Electrokinetic Flow in a Circular Capillary with a Surface Charge Layer

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An analytical study is presented of the steady electrokinetic flow in a long uniform circular capillary bearing a layer of adsorbed polyelectrolytes on its inside wall. In this solvent-permeable and ion-penetrable surface charge layer, idealized polyelectrolyte segments are assumed to distribute at a uniform density. The electrical potential and space charge density distributions on a cross section of the capillary are obtained by solving the linearized Poisson-Boltzmann equation. The fluid velocity profile due to the application of an electric field and a pressure gradient through the capillary is obtained from the analytical solution of a modified Navier-Stokes equation. Explicit formulas for the volumetric flow rate, the electro-osmotic velocity, the electric current and the streaming potential in the capillary are also derived. The results demonstrate that the structure of the surface charge layer can result in an augmented or a diminished electrokinetic flow relative to that in a capillary with bare walls, depending on the characteristics of the electrolyte solution, of the surface charge layer, and of the capillary. The Onsager reciprocal relation is found to be satisfied in the general case. © 1995 Academic Press, Inc.

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INTRODUCTION

In the study of phenomena occurring at charged solid-liquid interfaces, electrokinetic methods have proved to be useful tools. Although the basic relationships involved in electrokinetic phenomena were derived mainly by using the traditional model of plain distribution of surface charges, quite a number of investigations have applied these methods to the study of the effects of polyelectrolyte adsorbates. Several theoretical studies were made on the electrophoresis of a colloidal particle coated with an ion-penetrable layer of adsorbed, charged polymers (1-7), in relation to the electrophoresis of biocolloids such as cells. The electrophoretic mobility of such particles was found to be different from that of bare particles (8, 9).

On the other hand, Donath and Voigt (10) studied the electrokinetic flow in a rectangular chamber consisting of two parallel polyelectrolyte-coated surfaces and discussed the

streaming current and streaming potential. Ohshima and Kondo (11) also considered the electrokinetic flow between two parallel plates with permeable surface charge layers and evaluated the electro-osmotic velocity and streaming potential. Their results are also different from those obtained for the electrokinetic flow in a capillary slit with bare walls (12).

In this paper we shall be concerned with the electrokinetic flow in a long uniform circular capillary bearing permanently adsorbed or covalently bound polyelectrolytes on its inside wall. The charge and segment densities of adsorbed polymers are assumed to be uniform throughout the surface charge layer and the linearized Poisson-Boltzmann equation for the electrical potential is employed. However, no assumptions will be made as to the thickness of the electrical double layer relative to the radius of the capillary or the thickness of the surface charge layer. We shall derive explicit formulas for the profiles of electrical potential, of space charge density, and of fluid velocity due to the application of an electric field and a pressure gradient in the capillary. The volumetric flow rate, the electro-osmotic velocity, the electric current, and the streaming potential for the electrokinetic flow in the capillary will also be analytically calculated. When there is no polymer attached to the capillary wall, our results are consistent with those obtained by Rice and Whitehead (13) who analyzed the electrokinetic flow in a polymer-free capillary with a constant potential at its inside wall.

ELECTRICAL POTENTIAL DISTRIBUTION

We first consider the electrostatic potential distribution in a long uniform circular capillary tube of radius R . The inside wall of the tube is covered by a layer of adsorbed, charged polymers in equilibrium with the surrounding electrolyte solution. The polymer layer is treated as an ion-penetrable surface charge layer of constant thickness $d = R - r_1$ in which fixed-charged groups of valence z are distributed at a uniform density N . This assumption ignores the discrete nature of the charges both parallel and perpendicular to the capillary wall. If $\rho(r)$ represents the space charge density resulting from the electrolyte ions at a point distance r from the axis and $\psi(r)$ denotes the electrical potential at this point relative to the bulk solution phase, then the Poisson's equation gives

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$$\frac{1}{r} \frac{d}{dr} \left(r \frac{d\psi}{dr} \right) = -\frac{4\pi}{\epsilon} \rho, \quad \text{if } 0 \leq r < r_1; \quad [1a]$$

$$\frac{1}{r} \frac{d}{dr} \left(r \frac{d\psi}{dr} \right) = -\frac{4\pi}{\epsilon} (\rho + zeN), \quad \text{if } r_1 < r < R. \quad [1b]$$

Here, e is the charge of a proton; $\epsilon = 4\pi\epsilon_0\epsilon_r$, where ϵ_r is the relative permittivity of the electrolyte solution which is assumed to be constant and ϵ_0 is the permittivity of free space. Experimental values for human erythrocytes (4, 14), rat lymphocytes (15), and grafted polymer microcapsules (16) indicate that d ranges from 7.8 nm to 3.38 μm and N can be as high as 0.03 M, depending on the pH and ionic strength of the electrolyte solution.

The space charge density ρ can also be related to the electrical potential ψ by the Boltzmann equation,

$$\rho = \sum_i z_i e C_{i\infty} \exp\left(\frac{-z_i e \psi}{kT}\right), \quad [2]$$

where z_i is the valence of type- i ions, $C_{i\infty}$ is the bulk concentration of these ions, k is the Boltzmann constant, and T is the absolute temperature. Substitution of Eq. [2] into Poisson's equation leads to the well-known Poisson-Boltzmann equation. For small values of ψ (Debye-Huckel approximation), the Poisson-Boltzmann equation can be linearized, and Eq. [1] becomes

$$\frac{1}{r} \frac{d}{dr} \left(r \frac{d\psi}{dr} \right) = \kappa^2 \psi, \quad \text{if } 0 \leq r < r_1; \quad [3a]$$

$$\frac{1}{r} \frac{d}{dr} \left(r \frac{d\psi}{dr} \right) = \kappa^2 \psi - \frac{4\pi zeN}{\epsilon}, \quad \text{if } r_1 < r < R. \quad [3b]$$

Here, κ is the reciprocal of the Debye screening length defined by

$$\kappa = \left(\frac{4\pi e^2}{\epsilon kT} \sum_i z_i^2 C_{i\infty} \right)^{1/2}. \quad [4]$$

The boundary conditions for ψ are

$$\psi(r=0) \text{ is finite}, \quad [5a]$$

$$\psi(r=r_1^-) = \psi(r=r_1^+), \quad [5b]$$

$$\frac{d\psi}{dr}(r=r_1^-) = \frac{d\psi}{dr}(r=r_1^+), \quad [5c]$$

$$\frac{d\psi}{dr}(r=R) = \frac{4\pi\sigma}{\epsilon}. \quad [5d]$$

Equations [5b] and [5c] are the continuity requirements of ψ and of $d\psi/dr$ at $r = r_1$. Equation [5d] is the Gauss con-

dition at the capillary wall, with σ equal to the surface charge density of the bare wall. Note that the magnitudes of the dimensionless parameters $4\pi\sigma e/\epsilon\kappa kT$ and $4\pi ze^2 N/\epsilon\kappa^2 kT$ must be small for the potential ψ to remain small.

The solution to Eq. [3] satisfying the above boundary conditions is

$$\psi = AI_0(\kappa r), \quad \text{if } 0 \leq r < r_1; \quad [6a]$$

$$\psi = BI_0(\kappa r) + CK_0(\kappa r) + \frac{4\pi zeN}{\epsilon\kappa^2}, \quad \text{if } r_1 < r < R, \quad [6b]$$

with

$$A = \frac{4\pi\sigma}{\epsilon\kappa I_1(\kappa R)} + \frac{4\pi zeN}{\epsilon\kappa^2} \times \frac{I_1(\kappa R)K_1(\kappa r_1) - I_1(\kappa r_1)K_1(\kappa R)}{I_1(\kappa R)[I_1(\kappa r_1)K_0(\kappa r_1) + I_0(\kappa r_1)K_1(\kappa r_1)]}, \quad [7a]$$

$$B = \frac{4\pi\sigma}{\epsilon\kappa I_1(\kappa R)} - \frac{4\pi zeN}{\epsilon\kappa^2} \times \frac{I_1(\kappa r_1)K_1(\kappa R)}{I_1(\kappa R)[I_1(\kappa r_1)K_0(\kappa r_1) + I_0(\kappa r_1)K_1(\kappa r_1)]}, \quad [7b]$$

$$C = -\frac{4\pi zeN}{\epsilon\kappa^2} \frac{I_1(\kappa r_1)}{I_1(\kappa r_1)K_0(\kappa r_1) + I_0(\kappa r_1)K_1(\kappa r_1)}. \quad [7c]$$

Here, I_n and K_n are modified Bessel functions of order n of the first and second kinds, respectively. If the boundary condition [5d] for the case of constant surface charge density is replaced by the boundary condition for the case of constant surface potential,

$$\psi(r=R) = \psi_R, \quad [8]$$

then the solution in the form of Eq. [6] is also valid, with

$$A = \frac{\psi_R}{I_0(\kappa R)} - \frac{4\pi zeN}{\epsilon\kappa^2} \frac{1}{I_0(\kappa R)} \times \left[1 - \frac{I_1(\kappa r_1)K_0(\kappa R) + I_0(\kappa R)K_1(\kappa r_1)}{I_1(\kappa r_1)K_0(\kappa r_1) + I_0(\kappa r_1)K_1(\kappa r_1)} \right], \quad [9a]$$

$$B = \frac{\psi_R}{I_0(\kappa R)} - \frac{4\pi zeN}{\epsilon\kappa^2} \frac{1}{I_0(\kappa R)} \times \left[1 - \frac{I_1(\kappa r_1)K_0(\kappa R)}{I_1(\kappa r_1)K_0(\kappa r_1) + I_0(\kappa r_1)K_1(\kappa r_1)} \right], \quad [9b]$$

and C is still given by Eq. [7c].

Substituting Eq. [6] into Eq. [1], one obtains the space charge density distribution of the electrolyte solution:

$$\rho = -\frac{\epsilon\kappa^2}{4\pi} AI_0(\kappa r), \quad \text{if } 0 \leq r < r_1; \quad [10a] \quad u = \frac{P}{4\eta} (r_1^2 - r^2) - \frac{\epsilon E}{4\pi\eta} A[I_0(\kappa r_1) - I_0(\kappa r)]$$

$$\rho = -\frac{\epsilon\kappa^2}{4\pi} [BI_0(\kappa r) + CK_0(\kappa r)] - zeN, \quad \text{if } r_1 < r < R. \quad [10b]$$

$$+ \frac{\epsilon E}{4\pi\eta} \left(\frac{\kappa^2}{\kappa^2 - \lambda^2} \right) [BI_0(\kappa r_1) + CK_0(\kappa r_1)]$$

$$+ (G_1 P + G_2 E) I_0(\lambda r_1) + (H_1 P$$

$$+ H_2 E) K_0(\lambda r_1) + \frac{1}{\eta\lambda^2} (P - zeNE),$$

$$\text{if } 0 \leq r < r_1; \quad [13a]$$

FLUID VELOCITY DISTRIBUTION

We now consider the steady flow of an electrolyte solution through a long capillary tube with its inside wall covered by a layer of charged polymers under the influence of a uniform electric field E and a constant pressure gradient P , both applied axially. The fluid velocity in the axial direction, $u(r)$, is governed by the modified Navier-Stokes equation,

$$\frac{1}{r} \frac{d}{dr} \left(r \frac{du}{dr} \right) = -\frac{1}{\eta} (P + \rho E), \quad \text{if } 0 \leq r < r_1; \quad [11a]$$

$$\frac{1}{r} \frac{d}{dr} \left(r \frac{du}{dr} \right) - \frac{1}{\eta} fu = -\frac{1}{\eta} (P + \rho E), \quad \text{if } r_1 < r < R. \quad [11b]$$

Here, η is the viscosity of the fluid and f is the friction coefficient of the polymer layer per unit volume of the fluid; both are assumed to be constant. If the polymer segments have a uniform number density N_p and a common effective Stokes radius a , then $f = 6\pi\eta a N_p$. The charge density $\rho(r)$ in Eq. [11] has been obtained in Eq. [10], based on the assumption that the equilibrium radial charge distribution is not affected by the axially applied electric field.

The boundary conditions for u are

$$u(r=0) \text{ is finite}, \quad [12a]$$

$$u(r=r_1^-) = u(r=r_1^+), \quad [12b]$$

$$\frac{du}{dr}(r=r_1^-) = \frac{du}{dr}(r=r_1^+), \quad [12c]$$

$$u(r=R) = 0. \quad [12d]$$

In Eq. [12d], we have assumed that the shear plane coincides with the surface of the bare wall. Equations [12b] and [12c] express the continuity conditions of u and of du/dr at $r = r_1$.

The solution to Eq. [11] subject to the above boundary conditions gives the fluid velocity profile in the capillary:

$$u = \frac{\epsilon E}{4\pi\eta} \left(\frac{\kappa^2}{\kappa^2 - \lambda^2} \right) [BI_0(\kappa r) + CK_0(\kappa r)]$$

$$+ (G_1 P + G_2 E) I_0(\lambda r) + (H_1 P$$

$$+ H_2 E) K_0(\lambda r) + \frac{1}{\eta\lambda^2} (P - zeNE),$$

$$\text{if } r_1 < r < R, \quad [13b]$$

where

$$\lambda = \left(\frac{f}{\eta} \right)^{1/2}, \quad [14]$$

$$G_1 = -\left[\frac{r_1}{2\eta\lambda} K_0(\lambda R) + \frac{1}{\eta\lambda^2} K_1(\lambda r_1) \right] [I_1(\lambda r_1) K_0(\lambda R)$$

$$+ I_0(\lambda R) K_1(\lambda r_1)]^{-1}, \quad [15a]$$

$$H_1 = \left[\frac{r_1}{2\eta\lambda} I_0(\lambda R) - \frac{1}{\eta\lambda^2} I_1(\lambda r_1) \right] [I_1(\lambda r_1) K_0(\lambda R)$$

$$+ I_0(\lambda R) K_1(\lambda r_1)]^{-1}, \quad [15b]$$

$$G_2 = \left\{ \frac{zeN}{\eta\lambda^2} K_1(\lambda r_1) + \frac{\epsilon\kappa}{4\pi\eta\lambda} AI_1(\kappa r_1) K_0(\lambda R) \right.$$

$$- \frac{\epsilon}{4\pi\eta} \left(\frac{\kappa^2}{\kappa^2 - \lambda^2} \right) \left[\frac{\kappa}{\lambda} BI_1(\kappa r_1) K_0(\lambda R) \right.$$

$$+ BI_0(\kappa R) K_1(\lambda r_1) - \frac{\kappa}{\lambda} CK_0(\lambda R) K_1(\kappa r_1)$$

$$+ CK_0(\kappa R) K_1(\lambda r_1) \left. \right] \left. \right\} \times [I_1(\lambda r_1) K_0(\lambda R)$$

$$+ I_0(\lambda R) K_1(\lambda r_1)]^{-1}, \quad [16a]$$

$$H_2 = \left\{ \frac{zeN}{\eta\lambda^2} I_1(\lambda r_1) - \frac{\epsilon\kappa}{4\pi\eta\lambda} AI_0(\lambda R) I_1(\kappa r_1) \right.$$

$$- \frac{\epsilon}{4\pi\eta} \left(\frac{\kappa^2}{\kappa^2 - \lambda^2} \right) \left[BI_0(\kappa R) I_1(\lambda r_1) \right.$$

$$- \frac{\kappa}{\lambda} BI_0(\lambda R) I_1(\kappa r_1) + \frac{\kappa}{\lambda} CI_0(\lambda R) K_1(\kappa r_1)$$

$$+ CI_1(\lambda r_1) K_0(\kappa R) \left. \right] \left. \right\} \times [I_1(\lambda r_1) K_0(\lambda R)$$

$$+ I_0(\lambda R) K_1(\lambda r_1)]^{-1}. \quad [16b]$$

Note that the reciprocal of the parameter λ has the dimension of length and characterizes the extent of flow penetration inside the surface charge layer. For the surface charge layer of human erythrocytes (11, 14), rat lymphocytes (15), and grafted polymer microcapsules (16), experimental values of $1/\lambda$ range from 1.35 to 3.7 nm.

When there is no polymer adsorbed on the wall of the capillary tube, one has $d = 0$, $r_1 = R$, $N = 0$, and $\lambda = 0$. Then, Eqs. [6], [10], and [13] reduce to

$$\psi = A_0 I_0(\kappa r), \quad [17]$$

$$\rho = -\frac{\epsilon \kappa^2}{4\pi} A_0 I_0(\kappa r), \quad [18]$$

$$u = \frac{P}{4\eta} (R^2 - r^2) - \frac{\epsilon E}{4\pi\eta} A_0 [I_0(\kappa R) - I_0(\kappa r)], \quad [19]$$

where

$$A_0 = \frac{4\pi\sigma}{\epsilon \kappa I_1(\kappa R)} \quad [20]$$

for the situation of constant surface charge density, and

$$A_0 = \frac{\psi_R}{I_0(\kappa R)} \quad [21]$$

for the situation of constant surface potential. Equations [17]–[19] with Eq. [21] agree with the results obtained by Rice and Whitehead (13).

For the case of a capillary coated with an uncharged polymer layer ($N = 0$) at its inside wall, Eqs. [17] and [18] for the potential and charge distributions are also applicable and the fluid velocity distribution can be evaluated from Eq. [13] by setting $N = 0$.

When $\lambda \rightarrow \infty$ (very high segment density), the resistance to the fluid motion inside the surface charge layer is infinitely large. For this limiting case, Eq. [13] becomes

$$u = \frac{P}{4\eta} (r_1^2 - r^2) - \frac{\epsilon E}{4\pi\eta} A [I_0(\kappa r_1) - I_0(\kappa r)], \quad [22a]$$

if $0 \leq r < r_1$;

$$u = 0, \quad \text{if } r_1 < r < R. \quad [22b]$$

Equation [22] shows that the fluid flow in the surface charge layer disappears and the velocity profile of the remaining fluid is similar to that in a polymer-free capillary of radius r_1 with a modified surface charge density or surface potential at the wall.

When $\lambda \rightarrow 0$ (very low segment density), the adsorbed polymers do not exert resistance to the fluid motion in the capillary tube. In this limit, Eq. [13] becomes

$$u = \frac{P}{4\eta} (R^2 - r^2) - \frac{\epsilon E}{4\pi\eta} A [I_0(\kappa r_1) - I_0(\kappa r)] - \frac{zeNE}{4\eta} \times \left(R^2 - r_1^2 + 2r_1^2 \ln \frac{r_1}{R} \right) - \frac{\epsilon E}{4\pi\eta} \{ B [I_0(\kappa R) - I_0(\kappa r_1)] - C [K_0(\kappa r_1) - K_0(\kappa R)] \}, \quad \text{if } 0 \leq r < r_1; \quad [23a]$$

$$u = \frac{P}{4\eta} (R^2 - r^2) - \frac{zeNE}{4\eta} \left(R^2 - r^2 + 2r_1^2 \ln \frac{r}{R} \right) - \frac{\epsilon E}{4\pi\eta} \{ B [I_0(\kappa R) - I_0(\kappa r)] - C [K_0(\kappa r) - K_0(\kappa R)] \}, \quad \text{if } r_1 < r < R. \quad [23b]$$

If the adsorbed polymers are uncharged ($N = 0$), the above expression for the velocity profile again reduces to Eq. [19].

When the capillary tube is filled with the adsorbed polymers, r_1 can be taken as zero. Then, Eqs. [6], [10], and [13] reduce to

$$\psi = B_1 I_0(\kappa r) + \frac{4\pi zeN}{\epsilon \kappa^2}, \quad [24]$$

$$\rho = -\frac{\epsilon \kappa^2}{4\pi} B_1 I_0(\kappa r) - zeN, \quad [25]$$

$$u = \frac{\epsilon E}{4\pi\eta} \left(\frac{\kappa^2}{\kappa^2 - \lambda^2} \right) B_1 \left[I_0(\kappa r) - \frac{I_0(\kappa R)}{I_0(\lambda R)} I_0(\lambda r) \right] + \frac{P - zeNE}{\eta \lambda^2} \left[1 - \frac{I_0(\lambda r)}{I_0(\lambda R)} \right], \quad [26]$$

where

$$B_1 = \frac{4\pi\sigma}{\epsilon \kappa I_1(\kappa R)} \quad [27]$$

for the situation of constant surface charge density, and

$$B_1 = \frac{1}{I_0(\kappa R)} \left(\psi_R - \frac{4\pi zeN}{\epsilon \kappa^2} \right) \quad [28]$$

for the situation of constant surface potential.

The volumetric flow rate of the fluid, V , is obtained by integrating Eq. [13] for $u(r)$ over a cross section of the capillary tube,

$$V = 2\pi \int_0^R u(r) r dr, \quad [29]$$

and the result can be written in terms of the Onsager transport coefficients L_{11} and L_{12} (10, 17) as

$$V = L_{11}P + L_{12}E, \quad [30]$$

where

$$L_{11} = \pi \left\{ \frac{r_1^4}{8\eta} + \frac{R^2}{\eta\lambda^2} + G_1 \left[r_1^2 I_0(\lambda r_1) + \frac{2R}{\lambda} I_1(\lambda R) - \frac{2r_1}{\lambda} I_1(\lambda r_1) \right] + H_1 \left[r_1^2 K_0(\lambda r_1) - \frac{2R}{\lambda} K_1(\lambda R) + \frac{2r_1}{\lambda} K_1(\lambda r_1) \right] \right\}, \quad [31a]$$

$$L_{12} = \pi \left\{ \frac{\epsilon A}{4\pi\eta} \left[\frac{2r_1}{\kappa} I_1(\kappa r_1) - r_1^2 I_0(\kappa r_1) \right] + \frac{\epsilon}{4\pi\eta} \left(\frac{\kappa^2 r_1^2}{\kappa^2 - \lambda^2} \right) [BI_0(\kappa r_1) + CK_0(\kappa r_1)] + \frac{\epsilon}{2\pi\eta} \left(\frac{\kappa}{\kappa^2 - \lambda^2} \right) [BRI_1(\kappa R) - Br_1 I_1(\kappa r_1) - CRK_1(\kappa R) + Cr_1 K_1(\kappa r_1)] + G_2 \left[r_1^2 I_0(\lambda r_1) + \frac{2R}{\lambda} I_1(\lambda R) - \frac{2r_1}{\lambda} I_1(\lambda r_1) \right] + H_2 \left[r_1^2 K_0(\lambda r_1) - \frac{2R}{\lambda} K_1(\lambda R) + \frac{2r_1}{\lambda} K_1(\lambda r_1) \right] - \frac{zeNR^2}{\eta\lambda^2} \right\}. \quad [31b]$$

In the limit that $N = 0$ and $\lambda = 0$, Eq. [30] reduces to

$$\frac{V}{\pi R^2} = \frac{PR^2}{8\eta} - \frac{\epsilon E}{4\pi\eta} A_0 \left(I_0(\kappa R) - \frac{2}{\kappa R} I_1(\kappa R) \right). \quad [32]$$

It can be found by a comparison between Eqs. [30] and [32] that the structure of the surface charge layer can result in an augmented or a diminished volumetric flow rate relative to that in a capillary with bare wall, depending on the characteristics of the capillary, of the surface charge layer, and of the electrolyte solution. In general, the flow rate might be increased when the fixed-charged groups in the polyelectrolyte layer have the same sign as the charges on the bare wall. On the other hand, when z and σ (or ψ_R) are opposite in sign or when the value of λd is large, a decrease in the flow rate might be expected.

ELECTRO-OSMOSIS

The electro-osmotic velocity distribution in the capillary tube is given by Eq. [13] under conditions of no applied pressure gradient (viz. $P = 0$). If we consider the situation that $\kappa r_1 \rightarrow \infty$ and $\lambda r_1 \rightarrow \infty$ (which also imply that $\kappa R \rightarrow$

∞ and $\lambda R \rightarrow \infty$), the fluid velocity at a large distance from the wall of the tube (i.e., $\kappa(r_1 - r) \rightarrow \infty$) can be evaluated from Eq. [13a] noting that $\psi(r) \rightarrow 0$ far from the wall. The result of this electro-osmotic velocity, U_e , is

$$U_e = -\frac{\epsilon E}{4\pi\eta} \operatorname{sech} \lambda d \left\{ \frac{\kappa^2}{\kappa^2 - \lambda^2} \left[\frac{4\pi\sigma}{\epsilon\kappa} - \frac{4\pi zeN}{\epsilon\kappa^2} (e^{-\kappa d} - \cosh \lambda d) \right] - \frac{\lambda^2}{\kappa^2 - \lambda^2} \left(\cosh \lambda d + \frac{\kappa}{\lambda} \sinh \lambda d \right) \left[\frac{4\pi\sigma}{\epsilon\kappa} e^{-\kappa d} + \frac{2\pi zeN}{\epsilon\kappa^2} (1 - e^{-2\kappa d}) \right] \right\} - \frac{zeNE}{\eta\lambda^2} (1 - \operatorname{sech} \lambda d) \quad [33]$$

for the case of constant surface charge density, and

$$U_e = -\frac{\epsilon E}{4\pi\eta} \operatorname{sech} \lambda d \left\{ \frac{\kappa^2}{\kappa^2 - \lambda^2} \left[\psi_R - \frac{4\pi zeN}{\epsilon\kappa^2} (1 - \cosh \lambda d) \right] - \frac{\lambda^2}{\kappa^2 - \lambda^2} \left(\cosh \lambda d + \frac{\kappa}{\lambda} \sinh \lambda d \right) \left[\psi_R e^{-\kappa d} + \frac{2\pi zeN}{\epsilon\kappa^2} (1 - e^{-\kappa d})^2 \right] \right\} - \frac{zeNE}{\eta\lambda^2} (1 - \operatorname{sech} \lambda d) \quad [34]$$

for the case of constant surface potential. Equation [33] is consistent with the result obtained by Ohshima and Kondo (11) for the electro-osmotic flow between two parallel plates with surface charge layers and with $\sigma \approx 0$. Also, the ratio $-U_e/E$ given by Eq. [33] agrees with the expression for the electrophoretic mobility μ of a large polyelectrolyte-coated colloidal particle derived by Ohshima *et al.* (6).

When there is no polymer attached to the capillary wall ($N = 0$ and $\lambda = 0$), both Eqs. [33] and [34] reduce to the classical Helmholtz formula

$$U_e = -\frac{\epsilon\psi_R}{4\pi\eta} E, \quad [35]$$

knowing that

$$\psi_R = \frac{4\pi\sigma}{\epsilon\kappa} \quad [36]$$

for the situation considered.

The volumetric flow rate contributed by electro-osmosis through the capillary tube is given by $V = L_{12}E$ from Eq. [30] with $P = 0$. Also, the electro-osmotic counter pressure can be obtained by $P = -(L_{12}/L_{11})E$ from using Eq. [30]

under conditions of no net volume transport (i.e., $V = 0$). If this counter pressure is substituted into Eq. [13], the expression for the velocity distribution in the case of no total flow is obtained.

ELECTRIC CURRENT AND STREAMING POTENTIAL

The electric current density $i(r)$ flowing in the axial direction of the capillary tube at a radial position r in the electrolyte solution can be expressed as

$$i(r) = u(r)\rho(r) + \Lambda(r)E. \quad [37]$$

Here, $\Lambda(r)$ is the local electric conductivity of the solution and can be written as (11, 18)

$$\Lambda = \sum_i z_i^2 e^2 C_{i\infty} \exp\left(-\frac{z_i e \psi}{kT}\right) m_i, \quad [38]$$

where m_i is the mobility of ions of type i . Under the Debye-Huckel approximation, the above formula has its linearized form,

$$\Lambda = \sum_i z_i^2 e^2 C_{i\infty} \left(1 - \frac{z_i e \psi}{kT}\right) m_i. \quad [39]$$

In this linearized form, Λ will be constant for symmetric electrolytes with constant and equal ionic mobilities. The first term on the right-hand side of Eq. [37] is the contribution due to transport of electrolyte ions by the convection of fluid and the second term corresponds to the conduction current.

The total electric current I in the tube is given by

$$I = 2\pi \int_0^R i(r) r dr. \quad [40]$$

Substituting Eqs. [10], [13], and [39] for ρ , u , and Λ into Eq. [37] for i , one can evaluate the above integral using appropriate formulas for Bessel functions (19) to obtain the following expression in terms of the Onsager transport coefficients L_{21} and L_{22}

$$I = L_{21}P + L_{22}E, \quad [41]$$

where $L_{21} = L_{12}$ (given by Eq. [31b]), as can be shown and expected from the Onsager reciprocity principle (10, 13, 17), and

$$\begin{aligned} L_{22} = & -\frac{e^2 A^2}{16\pi\eta} \kappa r_1 [\kappa r_1 I_0^2(\kappa r_1) \\ & - 2I_0(\kappa r_1)I_1(\kappa r_1) - \kappa r_1 I_1^2(\kappa r_1)] - \frac{e^2 A}{8\pi\eta} \\ & \times \left(\frac{\kappa^3 r_1}{\kappa^2 - \lambda^2} \right) I_1(\kappa r_1) [BI_0(\kappa r_1) + CK_0(\kappa r_1)] \\ & - \frac{eA}{2} \kappa r_1 I_1(\kappa r_1) \left[G_2 I_0(\lambda r_1) + H_2 K_0(\lambda r_1) \right. \\ & \left. - \frac{zeN}{\eta\lambda^2} \right] - \frac{e}{2} \left(\frac{\kappa^2}{\kappa^2 - \lambda^2} \right) \{ BG_2 [\kappa R I_0(\lambda R) I_1(\kappa R) \\ & - \lambda R I_0(\kappa R) I_1(\lambda R) - \kappa r_1 I_0(\lambda r_1) I_1(\kappa r_1) \\ & + \lambda r_1 I_0(\kappa r_1) I_1(\lambda r_1)] + BH_2 [\lambda R I_0(\kappa R) K_1(\lambda R) \\ & + \kappa R I_1(\kappa R) K_0(\lambda R) - \lambda r_1 I_0(\kappa r_1) K_1(\lambda r_1) \\ & - \kappa r_1 I_1(\kappa r_1) K_0(\lambda r_1)] - CG_2 [\kappa R I_0(\lambda R) K_1(\kappa R) \\ & + \lambda R I_1(\lambda R) K_0(\kappa R) - \kappa r_1 I_0(\lambda r_1) K_1(\kappa r_1) \\ & - \lambda r_1 I_1(\lambda r_1) K_0(\kappa r_1)] - CH_2 [\kappa R K_0(\lambda R) K_1(\kappa R) \\ & - \lambda R K_0(\kappa R) K_1(\lambda R) - \kappa r_1 K_0(\lambda r_1) K_1(\kappa r_1) \\ & + \lambda r_1 K_0(\kappa r_1) K_1(\lambda r_1)] \} - \frac{e^2}{16\pi\eta} \left(\frac{\kappa^4}{\kappa^2 - \lambda^2} \right) \{ B^2 \\ & \times [R^2 I_0^2(\kappa R) - R^2 I_1^2(\kappa R) - r_1^2 I_0^2(\kappa r_1) + r_1^2 I_1^2(\kappa r_1)] \\ & + 2BC [R^2 I_0(\kappa R) K_0(\kappa R) + R^2 I_1(\kappa R) K_1(\kappa R) \\ & - r_1^2 I_0(\kappa r_1) K_0(\kappa r_1) - r_1^2 I_1(\kappa r_1) K_1(\kappa r_1)] \\ & + C^2 [R^2 K_0^2(\kappa R) - R^2 K_1^2(\kappa R) - r_1^2 K_0^2(\kappa r_1) \\ & + r_1^2 K_1^2(\kappa r_1)] \} + \frac{zeN\epsilon\kappa}{2\eta\lambda^2} \left(\frac{\kappa^2 - 2\lambda^2}{\kappa^2 - \lambda^2} \right) \\ & \times [BR I_1(\kappa R) - Br_1 I_1(\kappa r_1) - CR K_1(\kappa R) \\ & + Cr_1 K_1(\kappa r_1)] - 2\pi zeN \left\{ \frac{G_2}{\lambda} [RI_1(\lambda R) - r_1 I_1(\lambda r_1)] \right. \\ & \left. - \frac{H_2}{\lambda} [RK_1(\lambda R) - r_1 K_1(\lambda r_1)] - \frac{zeN}{2\eta\lambda^2} (R^2 - r_1^2) \right\} \\ & + \pi r_1^2 \sum_i z_i^2 e^2 C_{i\infty} m_{oi} - \frac{2\pi}{\kappa kT} Ar_1 I_1(\kappa r_1) \sum_i z_i^3 e^3 \\ & \times C_{i\infty} m_{oi} + \pi (R^2 - r_1^2) \sum_i z_i^2 e^2 C_{i\infty} m_{pi} - \frac{2\pi}{\kappa kT} \\ & \times \left[BR I_1(\kappa R) - Br_1 I_1(\kappa r_1) - CR K_1(\kappa R) + Cr_1 \right. \\ & \left. \times K_1(\kappa r_1) + \frac{2\pi zeN}{\epsilon\kappa} (R^2 - r_1^2) \right] \sum_i z_i^3 e^3 C_{i\infty} m_{pi}. \quad [42] \end{aligned}$$

Here, m_{0i} and m_{pi} are the mobilities of ions of type i in the polymer-free solution and in the surface charge layer, respectively; both are assumed to be constant in Eq. [42].

When there is no polymer anchored to the capillary wall ($N = 0$ and $\lambda = 0$), Eq. [41] reduces to

$$\frac{I}{\pi R^2} = E \left\{ \Lambda_0 - \frac{2}{kT\kappa R} I_1(\kappa R) \sum_i z_i^3 e^3 C_{i\infty} m_{0i} - \frac{\epsilon^2 \kappa^2}{16\pi^2 \eta} A_0^2 \left[I_0^2(\kappa R) - \frac{2}{\kappa R} I_0(\kappa R) I_1(\kappa R) - I_1^2(\kappa R) \right] \right\} - \frac{\epsilon P}{4\pi \eta} A_0 \left[I_0(\kappa R) - \frac{2}{\kappa R} I_1(\kappa R) \right], \quad [43]$$

where

$$\Lambda_0 = \sum_i z_i^2 e^2 C_{i\infty} m_{0i}, \quad [44]$$

which is the electric conductivity of the bulk electrolyte solution. The first term in Eq. [43] represents the current for electro-osmotic flow, while the second term is the contribution owing to the applied pressure gradient. A comparison between Eqs. [41] and [43] indicates that the surface structure can lead to an increase or a decrease in the current flow through a capillary, depending on the characteristics of the capillary, of the surface charge layer, and of the electrolyte solution. In general, the electric current might be increased if z has the same sign as σ (or ψ_R). When z is opposite in sign to σ (or ψ_R), when the value of λd is large, or when the ratio m_{pi}/m_{0i} is small, the decrease in the current flow might be expected.

The streaming potential is the steady potential difference which builds up across the capillary tube in the presence of an applied pressure gradient and which is just sufficient to prevent the net current flow. Putting $I = 0$ in Eq. [41] one obtains the streaming potential (gradient) as $E = -(L_{12}/L_{22})P$ for any given P . Substituting this streaming potential into Eq. [30] gives the apparent volumetric flow rate of the fluid under the applied pressure gradient.

Under the condition that $R \gg d$, $\kappa d \gg 1$ and $\lambda d \gg 1$, which holds for the surface of most biological pores, Eq. [41] can be simplified to a first approximation by

$$\frac{I}{\pi R^2} = \Lambda_0 E - \mu P, \quad [45]$$

where $\mu = -U_e/E$ with U_e given by Eq. [33] or [34].

CONCLUDING REMARKS

The steady electrokinetic flow in a long circular capillary tube with its inside wall covered by a layer of adsorbed poly-

electrolytes is analyzed in this work. The polyelectrolyte layer is treated as a solvent-permeable and ion-penetrable surface charge layer of constant thickness in which fixed-charged groups and frictional segments are distributed at uniform densities. Solving the linearized Poisson-Boltzmann equation and the modified Navier-Stokes equation applicable to the system, the electrical potential distribution, the space charge density distribution, and the fluid velocity profile under the influence of a uniform electric field and a constant pressure gradient are obtained in Eqs. [6], [10], and [13], respectively. Analytical expressions in explicit forms for the volumetric flow rate, the electro-osmotic velocity, and the electric current in the tube are also presented in Eqs. [30], [33], or [34], and [41], respectively. The explicit formula for the streaming potential can easily be derived from Eq. [41] by letting the net current in the tube be zero.

It is worth repeating that the above formulas for various electrokinetic phenomena have been obtained on the basis of the Debye-Huckel approximation for the space charge density in the double layer. This means that these results are satisfactory when used for low values of ψ_R , but that they can only be used tentatively for higher values of ψ_R . Moreover, the decay of the density distributions of polymer segments and fixed charges in the surface charge layer with the distance from the capillary wall has not been considered in our calculations. In order to see whether our theory can be reasonably extended to the higher values of ψ_R or to the nonuniform density distributions of polymer segments and charges, we propose to obtain a numerical solution of the Poisson-Boltzmann equation allowing the use of arbitrary distributions of charge and fluid drag components in the direction normal to the capillary wall and compare it with the approximate solution.

APPENDIX: NOMENCLATURE

a	Effective Stokes radius of a polymer segment, m
A, B, C	Quantities defined by Equation [7] or Equation [9], V
A_0	Quantities defined by Equation [20] or Equation [21], V
B_1	Quantities defined by Equation [27] or Equation [28], V
$C_{i\infty}$	Bulk concentration of type- i ions, m^{-3}
d	Thickness of the surface charge layer on the capillary wall, m
e	Protonic charge, C
E	Applied electric field through the capillary, $\text{V} \cdot \text{m}^{-1}$
f	Friction coefficient of the polymer layer per unit volume of fluid, $\text{Kg} \cdot \text{m}^{-3} \cdot \text{s}^{-1}$
G_1, H_1	Quantities defined by Equation [15], $\text{m}^4 \cdot \text{N}^{-1} \cdot \text{s}^{-1}$
G_2, H_2	Quantities defined by Equation [16], $\text{m}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$

i	Electric current density, $A \cdot m^{-2}$	κ	Reciprocal Debye screening length, m^{-1}
I	Total electric current in the capillary, A	λ	$=(f/\eta)^{1/2}$, m^{-1}
I_n, K_n	Modified Bessel functions of order n of the first and second kinds	Λ	Electric conductivity, $\Omega^{-1} \cdot m^{-1}$
k	The Boltzmann constant, $1.38 \times 10^{-23} J \cdot K^{-1}$	Λ_0	Electric conductivity of the bulk electrolyte solution, $\Omega^{-1} \cdot m^{-1}$
L_{11}	Onsager transport coefficient defined by Equation [30], $m^6 \cdot N^{-1} \cdot s^{-1}$	μ	Electrophoretic mobility of a large colloidal particle coated with a surface charge layer, $m^2 \cdot V^{-1} \cdot s^{-1}$
L_{12}	Onsager transport coefficient defined by Equation [30], $m^4 \cdot V^{-1} \cdot s^{-1}$	ρ	Space charge density resulting from the electrolyte ions, $C \cdot m^{-3}$
L_{21}	Onsager transport coefficient defined by Equation [41], $A \cdot m^3 \cdot N^{-1}$	σ	Surface charge density of the capillary wall, $C \cdot m^{-2}$
L_{22}	Onsager transport coefficient defined by Equation [41], $m \cdot \Omega^{-1}$	ψ	Electrical potential relative to the bulk solution, V
m_i	Mobility of ions of type i , $m \cdot N^{-1} \cdot s^{-1}$	ψ_R	Surface potential of the capillary wall, V
m_{0i}	Mobility of ions of type i in the polymer-free solution, $m \cdot N^{-1} \cdot s^{-1}$		
m_{pi}	Mobility of ions of type i in the surface charge layer, $m \cdot N^{-1} \cdot s^{-1}$		
N	Number density of fixed-charged groups in the surface charge layer, m^{-3}		
N_p	Number density of polymer segments in the surface charge layer, m^{-3}		
P	Applied pressure gradient through the capillary, $N \cdot m^{-3}$		
r	Point distance from the axis of the capillary, m		
r_1	$=R - d$, m		
R	Radius of the capillary with bare wall, m		
T	Absolute temperature, K		
u	Fluid velocity in the axial direction in the capillary, $m \cdot s^{-1}$		
U_e	Electro-osmotic velocity given by Eq. [33] or Equation [34], $m \cdot s^{-1}$		
V	Volumetric flow rate of fluid in the capillary, $m^3 \cdot s^{-1}$		
z	Valence of a fixed-charged group in the surface charge layer		
z_i	Valence of type- i ions		

Greek Letters

ϵ	$=4\pi\epsilon_0\epsilon_r$, $C^2 \cdot J^{-1} \cdot m^{-1}$
ϵ_0	Permittivity in vacuum, $8.854 \times 10^{-12} C^2 \cdot J^{-1} \cdot m^{-1}$
ϵ_r	Dielectric constant of the fluid
η	Fluid viscosity, $Kg \cdot m^{-1} \cdot s^{-1}$

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