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# Extension of External Voltage Control of Electroosmosis to High-pH Buffers

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**Control of electroosmosis by an applied external voltage field in capillary electrophoresis has been limited to buffer pH approximately 5 or below. This poor control at higher pH is caused by a high density of surface charge induced by chemical equilibrium overwhelming the influence of the external voltage-induced charges within the electric double layer. A *tert*-butyldiphenylchlorosilane treatment was used on fused-silica capillaries to minimize chemically generated $\zeta$-potential where this treatment allowed for control of electroosmosis over a large pH range (2−10). Blocking the surface with traditional polymer-based surface treatments does not work in this application since the polymers increase the viscosity within the electric double layer and impede electroosmosis. The surface created by this reaction is demonstrated in extremely narrow capillaries, down to 2-$\mu$m internal diameter. The treated surface is sterically hindered against acid- and base-catalyzed degradation reactions typically associated with organosilanes. This results in a surface that was stable to experimental buffer pH extremes, from pH 3 to pH 10, and was stable for at least 8 weeks exposed to both solution and air.**

Electroosmosis plays a central role in high-efficiency separation techniques and in microfluidics for the microinstrumentation recently appearing in the literature.[1,2] This mechanism of fluid propulsion has many inherent advantages. The flow profile is pluglike and limits dispersion to longitudinal diffusion alone. It can generate flow without pressure differential and will drive fluids in extremely small channels or capillaries (<2-$\mu$m diameter) as easily as in larger bore tubes (2−100-$\mu$m diameter). The flow generated impacts many aspects of separation science techniques, including resolution, time of analysis, injection reproducibility and detector performance.

Examples of purposefully altering the electroosmotic flow include buffer additives,[3−7] altering buffer pH,[8−10] altering buffer concentration,[8,11−13] and coating the inner wall of the capillary.[3,4,14−16] These techniques permanently alter either the surface structure or buffer composition and result in a static, new electroosmotic mobility that cannot be intentionally altered in response to changing conditions within the channel or tube. Electroosmotic flow rate may be altered by the longitudinal voltage field, but this impacts all electrokinetic phenomena so that the electrophoretic migration of charged species may be unduly influenced when one attempts to control flow.

Dynamic control of electroosmosis (aside from the longitudinal field strength) has been demonstrated by applying an additional external voltage field across the wall of standard fused-silica capillaries used in conventional capillary electrophoresis.[17−21] The external voltage flow control technique requires no permanent changes in surface structure or altered buffers. Aside from the other advantages of controlling and optimizing flow, this technique promises to provide a method to decouple the electrophoretic migration rate of charged species and the bulk flow rate.

Radial voltage flow control was first demonstrated using resistive solutions or materials covering the majority of the outer surface of the capillary.[17] This design required resistive materials so that the radial potential gradient matched the potential gradient of the buffer on the interior of the capillary. Later work demonstrated that the effect could be generated by conductive materials or ionized gas and that the matching of the interior potential gradient was unimportant in obtaining the effect.[22−24] In fact, control was demonstrated while covering only very small portions

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(~4%) of the outer surface with a conductor.[24] Surface conductance within the electric double layer was attributed for the effective control where the induced charge from the radial voltage spread along the inner surface (although there is some controversy as to the mechanism).[22,25−27] Regardless of the mechanism, this work indicated that the external voltage affected the ζ-potential over the entire capillary length, which effectively induced the change in electroosmosis.

One continuing limitation of electroosmosis for both capillary electrophoresis and microchip fluidic applications is the lack of dynamic control and the poor reproducibility.[28,29] The external voltage field flow control work was an attempt to address these issues. This demonstrated control, but limitations were discovered and defined. Effective control, as defined by the ability to alter the electroosmotic mobility by more than $3 \times 10^{-4}$ cm$^2$/(V s), was limited to lower buffer pH (<5) in standard systems.[19,21] Furthermore, flow reversal and truly complete control of electroosmosis was limited to buffer pH 3 or lower in these systems. To extend radial voltage flow control to higher buffer pH, the surface charge generated by the chemical equilibrium of buffer/wall interface must be minimized.[21, 30]

Many of the coatings designed to minimize surface charge noted the literature are unsuitable for the external voltage flow control application. These coatings, constructed with polymers, successfully eliminate the chemical equilibrium-based surface charge but also increase local viscosity.[29] The primary purpose of these coatings is to minimize protein adsorption and eliminate or permanently change electroosmosis.[16,29,31] An excellent review of capillary coatings appears in Srinivasan et al. which will not be repeated here.[31] This class of surface coatings is unsuitable because of the increased viscosity within the electric double layer. This inhibits the migration of ions with these layers and impedes electroosmosis—regardless of the magnitude to the double-layer potential fields. This effect renders the external voltage flow control impotent for altering electroosmosis.[19]

Other surface coatings based on organosilanes have been reported. Some are designed to form polymers on the surface and are also unsuitable. Others, which do not form polymers, use organosilanes with a single reactive group. This allows for reaction with surface functional groups, but does not allow for further extension of the molecule. The largest application of this approach is to form stationary phases for liquid and gas chromatographic columns. These coatings are designed to have a significant thickness (through use of long-chain substituents) to provide sufficient volume for the stationary phase and are also inappropriate for a flow control surface. Thin coatings have appeared, most notably as "deactivated" surfaces. However, due to the resulting labile silicon−oxygen−silicon−carbon bond system, previous organosilane treatments were not stable at buffer pH extremes, either high or low.[32,33] Sterically hindered triorganosilane reagents have demonstrated increased stability to the acid- and base-catalyzed reactions at this bond system with small organic molecules and therefore are a promising alternative for the present application.[34]

Surface treatments that are specific to improved flow control have also appeared. One example was the use of commercially "deactivated" tubing, where the authors merely mention that it "yields effective EOF [electroosmotic flow] control by applied radial voltage".[20] The authors indicate the surface was usable for weeks instead of days at pH 6 (compared to untreated capillary) and no data or claims of stability at pH extremes were stated. A butylsilane surface was also used to improve the effectiveness of flow control, but the surface was unstable above pH 5 and no detailed studies were described.[19,35]

In the present study, the properties of capillaries that were treated with the triorganosilane *tert*-butyldiphenylchlorosilane were examined for stability and improved flow control for a large buffer pH range (2−10). The same treatment was also applied to small-bore capillaries, down to 2-μm internal diameter. The surface was stable at both low-pH (pH 3) and high-pH (pH 10) buffers for 8 weeks with both solution and air exposure. The effectiveness of an applied radial voltage field on the control of electroosmosis was demonstrated even at high buffer pH (up to 10), where no effects from the radial field are observed for control (uncoated) capillaries.

## THEORY

The application of an external voltage to the capillary wall to influence the electroosmotic flow has been established in theory and in practice.[17,18,20] A comprehensive review of work prior to 1994 has appeared.[36] Electroosmotic flow rate ($\nu_{eof}$) is defined by the following equation:

$$\nu_{eof} = \zeta(\epsilon_b/\eta)E_{app} = \mu_{eof}E_{app} \quad (1)$$

where ζ is the potential drop across the diffuse layer of the electric double layer (commonly referred to as the ζ-potential), $\epsilon_b$ is the permittivity of the buffer solution, $\eta$ is the viscosity of the buffer solution, $\mu_{eof}$ is the electroosmotic mobility, and $E_{app}$ is the voltage gradient across the length of the capillary. Through the measurement of the velocity of a neutral marker and eq 1, the ζ-potential and electroosmotic mobility can be determined.[36,37] The external voltage flow control effect is directly related to the ζ-potential through the changes in the surface charge density of the channel. The total surface charge density results from chemical ionization ($\sigma_{si}$) and the charge induced by the radial voltage field ($\sigma_{rv}$).[20] According to the capacitive model the $\sigma_{rv}$ is described by the following equation:


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$$\sigma_{rv} = (\epsilon_Q V_r / r_i)(1/\ln(r_o/r_i)) \quad (2)$$

where $\epsilon_Q$ is the permittivity of the fused-silica capillary, $V_r$ is the applied radial voltage, $r_i$ is the inner radius of the capillary, and $r_o$ is the outer radius of the capillary. The surface charge density is related to the $\zeta$-potential by the following equation:[38−40]

$$\zeta = \exp(-\kappa x) E_{app} (\epsilon_b/\eta)(2kT/ze) \sinh^{-1}[(\sigma_{si} + \sigma_{rv})/ [8kT\epsilon_b n^0]^{1/2}] \quad (3)$$

where $\kappa = (2n^0 z^2 e^2/\epsilon_b kT)^{1/2}$, $n^0$ is the number concentration, $z$ is the electronic charge, $e$ is the elementary charge, $T$ is the temperature, $\kappa$ is the inverse Debye length, $x$ is the thickness of the counterion, and $k$ is the Boltzmann constant.

The voltage gradient across the capillary also induces an additional movement of charged species according to

$$\nu_{em} = (\mu_{eof} + \mu_{em}) E_{app} = \mu_{obs} E_{app} \quad (4)$$

where $\nu_{em}$ is migration rate of a charged species, $\mu_{em}$ is the electrophoretic mobility of the charged species, $\mu_{obs}$ is the observed mobility, and $\mu_{obs} = \mu_{eof} + \mu_{em}$. Since $\mu_{em}$ is constant under these experimental conditions, any change in $\nu_{em}$ may be attributed to changes in $\mu_{eof}$.

To obtain an expression directly relating changes in elution time ($\Delta t_{el}$) and the change in surface charge density ($\Delta\sigma_t$), it is noted that elution time is $t_{el} = L/\nu_{em}$, where $L$ is the length of the capillary from the injector to the detector. The velocity of the analyte is described by eq 4 where the electrophoretic mobility of that charged species is a constant under these experimental conditions. Noting that $\mu_{eof} = \zeta(\epsilon_b/\eta)$ from eq 1, and the definition of $t_{el}$, the following expression can be derived:

$$t_{el} = L/[(\zeta(\epsilon_b/\eta) + \mu_{em}) E_{app}] \quad (5)$$

Equation 3 gives a function of $\zeta$ that includes a term for surface charge ($\sigma_{si} + \sigma_{rv}$) for both the chemically generated surface charge and the external voltage-induced charge. For the surface coating assessments $\sigma_{rv} = 0$, and $\sigma_{si}$ is a function of the surface coating. It follows that, upon coating the surface, the measured change in elution time can be used directly to calculate the change in the surface charge from the following equation:

$$\Delta t_{el} = L/[(\{\exp(-\kappa x)(2kT/ze) \times \sinh^{-1}[(\Delta\sigma_{si})/[8kT\epsilon_b n^0]^{1/2}](\epsilon_b/\eta)\} + \mu_{em}) E_{app}] \quad (6)$$

or by substituting $A = (\exp(-\kappa x)(\epsilon_b/\eta)(2kT/ze)$ and $B = 1/[8kT\epsilon_b n^0]^{1/2}$ this simplifies to

$$\Delta t_{el} = L/[(A \sinh^{-1}[B\Delta\sigma_{si}] + \mu_{em}) E_{app}] \quad (7)$$

and rearrangement results in a more useful form of this equality:

$$\Delta\sigma_{si} = [\sinh\{([L/(\Delta t_{el} E_{app})] - \mu_{em})/A\}]/B \quad (8)$$

Note that all variables in this expression except $\Delta t_{el}$ are constant under these experimental conditions.

An alternative theoretical treatment for the effects of an applied radial voltage field on electroosmosis has recently appeared.[30] The method produced results that more closely match previously published data but it fails to address chemical equilibrium-generated surface charge and the effects from the areas of the capillary not under direct radial voltage flow control, both of which impact this discussion.

## EXPERIMENTAL SECTION

**Chemicals.** Rhodamine 123 (Molecular Probes, Eugene, OR), *tert*-butyldiphenylchlorosilane (United Chemical Technologies, Bristol, PA), anhydrous ethyl alcohol, and HPLC-grade phosphoric acid (Aldrich Chemical, Milwaukee, WI) were analytical-reagent grade and were used as received. Deionized ultralow organic content NANOpure UV (Barnstead, Dubuque, IA) reagent-grade water was used throughout this study. Nitrogen gas was filtered through a Drierite gas purifier (W. A. Hammond Drierite, Xenia, OH). Rhodamine 123 solution (1 mg/mL) was prepared by dissolving in ethanol. Electrophoretic buffers were prepared with phosphoric acid (25 mM) and titrated with 1 M NaOH solution to adjust pH. All buffers were degassed and filtered (0.5-$\mu$m filter unit, Millipore, Bedford, MA) prior to use.

**Instrumentation.** Electrophoretic separations were performed on a Crystal Series 310 electropherograph (Thermo Capillary Electrophoresis, Franklin, MA) with a FD-500 fluorescence detector (Groton Technology, Concord, MA) which operated at an excitation wavelength of 500 nm and an emission wavelength of 536 nm. External voltage to the outside of the capillary wall was applied by a CZE 1000R high-voltage system (Spellman High Voltage, Hauppauge, NY). Fused-silica capillaries (Polymicro Technologies Inc., Phoenix, AZ) were used with an effective length of 44.5 cm and total length of 70 cm, except for the radial voltage experiments. These were 94 cm long (68.5 cm effective length) for the uncoated experiments and 90 cm (64.5 effective length) for the coated inner-surface experiments. Capillaries were 50-, 5-, and 2-$\mu$m internal diameter (i.d.) and 365-, 365-, and 150-$\mu$m outer diameter (o.d.), respectively. Data collection and processing were accomplished with a DAS 801 A/D converter (sampling rate of 10 Hz) and personal computer running a 4880 data-handling system (ATI Unicam, Cambridge, U.K.). All samples were injected by pressure with parameters set to produce a 1% of capillary length sample plug. Electrophoresis was performed at 30 kV (unless indicated otherwise) and at room temperature.

**Capillary Column Preparations.** Capillaries were prepared by exposing the inner surface to a solution of 3% *tert*-butyldiphenylchlorosilane in anhydrous ethanol solution for 3−4 h at 30−40 °C. The anhydrous solution was filtered (0.5 $\mu$m) and initially added to the capillaries with 12, 20, and 35 psi of nitrogen gas for 50-, 5-, and 2-$\mu$m i.d. capillaries, respectively. The capillaries were

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then dried with nitrogen and stored for 24 h at room temperature. Capillaries were flushed with the electrophoretic running buffer for 10 min prior to use. Stability studies (10 weeks total duration) were performed five times each day for the first 3 weeks and every 2 days after that. After the runs each day, the capillaries were flushed with compressed air and stored. All phosphate buffers were made fresh.

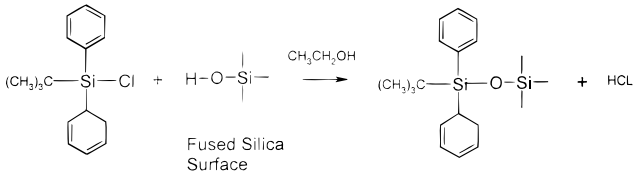
**Applied External Voltage.** Voltage (−10 to +10 kV) was applied to the outside of capillary wall via a 3-in. aluminum plate which was insulated by an interlock plexiglass box. The box was placed between the Crystals Series 310 electropherograph and the FD-500 fluorescence detector. The radial voltage was applied 20 s after each run had begun. The calculated buffer potential at the center of the external plates and the voltage applied to the outside surface were used to calculate the effective radial voltage (the actual potential field across the wall). Since the absolute magnitude of the $\mu_{obs}$ can vary dramatically with pH, data sets were normalized to the most negative effective radial voltage $\mu_{obs}$ value, thereby emphasizing the change in electroosmosis with applied external voltage.

## RESULTS AND DISCUSSION

An optimal inner-surface coating for the radial voltage control of electroosmosis (an electroosmotic surface) requires three properties. First, the surface must retain low chemical-generated surface charge density in the presence of the aqueous buffers typically used in capillary electrophoresis.[21,30] Second, this low surface charge density should be insensitive to pH changes of the buffer, thus remaining consistent over a large range of normally encountered pHs (2−11) and buffer types. The third concerns the viscosity of the buffer surface layers. The coating must not increase the viscosity of the layer of buffer near the capillary surface. This may be explained by observing that electroosmosis obeys the general relationship shown in eq 1. For the purposes of this equation, $\eta_o$ is approximated by the buffer viscosity, but actually it is the viscosity of the double layer that governs this velocity. A high-viscosity double layer impedes the migration of ions entrained in this layer. These high-viscosity surface coatings, common to polymers, gels, and polymer-forming agents, is predicted to stop electroosmosis altogether, and in fact, this effect has been demonstrated.[15,16,19] The effects of an applied radial voltage field influence the $\zeta$-potential term only; if the viscosity is too great then the effects of the applied field will be negligible. A strategy of avoiding the use of polymers or polymer-forming reactants, or by using monolayer surface coverage, averts increases in local viscosity. It is important to note that this requirement precludes the use of many previous surface coating strategies both from commercial sources and from the literature.[3,4,14,31,41,42] While these other coatings and treatments have merit in minimizing adsorption or in obtaining static control of electroosmosis, they are unacceptable for improved control of electroosmosis with an applied external voltage field.

A promising approach has been described with triorganochlorosilanes. The formation of hydrolytically stable silyl ethers has been accomplished for the purpose of protecting hydroxyl groups

Scheme 1




for synthetic stratagem.[34,43] A variety of triorganosilyl groups have been investigated for their stability when exposed to extremes of pH. One of the most robust of these structures is *tert*-butyldiphenylchlorosilane.[34] Since this reactant contains only one reactive site, it will not form polymers, and will therefore not adversely influence the surface layer viscosity. The combination of increased hydrolytic stability and the non-polymer-forming properties of this reagent appear to be consistent with properties required to form an electroosmotic surface.

Several special considerations must be made to characterize this system. First, fluorescence detection was used for the surface charge density assessment by capillary zone electrophoresis. This sensitive detection technique was required to identify elution time for the dye for the small-bore capillaries (2-$\mu$m internal diameter). The small-bore capillaries result in few molecules being present in the detection volume and the path length is quite short for spectroscopic techniques. Second, since electroosmosis was being suppressed in these experiments a neutral species would not elute. Therefore, a charged species was used to obtain elution time data. This is not a particular problem since it can be assumed that the electrophoretic mobility of the charged dye is constant. This is a reasonable assumption if the adsorption to the wall is negligible and the background buffer remains constant. With a constant buffer, the intermolecular forces that define electrophoretic mobility remain unchanged regardless of electroosmotic flow rate. In this case, any changes in elution time can be attributed to changes in electroosmosis and from which the change in surface charge density can be calculated directly (eqs 1 and 8).

Using this technique, experiments were performed on both treated and untreated capillaries. The change in elution time for the charged dye was used to calculate the change in the observed mobility ($\Delta\mu_{obs}$) and the surface charge density ($\Delta\sigma_{Si}$) with eqs 1 and 8. For capillaries of 50-$\mu$m i.d., the coating of the inner-surface according to Scheme 1 reduced $\mu_{obs}$ by $3.6 \times 10^{-4}$ cm$^2$/(V s) at pH 10 and a corresponding reduction of surface charge density of 0.075 C/m$^2$ (eq 8, Figure 1). At low pH (pH 2 and 3) the reduction of $\mu_{obs}$ was an average of $1.25 \times 10^{-4}$ cm$^2$/(V s) (0.022 C/m$^2$). This smaller reduction upon treatment is due the smaller amount of surface charge density initially at low pH for the uncoated control capillary surface. These capillaries were not prerinsed prior to exposure to the silane. This is somewhat unconventional, but the process yielded consistent results for more than 50 capillaries that were fabricated. So apparently, in this specific instance, the additional fabrication step is unwarranted. The mobility of a neutral species (mesityl oxide) at pH 10 in an uncoated tube was $(4.44 \pm 0.02) \times 10^{-4}$ cm$^2$/(V s) (0.10 C/m$^2$, $n$ = 10), consistent with other experimental values from the literature.[9−13,21,39,44,45] These neutral marker method data combined

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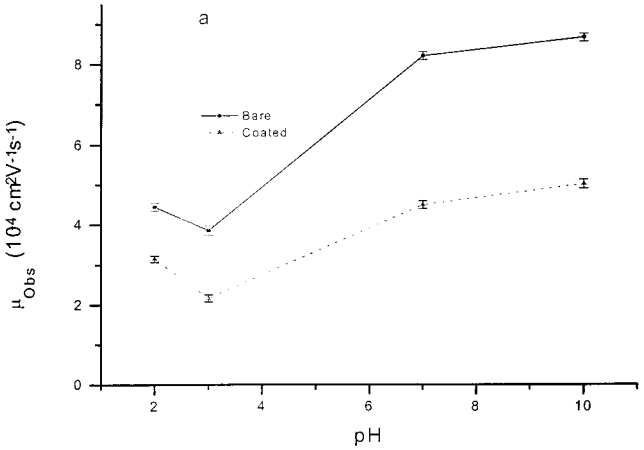


Figure 1. Observed mobility ($\mu_{obs}$) for rhodamine 123, a positively charged fluorescent dye, versus buffer pH. Observed mobility reflects both electrophoretic ($\mu_{em}$) mobility and electroosmotic mobility ($\mu_{eo}$) where changes in $\mu_{obs}$ are assumed to be reflective of changes in electroosmotic mobility (see text). Data are for untreated (labeled "bare") and *tert*-butyldiphenylchlorosilane treated (labeled "coated") 50-$\mu$m-i.d. fused-silica capillaries. The variability of $\mu_{obs}$ versus pH for both coated and bare data reflects changes in electrophoretic mobility; however, at a constant pH, electrophoretic mobility is constant and independent of electroosmosis.

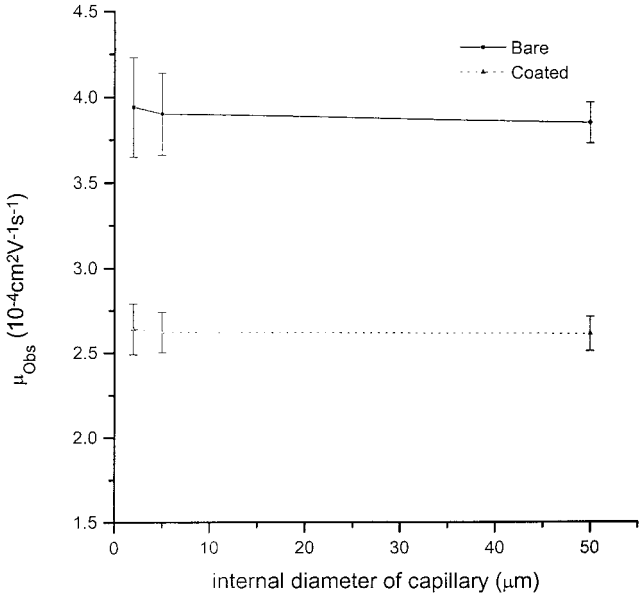


Figure 2. Treated and control capillaries with varying internal diameter. The observed mobility for rhodamine 123, a positively charged fluorescent dye, in untreated and *tert*-butyldiphenylchlorosilane treated capillary columns at pH 3 versus capillary internal diameter. Capillaries were standard polyimide-coated fused-silica where the outer diameter was 365 $\mu$m for the 50- and 5-$\mu$m i.d. and 150 $\mu$m for the 2-$\mu$m i.d.

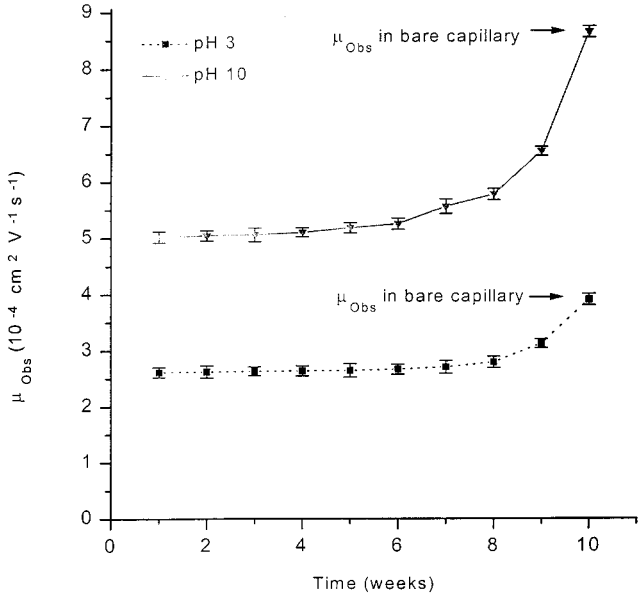


Figure 3. Stability study of treated fused-silica capillaries. The observed mobility for rhodamine 123, a positively charged fluorescent dye, in *tert*-butyldiphenylchlorosilane-treated capillaries for an extended period of time. Experimental protocol included exposure to both buffer and air storage conditions.

with the observed mobility data indicate that the surface charge was largely suppressed upon coating the tube (Figure 1, 0.075 C/m$^2$ suppressed).

The same surface chemistry was used for the coating of smaller bore tubes. Small-bore tubes have been utilized in biological sampling and these channel dimensions will be useful on future microinstrumentation.[1,46] The smaller bore coating experiments resulted in the reduction of $\mu_{obs}$ by $1.2 \times 10^{-4}$ cm$^2$/(V s) at pH 3.0 for all diameters tested (Figure 2). The data indicate that the fabrication of narrow-bore tubes with this unique surface coating is possible and that the behavior of the coated tubes is consistent with the performance of the larger bore tubes.

The coating was also tested for stability for acute exposure to high- and low-pH buffers and was tested for longer term stability in a typical-use pattern (testing and storage). The coating remained stable for 8 weeks at pH 10 under the experimental conditions described above (Figure 3). This stability was demonstrated by $\mu_{obs}$ remaining less than $5.5 \times 10^{-4}$ cm$^2$/(V s) (maintaining reduced surface charge density by 0.075 C/m$^2$ compared to uncoated, see Figure 1). At pH 3 the coating also remained stable, where $\mu_{obs}$ remained below $2.75 \times 10^{-4}$ cm$^2$/(V s) for 8 weeks (Figures 1 and 3). This study allowed the treated surface to undergo both solution- and air-aging phenomenoa. Other longer term studies under a variety of conditions are under way in our laboratory. The stability is consistent with the hindered-silane bonding system in small organic molecules, where this functional group remains stable 2 orders of magnitude longer than *n*-butylsilane to pH extremes.[34] After 10 weeks, the coatings had apparently completely degraded where the measured $\mu_{obs}$ increased to greater than $8.5 \times 10^{-4}$ cm$^2$/(V s) for pH 10 measurements and $3.5 \times 10^{-4}$ cm$^2$/(V s) for pH 3 measurements.

The difference between the observed mobility of the newly coated capillaries and the aged capillaries is exactly the same as the difference between coated and uncoated capillaries ($\Delta\mu_{obs} = 3.6 \times 10^{-4}$ cm$^2$/(V s) (pH 10), $\Delta\mu_{obs} = 1.25 \times 10^{-4}$ cm$^2$/(V s) (pH 3)).

While stability and reduction of surface charge density are important factors for an electroosmotic surface, the real functionality of this surface is the extension of control of electroosmosis by an applied external voltage field to higher pH buffers. Without

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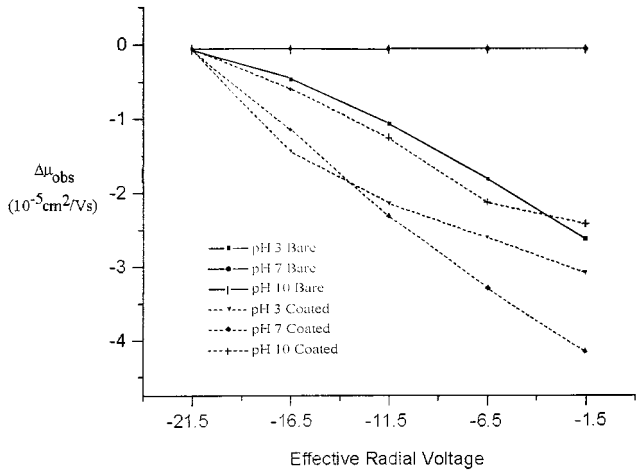


Figure 4. Demonstration of the extended control of electroosmosis with an applied radial voltage field with an electroosmotic surface. The change in observed mobility ($\Delta\mu_{obs}$) for rhodamine 123, a positively charged fluorescent dye, in uncoated and *tert*-butyldiphenylchlorosilane treated 50-$\mu$m i.d./375 $\mu$m o.d. capillaries versus an applied radial voltage field. The data groups for pH 7 Bare and pH 10 Bare completely overlap and do not respond to the radial voltage field. All data sets were normalized by subtracting the −21.5-kV effective radial voltage observed mobility value from each data point within that set. Note that equivalent flow control is demonstrated for all pH values for the treated capillaries ("coated" data) to that of the most favorable conditions of the "bare" or untreated pH data.

this feature, these treated capillaries would simply be one of a large number of organosilane-based capillary surface treatments.

To test this most important feature, the effectiveness of the control of electroosmosis by an external voltage field was tested on coated tubes of 50-$\mu$m i.d./375-$\mu$m o.d. For application of the radial field, 8.1% of the capillary was placed between two aluminum plates for which the voltage could be varied from −10 to +10 kV. Control experiments were performed on uncoated tubes at buffer pH 3, 7, and 10. The results of these control experiments were consistent with published relationships, where control was demonstrated at pH 3 (Figure 4) and was absent at pH 7 and pH 10. The experiments conducted at pH 3, where $\mu_{obs}$ changed by $2.5 \times 10^{-5}$ cm$^2$/(V s), represent the most favorable condition for flow control in this experimental apparatus since the surface charge density from chemical equilibrium is minimized from pH effects. The absolute magnitude of changes in flow by an applied radial field is limited by the physical modifications that could be made to the commercial capillary electrophoresis system. Since the buffer pH 3 uncoated capillary control experiment produced quantifiable results, the assessment of the effective control of electroosmosis for these capillaries could be performed.

Over a large pH range, in fact from 3 to 10, the coated capillaries responded to the radial voltage fields equivalent to or better than the pH 3 response with the uncoated tubes. At the experimental extreme of buffer pH 10, the change in $\mu_{obs}$ upon application of the radial voltage field was $2.5 \times 10^{-5}$ cm$^2$/(V s), consistent with the best control of flow at low pH in unmodified capillaries. The control was even better at the lower buffer pH values, where $\Delta\mu_{obs}$ was $3.0 \times 10^{-5}$ cm$^2$/(V s) at pH 7 and $4.0 \times 10^{-5}$ cm$^2$/(V s) at pH 3. These data indicate that the surface coating diminishes the competing surface charge from buffer/surface chemical equilibria on the inner surface of the tube, thus allowing control of electroosmosis with an applied radial voltage field over a wide variety of conditions. This surface has fulfilled the requirements of an electroosmotic surface and enabled the extension of the radial voltage flow control technique to high-pH buffers with good stability.

A variety of other hindered triorganosilanes may function in this role, and these are the subject of ongoing investigations within this laboratory. However, this one treatment completely fulfilled the requirements of an electroosmotic surface. It reduced the surface charge density, which allowed the external voltage flow control to be effective over a large buffer pH range. The surface remained stable to acute contact with both high- and low-pH buffers and remained stable to aging while exposed to both buffer and air.

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