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Short Communication

Short communication: A simple and accurate method of measuring the zeta-potential of microfluidic channels

We describe an improved method for determining the electroosmotic mobility and zeta potential of surfaces based on a current-monitoring method. This technique eliminates the requirement for measurements of channel dimensions and sample conductivities, leading to a simple high precision measurement. The zeta potential of PDMS is measured for native surfaces and surfaces treated with a nonionic surfactant in low-conductivity electrolytes.

Keywords:

Current-monitoring method / Electroosmosis / PDMS / Zeta-potential

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The zeta potential (ζ) is widely used to characterize the properties of a surface in contact with an electrolyte, particularly the surface charge density [1]. Determination of the zeta potential after surface chemical modification provides a means of characterising the effects of these modifications on polymer substrates which are widely used in microfluidic devices [2–5]. It is also important for applications such as capillary zone electrophoresis, where charged substances such as biopolymers are separated based on their electrophoretic mobilities [6].

Many different microfluidic techniques have been developed to determine the zeta potential of materials, and a summary and detailed comparison of these methods can be found in [7]. The most widely used method for fast and simple measurement of zeta potential is the so-called current-monitoring method, first reported by Huang et al. [8], which measures the electroosmotic velocity u_{EO} inside a channel. The principle involves measuring the DC current flowing through a microchannel when an interface between two electrolytes of slightly different conductivity move through the channel due to electroosmosis. A common experimental setup is shown in Fig. 1 and the experimental procedure is as follows.

Electroosmosis arises from the action of the electric field on the counterions that screen the surface charges. Assuming negative surface charges, electroosmosis drives the fluid from left to right in Fig. 1 if the applied voltage is positive. One electrolyte with a known conductivity is loaded in reservoir 1 while another electrolyte with a slightly different conductivity fills the channel and reservoir 2. When the DC voltage is applied, the electrical resistance of the device is dominated by the conductivity of the electrolyte in the channel because of

its small cross-section compared to the reservoirs. That is, the resistance of the device R_{ch} is given by

$$R_{ch} = \frac{1}{A} \left(\frac{L_1}{\sigma_1} + \frac{L_2}{\sigma_2} \right), \quad (1)$$

where A is the cross section of the channel and L_i is the length of the channel occupied by the electrolyte with conductivity σ_i ($i = 1, 2$). Thus, $L_1 + L_2 = L$ is the total length of the channel.

As the electrolyte in reservoir 1 slowly replaces the electrolyte that initially filled the channel, the resistance of the channel changes. This variation in resistance is monitored by measuring the voltage drop (V) across a series resistor with resistance R ; see Fig. 1. The voltage drop V changes until the original electrolyte is completely replaced. The electroosmotic velocity u_{EO} is obtained from a measurement of the time it takes for one of the solutions to replace the other, which in turn is determined from the duration of the voltage (or current) transient described above. The zeta potential is then obtained from the velocity of the fluid displacement through the Helmholtz–Smoluchowski equation:

$$u_{EO} = -\frac{\varepsilon\zeta}{\eta} \mathbf{E}, \quad (2)$$

where ε and η are, respectively, the electrical permittivity and dynamic viscosity of the electrolyte, and \mathbf{E} is the applied electric field.

This simple method has been widely used and improved, particularly with respect to the S/N of the current [9] and throughput and repeatability [10]. Most techniques now use the so-called “slope method” for determining u_{EO} [11], which addresses the problem of the lack of precision in timing the liquid displacement owing to the gradual transitions at the end of the process. With this method only the rate of change in the current is measured when the displacing electrolyte interface is at the central position of the microchannel.

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Color online: See article online to view Figs. 2 and 3 in color.

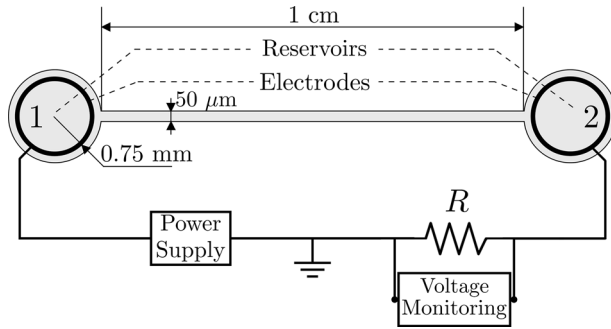


Figure 1. Diagram of an experimental setup of the current-monitoring method along with device dimensions used for measurements.

In this work, we describe an improved current monitoring method that significantly reduces the number of experimental parameters while increasing the precision of the measurements; all performed on-chip. The complexity and size of the device is reduced meaning that experiments can be performed with short channels. The zeta potential was measured for a PDMS microchannel of $50 \mu\text{m} \times 50 \mu\text{m}$ cross-section and 1 cm long (see Fig. 1). This is a significant reduction in size compared to the most recent reported work [9], where the channels were 6 cm long, 1 mm wide, and $35 \mu\text{m}$ tall. In the original work by Huang et al. [8], a capillary of $75 \mu\text{m}$ of inner diameter and a length of 63 cm is used.

Two metallic cylinders were inserted in the inlet and outlet of the PDMS channel—these acted as reservoirs as well as electrodes (see Fig. 1). Three different KCl electrolytes were used with conductivities of 1.5, 5.2, and 11.4 mS/m. For each conductivity, a second solution was prepared with a concentration at 95% of the original solution [8]. The electrical current was measured from the voltage drop across a resistor R connected in series with the channel (Fig. 1). The applied voltage (V_0) was selected so that the transient time of the conductivity displacement is approximately one minute. The resistance R was much smaller than the channel resistance ($R \ll R_{\text{ch}}$) and, therefore, the field in the channel can be calculated from $E = V_0/L$. However, R was large enough for the voltage drop across the resistor to be accurately measured. This meant that R was in the range between 1 and 10 M Ω , for an applied voltage of $V_0 = 20 \text{ V}$.

The channel was initially filled with the electrolyte with a higher conductivity. The voltage across the resistor therefore decreases during the current transient. If the change in current is only due to differences in bulk electrolyte conductivity, the rate of change of current with time $m_I = \Delta I/\Delta t$ is [11]:

$$m_I = \frac{EA(\sigma_1 - \sigma_2)}{\Delta t} = \mathbf{u}_{\text{EO}} \frac{EA(\sigma_1 - \sigma_2)}{L}, \quad (3)$$

where E is the applied field, which can be considered constant because of the small change in conductivity. The two conductivities of the electrolytes are σ_1 and σ_2 , which are measured independently. Finally, using (2) to relate the velocity with the zeta potential:

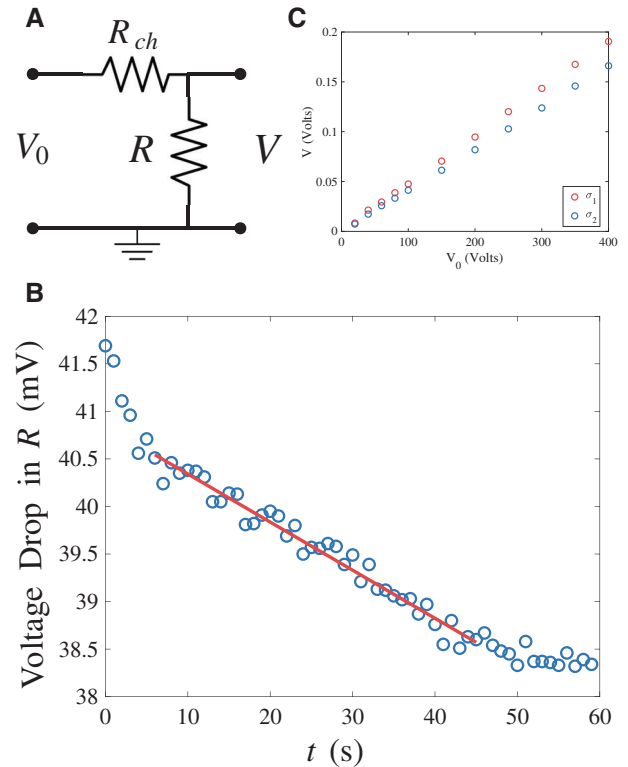


Figure 2. Technique for measuring the prefactors in Eq. (4). (A) Voltage divider with channel and test resistor. (B) Voltage drop across the resistor as a function of time for a conductivity of 5.2 mS/m. The electric field is applied at $t = 0 \text{ s}$. The red line represents a linear fit to the data points between 5 and 45 s, which correspond to the transient due to the displacement of the higher conductivity electrolyte. (C) Example of voltage sweep experiment for two electrolyte conductivities: $\sigma_1 = 1.7 \text{ mS/m}$ and $\sigma_2 = 0.95\sigma_1$.

$$\zeta = \frac{\eta m_I L}{\varepsilon E^2 A (\sigma_1 - \sigma_2)}, \quad (4)$$

which is the common expression used to determine the zeta potential for the state-of-the-art slope method. However, this approach requires at least five independent experimental measurements, namely, channel cross section and length, two electrolyte conductivities and the slope of the current-time plot, each of which can contribute to a final relatively large experimental error.

As stated above, in this method the current is evaluated by measuring the voltage drop across a series resistor R , according to

$$m_I = \frac{\Delta I}{\Delta t} = \frac{1}{R} \frac{\Delta V}{\Delta t} = \frac{m_V}{R},$$

where V is the voltage drop across the resistor, and we have defined the rate of change of voltage with time as $m_V = \Delta V/\Delta t$. In doing so, the circuit becomes a voltage divider from which the total resistance of the channel R_{ch} can be estimated, as shown in Fig. 2A.

Figure 2B is an example of the voltage drop across the resistor as a function of time for an electrolyte of 5.2 mS/m

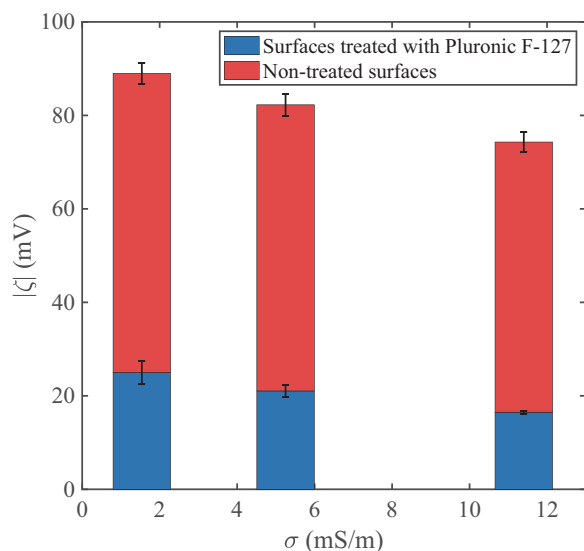


Figure 3. Estimation of zeta potential of PDMS for KCl electrolytes of 1.5, 5.2, and 11.4 mS/m. The ratio of zeta potential for treated and nontreated surfaces is 3.5, 3.9, and 4.5, respectively.

conductivity. Upon application of the electric field, a sudden decrease in voltage is observed, which does not seem related to the movement of the fluid. After a few seconds, the voltage decreases linearly with time, which corresponds to the change in channel electrical resistance due to the displacement of the more conductive solution. Finally, a plateau is reached corresponding to when the channel is filled with the lower conductivity electrolyte. The rate of change of the voltage m_V is obtained by fitting the data of the linear transient part of the graph as shown in the figure (solid line).

The channel resistance is $R_{ch}(\sigma) = L/(\sigma A)$ when filled with a homogeneous electrolyte of conductivity σ . By defining the ratio of channel resistance to R as $r_{\sigma_i} = R_{ch}(\sigma_i)/R$, Eq. (4) can be rewritten as

$$\zeta = \frac{\eta}{\varepsilon E^2} \frac{r_{\sigma_1} r_{\sigma_2}}{r_{\sigma_2} - r_{\sigma_1}} m_V. \quad (5)$$

It is clear that the important parameters are r_{σ_i} , the ratios of the channel resistances to R , which can be accurately measured through the slope of a voltage sweep when the system is filled entirely with one of the two conductivities, as shown in Fig. 2C. Significantly, this method circumvents the need for quantification of the resistances of both channel and resistor, cross section and conductivities of the solutions.

The above method was used to experimentally determine the zeta potential of PDMS. The results are summarized in Fig. 3, and are in agreement with the results in [12]. Experiments using PDMS pretreated with 0.1% w/v Pluronic F-127 for at least 30 min were also performed and strong reduc-

tion of electroosmotic mobility was found, consistent with data in the literature [13]. The zeta potential was reduced by the following ratios: 3.5, 3.9, and 4.5 for the 1.5, 5.2, and 11.4 mS/m conductivity solutions, respectively, in accordance with our estimation for the electroosmotic mobility reduction on PDMS surfaces due to the Pluronic treatment [14].

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The authors have declared no conflict of interest.

Data availability statement

The data that support the findings of this study are openly available in the University of Southampton repository at doi: 10.5258/SOTON/D1.

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