from 200 to 105 mV over 0.845% of the total length of the microchannel. Therefore, the variation of the zeta potential over almost the total length of the microchannel (i.e., 99.155% of the total length) is smaller (i.e., from 105 to 10 mV) in comparison with that in the case of equal section size, where the variation of the zeta potential over the same distance is approximately 190 mV. Recalling that the induced-pressure gradient is introduced because of the nonuniform zeta-potential distribution, it is easy to understand that the smaller the variation of the zeta potential, the smaller the induced-pressure gradient.

CONCLUSION

The electroosmotic flow in a microchannel with nonuniform zeta potential is studied in this paper. The results show that the different types of velocity profiles in the upstream and the downstream sections are caused by the nonuniform zeta-potential distribution. The effects of the unequal section size and the direction of the zeta-potential change in the flow direction on the induced-pressure distribution are also demonstrated. The induced-pressure distribution is different when the trend of the zeta-potential variation in the flow direction changes. For the unequal-section-size system, the induced pressure is smaller than that in the system of equal section size, because the variation of the zeta potential over almost the total length of the channel in this case is smaller than that in the system with equal-size sections. Overall, the results of theoretical model simulation of electroosmotic flow in heterogeneous microchannels revealed possible effects on bioadhesion in microchannels on the electroosmotic flow in biochip devices.

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