A numerical study of electrophoretic focusing of ionic species

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Abstract

Electrophoretic focusing of ionic species in a solution moving from a large reservoir into a small capillary is investigated numerically. The system set-up corresponds to the experiment of Polson, Savin & Hayes ¹ where the bulk flow into a fused silica capillary is driven by a pressure differential. The ionic species migrate with a velocity which is the sum of the fluid velocity \( u \) and the electrophoretic velocity \( u_{ep} \) of a charged particle relative to a static fluid. For the species to focus near the capillary entrance, all particle trajectories determined by the velocity \( u + u_{ep} \) must terminate at the ground electrode location which is placed near the capillary entrance. The key parameter for controlling focusing is the ratio between a characteristic electrophoretic velocity and a characteristic fluid velocity, \( S \). It is found that focusing can only occur when \( S \) is greater than a critical value which is computed for the system considered in this paper.

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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, microcrystallizations, distillations, electrophoresis and electrochemistry all depend on differential behaviors of the species based on their molecular/atomic structures. Nearly all analytical chemistry techniques require some set of physical constraints on the properties of the sample, either in terms of bulk properties, interferences, or concentration. Sample preparation includes adjustment of bulk properties of the sample (pH, ionic strength, refractive index, etc.), increased analyte concentration, and removal of unwanted constituents to improve sample throughput and reproducibility. Increased concentration is required by many of the new microfluidic devices. These small-volume devices have many advantages. It can provide for many sample replications or parallel analysis with limited sample and uses incredibly small volumes of solvent. However, this does present a challenge for dilute samples. While ultrasmall volume techniques can exhibit impressive mass detection limits—even single molecules, their concentration limits are necessarily poor and some type of preconcentration is required for detection. Even for sufficiently concentrated samples there is an advantage to pre-concentrating or focusing. The process can allow for a faster separation (offset somewhat by longer sampling times) by virtue of the narrow sample plug and subsequent efficient analysis. The column can be shortened or the flow rate increased since the peaks need not be pulled apart as far to gain resolution; in this way the injection band-width directly influences time-of-analysis and resolution. These advantages have inspired several preconcentration techniques, both on-column and off-column. On-column is the method of choice for ultrasmall volumes because of sample handling issues. Preconcentration techniques include partition-based preconcentration zones, porous membrane filtration, sample stacking (field amplification), and isotachophoretic effect\(^2\)\(^-\)\(^12\).
Others have recognized that setting flow and field gradients opposing one another can effectively cause differential transport for preconcentration or separation \(^1, 13-20\). 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, Savin & Hayes \(^1\). The system used in the experiment is shown schematically in Figure 1, where the bulk flow into a fused silica capillary (towards the left) is 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 inner diameter (i.d.) capillary with 400 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 is about 2 cm, giving an aspect ratio (or contraction ratio) of 1,000: 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 focusing will occur near the capillary. 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 (Figure 2). The electric field strength was empirically balanced to allow a concentrated plug of spheres to form at the entrance to the capillary. The image prior to focusing (left) is shown where the capillary face, the inner bore and the surrounding solution are visible (the general set-up is
similar to the cartoon in Figure 1). On the right, the bright area at the immediate entrance to the capillary indicates a dramatically increased local concentration of the particles. This data clearly show a focusing of the materials near the point where the electric field is initiated.

While there are many experimental investigations on preconcentrating/focusing, only simplified one-dimensional models have been used so far to study the focusing process from the transport point of view \textsuperscript{19,20}. These efforts are limited to the simple balance between the focusing effect and the convection/diffusion effect along a single line. In this paper, we perform numerical simulations of electrophoretic focusing for a two-dimensional channel, similar to the arrangement used in the experiment of Polson, Savin & Hayes \textsuperscript{1}. The physical mechanism of focusing is explored. Key parameters controlling focusing and concentration distribution are identified. It is found that a necessary condition for achieving focusing is that the particle migration velocity $u + u_{ep}$ along the centerline of the channel be brought to zero near the channel entrance. This condition is solely determined by a single dimensionless parameter $S$ which is the ratio between the electrophoretic migration velocity of the species and that of a characteristic fluid flow velocity.

2. Mathematical formulation

Electrophoretic focusing in a pressure-gradient-driven flow can be numerically studied by solving the governing equations for the motion of the buffer fluid and the species. In the experiments of Polson, Savin & Hayes \textsuperscript{1}, the inner surfaces were intentionally treated so that there were no surface charges on the walls of the reservoir and the capillary. Therefore electro-osmotic flow was absent. This simplifies the control of the experiment for achieving focusing
condition. In this situation, the fluid flow field 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 (Figure 1 and Figure 3). The steady velocity field $\mathbf{u}$ of the fluid is determined by solving the continuity and the steady Navier-Stokes equations

\[
div \mathbf{u} = 0, \quad (1)
\]

\[
\rho \mathbf{u} \cdot \nabla \mathbf{u} = -\nabla p + \eta \nabla^2 \mathbf{u}, \quad (2)
\]

together with the no-slip condition $\mathbf{u} = 0$ on all walls, and parabolic velocity profiles far up-stream in the reservoir and far down-stream in the capillary (Figure 4). In equation (2), $p$ is the hydrodynamic pressure, $\rho$ is the fluid density and $\eta$ is the fluid viscosity. Computations are carried out for a two-dimensional channel, and similar results are expected for cylindrical geometries. The prescribed volumetric flow rate is $Q$, the height of the capillary is $D_1$ and the height of the reservoir is $D_2$. The origin of the coordinate system is located at the mid-plane at the capillary entrance, with flow in the positive x-direction, from left to right in Figure 3.

For uncharged species, the micro-particles move with the local fluid velocity $\mathbf{u}$. If 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 $\mathbf{u}_{ep} = \mu_{em} E$, with $\mu_{em}$ being the electrophoretic mobility and $E$ the local applied electric field. For a spherical particle with radius $r$ and surface charge $q$, $\mu_{em} = (q/6\pi \eta r)$. The simple relation between the electrophoretic migration velocity $\mathbf{u}_{ep}$ and the electric intensity $E$ holds even if $E$ varies over distances comparable to the particle size (Keh & Anderson). For definiteness, we assume that all
particles carry positive charges on their surfaces, so that $u_{ep}$ is in the opposite direction of the flow (Figure 3). 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 inter-particle 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 inter-particle interactions. With these assumptions, the micro-particles then move with the velocity $u + u_{ep}$ relative to a fixed frame of reference. The concentration of the species $c$ is determined from the convection-diffusion equation

$$\frac{\partial c}{\partial t} + (u + u_{ep}) \cdot \nabla c = D \nabla^2 c,$$

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 $E$ is related to the electric potential $\phi$ by $E = -\nabla \phi$. The electric potential $\phi$ satisfies the Laplace equation

$$\nabla^2 \phi = 0.$$

On the capillary wall and the sidewalls of the reservoir, insulation condition is imposed. We prescribe the value for the electric potential $\phi$ at the downstream electrode location $x = L_1$, $\phi \big|_{x=L_1} = v_0$, which is the applied voltage. In the experiment of Polson, Savin & Hayes, the ground electrode is located just slightly inside the capillary when the thickness of the reservoir wall is taken into account (see Figure 1). Thus at $x = x_1$, $\phi \big|_{x=0} = 0$, with $x_1$ being the thickness
of the reservoir wall. Far upstream in the reservoir, \( x \to -\infty \), the electric potential does not change, \( \partial \phi / \partial x = 0 \). With these boundary conditions, the electric potential \( \phi \) can be calculated, and the electric field \( E \) is obtained by \( E = -\nabla \phi \). This completely determines the electrophoretic velocity \( u_{ep} \) in the flow domain.

To make the problem dimensionless, we scale length with \( D_1 \), velocity with \( U = 2Q/D_1 \), 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)

\[
div \mathbf{u} = 0, \quad (5)
\]

\[
Re \mathbf{u} \cdot \nabla \mathbf{u} = -\nabla p + \nabla^2 \mathbf{u}, \quad (6)
\]

\[
\frac{\partial c}{\partial t} + (\mathbf{u} + S \mathbf{E}) \cdot \nabla c = \frac{1}{Pe} \nabla^2 c, \quad (7)
\]

where the controlling dimensionless parameters are

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

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

\[
S = \frac{\mu_{en} E_{app}}{U}.
\]

The Reynolds number \( Re \), which is a measure of the importance of inertia force relative to viscous force, is very small in our applications, \( Re \ll 1 \). The Peclet number \( Pe \) is a measure of the strength of the convection effect relative to the diffusion effect. Large Peclet number indicates small diffusion effect. The parameter \( S \) is a measure of the electrophoretic migration velocity relative to the fluid convection velocity. \( E_{app} \) is the apparent electric intensity which is the applied voltage divided by the distance between the electrodes.
A numerical code for general incompressible viscous flow is used for the computation of the velocity field. A non-staggered non-uniform grid layout is employed in this analysis. We use a semi-implicit time-advancement scheme with the Adams-Bashforth method for the explicit terms and the Crank-Nicolson method for the implicit terms. The discretized equations corresponding to the unsteady forms of (5) and (6) are

\[
\frac{u^* - u^{k-1}}{\Delta t} = \frac{1}{2} (u^* + u^{k-1}), \tag{9a}
\]

\[
\nabla^2 \phi^k = \frac{\nabla \cdot u^*}{\Delta t}, \tag{9b}
\]

\[
u^k = u^* - \Delta t \nabla \phi^k, \tag{9c}
\]

\[
p^k = \phi^k - \frac{1}{2} \Delta t \nabla^2 \phi^k, \tag{9d}
\]

where \(u^*\) is the intermediate velocity and it is not constrained by continuity; \(p\) is the pressure, \(\phi\) is the pseudo-pressure, \(\Delta t\) 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 multi-grid 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.

Similarly, the discretized form of equation (7) is

\[
\frac{c^k - c^{k-1}}{\Delta t} = \frac{3}{2} \left( \left[ (u + u_{ep}) \cdot \nabla \right] c \right)^{k-1} - \frac{1}{2} \left( \left[ (u + u_{ep}) \cdot \nabla \right] c \right)^{k-2} + \frac{1}{2Pe} \nabla^2 (c^k + c^{k-1}), \tag{10}
\]
where $c$ is the concentration. The spatial derivatives are discretized using a variation of QUICK (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 & Peck\(^{24}\), and Pacheco\(^{25}\) for more in-depth technical details.

3. Numerical simulation: results

Simulations are carried out for the following geometry: the reservoir has a height of 13, and length of 12. The capillary channel has a height of 1, length of 12. Thus, the contraction ratio from the reservoir to the channel is 13. 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. A voltage is applied at $x = 10$. Since the capillary height is used as the length scale, the electrode downstream in the capillary is located at a very large value of $x$. However, the electric potential $\phi$ 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 capillary (dimensionless) for computation. In the simulation, we impose a voltage at $x = 10$, the value of this voltage can be interpolated from the true applied voltage using the linearity of the electric potential $\phi$ far away from $x = 0$. In dimensionless terms, this interpolated voltage is set to unity. The dimensionless velocity field $u$ and the electrostatic potential field $\phi$ can be computed independently.

Two types of initial concentration conditions are considered in the numerical simulations: 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.

3.1 Low concentration species initially confined to a circle in the reservoir

A blob of radius one containing the diluted species is initially centered at $x = -4$, with a concentration of $c_0$. Even though the evolution of the concentration field is determined by the convection-diffusion equation (7), it is perhaps most helpful to start our discussion from the case of non-diffusive species. For non-diffusive species, once released, they migrate toward the entrance of the capillary with velocity $u + SE$. The electric field $E$ is required to oppose the fluid velocity field $u$ so that the particles slow down when they approach the capillary entrance as the electrophoretic focusing effect takes place. Figures 4(a)(b)(c) show the time sequence of the migration process for $S = 3$, $Pe = 10$. The curves with arrows are the computed particle trajectories from the velocity $u + SE$, or pseudo-streamlines. As shown in Figure 5(a), at this low value of $S$, the trajectories around the centerline $y = 0$ squeeze through the capillary entrance and further extend to infinity downstream in the capillary, indicating that the particles around this core region travel through the entrance without being focused. To achieve focusing near the capillary entrance, the species migration velocity $u + SE$ needs to drop to zero near the capillary entrance. Since the strongest fluid velocity occurs at the centerline $y = 0$, this implies that the pseudo-streamline along the centerline generated by the velocity $u + SE$ needs to have a
stagnation point near the entrance. Otherwise the species will be “leaked” into the capillary as in the case of $S = 3$ shown in Figures 5. Thus, for a given geometry and Peclet number $Pe$, the key parameter that determines whether focusing near the capillary entrance can occur is the parameter $S = \frac{\mu_{em} E_{app}}{U}$, which is the ratio of the characteristic electrophoretic migration velocity of the particle over the characteristic fluid velocity. For a given flow rate $Q$, and particle electrophoretic mobility $\mu_{em}$, a large value of $S$ corresponds to a strong electric field. If the electric intensity is fixed, a large value of $S$ corresponds to species with a large electrophoretic mobility $\mu_{em}$.

Numerical simulation shows that the critical condition for the appearance of a stagnation point along the central pseudo-streamline is $S = 10$. When $S < 10$, the electric field is not strong enough to stop the forward movements of the species near the central pseudo-streamline, and species in the central core region will enter the capillary and move away from the entrance zone. The simulation for the critical condition of $S = 10$ and $Pe = 10$ is shown in Figures 5(a)(b)(c). Pseudo-streamlines are also depicted in these figures. At this value of $S$, the core “opening” is completely closed, making all trajectories in the core to reverse directions and terminate at the ground electrode location. All particles are then blocked at the capillary entrance and accumulated at the electrode locations. No particles will be able to travel any significant distance into the capillary because of the appearance of the stagnation point. This focusing effect is obviously mediated by diffusion effect as species may still penetrate into the capillary by diffusion. An equilibrium concentration distribution in the system is then established which is shown in Figure 5(e). Diffusion also forms a “cloud” in the reservoir near the capillary entrance and traps some species into the recirculation zone. In the limit of infinity Peclet number (zero
diffusion limit), all species initially centrally located in the reservoir will be collected at the ground electrode location for $S = 10$. A close-up view of the equilibrium concentration field near the entrance for $S = 10$ and $Pe = 10$ is shown in Figure 6. The highest concentration occurs at the electrode location with $c/c_0 = 2$ for this highly diffusive case.

Simulations are also carried out for higher values of $S$ (or supercritical case). Equilibrium concentration fields near the capillary entrance for $S = 11, 15$ are shown in Figures 7, 8, respectively. For both cases, the stagnation point along the centerline has been pushed outward toward the reservoir, and two high concentration blobs appear near the ground electrode locations. For a circular capillary, there will be a concentrated ring of species forming near the electrodes.

3.2 Initially uniform distribution of species in the reservoir

In this case, 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 $S < 10$, there is no stagnation point on the pseudo-streamline along the centerline (subcritical). This central pseudo-streamline as well as the ones closely surrounding it pass through the capillary entrance and extend to infinity down the capillary. Species will continuously move into the capillary through these open pseudo-streamlines near the centerline, and a steady-state equilibrium concentration distribution could be established. As discussed above in Section 3.1, in order to achieve focusing, the electric field has to be strong so that $S \geq 10$ (supercritical). When this happens, a stagnation point appears on the center pseudo-streamline, just slightly inside the capillary. All pseudo-streamlines then terminate at the
electrode location. No species are “leaked” into the capillary other than those by the slow diffusive transport. Since there is a continuous supply of species upstream, and the species are blocked from entering the capillary, the concentration of the species in the reservoir will continue to increase in time. No equilibrium concentration distribution in the system can be reached.

Concentration distribution in the system at $t = 400$ for $Pe = 5$ and various values of $S$ are shown Figures 9(a)(b)(c)(d)(e). For $S = 5$, even though the concentration is increased significantly from the background level, the species spread over a large portion in the capillary due to the open pseudo-streamlines (Figure 9(a)). Increasing the value of $S$ strengthens the electrophoresis focusing effect. At $S = 7$, concentration increases significantly near the entrance (Figure 9(b)). At the location of the ground electrode, the concentration increased to $c/c_0 = 3.5$. Further increase in the electric field to a larger value $S = 9$ magnifies the focusing effect, as indicated by the shrinking lengths of the “green tongues” in the capillary shown in Figure 9(c). At the critical value of $S = 10$, complete blocking of the species occurs as the central pseudo-streamline encounters a stagnation point (Figure 9(d)). Species are accumulated near the electrode location as well as in the region in the reservoir near the capillary entrance. Figure 9(e) shows the focusing for $S = 25$, where the species are pushed back into the reservoir.

To quantitatively characterize the focusing effect, in Figure 10 we plot the concentration distributions along the centerline $y = 0$ for $S = 5, 7, 9, 10, 11, \text{ and } Pe = 5$. For $S = 5$, the concentration increases along the centerline as the capillary entrance is approached. The concentration increases from the background value to $c/c_0 = 2.6$ near the entrance $x = 0$, and flattens out deep into the capillary. There is no peak in the concentration profile. For $S = 7$, the
concentration profile along the centerline forms a peak near \( x = 0.036 \), which is where the ground electrode is located. The peak concentration is about \( \frac{c}{c_0} = 3.5 \), a significant increase from the background value, and much higher than 2.6 for \( S = 5 \). The concentration drops off significantly as one moves into the capillary. As the \( S \) value is increased to 9, the concentration peak is further sharpened, with a narrower width, and a much faster and severe drop off inside the capillary. This is due to stronger focusing effect from the electric field. Notice, however, the peak value in the concentration is also reduced, from \( \frac{c}{c_0} = 3.5 \) for \( S = 7 \), to 2.4 for \( S = 9 \). This can be attributed to the fact that the location of the concentration peak is slightly pushed backward towards the reservoir due to the stronger focusing effect, and there is a laterally larger cluster of higher concentration area outside of the capillary entrance in the reservoir, which is due to stronger lateral diffusion caused by the shift of the peak. This phenomenon also occurs for the critical case \( S = 10 \), which has an even narrower bandwidth, and lower peak concentration value. This conclusion is also evident from Figures 9 (b) (c) (d). Thus, stronger lateral diffusion is the cause of the reduced peak value for higher values of \( S \). The correct interpretation of Figure 10 is only possible from a two-dimensional simulation. It is also noted that the concentration distribution curve along the centerline is clearly not symmetric about its peak. 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. Notice that for subcritical cases \( S < 10 \), no focusing of the species occur, as the open psuedo-streamlines allow significant amount of species move into the capillary. Thus the concentration distributions of most interest are those with \( S \geq 10 \). Clearly, the critical case of \( S = 10 \) gives the highest peak value in concentration for all supercritical conditions.
The time history of cross-section averaged concentration at x = 0 is plotted in Figure 11. No equilibrium concentration can be achieved for supercritical cases \( S \geq 10 \). At \( t = 400 \) time units, the cross-section averaged concentration \( c/c_0 = 2.8 \) for the critical case \( S = 10 \). For a micro-channel with \( D_t = 20 \) \( \mu \)m, flow velocity of 0.01 cm/s, this is equivalent to 1 minute and 20 seconds run-time.

Snap-shots of the focusing process are provided in Figures 12(a)-(d) for the critical case \( S = 10 \). At \( t = 1 \), a concentration maximum near the tip of the electrodes starts to appear, as indicated by the two yellow dots in Figure 12(a). As time progresses to \( t = 5 \), the concentration near the tip is further increased (Figure 12(b)). At \( t = 40 \), two blobs with high concentration near the capillary entrance appear, and the highest concentration occurs near the electrode location (Figure 12(c)). The time history of the concentration along the centerline of the system, \( y = 0 \), is plotted in Figure 13. The distribution curves are clearly asymmetric about its peak. The particles move a short distance into the capillary due to diffusion effect only.

Diffusion has a significant effect on the centerline concentration distribution and this effect varies depending on whether the condition is subcritical or supercritical. When the condition is subcritical, there are significant amount of species in the core region surrounding the centerline since the trajectories in this zone pass through the entrance and extend to infinity. Increasing diffusion (decreasing Peclet number) increases the spread of the species along the centerline, thus broadens the width of the peak and reduces the peak value, as shown in Figure 14 for \( S = 7, Pe = 1.25, 2.5, 5 \). The curve for \( Pe = 1.25 \) has the smallest peak value and broadest band and the curve for \( Pe = 5 \) has the highest peak value and narrowest band. However, the situation becomes dramatically different when the condition is critical or supercritical. In such
cases, all the trajectories terminate at the electrode location and species are accumulated there. The central core region would be free of species if there were no diffusion. Thus all the species in the central core region is due to diffusion from the high concentration region near the electrode location. Increasing diffusion increases the concentration peak along the centerline, as evident from Figure 15 for the critical case $S = 10$ and $Pe = 2.5, 5, 10$. The bandwidth however, still increases with increased diffusion.

5. Discussions and concluding remarks

We have studied electrophoretic focusing of dilute soluble ionic species in a two-dimensional system with the flow driven by an applied pressure differential. We found that a necessary condition for achieving focusing is that the particle migration velocity $u + u_{ep}$ along the centerline of the channel be brought to zero near the channel entrance. Otherwise significant amount of particles will move deep into the channel. When this necessary condition for focusing is satisfied, all the particle trajectories entered the channel terminate at the ground electrode location. Particles are then completely blocked from traveling further downstream and they accumulate near the entrance. This condition is solely determined by the dimensionless parameter $S$ when the geometry of the system is prescribed. This parameter is the ratio between the electrophoretic migration velocity of the species and that of a characteristic fluid flow velocity. For the system studied in this paper, the minimum value of $S$ for which this necessary condition is satisfied is $S = 10$.

Numerical simulation shows that for the supercritical cases $S \geq 10$ for which focusing is possible, the highest concentration peak occurs at the critical condition $S = 10$. An increase in the value of $S$ beyond this critical value actually decreases the concentration peak, and the
species form a large cloud in the reservoir with concentrations much lower than the peak value. Equilibrium concentration distribution is possible when the low concentration species in the reservoir is finite. If there is a constant supply of the low concentration species from upstream in the reservoir, the concentration in the system will continue to increase in time when $S \geq 10$ because no particles can enter the capillary.

In the experiments of Polson, Savin & Hayes $^1$, the concentration near the capillary entrance reached $c/c_0 = 1.2$ at two minutes mark. The exact electrophoretic mobility $\mu_{em}$ of the particles is however unknown, but it’s generally in the order of $10^{-4}$ cm$^2$/volt s. Using the data reported in the experiments, we come up with $S = 2.76$ for the corresponding focusing condition. This is of the same order of magnitude as the critical value $S = 10$ from our computation. Consider the uncertainty in the value of the electrophoretic mobility, and the difference in the contraction ratio (1,000 for the experiment, and 13 for the computation), this qualitative agreement is promising. Of course further experimentation is required for quantitative comparison.

Further understanding of the focusing process can be obtained from the numerical results. For a finite amount of mono-dispersed particles in the reservoir, by starting from the maximum applied voltage and gradually reducing its value in a step fashion towards the critical value $S = 10$, the mono-dispersed particles are guaranteed to be focused near the capillary entrance. For a poly-dispersed system of particles with different electrophoretic mobilities, gradually varying the applied voltage can remove the unwanted constituents, and separate particles with different electrophoretic mobilities.
References


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**Figure 1.** Cartoon of the basic concept of electrophoretic focusing using the bulk flow versus electric field to capture and concentrate charged molecules or particles.

**Figure 2.** (Left) Fused silica capillary entrance prior to electrophoretic focusing. The initial concentration of the fluorescent latex spheres was $10^{-11}$ M. (Right) Flow and electric field empirically adjusted to concentrate latex spheres at entrance for 4 min.

**Figure 3** Schematic of the contraction flow from the reservoir to the capillary in a pressure-driven flow.

**Figure 4** Disappearance of a blob of species in a weak electric field, $S = 3$. $Pe = 10$. (a) $t = 0$, particles are confined to the circle centered at $x = -8$, and the initial concentration is 0.1. The lines with arrows are the trajectories of the particles. Notice that near the center $y = 0$, the trajectories squeeze through the entrance and extend to far downstream in the capillary; (b) $t = 50$, significant amount of particles entered the capillary. (c) $t = 200$. Particles are disappearing from the domain. Notice that the blob is placed near the center of the reservoir, $y = 0$, and all the trajectories past through the initial blob enter the capillary. Thus there are no particles trapped at the corners of the reservoir.

**Figure 5** Time sequence of focusing of a blob of species at critical condition, $S = 10$, $Pe = 10$. (a) $t = 1$; (b) $t = 50$. $t = 200$. The appearance of the stagnation point along the central pseudo-streamline blocks the inward movements of the species.

**Figure 6** Close-up view of the equilibrium concentration distribution near the capillary entrance for the critical case of $S = 10$, $Pe = 10$.

**Figure 7** Focusing of a blob. Equilibrium concentration near the capillary entrance for supercritical case $S = 11$, $Pe = 10$.

**Figure 8** Focusing of a blob. Equilibrium concentration near the capillary entrance for supercritical case $S = 15$, $Pe = 10$. Species are being pushed back towards the reservoir.
Figure 9 Focusing from uniform initial concentration distribution and with a constant supply of low concentration solution. Concentration fields at $t=400$ for $Pe = 5$ for different values of $S$. The lines with arrows are the particle trajectories. Initially the concentration in the reservoir is 0.1 and uniform, and zero in the capillary. (a) $S = 5$. The electric field is too weak to create focusing, and most of the species have entered the capillary; (b) $S = 7$. Accumulation occurs near the capillary entrance at $x = 0$; (c) $S = 9$. (d) $S = 10$, appearance of first stagnation point; (e) $S = 25$. Very strong focusing occurs near the capillary entrance at $x = 0$.

Figure 10 Concentration distributions along the centerline for various values of $S$. $Pe = 5$ and $t=400$.

Figure 11 Cross-section averaged concentration at the capillary entrance $x = 0$ as a function of time for various values of $S$, and $Pe = 5$.

Figure 12 Snap shots of focusing process at different times. $S = 10$, $Pe = 5$. Initially the concentration in the reservoir is $c = 0.1$ and uniform, and zero in the capillary. (a) $t = 5$; (b) $t = 20$; (c) $t = 40$; (d) $t = 400$.

Figure 13 Time-evolution of concentration profile along the centerline when the initial concentration is uniform in the reservoir. $S = 10$, $Pe = 5$, and the initial uniform concentration in the reservoir is 0.1.

Figure 14 Effect of diffusion on the centerline concentration profiles for subcritical case $S = 7$. Small diffusion (large Peclet number) makes the peak sharper and the band narrower.

Figure 15 Effect of diffusion on the centerline concentration profiles for critical case $S = 10$. Large diffusion (small Peclet number) broadens the band and increases the peak value.
Figure 1. Cartoon of the basic concept of electrophoretic focusing using the bulk flow versus electric field to capture and concentrate charged molecules or particles.

<table>
<thead>
<tr>
<th>Background Concentration</th>
<th>Post-Electrophoretic Focusing</th>
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<td>capillary entrance</td>
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Figure 2. (Left) Fused silica capillary entrance prior to electrophoretic focusing. The initial concentration of the fluorescent latex spheres was $10^{-11}$ M. (Right) Flow and electric field empirically adjusted to concentrate latex spheres at entrance for 4 min.
Figure 3 Schematic of the contraction flow from the reservoir to the capillary in a pressure-driven flow.
Figure 4 Disappearance of a blob of species in a weak electric field, $S = 3$. $Pe = 10$. (a) $t = 0$, particles are confined to the circle centered at $x = -8$, and the initial concentration is 0.1. The lines with arrows are the trajectories of the particles. Notice that near the center $y = 0$, the trajectories squeeze through the entrance and extend to far downstream in the capillary; (b) $t = 50$, significant amount of particles entered the capillary. (c) $t = 200$. Particles are disappearing from the domain. Notice that the blob is placed near the center of the reservoir, $y = 0$, and all the trajectories past through the initial blob enter the capillary. Thus there are no particles trapped at the corners of the reservoir.
Figure 5 Time sequence of focusing of a blob of species at critical condition, $S = 10$, $Pe = 10$. (a) $t = 1$; (b) $t = 50$, $t = 200$. The appearance of the stagnation point along the central pseudo-streamline blocks the inward movements of the species.
Figure 6 Close-up view of the equilibrium concentration distribution near the capillary entrance for the critical case of $S = 10$, $Pe=10$. 

$c/c_o$
Figure 7 Focusing of a blob. Equilibrium concentration near the capillary entrance for supercritical case $S = 11$, $Pe = 10$. 


Figure 8 Focusing of a blob. Equilibrium concentration near the capillary entrance for supercritical case $S = 15, Pe = 10$. Species are being pushed back towards the reservoir.
Figure 9 Focusing from uniform initial concentration distribution and with a constant supply of low concentration solution. Concentration fields at $t = 400$ for $Pe = 5$ for different values of $S$. The lines with arrows are the particle trajectories. Initially the concentration in the reservoir is 0.1 and uniform, and zero in the capillary. (a) $S = 5$. The electric field is too weak to create focusing, and most of the species have entered the capillary; (b) $S = 7$. Accumulation occurs near the capillary entrance at $x = 0$; (c) $S = 9$. (d) $S = 10$, appearance of first stagnation point; (e) $S = 25$. Very strong focusing occurs near the capillary entrance at $x = 0$. 

9(e)
Figure 10 Concentration distributions along the centerline for various values of $S$. $Pe = 5$ and $t=400$. 
Figure 11 Cross-section averaged concentration at the capillary entrance $x = 0$ as a function of time for various values of $S$, and $Pe = 5$. 
Figure 12 Snap shots of focusing process at different times. $S = 10$, $Pe = 5$. Initially the concentration in the reservoir is $c = 0.1$ and uniform, and zero in the capillary. (a) $t = 5$; (b) $t = 20$; (c) $t = 40$; (d) $t = 400$.

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