Electrokinetic sample transport in a microchannel with spatial electrical conductivity gradients

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Abstract

Studies of the sample transport in a microchannel with the electrical conductivity gradient are critical to develop techniques for on-chip sample transport control. A numerical model presented in this paper, consisting of the electrical potential equation, full Navier–Stokes equation and species conservation equation, is used to simulate sample transport in a microchannel with the consideration of the conductivity gradient. There are two situations studied here, sample pumping (where sample separation is minimized by employing a high-conductivity buffer in the sample region), and sample stacking (where sample separation is expedited by using a low-conductivity buffer as the sample carrier). The effects of applied electrical potential, sample diffusion coefficient and the ratio of conductivity of the driving buffer over the sample carrying buffer are investigated by using the developed model.

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1. Introduction

Microfluidic chips have drawn significant attention in the past decade due to their wide range of applications in biomedical and chemical analysis such as capillary electrophoresis [1,2], flow cytometry [3,4], DNA amplification [5,6], and protein analysis [7,8]. In most of these applications, sample manipulation is crucial to the overall performance of the chip. Many studies have been conducted to improve liquid manipulation techniques and chip performance. For example, Vijayendran et al. [9] reported the effects of analyte transport in a poly(dimethylsiloxane) PDMS microfluidic chip on the performance of the surface-based biosensor, which was integrated with this microfluidic chip. Fu et al. [10,11] studied the sample injection in cross- and multi-T-form microfluidic systems and found that the injected sample plugs were critical to the next step process such as sample separation. Sinton et al. [12] reported a three-step sample injection technique to improve detection signal by dynamically controlling the sample size at the original sample concentration. In many of these microfluidic applications, sample carrying buffer has the same concentration as the running buffer, which gives rise to a uniform electrical conductivity along the microchannel length or cross the entire chip.

However, in many other practical applications, electrical conductivity gradients do exist and are often utilized to improve analyte detection using field amplified sample stacking (FASS) technique [13–18] or to minimize sample separation [19,20]. The detailed principles of sample stacking are described in [16] and the mechanism of reduced sample separation can be found elsewhere [20]. Fig. 1 schematically shows the mechanisms for both applications. The typical velocity fields near the sample region obtained through numerically solving the model described later are also shown in Fig. 1 to illustrate the velocity variation in this region. Brief explanations of these two principles are given below. The electrophoretic motion of the sample species is linearly
Fig. 1. Schematic diagram of the mechanisms of the pumping and stacking protocols and typical velocity fields near the sample region obtained numerically.

Proportional to the applied electrical potential strength and is described by $\vec{V}_{i,\text{ep}} = \mu_{i,\text{ep}} \vec{\nabla} \phi$, where $\vec{V}_{i,\text{ep}}$ and $\mu_{i,\text{ep}}$ are the electrophoretic velocity vector and mobility of the $i$th species, respectively, and $\vec{\nabla} \phi$ is the applied electrical potential gradient. Take a negative sample species as an example. When a lower buffer concentration (and hence a lower electrical conductivity) is employed in the sample region, which results in a higher electrical field, the negative sample molecules will quickly migrate to the running buffer region where a lower electrical field is present and the migration of the samples suddenly slows down there. As a result, the samples will stack at the interface between solutions with high/low electrical conductivities. On the other hand, when a higher buffer concentration is used in the sample region, a lower electrical field is achieved in this region, which will inhibit sample separation. This can be understood as below. The separation distance between different species is proportional to the local electrical field through the formula of $\Delta l = \Delta \mu_{\text{ep}} \cdot \nabla \phi$. Therefore, the reduced electrical field (i.e., $\nabla \phi$) will result in a reduced separation distance. In other words, separation is inhibited.

Field amplified sample stacking was initially discussed by Mikkers et al. [21] and was first implemented into microfluidic chip applications by Jacobson and Ramsey [13] to improve signal detection, which is proportional to the concentration of the sample. Since then, many studies have been performed [15–18] with a signal strength further improved to 560 fold [18] and even more than 1000 fold [16]. As compared to FASS, less attention has been paid to minimize sample separation by establishing an electrical conductivity gradient in microfluidic chips. Most studies on FASS have focused on experimentally exploring different combinations of microfluidic chip geometry, electrical conductivity gradient and detection system, aiming to gain high signal strength. Numerical simulation is an excellent alternative to study the physics underlying the observed phenomena because it can explore an optimized configuration such as the channel geometry and the conductivity gradient without running expensive experiments. There have been many numerical studies of microfluidic chips [22–24]. A recent review [25] can be found elsewhere. However, up to date, there are a few numerical studies on sample transport in microchannel with the consideration of the conductivity gradient. This is because the introduction of the conductivity gradient into the governing, partial-differential equations of the coupled electric field, flow field and the concentration field brings the nonlinearity into the model and significantly complicates the numerical simulations.

Sounart and Baygents [19] studied the transport of a sample plug with significantly higher conductivity than that of the bulk fluid. Flow separation in the velocity field was predicted in the varying conductivity regions and this gives rise to solute mixing and dispersion. In their study, a Stokes flow was assumed. This assumption neglects both the transient and convection terms in the full Navier–Stokes equation. More recently, Lin et al. [26] presented a comprehensive model of the conditions which lead to electrokinetic instability and nonlinear numerical simulations of the predicted transport field which agreed well with experimental results reported by the same group [27,28]. In their works, electri-
cal conductivity is established in the direction perpendicular to the bulk flow direction, which enhances mixing between two parallel flow streams with different conductivities.

As discussed above, the presence of electrical conductivity gradient in a microchannel can be utilized to enhance mixing, improve signal detection and minimizing sample separation. The fundamental understanding of transport phenomena in microfluidic devices with the consideration of electrical conductivity gradient will allow more operational control of microfluidic chips and provide insight into the physics underlying the observed transport phenomena. Therefore, in this work, a numerical model, consisting of the equation of applied electrical potential, the full Navier–Stokes equation, and the species conservation equation, is developed to study sample transport with conductivity difference along the microchannel. The simultaneous solution to this model will be used to describe the time-dependent applied electrical potential field, flow field and the species concentration field. The effects of electrical field strength, sample diffusion coefficient, and the conductivity gradient cross the channel length on sample control are examined as well. Potentially, the developed model can be used to find an optimized configuration for sample control in a microchannel with the electrical conductivity gradient in the flow direction.

2. Channel configuration and chemicals

Here we consider a sample transport system as illustrated in Fig. 2. A sample region, a buffer solution carrying the sample species, is initially sandwiched in between two regions filled with the driving buffer. The overall channel length is 1 mm, the length of the initial sample plug is 50 µm, and the channel width is 50 µm. The sample carrying buffer has the same chemical composites as that of the driving buffer, but a different concentration. The initial concentration distribution for both the sample and buffer are shown in this figure as well. An average electric field ranging from 10 to 30 kV m$^{-1}$ is applied along the channel to pump liquids. The variation of buffer concentration results in the conductivity gradients, which in turn alters the electrical field causing nonuniform electroosmotic flow.

Two fluorescent dyes are used in this study as the sample, Rhodamine 110 standard as supplied by Fisher Scientific, and Fluorescein as supplied by Molecular Probes. The driving buffer is sodium carbonate buffer of pH 9. Depending on the application, the concentration of buffer varies. The electrophoretic mobilities of Fluorescein and Rhodamine 110 are $\mu_{ep, F} = -3.3 \times 10^{-8}$ and $\mu_{ep, R} = -1.65 \times 10^{-8}$ m$^2$ V$^{-1}$ s$^{-1}$, respectively, as experimentally determined previously [12].

![Fig. 2. Schematic diagram of the microchannel and initial concentration distribution of sample and buffer for the pumping and stacking protocols.](image-url)

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Note: The image should be replaced with an actual figure related to the text content.
3. Theoretical model

A mathematical model of electrokinetic transport phenomena in a microchannel is developed here with the consideration of spatial gradient of electric conductivity. This model considers that the process is two-dimensional (in the plane of the chip), which is common in the modeling of similar processes [22,23]. It is assumed that the dependent variables do not exhibit significant gradients in the third, thickness dimension. Through comparing both two- and three-dimensional models, Patankar and Hu [24] showed this assumption to be reasonable in electroosmotic flows in similar configurations. This model consists of a set of 2-D governing equations describing the potential field, flow field and concentration field during transport processes as described below.

3.1. Electric potential field

Most buffer concentrations employed in microfluidic applications are higher than 10 mM, giving rise to an electrical double layer thickness less than 3 nm. For a microchannel with a channel width on the order of 10–100 µm, the electrical double layer thickness is less than 0.1% of the channel width and can be treated as a thin layer with electrical charges. When an electrical field is applied to the liquid in the microchannel, the driving force only exists within this thin layer provided that the electrical neutrality exists in the bulk liquid. The liquid in the charged thin layer will be driven to move. In this way, the electroosmotic flow can be considered as the slip flow boundary condition, and the electrical driving force can be neglected in the momentum equation for bulk liquid motion. Therefore, the electrical potential inside the thin double layer will not be studied here and only the applied electrical potential in the bulk liquid along the channel will be examined in this study.

When an electric field is applied along a microchannel, the current is setup along the channel and the local electric current vector is given by [29]

$$\vec{i} = e \vec{u} \sum_j z_j n_j - \sum_j D_j \vec{z}_j \nabla n_j - \frac{e^2 \nabla \phi}{k_B T} \sum_j z_j^2 D_j n_j,$$  \hspace{1cm} (1)

where $\vec{i}$ is the local electric current density vector, $\vec{u}$ is the local velocity vector, and $\phi$ is the local electrical potential. The $j$th ionic species has a valence $z_j$, a diffusion coefficient $D_j$ and an ionic number concentration $n_j$. Here, $e$, $k_B$, and $T$ represent the fundamental elementary charge, Boltzmann constant and the system absolute temperature, respectively. For a microchannel with large $\kappa a$ (here $a$ is the hydraulic diameter of the capillary and $\kappa^{-1}$ is the Debye double layer thickness), that is, the electric double layer is very thin, electroneutrality is assumed to dominate in the channel and the first term of Eq. (1) defining the current transport due to convection can be neglected. It is true that electroneutrality may not exist near the interface region between the sample and the carrying buffer due to the presence of the gradient of electric field strength such as described by $\rho_e = \epsilon_e \epsilon_0 \nabla E^2$, where $\epsilon_e$ and $\epsilon_0$ are the dielectric constant of the solution and the permittivity of vacuum, respectively, $\rho_e$ is the net charge density and $\nabla E$ is the gradient of electric field strength. However, it should be noticed that net charges only appear near the interface region, which is very small as compared to the whole channel length filled with uniform buffer solution. Therefore, the assumption of electroneutrality will not bring much error in evaluating electrical conductivity, which mainly depends on the concentration of the buffer solution, and in turn no appreciable effects on electrical current. Similarly, the effects of the gradient of electrical field strength at the interface region will not affect appreciably in the electrical driving force, which is mainly dominated by the electrical driving forces exerted on the net charges within the double layer region. This condition is applicable to most microfluidic applications, for example, $\kappa a \approx 10,000$ for a 10 mM solution in a 50 µm-diameter microchannel. Normally, one can neglect the second term in Eq. (1) which defines the current due to diffusion and is found small as compared with the third term [30]. Consequently, for large $\kappa a$ flows, one can write the electric current in terms of molar concentration as

$$\vec{i} = -\frac{e^2 N_A \nabla \phi}{k_B T} \sum_j z_j^2 D_j C_j,$$  \hspace{1cm} (2)

where $N_A$ is Avogadro number and the molar concentration is given by $C_j = n_j / N_A$. For a given electrolyte solution, Eq. (2) can be rewritten as

$$\vec{i} = \lambda \nabla \phi,$$  \hspace{1cm} (3)

where $\lambda$ is the electric conductivity of electrolyte solution and takes the form of

$$\lambda = \frac{e^2 N_A}{k_B T} \sum_j z_j^2 D_j C_j.$$  \hspace{1cm} (4)

Equation (4) is an expression of Ohm law for electrically neutral dilute solutions or solutions in a microchannel having large $\kappa a$, where $C_j$ can be determined by a set of concentration equations. The charge conservation in the liquid has to be satisfied, which is described by

$$\nabla \cdot \vec{i} = 0.$$  \hspace{1cm} (5)

Substituting Eq. (3) into Eq. (5), the equation of the electrical potential field is obtained as

$$\nabla \cdot (\lambda \nabla \phi) = 0.$$  \hspace{1cm} (6)

With the given concentration field and proper boundary conditions, Eqs. (4) and (6) can provide the distribution of the applied electric field, $\phi$, in the microchannel. It should be pointed out that if there is no spatial conductivity gradient, $\lambda$, is a constant, and hence Eq. (6) is reduced to

$$\nabla \cdot (\nabla \phi) = \nabla^2 \phi = 0.$$  \hspace{1cm} (6a)
Equation (6a) is commonly used to describe the applied electrical potential field in microfluidic devices with uniform conductivity [22–24,31]. The insulation boundary conditions are applied to the walls of the channel, the inlet potential is 10 V, and the outlet is grounded.

3.2. Flow field

The flow field is described by the modified Navier–Stokes equation as follows:

\[
\rho \left[ \frac{\partial \vec{V}}{\partial t} + (\vec{V} \cdot \nabla) \vec{V} \right] = -\nabla P + \mu \nabla^2 \vec{V} + \rho_e \nabla \phi, \tag{7}
\]

\[\vec{V} \cdot \vec{V} = 0, \tag{8}\]

where \(\vec{V}\) stands for the mass average velocity vector, \(\rho\) is the density of liquid, \(P\) is the pressure, \(\mu\) is the viscosity of the liquid, and \(\rho_e\) is the net charge density in the solution. As discussed earlier, for high ionic concentration solutions commonly used in on-chip microfluidic processes, the electric double layer usually is very thin, i.e., less than 0.1% of channel width. As explained before, the electroosmotic flow can be considered as the slip flow boundary condition, and the electrical driving force can be neglected in the momentum equation for bulk liquid motion (the third term on the right-hand side of Eq. (7)). Mathematically, this slip boundary condition is given by

\[\vec{V}_{|\text{wall}} = \mu_{eo} \vec{V} \phi, \tag{9}\]

where \(\mu_{eo}\) is the electroosmotic mobility of the buffer solution.

Since two reservoirs are open to atmosphere and we do not apply pressure to the liquid, the pressure gradient in Eq. (7) is the induced pressure gradient due to the presence of electrical conductivity gradient. The electrical conductivity alters the electrical field resulting in a nonuniform axial velocity distribution. The requirement of linear momentum conservation requires a pressure gradient to balance this nonuniformity in velocity. The slip velocity conditions are applied to the walls of the channel, the inlet velocity is specified to be equal to the wall velocity at the inlet, and the zero-flux boundary condition is applied at the outlet of the channel. The pressure at both the inlet and the outlet are the same as the atmospheric pressure and the insulation boundary conditions are applied to all the walls.

3.3. Concentration field

In most microfluidic applications, the sample concentration is very low (i.e., \(\mu\)M) as compared with buffer concentration, which is of the order of mM. In this case, the electrical conductivity of solution will be dominated by the buffer solution. In this study, we consider the different concentrations for the sample carrying buffer and the driving buffer, therefore, the spatial gradients of buffer concentration and the conductivity exist and the gradients are time dependent since the concentration distribution will change with time. The time dependent characteristics have significant effects on the electrical potential field and the flow field during the transport process. In order to monitor the variation of electrical conductivity, the buffer concentration field must be modeled simultaneously at each time step. The concentration field is governed by the mass conservation and can be described by

\[\frac{\partial C_i}{\partial t} + \vec{v} \cdot (\vec{V}_{\text{bulk}} + \vec{V}_{\text{ep}}) C_i = D_i \nabla^2 C_i, \tag{10}\]

\[\frac{\partial C_{\text{buffer}}}{\partial t} + \vec{V}_{\text{bulk}} \cdot \nabla C_{\text{buffer}} = D_{\text{buffer}} \nabla^2 C_{\text{buffer}}, \tag{11}\]

where \(\vec{V}_{\text{ep}}\) is the electrophoretic velocity of the \(i\)th species, given by \(\vec{V}_{\text{ep}} = \mu_{i \text{ep}} \vec{V} \phi\), where \(\mu_{i \text{ep}}\) is the electrophoretic mobility of this species. Please note that Eqs. (10) and (11) describe the concentration fields of the sample and the buffer, respectively. The insulation boundary is applied on the walls of the channel, the applied concentration value is applied at the inlet of the channel as listed in Table 1 and shown in Fig. 2, and the zero-flux boundary condition is applied to the outlet of the channel.

3.4. Numerical scheme

The complete set of equations, Eqs. (4), (6)–(8), and (10)–(11), were normalized by the following parameters, \(\Phi = \phi/\phi_{\text{max}}, \bar{X} = x/H, \bar{U} = (\rho \mu H)/\mu, \bar{P} = (p-p_a)/[\rho (\mu H)^2], \bar{C} = C/C_{\text{max}}, \text{ and } \bar{\tau} = (t \cdot \mu)/(\rho H^2),\) and numerically solved to obtain the variables of interest. In brief, the applied electrical potential field is obtained by solving Eqs. (4) and (6), the bulk velocity is obtained by solving Eqs. (7) and (8) using the semi-implicit method for pressure-linked equation (SIMPLE) algorithm developed by Patankar [32], and the concentration fields for both buffer solution and sample are obtained by solving Eqs. (10) and (11). The algorithm is based on a finite control volume discretization of the governing equations and a staggered grid scheme is applied in solving the momentum equations in this study. Grid independence has been checked in our numerical simulation and 20 and 15 control volumes are chosen for per unit nondimensional length in the width and length directions, respectively. The time step was chosen as 0.5 ms considering the process is on the order of seconds. Different convergence criteria have been checked for the numerical simulation to obtain a balance between reasonable computational cost and accuracy. Specifically, for the potential and concentration equations, \(|\Phi_{i,j}^{\text{new}} - \Phi_{i,j}^{\text{old}}| < 10^{-8}\) is chosen, while for the momentum equation, the residual of continuity is monitored and the iteration is stopped when the residual for all the control volumes is smaller than \(|B_{i,j}| < 10^{-5}\). The same convergence criteria have been applied in previous studies, which were also validated by experimental studies [33]. In this implementation, the solution to this set of equations is obtained by an iterative procedure. During each
4. Results and discussion

The conductivity difference between the sample carrying buffer and the driving buffer can be applied to pump multiple sample species without separation or enhance separation by stacking sample. When a sample plug is pumped through a microchannel, individual sample species moves at a velocity equal to the summation of the bulk electroosmotic velocity and its specific electrophoretic velocity, i.e., $V_i = V_{\text{bulk}} + \mu_i \nabla \phi$. The distance between any two analytes can be determined by $\Delta l_{a,b} = \Delta V_{a,b} \cdot t$, where $t$ is the time that the sample has traveled and $\Delta V_{a,b}$ is the velocity difference between two analytes, which can be further expressed as $\Delta V_{a,b} = \Delta V_{\text{bulk},a,b} + \Delta \mu_{ep,a,b} \nabla \phi$. If the conductivity is uniform along the channel length, the bulk velocity and electrical field strength are constant throughout the channel, and the distance between different species is dependent only on the difference of their electrophoretic velocities and the time that the sample has traveled, that is, $\Delta l_{a,b} = \Delta \mu_{ep,a,b} \nabla \phi \cdot t$. Because different species have different electrophoretic mobilities, such as Rhodamine 110 standard and Fluorescein ($\mu_{ep,F} = -3.3 \times 10^{-8}$ and $\mu_{ep,R} = -1.65 \times 10^{-8}$ m$^2$ V$^{-1}$ s$^{-1}$), they are separated when pumped downstream as seen in Fig. 3, which shows this separation process by the sequences of sample centerline concentration plots for each analyte. The fast one is Rhodamine due to its less negative electrophoretic mobility. As one can see that, at the beginning ($t = 0$ s), the two analytes were loaded together showing the same concentration plug. When the sample is transported downstream, the two species are gradually separated as shown in the plots at $t = 0.2$, $0.4$, and $0.6$ s (details are listed in Table 1).

This separation is common practice in many chip-based electrophoresis applications, however, in many other applications, a multi-component sample is required to be pumped downstream without separation (i.e., a large number of sample species screening) [20]. In order to achieve this goal, it is ideal that the sample-carrying buffer has a higher concentration than that of the driving buffer to obtain a local low electrical field and low velocity. Fig. 4 shows the sequence plots of centerline (i.e., along the symmetric axis of the channel in the length direction) concentration for a sam...
ple with two species (Rhodamine and Fluorescein) during the transport. In this case, the sample-carrying buffer has a concentration 5 times that of the driving buffer and the conductivity ratio of the driving buffer over the sample carrying buffer is assumed to be the same as that of concentration, that is, \( \gamma = \frac{\lambda_{\text{driving buffer}}}{\lambda_{\text{sample carrying buffer}}} = 0.2 \). Due to the high concentration and high electrical conductivity in the sample region, the local electrical field strength is lower as compared to that of the driving buffer regions. As discussed earlier, the separation distance depends on the local electrical field strength. When the local electrical field strength is reduced, the separation distance is decreased, or in other words, the separation is minimized. As shown in Fig. 4, the sample species are indeed kept together when pumped downstream within a certain time period (e.g., separation bands may be observed after 40 s under this set of specific conditions) due to the presence of high electrical conductivity in this region. In order to clearly show the minimized separation effect, the initial concentration for two species is

(a)

(b)
set differently, $C_{0, \text{Rhodamine}} = 40 \mu M$ and $C_{0, \text{Fluorescein}} = 32 \mu M$, so the curves for these two species have different heights.

**Fig. 5** shows the effects of the applied electrical field strength on the sample transport for the pumping process, where the concentration and the electrical conductivity in the sample region are higher than that in the driving buffer. The left column of this figure is the sample concentration profile and the right column is the corresponding buffer concentration profile in the sample region, where centerline (i.e., along the symmetric axis of the channel in the length direction) profiles are plotted at 0.1 s intervals. Since the pumping process can keep Rhodamine and Fluorescein together and the purpose here is to investigate the effects of the electrical field strength, only one sample species, Rhodamine, is considered for this case. As shown in **Fig. 5**, the sample moves faster when the electrical field strength is increased since the velocity is proportional to the electrical field strength. It should be noted that the sample shape is expanded when the electrical field strength is increased, as shown in **Fig. 5**. The sample plug size is dependent on the Péclet number (the ratio of convection effect over diffusion effect). The higher the Péclet number is, the closer the sample plug size to the original one. This is because diffusion effects tend to expand the sample size during the transport. The contrary results shown in **Fig. 5** can be understood as follows. In most Lab-on-a-chip applications, the sample concentration is very low as compared with the buffer solution and the channel length is much longer than the sample length, and thus the bulk electroosmotic flow velocity is dominated by the electroosmotic flow rate of the driving buffer. The electrophoretic velocity of the sample, however, depends directly on the local electrical field gradient. When the electrical field strength is increased, the negative electrophoretic velocity (tends to help the diffusion backward and thus expand the sample band) is increased linearly with the electrical field strength. Thus, the back (left boundary) of the sample is left within the low conductivity region (the driving buffer zone as shown in the right column of **Fig. 5b**), the local high electrical field strength in the driving buffer region will give rise to a even higher negative electrophoretic velocity. In addition, the pressure-driven flow in the low conductivity region, which is induced due to non-uniformity of flow field between the sample and running buffer region, will further enhance the sample transport back to the inlet of the channel and cause the spreading of the sample in this region. The detailed discussion about induced pressure driven flow on electroosmotic flow and sample transport in microfluidic chips can be found in our previous study [33]. As a result, the increased negative electrophoretic velocity enhances the diffusion backward in this
region resulting in the expanded sample plug as shown in left column of Fig. 5b.

As explained earlier, field amplified sample stacking (FASS) is a technique to increase signal-to-noise ratio through pre-concentrating the sample before analysis. In this process, the sample (stored in a low ionic strength buffer) is introduced into a channel as a discrete band, sandwiched between high ionic strength buffers on both sides, as shown in Fig. 2c. When an electric field is applied along the channel, the sample region experiences a higher electric field due to its high electrical resistance. In this study, a fluorescein/rhodamine sample mixture is assumed to be dissolved in a sample-carrying buffer that has a lower concentration than that of the driving buffer (details in Table 1). In Fig. 6, concentration profiles are plotted for both the buffer solution and the analytes at different time, as indicated in this figure.

In this figure, the length scale is normalized by the channel width, \( H \). The analytes are noticeably depleted at the beginning of transport, which is also observed in cross-linked microchannels [34]. This is because the high electrical field strength in the sample zone results in a high negative electrophoretic velocity and the low electrical field in the bulk region gives rise to a low bulk flow velocity. The sample velocity, which is a summation of the bulk electroosmotic velocity and its electrophoretic velocity, becomes very small. In such a case, diffusion dominates the transport at the beginning period and sample concentrations decrease significantly as shown in Fig. 6a at \( t_2 = 0.2 \) s. It should be noted that the induced pressure-driven flow in the sample region, which is in the opposite direction to the bulk electroosmotic flow, will contribute sample diffusion as well. Later on, the sample-stacking mechanism takes effect and the stacking is observed as Rhodamine moves toward downstream generating the increased maximum concentration as shown in Fig. 6a at \( t_3 = 0.3 \) s. However, not much stacking is observed in Fluorescein. This is because that fluorescein has a higher negative electrophoretic velocity and thus is left within the high conductivity region (see Fig. 6c at \( t = t_1 \) for buffer concentration profile), where the stacking effect is much weaker (not much conductivity difference is present). It is also noted that the band size of Fluorescein sample is much smaller in comparison with Rhodamine. The amount of these two analytes is the same in the sample. Fluorescein has a higher negative electrophoretic velocity, which results in a smaller net velocity or even a negative velocity. Thus diffusion effects dominate and quickly reduce Fluorescein sample size. Although the two species were totally separated at \( t_3 = 0.3 \) s, the two separate bands were seen clearly at \( t_2 = 0.2 \) s, which is faster than that with the uniform conductivity as shown in Fig. 3. This rapid separation is due to the high field strength in the sample region as explained earlier.

As explained above, the stacking occurs when the conductivity in the sample zone is lower than that in the driving buffer. The increase in conductivity difference enhances stacking as shown in Fig. 7. Since the purpose here is to show the effects of the conductivity ratio, \( \gamma \), on sample transport, only one sample species, Rhodamine is studied for this case. In this figure, centerline concentration profiles are plotted at 0.1 s intervals. The initial electrical conductivity ratio between the buffer region and the sample region, \( \gamma \), is increased from \( \gamma = 5 \) in Fig. 7a to \( \gamma = 10 \) in Fig. 7b. Comparing Fig. 7a with Fig. 7b, we see that a stronger stacking effect (i.e., higher centerline concentration) was achieved by lowering buffer concentration in the sample region, i.e., the height of sample centerline concentration was increased as it was transported downstream. Although this two-dimensional plot makes it much easier to see the stacking effects, it might be misleading that the mass conservation is violated because the concentration of the sample increases. However, it must be realized that this is the centerline concentration profile only. The mass conservation is satisfied and can be seen from Fig. 6 (\( t_2 = 0.2 \) and \( t_3 = 0.3 \) s), which shows the increase in the centerline concentration of the sample is compensated by the decrease of the concentration in the rest region of the channel cross area.

5. Summary

Conductivity differences between the sample carrying buffer and the driving buffer can influence the sample trans-
port in microchannels significantly. This work investigated the following two situations, sample pumping where a high-conductivity sample buffer is employed to minimize sample separation, and sample stacking where a low-conductivity buffer is employed in the sample region. It was found that the conductivity differences have significant effects on the sample transport compared with the uniform conductivity case. In order to control effectively the sample size and shape, an optimized combination of the conductivity of the sample carrying buffer and the driving buffer is required. The model developed here can provide guidance to search for this optimized configuration through numerically investigating the effects of these controlling parameters on sample transport in microchannels.

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