Mohammad Babar
Kaushlendra Dubey
Supreet Singh Bahga 🆔

Department of Mechanical
Engineering, Indian Institute of
Technology Delhi, Delhi, India

Research Article

Effect of surface conduction–induced electromigration on current monitoring method for electroosmotic flow measurement

Current monitoring method for measurement of EOF in microchannels involves measurement of time-varying current while an electrolyte displaces another electrolyte having different conductivity due to EOF. The basic premise of the current monitoring method is that an axial gradient in conductivity of a binary electrolyte in a microchannel advects only due to EOF. In the current work, using theory and experiments, we show that this assumption is not valid for low concentration electrolytes and narrow microchannels wherein surface conduction is comparable with bulk conduction. We show that in presence of surface conduction, a gradient in conductivity of binary electrolyte not only advects with EOF but also undergoes electromigration. This electromigration phenomenon is nonlinear and is characterized by propagation of shock and rarefaction waves in ion concentrations. Consequently, in presence of surface conduction, the current–time relationships for forward and reverse displacement in the current monitoring method are asymmetric and the displacement time is also direction dependent. To quantify the effect of surface conduction, we present analytical expressions for current–time relationship in the regime when surface conduction is comparable to bulk conduction. We validate these relations with experimental data by performing a series of current monitoring experiments in a glass microfluidic chip at low electrolyte concentrations. The experimentally validated analytical expressions for current–time relationships presented in this work can be used to correctly estimate EOF using the current monitoring method when surface conduction is not negligible.

🖥 Additional supporting information may be found online in the Supporting Information section at the end of the article.

1 Introduction

Solid surfaces in contact with electrolyte solutions usually acquire a surface charge due to chemical equilibrium [1, 2]. The immobile surface charges attract oppositely charged mobile ions in the electrolyte, called the counter-ions, and repel the like-charged ions called the co-ions. This results in formation of an electrical double layer (EDL) near the surface. Under the application of an external electric field, the mobile ions in the EDL move and pull the bulk fluid along due to viscous

drag, resulting in bulk motion of fluid termed as electroosmotic flow (EOF) [1, 2]. Unless suppressed [3], EOF is always present during electrophoresis experiments [4, 5]. EOF is often leveraged in electrophoresis for sample injection and simultaneous detection of anions and cations [5]. Besides electrophoresis, EOF is used in variety of microfluidic applications such as pumping [6], micromixing [7], and cell sorting [8]. Therefore, it is essential to characterize EOF in microfluidic channels and capillaries [9–14].

The EOF velocity is proportional to the applied electric field and the proportionality constant is termed as the EOF mobility. Current monitoring method is one of the most convenient methods of measuring EOF mobility in capillaries and microchannels [10–17]. The basic principle of the current monitoring method is illustrated in Fig. 1. In this method,

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Correspondence: Dr. Supreet Singh Bahga, Department of Mechanical Engineering, Indian Institute of Technology Delhi 110016, Delhi, India
E-mail: bahga@mech.iitd.ac.in

Abbreviation: EDL, electrical double layer

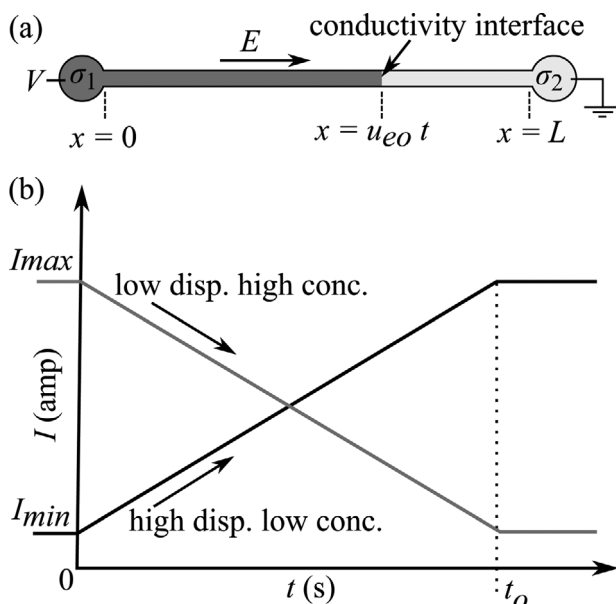**Color online**: See article online to view Figs. 2 and 3 in color.

Figure 1. Schematic illustrating the basic principle of current monitoring method. The channel and the right reservoir are initially filled with a binary electrolyte, called the displaced electrolyte, having conductivity σ_2. The left reservoir is filled with the displacing electrolyte having same composition as the displaced electrolyte but with different conductivity σ_1. At time $t = 0$, fixed voltage difference is applied across the channel which drives EOF towards the right. This causes the electrolyte with conductivity σ_1 to displace the electrolyte with conductivity σ_2. Due to changing resistance of the channel, the current rises or falls if the displacing electrolyte has higher or lower conductivity than the displaced electrolyte, respectively. The current attains a steady value when the displacing electrolyte completely fills the channel. The temporal variation of current is then related with the EOF assuming that the conductivity gradient advects only due to EOF.

the channel is first filled with a solution of a binary electrolyte consisting of a single anionic and cationic species. One of the reservoir is emptied and then filled with the same electrolyte but having a different concentration (and conductivity). Upon application of the electric field, EOF causes the electrolyte in the reservoir to replace the electrolyte in the channel, resulting in a temporal change in electrical resistance of the channel. When conductivity of the bulk solution is significantly larger than the conductivity of EDL, a conductivity gradient in a binary electrolyte migrates only due to EOF and not due to electromigration [18]. In such cases, measurement of current passing through the channel, for a fixed voltage, gives an estimate of the EOF. In particular, for small conductivity difference between the two electrolytes, the current increases (decreases) linearly with time if the displacing electrolyte has higher (lower) conductivity than the displaced electrolyte, as illustrated in Fig. 1. The time taken to completely displace the electrolyte initially filled in the channel can be related with EOF mobility [10, 12]. Alternatively, if the beginning or the end of the displacement process is difficult to identify due to current fluctuations, the slope of the current–time curve can be used to estimate the EOF [11–14].

Based on the principle described above, the displacement time in current monitoring method should be independent of whether a high conductivity electrolyte displaces a low conductivity electrolyte or vice versa. This is indeed true for most current monitoring experiments. However, current monitoring experiments of Lim and Lam [15] with low concentration binary electrolyte (order 1 mM of potassium chloride and less) in glass capillaries exhibited directional dependence of displacement time. In particular, in the experiments of Lim and Lam [15] the time taken by the high-conductivity solution to displace the low-conductivity solution was always smaller than that for the opposite case. Moreover, the difference in displacement time increased with an increase in conductivity difference of the two electrolytes. Saucedo-Espinosa and Lapizco-Encinas [14] have also reported statistically significant directional dependence of displacement times in current monitoring experiments, while using low conductivity electrolytes. These experimental observations suggest that, under certain conditions, the motion of conductivity gradient inside the channel is governed by a nonlinear, irreversible phenomenon. This is in contrast to the assumption inherent in the current monitoring method that the conductivity gradient advects with the EOF and hence its motion is a linear, reversible phenomenon; diffusion is ignored in the current monitoring method.

Because the directional dependence of displacement time in current monitoring method is observed only while using very low bulk conductivity electrolytes, it is plausible that this irreversibility results when surface conduction [19] through the EDL is comparable to bulk conduction. As shown by Bahga et al. [18] and Mani and Bazant [20], the effects of surface conduction on bulk electrophoretic transport of ions can become important in narrow microchannels with high surface-to-volume ratio and at low electrolyte concentrations. When surface conduction is negligible compared with bulk conduction, the only effect of EDL on bulk ion-transport is due to EOF [18]. For negligible surface conduction, concentration gradients in a binary electrolyte in the presence of collinear electric field remain stationary in the frame of moving fluid; the concentration gradients, of course, diffuse due to molecular diffusion. However, when surface conduction is comparable with bulk conduction, the nonlinearity induced by surface conduction causes a gradient in binary electrolyte to either sharpen to form a shock wave [18], similar to that in isotachophoresis (ITP) [21, 22], or disperse to form a rarefaction wave such as that in transient-ITP [22]. Here, the term "wave" is used to denote a migrating disturbance in conductivity or ion concentration [23, 24]. Therefore, in the presence of significant surface conduction, the concentration gradient in the current monitoring method can also electro-migrate as a nonlinear wave in addition to advection due to EOF.

Existence of nonlinear concentration waves in the current monitoring method and their effect on measurement of EOF mobility has not been studied till date. We note that previous experimental studies on current monitoring method do account for surface conduction in the current measurements [10, 13, 14]. However, all these studies neglect surface

conduction–induced electromigration of the conductivity gradient and assume that the conductivity gradient migrates only due to EOF. For example, Arulanandam and Li [10] experimentally showed that for 1 mM potassium chloride solution in 200 μm glass capillary, contribution of surface conduction to the total current can be as high as ten percent. Despite such significant surface conduction Arulanandam and Li [10] assumed that the displacement process is solely due to EOF, an assumption that is valid only when surface conduction is negligible compared with bulk conduction [18, 20].

In the current work, using theory and experiments, we elucidate the effect of surface conduction–induced nonlinear concentration waves on the current monitoring method for measurement of EOF mobility. We present analytical expressions for current–time relationship in the regime when surface conduction is comparable to the bulk conduction. Further, we validate these relations with experimental data by performing current monitoring experiments in a glass microfluidic chip. Our theory and experiments give a conclusive evidence that directional dependence of displacement time in current monitoring method is a consequence of surface conduction–induced nonlinear electromigration. We show that, when high (low) conductivity electrolyte displaces a low (high) conductivity electrolyte in a negatively charged channel such as that made of glass, it results in formation of a shock (rarefaction) wave. Both of these concentration waves propagate in the direction opposite to the EOF and result in directional dependence of displacement times.

2 Theory

2.1 Principle of current monitoring method: without surface conduction

The basic principle of current monitoring method for measurement of EOF has been discussed in detail by Ren et al. [11] and Saucedo-Espinosa and Lapizco-Encinas [14]. Here, we briefly review the theory on which this method is based to highlight the differences with the case when surface conduction becomes relevant. In the current monitoring method, the effect of surface conduction is assumed to be negligible compared with bulk conduction. As explained by Bahga et al. [18], surface conduction can be ignored if $\rho_w P/(zcFA) \ll 1$, where ρ_w is the surface charge density on the channel surface, F is the Faraday's constant, P and A are perimeter and cross-sectional area of the channel, and z and c are the characteristic valence and concentration of ions in the bulk solution.

In current monitoring method, illustrated in Fig. 1, a channel of length L and the right reservoir are filled with a binary electrolyte (denoted by 2) and the left reservoir is filled with similar electrolyte but with different conductivity (denoted by 1). Next, a voltage $V > 0$ is applied at the left reservoir and the right reservoir is grounded. Application of external electric field across the channel results in EOF towards the right (for negatively charged walls), which causes electrolyte 1 to displace electrolyte 2. In the absence of surface conduction

and neglecting slow molecular diffusion, the conductivity of a binary electrolyte within the channel is governed by:

$$\frac{\partial \sigma}{\partial t} + u_{eo}\frac{\partial \sigma}{\partial x} = 0, \quad u_{eo} = \frac{\mu_{eo}V}{L}, \tag{1}$$

where σ denotes the local electrical conductivity, t the time, x the axial coordinate, and u_{eo} the average EOF velocity. The EOF velocity depends on the EOF mobility μ_{eo} and electric field V/L as $u_{eo} = \mu_{eo}V/L$. Throughout this paper, we assume that the EOF mobility is uniform along the channel, which is valid if the axial variation in conductivity is not large [1]. As a result, the EOF velocity u_{eo} remains constant over time.

Equation (1) is a linear hyperbolic equation which has a solution:

$$\sigma = \sigma_o(x - u_{eo}t), \tag{2}$$

where $\sigma_o(x)$ is the initial conductivity profile. In the current case, the initially sharp gradient between regions having conductivities σ_1 (displacing fluid) and σ_2 (displaced fluid) simply advects along the channel with uniform speed u_{eo}. These two zones of different conductivity act as two electrical resistors in series and hence the time-varying current is given by:

$$I(t) = \frac{VA}{\left(\dfrac{L - u_{eo}t}{\sigma_2} + \dfrac{u_{eo}t}{\sigma_1}\right)}, \tag{3}$$

where A denotes the cross-sectional area of the channel. For a small difference in conductivities of the two solutions ($\Delta\sigma/\sigma_2 \ll 1$, $\Delta\sigma = \sigma_1 - \sigma_2$), Eq. (3) yields a linear variation of current with time:

$$I(t) = I_0\left(1 + \mu_{eo}\frac{Vt}{L^2}\frac{\Delta\sigma}{\sigma_1}\right), \quad I_0 = \frac{\sigma_2 VA}{L}. \tag{4}$$

The current rises from its initial value I_0 when the high-conductivity solution displaces initially filled low-conductivity solution ($\Delta\sigma > 0$) and vice versa. The slope of current versus time data or the total displacement time when current attains a new steady value (see Fig. 1) is used to determine the EOF velocity and mobility. Note that if the displaced and displacing electrolytes are swapped, displacement time remains same in the absence of surface conduction.

2.2 Current–time relationship in presence of surface conduction

To model the current–time relationship in the current monitoring method in the regime when surface conduction is comparable to bulk conduction, we consider a binary electrolyte filled in a channel with negatively charged walls. The valences and electrophoretic mobilities of anion and cation are denoted by $z_\pm$ and $\mu_\pm$, respectively. Note that, mobility is a signed quantity and hence $\mu_- < 0$ and $\mu_+ > 0$. We consider a regime where the EDL thickness is significantly smaller than the channel dimensions but surface conduction is comparable with bulk conduction. For example, for 1 mM aqueous solution of potassium chloride the EDL thickness is 10 nm [2]. For a circular channel with 10 μm diameter and surface

charge density $\rho_w = 0.1$ C/m^2, the ratio of current conducted by the EDL to that conducted through the bulk, which scales as $\rho_w P/(zcFA)$ [18], is of order 0.4 indicating that surface conduction is comparable with bulk conduction. The mathematical model for incorporating the effect of surface conduction on bulk electrophoretic transport in this regime has been presented earlier by Mani and Bazant [20] for a binary electrolyte and subsequently generalized for multi-species systems by Bahga et al. [18]. The transport equation for bulk conductivity σ of a binary electrolyte is given by [18, 20]:

$$\frac{\partial \sigma}{\partial t} + u_{eo} \frac{\partial \sigma}{\partial x} + \frac{\mu_- j(t) k}{(\sigma + k)^2} \frac{\partial \sigma}{\partial x} = 0, \tag{5}$$

where $\sigma = z_+ \mu_+ c_+ F + z_- \mu_- c_- F = z_-(\mu_- - \mu_+)c_- F$ is the conductivity of the bulk fluid outside the EDL and $k = -\mu_+ \rho_w P/A > 0$ is the surface conductance per unit cross-sectional area of the channel. In Eq. (5), $j(t) = I(t)/A$ is the current density. Equation (5) shows that when surface conduction is not negligible, a disturbance in conductivity also undergoes electromigration in addition to advection due to EOF. Moreover, as shown by Eq. (5), the electromigration velocity is opposite to EOF because $\mu_- < 0$. Therefore, surface conduction reduces the propagation speed of concentration waves for the same magnitude of total current.

Equation (5) is a quasilinear hyperbolic equation in which the electromigration speed (or wave speed) itself depends on the bulk conductivity. As shown by Bahga et al. [18], depending upon the initial conditions, this equation exhibits solutions with self-sharpening concentration gradients, termed as shock waves, and continuously dispersing waves, termed as rarefaction waves. To use the analytical solutions to Eq. (5), given earlier by Bahga et al. [18], we consider the electrophoretic system in the frame of moving fluid by introducing the axial co-ordinate $X = x - u_{eo}t$; note that u_{eo} remains constant over time. Next, instead of the time co-ordinate we use the charge transported per unit cross-sectional area $\tau = \int_0^t j(\xi)d\xi$. The latter transformation is required because for a fixed voltage, the current changes over time and continuously changes the electromigration speed. Whereas, using τ instead of t yields a constant electromigration speed which simplifies our analysis. In terms of X and τ, Eq. (5) simplifies to:

$$\frac{\partial \sigma}{\partial \tau} + \frac{\mu_- k}{(\sigma + k)^2} \frac{\partial \sigma}{\partial X} = 0. \tag{6}$$

This equation is in the form for which analytical solutions are available in the literature [18, 20]. Based on these solutions, we now derive the current–time relationship in the current monitoring method of EOF measurement in the regime when surface conduction is comparable with bulk conduction.

2.2.1 High-conductivity electrolyte displacing low-conductivity electrolyte: shock wave

When a high-conductivity electrolyte displaces a low-conductivity electrolyte, the interface separating the zones with different conductivities sharpens to form a shock wave, similar to that observed in ITP. For an initial condition having a sharp interface at $X = 0$ separating zones of high conductivity ($\sigma = \sigma_H$, $X < 0$) and low conductivity ($\sigma = \sigma_L$, $X > 0$), Bahga et al. [18] showed that a shock wave propagates at a speed:

$$v_s = \frac{dX_s}{d\tau} = \frac{\mu_- k}{(\sigma_H + k)(\sigma_L + k)}. \tag{7}$$

Here X_s denotes the location of shock wave in the reference frame of the moving fluid. Because $\mu_- < 0$, $v_s < 0$ and hence the wave travels opposite to the direction of EOF. This shock wave separates zones of uniformly high and low conductivity (σ_H and σ_L). Figure S1A depicts the solution in stationary reference frame, x. The distribution of the bulk-conductivity in stationary frame is given by:

$$\sigma(x, t) = \begin{cases} \sigma_H, & 0 < x < u_{eo}t + v_s \tau(t) \\ \sigma_L, & u_{eo}t + v_s \tau(t) < x < L \end{cases}, \tag{8}$$

if the EOF speed $u_{eo} = \mu_{eo}V/L$ is higher than the speed of shock travelling in the opposite direction. Note that, in constant voltage operation the current varies with time and hence the charge transferred per unit area τ is not directly proportional to time t. To obtain the dependence of current I and τ on time, we first substitute the conductivity distribution given by Eq. (8), in the Ohm's law:

$$I(t) = \frac{V}{R(t)}, \qquad R(t) = \int_0^L \frac{dx}{A(\sigma(x, t) + k)}. \tag{9}$$

Here $R(t)$ is the resistance of the channel. Next, solving the differential equation $d\tau/dt = I(t)/A$, with initial condition $\tau(0) = 0$ yields an analytical expression for time, parameterized by τ:

$$t(\tau) = \frac{-v_s}{u_{eo}} \tau + \left(b_1 + \frac{v_s}{u_{eo}}\right) \left(\frac{1 - e^{-a_1 u_{eo} \tau}}{a_1 u_{eo}}\right),$$

$$\text{where } a_1 = \frac{1}{V}\left(\frac{1}{(\sigma_L + k)} - \frac{1}{(\sigma_H + k)}\right) \text{ and } b_1 = \frac{L}{V(\sigma_L + k)}. \tag{10}$$

Knowing $t(\tau)$, Eq. (9) along with Eq. (8) yields an analytical expression for current, parameterized by τ:

$$I(\tau) = \frac{A u_{eo}}{-v_s + (u_{eo}b_1 + v_s)e^{-a_1 u_{eo} \tau}}. \tag{11}$$

Equations (10) and (11) can be used together to obtain the current versus time relationship when a high-conductivity electrolyte displaces a low-conductivity electrolyte. A step-by-step derivation of above expressions is provided in the Supporting Information.

2.2.2 Low-conductivity electrolyte displacing high-conductivity electrolyte: rarefaction wave

When a low-conductivity electrolyte displaces a high-conductivity electrolyte, an initially sharp interface undergoes electromigration dispersion to form a rarefaction wave. This continuously expanding wave propagates opposite to the direction of EOF and is shown schematically in Fig. S1B. Adapting the analytical solution provided by Bahga et al. [18] to this case, the variation of bulk conductivity at later times is given by:

$$\sigma(x,t) = \begin{cases} \sigma_L, & 0 < x < u_{eo}t + v_l \tau(t) \\ \left(\dfrac{\mu_- k \tau(t)}{(x - u_{eo}t)} \right)^{1/2} - k, & v_l \tau(t) < x - u_{eo}t < v_r \tau(t) \\ \sigma_H, & u_{eo}t + v_r \tau(t) < x < L \end{cases}$$

(12)

where

$$v_l = \frac{\mu_- k}{(\sigma_L + k)^2} \quad \text{and} \quad v_r = \frac{\mu_- k}{(\sigma_H + k)^2}$$

(13)

are the electromigration speeds of left and right edge of the rarefaction wave, depicted in Fig. S1. When the rarefaction wave lies completely within the channel, the channel resistance and current–time relationship can be found using the method described for the case of a shock wave in Section 2.2.1. The current–time relation, parameterized by τ, is given by:

$$t(\tau) = \frac{-b_2 \tau}{a_2} + \left(c_2 + \frac{b_2}{a_2} \right) \left(\frac{e^{a_2 \tau} - 1}{a_2} \right),$$

$$I(\tau) = \frac{A a_2}{-b_2 + (a_2 c_2 + b_2) e^{a_2 \tau}},$$

(14)

where

$$a_2 = \frac{u_{eo}}{V} \left(\frac{1}{\sigma_L + k} - \frac{1}{\sigma_H + k} \right),$$

$$b_2 = \frac{\mu_1 k}{3V} \left(\frac{1}{(\sigma_L + k)^3} - \frac{1}{(\sigma_H + k)^3} \right),$$

$$c_2 = \frac{L}{V(\sigma_H + k)}.$$

(15)

A step-by-step derivation of these expressions is provided in the Supporting Information. At later times, the EOF advects the right edge of rarefaction wave outside the channel and only a part of the rarefaction wave remains in the channel. For such a case, a closed form analytical solution for current–time relationship is difficult to obtain. In this regime, the current–time relationship can be obtained by numerically solving the differential equation $d\tau/dt = I(t)/A$, with initial condition $\tau(0) = 0$, where $I(t)$ is given by Eq. (9) and resistance is given by (see Supporting Information):

$$R(\tau, t) = \frac{u_{eo}t}{A(\sigma_L + k)} + \frac{\mu_- k \tau}{3A(\sigma_L + k)^3}$$

$$+ \frac{2(L - u_{eo}t)}{3A} \sqrt{\frac{L - u_{eo}t}{\mu_- k \tau}}.$$

(16)

In this work, we solved the above differential equation numerically using ode45 function in MATLAB, which is based on the Runge–Kutta method.

2.2.3 Limit of small conductivity difference: linear wave

In the limit of small conductivity difference between the displaced and the displacing electrolyte, we can consider that conductivity varies over a base-state value $\bar{\sigma}$ as $\sigma(x,t) = \bar{\sigma} + \sigma'(x,t)$ where $\sigma' \ll \bar{\sigma}$. Substituting this form of $\sigma(x,t)$ in Eq. (5) and linearizing the equation over the base-state conductivity $\bar{\sigma}$ yields a linearized transport equation for bulk conductivity:

$$\frac{\partial \sigma'}{\partial t} + (u_{eo} + \bar{u}) \frac{\partial \sigma'}{\partial x} = 0, \quad \bar{u} = \frac{\mu_- j(t) k}{(\bar{\sigma} + k)^2}.$$

(17)

Irrespective of whether the displacing electrolyte has high or low conductivity compared with the displaced electrolyte, for small conductivity differences a linear wave propagates opposite to the direction of EOF with speed $\bar{u}$. The current–time relationship in this case can be obtained using solutions for shock or rarefaction wave in the limit that $\sigma_L = \bar{\sigma}$ and $\sigma_H = \bar{\sigma} + \Delta\sigma$, where $\Delta\sigma \ll \bar{\sigma}$. The resulting current–time relationship is linear and is given by

$$I = I_0 \left(1 + t \frac{V}{L^2} \frac{\Delta\sigma}{(\bar{\sigma} + k)} \left(\mu_{eo} + \frac{\mu_- k}{\bar{\sigma} + k} \right) \right),$$

$$I_0 = (\bar{\sigma} + k) \frac{VA}{L}.$$

(18)

Note that in the limit of negligible surface conduction $k/\bar{\sigma} \ll 1$, this equation simplifies to the current–time relationship given by Eq. (4). Equation (18) shows that in the presence of surface conduction, even with a small conductivity difference, the slope of current versus time data has a bias of $\mu_- k/(\bar{\sigma} + k)$. This bias always has a sign opposite to that of EOF mobility, that is, the linear wave electromigrates opposite to the EOF. Therefore, if a current–monitoring experiment is performed under conditions where surface conduction is not negligible, using the slope of current versus time data to estimate EOF mobility (using Eq. (4)) will always underpredict the actual EOF mobility. However, in this limit of small conductivity difference between the two electrolytes, there is no directional dependence of the displacement time as the wave propagation phenomenon is linear.

2.3 Theoretical current–time relationship

To elucidate the effect of surface conduction in the current monitoring method for EOF measurement, we use the mathematical model described above to predict current–time relationship for different electrolyte conductivities and surface charge densities. For our calculations, we consider a system similar to the experiments of Lim and Lam [15], who used

aqueous solution of potassium chloride (KCl) as the binary electrolyte in a glass microchannel with nominal diameter 100 µm and length 8 cm. A voltage drop of 1000 V was applied at the channel ends. For our calculations the electrophoretic mobilities were taken as $\mu_{\pm} = \pm 80 \times 10^{-9}$ m^2/V/s and the EOF mobility was $\mu_{eo} = 50 \times 10^{-9}$ m^2/V/s.

Figure 2A shows the current–time relationship in the limit of small concentration difference between the displaced and displacing electrolytes (0.95 mM and 1 mM), for varying surface charge densities. To show that small concentration differences lead to linear current–time relationship, for plotting Fig. 2A we used the nonlinear expressions for shock and rarefaction waves derived in Sections 2.2.1 and 2.2.2. As the magnitude of surface charge density increases, the steady state current before replacement and after complete displacement increases due to increased surface conduction. Therefore, for easier comparison of displacement times, in Fig. 2 we present current values that are normalized using the maximum (I_{max}) and minimum (I_{min}) values as $(I - I_{min})/(I_{max} - I_{min})$. The ascending curves correspond to the case when high conductivity electrolyte displaces low conductivity electrolyte and descending curves for the reverse displacement. In the limit of small concentration difference between the two electrolytes, shown in Fig. 2A, the current–time curves are linear. However, for higher magnitude of surface charge the displacement process takes longer time, even though the EOF mobility is same. As discussed in Section 2.2.3, this is because the conductivity gradient electromigrates due to surface conduction as a linear wave, in the limit of small conductivity differences, in the direction opposite to the EOF. Note that, there is no directional dependence of displacement time in this case due to linear behavior of the system for small conductivity differences. In the inset of Fig. 2A, we show the axial variation in conductivity when 1 mM KCl solution displaces 0.95 mM KCl solution (black line) and when 0.95 mM KCl solution displaces 1 mM KCl solution (gray line) for $\rho_w = -0.5$ C/m^2. Because we have neglected diffusion, in both cases the concentration gradient migrates as a step variation in concentration.

Figure 2B shows the current–time relationship for the case when 1 mM KCl solution displaces 0.5 mM KCl solution and vice versa, for varying surface charge densities. For zero surface charge density, the concentration gradient advects only with EOF and hence the displacement times for both processes are identical and the current–time curves are symmetric. The displacement times are higher in the presence of surface conduction due to finite surface charge density. However, in the presence of surface conduction, the time taken by high-conductivity electrolyte to displace a low-conductivity electrolyte is always lower than the time taken by low-conductivity electrolyte to displace a high-conductivity electrolyte. This difference in displacement times becomes more pronounced at higher magnitudes of surface charge. As discussed in Sections 2.2.1 and 2.2.2, the directional dependence of displacement times in current monitoring experiments is due to propagation of nonlinear waves in presence of surface conduction. When high-conductivity electrolyte displaces
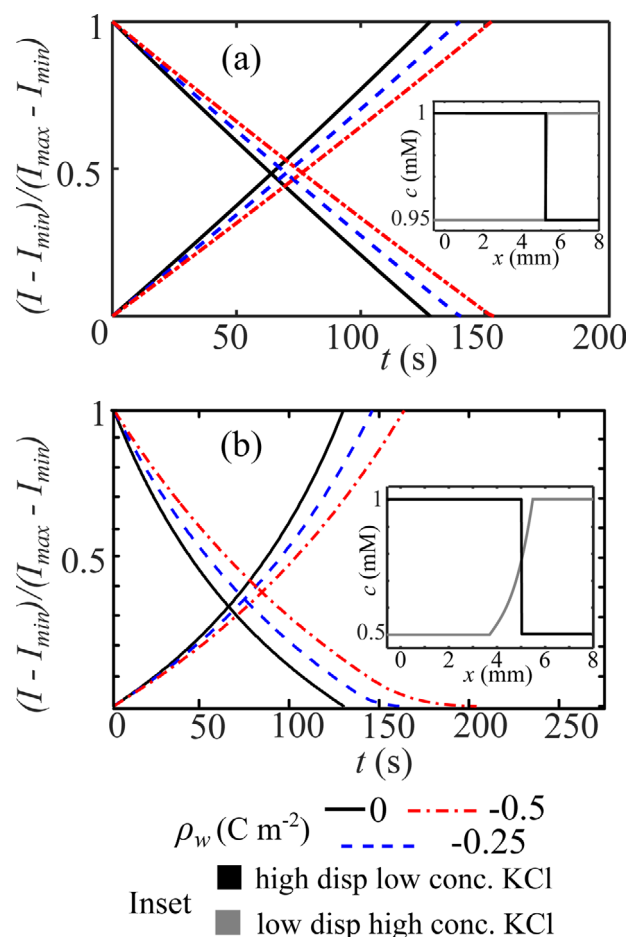

Figure 2. Normalized current time characteristics predicted by the mathematical model for (A) 0.95–1 mM KCl solutions and (B) 0.5–1 mM KCl solutions for varying surface charge density of $\rho_w = 0, -0.25,$ and -0.5 C/m^2. (A) For small conductivity difference between the displaced and displacing electrolytes, the current–time relationships for forward and reverse displacement processes are linear and symmetric. The time taken for complete displacement increases with an increase in magnitude of surface charge. The inset of (A) shows the concentration gradients when 1 mM KCl displaces 0.95 mM electrolyte (black line) and vice versa (gray line). In both cases, the conductivity gradient migrates as a linear wave. (B) For higher conductivity difference between the two electrolytes, the predicted current–time relationships are nonlinear and asymmetric. As shown in the inset of (B), when high conductivity electrolyte displaces a low conductivity electrolyte, the conductivity gradient migrates as a shock wave (black line). In the opposite case, the conductivity gradient migrates as a dispersed rarefaction wave (gray line). The following values of various parameters were used in these calculations: $V = 1000$ V, $L = 8$ cm, $d = 100$ µm, $\mu_{\pm} = \pm 80 \times 10^{-9}$ m^2/V/s and $\mu_{eo} = 50 \times 10^{-9}$ m^2/V/s. The concentration gradients in the insets were plotted with charge density $\rho_w = -0.5$ C/m^2 at $t = 100$ s.

a low-conductivity electrolyte, the concentration gradient electromigrates as a shock wave opposite to the direction of EOF. This shock wave is shown as black line in the inset of Fig. 2B. On the other hand, when low-conductivity electrolyte displaces a high-conductivity electrolyte, the concentration gradient disperses to form a rarefaction wave, shown as grey

line in the inset of Fig. 2B. The left edge of this rarefaction wave always lags the shock wave and hence the time taken by low-conductivity electrolyte to displace the high-conductivity electrolyte is always higher than the opposite case.

3 Experiments

3.1 Materials and methods

We performed a series of current monitoring experiments to validate the mathematical model described in Section 2. Experiments were conducted in a standard cross-shaped, glass microchannel (Micronit, The Netherlands). The microchannels connecting the north (N), south (S), and west (W) reservoirs to the junction were 5 mm long, and the main channel connecting the junction to the east (E) reservoir was 35 mm long. All microchannels were isotropically etched with a D-shaped cross-section of 50 μm width and 20 μm depth. To prevent the adverse effects of electrolysis during current monitoring experiments, large reservoirs of more than 100 μL volume were fixed at the channel ends. All reservoirs were filled with equal volume of fluid (60 μL) and care was taken to avoid undesirable pressure heads. Current monitoring experiments were performed in two steps: (i) filling the straight channel between E and W ends with electrolyte solution, and (ii) replacing the E reservoir with the displacing electrolyte, followed by application of axial electric field between E and W reservoirs. External electric field was applied by applying a potential of 1000 V from the DC power supply (Ionics, India, max. 2 kV and 10 mA) on the platinum electrode dipped in the E reservoir and grounding the platinum electrode dipped in the W reservoir. No voltage was applied at N and S reservoirs. Consequently, EOF in the direction of E and W reservoir was established. The current flowing though the microchannel was measured by recording the voltage difference across a 9.4 MΩ resistor connected in series with the channel. The voltage difference across the resistor was measured using Arduino microcontroller.

For all our experiments, the high conductivity electrolyte was 1 mM KCl (measured conductivity $\sigma_H = 150 \times 10^{-4}$ S/m) solution. We performed three sets of experiments using 0.2 mM, 0.5 mM, and 0.9 mM KCl solutions as the low-conductivity solutions (measured conductivities $\sigma_L = 26 \times 10^{-4}$ S/m, $\sigma_L = 72 \times 10^{-4}$ S/m, and $\sigma_L = 140 \times 10^{-4}$ S/m, respectively). Each set of experiments consisted of three repetitions each of high-conductivity displacing low-conductivity electrolyte and reverse. The high and low conductivity electrolyte solutions were prepared by diluting 1 M stock solution of KCl (CDH, India) solution using Millipore deionized water.

3.2 Validation of mathematical model with experiments

Figure 3 shows the measured variation of current (I/I_{max}) with time in current monitoring method for three cases
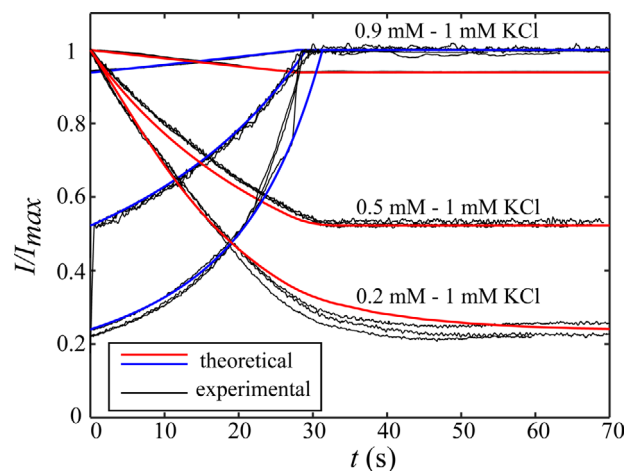

Figure 3. Comparison of experimentally measured and theoretically predicted current–time relationships for three different electrolyte systems. The current data has been normalized by the maximum current. For 0.9 mM-1 mM KCl system, a linear and symmetric response was observed. Whereas, for 0.5 mM-1 mM KCl and 0.2 mM-1 mM KCl systems nonlinear asymmetric current–time relationships were observed. The current–time relationships predicted using the mathematical model are in quantitative agreement with all the experimental data. The parameters of the model were chosen as $\mu_{eo} = 63.8 \times 10^{-9} \text{m}^2/\text{V/s}$ and $\rho_w = -0.11$ C/m^2 to give least squares error between theory and experiments. Other parameters used in calculations were: $V = 1000$ V, $L = 40$ mm, $P = 122.8 \times 10^{-6}$m, $A = 828.3 \times 10^{-12}$ m^2, and $\mu_{\pm} = \pm 80 \times 10^{-9}$ m^2/V/s.

wherein the high-conductivity electrolytes was 1 mM KCl and low-conductivity electrolytes were 0.2 mM, 0.5 mM, and 0.9 mM KCl solutions. The data with increasing (decreasing) current with time corresponds to the case when high (low) conductivity electrolyte displaces a low (high) conductivity electrolyte. As expected, the current–time curves are symmetric and linear when the two electrolytes are of similar concentration (1 mM and 0.9 mM KCl). As shown in Fig. 3, the measured current–time curves are nonlinear for higher concentration difference between the displaced and displacing electrolytes. Moreover, the displacement times are longer when a low-conductivity electrolyte displaces a high-conductivity electrolyte. In Fig. 3, we also show the comparison of experimental data with predictions of the mathematical model. The theoretical predictions considering EOF mobility $\mu_{eo} = 63.8 \times 10^{-9} \text{m}^2/\text{V/s}$ and surface charge density $\rho_w = -0.11$ C/m^2 compare well with all the experimental data. We note that, this value of EOF mobility is typical of glass substrates [3]. Also, the surface charge density of $\rho_w = -0.11$ C/m^2 compares well with typical values of order -0.1 C/m^2, measured by charge titration [25] and those estimated by measuring conductance of aqueous-filled silica nanochannel [26]. The quantitative agreement between experimental data and theoretical predictions gives a conclusive evidence that the directional dependence of displacement times in the current monitoring method for EOF measurement is due to surface conduction–induced nonlinear electromigration of conductivity gradients.

4 Concluding remarks

We have described the effect of surface conduction on the current–time relationship in the current-monitoring method for measurement of EOF. Using theory and experiments, we have shown that, in the regime when surface conduction is comparable with bulk conduction, the basic premise of the current monitoring method that the gradient in conductivity of a binary electrolyte advects only with EOF is not valid. In presence of surface conduction, a gradient in conductivity of binary electrolyte not only advects with EOF but also undergoes electromigration. This electromigration phenomenon is nonlinear and is characterized by propagation of shock and rarefaction waves in ion-concentrations. Consequently, the time taken for displacement of one electrolyte by another is dependent on whether the displacing electrolyte has higher or lower conductivity than the displaced electrolyte.

We have presented analytical expressions for current–time relationship for current monitoring method in the regime when surface conduction is comparable with bulk conduction and validated these relations with experimental data. Our analysis suggests that conventional theory of current monitoring method is strictly applicable only when surface conduction is negligible compared with bulk conduction ($\rho_w P/(zcFA) \ll 1$). Surface conduction can become comparable with bulk conduction when bulk concentration of electrolyte is low, microchannels are narrow, and surface charge density is high. Because surface conduction–induced electromigration is always opposite to the direction of EOF, ignoring surface conduction effects in current monitoring method can significantly under-predict the EOF mobility.

To know whether surface conduction effects are present during current monitoring experiments, one can perform displacement experiments using electrolytes with significantly different conductivities. If the measured current–time curves are asymmetric for forward and reverse displacement, then surface conduction effects are present and must be accounted for. In such cases, the modified current–time relations provided in this paper can be used to infer the EOF mobility. We note that, if conductivities of two electrolytes are similar, the current–time curves are linear and symmetric even if surface conduction is present; the slope of these curves depends on surface conductance. Therefore, in current monitoring experiments, it is impossible to know whether surface conduction effects are relevant if the conductivities of displaced and displacing electrolytes are not significantly different.

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