

Streaming Potential and Streaming Current Methods for Characterizing Heterogeneous Solid Surfaces

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By monitoring changes in electrokinetic parameters, the streaming potential technique has been used as a method of characterizing heterogeneous surfaces, for example, due to protein adsorption. In general it is assumed that the change in the streaming potential is proportional to the degree of heterogeneity. In this study a simple model of the electrokinetic flow through heterogeneous slit channels has been developed with the goal of comparing the streaming potential and streaming current techniques and determining under what conditions the aforementioned proportionality assumption will produce erroneous results. The flow simulations have shown that, when the streaming potential induces significant flow impedance, a severe deviation from the linear assumption is observed. Since streaming current measurements are unaffected by electrokinetic flow effects, more consistent results are predicted and they are preferred for measurements made in small channels. Additionally it has been shown that the distribution of the heterogeneous coverage has a negligible effect on both the streaming potential and the streaming current in cases where the double-layer overlap is not significant.

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Key Words: heterogeneous surfaces; streaming potential; streaming current; electrokinetic flow; microchannel.

1. INTRODUCTION

Electrokinetic means are a popular method of surface characterization for biomedical polymers (1, 2). It is well known that electrokinetic phenomena can be used as a method of measuring the degree of surface heterogeneity, for example, due to the adsorption of surface active substances (3). More recently, pioneering works by Norde and co-workers (4, 5) and others (6, 7) have shown that the streaming potential technique can be an effective tool for the study of protein adsorption onto polymer materials, which is a key process with regard to the biocompatibility of medical devices.

When substances such as the aforementioned proteins are adsorbed onto a surface, the average electrokinetic properties of the surface change. Norde and Rouwnthal (4) proposed that the degree of surface heterogeneity, Γ , could be related to the change

in the zeta potential, $\Delta\zeta$, through a linear relation,

$$\Gamma = F\Delta\zeta, \quad [1]$$

where F is a proportionality constant. The value of F is determined through knowledge of the ζ -potentials of the homogeneous surface and the surface with some known degree of heterogeneity. In the case of protein adsorption, for example, the observed maximum or minimum in zeta potential was assumed to correspond to maximum interfacial protein concentration, which could be measured directly through some other technique like ellipsometry (5).

In all of the above studies, the proteins were mixed in a solution that was then forced to flow through either a slit microchannel or a capillary tube. As the proteins were adsorbed to the surface, $\Delta\zeta$ was deduced from the change in the measured streaming potential, E_s , using the Smoluchowski equation. Since this equation predicts a linear relation between E_s and $\Delta\zeta$, this proportionality can be added to that shown above to determine the working form of Eq. [1],

$$\Gamma = R_1\Delta E_s, \quad [2a]$$

where R_1 is a new proportionality constant.

Though not yet applied to study heterogeneous surfaces, a number of recent papers (8, 9) have described the streaming current technique as an alternative method of electrokinetic characterization. The two techniques are illustrated in Fig. 1. In the streaming current technique the microchannel is short-circuited, therefore eliminating E_s , and the streaming current, I_s , is measured directly. Since changes in I_s , should also be proportional to $\Delta\zeta$, a relation similar to Eq. [2a] can be developed for streaming current measurements,

$$\Gamma = R_2\Delta I_s, \quad [2b]$$

where R_2 is a proportionality constant, different from R_1 .

Each technique has its analytic and experimental advantages and disadvantages. Generally E_s is on the order of 10–100 mV/kPa pressure drop along the channel and as such is relatively easy to measure. In recent studies (10–12), however, it has been shown that the presence of E_s can have significant effects on the velocity profile and the volume flow rate (i.e.,

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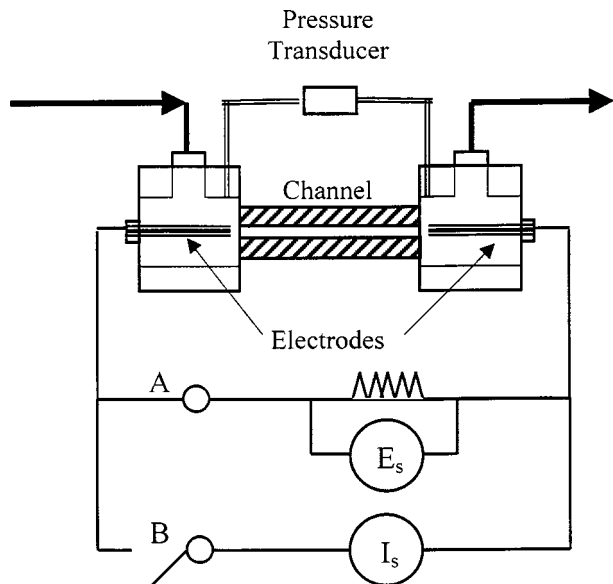


FIG. 1. Typical streaming potential and streaming current apparatus (A open, B closed = streaming current measurement; A closed, B open = streaming potential measurement).

the electroviscous effect). This fact was not considered in the derivation of Eq. [2a]. The streaming current method avoids this difficulty, but the current can be on the order of 1 nA/kPa pressure drop (8), making an accurate measurement more difficult.

In this paper the effectiveness of the streaming potential and streaming current techniques for determining the degree of surface heterogeneity will be examined theoretically. By using a numerical solution to the modified Navier–Stokes equation, the sensitivity and accuracy of the two methods will be investigated, as well as the effects of the channel height, the distribution of the heterogeneity, the magnitude of $\Delta\zeta$, and the electrolyte concentration. Furthermore this study will investigate under what conditions the linear relations, assumed in Eqs. [2], fail to be accurate.

2. FLOW THROUGH INHOMOGENEOUS SLIT MICROCHANNELS

As mentioned above, the objective of this paper is to examine qualitatively the sensitivity of the streaming potential and the streaming current to the degree of surface heterogeneity. Therefore, to simplify the mathematical analysis, we consider a slit microchannel with strip-wise heterogeneity parallel to the flow axis for both symmetric and nonsymmetric distributions, as illustrated in Fig. 2. The flow model will be developed in such a manner that the zeta potential, ζ , can vary arbitrarily along the channel cross section. Unlike previous models (13) this paper will concentrate on the electrokinetic flow effects rather than the impedance due to the shape of the adsorbed particle.

As most streaming potential and streaming current measurements are made using a slit microchannel setup (14), this geometry was selected here. In previous analysis of such slit chan-

nels (15), the analysis was reduced to the 1-D case, since the height to width ratio was much less than one ($H/W \ll 1$). However here the existence of a changing surface potential along the x axis prohibits this simplification, and thus, a 2-D model must be used.

The steady-state, laminar flow of fluids with constant viscosity and density through microchannels is described by the Navier–Stokes equation for momentum,

$$\rho \bar{u} \nabla \bar{u} = -\nabla P + \mu \nabla^2 \bar{u} + \bar{F}, \quad [3a]$$

where \bar{u} is the velocity vector, ρ is the fluid density, P is the relative pressure, and \bar{F} represents any additional body forces applied to the fluid continua. For fully developed laminar flow, the kinetic energy terms on the left-hand side of Eq. [3a] can be neglected, as well as any additional components of velocity in the x and y directions. Under these conditions Eq. [3a] is reduced to

$$\mu \nabla^2 u_z = \frac{\partial P}{\partial z} - F_z. \quad [3b]$$

If the gravity effect is negligible, the only significant body force is that caused by the streaming potential, which is described by

$$F_z = F_e = \frac{\partial E_s}{\partial z} \rho_e(x, y), \quad [4]$$

where $\partial E_s / \partial z$ is the instantaneous rate of change of the streaming potential along the z (flow) axis and ρ_e is the local net charge density per unit volume. The problem becomes well defined by subjecting the above equations to the no slip boundary condition. As alluded to earlier, a consequence of streaming current technique is that E_s is eliminated due to the short-circuiting of

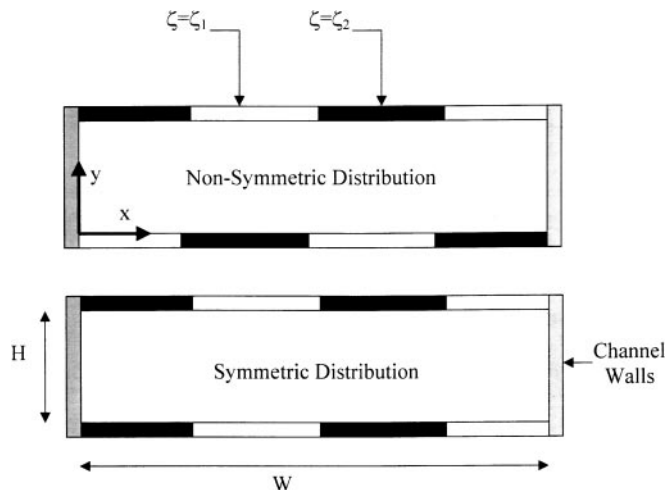


FIG. 2. Symmetric and nonsymmetric heterogeneous distributions along channel cross-section. The z axis is out of the page, corresponding to the pressure driven flow direction.

the two ends of the channel. Thus for this case $F_e = 0$, and Eq. [3b] is reduced to a form to which an exact analytical solution is available using a separation of variables technique.

2.1. Electrical Double-Layer (EDL) Field

According to the theory of electrostatics, the relationship between the net local charge density per unit volume, ρ_e , and the local electrostatic potential of the EDL, ψ , is given by

$$\nabla^2 \psi = \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} = -\frac{\rho_e}{\varepsilon \varepsilon_0}, \quad [5]$$

where ε is the dielectric constant of the fluid and ε_0 is the permittivity of a vacuum. Assuming that the equilibrium Boltzmann distribution is applicable, it can be shown (12) that ρ_e is related to ψ by the equation

$$\rho_e(x, y) = -2z_e e n_o \sinh\left(\frac{z_e e \psi(x, y)}{k_b T}\right), \quad [6]$$

where z_e is the valence of the ions in the electrolytic solution, e is the charge of an electron, n_o is the ionic concentration, k_b is the Boltzmann constant, and T is the absolute temperature. By defining the Debye–Hückel parameter as $\kappa^2 = 2z_e^2 e^2 n_o / \varepsilon \varepsilon_0 k_b T$, the hydraulic diameter as $D_h = 2HW/(H + W)$, and introducing the following nondimensional parameters $\psi^* = z_e e \psi / k_b T$, $\kappa^* = \kappa D_h$, and $x^* = x/D_h$, $y^* = y/D_h$, the nondimensional EDL profile can be described by combining Eqs. [5] and [6] to yield

$$\frac{\partial^2 \psi^*}{\partial x^{*2}} + \frac{\partial^2 \psi^*}{\partial y^{*2}} = \kappa^{*2} \sinh \psi^*, \quad [7a]$$

which is subject to the following Dirichlet boundary conditions at the shear plane,

$$\begin{aligned} \psi^*(x^*, y^* = 0) &= \zeta_b^*(x^*) \\ \psi^*(x^*, y^* = H/D_h) &= \zeta_t^*(x^*) \\ \psi^*(x^* = 0, y^*) &= \zeta_l^*(y^*) \\ \psi^*(x^* = W/D_h, y^*) &= \zeta_r^*(y^*), \end{aligned} \quad [7b]$$

where ζ_b^* , ζ_t^* , ζ_l^* , and ζ_r^* are the nondimensional zeta-potentials for the bottom, top, left, and right surfaces, respectively, defined by $\zeta^* = z_e e \zeta / k_b T$. For the slit geometry, where $H \ll W$, the actual value of ζ^* on the left and right boundary is for all practical purposes irrelevant to the final solution; however, they are mathematically required to ensure that the problem is well defined.

2.2. Streaming Potential and Streaming Current

The streaming current can be found by integrating the product of the net charge density and the z component of the velocity

over the cross section of the channel as:

$$I_s = \int_{y=0}^{y=H} \int_{x=0}^{x=W} \rho_e(x, y) u_z(x, y) dx dy. \quad [8]$$

For streaming current measurements, I_s is measured directly. In the streaming potential technique the presence of E_s induces a conduction current opposite the direction of the flow, defined by

$$I_c = \lambda_o A_c \frac{\partial E_s}{\partial z}, \quad [9]$$

where A_c is the effective cross-sectional area of the channel and λ_o is the bulk conductivity of the channel. The conduction current in turn will generate a liquid flow in the opposite direction of the pressure-driven flow. Consequently, the net flow rate in the pressure-driven direction is reduced. This is the well-known electroviscous effect (10–12). When $I_s + I_c = 0$ (i.e., no net current through the channel), the system is said to be at a steady state and it is through this equivalence that the steady-state streaming potential is determined,

$$\frac{\partial E_s}{\partial z} = \frac{E_s}{L} = -\frac{1}{\lambda_o A_c} \int_{y=0}^{y=H} \int_{x=0}^{x=W} u_z(x, y) \rho_e(x, y) dx dy, \quad [10]$$

where L is the length of the channel.

By introducing the following dimensionless groups, $E_s^* = E_s \lambda_o A_c / 2z_e U e L n_o D_h^2$, $u_z^* = u_z / U$, where U is a velocity scaling factor on the order of the maximum flow velocity, and $z^* = z/L$, where z is the co-ordinate variable in the direction of the pressure driven flow, Eq. [10] can be nondimensionalized to the form:

$$\frac{\partial E_s^*}{\partial z^*} = \int_{y^*=0}^{y^*=H/D_h} \int_{x^*=0}^{x^*=W/D_h} u_z^* \sinh \psi^* dx^* dy^*. \quad [11]$$

2.3. Velocity Profile

Defining nondimensional pressure as $P^* = P/P_o$, where P_o is the entrance pressure, and recognizing that $\partial P^* / \partial z^* = -1$ if a linear pressure drop is assumed, the nondimensional version of Eq. [3b] is developed as

$$\frac{\partial^2 u_z^*}{\partial x^{*2}} + \frac{\partial^2 u_z^*}{\partial y^{*2}} = -G_1 + G_2 \frac{\partial E_s^*}{\partial z^*} \sinh(\psi^*), \quad [12]$$

where the nondimensional groups G_1 and G_2 are defined as $G_1 = D_h^2 P_o / \mu U L$ and $G_2 = 4(z_e e D_h^2 n_o)^2 / \mu \lambda_o A_c$. Of note here is that a linear pressure drop implies that the velocity profile is quasi-constant at each point in the z direction. As a result this model assumes that the heterogeneous strips have a constant width along the flow axis.

2.4. Numerical Technique and Solution Scheme

Equations [7a] and [12] are nonlinear partial differential equations, which must be solved numerically. In both cases a finite difference scheme using a divided difference polynomial, which allowed for variable grid spacing, was developed to discretize the equations. The variable spacing was then used to tighten up the grid spacing in the region nearest the channel wall, where EDL effects are most significant. The resulting set of algebraic equations was then solved using Newton's method.

While solving for the EDL profile in this manner is straightforward, the velocity profile solution is significantly more difficult because Eq. [12] must be coupled to the streaming potential relation Eq. [11]. As a result an iterative scheme was used to successively update the value of $\partial E_s^*/\partial z^*$ in Eq. [12] with that

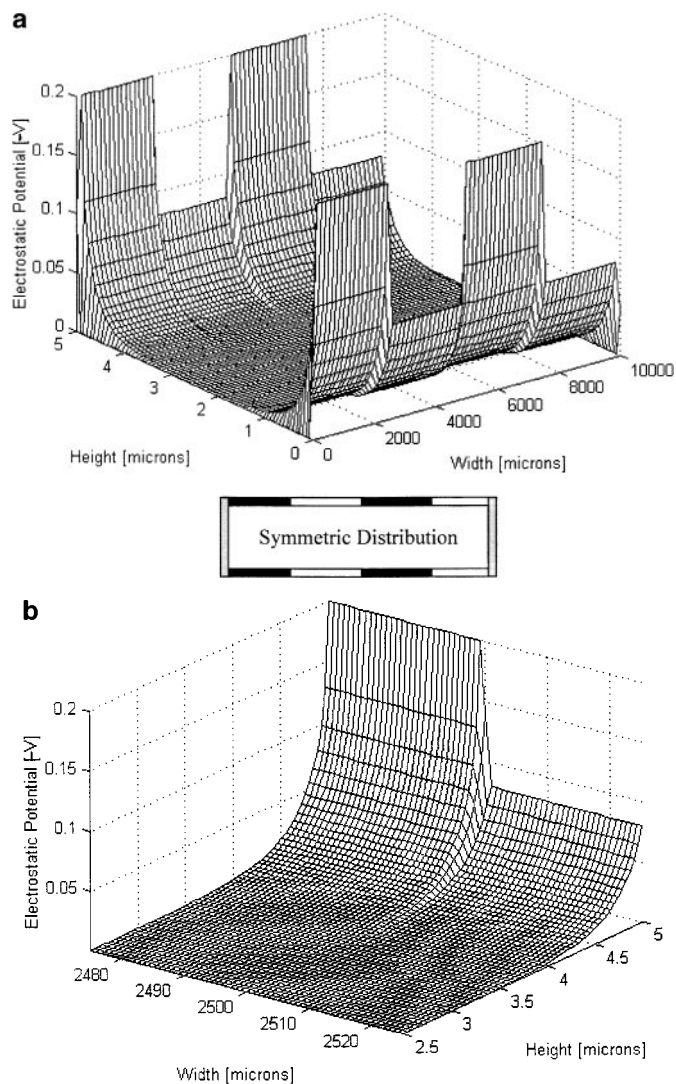


FIG. 3. (a) Cross-sectional view of the EDL field in a slit microchannel with 50% heterogeneous strip surface coverage ($\zeta_o = -0.2$ V and $\zeta_h = -0.08$ V, $n_o = 10^{-6}$ M KCl). (b) Close-up view of the EDL transition zone between a strip of the solid surface of a heterogeneous strip.

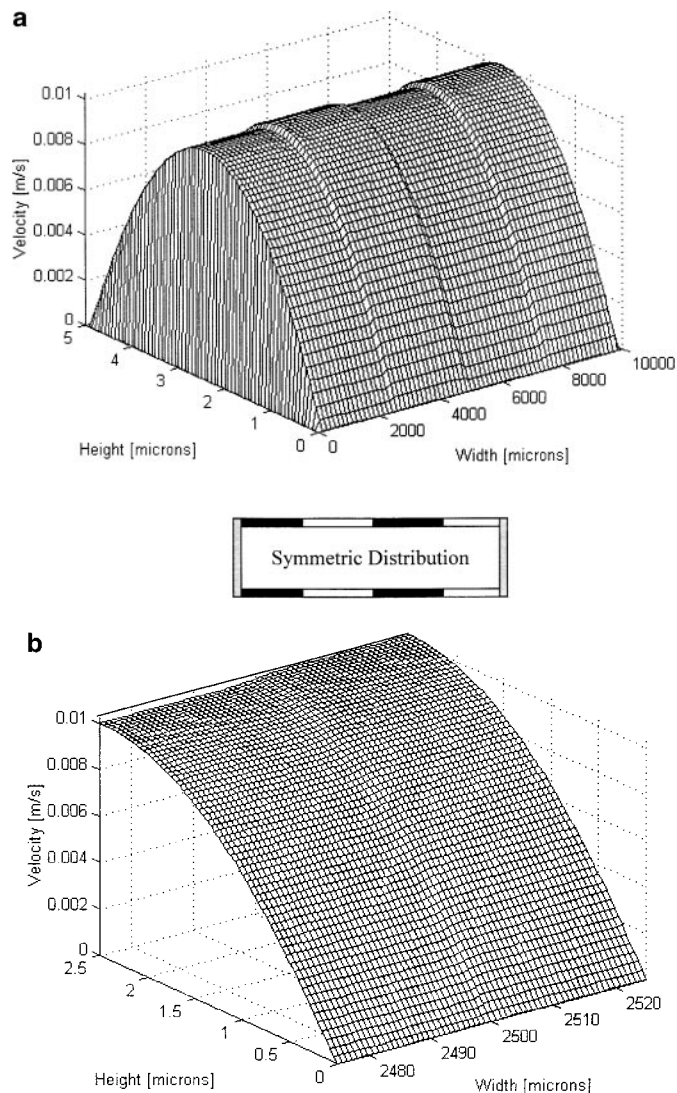


FIG. 4. (a) Steady-state, fully developed, velocity profile in a slit microchannel with 50% heterogeneous strip surface coverage ($\zeta_o = -0.2$ V and $\zeta_h = -0.08$ V, $n_o = 10^{-6}$ M KCl). (b) Close up of the velocity transition zone between a strip of the solid surface and a heterogeneous strip.

calculated from Eq. [11], by using the previous velocity profile. For the streaming current analysis this step is not required since $\partial E_s^*/\partial z^* = 0$. In cases where the streaming potential significantly affects the velocity profile, a relaxation factor less than 1 was applied to the updated value $\partial E_s^*/\partial z^*$.

Figures 3 and 4 show the EDL and velocity profiles in a slit microchannel for a surface of $\zeta_o = -0.2$ V with a 50% symmetric heterogeneous coverage with $\zeta_h = -0.08$ V. In Fig. 3a it is apparent that the heterogeneities have a sharp effect on the EDL profile and there is no gradual transition from one region to another as might be expected. This is confirmed in Fig. 3b, which shows a close-up view of the transition zone between the two heterogeneous regions.

Figure 4a shows that indeed the surface inhomogeneity can have a dramatic effect on the velocity profile along the length of

the channel. While this figure seems to suggest that the velocity profile also experiences sharp changes along the x axis, a close-up look in Fig. 4b shows the transition to be quite gradual over a large region, greater than 20 times the half height of the channel. By comparing Figs. 3a and 4a, it can be noted that in the regions of high ζ -potential, the local velocity is lower than that in the low ζ -potential regions. At a given distance from the wall, $\rho_e(x, y)$ is of greater magnitude in the regions of high ζ -potential. As such the electrokinetic body force is greater, resulting in a more significant impact on the velocity profile than in the lower ζ -potential regions.

3. RESULTS AND DISCUSSION

By using the above algorithm, the dependence of the streaming potential, streaming current, and volume flow rate on the degree of heterogeneity has been investigated. The first section will consider how the degree of heterogeneity will affect these quantities and under what conditions the channel height and distribution of the inhomogeneity cause significant deviation from the linear relation described by Eqs. [2]. In the second part the effect of the $\Delta\zeta$ will be investigated. Finally the third section will consider the effects of the bulk ionic concentration.

3.1. Effect of Surface Coverage

Figures 5a, 5b, and 5c compare the changes in streaming potential, streaming current, and volume flow rate with the degree of heterogeneity for channel heights ranging from 20 to 5 μm in height. In Figs. 5a and 5b the results have been scaled by the value predicted for a homogenous channel, whereas Q in Fig. 5c is scaled by the ideal Poiseuille volume flow rate (i.e., without electroviscous effects). To determine when the location of the heterogeneity becomes important, simulations have been conducted for both a symmetric (dashed line) and a nonsymmetric distribution (solid line). In each case the homogenous surface of $\zeta = -0.2\text{V}(\zeta_o)$ and heterogeneity of $\zeta = -0.08\text{V}(\zeta_h)$ in a streaming solution of 10^{-6}M KCl were considered.

From Fig. 5a it is apparent that in the smaller channels the streaming potential deviates significantly from the linear prediction. The explanation for this can be deduced from Fig. 5c, which indicates that there is significant flow impedance in the smaller channels due to the presence of the streaming potential. Referring back to Eq. [10], it is apparent that if u_z is constant, as is the case for the larger channels, E_s should change proportionally with ρ_e . In smaller channels, however, the decreasing E_s with ρ_e is partially offset with an increase in u_z . As a result the change in streaming potential with Γ is less significant than it is predicted from Eq. [2a]. In other words, if such a linear relation were assumed, the percentage heterogeneous coverage would be significantly underestimated. Also from Fig. 5a, the streaming potential technique is less sensitive for smaller channels, in that ΔE_s for a given $\Delta\Gamma$ becomes smaller as H decreases.

Since the streaming current measurements are unaffected by electrokinetically caused flow impedance (i.e., $Q/Q_0 = 1$), it

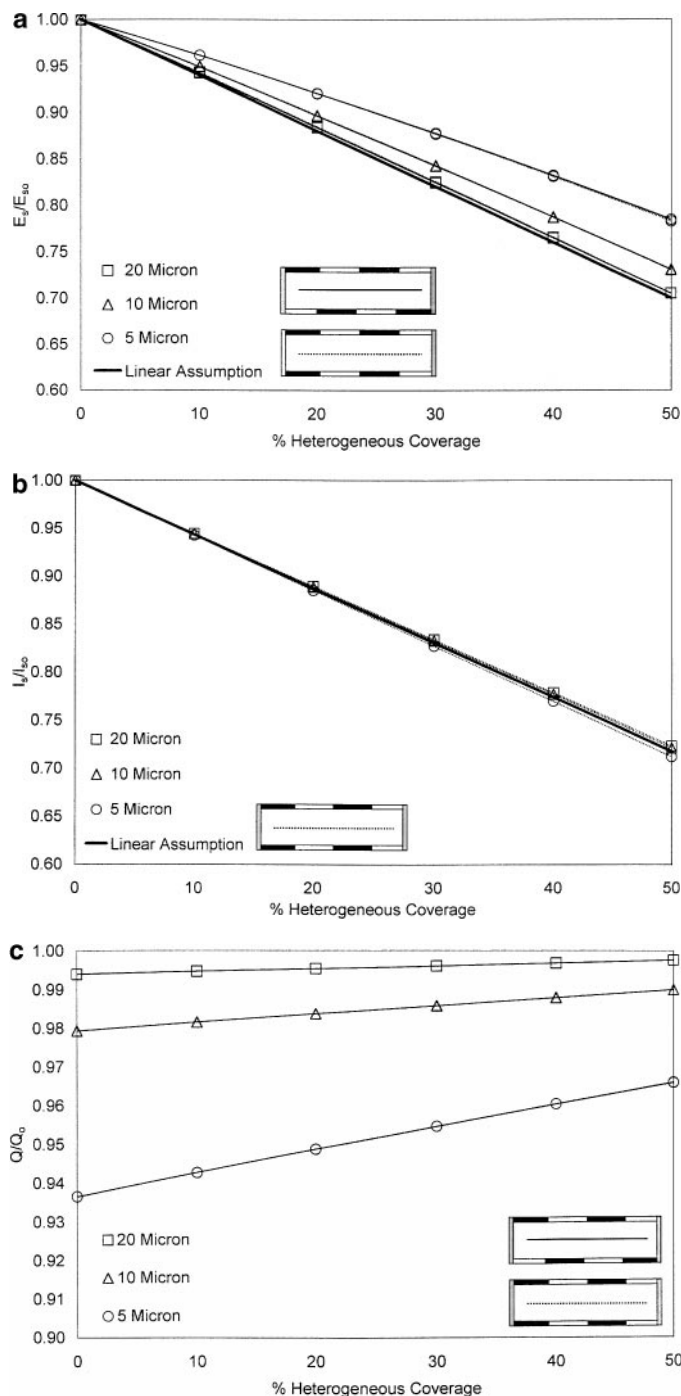


FIG. 5. Effect of the degree of surface heterogeneity on the (a) streaming potential, (b) streaming current, and (c) volume flow rate ($\zeta_o = -0.2\text{V}$ and $\zeta_h = -0.08\text{V}$, $n_o = 10^{-6}\text{M}$ KCl).

would be expected that the scaled streaming current should be nearly linear in all cases. As can be seen from Fig. 5b, the curves for all channels never deviate more than 1 or 2% from the linear relation, confirming this hypothesis and suggesting that this technique is favorable for determining Γ especially in small channels. Additionally the results of the calculations, as can be

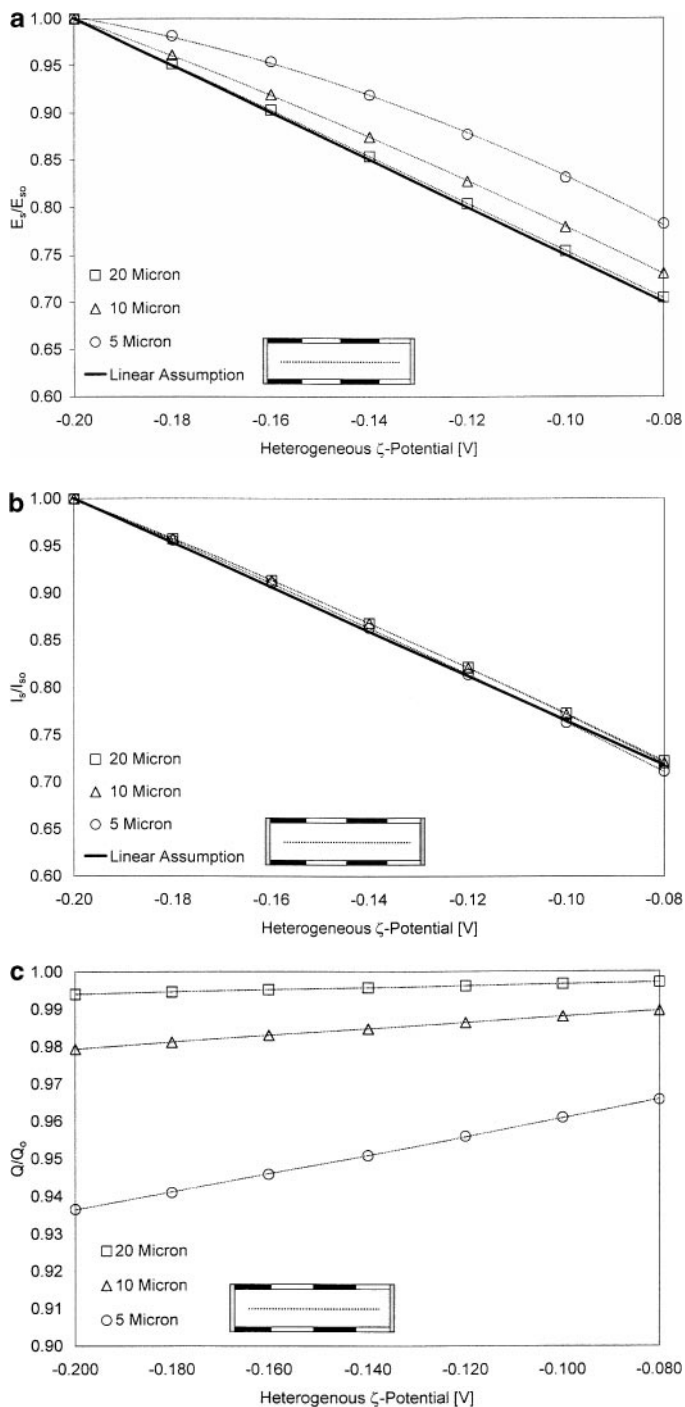


FIG. 6. Effect of the magnitude of the heterogeneous surface ζ -potential on the (a) streaming potential, (b) streaming current, and (c) volume flow rate (constant 50% strip-wise heterogeneous coverage, $\zeta_o = -0.2$ V, $n_o = 10^{-6}$ M KCl).

seen in Figs. 5a and 5c, revealed that the distribution of the heterogeneous coverage had a negligible effect on all of the parameters of interest. This suggests that, when no double layer overlap is present, the location of the inhomogeneity is inconsequential and only the percentage of heterogeneity matters.

3.2. Effect of $\Delta\zeta$

Figures 6a, 6b, and 6c consider the effects of the magnitude of the ζ -potential of the heterogeneity on the quantities of interest. As before a streaming solution of 10^{-6} M KCl and a surface of ζ -potential of -0.2 V were used. The ζ_h was varied from

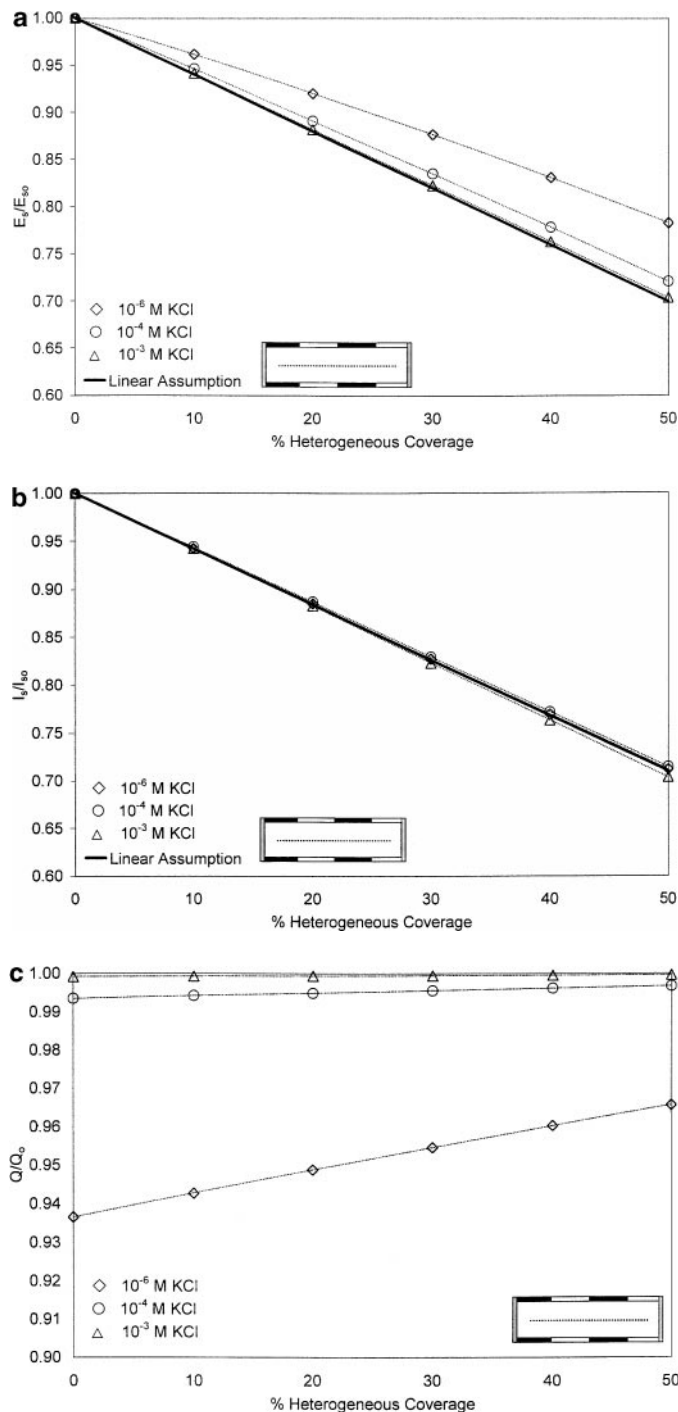


FIG. 7. Effect of bulk ionic concentration in a 5- μ m channel with a varying degree of heterogeneous coverage on the (a) streaming potential, (b) streaming current, and (c) volume flow rate ($\zeta_o = -0.2$ V and $\zeta_h = -0.08$ V).

−0.2 to −0.08 V at a constant 50% heterogeneous coverage in channels ranging in height from 5 to 20 μm .

Analogous to the previous section, the simulation predicts a linear change in E_s with ζ only for the larger channels. As the channel height is decreased, E_s begins to deviate significantly from the linear assumption due to the significance of the flow impedance shown in Fig. 6c. As a result, if $\Delta\zeta$ is known, Eq. [2a] will underestimate the value of Γ for small channels. As in the previous case the streaming current measurements show a perfectly linear relationship with changing ζ_h for all channel heights.

3.3. Effect of Bulk Ionic Concentration

Figures 7a, 7b, and 7c demonstrate the effects of bulk ionic concentration of the streaming solution on the quantities of interest. Four aqueous KCl solutions were examined, varying in concentration from 10^{-6} to 10^{-3} M. Results are presented for a 5- μm channel with a surface ζ -potential of −0.2 V and a ζ_h of −0.08 V varying in Γ from 0 to 50%.

Figures 7a and 7c show trends similar to those above, where the flow impedance is greater, such as in the case of the lower concentration solutions, where the streaming potential will always be higher than expected. Again failure to account for this will lead to a severe overestimation of Γ . When the concentration increases, the double-layer thickness decreases and the flow impedance becomes less significant. As a result the highest ionic concentration shows almost no deviation from the linear assumption. Figure 7b again shows that the streaming current simulations produced results very similar to the linear assumption.

4. CONCLUSIONS

A number of recent studies have used the streaming potential technique as a method of characterizing heterogeneous surfaces. In those works it was assumed that a linear relation exists between the change in the streaming potential and the percentage heterogeneous coverage. The purpose of this paper was to develop a model for the electrokinetic flow in channels with heterogeneous surface properties and to use this model to determine under what conditions the error associated with this linear assumption is significant.

The results have shown that, when the presence of the streaming potential causes significant flow impedance, a severe deviation from the linear assumption is observed and large errors are induced. In general this will lead to an overestimation of the degree of heterogeneity. Since there is no electrokinetic flow impedance associated with the streaming current measurements, the model predicts that I_s does not deviate significantly from the linear assumption. As such the streaming current method is preferred, especially when measurements are to be made in small channels with a streaming solution of low ionic concentration. In all cases results were nearly identical for symmetric and nonsymmetric heterogeneous patterns, suggesting that the distribution of the surface heterogeneity has very little effect on either E_s or I_s in cases where no double-layer overlap occurs.

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