

Diffusioosmosis of electrolyte solutions in a capillary slit with surface charge layers

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Abstract

The steady diffusioosmotic flow of an electrolyte solution in a fine capillary slit with each of its inside walls covered by a layer of adsorbed polyelectrolytes is analytically studied. In this solvent-permeable and ion-penetrable surface charge layer, idealized polyelectrolyte segments are assumed to distribute at a uniform density. The electric double layer and the surface charge layer may have arbitrary thicknesses relative to the gap width between the slit walls. The Debye–Hückel approximation is used to obtain the electrostatic potential distribution on a cross section of the slit. The macroscopic electric field induced by the imposed electrolyte concentration gradient through the slit is determined as a function of the lateral position rather than taken as its constant bulk-phase quantity. Explicit formulas for the fluid velocity profile are derived as the solution of a modified Navier–Stokes/Brinkman equation. The effect of the lateral distribution of the induced axial electric field in the slit on the diffusioosmotic flow is found to be of dominant significance in most practical situations and to drive the fluid towards the end of higher electrolyte concentration. The existence of the surface charge layers can lead to a quite different diffusioosmotic flow from that in a capillary with bare walls.

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1. Introduction

The flow of electrolyte solutions in a small pore with a charged wall is of much fundamental and practical interest in various areas of science and engineering. In general, driving forces for this electrokinetic flow include dynamic pressure differences between the two ends of the pore (a streaming potential is developed as a result of zero net electric current) and tangential electric fields that interact with the electric double layer adjacent to the pore wall (electroosmosis). Problems of fluid flow in pores caused by these well-known driving forces were studied extensively in the past century [1–8].

Another driving force for the electrokinetic flow in a micropore, which has commanded less attention, involves tangential concentration gradients of an ionic solute that interacts with the charged pore wall. This solute-wall interaction is electrostatic in nature and its range is the Debye screening

length κ^{-1} (defined right after Eq. (3)). The fluid motion associated with this mechanism, known as “diffusioosmosis”, has been analytically examined for solutions near a plane wall [4,9–12] and inside a fine capillary [13–16]. Electrolyte solutions with a concentration gradient of order 100 kmol/m^4 ($=1 \text{ M/cm}$) along solid surfaces with a zeta potential of order kT/e ($\sim 25 \text{ mV}$; e is the charge of a proton, k is the Boltzmann constant, and T is the absolute temperature) can flow by diffusioosmosis at velocities of several micrometers per second.

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 phenomena to the study of the effects of polyelectrolyte adsorbates. The electroosmotic flows in capillaries with thin polymer layers on the inside walls were theoretically examined for the cases of a slit [17,18] and a tube [19] with thin double layers. On the other hand, analytical formulas for the electroosmotic velocity profile of electrolyte solutions on the cross section of a capillary with its inside wall covered by a finite layer

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of adsorbed polyelectrolytes were obtained by solving the linearized Poisson–Boltzmann equation for the case of an arbitrary value of κR or κh , where R is the radius of a capillary tube and h is the half thickness of a capillary slit [20,21]. Recently, the diffusioosmotic flow of a symmetric electrolyte solution in a fine capillary slit bearing adsorbed polyelectrolytes on its inside walls was theoretically investigated for the case of small potentials or low fixed-charge densities, and an analytical formula for the fluid velocity profile on the cross section of the slit was obtained [22]. In this study, however, the effect of lateral distributions of the counter-ions and co-ions on the local macroscopic electric field induced by the imposed electrolyte concentration gradient in the axial direction, which can be dominantly important, was neglected.

The objective of this work is to analyze the steady diffusioosmosis of an electrolyte solution with a constant imposed concentration gradient through a capillary slit bearing permanently adsorbed or covalently bound polyelectrolytes on its inside walls. The charge and segment densities of the adsorbed polymers are assumed to be uniform throughout the surface charge layer, and the Debye–Hückel approximation for the electrostatic potential is employed. However, no assumptions will be made about the thickness of the electric double layer or the thickness of the surface charge layer relative to the gap width between the slit walls, and the lateral distribution of the induced axial electric field is allowed. We shall derive explicit formulas for the local and average fluid velocities due to the application of an electrolyte concentration gradient along the slit walls. These results show that the effect of the deviation of the induced axial electric field in the slit from its bulk-phase quantity on the diffusioosmotic velocity of the fluid is dominantly significant in most practical situations.

2. Electrostatic potential distribution

In this section, we consider the electrostatic potential distribution in the fluid solution of a symmetrically charged electrolyte on a cross section of the narrow channel between two large identical parallel plates of length L at separation distance $2h$ with $h \ll L$, as illustrated in Fig. 1. Each of the inside walls of the capillary slit is coated with a layer of adsorbed,

charged polymers in equilibrium with the surrounding solution. The polymer layer is treated as a solvent-permeable and ion-penetrable surface charge layer of constant thickness $d = h - b$ in which fixed-charged groups of valence q are distributed at a uniform density N . Experimental values for human erythrocytes [23], rat lymphocytes [24], and grafted polymer macrocapsules [25] indicate that d ranges from 7.8 nm to 3.38 μm and N can be as high as 0.03 kmol/m^3 , depending on the pH and ionic strength of the electrolyte solution.

The prescribed electrolyte concentration gradient ∇n^∞ is a constant along the axial direction in the capillary, where $n^\infty(z)$ can be interpreted as the equivalent electrolyte concentration in the bulk solution phase (outside the capillary) at equilibrium with the fluid in the slit cross section at axial position z . Since the electrolyte ions can diffuse freely along the capillary (inside and outside the surface charge layers), there exists no regular osmotic flow of the solvent. It is assumed that $L|\nabla n^\infty|/n^\infty(0) \ll 1$, where $z=0$ is set at the midpoint through the capillary slit. Thus, the variation of the electrostatic potential (excluding the macroscopic electric field induced by the prescribed electrolyte gradient, which will be discussed in the next section) and ionic concentrations in the slit with the axial position is negligible.

Because of 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 a normal direction. If $\psi(y)$ represents the electrostatic potential at the position y relative to that in the bulk solution and $n_+(y, z)$ and $n_-(y, z)$ denote the local concentrations of the cation and anion, respectively, of the symmetric electrolyte with valence Z (which is positive), then Poisson's equation gives

$$\frac{d^2\psi}{dy^2} = -\frac{4\pi e}{\varepsilon} \{Z[n_+(y, 0) - n_-(y, 0)] + H(y)qN\} \quad (1)$$

Here, $H(y)$ is a unit step function which equals unity if $b < y < h$, and zero if $0 \leq y < b$; $\varepsilon = 4\pi\varepsilon_0\varepsilon_r$, where ε_r is the relative permittivity of the electrolyte solution which is assumed to be constant and ε_0 is the permittivity of a vacuum.

The local concentrations n_+ and n_- are also related to ψ by the Boltzmann equation:

$$n_\pm = n^\infty \exp\left(\mp \frac{Ze\psi}{kT}\right) \quad (2)$$

The substitution of Eq. (2) into Eq. (1) leads to the well-known Poisson–Boltzmann equation. For small values of ψ (or $Ze\psi/kT \ll 1$, known as the Debye–Hückel approximation), the Poisson–Boltzmann equation can be linearized and Eq. (1) becomes

$$\frac{d^2\psi}{dy^2} = \kappa^2\psi - H(y)\frac{4\pi qeN}{\varepsilon}, \quad (3)$$

where $\kappa = [8\pi(Ze)^2n^\infty(0)/\varepsilon kT]^{1/2}$ is the Debye screening parameter.

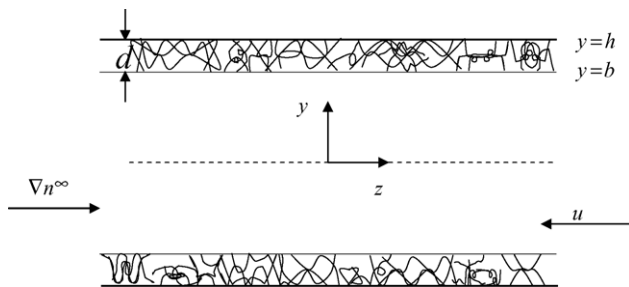


Fig. 1. Geometrical sketch for the diffusioosmosis in a capillary slit with each of its inside walls covered by a layer of adsorbed polyelectrolytes.

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