Research Article

A study on the condition for differential electrophoretic transport at a channel entrance

Electrophoretic differential transport of ionic species in a solution moving from a large reservoir into a small channel is investigated numerically. The system setup is similar to the experiments of Polson, Savin, and Hayes (J. Microcol. Sep. 2000, 12, 98), where the bulk flow into a fused-silica capillary was driven by a pressure differential. A critical condition for achieving the defined differential transport near the channel entrance is found and this condition is solely determined by a dimensionless parameter when the geometry of the system is prescribed. This dimensionless parameter is the ratio between the electrophoretic migration velocity of the species based on the apparent electric intensity and the centerline fluid velocity of the fully developed channel flow. Species concentration distributions are also computed for various conditions. A separation technique can be derived from the experimental condition where a targeted division of species can be created at the channel entrance.

Keywords:
Electrokinetic effects / Electrophoretic focusing / Low Reynolds number flow

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1 Introduction

Manipulation of specific chemical species in a solution forms the basis for many important processes. Small-scale analytical chemistry applications, such as chromatography, microcristallizations, distillations, electrophoresis, and electrochemistry, all depend on differential behaviors of the species based on their molecular or atomic structures. Generally, these are carried out in a continuous system where kinetics and thermodynamic driving forces are used to generate a separation in time or space, or some sort of gradient/equilibrium state is allowed to occur [1–11]. Other, rather low-resolution approaches separate at some interface (filtration for example). There is a growing interest in generating a high-resolution separatory capability at an interface. Juxtaposing a flow field across the initiation of an electric field may provide this capability.

It has been recognized that setting flow and field gradients opposing one another can effectively cause differential transport for preconcentration or separation [12–20]. An early study by Hori et al. [14] showed the connection of a large diameter tube (1.5 mm) between two reservoirs containing several milliliters of solution, where the flow was set to oppose the electrophoretic migration of selected species. The electrophoretic migration was larger than the flow rate, which prevented the charged species from being transferred from the reservoir thus concentrating those materials. More recently, an electrophoretic focusing preconcentration technique for small-volume ionic species was examined by Polson et al. [12]. For the system used in the experiments, the bulk flow into a fused-silica capillary was driven by a pressure differential. The fluid velocity which convects the 200 nm diameter carboxylated fluorescent latex spheres was balanced by the electrophoretic migration of these particles near the entrance to the capillary. These data were collected with a 20 μm id capillary with 350 V/cm field strength, pH 5 (25 mM) phosphate buffer and a pressure drop of about 0.04 atm. The inner diameter of the reservoir was about 2 cm, giving an aspect ratio (or contraction ratio) of 1000:1. The capillary tip was sputter-coated with chromium and then gold to form an integral electrode. This conductive material was in electrical contact with an electrode encircling the reservoir, thus ensuring a nearly flat potential field within that volume. With such a large contraction ratio, the electric field is essentially zero in the reservoir, which guarantees that the differential transport will occur near the capillary entrance. Single spheres or small groups of spheres were clearly visible under the fluorescence microscope allowing easy observation of the effects of both flow and electric fields on these charged species. The electric field strength was...
empirically balanced to allow a concentrated plug of spheres to form at the entrance to the capillary. The experimental data clearly shows a differential transport and hence minor focusing of the materials near the point where the electric field is initiated. The focus of this earlier work was to pre-concentrate the materials at the capillary entrance, whereas the work here attempts to understand the ability of this interface to generate high fidelity differential transport allowing very similar species to be separated at the interface without regard for the increased concentration at the interface.

While there are many experimental investigations on flow field/electric field interfaces, only simplified 1-D models have been used so far to study the focusing process from the transport point of view [12]. Furthermore, these models ignored the potential for high-resolution differential transport. The interface was modeled as a partially rejecting barrier with an exponentially decaying velocity from the barrier. Concentration distribution along a single line near the barrier was obtained under steady-state operation. The obvious limitation of such an analysis is its qualitative nature due to the 1-D assumption and the assumed velocity profile. In addition, no differential transport condition can be obtained since no knowledge of the electric field shape near the barrier is available. In this paper, we study differential transport conditions for a 2-D reservoir-channel configuration, similar to the arrangement used in the experiments of Polson et al. [12]. The experiments of Polson et al. [12], carried out more than seven years ago, were of exploratory nature and they used a cylindrical geometry. However, current interest in this area is to employ this technique for microfluidic applications which correspond to 2-D channel geometry. For this reason, the results reported here are carried out for a 2-D channel. Similar results are expected for cylindrical geometries. This issue will be further discussed in later sections of the paper. The physical mechanism of transport is explored. Key parameters controlling transport conditions and concentration distribution are identified. A necessary condition for achieving effective differential transport is that the migration velocity $\bar{u} + \bar{u}_e$ along the centerline of the channel be brought to zero near the channel entrance, or the pseudovelocity field $\bar{u}_e$ must possess a stagnation point along the centerline of the channel. For large reservoir-to-channel contraction ratios, this condition is solely determined by a single dimensionless parameter $S$ which is the ratio between a characteristic electrophoretic migration velocity of the species based upon the apparent electric intensity and the velocity of the fluid at the channel centerline in the fully developed zone. The critical value of $S$ corresponding to this condition varies with the location of the stagnation point along the centerline of the channel. Species concentration distributions for various conditions are reported. Comparisons with experiments are provided and application of this transport condition to separation of species is also discussed.

2 Mathematical formulation

In preparation to examine differential transport, the original electrophoretic focusing in a pressure-gradient-driven flow can be studied by solving the governing equations for the motion of the buffer fluid and the species. In the experiments of Polson et al. [12], the inner surfaces were intentionally treated so that there were no surface charges on the walls of the reservoir and the capillary. Therefore, EOF was absent. This simplifies the control of the experiment for achieving the focusing condition. In this situation, the flow field of the fluid is decoupled from the applied electric field which is generated by applying a voltage $V_0$ across the two electrodes at two locations in the capillary (Fig. 1). The steady velocity field $\bar{u}$ of the fluid is determined by solving the continuity and the steady Navier–Stokes equations

$$\nabla \cdot \bar{u} = 0$$  \hspace{1cm} (1)

$$\rho \bar{u} \cdot \nabla \bar{u} = -\nabla p + \eta \nabla^2 \bar{u}$$  \hspace{1cm} (2)

Figure 1. Schematic representation of the contraction flow from the reservoir to the capillary in a pressure-driven flow.
together with the no-slip condition \( \mathbf{u} = 0 \) on all walls, and parabolic velocity profiles far upstream in the reservoir and far downstream in the capillary. In Eq. (2), \( \rho \) is the hydrodynamic pressure, \( \rho \) is the fluid density, and \( \eta \) is the fluid viscosity. For a steady-state velocity field, the prescribed volumetric flow rate is \( Q \). The height of the channel is \( D_0 \) and the height of the reservoir is \( D_1 \). The origin of the coordinate system is located at the mid-plane at the channel entrance, with flow in the positive \( x \)-direction, from left to right as depicted in Fig. 1.

For uncharged species, the microparticles move with the local fluid velocity \( \mathbf{u} \). When the particles are charged and an external electric field is present, however, the particles migrate relative to the local fluid with an electrophoretic velocity \( \mathbf{u}_{ep} \). When the diameter of a spherical particle is large relative to the thickness of the electric double layer formed adjacent to the particle surface, the electrophoretic migration velocity of a single particle is given by \( \mathbf{u}_{ep} = \mu_{em} \mathbf{E} \), with \( \mu_{em} \) being the electrophoretic mobility and \( \mathbf{E} \) the local applied electric field. For a spherical particle with radius \( r \) and surface charge \( q_s \), \( \mu_{em} = q_s / 6 \pi \eta r \). This simple relation between the electrophoretic migration velocity \( \mathbf{u}_{ep} \) and the electric intensity \( \mathbf{E} \) holds even if \( \mathbf{E} \) varies over distances comparable to the particle size (Keh and Anderson [21]). For definiteness, we assume that all particles carry positive charges on their surfaces, so that \( \mathbf{u}_{ep} \) is in the opposite direction of the flow of the buffer fluid (Fig. 1). We shall further assume that the species are very dilute so that the above electrophoretic velocity formula for a single spherical particle can be adopted for our simulations. This implies that the interparticle interactions are neglected, even when the particles are being focused. This is of course a crude approximation which is probably only valid during the early stage of focusing. Nevertheless it is an approximation that allows the first simulation on electrophoretic focusing without the significant complication due to interparticle interactions. With these assumptions, the microparticles then move with the velocity \( \mathbf{u} + \mathbf{u}_{ep} \) relative to a fixed frame of reference. The concentration of the species \( c \) is determined from the convection–diffusion equation.

\[
\frac{\partial c}{\partial t} + (\mathbf{u} + \mathbf{u}_{ep}) \cdot \nabla c = D \nabla^2 c \tag{3}
\]

where \( D \) is the diffusion coefficient of the species in the solvent. On the walls, the no-penetration condition applies, and at the far ends of the capillary and the reservoir, \( c \) is specified.

The local external electric field \( \mathbf{E} \) is related to the electric potential \( \psi \) by \( \mathbf{E} = -\nabla \psi \). The electric potential \( \psi \) satisfies the Laplace equation

\[
\nabla^2 \psi = 0 \tag{4}
\]

On the capillary wall and the sidewalls of the reservoir, insulator condition is imposed. We prescribe the value for the electric potential \( \psi \) at the downstream electrode location \( x = L_1 \) on the wall, \( \psi = V_o \). In the experiment of Polson et al. [12], the ground electrode is located just slightly inside the capillary when the thickness of the reservoir wall is taken into account. Thus at \( x = x_1 \) on the wall, \( \psi = 0 \), with \( x_1 \) being the thickness of the reservoir wall. Far upstream in the reservoir and far downstream in the channel, \( x \to \pm \infty \), the electric potential does not change, \( \partial \psi / \partial x = 0 \). With these boundary conditions, the electric potential \( \psi \) can be calculated, and the electric field \( \mathbf{E} \) is obtained by \( \mathbf{E} = -\nabla \psi \). This completely determines the electrophoretic velocity \( \mathbf{u}_{ep} \) in the flow domain.

To make the problem dimensionless, we scale length with the height of the channel \( D_1 \), velocity with the centerline velocity of the fully developed channel flow \( U (U = 1.5 Q / D_1) \), and time with \( D_1 / U \). The channel width in the \( z \)-direction is unit length. Thus the dimensionless governing equations are (all quantities below are dimensionless):

\[
\text{div} \mathbf{u} = 0 \tag{5}
\]

\[
\text{Re} u \cdot \nabla u = -\nabla p + \nabla^2 u \tag{6}
\]

\[
\frac{\partial c}{\partial t} + (u + u_{ep}) \cdot \nabla c = \frac{1}{Pe} \nabla^2 c \tag{7}
\]

where the controlling dimensionless parameters are as follows:

\[
\text{Re} = \frac{\rho UD_1}{\eta} \quad \text{(Reynolds number)}
\]

\[
\text{Pe} = \frac{D_1 U}{\eta} \quad \text{(Peclet number)}
\]

\[
K = \frac{\mu_{em} V_0}{UD_1} = \frac{\mu_{em} V_0}{U(L_1 - x_1) / D_1} = \frac{L_1 - x_1}{D_1} \tag{8}
\]

\[
S = \frac{\mu_{em} V_0}{U(L_1 - x_1) / D_1} = \frac{\mu_{em} E_{app}}{U}
\]

\[
E_{app} = \frac{V_0}{L_1 - x_1}
\]

The Reynolds number \( \text{Re} \), which is a measure of the importance of inertia force relative to viscous force, is very small in our applications, \( \text{Re} \ll 1 \). The Peclet number \( \text{Pe} \) is a measure of the strength of the convection effect relative to the diffusion effect. The same dimensionless geometric configuration is used to compute the dimensionless fluid velocity field and electric field. Since the channel height \( D_1 \) is used as the length scale, the scale for the electric intensity is then \( V_0 / D_1 \).

\[
E_{app} = \frac{V_0}{L_1 - x_1} \quad \text{is the apparent electric intensity which is the applied voltage divided by the distance between the electrodes. Thus, the dimensionless electric field is related to the computed dimensionless electric field} \ E \quad \text{by the relation} \ \frac{V_0}{D_1} E = E_{app} \frac{L_1 - x_1}{D_1} E. \quad \text{The parameter} \ S \quad \text{is the ratio between a characteristic electrophoretic migration velocity of the species based upon the apparent electric intensity and the velocity of the fluid at the channel centerline in the fully developed zone, a measure of the electrophoretic migration velocity relative to the fluid convection velocity.} \]
A numerical code for general incompressible viscous flow is used for the computation of the velocity field using the pseudotransient technique. The steady-state velocity field is obtained by computing the corresponding unsteady state until the solution converges in time. A nonstaggered non-uniform grid layout was employed in this analysis. We used a semi-implicit time-advancement scheme with the Adams–Bashforth method for the explicit terms and the Crank–Nicholson method for the implicit terms. The discretized equations corresponding to the unsteady forms of (5) and (6) are

\[ \frac{u^* - u^{k-1}}{\Delta t} = \frac{1}{2} (u^* + u^{k-1}) \]  
\[ \nabla^2 \phi^k = \frac{\nabla \cdot u^*}{\Delta t} \]  
\[ u^k = u^* - \Delta t \nabla \phi^k \]  
\[ p^k = \phi^k - \frac{1}{2} u^2 \nabla^2 \phi^k \]

where \( u^* \) is the intermediate velocity and it is not constrained by continuity; \( p \) is the pressure, \( \phi \) is the pseudopressure, \( \Delta t \) is the time increment, and \( k \) is the time-step. To obtain \( u^* \), we employ the approximate factorization technique. The variable \( \phi \) is obtained by solving the Poisson equation using a multigrid method. The diagonal viscous terms are treated implicitly in order to remove the viscous stability limit. The spatial derivatives are discretized using second-order central differences.

The discretized form of the convection–diffusion Eq. (7) is as follows:

\[ \frac{c^k - c^{k-1}}{\Delta t} = -\frac{3}{2} \left( (\nabla c)^2 \right)^{-1} \left[ (\nabla \cdot u_{eq}) \cdot \nabla c \right] c^{k-2} - \frac{1}{2} \left[ (\nabla \cdot u_{eq}) \cdot \nabla c \right] c^{k-1} + \frac{1}{2 Pe} \nabla^2 (c^k + c^{k-1}) \]

where \( c \) is the concentration and \( u_{eq} = K \varepsilon. \) The spatial derivatives are discretized using a variation of QUICKC (Leonard [22]) which calculates the face value from the nodal value with a quadratic interpolation scheme. The upwinding schemes are carried out by computing negative and positive volume fluxes. Readers may consult Zhang et al. [23], Pacheco and Peck [24], and Pacheco [25] for more in-depth technical details.

3 Results

3.1 Focusing condition

For the contraction flow from the reservoir to the channel, the streamwise fluid velocity (x-component of \( u \)) is the largest along the centerline \( y = 0 \). Thus, a necessary condition for focusing species near the channel entrance is that the electric field is strong enough so that along the channel centerline the pseudovelocity \( u + \bar{u}_{eq} \) becomes zero near the channel entrance (or the pseudovelocity possesses a stagnation point). Near the channel entrance, however, both the fluid velocity field \( \bar{u} \) and the electric field \( \varepsilon \) are not fully developed. Thus \( u + \bar{u}_{eq} \) varies with the distance to the channel entrance (recall \( \bar{u}_{eq} = \mu \varepsilon \)). This variation with the distance to the channel entrance can only be obtained from numerical computations from which the necessary condition for focusing can be quantified. On the other hand, further downstream in the channel beyond the entrance region, both the velocity field and the electric field are fully developed. In this region, along the centerline, \( u + \bar{u}_{eq} = (U - \mu \varepsilon E_{app}) \) along the centerline in the fully developed zone. A stagnation point in the pseudovelocity along the centerline appears when \( S = \frac{\mu \varepsilon E_{app}}{U} = 1 \). This serves as an asymptotic limit for the critical value of \( S \) for focusing.

Computations of the velocity field and the electric field are carried out for the following geometries: the channel has a height of 1, length of 12; the reservoir has a length of 12, and various heights (13, 30, 40, 50). Thus, the contraction ratio from the reservoir to the channel, \( A \), varies from 13 to 50. The ground electrode is located at \( x = 0.036 \). The distance of 0.036 between the entrance \( x = 0 \) and the ground electrode accounts for the thickness of the reservoir wall. Since the channel height is used as the length scale, the actual downstream electrode in the capillary is located at a very large value of \( x \). However, the electric potential \( \psi \) becomes a linear function of \( x \) quickly as \( x \) is increased due to the nature of the solution of the Laplace equation. This facilitates the use of a much shorter channel (dimensionless) for computation. In the simulation, at \( x = 10 \), we impose a voltage which in dimensionless terms is set to unity. The dimensionless velocity field \( u \) and the electrostatic potential field \( \psi \) can be computed independently. Figure 2 shows the dimensionless velocity and dimensionless electric intensity along the channel centerline \( y = 0 \). The velocity approaches fully developed state (value of one) when \( x = 0.5 \), and the electric intensity becomes a constant when \( x = 0.8 \).

By setting the centerline pseudovelocity to zero, the focusing condition can be expressed in terms of a critical value of the dimensionless parameter \( S \), which can be obtained from the computed velocity and electric intensity along the centerline, such as those shown in Fig. 2 for \( A = 40 \). Figure 3 shows the critical values \( S_c \) as a function of the location of the stagnation point for various contraction ratios. \( S_c \geq 1 \) for all these curves and they asymptote to \( S = 1 \) from above when \( x \) is increased, which correspond to the fully developed zone as discussed above. As expected, \( S > 1 \) is required to push the stagnation point outward from inside the channel towards the channel entrance at \( x = 0 \). As the contraction ratio is increased, the critical value \( S_c \) is
Figure 2. Dimensionless fluid velocity and electric intensity variation along the centerline near the channel entrance when contraction ratio $A = 40$. The centerline velocity $u_c$ reaches the fully developed value one when $x$ is around 0.5 (one-half of channel height). The electric intensity reaches a constant (0.1) when $x$ is around 0.8. Notice that $x$ is scaled with the height of the channel.

decreased. This is due to the fact that the approaching velocity of the fluid is reduced for a larger reservoir when the flow rate is fixed. There is little difference between the curves for contraction ratio of 40 and 50 when $x \geq 0$. This remains true when the contraction ratio is further increased. Thus, the curve corresponding to contraction ratio of 40 can be used for very large contraction ratio reservoirs, which are of the greatest interest in microfluidics applications. For such large reservoirs, the stagnation point is located at $x = 0$ when $S = 1.3$. Thus a nondiffusive particle is blocked from entering the channel when $S \geq 1.3$.

3.2 Concentration distribution

Species concentration distribution can be obtained from the solution of the convection–diffusion equation (Eq. 7). Two types of initial concentration conditions are considered: a given amount of species confined to a small sphere (for planar case, a circle) and the second case of low concentration species uniformly distributed throughout the reservoir. In the first case, no new supply of the species is provided, while for the second case the concentration far upstream of the reservoir is maintained at its initial value, corresponding to the situation that a constant low concentration solution is supplied from the upstream of the reservoir. Starting from these initial conditions, the instantaneous species concentrations in the system at subsequent times are computed for a given set of parameters ($Pe$, $S$). Since the convection–diffusion equation is linear in the concentration $c$, the ratio $c/c_0$ is computed, where $c_0$ is the initial concentration level. Results are presented for the contraction ratio $A = 40$.

3.2.1 Low-concentration species initially confined to a circle in the reservoir

To examine the proposed modeling reflects the published data, one approach is to initially set a bolus of materials within the reservoir. A blob of radius one containing the diluted species is initially centrally located at $x = -4$, with a concentration of $c_0$. Numerical simulation confirms that when $S < 1$, all the species enter the channel, move away from the entrance zone, then completely disappear from the computational domain. The simulation for the critical condition of $S = 1$ and $Pe = 10$ is shown in Fig. 4. Pseudostreamlines, defined in terms of the pseudovelocity $\vec{u} + \vec{u}_p$, represent the trajectories of the particles and they are also depicted Fig. 4. At this value of $S$, there is a stagnation point on the central pseudostreamline, located around $x = 0.5$, and all the trajectories in the core reverse directions and terminate at the ground electrode location. All particles are then blocked near the channel entrance and accumulated at the electrode locations. This focusing effect is obviously mediated by diffusion effect as species may still penetrate beyond the stagnation point by diffusion. An equilibrium concentration distribution in the system can be established for this setup. This distribution is shown in Fig. 4. Diffusion also forms a “cloud” in the reservoir near the channel entrance. The highest concentration occurs at the electrode location with $c/c_0 = 1.5$ for this highly diffusive case.
3.2.2 Initially uniform distribution of species in the reservoir

Again, to test the model against the published experimental data, low concentration species are initially distributed uniformly in the reservoir and we assume that a constant supply of such low concentration solution is provided from an upstream location of the reservoir. There are two scenarios associated with this situation. When the electric field is weak and the parameter $S < 1$, there is no stagnation point on the pseudostreamline along the centerline (the “subcritical” case). This open central pseudostreamline as well as the ones closely surrounding it pass through the channel entrance and extend to infinity down the channel. Species will move continuously into the channel through these open pseudostreamlines, and a steady-state equilibrium concentration distribution could be established. For $S \geq 1$ (“supercritical” operation), a stagnation point appears on the central pseudostreamline. All pseudostreamlines then terminate at the electrode location. No species are “leaked” deep into the channel beyond the stagnation point other than those by the slow diffusive transport. Since there is a continuous supply of species upstream and the species are essentially blocked from entering the channel, the concentration in the reservoir will continue to increase in time and no equilibrium concentration distribution in the system can be reached. Concentration distribution in the system at $t = 400$ for $S = 1.3, Pe = 5$ is shown in Fig. 5. For a microchannel with $D_i = 20 \mu m$, flow velocity of 0.01 cm/s, $t = 400$ is equivalent to 1 min and 20 s of run time. Species are accumulated near the electrode location as well as in the region in the reservoir near the channel entrance. The highest concentration $c/c_0 = 5$ occurs near the electrode location where the central region of the channel has relatively lower concentration.

To quantitatively characterize the transport effects, in Fig. 6 we plot the concentration distributions at $t = 400$ along the centerline $y = 0$ for $S = 0.7, 1, 1.3$, and $Pe = 5$. The concentration along the centerline experiences a dramatic increase within a short distance as the channel entrance is approached, and it forms a peak near $x = 0.036$, which is where the ground electrode is located. For the subcritical case $S = 0.7$, the peak concentration is about $c/c_0 = 3.2$, a significant increase from the background value. The concentration drops off gradually when one moves into the channel. We emphasize that even though there is a large concentration peak for the subcritical case $S = 0.7$, the species are NOT blocked from entering the channel, and the concentration curve extends far downstream into the channel, a key issue in moving forward to differential transport. When $S$ is increased to 1, the concentration peak is significantly sharpened, with a narrower width, and a much faster and severe drop-off inside the channel. The peak value in the concentration is also reduced, from $c/c_0 = 3.2$ for $S = 0.7$, to 2 for $S = 1$. When $S = 1$, the appearance of a stagnation point on the central pseudostreamline “blocks” the species from entering the channel and “pushes” the species to the elec-
Figure 5. Initially uniformly distributed species. Concentration distribution at $t = 400$, for $A = 40$, $S = 1.3$, $Pe = 5$. A large diffusion cloud is formed in the reservoir near the channel entrance.

Figure 6. Concentration distributions along the centerline at $t = 400$ for different values of $S$, $Pe = 5$, and $A = 40$. Particles are initially uniform in the reservoir. For subcritical case $S = 0.7$, the species enter the channel, and they are being depleted from the system. Its concentration curve extends to infinity. For supercritical cases, $S = 1, 1.3$, species are completely blocked from entering the channel, and their concentrations drop-off to zero quickly.

trode location. This lowers the concentration in the central region but increases the concentration near the electrode location. This is true for all the supercritical cases. The steep but smooth drop-off in the concentration in the channel is due to diffusion effects, without which the drop-off to zero would be step-like. When $S$ is increased to 1.3, the stagnation point is moved to the channel entrance $x = 0$, and the peak concentration value along the centerline is further reduced to 1.5. This can be attributed to the stronger focusing effect and stronger lateral diffusion ($y$-direction diffusion) in the reservoir caused by the push-out of the stagnation point. This lateral diffusion in the reservoir is evident from the formation of clusters of higher concentration area outside of the channel entrance in the reservoir as shown in Fig. 5. Obviously, the correct interpretation of Fig. 6 is only possible from a 2-D analysis. In a 1-D theory, one would expect that higher value of $S$ will produce a higher concentration peak. It is also noted that the concentration distribution curve along the centerline is clearly not symmetric about its peak. In the supercritical case, the forward portion of the concentration curve is reminiscent of the Gaussian curve of a pure diffusion, with a gentle slope. The back portion is typical of the shape from the balance of convective transport and backward diffusion, with a steep slope.

The Peclet number $Pe$ can also be used to discuss diffusion effects on the focused supercritical cases. For such cases, all the trajectories terminate at the electrode location and species get accumulated there. The central core region thus has relatively lower concentration. Diffusion from the high concentration region near the electrode location to the core region increases the concentration along the centerline. This is evident from Fig. 7 where the centerline concentra-
not known from the experiment, this value is very close to 1.3 predicted from our computation for very large contraction ratio reservoirs with stagnation point located right at the entrance \( x = 0 \).

Fluorescence signals monitored during the experiments indicated a 1.5-fold increase in the local concentration on the centerline at 19.2 \( \mu m \) from the capillary entrance in the reservoir 9 min after initiation of focusing in one run. In another run, a 1.2-fold increase was observed in the concentration at the capillary entrance on the centerline 4 min after initiation. The Peclet number \( Pe \) corresponding to these experiments, however, are not known, since the diffusion coefficient of the particles in the solvent was not measured. Thus a direct comparison between the computed concentration amplification factors \( c/c_0 \) and the ones from the experiments is difficult since \( c/c_0 \) varies significantly with the Peclet number as shown in Fig. 7. Also worth mention is that under supercritical operating condition \( S \geq 1 \), the concentration in the system will continue to rise in time if a constant supply of low concentration solution is maintained upstream.

In summary, we have quantified electrophoretic focusing condition from previous work to establish a strategy for high resolution differential transport of dilute soluble ionic species in a 2-D system in terms of a dimensionless parameter \( S \). Focusing is achieved when \( S \) is greater than a critical value. This critical value depends on the location of the stagnation point, which for a very large reservoir, is located between \( x = 0 \) and 0.5. This focusing condition is also clearly a criterion for blocking species from entering the channel. For very large reservoir-to-channel contraction ratios, \( S = 1.3 \) is required to block a nondiffusive particle from entering the channel completely (stagnation point at \( x = 0 \)). This criterion is directly applicable to device design. For example, in order to prevent a species with an electrophoretic mobility \( \mu_{em} \) from entering the channel, a current with an apparent electric intensity \( E_{app} = \frac{1.95 Q}{\mu_{em} D_1} \) should be applied within the channel (\( Q \) is the volumetric flow rate of the fluid and \( D_1 \) is the channel height). This criterion can be further extended to other separation applications where a mixture of species with different electrophoretic mobilities can be effectively separated.

Equilibrium concentration distribution is possible when the low concentration species in the reservoir is finite. When there is a constant supply of low concentration species upstream in the reservoir, the concentration in the system will continue to increase under supercritical conditions \( S \geq 1 \), since no particle can enter the channel. Increasing the field strength (or \( S \) value) does not increase the concentration near the central portion of the channel as particles are forced to move to the electrodes. Increase in diffusion, however, increases the concentration near the central region due to stronger diffusive transport from the higher concentration region near the electrodes to the lower concentration region near the center. These 2-D effects are opposite to those from a 1-D analysis.

4 Discussion

Even though the analysis reported here is for a 2-D channel, no qualitatively significant change is expected when the geometry is circular. In particular, there should be little difference between the critical values of \( S \) for achieving focusing for these two geometries, as this condition is the reflection of the balance between the convective fluid velocity and the electrophoretic migration velocity near the stagnation point along the centerline of the channel/capillary. In the experiments of Polson et al. [12], the inner diameter of the circular capillary was 20 \( \mu m \), and the inner diameter of the reservoir was about 2 cm, giving a contraction ratio of 1000. The pressure drop was 0.04 atm over 40 cm. Using the viscosity of water, the centerline velocity of the fully developed flow in the capillary was then \( U = 0.0254 \text{ cm/s} \). Electrophoretic focusing was achieved when a voltage of 14 kV was applied between the two electrodes which were located 40 cm apart. This gave an apparent electric intensity \( E_{app} = 350 \text{ V/cm} \) at the critical condition. The exact electrophoretic mobility \( \mu_{em} \) of the particles used is however unknown, but it is generally in the order of \( 10^{-4} \text{ cm}^2/\text{V-s} \). Thus when focusing was achieved in the experiment, the value of \( S \) is \( 10^{-4} \times 350/0.0254 = 1.38 \). Even though the location of the stagnation point of the pseudovelocity was...
5 References