Mass Transfer and Flow in Electrically Charged Micro- and Nanochannels

A. T. Conlisk* and Jennifer McFerran

Department of Mechanical Engineering, The Ohio State University, Columbus, Ohio 43210-1107

Zhi Zheng and Derek Hansford

Biomedical Engineering Program, The Ohio State University, Columbus, Ohio 43210-1107

In this work, the fluid flow and mass transfer due to the presence of an electric field in a rectangular channel is examined. We consider a mixture of water or another neutral solvent and a salt compound, such as sodium chloride, for which the ionic species are entirely dissociated. Results are produced for the case in which the channel height is much greater than the electric double layer (EDL) (microchannel) and for the case in which the channel height is of the order of the width of the EDL (nanochannel). Both symmetric and nonsymmetric velocity, potential, and mole fraction distributions are considered, unlike previous work on this problem. At small electrolyte concentrations, the Debye–Hückel picture of the electric double layer is recovered; at larger concentrations, the Gouy–Chapman picture of the electric double layer emerges naturally. The numerical results presented here agree with analytical solutions of a singular perturbation analysis, which is valid as the channel height increases. In the symmetric case for the electroosmotic flow so induced, the velocity field and the potential are similar. In the asymmetric case corresponding to different wall potentials, the velocity and potential can be vastly different. The fluid is assumed to behave as a continuum, and in the volume flow rate is observed to vary linearly with height, potential, and mole fraction distributions are considered, unlike previous work on this problem. At small electrolyte concentrations, the Debye–Hückel picture of the electric double layer is recovered; at larger concentrations, the Gouy–Chapman picture of the electric double layer emerges naturally. The numerical results presented here agree with analytical solutions of a singular perturbation analysis, which is valid as the channel height increases. In the symmetric case for the electroosmotic flow so induced, the velocity field and the potential are similar. In the asymmetric case corresponding to different wall potentials, the velocity and potential can be vastly different. The fluid is assumed to behave as a continuum, and in the volume flow rate is observed to vary linearly with height.

When the electrolyte mixture is not dissociated and when the region of flow is sufficiently large, the most common mass transfer balance is one between Fickian diffusion and convection. The case of a concentrated salt solution of undissociated components is an important problem in the analysis of the performance of an absorption heat pump. In the present case however, we consider not only the case of a small conduit, but also the presence of an electric field, which drives the motion of the fluid. Moreover, since the dimensions of the conduit are so small, inertial effects are negligible; replacing the mode of convection at small scales is the presence of an electric field, which is an efficient mode of transferring fluid from one place to another.

Problems of this type have been investigated for a long time. There are a number of textbooks on the subject of flow driven by the presence of an electric field among many others. The flow induced by electric fields is also an old subject, and in this paper, we consider the case of electroosmosis, which is defined as the motion of a fluid due to an externally applied electric field. In addition, it is shown that an electric field is generated in a direction transverse to the primary flow direction; in turn, a pressure gradient in the direction normal to the primary flow direction is set up.

The electroosmotic problem without flow for channel heights on the order of the electric double layer had been developed. There the solution for the potential is based on a Boltzmann distribution for the number concentration of the ions; the potential is calculated on the basis of a symmetry condition at the centerline. Qu and Li have recently produced solutions that do not require

* Corresponding author. E-mail: conlisk.1@osu.edu.

the Boltzmann distribution, but they also assume symmetry at the centerline; the results show significant differences from the results of Verwey and Overbeek. The results of Qu and Li are valid for low voltages, since the Debye-Huckel approximation is invoked.

The first work on the electroosmotic flow problem discussed here appears to have been done by Burgeen and Nakache, who considered channel heights of the order of the electric double layer thickness. They produced results for the velocity field and potential for two equally charged ions of valence \( z \); a Boltzmann distribution is assumed for the number of ions in solution. The convective terms in the velocity momentum equation are assumed to be negligible, and the solution for the velocity and potential is assumed to be symmetric about the centerline of the channel. Additional work of a similar nature for double layer thicknesses that are small as compared to the channel height has also appeared in the open literature.

In this paper, we examine the behavior of the flow in a rectangular channel of a mixture consisting of two monovalent ions plus an aqueous solvent; we consider a NaCl–H2O mixture under the action of an electric field in the primary direction of motion. In particular, we calculate the mole fractions of the ions and the potential and velocity numerically. Because of this fact, we need not assume symmetry; therefore, we consider both symmetric and asymmetric flow. Moreover, although we focus on a salt solution, the present theory can be applied to any combination of ionic constituents of arbitrary valences; all of the previous work described above requires that the ionic species be pairs of ions of equal and opposite valence. We consider the case of charged walls. In the case of a negatively charged wall, we expect a surplus of cations near the wall, but in the case of a positively charged wall, we would expect a surplus of anions.

The dominant physics of the mass transfer problem is located within the electric double layer (EDL) near the surfaces of the channel. The thickness of the EDL is estimated by

\[
\lambda = \frac{\sqrt{\varepsilon_e R T}}{F \left( \sum z_i c_i \right)^{1/2}}
\]

where \( F \) is Faraday’s constant, \( \varepsilon_e \) is the electrical permittivity of the medium, \( c_i \) is the concentrations of the electrolyte constituents, \( R \) is the gas constant, \( z_i \) is the valence of species \( i \), and \( T \) is the temperature.

Typically, the width of the electric double layer is on the order of 1–10 nm for a dilute mixture; therefore, if the channel height \( h \) is not too small, then \( \lambda / h \ll 1 \). In this case, the problem for the electric potential and the mole fraction of the ions is a singular perturbation problem, and the fluid away from the electric double layers is electrically neutral. We also consider the case for which \( \lambda / h \) is of the order of magnitude 1 (\( \lambda / h = O(1) \)), in which case the channel height is of the order of the EDL thickness. In this case, electroneutrality need not be preserved anywhere in the channel. The geometry is depicted in Figure 1. We assume that the temperature is constant and that the ionic components of the mixture are dilute.

The plan of the paper is as follows: In the next section, the governing equations are derived; the flow field, the electric field...
and the mass transfer problems are fully coupled. Additionally, in particular, if the mixture is dilute, the mass transfer equations reduce to the Poisson–Nernst–Planck equations for the ion mole fractions. We then present some results for several different channel heights and for different wall mole fraction distributions. In the following section, we solve the equations both for the case of a double layer that is much thinner than the channel height and for λ/h = O(1) and calculate the volume flow rate through the channel.

GOVERNING EQUATIONS

Let us now consider the mass transport in a liquid mixture of three components flowing in the channel depicted in Figure 1. We have in mind the mixture consisting of water and a salt, such as sodium chloride. We consider the case for which the salt is dissociated so that the mixture consists of positively and negatively charged ions, say Na⁺ and Cl⁻. The driving forces for mass transfer are assumed to be ordinary Fick diffusion, pressure diffusion, and migration due to the presence of an electric field. The electric field in general can be composed of two components: an externally imposed electric field, E₀, and a local electric field present near the solid surfaces of the channel corresponding to the presence of an electric double layer. In dimensional form, the molar flux of species A for a dilute mixture is a vector given by:

\[ \mathbf{J}_A = -c D_{AB} \nabla X_A - \frac{D_{AB} M_A}{RT} X_A(1 - X_A) \nabla p + u_A z_A F X_A \bar{E}^* + c_{X_A^*} \bar{u}^* \]  

(2)

Here, D_{AB} is the diffusion coefficient; c is the total concentration; X_A is the mole fraction of species A, which can be either the anion or the cation; p is the pressure; M_A is the molecular weight; R is the gas constant; T is the temperature; u_A is the mobility; z_A is the valence; F is Faraday’s constant; \bar{E}^* is the total electric field; and \bar{u}^* is the mass average velocity of the fluid. The mobility u_A is defined by the Nernst–Planck equation as

\[ u_A = \frac{D_{AB}}{RT} \]

The mass transport equation for steady state is then

\[ \nabla \cdot \mathbf{J}_A = 0 \]  

(3)

In the present paper, we focus on the migration of ions due to the electric field. As a result, we consider only the case in which the externally imposed pressure gradient vanishes. In nondimensional form, the equation becomes

\[ \frac{\partial^2 X_A}{\partial y^2} + \epsilon_1 \frac{\partial^2 X_A}{\partial x^2} + \epsilon_2 \frac{\partial^2 X_A}{\partial z^2} = \text{ReSc} \left( \epsilon_1 u_A \frac{\partial X_A}{\partial x} + \epsilon_2 u_A \frac{\partial X_A}{\partial z} \right) + \left( \alpha_x \epsilon_1 \frac{\partial X_A}{\partial x} + \alpha_y \epsilon_2 \frac{\partial X_A}{\partial y} + \alpha_z \epsilon_2 \frac{\partial X_A}{\partial z} \right) \]  

(4)

Here, we note that \( \alpha_i \) are scale factors for the potential field; for the configuration of interest,

\[ \alpha_x = \frac{hE_{0z}F}{RT} \]

\[ \alpha_y = \frac{\phi_y z_A F}{RT} \]

\[ \alpha_z = \frac{\phi_z z_A F}{RT} \]

and we have assumed that the fluid and transport properties are constants. The externally imposed electric field, E₀, is constant in the x direction, whereas variations in the potential in the y and z directions are permitted. The coordinates (x, y, z) are nondimensional; for example, x = x/\( x_0 \), and the scaling lengths in the three directions are (L, h, W), as depicted in Figure 1. In addition, (u, v, w) are the dimensionless velocities in each of the coordinate directions (x, y, z); for example u = u*/\( U_0 \), where u* is dimensional. Here, \( \epsilon_1 = h/L \) and \( \epsilon_2 = h/W \). We assume h ≪ W, L so that both \( \epsilon_1 \) and \( \epsilon_2 \) are small. \( \text{Re} = U_0 h/\nu \) is the Reynolds number and \( \text{Sc} = \nu/\text{Da}_B \) is the Schmidt number, where \( \nu \) is the kinematic viscosity. The valence z_A is 1 for the positive ion and z_A = −1 for the negative ion, although generalization to arbitrary valence is obvious. The determination of the velocity scale \( U_0 \) will be discussed below.

The mass transfer equation is subject to boundary conditions at a solid surface. Consider the wall at y = 0. Then if A refers to either of the ion distributions, it follows that we can specify the ion concentration or the flux at the surface. For the case of specified mole fraction,

\[ X_A = X^0 \quad y = 0 \]

and

\[ X_A = X^1 \quad y = 1 \]

where \( X^0 \) is the mole fraction at y = 0 and \( X^1 \) is the mole fraction at y = 1. Similar boundary conditions will hold at z = 0 and z = 1. We defer comment on the boundary conditions in x, the flow direction.

The mass transfer equation must be supplemented by an equation for the electric field. The electric field \( \bar{E}^* \) in the steady flow case must satisfy Maxwell’s equations in the form

\[ \nabla \times \bar{E}^* = 0 \]  

(5)

which along with the Poisson equation given by

\[ \nabla^2 \psi = \frac{\rho}{\epsilon_0} \]

(6)

\[ \text{Re} \frac{\partial \psi}{\partial z} = \frac{\epsilon_1 \epsilon_2}{\epsilon_0} \frac{\partial^2 \psi}{\partial x^2} + \frac{\epsilon_1 \epsilon_2}{\epsilon_0} \frac{\partial^2 \psi}{\partial z^2} \]  

(7)

\[ \psi = \frac{\epsilon_0}{\epsilon_1 \epsilon_2} \frac{\epsilon_0 \phi_y z_A F}{\alpha_y} \frac{\partial X_A}{\partial y} + \frac{\epsilon_0}{\epsilon_1 \epsilon_2} \frac{\epsilon_0 \phi_z z_A F}{\alpha_z} \frac{\partial X_A}{\partial z} \]  

(8)

\[ \frac{\epsilon_0}{\epsilon_1 \epsilon_2} \frac{\epsilon_0 \phi_y z_A F}{\alpha_y} \frac{\partial X_A}{\partial y} + \frac{\epsilon_0}{\epsilon_1 \epsilon_2} \frac{\epsilon_0 \phi_z z_A F}{\alpha_z} \frac{\partial X_A}{\partial z} \]

where we have assumed that \( \epsilon_1 \) and \( \epsilon_2 \) are small and \( \epsilon_1 \) and \( \epsilon_2 \) are large.
\[ \nabla \cdot (\varepsilon \vec{E}) = -\nabla \cdot \rho \quad (6) \]

determines the potential. Here, \( \rho \) is the charge density per unit volume, \( \varepsilon \) is the permittivity, and the * denotes a dimensional quantity. The charge density is defined by

\[ \rho = -F \sum_i z_i c_i = -F \sum_i z_i X_i \quad (7) \]

where \( c_i \) is the molar concentration of species \( i \), and \( c \) is the total molar concentration and is assumed constant.

Most often in these problems, the channel is connected to large baths upstream and downstream. In this case, the electric field in both baths and the channel should be calculated. This is a formidable task. To simplify the problem, we have assumed the electrodes are placed at the inlet and outlet of the channel. To further simplify the problem we have assumed that the \( x \) component of the electric field is constant. This means that the dimensional potential is of the form

\[ \phi^* = -y^* x^* + \phi^* \quad (y^*, z^*) \]

where it is seen that \( \phi^* \) is the perturbation potential, and \( y^* \) is a constant. This form of the potential is consistent with the situation within the channel for a liquid, assuming a uniform dielectric constant across the channel. Note that a variable dielectric constant could be easily incorporated into our analysis as a function of \( y^* \) to accommodate changes in concentration and temperature.

Nondimensionalizing the equation for the potential as above and assuming \( \phi_0 = \phi_0 \), \( \phi = \phi^*/\phi_0 \)

\[ \frac{\partial^2 \phi}{\partial y^2} + \frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial z^2} = -\frac{F c h^2}{\varepsilon \phi_0} (X^+ - X^-) \]

where \( \phi \) is the dimensionless perturbation potential and we have assumed a pair of oppositely charged ions. In addition, we have written \( X^+ = X_A \) and \( X^- = X_B \).

Since only differences in potential are important in this analysis, we can specify the potential boundary conditions as

\[ \phi = 0 \quad y = 0 \]

and

\[ \phi = \phi^* \quad y = 1 \]

The velocity field is coupled to the mass transfer equations and the equation for the potential. The governing equations of fluid flow express conservation of linear momentum along with the continuity equation, which expresses conservation of mass.

Conservation of mass requires

\[ \varepsilon_1 \frac{\partial u}{\partial x} + \varepsilon_1 \frac{\partial v}{\partial y} + \varepsilon_2 \frac{\partial w}{\partial z} = 0 \quad (9) \]

The x direction is the primary direction of flow. Here it is noted that the velocity \( v \) is small and of \( O(\max(x_1, x_2)) \). We assume that the flow may be driven by an electrical body force oriented in the \( x \) direction. The three momentum equations for an incompressible, steady flow, in dimensionless form, are

\[ \text{Re} \left( \varepsilon_1 \frac{\partial u}{\partial x} + \varepsilon_2 \frac{\partial v}{\partial y} + \varepsilon_2 \frac{\partial w}{\partial z} \right) = \frac{F c \varepsilon_1}{\mu U_0} (X^+ - X^-) + \nabla^2 u \quad (10) \]

\[ \text{Re} \left( \varepsilon_2 \frac{\partial v}{\partial y} + \varepsilon_2 \frac{\partial w}{\partial z} \right) = -\frac{\partial p}{\partial y} + \frac{F c \varepsilon_1}{\mu U_0} (X^+ - X^-) + \nabla^2 v \quad (11) \]

\[ \text{Re} \left( \varepsilon_2 \frac{\partial w}{\partial z} \right) = -\frac{\partial p}{\partial z} + \frac{F c \varepsilon_1}{\mu U_0} (X^+ - X^-) + \nabla^2 w \quad (12) \]

where \( \text{Re} \) is the Reynolds number

\[ \text{Re} = \frac{\rho U h}{\mu} \]

and \( U_0 \) is the velocity scale. These equations are the classical Navier–Stokes equations for constant density and viscosity that govern fluid flow of Newtonian liquids in a continuum. Here \( p = p^*/[\mu U_0 h] \) is the dimensionless pressure and

\[ \nabla^2 = \frac{\partial^2}{\partial y^2} + \varepsilon_1 \frac{\partial^2}{\partial x^2} + \varepsilon_2 \frac{\partial^2}{\partial z^2} \]

Note that these equations are highly nonlinear and are coupled equations. The Navier–Stokes equations are rarely solved in the form shown here, since the equations are fully three-dimensional, highly nonlinear and coupled. Thus, approximations need to be made, and these are described in the next section.

**ELECTRIC-FIELD-DRIVEN FLOW AND MASS TRANSFER IN A LONG, SLENDER CHANNEL**

Since the channel is long and narrow (\( h \ll W, L \)) and we wish to consider the EDL thickness \( \lambda \sim h \), it is evident that the variation of the variables in the \( y \) direction will be dominant. The mixture is a three-component mixture containing the ionic species plus the solvent water. Because the mole fractions sum to 1, it is sufficient to consider only the equations governing the ionic species.

Now, the potential scale is defined by taking \( \alpha = \alpha_0 = 1 \), which means that the potential scale, \( \phi_0 \), is \( RT/F \). Substituting for \( F \varepsilon c \) in eq 8, we have

\[ \varepsilon_1 \frac{\partial^2 \phi}{\partial y^2} + \varepsilon_1 \frac{\partial^2 \phi}{\partial x^2} + \varepsilon_2 \frac{\partial^2 \phi}{\partial z^2} = -\beta (X^+ - X^-) \quad (13) \]

where now \( \varepsilon_1 = \lambda / L \) and \( \varepsilon_2 = \lambda / W \) and
\[ \beta = 1 + \frac{c_3}{c} \]

where \( c_3 \) is the concentration of the solvent, \( \epsilon \) is \( \lambda / h \), and \( c \) is the ionic strength. For very wide channels, \( \epsilon \gg \epsilon_1, \epsilon_2 \); in addition, it is important to note that there will be boundary layers near the entrance and the exit of the channel and near the side walls where all of the independent variables vary rapidly. However, these regions are small, and in particular, for very wide channels, the influence of the side wall boundary layers will be negligible.

The inertial terms in the mass transfer equations are of the order of \( \epsilon \Re \text{Sc} \), and the value of \( \epsilon_2 \) is \( \sim 0.03 \). At most, the magnitude of the inertial terms is \( \sim 10^{-2} \) (\( \Re \sim 10^{-3} \) or smaller), and the governing equations become, to leading order,

\[
\frac{a}{\partial y} \left( \frac{\partial X_+}{\partial y} + \alpha X_+ \frac{\partial \phi}{\partial y} \right) = 0 \quad (14)
\]

\[
\frac{a}{\partial y} \left( \frac{\partial X_-}{\partial y} - \alpha X_- \frac{\partial \phi}{\partial y} \right) = 0 \quad (15)
\]

\[
e^{2} \frac{\partial^2 \phi}{\partial y^2} = -\beta (X_+ - X_-) \quad (16)
\]

and

\[
e^{2} \frac{\partial^2 u}{\partial y^2} = -\beta e \epsilon_{0} \frac{RT}{\mu U_0} (X_+ - X_-) \quad (17)
\]

Here, \( E_0 \) is the driving electric field in the \( x \) direction and will be specified so that the dimensionless electric field \( E_z = 1 \), as discussed previously. Equations 14–17 are four equations in four unknowns for the mole fractions of the ions, the potential, and the fluid velocity. It should be pointed out that a set of equations similar to those given above apart from the fluid flow equations also describe the physical processes that take place in semiconductor devices \(^{20} \) and in the collisionless Boltzmann equation or Vlasov equation, which describes the behavior of a highly ionized gas \(^{21,22} \).

Equation 17 then sets the velocity scale as

\[ U_0 = \frac{e \epsilon E \phi_0}{\mu} \]

which is recognized as the electroosmotic velocity. Note that the equations for the velocity and potential are the same, and if the boundary conditions are the same, the velocity and the potential are said to be similar.\(^ {14,15} \) Moreover, we do not require streamwise and spanwise variations in the dependent variables to vanish, only that these variations be much smaller than those in the \( y \) direction. In this case, the velocity, \( v \ll u \) nominally, and in fact, since \( v = 0 \) at \( y = 0, 1 \), in the present problem, \( v = 0 \). A similar comment applies to the \( w \) velocity, therefore, the flow field is one-dimensional. In addition, note that to leading order, we do not need boundary conditions in the \( x \) direction. In addition, from the governing equations, there is a pressure gradient in the \( y \) direction that is proportional to the potential gradient in the \( y \) direction.

For clarity and completeness, we repeat the boundary conditions for the simplified problem (with \( X_+ = g \) and \( X_- = f \)) as

\[
\phi = 0 \text{ at } y = 0 \quad (18)
\]

\[
\phi = \phi^1 \text{ at } y = 1 \quad (19)
\]

\[
f = f^0 \text{ at } y = 0 \quad (20)
\]

\[
f = f^1 \text{ at } y = 1 \quad (21)
\]

\[
g = g^0 \text{ at } y = 0 \quad (22)
\]

\[
g = g^1 \text{ at } y = 1 \quad (23)
\]

\[
u = 0 \text{ at } y = 0, \text{ and } y = 1 \quad (24)
\]

The last equation is the no-slip condition for the velocity.

**SINGULAR PERTURBATION ANALYSIS FOR \( \epsilon \ll 1 \)**

Equations 16 and 17 suggest clearly the nature of the solution as a function of \( \epsilon \). For \( \epsilon \ll 1 \), eqs 16 and 17 reduce to

\[ g - f = 0 \]

As a result, the core region away from the walls the fluid is electrically neutral. Near the walls, the velocity and potential vary rapidly. As a result, we define the new variable appropriate in the region near \( y = 0 \) to be \( Y = y + \epsilon \), and for example, eq 17 becomes

\[ \frac{\partial^2 u}{\partial Y^2} = -\beta (g - f) \]

This is expected to be the situation in the case of a microchannel. On the other hand, when \( \epsilon = O(1) \), the fluid is nowhere electrically neutral and the whole problem must be solved in the entire domain \( 0 \leq y \leq 1 \). This is the case for a nanochannel.

Independent of the value of \( \epsilon \), one integration of eqs 14 and 15 shows that

\[
f = f^0 e^{-\phi} - \phi(0) \quad (25)
\]

\[
g = g^0 e^{-\phi} + \phi(0) \quad (26)
\]

Note that the functional form of eqs 25 and 26 are valid both inside and outside the electric double layer. For \( \epsilon \ll 1 \) far outside the double layer, we set \( \epsilon \) equal to 0 and we have

\[
f_o = g_o \quad (27)
\]

where the subscript 0 denotes the outer solution outside the double layers. Thus, the core flow is electrically neutral to leading order. It will be seen that for \( \epsilon = O(1) \), this is not the case.
Adding and subtracting eqs 14 and 15, we find that \( f \) and \( g \) can be at most linear in the outer region, and the result for the mole fraction and the potential is

\[ f_0 = g_0 = Ay + B \]  

(28)

To illustrate the wide variety of solutions, it is sufficient to consider the case where \( A = 0 \).

\[ \phi_0 = C \int_y^1 \frac{dy}{g_0} + D \]  

(29)

Now the dimensionless velocity in the outer region satisfies

\[ u_0 = \phi_0 + E y + F \]  

(30)

and in the inner region near \( y = 1 \), for example,

\[ u_i = \phi_i + G \]  

(31)

Near \( y = 0 \), we have

\[ u_i = \phi_i + K \]  

(32)

The unknown constants are obtained by matching the inner and the outer solutions. For example, near \( y = 0 \),

\[ \lim_{y \to 0} H_i = \lim_{y \to 0} H_0 \]  

(33)

where the function \( H_i \) denotes the inner distribution of any of \( f, g, \phi, u \). A similar equation holds at \( y = 1 \). The constants are easily found and

\[ B = \sqrt{g_0^{f0}} = \sqrt{g_0^{f1}} \]

\[ C = (\phi^0 - \phi^1 + \frac{1}{2} (\ln g^0 - \ln g^1)) \sqrt{g_0^{f0}} \]

\[ D = \phi^1 + \frac{1}{2} \ln (\frac{g^0}{g^1}) \]

\[ E = \phi^0 - \phi^1 \]

\[ F = -\phi^0 \]

and \( K = F \) and \( G = E + F \). It turns out that \( A = \sqrt{g_0^{f1}} - \sqrt{g_0^{f0}} \equiv 0 \) for the assumed mole fractions at the boundaries. The solution can now be obtained, once eq 29 is integrated and

\[ \phi_0 = \frac{C}{B} (1 - y) + D \]  

(34)

For the mole fractions and potentials considered here, \( C \) is very small; therefore, \( \phi_0 \sim D \).

Now consider the inner solution within the electric double layer. Substituting expressions 25 and 26 in the potential equation (eq 16) we can integrate once, but it is just as easy to calculate the solution numerically; the numerical methods used are discussed in the next section. However, much information may be obtained without performing the integration explicitly. The uniformly valid solution for the velocity is given by

\[ u_{uv} = u^0_v + (\phi^0 - \phi^1) y + u^1_v \]  

(35)

where \( u^0_v \) is the inner solution near \( y = 0 \), for example. Note that near \( y = 0, u_{uv} = \phi^0 (\phi^0 = 0) \) and \( u_{uv} = \phi^1 - \phi^1 \) near \( y = 1 \), where \( \phi^0 \) is the inner solution for the potential near \( y = 0 \). Both of these characteristics are confirmed in the numerical solutions given below.

In particular, for the symmetric case \( \phi^0 = \phi^1 \), the dimensionless velocity and potential are given by

\[ u_0 = \phi_0 = \frac{1}{2} (\ln (\frac{g^0}{f^0})) \]  

(36)

\[ f_0 = \sqrt{g_0^{f0}} = g_0 \]  

(37)

Note that both positive and negative velocities may occur, on the basis of the relative values of the mole fractions \( f^0 \) and \( g^0 \).

RESULTS

Numerical Methods. For both the symmetric and the asymmetric case, we use second-order central differences to approximate the derivatives in the governing equations and to solve each set of difference equations by the Thomas algorithm. The equations are nonlinear and coupled so that the solution procedure requires iteration. The program is very short and requires less than 20 iterations to converge for smaller values of the channel height \( h \). The iteration procedure is said to converge if

\[ \left| \frac{g_{\text{new}} - g_{\text{old}}}{g_{\text{new}}} \right| < \delta \]

at all grid points where \( \delta = 10^{-4} \). For larger values of the channel height, \( \delta = 10^{-5} \) was used. In general, four-digit accuracy was achieved in solutions for 81 and 161 points across the channel in all of the variables for all of the runs made. For \( h = 24 \text{ nm} \), four-digit accuracy was achieved for 161 and 321 points across the channel. Because central difference formulas are used, the accuracy increases quadratically, and the grid spacing is decreased. For channel heights above 24 nm, a separate program was written to solve for the velocity, ion mole fraction and the potential inside the electric double layer on the basis of the singular perturbation analysis discussed above with, for example, in the symmetric case, eqs 36 and 37 as boundary conditions. It should be noted that the analysis presented here is valid up to and including the entire microchannel regime.

We assume the solvent is water at a temperature \( T = 300^\circ \text{K} \). The pressure gradient along the channel vanishes, and the magnitude of the externally imposed potential is 6 V applied over a length of 3.5 \( \mu \text{m} \). The dielectric constant of the medium has been taken to be that of water, 78.54. We assume two monovalent ions.

\[ (23) \text{Kevorkian, J.; Cole, J. D. Multiple Scale and Singular Perturbation Methods, Springer, New York, 1996.} \]
ions, say Na$^+$ and Cl$^-$, although this assumption is not necessary and it is easy to extend the numerical calculations to mixtures of arbitrary valence, as discussed earlier. The baseline mixture wall mole fractions correspond to a concentration of Na equal to 0.154 M; Cl, 0.141 M; and water, 55.6 M for which $\lambda$ is 190. Results are also produced for other concentrations, as noted. The width of the channel is assumed to be 3 $\mu$m. The primary variable is the volume flow rate, and when the EDLs are thin, the flow rate is given to leading order

$$Q_e = u_0 U_0 h W$$  \hspace{1cm} (38)

Here we see that the flow rate is proportional to $h$, and not $h^3$, as for pressure-driven flow for which the volume flow rate is

$$Q_p = \frac{W h^3}{12 \mu L} \Delta p$$  \hspace{1cm} (39)

where $\Delta p$ is the pressure drop.

**The Symmetric Case.** Figure 3 shows results for $h = 1$ nm. Note that the mole fractions are almost constant and that the velocity and potential are similar; that is, they have the same distribution. For this case, $\epsilon \sim 0.8$, and the core is not electrically neutral. The volume flow rate is $Q = 2.8 \times 10^{-14}$ L/min. Figure 4 illustrates the case of $h = 4$ nm. In this case, we find the EDL thickness is about 0.8 nm; therefore, $\epsilon \sim 0.2$. Figure 4a shows the velocity and potential. Figure 4b shows the mole fractions, and again, electrical neutrality is not preserved in the core. The total flow rate is $Q = 5.9 \times 10^{-13}$ bL/min for this case.

Figure 5 shows the results for $h = 24$ nm; here, $\epsilon \sim 0.03$. Note the plug flow nature of the velocity; this is the classical electroosmotic velocity, as depicted in textbooks. Figure 5b shows the mole fractions; note that electrical neutrality is preserved over the entire core of the channel. In this case, the flow rate is about $Q = 5.7 \times 10^{-12}$ L/min, and the velocity in the core region has reached the value of 0.0439, which is close to the singular perturbation solution of 0.0441. It is rather surprising that the plug flow nature of the

---

**Figure 3.** Results for the dimensionless velocity and potential along with mole fractions for the symmetric case of a NaCl–water mixture. Here, the electric field corresponds to 6 V over a channel of length $L = 3.5 \mu$m; the channel height, $h$, is 1 nm. (a) Velocity and potential. (b) Mole fractions for $f_0 = f_1 = 0.00252$ and $g_0 = g_1 = 0.00276$.

**Figure 4.** Results for the dimensionless velocity and potential along with mole fractions for the symmetric case of a NaCl–water mixture. Here, the electric field corresponds to 6 V over a channel of length $L = 3.5 \mu$m; the channel height, $h$, is 4 nm. (a) Velocity and potential. (b) Mole fractions for $f_0 = f_1 = 0.00252$ and $g_0 = g_1 = 0.00276$. 
velocity profile emerges at such a small value of the channel height; this situation will change as the concentrations of the electrolytes change. Indeed, overlapped double layers can occur at much higher channel heights for smaller concentrations.

Results for $h = 100$ nm are depicted in Figure 6. In both of these figures only the flow in the EDL is depicted. Note that the velocity approaches a constant in the core of the channel given by the value in eq 36. Also plotted in Figure 6b is the analytical solution for the mole fractions as given in eqs 25 and 26; the numerical results and the analytical results are virtually indistinguishable. Moreover, the constant bulk velocity for this case is essentially the same as that for $h = 24$ nm, and the Debye-Huckel picture of the electric double layer is recovered. The flow rate for this case is $Q = 2.4 \times 10^{-11}$ L/min. It should be noted that Figure 6a is similar to the sketch presented on page 81 of Newman, and in Figure 2.7 of Hunter.

For all of the cases presented so far, the Debye-Huckel picture of the EDL is approximately recovered, although the Debye-Huckel approximation is not invoked. That is, the mole fraction distributions of the cations and the anions are symmetric about a mean value. For example, note the results of Figure 5b. If the concentration of sodium is significantly increased, the Gouy-Chapman model emerges. Figure 7 illustrates the results for a 0.308 M concentration of Na with the Cl concentration the same as before. The result depicted in Figure 7b is also sketched in Hunter. The flowrate in Figure 7 is $4.83 \times 10^{-11}$ L/min.

The behavior of the flow rate as the difference $g^0 - f^0$ increases is depicted in Table 1. Here, $f^0 = 0.0025$, and it is fixed. Note the linear behavior of the flow rate, as should be the case.

The Asymmetric Case. In the asymmetric case, the wall mole fractions at $y = 0$ do not equal those values at $y = 1$. This could be the case for when two streams of different compositions are mixed or for channels with unequal surface potentials. A major strength of the numerical model is the ability to consider this situation, and results are shown in the next few figures. The relationship between the wall mole fractions and the potential drop in the $y$ direction is established by setting the electrochemical potentials at $y = 0, 1$ to be equal. This condition is automatically satisfied in the symmetrical case. The potential is then scaled to be 0 at the wall $y = 0$. In these cases, the potential field and the
velocity are no longer similar, as a result of the symmetrical assumption of zero velocity at both walls.

Figures 8, 9, and 10 show the concentration, velocity, and potential profiles across channels of different heights, corresponding to both walls having different but negative surface potentials. The mole fractions in Figures 8, 9, and 10 correspond to concentrations of Na equal to 0.308 M and of Cl equal to 0.141 M at $y = 0$ with the value of the concentration of Na at $y = 1$ equal to 0.8 of the value at $y = 0$. The Cl concentration at $y = 1$ is dictated, then, by the condition of equal electrochemical potentials for each species at $y = 0, 1$. Figure 8 shows the values for $h = 1$ nm. As in the symmetrical case, the variation of the mole fractions across the channel is mild, and the potential is nearly linear. For $h = 4$ nm, the core is still not electrically neutral (Figure 9), but at $h = 24$ nm, electroneutrality is preserved, as shown in Figure 10. Note that the solutions for dimensionless velocity and potential are the same near $y = 0$ and are a constant apart near $y = 1$, as predicted by the singular perturbation analysis. For this case, the constant $C$ is very small. Note that the numerical and outer solutions for the potential and velocity agree very well. The numerical value of $\phi_0$ is $\sim 0.3907$, which is seen to be close to the numerical value of 0.3905. In addition, the slope of the velocity in the core from the perturbation analysis is $\partial u_d / \partial y = -0.2238$, but a direct numerical calculation yields $\partial u_d / \partial y = -0.2235$. Clearly, the singular perturbation solutions are predicted by the numerical solutions. The flow rates for the profiles in Figures 8–10 are $Q = \ldots$

### Table 1. Flow Rate and EDL Thickness as $g^0$ Is Varied

<table>
<thead>
<tr>
<th>$g^0$</th>
<th>molar</th>
<th>$\lambda$ (m)</th>
<th>flow rate (L/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0026</td>
<td>0.145</td>
<td>$8.07 \times 10^{-10}$</td>
<td>$1.70 \times 10^{-13}$</td>
</tr>
<tr>
<td>0.0027</td>
<td>0.150</td>
<td>$8.00 \times 10^{-10}$</td>
<td>$3.82 \times 10^{-12}$</td>
</tr>
<tr>
<td>0.0028</td>
<td>0.155</td>
<td>$7.93 \times 10^{-10}$</td>
<td>$5.85 \times 10^{-12}$</td>
</tr>
<tr>
<td>0.0029</td>
<td>0.160</td>
<td>$7.86 \times 10^{-10}$</td>
<td>$7.81 \times 10^{-12}$</td>
</tr>
<tr>
<td>0.0030</td>
<td>0.165</td>
<td>$7.79 \times 10^{-10}$</td>
<td>$9.71 \times 10^{-12}$</td>
</tr>
<tr>
<td>0.0031</td>
<td>0.175</td>
<td>$7.67 \times 10^{-10}$</td>
<td>$1.34 \times 10^{-11}$</td>
</tr>
<tr>
<td>0.0032</td>
<td>0.180</td>
<td>$7.61 \times 10^{-10}$</td>
<td>$1.51 \times 10^{-11}$</td>
</tr>
</tbody>
</table>

*Here, $f^0 = 0.0025$ and is fixed.*

---

Figure 7. Results for the dimensionless velocity and potential along with mole fractions in the electric double layer near the wall at $y = 0$ for the symmetric case of a NaCl–water mixture. Here, the electric field corresponds to 6 V over a channel of length $L = 3.5 \mu$m; the channel height, $h$, is 24 nm. (a) Velocity and potential. (b) Mole fractions for $f^0 = 0.00252$ and $g^0 = 0.00550$. The Gouy–Chapman model for the EDL emerges naturally.

Figure 8. Results for the dimensionless velocity and potential along with mole fractions for the asymmetric case of a NaCl–water mixture. Here, the electric field corresponds to 6 V over a channel of length $L = 3.5 \mu$m; the channel height, $h$, is 1 nm. (a) Velocity and potential. (b) Mole fractions for $f^0 = 0.00252$, $f^1 = 0.00314$, $g^0 = 0.00550$, and $g^1 = 0.00440$.
2.4 × 10^{-13} \ L/min, 4.1 × 10^{-12} \ L/min, and 3.4 × 10^{-11} \ L/min, respectively.

Figures 11 and 12 demonstrate the concentration, velocity, and potential profiles across channels of different heights and oppositely charged surfaces. That is, y = 0 corresponds to a negatively charged surface and y = 1 corresponds to a positively charged surface. Accordingly, the ionic wall mole concentrations show an increase in the counterion for each surface, leading to increased concentrations of opposing ions at the opposite walls. For these simulations, the same mole fractions were used at y = 0 as in Figures 8–10, with the Na concentration at y = 1 equal to 0.5 that of the concentration at y = 0. Again, the Cl concentration at y = 1 is dictated by the condition of equal electrochemical potentials. Figure 11 presents results for a channel of h = 4 nm. Note that within the channel, there is flow in opposing directions as a result of competing electroosmotic effects at the two surfaces. This gives the considerably lower flow rate of Q = 6.5 × 10^{-13} \ L/min. Figure 12 presents the results for a channel with h = 24 nm; note again that flow in both directions is present within the channel, and the flow rate is Q = 5.06 × 10^{-12} \ L/min. Again, the outer solution corresponding to the singular perturbation solutions agree very well with the numerical solutions for the velocity and potential, although the mole fractions vary slightly in the core, possibly indicating the limit of the validity of the numerical approach with height.

Figures 8–12 represent the power of the present model to evaluate concentration, velocity, and potential profiles across a channel with arbitrary solid surface conditions and species concentrations. This allows the model to accurately demonstrate the profiles that can be expected in nonideal nanochannels with different channel surface conditions within a tightly confined space.

Comparison with Experiment. We have received experimental data from iMEDD, Inc. and have compared the experimental results with our numerical computations. The results are depicted in Table 2. The solution is phosphate buffered saline (PBS) at concentrations of Na and Cl 10 times less than concentrations considered in Figure 3. The flow is assumed to
be symmetric about the center line, and the wall mole fractions are calculated from a Donnan equilibrium analysis. The agreement is fairly good, and we are continuing to compare with other data sets as they become available.

**SUMMARY**

In this work, we have developed a model for electric-field-driven flow in micro- and nanochannels. The model consists of a system of partial differential equations that govern the velocity field, potential, and mole fractions of the ionic species in a dilute aqueous solution and corresponds to classical electroosmotic flow discussed in textbooks. The primary difference between this work and classical analyses and others is that numerical solution of the governing equations allows asymmetry of the flow, potential, and mole fractions (Figures 8–12), and the Debye–Huckel approximation is not invoked. In addition, the present model is valid from channels of height on the nanometer scale up through channels that have heights on the micrometer scale. Moreover, the Gouy–Chapman picture of the EDL emerges naturally at higher cation–anion concentration differences. In addition, the numerical results reduce to the singular perturbation results as the height of the channel gets larger.

It is useful to note that all previous work on this problem has assumed that there is a single anion and a single cation of given

---

**Table 2. Experimental Flow Rate Data Compared with the Calculated Values**

<table>
<thead>
<tr>
<th>height (nm)</th>
<th>VD</th>
<th>Q&lt;sub&gt;expt&lt;/sub&gt;</th>
<th>Q&lt;sub&gt;calc&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>0.105</td>
<td>0.48</td>
<td>0.36</td>
</tr>
<tr>
<td>13</td>
<td>0.105</td>
<td>0.81</td>
<td>0.74</td>
</tr>
<tr>
<td>20</td>
<td>0.028</td>
<td>0.77</td>
<td>0.87</td>
</tr>
</tbody>
</table>

The experimental data is from iMEDD, Inc. of Columbus, Ohio, and is used with permission. VD is the voltage drop calculated by iMEDD, and the fluid is phosphate buffered saline (PBS) at concentrations of Na and Cl 10 times less than concentrations considered in this paper. The flow is assumed to be symmetric about the center line and the wall mole fractions are calculated from a Donnan equilibrium analysis.
equal and opposite valences; the present work contains no such restrictions, and we are presently considering more complex mixtures with components of arbitrary valence. Furthermore, the coupling of the ion-induced potential field with the flow and mass transfer of ions generates a finite pressure gradient normal to the walls of the channel (eq 11).

The main results of this paper are that, depending on the relative magnitude of the mole fractions at the walls of the channel, both forward and reversed flow may occur, and the volume flow rate is observed to vary linearly with channel height for electrically driven flow, in contrast to pressure-driven flow, which varies as height cubed. Moreover, useful volume flow rates may be obtained at a very low driving voltage. For the voltages used in the present calculations, for $h = 10$ nm, it would require a pressure drop of over 8 atm, but for $h = 100$ nm, a pressure drop of about 0.08 atm is required. Clearly, this is an important consideration in nanoscale fluid mechanics.

In addition, it is observed that beyond a value of the channel height of about 20–25 nm, the bulk velocity is constant (Figures 5 and 6) and corresponds to the classical electroosmotic profile for the given values of wall mole fraction. Of course, the precise channel height where the electroosmotic profile emerges depends on the mole fraction.

It is useful to note that the present model is a continuum and does give good agreement with experimental data, as shown in Table 2; the results of additional comparisons will be reported in a separate paper. The continuum assumption is justified by the success of similar analysis of natural nanochannels\textsuperscript{17}–\textsuperscript{19} although plans are underway to compare the present continuum results with molecular simulations.

ACKNOWLEDGMENT

This work is funded by DARPA under agreement number F30602-00-2-0613. The authors are grateful to the contract monitors Dr. Anantha Krishnan (DARPA), Mr. Clare Thiem and Mr. Duane Gilmour of the Air Force Research Lab (IFTC) for their support. A.T.C. is especially grateful for extensive discussions with Carl Grove, Rob Walczak, and Tony Boiarski of iMEDD and to Dr. Mauro Ferrari who got him involved in this work.

Received for review November 20, 2001. Accepted February 16, 2002.

AC011198O