Transient electro-osmotic flow in cylindrical microcapillaries containing salt-free medium

Shih-Hsiang Chang^{a)}

Department of Mechanical Engineering, Far East University, Tainan 744, Taiwan

(Received 22 September 2008; accepted 11 December 2008;

published online 7 January 2009)

A theoretical study on the transient electro-osmotic flow through a cylindrical microcapillary containing a salt-free medium is presented for both constant surface charge density and constant surface potential. The exact analytical solutions for the electric potential distribution and the transient electro-osmotic flow velocity are derived by solving the nonlinear Poisson-Boltzmann equation and the Navier-Stokes equation. Based on these results, a systematic parametric study on the characteristics of the transient electro-osmotic flow is detailed. The general behavior of transient electro-osmotic flow in a cylindrical tube is similar to that observed in a microchannel containing an electrolyte solution. However, the steady-state electro-osmotic flow significantly deviates from the typical plug flow at higher surface charge and the rate of increase in the electro-osmotic mobility is strongly suppressed due to the effect of counterion condensation. In addition, the applicability limit of these solutions is also discussed. © 2009 American Institute of Physics.
[DOI: [10.1063/1.3064113](https://doi.org/10.1063/1.3064113)]

I. INTRODUCTION

Electrokinetic phenomena for colloidal particles such as electrophoresis¹⁻⁹ and electro-osmosis¹⁰ in a salt-free medium containing only counterions are quite different from those in an electrolyte solution. This difference is caused by the fact that most of the counterions are condensed in a very thin layer around the highly charged surface, which is called the counterion condensation. Typical examples of salt-free media are the nonaqueous media or electrolyte-free aqueous media.³ Aqueous polyelectrolyte dispersion can also be treated as a salt-free medium when the concentrations of hydrogen ions and hydroxide ions are much lower than the concentration of counterions dissociated from polyelectrolytes such as proteins, nucleic acids, DNA, and polyacrylic acid (PAA).⁹

Most of the theoretical studies on electrokinetic flow in a salt-free medium are limited to the fully developed steady-state transverse flow and specifically focus on colloidal particles. However, in practical situation, the efficiency of electrophoretic separation in an electrolyte solution has been observed to strongly depend on the duration of sample injection,¹¹ which in turn is related to the unsteady electro-osmotic flow (EOF) field.¹²⁻¹⁴ Further, the cylindrical capillary has been widely used in biological chips such as micropumps,¹⁵ capillary electrophoretic devices for separation of proteins,¹⁶ and coaxial jet mixing devices used in chemical analysis and biomedical diagnostics.^{17,18} Therefore, it is necessary to study the transient response of EOF in a cylindrical microcapillary containing a salt-free medium.

In this paper, the exact analytical solutions for the electric potential distribution and the transient EOF velocity of a salt-free medium containing only counterions in cylindrical capillaries are derived. No assumption is made about the electrokinetic radius, ka , and the surface potential or surface charge density. Here, k and a are the inverse Debye length and the radius of the

^{a)}Electronic mail: shchang@cc.feu.edu.tw.

FIG. 1. Schematic diagram of a charged cylindrical capillary of radius a , which is filled with a salt-free medium containing only counterions.

cylinder, respectively. Both cases of constant surface charge density and constant surface potential are considered. Theoretical results are presented for the effect of various parameters including the total surface charge per unit length (or zeta potential), the Debye length, and the radius of cylinder on the characteristics of the transient EOF. Although the general behavior of transient electro-osmotic flow in a cylindrical tube is similar to that observed in a microchannel containing an electrolyte solution,^{13,14,19} the Debye length has no effect on such a transient behavior for the case of constant surface charge density, and the steady-state electro-osmotic flow significantly deviates from the typical plug flow for high surface charge. Furthermore, the electro-osmotic mobility increases nonlinearly with the total surface charge; however, the increase in this mobility is considerably suppressed because the counterion condensation occurs at higher surface charge. In addition, the limit of applicability of these solution is discussed.

II. ELECTRIC POTENTIAL FIELD

Consider an EOF in a long uniform cylindrical capillary of radius a , filled with a salt-free medium containing only counterions, with a surface charge density σ or total surface charge $q = 2\pi a\sigma$ per unit length as shown in Fig. 1. Note that the counterions are distributed so that the electroneutrality of the whole system is satisfied. Because the time scale related to electromigration in the electric double layer (EDL), which is of order 10^{-8} – 10^{-7} s,²⁰ is at least two orders smaller than that associated with the evolution of EOF, which is of order 10^{-5} – 10^{-3} s,^{13,14} the transient effect of the EDL can then be neglected and the local volumetric charge density $\rho_e(r)$ can be described by the Poisson equation²¹

$$\frac{1}{r} \frac{d}{dr} \left(r \frac{d\psi}{dr} \right) = - \frac{\rho_e}{\epsilon \epsilon_0} \quad (1)$$

where $\psi(r)$ is the electric potential of the EDL, ϵ is the dielectric constant of the medium, and ϵ_0 is the permittivity of the vacuum.

In fact, the distribution of ionic concentration may be distorted by the fluid motion since the ions convect with flow. However, this distribution can be safely assumed to obey the Boltzmann distribution if the flow is in a fully developed unsteady state and the frequency of external electric field is less than 1 MHz.¹⁴ As a result, the local volumetric charge density in a salt-free medium containing only counterions with the valence $-z$ can be expressed as

$$\rho_e(r) = -zen_0 \exp\left(\frac{ze}{k_b T_a} \psi\right), \quad (2)$$

where n_0 is the concentration of counterions at points where $\psi(r)=0$, e is the elementary charge, k_b is the Boltzmann constant, and T_a is the absolute temperature. Combining Eqs. (1) and (2), we obtain the Poisson-Boltzmann equation

$$\frac{1}{r} \frac{d}{dr} \left(r \frac{d\psi}{dr} \right) = \frac{zen_0}{\epsilon \epsilon_0} \exp\left(\frac{ze}{k_b T_a} \psi\right). \quad (3)$$

Since only differences in electric potential are physically meaningful, we may introduce a new function $y(R) = \Psi(R) - \Psi_0$ and nondimensionalize Eq. (3) as

$$\frac{1}{R} \frac{d}{dR} \left(R \frac{dy}{dR} \right) = (ka)^2 e^{\Psi_0} e^y \quad (4)$$

subject to the boundary conditions

$$y(0) = 0, \quad \left. \frac{dy}{dR} \right|_{R=0} = 0, \quad \left. \frac{dy}{dR} \right|_{R=1} = Q, \quad (5)$$

where Ψ_0 is the unknown scaled value of electric potential at center ($R=0$) and

$$R = \frac{r}{a}, \quad \Psi = \frac{ze}{k_b T_a} \psi, \quad k = \left(\frac{z^2 e^2 n_0}{\epsilon \epsilon_0 k_b T_a} \right)^{1/2}, \quad Q = \frac{aez\sigma}{\epsilon \epsilon_0 k_b T_a} = \frac{ezq}{2\pi \epsilon \epsilon_0 k_b T_a}. \quad (6)$$

Note that k^{-1} is the Debye length, which represents the characteristic thickness of the EDL, and the scaled total surface charge Q per unit length is positive since σ and z are in the same sign.

When $\Psi_0=0$, the solution to Eq. (4) together with the first two boundary conditions is^{22,23}

$$y(R) = -\ln \left(1 - \frac{k^2 a^2}{8} R^2 \right)^2. \quad (7)$$

Based on this fact, the solution to Eq. (4) with the same boundary conditions for arbitrary Ψ_0 can then be derived as

$$y(R) = -\ln \left(1 - \frac{k^2 a^2}{8} e^{\Psi_0} R^2 \right)^2. \quad (8)$$

By imposing the boundary condition at $R=1$ on Eq. (8), we obtain

$$\Psi_0 = \ln \left[\frac{8Q}{(4+Q)k^2 a^2} \right]. \quad (9)$$

Substitute Eq. (9) into Eq. (8) to yield

$$y(R) = -2 \ln \left(1 - \frac{Q}{4+Q} R^2 \right) \quad (10)$$

from which we find the scaled surface potential

$$\Psi_s = \ln \left[\frac{Q(4+Q)}{2k^2 a^2} \right]. \quad (11)$$

Obviously, the potential difference $y(R)$ depends only on Q , not on ka . Further, for high surface charge density ($\sigma \gg 0$), corresponding to high scaled total surface charge ($Q \gg 0$), Eq. (10) becomes

$$y(R) = -2 \ln(1 - R^2), \quad (12)$$

which is not dependent on Q .

As suggested by Ohshima¹⁻⁷ for salt-free media, the zeta potential can be defined as $\zeta = \psi_s - \psi_0$ or the scaled zeta potential as $y_s = \Psi_s - \Psi_0$. Thus, it follows from Eqs. (9) and (11) that

$$y_s = 2 \ln \left(1 + \frac{Q}{4} \right). \quad (13)$$

Note that y_s is positive because Q is positive. If $Q \ll 4$, then $y_s \cong Q/2$. This implies that

$$\zeta = \frac{q}{4\pi\epsilon\epsilon_0}, \quad (14)$$

which is the unscreened Coulomb potential of a charged cylinder. That is, the zeta potential in this limit is the same as if the counterions were absent.²

The present analysis is also applicable to the case where the surface potential is maintained at a constant value ψ_s . In this case, the boundary conditions expressed in Eq. (5) become

$$y(0) = 0, \quad \left. \frac{dy}{dR} \right|_{R=0} = 0, \quad y(1) = \Psi_s - \Psi_0. \quad (15)$$

Since the first two boundary conditions are the same as those for the case of constant surface charge density, it is obvious that the solution for electric potential will be identical to Eq. (10). Here, however, Q is a function of Ψ_s and ka and given by

$$Q = \sqrt{2k^2 a^2 e^{\Psi_s} + 4} - 2. \quad (16)$$

This indicates that the potential difference $y(R)$ in this case is not only dependent on Ψ_s but also on ka . Similarly, for high surface potential ($\Psi_s \gg 0$) or high electrokinetic radius ($ka \gg 0$), corresponding to high scaled total surface charge ($Q \gg 0$), this potential difference will also become Eq. (12), irrespective of both parameters.

III. ELECTROOSMOTIC FLOW FIELD

The salt-free medium is idealized as an incompressible Newtonian fluid with a constant viscosity μ and density ρ . A uniform electric field E is applied along the axial direction starting at the time $t=0$. For a fully developed unsteady laminar flow, the axial velocity $u(r, t)$ through the cylinder due to electro-osmosis is governed by the Navier-Stokes equation

$$\rho \frac{\partial u}{\partial t} = \mu \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial u}{\partial r} \right) + \rho_e(r) E, \quad (17)$$

Substitute Eq. (1) into Eq. (17) to give

$$\rho \frac{\partial u}{\partial t} = \mu \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial u}{\partial r} \right) - \epsilon \epsilon_0 E \frac{1}{r} \frac{d}{dr} \left(r \frac{d\psi}{dr} \right). \quad (18)$$

The appropriate initial and boundary conditions applied for this governing equation are

$$u(0, r) = 0, \quad \left. \frac{\partial u}{\partial r} \right|_{r=0} = 0, \quad u(t, a) = 0, \quad \left. \frac{d\psi}{dr} \right|_{r=0} = 0, \quad \psi(a) = \psi_s \quad (19)$$

The solution to Eq. (18) subject to the above conditions has been derived by Keh and Tseng¹⁹ in the form of $\psi(r)$. By substituting Eq. (10) into their solution and making some manipulation, we have

$$u(T, R) = -\frac{\varepsilon \varepsilon_0 E k_b T_a}{\mu z e} \left[y_s + 2 \ln \left(1 - \frac{Q}{4+Q} R^2 \right) - \sum_{n=1}^{\infty} B_n \frac{J_0(\beta_n a R)}{J_1(\beta_n a)} \exp(-\beta_n^2 a^2 T) \right], \quad (20)$$

where

$$T = \frac{\mu t}{\rho a^2}, \quad B_n = 2 \int_0^1 \left[y_s + 2 \ln \left(1 - \frac{Q}{4+Q} R^2 \right) \right] \frac{J_0(\beta_n a R)}{J_1(\beta_n a)} R dR. \quad (21)$$

Note that J_n is the Bessel function of the first kind of order n , and the eigenvalues β_n are the positive roots of the equation $J_0(\beta_n a) = 0$.

The average flow velocity over a cross section of the cylindrical capillary is obtained by

$$\bar{u}(t) = \frac{2}{a^2} \int_0^a u(t, r) r dr = -\frac{\varepsilon \varepsilon_0 E k_b T_a}{\mu z e} \mu_{eo} = -\frac{\varepsilon \varepsilon_0 y_s}{\mu} EG, \quad (22)$$

where $G = \mu_{eo}/y_s$ and

$$\begin{aligned} \mu_{eo}(Q, T) &= 2 \int_0^1 \left[y_s + 2 \ln \left(1 - \frac{Q}{4+Q} R^2 \right) \right] R dR - \sum_{n=1}^{\infty} \frac{2B_n}{\beta_n a} \exp(-\beta_n^2 a^2 T) \\ &= \left(1 + \frac{4}{Q} \right) y_s - 2 - \sum_{n=1}^{\infty} \frac{2B_n}{\beta_n a} \exp(-\beta_n^2 a^2 T). \end{aligned} \quad (23)$$

Here, μ_{eo} represents an unsteady scaled electro-osmotic mobility and it depends on the time T and total surface charge Q . It should be also noted that Q is given by Eq. (16) for the case of constant surface potential. Further, G can be regarded as a correction factor to the Smoluchowski equation²¹ and its steady-state value will approach to 1 as $Q \rightarrow \infty$, corresponding to $y_s \rightarrow \infty$.

IV. RESULTS AND DISCUSSION

All of the analytical solutions derived above are based on the classical Poisson-Boltzmann theory. Unfortunately, the ionic concentration predicted using this theory will exceed the maximum concentration, d^{-3} , of counterions packed with typical spacing d near a highly charged surface. Hence, the upper bound for surface potential can be estimated as

$$\Psi_{\max} = \frac{k_b T_a}{z e} \left(\frac{1}{d^3 n_0} \right). \quad (24)$$

Substituting this maximum surface potential into Eq. (16) and using the fact that $Q \gg 4$ for high surface charge, we obtain

$$Q_{\max} = \sqrt{\frac{2k^2 a^2}{d^3 n_0} + 4} - 2 \doteq \sqrt{\frac{2k^2 a^2}{d^3 n_0}}, \quad (25)$$

from which the threshold surface charge density can be calculated as

FIG. 2. Spatial distribution of the scaled electrical potential difference in a cylinder for various scaled total surface charges Q .

$$\sigma_{\max} \doteq \sqrt{\frac{2\epsilon\epsilon_0 k_b T_a}{d^3}}. \quad (26)$$

Note that this value is independent of electrokinetic radius, ka , and the valence of counterion, z . For the case where the medium is water at 25 °C ($\epsilon=78.5$) containing only counterions with effective ion size $d=1$ nm, taking into account hydration effects and ion-ion correlations,²⁴ the value of $\sigma_{\max}$ is about 0.076 C m⁻¹. Another criterion for estimating the upper bound for surface potential is²⁴⁻²⁶

$$\text{Du}(\Psi, ka, m) = \frac{K_S}{aK_L} \ll 1, \quad (27)$$

where Du is the Dukhin number, K_S is the surface conductivity, K_L is the bulk conductivity, and

$$m = \left(\frac{k_b T_a}{ze} \right)^2 \frac{2\epsilon\epsilon_0}{\mu D} \quad (28)$$

is a dimensionless number giving the relative importance of electro-osmosis to electromigration, and D is the ionic diffusivity. For $\text{Du} \ll 1$, the surface conduction and concentration polarization can be safely ignored and the EDL remains in thermal quasiequilibrium.^{24,25} However, there is no concentration gradient buildup in the direction of flow, because the applied electric field is tangent to the fix-charge cylindrical solid surface in this study. The work is underway to derive the closed form of the Dukhin number.

The spatial distribution of the scaled electrical potential difference in a cylindrical microcapillary containing a salt-free medium for various scaled total surface charges Q is shown in Fig. 2. It is seen clearly that the potential difference profile is far away from the nearly flat distribution and moves outward as Q increases, indicating that the EDL exists over the entire portion of the

FIG. 3. Variation in scaled zeta potential y_s^* with scaled total surface charge Q^* at different values of z . Note that $y_s^* = y_s/z$ and $Q^* = Q/z$.

microchannel, regardless of the values of Q . This feature is significantly different from that observed in an electrolyte solution, which in turn affects the EOF field, especially for the steady-state flow, as will be shown later. Another interesting result is that this profile will approach an asymptotic state when $Q > 100$, as indicated by Eq. (12). This behavior is a consequence of the fact that at higher Q , the more counterions in the liquid phase are attracted to the region near the surface owing to the Coulomb attractions and the counterion condensation occurs. Figure 3 shows the variation in scaled zeta potential y_s^* with scaled total surface charge Q^* at different values of counterion's valence z . Here, $y_s^* = y_s/z$ and $Q^* = Q/z$ so that the effect of counterion's valence can be shown. Obviously, y_s^* increases with Q^* nonlinearly, as indicated by Eq. (13). However, the increase rate is strongly suppressed due to the effect of counterion condensation, and this suppression is more significant as z increases. This phenomenon is expected because the counterions with a higher valence are more easily attracted to the surface than those with a lower valence. Similar results have been predicted theoretically by Ohshima^{1,2} and Chiang *et al.*⁹ for colloidal particles in a salt-free medium.

Time evolution of nondimensional electro-osmotic velocity profile in a cylindrical microcapillary containing a salt-free medium for various values of Q is shown in Fig. 4. Here, the reference velocity is chosen as $u_r = -(\epsilon\epsilon_0/\mu)E(k_b T_a / ze)$ so that the zeta potential effect can be taken into account. It is observed that the flow is first activated in a thin layer adjacent to the wall, i.e., the high potential region, and its velocity increases rapidly from zero on the surface to a maximum within the high potential region and then drops gradually to a smaller value as the distance is away from the surface. Also, this maximum velocity occurs at a position closer to the surface as Q increases at a given time. This unique profile is attributed to the fact that the flow is driven by the electric force arising from the interaction of an applied electric field and the EDL and such driving force is dominant within this boundary layer. As the time elapses, the flow gradually extends to the center of the cylinder due to the viscous drag force originated from the liquid viscosity, and the location of the maximum velocity will also shift toward the center. These transient EOF behaviors

FIG. 4. Time evolution of nondimensional electro-osmotic velocity profile in a cylinder for various scaled total surface charges Q . Note that $U(R,T)=u(R,T)/u_r$, where $u_r=-(\epsilon\epsilon_0/\mu)E(k_b T_a/z e)$ is a reference velocity.

were also observed in a microchannel containing an electrolyte solution.^{13,14,19} When the steady state is reached, however, even at higher Q the fluid velocity distribution strongly deviates from the typical plug-like flow pattern observed in an electrolyte solution. This result is expected since the shape of steady-state EOF is only determined by the electric potential difference field, which exhibits a completely different behavior on Q as compared with that observed in an electrolyte solution (see Fig. 2). Furthermore, closer examination of Fig. 4 reveals that the characteristic time for the EOF to reach the steady state can be taken as $T=\mu t_{ss}/\rho a^2=1$. Hence, we obtain $t_{ss}=\rho a^2/\mu=a^2/\nu$, where ν is the kinetic viscosity of the medium. This expression shows that the characteristic time associated with the evolution of EOF is proportional to the square of the radius of cylinder a and, surprisingly, independent of any EDL parameter such as zeta potential. Similar expression has also been derived by Yang and his co-workers^{13,14} on studying the evolution of EOF through a microchannel containing an electrolyte solution. It should be noted that the charging time scale, $\tau_c=a/kD$, observed in induced-charge electro-osmosis (IECO) flow,²⁵ does not appear in this study. This is because the surface charge (or zeta potential) in this paper is fixed and constant, not induced by the applied electric field.

In Fig. 5(a), the time evolution of the scaled electro-osmotic mobility μ_{eo} is plotted as a

FIG. 5. Time evolution of (a) the scaled electro-osmotic mobility μ_{eo} and (b) the correction factor to the Smoluchowski equation G as a function of the scaled total surface charge Q .

function of Q . It is clear that the mobility μ_{eo} increases as T or Q increase. However, the rate of increase in μ_{eo} with Q is considerably suppressed due to the effect of counterion condensation. The qualitative behavior of μ_{eo} observed in Fig. 5(a) as Q varies is similar to the result for the scaled zeta potential as shown in Fig. 3. This similarity is expected since the electro-osmotic velocity almost increases with the zeta potential linearly. The effects of Q and T on the correction factor to the Smoluchowski equation G are shown in Fig. 5(b). As expected, this correction factor increases with increasing T or Q . However, the steady-state value of G is only around 0.82 even for such a high surface charge $Q=1000$. This result suggests that the EDL-related correction must be taken into account when the Smoluchowski equation is applied to estimate the average steady-state EOF velocity in a microchannel containing a salt-free medium.

V. CONCLUSIONS

A theoretical study on the transient EOF through a cylindrical microcapillary containing a salt-free medium has been presented in this paper. Both cases of constant surface charge density and constant surface potential are considered. The exact analytical solutions for the electric potential distribution and the electro-osmotic velocity are derived by solving the nonlinear Poisson-Boltzmann equation and the Navier-Stokes equation. The total surface charge (or zeta potential) and the radius of the cylinder are found to have strong impact on the transient behavior of EOF. The radius of the cylinder determines the characteristic time for the EOF to reach the steady state while the total surface charge (or zeta potential) determines the magnitude of the electro-osmotic velocity, and hence the flow rate. Although the general behavior of transient electro-osmotic flow in a cylindrical tube is similar to that observed in a microchannel containing an electrolyte solution, the Debye length has no effect on such a transient behavior for the case of constant surface charge density and the steady-state electro-osmotic flow significantly deviates from the typical plug flow for high surface charge. Furthermore, the electro-osmotic mobility increases nonlinearly as the total surface charge increases; however, the increase in this mobility with the surface charge is strongly suppressed due to the effect of counterion condensation.

ACKNOWLEDGMENTS

This work was supported by the National Science Council, ROC, under Grant No. NSC 96-2221-E-269-015.

- ¹H. Ohshima, *J. Colloid Interface Sci.* **248**, 499 (2002).
- ²H. Ohshima, *J. Colloid Interface Sci.* **255**, 202 (2002).
- ³H. Ohshima, *J. Colloid Interface Sci.* **262**, 294 (2003).
- ⁴H. Ohshima, *J. Colloid Interface Sci.* **265**, 422 (2003).
- ⁵H. Ohshima, *Colloids Surf., A* **222**, 207 (2003).
- ⁶H. Ohshima, *J. Colloid Interface Sci.* **269**, 255 (2004).
- ⁷H. Ohshima, *Chem. Eng. Sci.* **61**, 2104 (2006).
- ⁸V. Lobaskin, B. Dunweg, and C. Holm, *J. Phys.: Condens. Matter* **16**, S4063 (2004).
- ⁹C. P. Chiang, E. Lee, Y. Y. He, and J. P. Hsu, *J. Phys. Chem. B* **110**, 1490 (2006).
- ¹⁰H. Ohshima, *Colloids Surf., B* **247**, 139 (2004).
- ¹¹Z. H. Fan and J. D. Harrison, *Anal. Chem.* **66**, 177 (1994).
- ¹²N. A. Patankar and H. H. Hu, *Anal. Chem.* **70**, 1870 (1998).
- ¹³C. Yang, C. B. Ng, and V. Chan, *J. Colloid Interface Sci.* **248**, 524 (2002).
- ¹⁴Y. Kang, C. Yang, and X. Huang, *Int. J. Eng. Sci.* **40**, 2203 (2002).
- ¹⁵Y. J. Song and T. S. Zhao, *J. Micromech. Microeng.* **11**, 713 (2001).
- ¹⁶A. J. O'Connor, H. R. C. Pratt, and G. W. Stevens, *Chem. Eng. Sci.* **51**, 3459 (1996).
- ¹⁷L. D. Scampavia, G. Blankenstein, J. Ruzicka, and G. D. Christian, *Anal. Chem.* **67**, 2743 (1995).
- ¹⁸V. P. Andreev, S. B. Koleshko, D. Holman, L. D. Scampavia, and G. D. Christian, *Anal. Chem.* **71**, 2199 (1999).
- ¹⁹H. J. Keh and H. C. Tseng, *J. Colloid Interface Sci.* **242**, 450 (2001).
- ²⁰J. P. Hsu, Y. C. Kuo, and S. J. Tseng, *J. Colloid Interface Sci.* **195**, 388 (1997).
- ²¹R. J. Hunter, *Zeta Potential in Colloid Science: Principles and Applications* (Academic, New York, 1981).
- ²²M. A. Lampert and R. U. Martinelli, *Chem. Phys.* **88**, 399 (1984).
- ²³H. K. Tsao, *J. Phys. Chem. B* **102**, 10243 (1998).
- ²⁴M. S. Kilic, M. Z. Bazant, and A. Ajdari, *Phys. Rev. E* **75**, 021502 (2007).
- ²⁵T. M. Squires and M. Z. Bazant, *J. Fluid Mech.* **509**, 217 (2004).
- ²⁶M. Z. Bazant, K. Thornton, and A. Ajdari, *Phys. Rev. E* **70**, 021506 (2004).