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LETTER TO THE EDITOR

Comment on "Theoretical Model of Electrode Polarization and AC Electroosmotic Fluid Flow in Planar Electrode Arrays"

Recent experiments have shown that an AC electric field induces steady fluid flow at or near the surfaces of microelectrodes. The flow velocity is a function of frequency and applied voltage and deriving a full theoretical model has proved difficult. Recently in this journal, M. Scott, K. V. I. S. Kaler, and R. Paul (*J. Colloid Interface Sci.* 238, 449 (2001)) presented a new theoretical model that not only is less comprehensive than previous ones but also is in direct contradiction to established fundamental principles of electrokinetics.

Key Words: **electroosmosis; electrode polarization; microelectrode; AC electrokinetics; electrohydrodynamics.**

This letter is in response to a letter to the editor recently published in this journal (1), in which Kaler and co-workers made several incorrect assertions about our recent work on AC electroosmotic fluid flow on microelectrodes (2–4). The authors derived a model for the electroosmotic velocity that directly contradicts fundamental electrokinetic principles. We rebut these assertions and point out the errors made by the authors.

Recent work has shown that the application of an AC electric field to a pair of co-planar interdigitated microelectrodes generates a steady (nonzero time averaged) fluid flow with a velocity which depends both on the applied potential and on the frequency (2–4). Measurements were recorded using a pair of 100-nm-thick electrodes with a 25-μm gap fabricated on a planar substrate and covered by a fluid (3). The electrodes were energized with a voltage of variable frequency and amplitude. Fluid movement was recorded as a function of position in the electrode plane, applied field frequency, and voltage using fluorescent latex beads as tracer particles. In our preliminary paper (2) we used a simple model based on an array of resistor–capacitor circuits to calculate the fluid flow. This model consisted of semicircular resistors bridging one electrode to the other, terminated at either end on an electrode by a capacitor representing the electrical double layer (2). This model was further refined by taking into account the full linear electrokinetic equations for the double layer and the electrolyte (4).

Scott *et al.* (1) stated that in our RC model (2) we ignored the diffuse character of the double layer. In fact, our model was based upon the standard Debye-Hückel treatment on the diffuse double layer (5–8). In this widely accepted theory, the excess volume charge density decreases exponentially from the electrode to the bulk with a typical decay length of a few nanometers, given by the Debye length, κ^{-1}. At distances from the surface, much greater than this, the fluid is electroneutral. From the linear Debye–Hückel theory, the relationship between the charge per unit area accumulated in the diffuse layer, σ_q, and the potential dropped across the diffuse layer, the zeta potential ζ, is given by

$$\sigma_q = -\varepsilon\kappa\zeta, \qquad [1]$$

where ε is the permittivity of the electrolyte. The surface charge density is obtained by integrating the volume charge from zero to infinity in the direction normal to the electrode surface. According to Eq. [1], the diffuse double layer can be modeled as a capacitor with specific capacitance (capacitance per unit area) $C_s = \varepsilon\kappa$. This widely accepted framework for the double layer was used by us to develop a resistor–capacitor circuit model (2), which predicted the approximate frequency dependence and velocity of fluid flow.

In addition to the simple circuit analysis, we have also developed a model based on the full electrokinetic equations. In Gonzalez *et al.* (4) we presented a full linear analysis of these equations, which were solved for small applied AC voltages to give the AC electroosmotic velocity of the fluid. Significantly, the results of this analysis were in good agreement with simpler resistor–capacitor model (2).

Returning to the resistor–capacitor circuit model, it could be argued that this model (2) considers only the static capacitance of the diffuse layer, ignoring the fact that for alternating electric fields, the double layer will be sensitive to the frequency. However, according to Gunning *et al.* (9), ionic diffusion effects begin to modify the standard differential capacitance when the period of the applied signal is on the order of the characteristic diffusion time of the ions across the diffuse layer length, κ^{-1}. This relaxation time is given by $\tau = \varepsilon/\sigma_c$, where σ_c is the conductivity of the fluid. The observed fluid motion (3) occurs at frequencies in the range from 10^1 to 10^4 Hz, several orders of magnitude smaller than the frequencies corresponding to τ^{-1} (10^6 to 10^8 s^{-1}). The double layer can therefore be assumed to be quasistatic; there is no free charge in the bulk, and the electric potential satisfies Laplace's equation (4).

The fluid velocity is calculated from the stress exerted on the fluid due to the action of the tangential component of the electric field, E_t, on the charges inside the diffuse double layer, since there is no net charge outside. The electroosmotic velocity is then obtained by integrating the tangential electrical stresses in the diffuse double layer and the result is the well-known Smoluchowski formula (5) for the electroosmotic velocity, which is widely used to model fluid flow in a capillary subjected to a DC electric field:

$$v = -\frac{\varepsilon}{\eta} E_t \zeta. \qquad [2]$$

In this equation, η is the viscosity of the fluid. This expression gives the fluid velocity close to the surface, just outside the double layer at a distance on the order of a few Debye lengths. For distances much greater than κ^{-1}, the fluid velocity is obtained from the solution of the Navier–Stokes equation with the electroosmotic velocity as a boundary condition.

Substituting for the zeta potential (Eq. [1]) into Eq. [2] gives the velocity in terms of the surface charge density:

$$v = \frac{\sigma_q E_t}{\eta\kappa}. \qquad [3]$$

This expression was used by us (2) to calculate the fluid velocity in an AC field, with the induced charge and tangential field both functions of frequency. Note that in this analysis the diffuse character of the double layer was not ignored, contrary to the assertion of Kaler and co-workers (1). Given the simplicity of the model, it is in surprisingly good agreement with more comprehensive solutions (4).

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In their letter, Scott *et al.* (1) state that the surface charge should be written as a function of distance x,

$$\sigma(x) = \frac{\varepsilon}{x}(V - \Psi(x))$$

(the meaning of a surface charge, which is a function of x, the direction normal to the surface, is not clear). Substituting this expression into Eq. [3] as in Scott *et al.* (1) gives an expression that relates the fluid velocity explicitly to the distance:

$$v(x) = \frac{\varepsilon E_t}{\eta\kappa}(V - \Psi(x))\frac{1}{x}. \quad [4]$$

Note that this expression differs from the Smoluchowski formula, Eq. [2].

We will now show that this expression is invalid by reference to the simple textbook problem of calculating the electroosmotic flow in an open capillary tube subjected to an axial DC field. We begin by defining the potential at the surface of the capillary, or at least at the slip plane as V. Assume that the capillary radius is much greater than the Debye length κ^{-1}. The solution for the electric potential in this case is well known; the potential decreases exponentially into the bulk and becomes negligible at distances several times κ^{-1}. Using the expression derived by Scott *et al.* (our Eq. [4], their Eq. [8]), in the bulk $\Psi(x \gg \kappa^{-1}) = 0$ and we see that the fluid velocity becomes inversely proportional to x:

$$v(x) = \frac{\varepsilon E_t}{\eta\kappa}\frac{V}{x}. \quad [5]$$

This expression directly contradicts the well-known fact that in an open capillary the fluid moves as a plug with a constant velocity across the capillary, except in a very thin region corresponding to the diffuse layer, where the velocity increases rapidly from zero at the wall (slip plane) to the maximum value in the bulk (5).

In our experiments with microelectrodes and AC fields, the fluid velocities were measured at a height of approximately 1 μm above the electrode surface (3). As explained by Gonzalez *et al.* (4) and observed experimentally (3), the velocity of the fluid does not vary significantly with height x above the electrode surface, for heights smaller than the typical distances of order 25 μm. Therefore, it is justifiable to compare the calculated AC electroosmotic slip velocity at the surface with the experimental results, since the velocities at 0.5 μm, 1 μm, or 2 μm are comparable and in fact do not vary as $1/x$ as suggested by Scott *et al.*

Scott *et al.* (1) continue by stating that the result produced by their analysis predicts the qualitative aspects of the experiments much better than that produced by our circuit analysis model. However, their model underestimates the velocity maxima by an order of magnitude. In addition, although their model predicts a decrease in velocity with increasing conductivity that approximately corresponds to our measurements for 5 V_{pk-pk} (3), the frequencies at which the peak values of velocity occur are incorrect (cf. Fig. 7a in Ref. (3)). In fact, their predicted frequency of maximum velocity for the lowest medium conductivity is nearly one order of magnitude higher than measured. Significantly, we have shown experimentally that at low voltages ($\sim$1 V_{pk-pk}) there is only a slight decrease in velocity with conductivity (Fig. 7b in Ref. (3)), a result which is in direct contradiction to the model proposed by Scott *et al.* (1). However, the models of Ramos *et al.* (2) and Gonzalez *et al.* (4) are in broad agreement with experiment.

The most plausible explanation for the variation of measured fluid velocity at different voltages and conductivities is that the double layer model becomes nonlinear at high electrode potentials (6). In addition, both in our early model (2) and in the model of Scott *et al.* (1), the effects of the immobile Stern layer were completely ignored. At high suspending-medium conductivities the reactive impedance of the diffuse layer becomes comparable with that of the Stern layer (4) (which is always present) and the latter becomes important in determining the potential drop across the double layer. At high suspending-medium conductivites, a substantial part of the applied potential is dropped across the immobile Stern layer, rather than the diffuse layer thus leading to a reduction in the fluid velocity.

In conclusion, the model proposed by Scott *et al.* (1) is incorrect and does not provide a more comprehensive understanding of the mechanism responsible for the observed fluid flow on microelectrodes in AC fields. Indeed, existing theories are able to account for the qualitative trend observed in the frequency spectra of the flow.

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