

Short communication

Characterizing electroosmotic flow in microfluidic devices

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Abstract

The current-monitoring method was used to measure the electroosmotic flow (EOF) in borosilicate glass capillaries and zeonor plastic microfluidic devices. The surface of the zeonor devices must be oxidized to support EOF and this treatment shows signs of aging within 6 days. Oxidized zeonor devices showed the same response to changes in applied field, pH, and ionic concentration as the capillaries. The effects of several common dynamic surfactant coatings on the walls were also studied (0.1%, v/v solutions of POP-6, POP-4, Pluronic L81, and NP-40). These generally significantly suppressed the EOF but required several days to stabilize.

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1. Introduction

One of the main goals for the rapidly growing field of microfluidics is to integrate multiple functions on a chip to provide micro-total analytical systems (mTAS) [1,2]. As a result, the benefits of reduced reagent consumption and increased analytical performance are materializing [3]. The promise of parallel and integrated analysis has great potential for fields such as drug discovery, genomics, and proteomics [4,5]. In microfluidic devices where channel diameters range from a few microns to hundreds of microns, surface effects can dominate volume effects thus it is important to understand the influence of the surface, especially to develop microfluidics into a more reliable tool.

Electroosmosis is a prominent mechanism for

controlling fluid flow in microchannels, requiring surface charges. The surface charge on the channel walls causes a diffuse layer of counterions (1 nm–1 μm thick) to form. When an electric field is applied, the mobile outer layer of ions is drawn toward the oppositely charged electrode dragging with it the bulk solution and producing a net flow referred to as electroosmotic flow (EOF) [6]. This mechanism of fluid motion produces a uniform velocity distribution across the channel, which is often advantageous. The electroosmotic velocity is $v_{\text{eof}} = \epsilon \zeta E / 4 \pi \eta$ where ϵ is the dielectric constant of the fluid, η is the fluid viscosity, E is the applied field strength, and ζ is the zeta potential of the surface [7]. The electroosmotic mobility (μ_{eof}) is the electroosmotic velocity normalized by the applied field: $\mu_{\text{eof}} = v_{\text{eof}} / E$. Thus, changing the applied field, the properties of the solution, or altering the surface charge can affect v_{eof} .

This study characterizes EOF in two common

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microfluidic materials, borosilicate glass and Zeonor plastic (zeonor). The zeonor polymer is used for embossed microfluidic devices [8] because it exhibits many favorable properties [9]: low water absorption ($< 0.01\%$), a relatively low glass transition temperature ($105\text{ }^\circ\text{C}$), and good chemical resistance to acids, alcohols, and ketones. We explore the effects of applied field strength, pH, ionic strength, and surface treatments on EOF in each of the materials.

2. Experimental

2.1. Chemical reagents and solutions

Tris–borate–EDTA buffer (TBE) at $5\times$ concentration (445 mM) was purchased from Sigma (St. Louis, MO, USA) and $10\times$ Tris–acetate–EDTA (TAE) buffer (400 mM) was obtained from GibcoBRL (Carlsbad, CA, USA). Stock solutions of 20 mM monobasic sodium phosphate (Mallinckrodt Baker, Paris, KY, USA) and 20 mM dibasic sodium phosphate (Fisher Scientific, Fair Lawn, NJ, USA) were prepared and then combined in the correct ratios to yield phosphate buffer solutions of pH 5.7, pH 7.0, and pH 8.0 [10]. The Nonidet P40 surfactant, NP-40 (USB, Cleveland, OH, USA), Pluronic L81 (a poly(ethylene oxide) and poly(propylene oxide) copolymer, BASF Performance Chemicals, Mt. Olive, NJ, USA), and Performance Optimized Polymers 4 and 6, POP-4 and POP-6, (linear polyacrylamides, Applied Biosystems, Foster City, CA, USA) were added to some of the buffer solutions to yield a 0.1% (v/v) solution. To make an EOF measurement, two different concentrations of the same solution are needed, a solution with concentration, C , and one with a concentration $C' = 0.9C$. All solutions were made at concentration C (e.g. 20 mM phosphate, pH 5.7, with 1% POP-6), then diluted to C' with ultrapure water (Milli-Q, Millipore, $18\text{ M}\Omega$).

2.2. Channels

Borosilicate glass capillaries (I.D. = $110\text{ }\mu\text{m}$) were purchased from Fisher Scientific (Pittsburgh, PA, USA) and used without any pretreatment. Standard photolithography and deep reactive ion etching were

used to fabricate silicon masters that are the negative pattern of the channels. The zeonor (Zeonor 1020R, a polycycloolefin resin, Zeon Chemicals, Louisville, KY, USA) devices were formed by hot embossing with the silicon master at $130\text{ }^\circ\text{C}$ and circa 250 p.s.i. for 10 min. To seal the channel, another piece of zeonor was thermally bonded ($85\text{ }^\circ\text{C}$, 250 p.s.i. , 7–10 min; $1\text{ p.s.i.} = 6894.76\text{ Pa}$) on top. The finished zeonor channels ($60\text{ }\mu\text{m}$ wide, $20\text{ }\mu\text{m}$ deep) were filled with water immediately after sealing with the top piece. For the oxidized zeonor channels, the zeonor pieces were oxidized in an oxygen plasma for 30 s (PlasmaTherm 72, 150 W , 0.06 Torr O_2 , 30 sccm ; $1\text{ Torr} = 133.322\text{ Pa}$) before the bonding step.

2.3. Measurement of electroosmotic flow

The current monitoring method [11] was used to measure EOF in the channels. The glass channels were initially filled with the higher conductivity buffer by capillary action. In the polymer channels, EOF was used to replace the initial filling water with the appropriate higher conductivity buffer. Just prior to the EOF measurement, the fluid reservoirs were emptied and equal aliquots of the appropriate ionic strength solution were put in each of the reservoirs to minimize errors from flow induced by differences in hydrostatic pressure. The voltage drop was monitored across a $10\text{ k}\Omega$ thin film metal resistor in series with the silica capillary (a $100\text{ k}\Omega$ resistor was used for the zeonor microfluidic channel) as the lower conductivity buffer replaced the initial higher conductivity buffer. The time (t) required for this replacement gave the electroosmotic velocity ($v_{\text{eof}} = L/t$ where L is the channel length) and electroosmotic mobility. At least three measurements of v_{eof} were made for each point in the explored parameter space.

3. Results and discussion

As expected, the EOF in the capillaries and in the oxidized zeonor channels is from the anode (+) electrode towards the cathode electrode. A negative surface charge attracts positive ions to form the mobile diffuse double layer. In the capillaries, partial ionization of the hydroxyl (OH) groups imparts a

negative surface charge [7]. Surface oxidation of the zeonor polymer must impart a similar chemical functionality as no EOF was detected in the untreated channels. The EOF velocity is linearly proportional to the applied potential [7] as long as the increased Joule heating is completely offset by the heat dissipation. All EOF measurements were made in the linear regime. For the oxidized zeonor microfluidic channels, an aging affect was noticed even for the devices filled with only deionized water. After about 6 days, three of the oxidized zeonor devices ceased to support EOF while two others started exhibiting erratic EOF behavior.

3.1. Effects of buffer on electroosmotic flow

Lukacs and Jorgenson [12] reported a sigmoidal dependence of the electroosmotic mobility on the buffer pH with the inflection point near pH 5.0. An increase in μ_{eof} is observed as more surface species become ionized at higher pH. Although the lowest buffer pH used for these EOF measurements was pH 5.7, the data for both the capillaries and the oxidized zeonor channels have this sigmoidal pattern (Fig. 1).

The buffer's ionic strength also affects the zeta potential [13]. Fig. 2 shows the dependence of electroosmotic mobility on the natural logarithm of the ionic strength. The electroosmotic mobility depends on the thickness of the electrical double layer. A thicker double layer produces a greater μ_{eof} and the thickness of the double layer is proportional to $c^{-1/2}$ where c is the concentration of electrolyte in solution [14]. Measurements were made of the μ_{eof} as a function of concentration in the capillaries for two common biological buffers, TBE and TAE, and they follow similar curves (Fig. 2). Substantially lower EOF mobilities are measured for TBE in the oxidized zeonor channels. However, these mobilities follow similar trends.

Locascio et al. have studied EOF in microfluidic channels imprinted in plastics without further surface treatments [15]. They used the current monitoring method [11] to measure electroosmotic mobilities at pH 7.0 ($C = 20 \text{ mM}$ phosphate buffer and $C' = 10 \text{ mM}$ phosphate buffer) of 1.8, 2.5, and $4.3 (\times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$ for polystyrene, acrylic, and copolyester, respectively. The EOF in microfluidic channels made of poly(dimethylsiloxane) (PDMS) have also

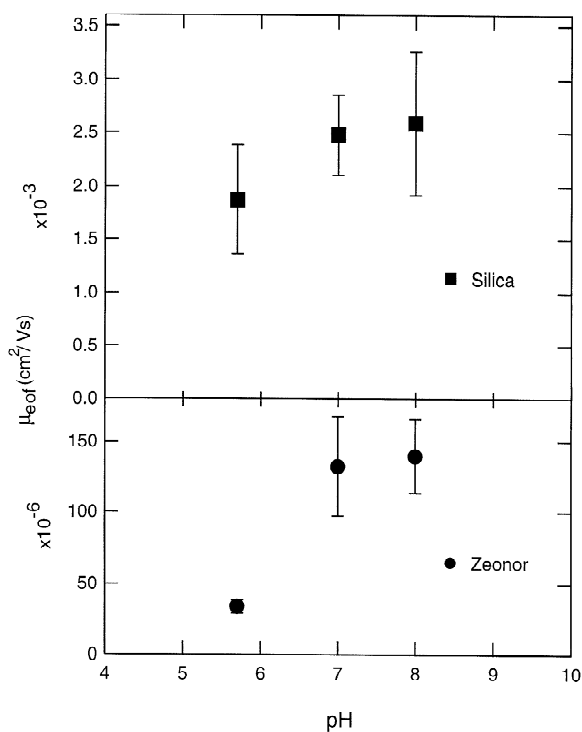


Fig. 1. Electroosmotic mobility as a function of buffer pH. Measurements were taken at constant ionic strength ($C = 20 \text{ mM}$ phosphate buffer) and the errors are reported at the 95% confidence limit.

been characterized [16] in the literature, finding that the EOF in oxidized PDMS is about four times higher than in the untreated PDMS ($1 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). The electroosmotic mobility for the oxidized zeonor channels is $1.1 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is somewhat lower but comparable to that observed in the other plastics. Zeonor, however, may be a less suitable substrate for supporting EOF since the surface must be treated before EOF can be sustained and this surface treatment is susceptible to aging effects. Often the goal of surface treatments is the suppression of EOF; zeonor makes an ideal substrate in this situation. Locascio et al. did not mention any aging effects in their studies and aging effects would not be expected since the polystyrene, acrylic, and copolyester did not require surface treatments. Aging effects were observed in the oxidized PDMS channels when exposed to air [16]; μ_{eof} dropped sharply after day four.

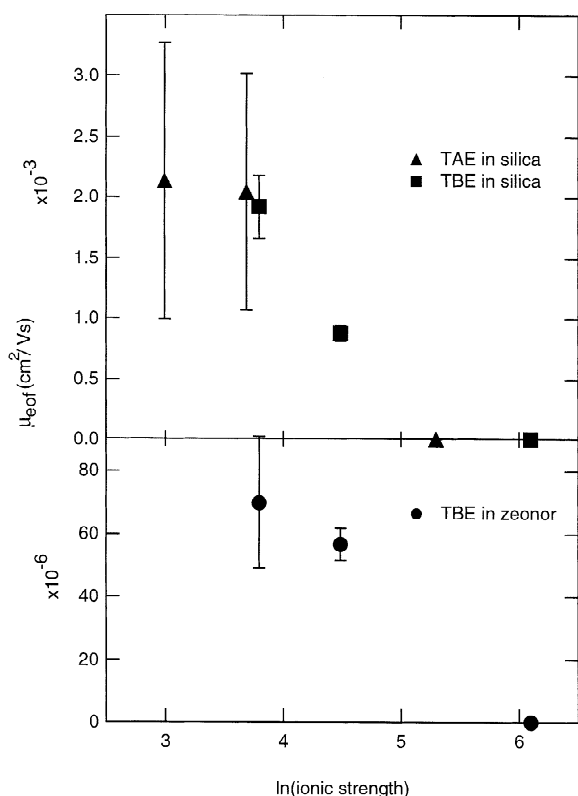


Fig. 2. Electroosmotic mobility as a function of buffer ionic strength. The errors are reported at the 95% confidence limit. Note that the μ_{eof} for the different buffers in the capillaries fall on the same line.

3.2. Effects of surfactant on electroosmotic flow

Surfactants are frequently added to running buffers, forming a dynamic coating of the walls, in capillary electrophoresis [17–19] and in microfluidic devices [20–22] to inhibit adsorption of analytes or fluorescent dyes and to suppress EOF. Characterizing

the effect of common surfactants on the EOF is an important step. Table 1 shows the electroosmotic mobilities for four different surfactants in the capillaries and one surfactant in the oxidized zeonor channels. For the capillaries, these measurements were made after the capillary tubes were soaked in the buffer solution with the 0.1% (v/v) surfactant for at least 4 days because EOF measurements made in freshly filled capillaries with NP-40 or POP-4 buffer solutions did not yield a reproducible measurement of μ_{eof} . The EOF in one POP-4 capillary was followed for over 48 h without seeing a stabilization in μ_{eof} . The POP-4 surfactant quenched the EOF in the oxidized zeonor channels without the need for a waiting period.

4. Conclusions

Oxidized zeonor microfluidic channels display the same EOF trends as borosilicate capillaries but μ_{eof} is lower by almost an order of magnitude. The unoxidized zeonor channels did not support detectable EOF. Furthermore, the oxidized zeonor devices showed signs of aging by day 6. The use of surfactants to dynamically coat the walls for control of the EOF in the borosilicate capillaries was explored. The surfactants studied generally suppressed the EOF but did not eliminate or reverse it. Of particular note is that the dynamic coating took days before it was stable enough to yield reproducible measurements of μ_{eof} . EOF is an important effect in capillary electrophoresis and for the developing field of microfluidics. An increased understanding of the factors affecting EOF is necessary for the continued development of these promising technologies.

Table 1

Effect of surfactants on electroosmotic mobilities (μ_{eof}) in borosilicate capillaries and oxidized zeonor channels

	μ_{eof}				
	Uncoated	POP-6	POP-4	L81	NP-40
Silica	18.7±2.7	12.8±1.6	9.5±2.6	6.8±1.0	21.0±2.9
Oxidized zeonor	0.34±0.05		0		

The units for all mobilities reported in the table are ($\times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and the errors are reported at the 95% confidence limit. See text for details.

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