The effect of divalent counterions on particle velocimetry studies of electrokinetically driven flows

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Abstract In particle-image velocimetry studies of the flow of aqueous electrolyte solutions in microchannels, the tracers are usually fluorescent polystyrene (PS) spheres a few μm or less in radius a. In many cases, the flows are driven by an electric field because the resulting electroosmotic flow (EOF) has a uniform velocity profile and hence less convective dispersion. This electric field affects only the hydrated ions in the thin electric double layer (EDL), which screens the charged surface of the microchannel wall.

The surfaces of the PS tracers suspended in the electrolyte solution also become charged, however, and so an EDL surrounds each particle. The electric field that drives EOF will therefore affect the particle tracers, a phenomenon known as electrophoresis. The velocity of a tracer particle \( u_p \) in such an electrokinetically driven flow will therefore be the superposition of the EOF and electrophoretic velocities \( u_{eo} \) and \( u_{ep} \), respectively.

The wall and particle surface charges, and hence \( u_{eo} \) and \( u_{ep} \), are determined by the wall and particle zeta-potentials \( \zeta_w \) and \( \zeta_p \), respectively. Changes in \( \zeta_w \) and \( \zeta_p \) will therefore affect the particle velocity. The zeta-potential of glass surfaces is known, for example, to be affected by the pH and ionic strength of the electrolyte solution, as well as the valence and type of electrolytes in the solution.

The flow of monovalent NaCl-NaOH and borate buffer-NaOH solutions with ionic strengths \( I = 0.2 \) mM to \( 10 \) mM driven by an electric field of magnitude \( E \leq 43 \) V/cm parallel to the channel wall was therefore studied in fused-silica microchannels with a depth of 33 μm. The effect of small amounts of the divalent cations Mg\(^{2+}\) and Ca\(^{2+}\), as well as the effect of varying solution pH from 8.5 to 10.5 and varying \( I \) by almost two orders of magnitude, was investigated by measuring the velocity of a \( a = 104 \) nm fluorescent carboxylated PS particles with evanescent-wave particle velocimetry. The effect of these solution parameters on \( \zeta_p \) was determined using dynamic light scattering. Finally, the EOF velocity was determined by subtracting the electrophoretic velocity of the particles from the measured particle velocity in this uniform flow, and the zeta-potential of the fused-silica channel walls was estimated by assuming that \( u_{eo} \) was directly proportional to \( \zeta_w \).

1. Introduction

Microfluidics, the study of flows with overall dimensions typically ranging from a few μm to a few hundred μm, has been the subject of a great deal of research over the last decade, motivated by the development of Lab on a Chip (LOC) or micro-Total Analysis System (μTAS) devices for high-throughput biomolecular and cellular separation, reaction and detection (Reyes et al. 2002; Ohno et al. 2008). Reducing the overall dimension of the flow has a number of advantages, including faster diffusion of mass and heat, and reduced sample and reagent volumes.

The flows in LOC are for the most part incompressible and low Reynolds number internal flows of aqueous solutions containing charged biomolecules and electrolytes. For a LOC fabricated in glass, the microchannel walls become negatively charged when exposed to an aqueous electrolyte solution at moderate pH due to deprotonation of surface silanol groups, and the charged wall attracts cations (i.e., counterions) from the fluid, forming a screening layer that neutralizes, or cancels, the negative surface charge of the wall. This screening layer, known as the electric double layer (EDL), consists of: \( i \) the inner Stern layer consisting of immobile counterions “attached” by electrostatic forces to the surface of the wall; and \( ii \) the outer diffuse layer containing mobile counterions subject to random thermal fluctuations (Probstein 2003). The electrostatic potential in the EDL decays exponentially with distance normal to the wall from its value at the outer edge of the Stern layer, the (wall) zeta-potential \( \zeta_w \). The length scale of this exponential decay is known as the Debye length scale \( \lambda_D \); for aqueous solutions at room temperature, \( \lambda_D \) is typically \( O(1–10 \) nm).
In electrokinetically driven flows (EDF), a voltage gradient, or electric field of magnitude $E$, is applied parallel to the wall. The field only drives the cations and fluid molecules in the EDL towards the anode, while the neutral fluid beyond the EDL is driven via viscous effects towards the anode. The resulting electroosmotic flow (EOF) has a uniform velocity profile outside the EDL, \textit{i.e.}, over most of the channel cross-section, and the “boundary layer-like” flow in the EDL recovers to 99% of the bulk velocity $\sim 4.6a_D$ from the wall. Electrokinetically driven flows are commonly used in LOC because its uniform velocity profile has less convective dispersion than parabolic Poiseuille flow.

A common velocimetry technique used in microfluidic devices is microscale particle-image velocimetry ($\mu$PIV), which measures the displacements of particle tracers, usually fluorescent polystyrene (PS) spheres of radii $a \leq 2 \, \mu m$ and density $\rho = 1.05 \, g/cm^3$, from two successive exposures of the tracers separated by a time interval $\Delta t$ (Santiago et al. 1998; Wereley and Meinhart 2010). The particle velocity is the particle displacement, which is usually determined from the average cross-correlation, divided by $\Delta t$. The fluid velocity is then assumed to be identical to the particle velocity.

The surface of the PS tracers will however also become charged in the presence of an aqueous electrolyte solution, with a surface charge characterized by the particle zeta-potential $\zeta_p$ which is again the electric potential at the outer edge of the Stern layer a counterion diameter away from the surface of the particle. The external electric field that drives the EOF will therefore also affect the particle tracers. If the PS tracers, like the wall, have a negative surface charge, $E$ will drive the tracers towards the cathode, a phenomenon known as electrophoresis. A tracer particle will therefore be convected by EOF and driven by electrophoresis in opposite directions (Fig. 1). The actual particle velocity will be the superposition of the EOF and electrophoretic velocities $u_{eo}$ and $u_{ep}$, respectively, and so the particle velocity will not, in general, be equal to the fluid velocity in EDF.

However, because the electric field affects only the fluid in the screening layer, EOF is very sensitive to changes in $\zeta_w$. As reviewed in Kirby and Hasselbrink (2004), the wall zeta-potential for silicate glasses depends upon the properties of the aqueous solution, such as:

- its pH, because this affects the extent of silanol deprotonation and the concentration of protons (Kirby and Hasselbrink 2004; Coreño et al. 2001; Kosmulski and Matijevic 1991);
- its ionic strength $I$, because this affects both the concentration of the counterions and the thickness of the EDL (and $\lambda_D$) (Kirby and Hasselbrink 2004; Coreño et al. 2001);
- the valence of the electrolytes, because multivalent counterions are known to reduce (the magnitude) of $\zeta_w$ more than monovalent counterions, presumably due both to nonspecific and specific adsorption (Datta et al. 2009).

Variations in solution pH, ionic strength and electrolyte valence could also affect $\zeta_p$, and hence velocity data obtained with particle tracers.

The changes in wall zeta-potential due to electrolyte or analyte adsorption have a major impact on capillary zone electrophoresis (CZE), which is commonly used to separate ionic species because changes affect the migration velocity of these species. Spatial variations in $\zeta_w$ can lead to nonuniform flows and even flow reversal, causing peak broadening, \textit{i.e.}, an increase in the width of the region where a given species is concentrated, and lower separation efficiencies. Towns and Regnier (1992) performed electrophoretic separation processes in fused-silica capillaries, using solutions of proteins with different isoelectric points pH (\textit{i.e.}, pH values where the protein in solution carries no charge) at pH3–11, and observed that positively charged species were preferentially adsorbed within a few cm of where the species were introduced at the capillary inlet, leading to variations in the migration speed of the proteins along the length of the capillary and lower separation efficiencies. Ermakov et al. (1995) modeled the

![Figure 1](image)

**Figure 1** A negatively charged particle near a negatively charged wall subject to electrophoresis and EOF. Note that only the cations in the EDL are shown near the wall.
interactions between fused silica capillary walls and various analytes (e.g. small monovalent cations, polycations, and proteins) as diffusion-driven absorption, and was able to reproduce many of the features observed in experimental studies. The capillaries and microchannels commonly used in CZE are often treated with polymeric coatings to minimize “fouling” due to analyte adsorption, as reviewed by Doherty et al. (2003).

As part of a study of the transport and near-wall dynamics of colloidal particles in EDF, the effect of counterion properties such as pH (which characterizes the concentration of only one type of monovalent counterion), ionic strength, and electrolyte valence on EDF was studied using evanescent-wave particle velocimetry. The objectives of this research were to quantify the effect of small amounts of the divalent cations Mg$^{2+}$ and Ca$^{2+}$, as well as the ionic strength and pH of the solution, the on the EOF of monovalent aqueous solutions, and the electrophoresis of $a = 104$ nm fluorescent carboxylate-terminated PS tracers suspended in these solutions. The particle velocity within ~400 nm of the wall was measured in steady uniform EDF in ~30 μm deep fused-silica channels driven by electric fields parallel to the axis of the channel at $E \leq 43$ V/cm. Particle zeta-potentials were measured using dynamic light scattering (DLS), and the EOF velocities and wall zeta-potentials were then determined under the assumption of thin EDLs where the electrophoretic and electroosmotic velocities are proportional to $\zeta_p$ and $\zeta_w$, respectively.

2. Experimental Description

2.1 Evanescent-wave particle velocimetry

In many microchannel flows, surface effects become significant because the surface area becomes relatively large compared with the volume. Such surface (e.g. electrostatic, capillary) effects can be exploited to develop new technologies for driving and controlling transport in LOC. Since these effects are usually significant only within 0.5 μm of the wall, characterizing transport by measuring the velocity field in this near-wall region is important in understanding how surface phenomena affect flows in microfluidic devices.

It is difficult, however, to resolve velocity fields even within 1 μm of the wall using μPIV, because: i) the spatial resolution of μPIV along the optical axis, based on the depth of correlation, typically exceeds 2 μm (Wereley and Meinhart 2010); and ii) μPIV images usually have significant optical interference near the wall because of stray reflections and glare. Since the focus of this work is the near-wall transport of colloidal particles driven by an external electric field, evanescent-wave particle velocimetry, which images only the particles within ~400 nm of the wall, was used instead.

When light undergoes total internal reflection (TIR) at a planar refractive-index interface, such as that between a glass wall and an aqueous solution, the waves with complex wavenumber are transmitted into the fluid. The resulting evanescent wave, which propagates in the fluid parallel to the wall, has an intensity $I$ that decays exponentially with distance normal to the wall $z$:

$$I(z) = I_0 \exp\{-z/\zeta_p\}$$  

where $I_0$, the maximum intensity of the evanescent wave, is the intensity at the surface of the wall, $z = 0$. The length scale of this decay, the intensity-based penetration depth $\zeta_p$, is a function of the wavelength of the illumination $\lambda$, the refractive indices of the glass and the solution, and the angle of incidence of the light, which must exceed the critical angle $\theta_c$ for there to be TIR. For the TIR of $\lambda = 488$ nm blue light at a glass-water interface, $\zeta_p \approx 100$ nm for values of $\theta_i$ a few degrees greater than $\theta_c$. The evanescent wave therefore only illuminates the region within a few hundred nm of the wall, and the actual $z$-extent of this region is usually determined by the minimum signal-to-noise ratio required to distinguish a particle from the background of the image.

Various tracers, including visible quantum dots with an effective diameter of about 11 nm, have been used in evanescent-wave particle velocimetry by Pouya et al. (2005). Most applications, however, use the same fluorescent PS spheres used for μPIV. The relatively weak signals from the tracers, imaged over a plane parallel to the wall, are isolated from the scattered light by wavelength filtering. Evanescent-wave particle velocimetry has been used to study Poiseuille flow (Huang et al. 2006; Li and...
Yoda 2010) and EOF (Sadr et al. 2004) in microchannels. In multilayer nano-particle tracking velocimetry (MnPTV), the particle edge-wall separation is determined from the particle image brightness \( I_p \) assuming that it has the same behavior as that of the evanescent wave (Eq. 1) (Li and Yoda 2008). The particle images are divided into “sub-layers,” or bins based upon their \( h \)-positions, and the particle velocities are determined in each sub-layer to obtain velocity data at different distances from the wall.

2.2 Electrokinetically driven flows
Electrokinetically driven flows were studied through fused-silica channels with a trapezoidal cross-section of depth 33 \( \mu \)m and an average width of ~320 \( \mu \)m (the width of these wet-etched channels varied from 277 \( \mu \)m to 360 \( \mu \)m). The flow was driven by electric fields parallel to the wall of magnitude \( E = 12 \text{ V/cm, } 21 \text{ V/cm, } 31 \text{ V/cm and } 43 \text{ V/cm created by a dc power supply (Stanford Research Systems, PS325) attached to platinum electrodes submerged in the reservoirs upstream and downstream of the microchannel. In all cases, Joule heating was negligible, and the temperature of the fluid was the ambient temperature which ranged from 19 \( ^\circ \text{C} \) to 21 \( ^\circ \text{C}. \)

2.2.1 Divalent cation effects
The first set of studies looked at the effect of the divalent counterions Mg\(^{++} \) and Ca\(^{++} \). Seven different electrolyte solutions, all of ionic strength \( I = 10 \text{ mM corresponding to a Debye length } \lambda_D = 3 \text{ nm, were studied:} \)

- a “base” monovalent electrolyte solution consisting of 9 mM sodium chloride (NaCl) and 1 mmol/L sodium hydroxide (NaOH) at pH10.5
- three different solutions with small amounts of the divalent cation Mg\(^{++} \) consisting of the base solution and enough magnesium chloride (MgCl\(_2\)) so that the divalent cation fraction \( \alpha \equiv [\text{Mg}^{++}] / [\text{Na}^+] = 0.5\%, 1\% \) and 2\%
- three different solutions with small amounts of the divalent cation Ca\(^{++} \) consisting of the base solution and enough calcium chloride (CaCl\(_2\)) so that the divalent cation fraction \( \alpha \equiv [\text{Ca}^{++}] / [\text{Na}^+] = 0.5\%, 1\% \) and 2\%.

Here, the ionic strength \( I = \sum_{i=1}^{N} z_i^2 c_i / 2 \) where \( z_i \) is the valence and \( c_i \) is the molar concentration of the \( i \)-th electrolyte species for all \( N \) species present in the solution. The divalent cation fractions studied here were limited to a maximum value of 2% because most of the tracer particles were immobilized (presumably due to electrostatic forces) on the microchannel wall at higher values of \( \alpha \).

To prepare the base solution, NaCl (Sigma-Aldrich S-9625) and NaOH were dissolved in distilled deionized water. A 20 mM MgCl\(_2\) solution was prepared by diluting a 1 M stock solution (Fluka 63020) with distilled deionized water, while a 20 mM CaCl\(_2\) solution was prepared by dissolving calcium chloride dehydrate (CaCl\(_2\) 2H\(_2\)O) (EMD CX0130-1) in distilled deionized water. The base solution, MgCl\(_2\) solution and CaCl\(_2\) solution were all filtered through glass microfiber filters with a 0.7 \( \mu \)m pore size (Whatman 1825070). The distilled deionized water used to prepare all these solutions had a resistivity exceeding 18 M\( \Omega \)-cm.

All seven solutions were seeded with fluorescent carboxylate-terminated polystyrene (PS) particles (Invitrogen F-8811) at a volume fraction \( \phi = 1.6 \times 10^{-4} \). The particles had an average radius \( a = 104 \pm 7 \text{ nm, a density } \rho = 1.05 \text{ g/cm}^3 \), and absorption and emission maxima at wavelengths of 505 nm and 515 nm, respectively, according to the manufacturer. The particle solution was sonicated for 15 min and filtered through syringe filters with 0.45 \( \mu \)m pore size (Millipore SLHV033RS), then used in all cases within a week. Immediately before the experiment, the solution is sonicated for 15 min and degassed by placing the fluid under a vacuum at an absolute pressure of \( O(10 \text{ kPa}) \) for another 15 min.

The particle zeta-potentials \( \zeta_\rho \) (average ± standard deviation) were measured using dynamic light scattering with a Malvern Zetasizer. In all cases, the average and standard deviation values were calculated over five independent Zetasizer runs. For the experiments with Mg\(^{++} \), the particle zeta-potentials for particles were suspended in the four different working fluids were:
• $\alpha = 0$ (base fluid): $\zeta_p = -49.1 \pm 1.2$ mV  
• $\alpha = 0.5\%$: $\zeta_p = -49.1 \pm 0.5$ mV  
• $\alpha = 1\%$: $\zeta_p = -47.1 \pm 1.0$ mV  
• $\alpha = 2\%$: $\zeta_p = -43.1 \pm 0.6$ mV  

The $\zeta_p$ values decrease in magnitude as $\alpha$ increases, suggesting that there is some adsorption of the Mg$^{++}$ on the negatively charged surface of the PS particles.

For the experiments with Ca$^{++}$, the particle zeta-potentials in the different working fluids were:

• $\alpha = 0$ (base fluid): $\zeta_p = -49.1 \pm 1.2$ mV  
• $\alpha = 0.5\%$: $\zeta_p = -49.1 \pm 0.8$ mV  
• $\alpha = 1\%$: $\zeta_p = -47.1 \pm 0.5$ mV  
• $\alpha = 2\%$: $\zeta_p = -44.8 \pm 0.4$ mV  

Again, $\zeta_p$ decreases in magnitude as $\alpha$ increases, implying that the Ca$^{++}$ adsors on the surface of the PS particles, and it appears that the decrease is slightly smaller than that observed for Mg$^{++}$ at $\alpha = 2\%$. The results at $\alpha = 2\%$, as well as results (not shown here) at higher divalent cation fractions, suggest that Ca$^{++}$ has slightly less affinity than Mg$^{++}$ for the surface of these PS particles.

2.2.2 pH and ionic strength effects
The next set of studies considered the effect of varying the pH and ionic strength of the working fluid.

Five different solutions were studied:
• a “base” monovalent borate buffer solution at $I = 10$ mM and pH8.5 consisting of sodium tetraborate (Na$_2$B$_4$O$_7$) and boric acid (H$_3$BO$_3$), and a trace amount of NaOH  
• two different $I = 10$ mM borate buffer and NaOH solutions at pH9.5 and 10.5;  
• two different borate buffer solutions (with a trace amount of NaOH) at pH8.5 at $I = 0.2$ mM and 1 mM  

The base solution and the pH 9.5 and 10.5 solutions were all prepared by mixing 5 mM Na$_2$B$_4$O$_7$ (Acros 419450010) and 10 mM H$_3$BO$_3$ (Acros 423485000) solutions (prepared from distilled deionized water with a resistivity of at least 18 M$\Omega$-cm), and titrating with 10 mM NaOH to obtain the required pH. The $I = 1$ mM solution was prepared by mixing 0.5 mM Na$_2$B$_4$O$_7$ and 1 mM H$_3$BO$_3$, and mixing with 1 mM NaOH to pH8.5. Finally, the $I = 0.2$ mM solution was prepared by mixing 0.1 mM Na$_2$B$_4$O$_7$ and 0.2 mM H$_3$BO$_3$, and mixing with 0.2 mM NaOH to pH8.5. Given the difficulties in keeping such a low ionic strength aqueous electrolyte solution at a stable pH and ionic strength, a fresh 0.2 mM solution was prepared before each experiment and used within 2 h. All the solutions were filtered through 0.7 μm pore size filters as described previously.

The solutions were seeded with $a = 104$ nm fluorescent PS particles as described previously. The zeta-potentials of the particles suspended in the five different working fluids (average ± standard deviation) measured using light scattering over five independent experiments for each case were:

• Base fluid (pH 8.5 and $I = 10$ mM): $\zeta_p = -44.0 \pm 1.0$ mV  
• pH9.5 and $I = 10$ mM: $\zeta_p = -44.0 \pm 0.8$ mV  
• pH10.5 and $I = 10$ mM: $\zeta_p = -43.5 \pm 0.9$ mV  
• $I = 1$ mM: $\zeta_p = -56.5 \pm 0.6$ mV  
• $I = 0.2$ mM: $\zeta_p = -57.1 \pm 1.7$ mV  

Although solution pH had little, if any effect on $\zeta_p$, the magnitude of the particle zeta-potential decreases by about 24% as the ionic strength of the monovalent solution increases by nearly two orders of magnitude.

2.2.3 Experimental description
The microchannel was mounted on the stage of an inverted epi-fluorescence microscope (Leica DMIREE2) and illuminated by evanescent waves over a roughly elliptical region 0.9 mm × 0.3 mm with a penetration depth $z_p = 142$ nm in a region next to the center of the bottom wall of the channel (i.e., away from the side walls) with a surface roughness of 3 nm. The evanescent waves were generated by the total internal reflection (TIR) of an argon-ion laser beam at a wavelength of 488 nm with an output power of
about 1 W at the silica-fluid interface, where the laser beam was coupled into the fused-silica substrate of the microchannel by a prism (Fig. 2).

Before each experimental run, the microchannels were rinsed by flowing acetone, methanol, deionized water, 1 M sodium hydroxide (NaOH), then the appropriate base solution with no particles. The fluorescence from the particles in a plane immediately adjacent to and parallel to the wall was imaged over a rectangular region 136 µm × 37 µm in the center of the illuminated region through a filter which separated the longer-wavelength fluorescence from the 488 nm illumination onto an electron multiplying CCD (EMCCD) camera (Hamamatsu C9100-13) through a 63 magnification, 0.7 numerical aperture microscope objective.

An acousto-optic modulator (AOM) was used to illuminate the particles with a pair of pulses 0.49 ms in width spaced Δt = 5 ms or 10 ms apart; the time interval between the pulses was adjusted to ensure that the particle displacement over Δt was at least 1 pixel, or 254 nm. Each pair of pulses was spaced 100–250 ms apart. A sequence of 500 512 × 144 pixels image pairs (= 1000 images) were acquired for each dataset over a total data acquisition time of 150 s.

After correcting the images for the nonlinear response of the EMCCD camera and removing images of flocculated and overlapping particles, as well as images of stationary particles attached to the wall, the particle edge-wall separation distance h was determined using Eq. 2 for the remaining particle images from the particle image intensity Ip, which was defined in this set of experiments to be an area-averaged integral over the grayscale values within the particle image in the frame. The intensity of particles at h = 0, or Ip”, was determined from calibrations that were performed at the end of the experimental run where a O(1 mM) aqueous calcium chloride (CaCl2) solution was injected into the channel to attach particles to the wall, and illuminated and imaged under conditions identical to those in the actual experiments. Only results for particles at h ≤ 400 nm ≈ 2.7 zp were included to ensure that there was sufficient contrast between the particle images and the background noise in each frame.

The particle displacements were found using the particle-tracking procedure as described by Li and Yoda (2008). The particle velocity parallel to the wall was then the displacement divided by Δt.

As discussed previously, the particle velocities measured by evanescent-wave particle velocimetry are the combination of the electrophoretic velocity uep and the electroosmotic velocity ueo (Fig. 1). Since λ/ao ≈ 1 in these experiments, the EDL is “thin,” and the EOF velocity profile is essentially uniform. By the Helmholtz-Smoluchowski relation, the electrophoretic and electroosmotic velocities are proportional to \( E \) and \( \zeta_p \) and \( \zeta_w \), respectively. The measured particle velocity

\[
\begin{align*}
\mathbf{u}_p &= \mathbf{u}_{ep} + \mathbf{u}_{eo} = \frac{e}{\mu} (\zeta_p - \zeta_w) \mathbf{E} \\
\end{align*}
\]

where \( e \) and \( \mu \) are the permittivity and dynamic viscosity of the fluid, respectively. Near the wall, the electrophoretic mobility of a particle is hindered by particle-wall hydrodynamic interactions (Keh and Anderson 1985) but this effect is usually negligible for evanescent-wave particle velocimetry (Kazoe and Yoda 2011). The electroosmotic flow velocity can then be estimated using Eq. 2 from the velocities measured by evanescent-wave particle velocimetry and the mean values for \( \zeta_p \) obtained from light scattering.
3. Results and Discussions

3.1 Divalent Cation Effects: Mg$^{++}$

The distribution of colloidal PS particles near the wall measured by evanescent-wave particle velocimetry is nonuniform due to the repulsive electrostatic forces due to particle-wall EDL interactions mediated by attractive van der Waals forces due to permanent and induced dipole interactions (Bevan and Prieve 1999), as described by the classic Derjaguin-Landau-Verwey-Overbeek (DLVO) theory of colloid science (Probstein 2003). A nonuniform particle distribution should have no effect on the velocity results for this flow, since the particle and EOF velocities are uniform. Although results are not shown here due to space limitations, it appears that Mg$^{++}$ or Ca$^{++}$, at least for $\alpha \leq 2\%$, has no effect on the particle distributions for $h \leq 400$ nm (Cevheri and Yoda 2012). These experimental studies also indicate that the electric field magnitude, as well as the ionic strength and pH of the solution, have no effect on the near-wall particle distribution.

Multilayer nano-particle tracking velocimetry may lack the sensitivity to detect the effect of the variations in particle and wall zeta-potentials, at least over this range of parameters. The particle distribution is also “blurred” by Brownian diffusion of the particles, since the exposure time of 0.49 ms is at least five orders of magnitude greater than the timescale of the Brownian fluctuations. Moreover, the particle-wall EDL interactions are likely attenuated by the background monovalent electrolytes in the solution: at a molar concentration of 10 mM, the number density of electrolytes is eight orders of magnitude greater than that of the particles.

Figure 3 shows the particle velocities $u_p$ measured with evanescent-wave particle velocimetry as a function of the applied electric field magnitude $E$ for all four solutions, namely the base pure NaCl-NaOH solution, or $\alpha = 0$ ( ), the NaCl-NaOH solution with $\alpha = 0.5\%$ Mg$^{++}$ ( ), the NaCl-NaOH solution with $\alpha = 1\%$ Mg$^{++}$ ( ), and the NaCl-NaOH solution with $\alpha = 2\%$ Mg$^{++}$ ( ). In all cases, these data are the average of four independent experiments performed in the same channel. The uniform nature of the particle velocity was verified by the experimental results, which gave similar results for $u_p$ at different $h$. The particle velocities were therefore averaged over $h = [100 \text{ nm} : 300 \text{ nm}]$. As expected, $u_p$ varies linearly with $E$; linear regression of these data (solid lines) gives intercepts of 0.3–5 µm/s. The error bars represent the standard deviations for these data. The results clearly show that the velocities at a given $E$ decrease as the Mg$^{++}$ fraction increases, consistent with adsorption of Mg$^{++}$ on the negatively charged surfaces of the fused-silica channel reducing $\zeta_w$.

The EOF velocity $u_{eo}$ was calculated from the data of Figure 3 using Eq. 2 and the $\zeta_p$ values given previously for the tracer particles in the four working fluids. Figure 4 graphs $u_{eo}$ as a function of $E$ using the same symbols as Figure 3. Again, the solid lines represent a linear curve-fit to these data. As expected, the EOF velocity decreases at a given $E$ as $\alpha$ increases.

The slope of these data, the electroosmotic mobility $\mu_{eo}$, is directly proportional to $\zeta_w$:

$$\mu_{eo} = \frac{\epsilon}{\mu} \zeta_w$$

(3)
The wall zeta-potentials obtained from linear regression of these data and Eq. 3 are:

- $\alpha = 0$ (base fluid): $\zeta_w = -90.7 \pm 2.2 \text{ mV}$
- $\alpha = 0.5\%$: $\zeta_w = -80.6 \pm 4.5 \text{ mV}$
- $\alpha = 1\%$: $\zeta_w = -69.1 \pm 5.3 \text{ mV}$
- $\alpha = 2\%$: $\zeta_w = -59.0 \pm 2.2 \text{ mV}$

Like the particle zeta-potentials, the trend where the wall zeta-potential values become less negative as the Mg$^{2+}$ fraction increases suggests that there is adsorption of Mg$^{2+}$ on the fused-silica wall, resulting in a one-third reduction in $|\zeta_p|$ (and $\zeta_{eo}$) at $\alpha = 2\%$. The relative reduction in wall zeta-potentials is larger than that in $|\zeta_p|$ at a given Mg$^{2+}$ fraction, suggesting that the Mg$^{2+}$ has a greater affinity for fused silica.

### 3.2 Divalent Cation Effects: Ca$^{2+}$

Figure 5 graphs the measured particle velocities $u_p$ as a function of the magnitude of the applied electric field $E$ for the pure NaCl-NaOH solution, or $\alpha = 0$ (○), as well as the same solution with $\alpha = 0.5\%$ (◇), 1% (Δ), and 2% (□) Ca$^{2+}$ solutions. The solid lines are curve-fits to the data obtained by linear regression; the error bars representing the uncertainties are smaller than the symbols.

The particle velocities again vary linearly with $E$, and linear regression of these data (solid lines) gives intercepts of 0.1–4 $\mu$m/s. Again, the velocities at a given $E$ decrease as $\alpha$ increases, consistent with adsorption of Ca$^{2+}$ on the negatively charged surfaces of the fused-silica channel reducing $\zeta_w$. 

- **Figure 4** Graph of the EOF velocities $u_{eo}$ for the Mg$^{2+}$ solutions as a function of electric field magnitude $E$; the legend is the same as the previous figure. The solid lines are curve-fits to the data obtained by linear regression; the error bars representing the uncertainty in these data based on the standard deviations in $u_p$ and $\zeta_p$ are smaller than the symbols.

- **Figure 5** Plot of the measured particle velocities $u_p$ as a function of electric field magnitude $E$ for the $\alpha = 0$ (○), 0.5% (◇), 1% (Δ) and 2% (□) Ca$^{2+}$ solutions. The solid lines are curve-fits to the data obtained by linear regression; the error bars denote the standard deviation of these data.

- **Figure 6** Electroosmotic flow velocities $u_{eo}$ as a function of electric field magnitude $E$ for the $\alpha = 0$ (○), 0.5% (◇), 1% (Δ) and 2% (□) Ca$^{2+}$ solutions. The solid lines are curve-fits to the data obtained by linear regression; the error bars representing the uncertainties are smaller than the symbols.
Figure 6 shows the EOF velocity $u_{eo}$, using the same symbols as those in the previous figure. The solid lines are a linear curve-fit to these data, and the wall zeta-potential values calculated from the slope of these data are:

- $\alpha = 0$ (base fluid): $\zeta_w = -90.7 \pm 1.7 \text{ mV}$
- $\alpha = 0.5\%$: $\zeta_w = -84.9 \pm 1.1 \text{ mV}$
- $\alpha = 1\%$: $\zeta_w = -76.3 \pm 2.5 \text{ mV}$
- $\alpha = 2\%$: $\zeta_w = -60.5 \pm 5.8 \text{ mV}$

The magnitude of the wall zeta-potentials decreases as the Ca$^{++}$ fraction increases, presumably again due to adsorption of the divalent cation on the fused-silica wall. Even at a relatively low fraction of $\alpha = 2\%$, Mg$^{++}$ and Ca$^{++}$ both reduce $|\zeta_w|$ and $u_{eo}$ by one-third.

### 3.3 pH and Ionic Strength Effects

Although results are not shown here, the particle velocities measured by evanescent-wave particle velocimetry were linear functions of $E$ for the EDF of all five borate buffer solutions at different pH and ionic strengths. Figure 7 shows $u_{eo}(E)$ (again calculated from $u_p$ and $\zeta_p$ averaged over four independent experiments using Eq. 2) for the $I = 10$ mM borate buffer solutions at pH8.5 ($\nabla$), 9.5 ($\square$) and 10.5 ($\diagonaleright$). As expected, $u_{eo}$ is a linear function of $E$, and linear curve-fits to the data (lines) with a maximum intercept of 6.4 $\mu$m/s, vs. the expected value of 0. The wall zeta-potentials obtained from the slopes of these data are:

- pH8.5 (base fluid): $\zeta_w = -72.4 \pm 2.9 \text{ mV}$
- pH9.5: $\zeta_w = -87.8 \pm 1.2 \text{ mV}$
- pH10.5: $\zeta_w = -90.7 \pm 1.0 \text{ mV}$

Although the pH of these solutions had a negligible effect on $\zeta_p$, pH clearly affects $\zeta_w$, with the wall zeta-potential magnitude decreasing with decreasing pH. These observations are consistent with the the zeta-potential values for fused silica reported in the literature, and consistent with the value for pI of 2.7 reported for fused silica (Kosmulski and Matijevic 1991; Kirby and Hasselbrink 2004).

Figure 8 shows the EOF velocity as a function of electric field magnitude for the $I = 0.2$ mM ($\triangleleft$), 1 mM ($\bigcirc$) and 10 mM ($\nabla$) borate buffer solutions, all at pH8.5. The error bars represent the uncertainty in $u_{eo}$ (those for $I = 1$ mM are smaller than the symbols).
The wall zeta-potential magnitude decreases as \( I \) increases; \(|\zeta_w|\) decreases by more than 40\% over a 50-fold change in the ionic strength and the number of mobile (monovalent) counterions in the solution that can adsorb onto the wall, increases. As seen in Figure 8, the standard deviation in \( u_{eo} \) (and \(|\zeta_w|\)) is greatest for \( I = 0.2 \) mM, again most likely due to variations in \( I \) and pH of the solution.

3. Conclusions

Evanescent-wave particle velocimetry using fluorescent 104 nm radius polystyrene particles was used to study the flow of aqueous electrolyte solutions with a maximum ionic strength of 10 mM through 33 µm deep fused-silica microchannels driven by a voltage gradient, or electric field, parallel to the channel wall. The effect of varying solution pH from 8.5 to 10.5 and varying the ionic strength by almost two orders of magnitude from 0.2 mM to 10 mM on the electroosmotic flow velocity, and the zeta-potential of the channel walls, was characterized. The effect of divalent cations Mg\(^{++}\) and Ca\(^{++}\) at molar fractions up to 2\% on the electrokinetically driven flow of a NaCl-NaOH solution at an ionic strength of 10 mM was also investigated as a simple model of (presumably) nonspecific adsorption of multivalent cations onto the channel walls.

Multilayer nano-particle tracking velocimetry, where the three-dimensional position of individual particles is determined from their image intensity and their position in the image, was used to determine both the particle velocity field components parallel to the wall and the steady-state distribution of particles with respect to the wall-normal direction for particle-wall separations up to 400 nm. The electroosmotic flow velocity, which is proportional to the wall zeta-potential, was determined by subtracting the electrophoretic velocity of the particles from the measured particle velocity in this uniform flow. The electrophoretic velocity was determined from dynamic light scattering measurements of the particle zeta-potential.

Although results are not shown here, both Mg\(^{++}\) and Ca\(^{++}\) were found to have a negligible effect on the near-wall particle distribution; variations in pH and ionic strength also appeared to have no effect on the near-wall particle distribution. Nevertheless, Mg\(^{++}\) and Ca\(^{++}\) had a significant effect on the magnitudes of the wall and particle-zeta-potentials, and 2\% of either cation was sufficient to reduce the wall zeta-potential by about 33\%. The particle and electroosmotic flow velocities are proportional to the electric field magnitude, in agreement with the Helmholtz-Smoluchowski relation. The results also suggest that Mg\(^{++}\) and Ca\(^{++}\) with ionic radii of 86 and 114 pm, respectively (http://en.wikipedia.org/wiki/Ionic_radius), have nearly identical relative effects on the wall zeta-potential, but that Mg\(^{++}\) has a slightly greater effect on the particle zeta-potential. This suggests that the adsorption of both of these divalent cations on the negatively charged fused-silica surface is nonspecific. These results disagree with our previous particle-velocimetry studies (Datta et al. 2009), although these studies did not characterize the particle zeta-potential and attributed all changes in the particle velocity to changes in the wall zeta-potential.

The magnitude of the wall zeta-potential decreased as pH decreased from 10.5 to 8.5, presumably because reducing the solution pH brings the electrolyte solution-fused silica interface closer to the isoelectric point of fused silica, which is about 2.7 (Kirby and Hasselbrink 2004). Varying the pH had little, if any, effect on the particle zeta-potentials, however; this result implies that protons have little adsorption on carboxylate-terminated polystyrene surface. And the magnitudes of the wall zeta-potential, and to a lesser extent, the particle zeta-potential decreased significantly as the ionic strength, and the concentration of mobile counterions in the solution, increased.

These results suggest that electroosmotic flow velocities can be accurately estimated from the particle velocities measured by evanescent-wave particle velocimetry, after accounting for particle electrophoresis, even in the presence of multivalent counterions. Indeed, Kazoe et al. (2009) used evanescent-wave particle velocimetry and what they termed nanoscale laser-induced fluorescence (nLIF) to measure spatial variations in wall zeta-potential in the electrokinetically driven flow of a monovalent electrolyte solution for a fused-silica surface patterned with octadecyltrichlorosilane (OTS). We plan next to use evanescent-wave particle velocimetry to measure near-wall velocity profiles in the shear flow driven by both pressure and voltage gradients through fused-silica microchannels.
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