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Electrokinetic Flow in Fine Capillaries Caused by Gradients of Electrolyte Concentration

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The steady electrokinetic flow of an electrolyte solution in a narrow capillary tube or slit generated by a uniform prescribed concentration gradient is analytically studied. The electric double layer adjacent to the charged capillary wall may have arbitrary thickness relative to the capillary radius. The electrostatic potential distribution on a cross section of the capillary is obtained by solving the linearized Poisson–Boltzmann equation, which applies to the case of low surface potential or low surface charge density at the capillary wall. Explicit formulas for the fluid velocity profile due to the gradient of electrolyte concentration through the capillary are derived as the solution of a modified Navier–Stokes equation. In the absence of a macroscopic electric field induced by the electrolyte gradient, the fluid flows (due to the chemiosmotic contribution) toward lower electrolyte concentration. With an induced electric field, competition between electroosmosis and chemiosmosis can result in more than one reversal in direction of the fluid flow over a small range of the surface potential. For a given concentration gradient of electrolyte in a capillary, the fluid flow rate does not always increase with an increase in the electrokinetic radius of the capillary, which is the capillary radius divided by the Debye screening length.

1. Introduction

The flow behavior of fluids in porous media is of much fundamental and practical interest. In general, driving forces for the fluid transport through micropores include dynamic pressure differences between the two ends of a capillary pore (convection), concentration differences of an impermeable solute between the two bulk solutions outside the pores (osmosis), and tangential electric fields that interact with the electric double layer adjacent to a charged pore wall (electroosmosis). Problems of fluid flow induced by these well-known driving forces were treated extensively in the past.

Another driving force for the flow of liquid solutions in a capillary pore, which has commanded less attention, involves concentration gradients of a permeable solute that interacts with the pore wall along the capillary. The fluid motion associated with this mechanism, which may be termed “diffusioosmosis”, has been discussed analytically for solutions of either ionic or nonionic solutes near a plane wall.^{1–5} In a solution of uncharged solute, the solute molecules interact with the wall through the van der Waals and dipole forces. For an electrolyte solution in contact with a charged wall, the solute–wall interaction is electrostatic in nature and its range is the Debye screening length κ^{-1} (defined by eq 4). Electrolyte solutions with a concentration gradient of order 1 M/cm along rigid surfaces with a zeta (ζ) potential of order kT/e (~ 25 mV; e is the charge of a proton, k is the Boltzmann constant, and T is the absolute temperature) can flow by diffusioosmosis at rates of several microns per second.

The analytical solution for the diffusioosmotic velocity of electrolyte solutions parallel to a charged plane wall³ can be applied to the corresponding flow in capillary tubes and slits when the thickness of the double layer adjacent to the capillary wall is small compared with the capillary radius. However, in some practical applications involving dilute electrolyte solutions in very fine capillaries, this condition is no longer satisfied and the dependence of the fluid flow on the electrokinetic radius κR or κh , where R is the radius of a capillary tube and h is the half thickness of a capillary slit, must be taken into account. In this paper we present an analysis of the diffusioosmosis of an electrolyte solution with a constant imposed concentration gradient through a capillary tube or slit. The electric potential at the capillary wall (or the surface charge density) is assumed to be uniform and low, but no assumption is made as to the electrokinetic radius κR or κh . Closed-form expressions for the fluid velocity profiles on cross sections of the capillary tube and slit are obtained in eqs 14 and 30, respectively.

2. Diffusioosmotic Flow in a Circular Capillary

In this section, the steady diffusioosmotic flow of an electrolyte solution in a straight capillary tube of radius R and length L with $R \ll L$, as illustrated in Figure 1a, is analyzed in the absence of an external electric field or a dynamic pressure gradient. The discrete nature of the surface charges, which are uniformly distributed over the capillary wall, is neglected. The valences of the electrolyte ions are z_1 and z_2 , where the subscripts 1 and 2 refer to the counterion and co-ion, respectively. Obviously, for a symmetrically charged electrolyte, $z_1 = -z_2$. The prescribed electrolyte concentration gradient along the axial (z) direction in the capillary tube is constant and can be expressed by $\alpha = dC_{1\infty}/dz = -(z_2/z_1) dC_{2\infty}/dz$, where $C_{1\infty}(z)$ and $C_{2\infty}(z)$ are the linear concentration distributions of the electrolyte ions in the bulk solution phase in equilibrium with the fluid inside the capillary. Both ions can diffuse freely along the capillary, so there exists no regular osmotic flow of the solvent. It is assumed that $\alpha L/C_{1\infty}$

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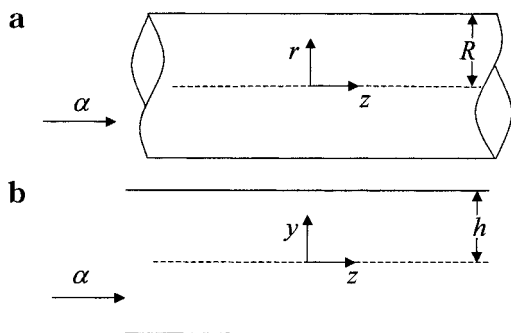


Figure 1. Geometrical sketch for the electrokinetic flow in a straight capillary due to a concentration gradient of the electrolyte: (a) a capillary tube; (b) a capillary slit.

(0) $\ll 1$, where $z = 0$ is set at the midpoint through the tube. Thus, the variation of the electrostatic potential (excluding the macroscopic electric field induced by the electrolyte gradient) and ionic concentrations in the electric double layer adjacent to the capillary wall with the axial position can be ignored.

2.1. Electrostatic Potential Distribution. We first consider the electric potential distribution on a cross section of the capillary tube. If $\psi(r)$ represents the electrostatic potential at a point distance r from the axis of the tube relative to that in the bulk solution and $C_1(r, z)$ and $C_2(r, z)$ denote the local concentrations of the electrolyte ions in the tube, then Poisson's equation gives

$$\frac{1}{r} \frac{d}{dr} \left(r \frac{d\psi}{dr} \right) = - \frac{4\pi e}{\epsilon} [z_1 C_1(r, 0) + z_2 C_2(r, 0)] \quad (1)$$

In this equation, $\epsilon = 4\pi\epsilon_0\epsilon_r$, where ϵ_r is the relative permittivity of the electrolyte solution and ϵ_0 is the permittivity of a vacuum. The local concentrations C_1 and C_2 can also be related to the electrostatic potential ψ by the Boltzmann equation

$$C_i = C_{i\infty} \exp\left(-\frac{z_i e \psi}{kT}\right), \quad i = 1, 2 \quad (2)$$

Substitution of eq 2 into eq 1 leads to the well-known Poisson–Boltzmann equation. For small values of ψ , the Poisson–Boltzmann equation can be linearized (known as the Debye–Hückel approximation), and eq 1 becomes

$$\frac{1}{r} \frac{d}{dr} \left(r \frac{d\psi}{dr} \right) = \kappa^2 \psi \quad (3)$$

where κ is the reciprocal of the Debye screening length defined by

$$\kappa = \left\{ \frac{4\pi e^2}{\epsilon kT} [z_1^2 C_{1\infty}(0) + z_2^2 C_{2\infty}(0)] \right\}^{1/2} \quad (4)$$

The boundary conditions for ψ are

$$r = 0: \quad \frac{d\psi}{dr} = 0 \quad (5a)$$

$$r = R: \quad \psi = \psi_w \quad (5b)$$

where ψ_w is the surface (ζ) potential at the capillary wall.

The solution to eqs 3 and 5 is

$$\psi = \psi_w \frac{I_0(\kappa r)}{I_0(\kappa R)} \quad (6)$$

where I_n is the modified Bessel function of the first kind

of order n . Due to the linearization of the Poisson–Boltzmann equation, the normalized potential distribution ψ/ψ_w is independent of the dimensionless parameters $z_i e \psi_w / kT$.

If the surface charge density σ , instead of the surface potential ψ_w , is known at the capillary wall, the boundary condition specified by eq 5b should be replaced by the Gauss condition

$$r = R: \quad \frac{d\psi}{dr} = \frac{4\pi\sigma}{\epsilon} \quad (7)$$

The solution for ψ given by eq 6 still holds for this condition, with the relation between ψ_w and σ for an arbitrary value of κR as

$$\psi_w = \frac{4\pi\sigma}{\epsilon\kappa} \frac{I_0(\kappa R)}{I_1(\kappa R)} \quad (8)$$

Note that we have set $z_1 \psi_w$ or $z_1 \sigma$ to be negative.

2.2. Fluid Velocity Distribution. We now consider the steady flow of an electrolyte solution through a capillary tube under the influence of a constant concentration gradient of the electrolyte prescribed axially. The momentum balances on the Newtonian fluid in the r and z directions give

$$\frac{\partial p}{\partial r} + e(z_1 C_1 + z_2 C_2) \frac{d\psi}{dr} = 0 \quad (9a)$$

$$\eta \frac{d}{dr} \left(r \frac{du}{dr} \right) = \frac{\partial p}{\partial z} - e(z_1 C_1 + z_2 C_2) E \quad (9b)$$

where $u(r)$ is the fluid velocity in the axial direction of increasing electrolyte concentration (satisfying the equation of continuity for an incompressible fluid), $p(r, z)$ is the pressure, and η is the viscosity of the fluid. The macroscopic electric field E in eq 9b arises spontaneously due to the imposed concentration gradient of the electrolyte and the difference in mobilities of the cation and anion of the electrolyte. Under the condition that there is no electric current generated by the cocurrent diffusion of the counterions and co-ions in an electrically neutral bulk solution, this induced electric field can be expressed as^{1,6,7}

$$E = \frac{kT}{z_1 e} \beta \frac{\alpha}{C_{1\infty}(0)} \quad (10)$$

which is a constant, where

$$\beta = \frac{D_1 - D_2}{D_1 - (z_2/z_1)D_2} \quad (11)$$

Note that the sign of β depends on that of ψ_w . The boundary conditions for u are

$$r = 0: \quad \frac{du}{dr} = 0 \quad (12a)$$

$$r = R: \quad u = 0 \quad (12b)$$

After the substitution of eq 2 for C_i into eq 9a and the application of the Debye–Hückel approximation, the pressure distribution can be determined, with the result

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(7) Pawar, Y.; Solomentsev, Y. E.; Anderson, J. L. *J. Colloid Interface Sci.* **1993**, *155*, 488.

$$p = p_0 - \frac{z_1(z_2 - z_1)C_{1\infty}}{2kT} \left[\frac{e\psi_w}{I_0(\kappa R)} \right]^2 \{ [I_0(\kappa R)]^2 - 1 \} + O(\psi_w^3) \quad (13)$$

where p_0 is the pressure on the axis of the capillary tube, which is a constant in the absence of applied pressure gradient. Substituting the ionic concentration distributions of eq 2, the pressure profile of eq 13, and the electric field of eq 10 into eq 9b and solving for the fluid velocity subject to the boundary conditions in eq 12, we obtain

$$u = \frac{(z_2 - z_1)e}{\eta\kappa^2} \alpha \left\{ \beta\psi_w\Theta_1(\kappa R, r/R) + \frac{e}{8kT}\psi_w^2 [z_1\Theta_2(\kappa R, r/R) - \beta(z_1 + z_2)\Theta_3(\kappa R, r/R)] + O(\psi_w^3) \right\} \quad (14)$$

where Θ_1 and Θ_2 are functions given by

$$\Theta_1 = 1 - \frac{I_0(\kappa r)}{I_0(\kappa R)} = 1 - \frac{\psi}{\psi_w} \quad (15a)$$

$$\Theta_2 = \frac{1}{[I_0(\kappa R)]^2} [H(\kappa R) - H(\kappa r)] \quad (15b)$$

and the term containing Θ_3 vanishes for a symmetrically charged electrolyte. In eq 15b, the function H is defined as

$$H(x) = x^2 \{ I_0(x)[I_0(x) + I_2(x)] - 2[I_1(x)]^2 - 1 \} \quad (16)$$

The average velocity $\langle u \rangle$ over a cross section of the capillary tube filled with a symmetric electrolyte can be expressed as

$$\langle u \rangle = \frac{(z_2 - z_1)e}{\eta\kappa^2} \alpha \left[\beta\psi_w\langle\Theta_1\rangle + \frac{z_1e}{8kT}\psi_w^2\langle\Theta_2\rangle + O(\psi_w^3) \right] \quad (17)$$

Here, the definition of the angle brackets is

$$\langle u \rangle = \frac{2}{R^2} \int_0^R u(r)r dr \quad (18)$$

It can be found that

$$\langle\Theta_1\rangle = 1 - \frac{2I_1(\kappa R)}{\kappa R I_0(\kappa R)} \quad (19)$$

but the analytical form of $\langle\Theta_2\rangle$ is quite complicated and it will be determined by numerical integration.

In the limiting situation that $\kappa R = 0$, eq 15 gives $\Theta_1 = \Theta_2 = 0$ at any position in the tube, which also leads to $\langle\Theta_1\rangle = \langle\Theta_2\rangle = 0$, as expected. If we consider the other limiting situation that $\kappa R \rightarrow \infty$, the fluid velocity at a large distance from the wall of the tube (i.e., with $\kappa(R - r) \rightarrow \infty$) can be evaluated from eq 14 noting that $\psi(r) \rightarrow 0$ far from the wall. For this particular case, $\Theta_1 = \Theta_2 = 1$ at an arbitrary position $r/R \neq 1$ (so $\langle\Theta_1\rangle = \langle\Theta_2\rangle = 1$, too) and eq 14 is consistent with the result obtained by Prieve et al.³ for the diffusioosmotic flow of a symmetric electrolyte solution near an infinite flat plane.

It is understood that the diffusioosmosis of an electrolyte solution in a capillary pore results from a linear combina-

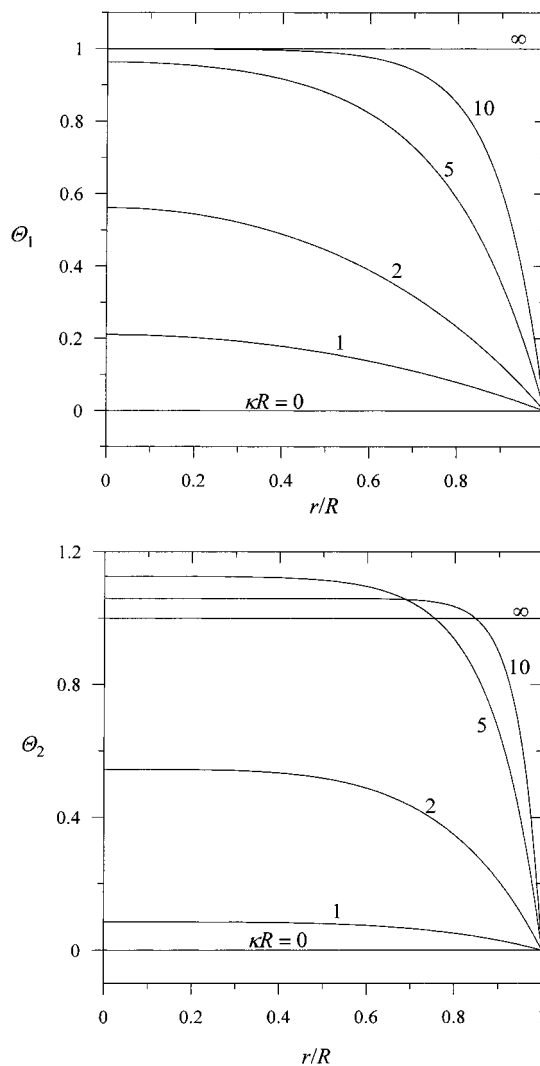


Figure 2. Plots of the functions Θ_1 and Θ_2 as calculated from eq 15 versus the normalized coordinate r/R for various values of the electrokinetic radius κR .

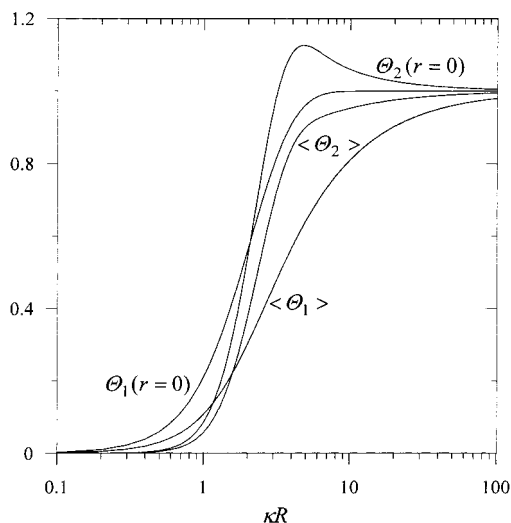
tion of two effects: (i) “chemiosmosis” due to the non-uniform adsorption of counterions in the electric double layer over the charged surface, which is analogous to the diffusioosmosis of a nonelectrolyte solution; (ii) “electroosmosis” due to the macroscopic electric field generated by the concentration gradient of the electrolyte and the difference in mobilities of the cation and anion of the electrolyte, given by eq 10. The terms in eqs 14 and 17 proportional to β (involving the functions Θ_1 , Θ_3 , and $\langle\Theta_1\rangle$) represent the contribution from electroosmosis, while the remainder terms (containing the functions Θ_2 and $\langle\Theta_2\rangle$) are the chemiosmotic component. It can be found that the function Θ_1 given by eq 15a is the same as that obtained by Rice and Whitehead⁸ for the normalized electroosmotic velocity of electrolyte solutions in a circular capillary with low surface potentials (so that the contribution from $O(\psi_w^2)$ is negligible). Note that the direction of the flow caused by electroosmosis is determined by the sign of the parameter β (since $z_2 - z_1\psi_w$ is always positive), while the fluid flow generated by chemiosmosis for small values of ψ_w is always in the direction of decreasing electrolyte concentration (since $z_1(z_2 - z_1)$ is always negative).

2.3. Results and Discussion. The functions Θ_1 and Θ_2 given by eq 15 represent dimensionless electroosmotic

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Table 1. Values of $\Theta_1(r=0)$, $\langle\Theta_1\rangle$, $\Theta_2(r=0)$, and $\langle\Theta_2\rangle$ for Various Values of κR

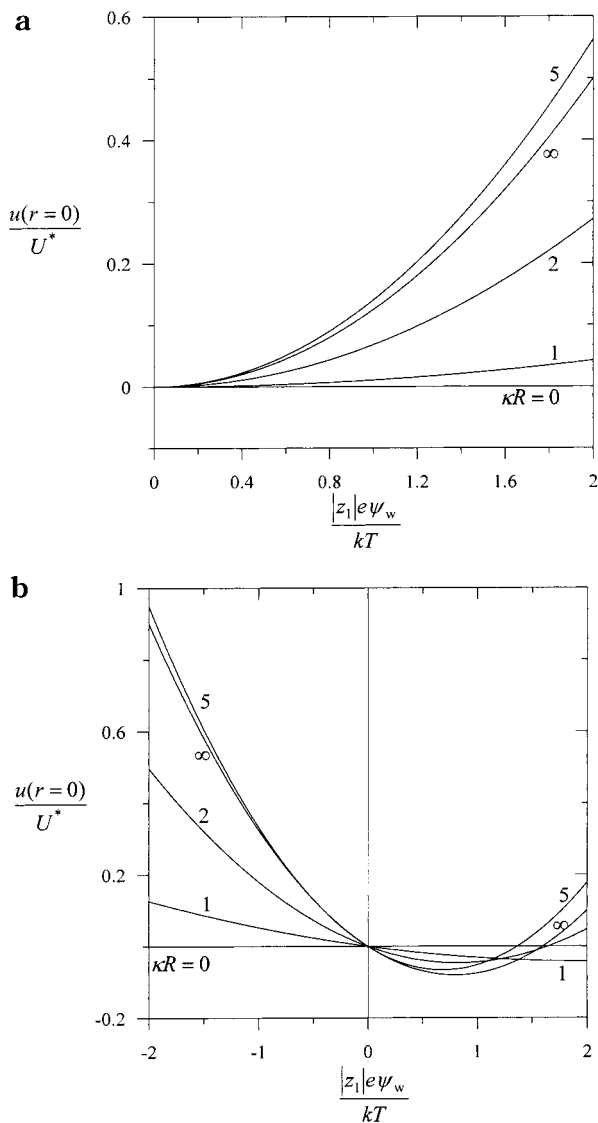
| κR | $\Theta_1(r=0)$ | $\langle\Theta_1\rangle$ | $\Theta_2(r=0)$ | $\langle\Theta_2\rangle$ |
|------------|-----------------|--------------------------|-----------------|--------------------------|
| 0 | 0 | 0 | 0 | 0 |
| 0.2 | 0.0099 | 0.0050 | 0.0002 | 0.0001 |
| 0.5 | 0.0596 | 0.0300 | 0.0071 | 0.0047 |
| 1 | 0.2101 | 0.1072 | 0.0848 | 0.0571 |
| 2 | 0.5613 | 0.3022 | 0.5440 | 0.3777 |
| 3 | 0.7951 | 0.4600 | 0.9529 | 0.6921 |
| 4 | 0.9115 | 0.5682 | 1.1051 | 0.8446 |
| 5 | 0.9633 | 0.6427 | 1.1258 | 0.9017 |
| 10 | 0.9997 | 0.8103 | 1.0597 | 0.9531 |
| 20 | 1.0000 | 0.9025 | 1.0271 | 0.9757 |
| 50 | 1.0000 | 0.9604 | 1.0103 | 0.9901 |
| ∞ | 1 | 1 | 1 | 1 |

**Figure 3.** Plots of the functions $\Theta_1(r=0)$, $\Theta_2(r=0)$, $\langle\Theta_1\rangle$, and $\langle\Theta_2\rangle$ versus the electrokinetic radius κR .

velocity of a symmetric electrolyte and chemiosmotic velocity of a general electrolyte, respectively, correct to $O(\psi_w^2)$. Their numerical results are plotted versus the dimensionless coordinate r/R in Figure 2 for various values of κR . As expected, for a specified value of κR , both Θ_1 and Θ_2 are monotonically decreasing functions of r/R from maxima at the axis of the tube (with $r=0$) to zero at the tube wall (with $r=R$). For a fixed value of r/R , Θ_1 increases monotonically with an increase in κR , while peculiarly, Θ_2 is not a monotonic function of κR and has a maximal value which is greater than unity. The maximum in Θ_2 occurs in the vicinity of $\kappa R=4.8$ at the axis of the tube, and its location shifts to larger κR as r/R increases. When the tube wall is approached ($r/R \rightarrow 1$), this maximum occurs at $\kappa R \rightarrow \infty$ and its value is close to unity.

The values of Θ_1 and Θ_2 at the axis of the tube and the values of the averaged $\langle\Theta_1\rangle$ and $\langle\Theta_2\rangle$ as functions of κR are presented in Table 1 and plotted in Figure 3. It can be seen that both functions $\langle\Theta_1\rangle$ and $\langle\Theta_2\rangle$ increase monotonically with an increase in κR . As expected, $\langle\Theta_1\rangle$ and $\langle\Theta_2\rangle$ are smaller than $\Theta_1(r=0)$ and $\Theta_2(r=0)$, respectively, for an arbitrary finite value of κR . Although the value of $\Theta_2(r=0)$ is greater than unity for cases with κR greater than about 3.2, the value of $\langle\Theta_2\rangle$ cannot be greater than unity for any given value of κR .

In Figure 4, the dependence of the diffusioosmotic velocity of an electrolyte solution at the axis of a capillary tube on the dimensionless surface (ζ) potential of the tube wall at various values of κR is displayed. The magnitude of the maximum fluid velocity is normalized by a characteristic value given by

**Figure 4.** Plots of the normalized diffusioosmotic velocity at the axis of a capillary tube versus the dimensionless surface potential $|z_1|e\psi_w/kT$ for various values of κR : (a) $\beta = 0$; (b) $z_1 = -z_2$ and $\beta = -0.2$.

$$U^* = \frac{(z_2 - z_1)\alpha kT}{z_1 \eta \kappa^2} = \frac{-\epsilon \alpha}{4\pi \eta C_{1\infty}(0)} \left(\frac{kT}{z_1 e} \right)^2 \quad (20)$$

The negative nature of this characteristic velocity means that its direction is opposite to that of the concentration gradient of the electrolyte. Figure 4a is drawn for the case of an arbitrary electrolyte that the cation and anion diffusivities are equal ($\beta = 0$). Only the results at positive surface potentials are shown because the fluid velocity, which is due to the chemiosmotic effect entirely, is an even function of the surface potential as illustrated by eq 14. Since our analysis is based on the assumption of small surface potential, the magnitudes of $|z_1|e\psi_w/kT$ considered are less than 2. It can be seen that, in this range of $|z_1|e\psi_w/kT$, the reduced diffusioosmotic velocity $u(r=0)/U^*$ (or u/U^* at any other location) increases monotonically with the increase of $|z_1|e\psi_w/kT$ for a given value of κR and, similar to the function $\Theta_2(r=0)$ illustrated in Figures 2b and 3, is not a monotonic function of κR for a fixed value of $|z_1|e\psi_w/kT$. On the other hand, the reduced average fluid velocity $\langle u \rangle/U^*$ increases monotonically with an increase in either $|z_1|e\psi_w/kT$ or κR , although this relation is not graphically

presented here for conciseness. There is no chemiosmotic motion of the fluid for the special cases of $|z_1|e\psi_w/kT=0$ or $\kappa R=0$.

Figure 4b is plotted for the reduced diffusioosmotic velocity $u(r=0)/U^*$ as a function of $|z_1|e\psi_w/kT$ at various values of κR for the case of a symmetric electrolyte whose cation and anion have different diffusion coefficients ($\beta = -0.2$ is chosen). In this case, both the chemiosmotic and the electroosmotic effects contribute to the fluid flow and the net diffusioosmotic velocity is neither an even nor an odd function of the surface potential of the tube wall. It can be seen that the fluid velocity is not necessarily a monotonic function of $|z_1|e\psi_w/kT$ given a constant value of κR . Some of the curves in Figure 4b indicate that the fluid might reverse direction of flow more than once as the surface potential of the capillary wall varies from negative to positive values. The reversals occurring at the values of $|z_1|e\psi_w/kT$ other than zero result from the competition between the contributions from chemiosmosis and electroosmosis. Again, for a specified value of $|z_1|e\psi_w/kT$, $u(r=0)/U^*$ (or u/U^* at any other location) is not necessarily a monotonic function of κR . Because of the competition between the chemiosmosis and electroosmosis, the net average velocity $\langle u \rangle/U^*$, which is not illustrated here, may not be a monotonic function of κR for some given values of $|z_1|e\psi_w/kT$.

Note that the situations associated with Figure 4a,b taking $z_1 = -z_2 = 1$ are close to the diffusioosmosis of the aqueous solutions of KCl and NaCl, respectively.

3. Diffusioosmotic Flow in a Capillary Slit

In this section, we deal with the steady diffusioosmotic flow of an electrolyte solution in a capillary channel between two identical parallel plates at separation $2h$, as shown in Figure 1b. Owing to the planar symmetry of the system, we need consider only the half region $0 \leq y \leq h$, where y is the distance from the median plane between the slit walls in the normal direction. The analysis for this case is similar to that presented in the previous section for the case of diffusioosmotic flow in a capillary tube.

3.1. Electrostatic Potential Distribution. Let $\psi(y)$ be the electrostatic potential at the position y and $C_1(y,z)$ and $C_2(y,z)$ be the local concentrations of the counterions and co-ions, respectively. Now, Poisson's equation has the form

$$\frac{d^2\psi}{dy^2} = -\frac{4\pi e}{\epsilon}[z_1 C_1(y,0) + z_2 C_2(y,0)] \quad (21)$$

where $z=0$ is set at the midpoint through the capillary. Substitution of eq 2 for C_1 and C_2 into the above equation and application of the Debye-Hückel approximation lead to

$$\frac{d^2\psi}{dy^2} = \kappa^2\psi \quad (22)$$

where the Debye parameter κ is defined by eq 4. Here, the boundary conditions for ψ are

$$y=0: \quad \frac{d\psi}{dy} = 0 \quad (23a)$$

$$y=h: \quad \psi = \psi_w \quad (23b)$$

The solution to eqs 22 and 23 is

$$\psi = \psi_w \frac{\cosh(\kappa y)}{\cosh(\kappa h)} \quad (24)$$

If the Gauss condition at the capillary wall

$$y=h: \quad \frac{d\psi}{dy} = \frac{4\pi\sigma}{\epsilon} \quad (25)$$

is used to replace eq 23b, the solution for ψ given by eq 24 is still valid, with

$$\psi_w = \frac{4\pi\sigma}{\epsilon\kappa} \frac{\cosh(\kappa h)}{\sinh(\kappa h)} \quad (26)$$

3.2. Fluid Velocity Distribution. For the steady flow of an electrolyte solution in a capillary slit acted upon by a constant concentration gradient of the electrolyte parallel to the slit walls, the equations of momentum balance for the fluid are

$$\frac{\partial p}{\partial y} + e(z_1 C_1 + z_2 C_2) \frac{d\psi}{dy} = 0 \quad (27a)$$

$$\eta \frac{d^2 u}{dy^2} = \frac{\partial p}{\partial z} - e(z_1 C_1 + z_2 C_2) E \quad (27b)$$

where $u(y)$ is the fluid velocity profile in the direction of electrolyte concentration gradient and $p(y,z)$ is the pressure distribution. The induced uniform electric field E is still given by eq 10 with β defined by eq 11. The boundary conditions for u become

$$y=0: \quad \frac{du}{dy} = 0 \quad (28a)$$

$$y=h: \quad u = 0 \quad (28b)$$

Substituting the linearized form of eq 2 into eq 27a, we solve for the pressure distribution to yield

$$p = p_0 - \frac{z_1(z_2 - z_1)C_{1\infty}}{2kT} \left[\frac{e\psi_w}{\cosh(\kappa h)} \right]^2 [\cosh^2(\kappa y) - 1] + O(\psi_w^3) \quad (29)$$

where p_0 is the pressure on the midplane between the slit walls. The fluid velocity u can be solved from eqs 27b and 28 by the substitution of eqs 2, 10, and 29, with the result

$$u = \frac{(z_2 - z_1)e}{\eta\kappa^2} \alpha \left\{ \beta\psi_w \Phi_1(\kappa h, y/h) + \frac{e}{8kT} \psi_w^2 [z_1 \Phi_2(\kappa h, y/h) - \beta(z_1 + z_2) \Phi_3(\kappa h, y/h)] + O(\psi_w^3) \right\} \quad (30)$$

where the functions Θ_1 and Θ_2 are

$$\Phi_1 = 1 - \frac{\cosh(\kappa y)}{\cosh(\kappa h)} = 1 - \frac{\psi}{\psi_w} \quad (31a)$$

$$\Phi_2 = \frac{1}{2 \cosh^2(\kappa h)} [\cosh(2\kappa h) - \cosh(2\kappa y) - 2\kappa^2(h^2 - y^2)] \quad (31b)$$

Table 2. Values of $\Phi_1(y=0)$, $\langle\Phi_1\rangle$, $\Phi_2(y=0)$, and $\langle\Phi_2\rangle$ for Various Values of κh

| κh | $\Phi_1(y=0)$ | $\langle\Phi_1\rangle$ | $\Phi_2(y=0)$ | $\langle\Phi_2\rangle$ |
|------------|---------------|------------------------|---------------|------------------------|
| 0 | 0 | 0 | 0 | 0 |
| 0.2 | 0.0197 | 0.0131 | 0.0005 | 0.0004 |
| 0.5 | 0.1132 | 0.0758 | 0.0169 | 0.0136 |
| 1 | 0.3519 | 0.2384 | 0.1601 | 0.1292 |
| 2 | 0.7342 | 0.5180 | 0.6467 | 0.5353 |
| 3 | 0.9007 | 0.6683 | 0.9013 | 0.7700 |
| 4 | 0.9634 | 0.7502 | 0.9772 | 0.8601 |
| 5 | 0.9865 | 0.8000 | 0.9953 | 0.8969 |
| 10 | 0.9999 | 0.9000 | 1.0000 | 0.9500 |
| 20 | 1.0000 | 0.9500 | 1.0000 | 0.9750 |
| 50 | 1.0000 | 0.9800 | 1.0000 | 0.9900 |
| ∞ | 1 | 1 | 1 | 1 |

and the term involving Φ_3 disappears for a symmetric electrolyte. The function Φ_1 given by eq 31a is consistent with that obtained by Burgreen and Nakache⁹ for the normalized electroosmotic mobility of electrolyte solutions in a capillary slit.

The average velocity $\langle u \rangle$ over a cross section of the slit filled with a symmetric electrolyte is

$$\langle u \rangle = \frac{(z_2 - z_1)e}{\eta\kappa^2} \alpha \left[\beta\psi_w \langle \Phi_1 \rangle + \frac{z_1 e}{8kT} \psi_w^2 \langle \Phi_2 \rangle + O(\psi_w^3) \right] \quad (32)$$

Here, the definition of the angle brackets becomes

$$\langle u \rangle = \frac{1}{h} \int_0^h u(y) dy \quad (33)$$

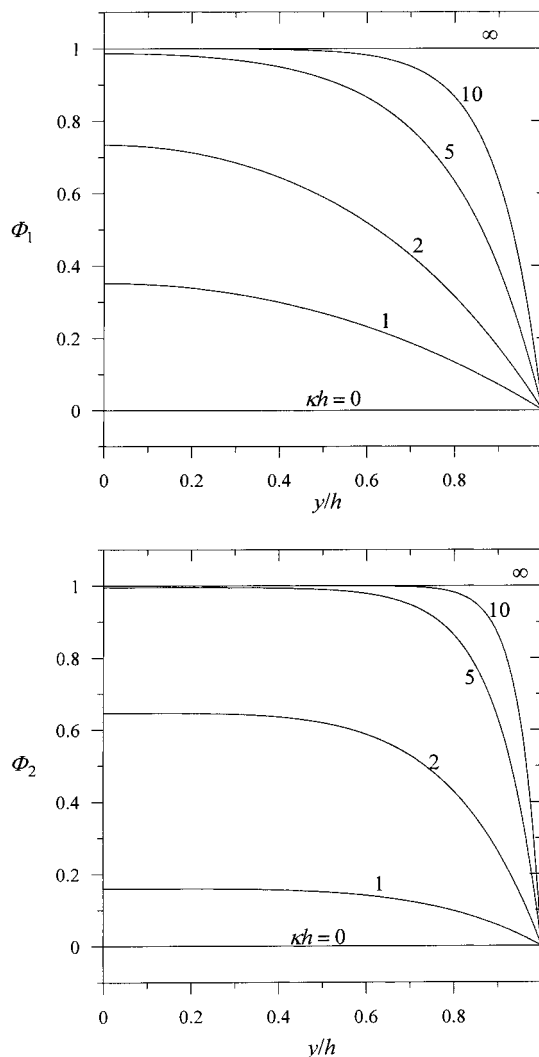
It can be shown that

$$\langle \Phi_1 \rangle = 1 - \frac{\sinh(\kappa h)}{\kappa h \cosh(\kappa h)} \quad (34a)$$

$$\langle \Phi_2 \rangle = \frac{1}{2 \cosh^2(\kappa h)} \left[\cosh(2\kappa h) - \frac{1}{2\kappa h} \sinh(2\kappa h) - \frac{4}{3}(\kappa h)^2 \right] \quad (34b)$$

In the limit $\kappa h = 0$, eqs 31 and 34 result in $\Phi_1 = \Phi_2 = 0$ at any position in the capillary and $\langle \Phi_1 \rangle = \langle \Phi_2 \rangle = 0$, respectively. Under the situation of $\kappa h \rightarrow \infty$, eqs 31 and 34 give that $\Phi_1 = \Phi_2 = 1$ at positions far from the capillary walls (i.e., with $\kappa(h - y) \rightarrow \infty$ or $y/h \neq 1$) and $\langle \Phi_1 \rangle = \langle \Phi_2 \rangle = 1$. In this case, the fluid velocity predicted by eq 30 also agrees with that obtained by Prieve et al.³ for the diffusioosmosis of symmetric electrolyte solutions near an infinite plane wall.

3.3. Results and Discussion. The functions Φ_1 and Φ_2 obtained in eq 31, whose physical meanings are the same as those of the functions Θ_1 and Θ_2 for the electrokinetic flow in a capillary tube discussed in the previous section, are plotted versus the normalized coordinate y/h in Figure 5a and Figure 5b, respectively, for various values of κh . The values of Φ_1 and Φ_2 at the midplane of the capillary slit (with $y = 0$) and their averaged results over a cross section of the slit as functions of κh are also presented in Table 2 and plotted in Figure 6. Similar to the case of fluid flow in a capillary tube, both Φ_1 and Φ_2 decrease monotonically with an increase in y/h for a constant value of κh , from maxima at the midplane of the capillary slit to zero at the slit wall (with $y = h$). For a given value of y/h , both Φ_1 and Φ_2 are monotonically increasing functions of κh and their values range from 0 to 1, partly different from the results for a capillary tube

**Figure 5.** Plots of the functions Φ_1 and Φ_2 as calculated from eq 31 versus the normalized coordinate y/h for various values of κh .

obtained in the previous section, in which the function Θ_2 has a maximal value greater than unity at some value of κR . Accordingly, both the functions $\langle \Phi_1 \rangle$ and $\langle \Phi_2 \rangle$ for the slit also increase monotonically with an increase in κh . It can be found that the relations $\Phi_1(\kappa h, y/h) > \Theta_1(\kappa R, r/R)$ and $\langle \Phi_1 \rangle(\kappa h) > \langle \Theta_1 \rangle(\kappa R)$ are always true for any given values of $0 < \kappa h = \kappa R < \infty$ and $0 \leq y/h = r/R < 1$. However, $\langle \Phi_2 \rangle$ is greater than $\langle \Theta_2 \rangle$ only for cases with $0 < \kappa h = \kappa R < 4.6$, and $\langle \Phi_2 \rangle$ is smaller than $\langle \Theta_2 \rangle$ otherwise.

The diffusioosmotic velocity of an electrolyte solution at the midplane of a capillary slit normalized by its characteristic value given by eq 20 is plotted as a function of the dimensionless surface potential $|z_1|e\psi_w/kT$ (with its magnitude less than 2) in Figure 7 for various values of κh . For the case of a general electrolyte that the cation and anion diffusivities are equal ($\beta = 0$), the normalized velocity $u(y=0)/U^*$ (or u/U^* at any other location or $\langle u \rangle/U^*$, which is not illustrated here) increases monotonically with an increase in $|z_1|e\psi_w/kT$ for a fixed value of κh and with an increase in κh for a constant value of $|z_1|e\psi_w/kT$. This behavior is different from the relevant results for a capillary tube, in which the normalized maximum velocity is not a monotonic function of κR for a given value of $|z_1|e\psi_w/kT$. For the case of a symmetric electrolyte whose cation and anion have unequal diffusion coefficients ($\beta \neq 0$), the fluid velocity is not necessarily a monotonic function of $|z_1|e\psi_w/kT$ for a fixed value of κh

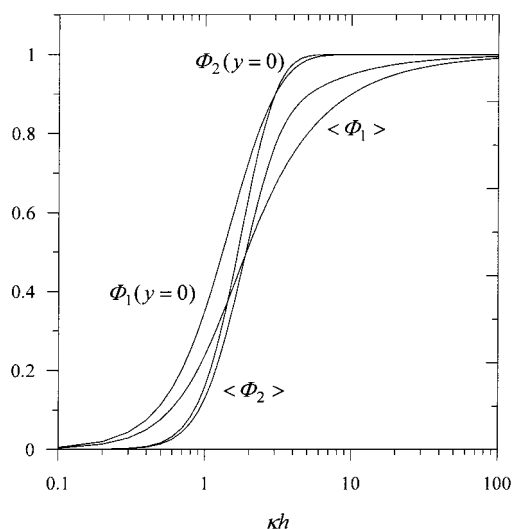


Figure 6. Plots of the functions $\Phi_1(y=0)$, $\Phi_2(y=0)$, $\langle\Phi_1\rangle$, and $\langle\Phi_2\rangle$ versus κh .

and the fluid flow might reverse its direction more than once as the surface potential of the capillary wall varies from negative to positive values, similar to the diffusioosmosis in a capillary tube. Owing to the competition between the chemiosmotic and electroosmotic contributions, the net local or average fluid velocity may not be a monotonic function of κh for some constant values of $|z_1|e\psi_w/kT$.

4. Concluding Remarks

The steady diffusioosmotic flow of electrolyte solutions in a fine capillary tube or slit is analyzed in this work. It is assumed that the fluid is only slightly nonuniform in the electrolyte concentration along the capillary axis, but no assumption is made as to the thickness of the double layer at the capillary wall relative to the radius of the capillary. The capillary wall may have either a constant surface potential or a constant surface charge density. Solving the linearized Poisson–Boltzmann equation and the modified Navier–Stokes equation applicable to the system, the electrostatic potential distribution and the fluid velocity profile under the influence of a constant gradient of the electrolyte concentration are obtained analytically. Closed-form formulas and numerical results for the average velocity over a cross section of the capillary are also presented. This analysis applies to a solution with general electrolytes for electroosmosis to $O(\psi_w)$ and for chemiosmosis (diffusioosmosis with $\beta = 0$) to $O(\psi_w^2)$. For a solution with symmetrically charged electrolytes, the $O(\psi_w^2)$ contribution to electroosmosis vanishes. Although the electroosmotic effects in a capillary tube and in a capillary slit are similar, the chemiosmotic effects in these two types of capillary are somewhat different qualitatively. The reason for this difference caused by the variation of the cross-sectional shape of a capillary remains unclear.

It is worth repeating that our analytical solutions for the diffusioosmotic velocity of electrolyte solutions in a capillary are obtained on the basis of the Debye–Hückel approximation for the potential distribution in the double layer. A similar solution for the diffusiophoretic velocity of a charged spherical particle with low surface (ζ) potential, in comparison with the corresponding numerical

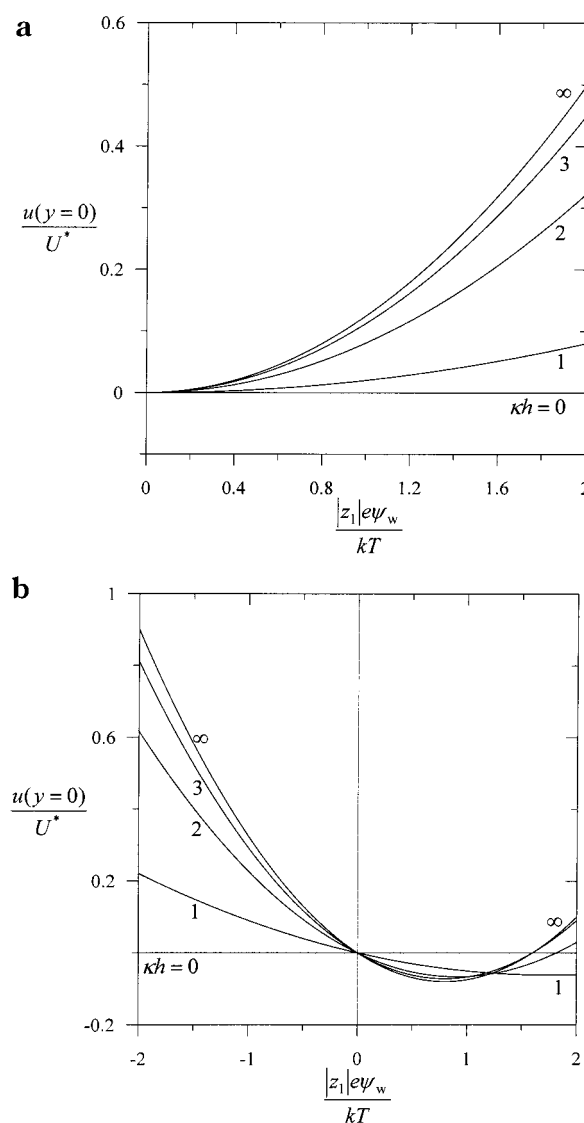


Figure 7. Plots of the normalized diffusioosmotic velocity at the midplane of a capillary slit versus the dimensionless surface potential $|z_1|e\psi_w/kT$ for various values of κh : (a) $\beta = 0$; (b) $z_1 = -z_2$ and $\beta = -0.2$.

solution valid for an arbitrary value of the surface potential,¹⁰ was shown to give an excellent approximation for the case of $\psi_w e/kT \leq 2$ in an aqueous KCl or NaCl solution.¹¹ Therefore, our results might be used tentatively for capillaries with surface potential in this range. To see whether our theory can be reasonably extended to the higher values of electric potential, we propose to obtain a numerical solution of the electrokinetic differential equations with no assumption on the magnitude of electric potential and compare it with the approximate solution.

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